Long-Lived Cyclopropylcarbinyl Cations

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Received July 22, 1991 (Revised Manuscript Received November 13, 1991)

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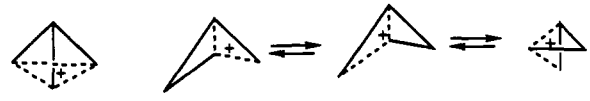
I. Introduction

Among the simple carbocationic systems, cyclopropylcarbinyl cations have been among the most extensively investigated, yet their structures have not yet been fully established. Bartlett's statement "Among nonclassical ions, the ratio of conceptual difficulty to molecular weight reaches a maximum with the cyclopropylcarbinyl–cyclobutyl system" still remains valid.[1a]

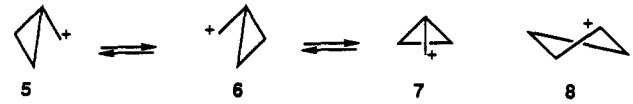
From extensive kinetic studies, which revealed unusually fast rates of solvolyses for cyclobutyl and cyclopropylcarbinyl systems, Roberts first proposed the symmetrical tricyclobutonium ion (1).[1-3] Historically, this was the first carbocationic structure to be named "nonclassical". The same intermediate was proposed to arise from the solvolysis of related cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl systems, since similar product composition resulted when each of these substrates was used as starting material. Deamination of cyclopropylcarbinylamine or cyclobutylamine with nitrous acid also gave nearly identical product mixtures of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl (3-butenyl) derivatives. Roberts' subsequent experiments necessitated the modification of the nature of the intermediate. Thus, solvolyses of 1-deuterio and 1-^{14}C labeled analogues of the cyclopropylcarbinyl substrates provided product cyclobutanols and cyclopropylcarbinols, with unequal distribution of the label among different positions. A symmetrical tricyclobutonium ion would be expected to distribute the label equally among all the methylene carbons. To account for these results, Roberts proposed equilibrating bicyclobutonium ions 2–4 as intermediates.[3] The kinetic studies on the



1 2 3 4

parent system was also extended to several cyclopropyl- or cyclobutyl-substituted hydrocarbons, and the effect of the alkyl or aryl substituents on the electron-delocalizing ability of the cyclopropyl group was systematically analyzed by several groups.[1c]

The nature of the carbocationic intermediate in solvolysis studies is not clearly established. Brown has obtained unequal product ratios of cyclopropylcarbinyl and cyclobutyl derivatives in the methanolysis of cyclopropylcarbinyl and cyclobutyl 2-naphthalenesulfonates and argued against the involvement of a bridged intermediate.[1e] He proposed the involvement of equilibrating cyclopropylcarbinyl cations (5–7), the



5 6 7 8

equilibrium occurring through a relatively unpopulated puckered cyclobutyl cation (8). He accounted for the relatively fast reactions of the cyclopropylcarbinyl substrates and relatively less negative *e* values for the solvolyses of these substrates as due to the σ-conjugation involving the cyclopropyl group, instead of the σ-participation, required for bridged structures.

Stable ion studies provided definitive structural assignments for several cyclopropylcarbinyl cations. Since ^{13}C NMR absorptions are related to the charge densities

0009-2665/92/0792-0069$10.00/0

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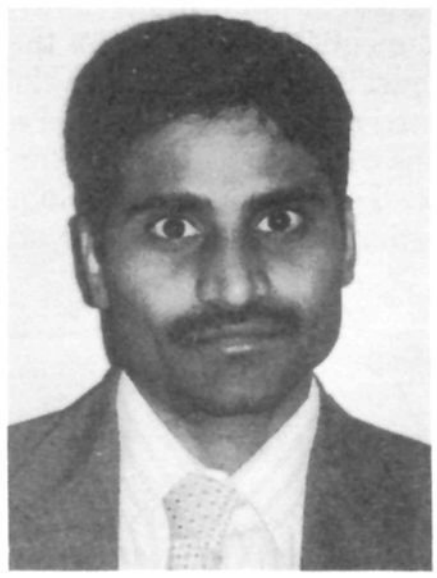

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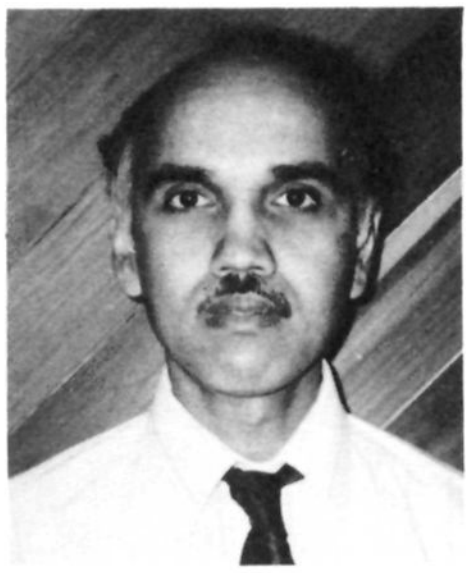
at the respective carbons, it is relatively straightforward to characterize and distinguish the classical cations from nonclassical cations. The low nucleophilicity of the superacids used for the preparation of carbocations eliminates any significant solvation, which is invariably associated with the solvolysis studies. Cyclopropylcarbinyl cations are stabilized by delocalization into the cyclopropyl rings, and the degree of delocalization of the charge into the cyclopropyl groups can be estimated by relative ^{13}C NMR chemical shifts of these carbons. It is also possible to distinguish the rapidly equilibrating (degenerate) cations from the static cations on the basis of their temperature-dependent average ^{13}C NMR chemical shifts. The deuterium isotopic perturbation technique developed by Saunders et al.[4] is capable of providing a convenient means to differentiate between rapidly equilibrating classical trivalent cations and nonclassical σ-bridged cations. Saunders and Vogel in 1971[4b] discovered that by asymmetrically introducing



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deuterium into carbocations that were known to undergo degenerate, very rapid, and reversible rearrangement process large splittings were produced in the NMR spectra. Although the ions were interconverting extremely rapidly and still gave averaged spectra, the presence of the isotope made the energies of two interconverting species slightly different and thus the equilibrium constant between them was no longer unity. Each ion, therefore, spent a little more time on one side of the equilibrium barrier than on the other side as a function of temperature. The weighted average peaks of the two carbon atoms that were interchanging by the rearrangement process thus no longer coincided. On the other hand, when deuterium was introduced into structures having a single minimum, i.e., nonequilibrating species, no such large splittings were observed. By using this technique cyclopropylcarbinyl and 1-methylcyclobutyl cations were shown to be equilibrating nonclassical structures. The field of cyclopropylcarbinyl cations was reviewed previously in 1972, including stable long-lived ions.[1b-d] Methods used in the study of degenerate cations were also reviewed by Ahlberg and co-workers.[1g] The present review deals with the newer structural characterization of cyclopropylcarbinyl cations under long-lived stable ion conditions, i.e., in superacidic, low-nucleophilic media, such as FSO_3H, FSO_3H–SbF_5, or SbF_5, dissolved in solvents, such as sulfuryl chloride fluoride, sulfuryl fluoride, and liquid sulfur dioxide. NMR spectroscopic characterization, including that of temperature-dependent equilibria, theoretical calculations, as well as the effect of substituents on charge delocalization will also be discussed. On the basis of historical perspective, the degenerate cations are discussed before the nondegenerate ones.

II. Primary Cyclopropylcarbinyl Cations

A. Equilibrating (Degenerate) Cations

1. $C_4H_7^+$ (Cyclopropylcarbinyl Cation)

The $C_4H_7^+$ ion was observed, and characterized by proton and carbon-13 NMR spectra under stable ion

conditions by Olah and co-workers in 1970.[5] Cyclopropylcarbinol or cyclobutanol on reaction with SbF_5–SO_2ClF at −80 °C gave identical ^1H and ^{13}C spectral characteristics. The proton spectrum of the cation showed a methine multiplet at δ 6.5 (two overlapping quartets, J_1 = 8 Hz, J_2 = 6.5 Hz), and two distinct methylene doublets at δ 4.64 and 4.21. The latter absorptions were shown to be due to the *endo*- and *exo*-methylene hydrogens, respectively, by the deuterium-labeling studies.[11] Thus the geminal methylene hydrogens are not stereochemically equivalent. This observation excludes classical cyclobutyl or cyclopropylcarbinyl cation structures. The ^{13}C spectrum shows only two absorptions: the methine carbon absorbs at δ 108.4, and the methylenes at δ 55.2 (J_{CH} = 180 Hz). The ^1H and ^{13}C NMR spectra complement each other to show that the methylene carbons are equivalent in the cation, but the methylene protons exist as two sets of three-proton doublets. A pentacoordinated σ-delocalized bicyclobutonium ion would account for the distinct NMR behavior of the geminal methylene protons. As pointed out by Schleyer,[1d] the puckered cyclobutyl cation can be ruled out, as the ring-inversion barrier for this structure would be expected to be too low, probably less than 1.4 kcal/mol. The facile ring inversion would make the geminal methylene hydrogens of this structure equivalent, contrary to the experimental observations. Olah, Roberts, and co-workers ionized cyclopropylcarbinol-1-^{13}C with SbF_5–SO_2ClF–SO_2F_2 at −125 °C, and the temperature dependence of the ion was examined between temperatures −61 to −132 °C.[6] At −70 °C, the ion shows absorptions at δ 107.56 and 57.41, corresponding to the methine and methylene carbons, respectively. The ^{13}C label was distributed nearly randomly between the CH_2 and CH carbons, indicating that 1,2-hydride migrations were occurring at this temperature. Decreasing the temperature causes substantial shifting of the methine and average methylene carbon resonances resulting in their deshielding and shielding, respectively. Thus, at −61 °C, δ ^{13}CH = 106.78, and δ $^{13}CH_2$ = 58.95, whereas at −132 °C, δ ^{13}CH = 111.32 and δ $^{13}CH_2$ = 50.89. Under the same conditions the static dimethylcyclopropylcarbinyl cation (vide infra) does not exhibit temperature-dependent chemical shift differences of any appreciable magnitude. The rather large temperature-induced chemical shift variation in $C_4H_7^+$ indicates equilibration of the bicyclobutonium ion with an additional energetically similar isomeric ion. The bisected cyclopropylcarbinyl cation was proposed as the minor equilibrating species.

It is interesting to note that 1,2-hydride migrations occur in the ion in superacids under stable ion conditions, while such shifts could not be observed in solvolytic reactions. Roberts and Staral found that ionization of cyclopropylcarbinol with SbF_5–SO_2ClF–SO_2F_2 below −70 °C gave a mixture of protonated cyclobutanol and $C_4H_7^+$ cation, but above −70 °C it was irreversibly converted to the $C_4H_7^+$ cation.[7] From the line width of the methylene carbon absorptions at −60 °C ($\upsilon_{1/2}$ < 10 Hz), the rate for the 1,2-hydride migration in the cyclobutyl system was calculated to be 65 s^{-1}, implying $\Delta G^{\ddagger}$ greater than 10 kcal/mol. This barrier for the hydride shift is greater than the degenerate 1,2-hydride shift in secondary cations, such as the cyclopentyl cation, by as much as 5 kcal/mol.[8] Thus, the rate of hydride migration is slow on the NMR time scale, and hence the cation shows distinct absorptions for the methylene and methine carbons.

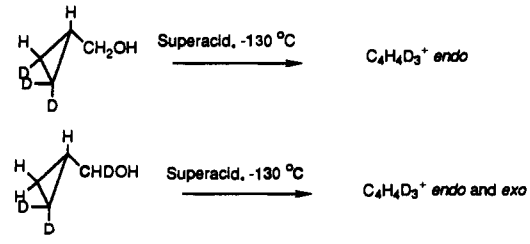
More direct evidence for the equilibration of the bicyclobutonium ion with a less populated isomer, the bisected cyclopropylcarbinyl cation or bent cyclobutyl cation, comes from deuterium isotope effect studies of the cation by Saunders and Siehl.[9,10] As discussed earlier, the presence of deuterium in the cation causes perturbation of the otherwise degenerate equilibria, and equilibrium isotope effects, as manifested in the splittings of the NMR absorptions, are observed in the relevant cases. The isotopic perturbation of resonance, on the other hand, exerts only a negligible splitting of the NMR lines.[4]

The ^{13}C NMR spectrum obtained from the ionization of the α,α-dideuteriated cyclopropylcarbinol showed two distinct methylene absorptions (deuteriated and nondeuteriated). The unlabeled methylene carbon was shielded by 1.77 ppm at −135 °C, and by 1.24 ppm at −107 °C, compared with the methylene carbons of perprotiated ion. Similar shieldings were also observed in the ^1H NMR, but only the upfield methylene absorptions showed such shifts, while downfield methylene peaks remained unchanged.[9] Equilibrating bridged cations were proposed on the basis of the observed temperature-dependent small equilibrium isotope effects.

α-Monodeuteriated cyclopropylcarbinol in SbF_5–SO_2ClF gave two distinct ions, differing in the deuterium stereochemistry.[10] It was observed that in one of the isomeric ions, the deuteriated carbon was shifted upfield (shielded) from the unlabeled carbon, while in the other isomer, the deuteriated carbon was shifted downfield (deshielded) from the corresponding unlabeled carbon. The magnitude of the downfield shift was twice as much as the upfield shift. Although it was not possible to unequivocally assign these absorptions to the endo- and exo-deuteriated cyclopropylcarbinyl cations, it is clear that these isomers exert different equilibrium isotope effects, opposite in sign and magnitude from each other. Hence, the C–H force constants between the rapidly equilibrating two sets of hydrogen are extremely different. This fact excludes the possibility of classical cyclopropylcarbinyl or the cyclobutyl cations as the main species, and leaves the pentacoordinated bicyclobutonium ion as the only indicated ground-state structure. In order to rationalize the observed equilibrium isotope effects, it was proposed that the bicyclobutonium ion is in equilibrium with a minor species, such as the bisected cyclopropylcarbinyl cation.

Roberts and co-workers[11] subsequently prepared stereoisomers of the trideuteriated cyclopropylcarbinyl cations as shown in Scheme 1.

SCHEME 1. Stereospecific Synthesis of *endo*- and *exo*-(Trideuteriocyclopropyl)carbinyl Cations



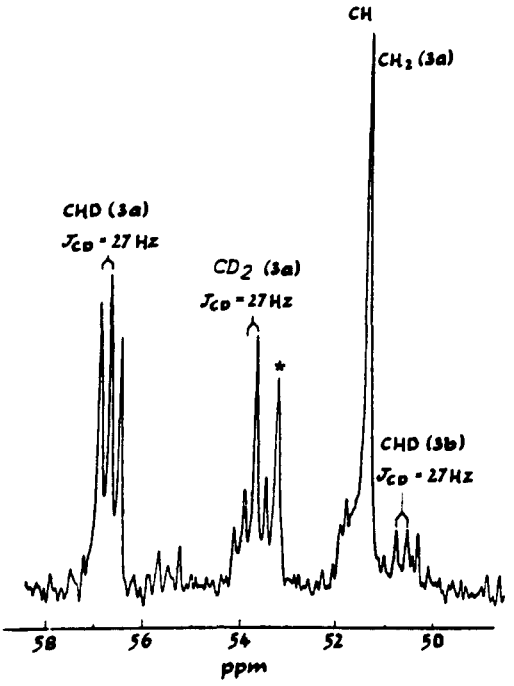


Figure 1. Methylene-shift region of the proton-decoupled 125.7-MHz ^{13}C FT NMR spectrum of *endo*-$C_4H_4D_3^+$ at −95 °C in SbF_5–SO_2ClF–SO_2F_2 solution. (The asterisk corresponds to an unknown resonance.) (Reprinted from ref 11; copyright 1984 American Chemical Society).

TABLE 1. ^{13}C Chemical Shifts (δ ^{13}C) of $C_4H_4D_3^+$ (endo and exo) at −95 °C

	CH_2	CHD	CD_2	CH
endo	51.35	56.59	53.68	109.81
exo	53.68	50.51	55.7	110.28

They demonstrated that the endo isomer shows deshielding of the deuteriated carbon and the exo isomer shows shielding. A ^{13}C NMR spectrum of the *endo*-deuterio compound at −96 °C is shown in Figure 1. The assignments were confirmed by C–D coupling constants and from a spectrum of equimolar mixture of the endo and exo isomers of the cation. The relative chemical shifts of the endo and exo isomers with respect to the corresponding shifts for the unlabeled isomer are CH_2, −3.0 (endo) and −0.7 (exo); CHD, 2.2 (endo) and −3.6 (exo); CH, 0.0 (endo) and 0.4 (exo); and CD_2, −0.8 (endo) and 1.0 (exo). The ^{13}C chemical shift assignments of the endo and exo isomers at −95 °C are shown in Table 1.

The *endo*-deuterio and *exo*-deuterio isomers were not interconverted at −90 °C for up to 4 h. Minimum free energy of activation was estimated for the interconversion as 14 kcal/mol at −90 °C[11] which complements Saunders' equilibrium isotope effect study in excluding a classical equilibrating cation. Only a pentacoordinated bicyclobutonium ion in equilibration with a relatively unpopulated minor isomer can explain the observed results. Attempts to assess the degree of 1,2-deuterium migration from the methylene to methine failed, as there was no deuterium migration to methine position, even after keeping the ion to extended periods above −80 °C.[11]

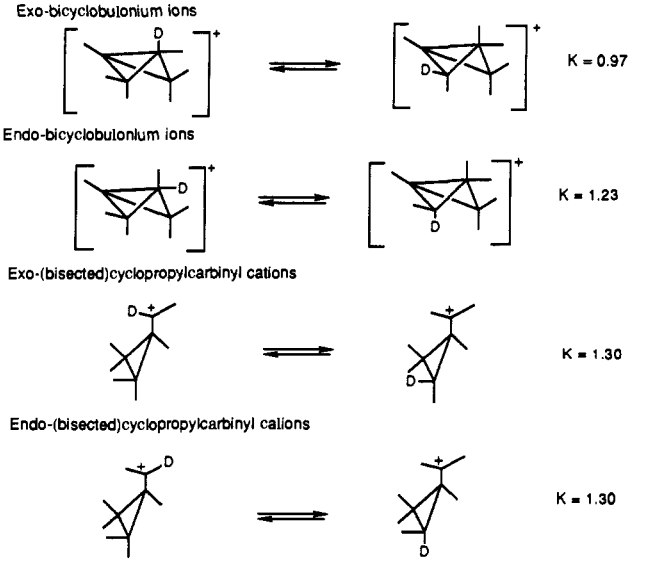
The observed chemical shifts of the ion are also in close agreement with calculated chemical shifts of the bicyclobutonium ion, using Kutzelnigg and Schlindler's IGLO (Individual Gauge for Localized Orbitals) method. The chemical shifts calculated for the bisected classical cyclopropylcarbinyl cation, using the same method deviate much more from the experimental values.[12] Table 2 also compares the experimental ^{13}C NMR chemical shift values with calculated chemical shifts (IGLO) of the bisected cyclopropylcarbinyl and bicyclobutonium ions. The deviation of the observed chemical shifts from the IGLO values suggests the presence of two isomers in equilibrium. The mole fraction of these isomers were determined by assuming the observed chemical shift as a weighted average of the chemical shifts of the static ion. The ratio of bicyclobutonium ion and bisected cyclopropylcarbinyl cations were calculated to vary from 74.8:25.2 at −61 °C to 84:16 at −132 °C. A Boltzmann population analysis showed that the bicyclobutonium ion is about 0.5 kcal/mol more stable than the bisected cyclopropylcarbinyl cation. These values can only be correct to the extent of accuracy of the IGLO calculations in reproducing the experimental chemical shifts.

TABLE 2. Comparison of Experimental and IGLO Calculated ^{13}C NMR Chemical Shifts for $C_4H_7^+$ Ions (at IIIZ//MP2/6-31G* Level of Calculation)[12]

	CH_2[a]	CH
IGLO		
(bisected)	125.7	65.8
(bicyclobutonium)	36.5	117.5
Experimental		
−61 °C	58.95	106.78
−80 °C	56.55	108.02
−106 °C	53.97	109.38
−115 °C	52.63	110.25
−132 °C	50.89	111.32

More recently, the equilibrium isotope effects were theoretically calculated for the endo- and exo-deuteriated isomers of the bicyclobutonium and bisected cyclopropylcarbinyl structures.[13] The values are shown in Scheme 2.

SCHEME 2. Calculated Equilibrium Isotope Effects for $C_4H_6D^+$ Isomers



The calculations predict that, in the exo isomer of the bicyclobutonium ion, deuterium prefers to be on the pentacoordinated rather than on the tetracoordinated adjacent carbon. In the endo isomer, on the other hand, the deuterium favors the methylene over the penta-

coordinated carbon. The observed chemical shifts of endo- and exo-deuteriated isomers can be well explained by the results of these calculations. Since the pentacoordinated carbon usually resonates upfield compared to the tetracoordinated methylenes, the equilibration of the isomeric bicyclobutonium ions through relatively unpopulated cyclopropylcarbinyl cations results in an upfield shift (shielding) for the exo-deuteriated methylene; similarly the downfield shift (deshielding) of the methylene carbon for the endo-labeled isomer can be explained. Thus experimentally observed isotope effects of opposite sign and magnitude are also reproduced by the theoretically calculated equilibrium isotope effects. Such calculations for the bisected cyclopropylcarbinyl cation do not show opposite effects. However, they show that in both the endo and exo isomers the deuterium is favored in the cyclopropyl ring rather than on the cationic carbon.

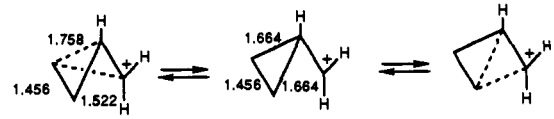
Myhre, Webb, and Yannoni[14] recently were able to freeze out the equilibria between bisected cyclopropylcarbinyl and bicyclobutonium ions below 60 K and recorded their ^{13}C NMR spectra using ultra-low temperature CPMAS techniques. At 60 K, they observed an absorption at $\delta(^{13}C)$ 235, attributable to the pentacoordinated methylene carbon of the bisected cyclopropylcarbinyl cation, the minor species. The IGLO calculated value for this carbon, $\delta(^{13}C)$ 245.2,[12] is in reasonable agreement with the experimental value. They also observed absorptions at $\delta(^{13}C)$ −15 and 55, assignable to the pentacoordinated carbon and the symmetrically related methylene carbons of the bicyclobutonium ion, the major isomer. The corresponding calculated IGLO values are $\delta(^{13}C)$ −24.7 and 67.1, respectively. It was not possible to assign the methine hydrogens of the bicyclobutonium ion, as the peaks were very broad at these extremely low temperatures. On the basis of the relative intensities of the peaks at $\delta(^{13}C)$ 235 (bisected cyclopropylcarbinyl cation) and $\delta(^{13}C)$ −15 (bicyclobutonium ion) at different temperatures, a $\Delta H°$ value of 0.05 kcal/mol was estimated for the equilibration of the bicyclobutonium ion with the bisected cyclopropylcarbinyl cation.

2. Conformational Barrier in $C_4H_7^+$ Cations and Their Potential Energy Surface Calculations

Cyclopropylcarbinyl cations can, in principle, adopt two conformations: bisected (**9**) and perpendicular (**10**). In the bisected conformation the vacant p orbital is parallel to the ring and is well aligned with the C1–C2 and C1–C3 bonds of the cyclopropane ring so that maximum overlap of the orbitals is achieved. In the perpendicular conformation, the vacant p orbital is perpendicular to the plane of the cyclopropane ring, and the overlap effectively becomes zero. Hence the bisected conformation is of lower energy than the perpendicular one.[15]

Sorensen and Kirchen[16] calculated, at the STO-3G level, the rotational barriers for the classical cyclopropylcarbinyl cation as 26.31 kcal/mol. They also estimated the barrier for interconversion from the NMR data; the cation was stable up to about −60 °C, and there was no line broadening at this temperature, and hence a minimum $\Delta G^{\ddagger}$ value of 11.4 kcal/mol was suggested. However, Koch and co-workers' recent theoretical calculations at correlated levels (MP4/6-311G**) show that the activation barrier for the interconversion of these isomers is only 0.6 kcal/mol, with the bisected conformer being more stable.[17] This value compares well with the experimentally estimated value of 1 ± 0.5 kcal/mol for the energy difference between the two isomers.[6] They further showed that 1-methylallyl cation was the global minimu, 9.0 kcal/mol more stable than the bisected conformer. Saunders and Schleyer's[12] and McKee's[18] calculations, on the other hand, indicated both conformers only as transition states. As shown by Koch,[17] only inclusion of correlation, at least up to MP2 level, predicts correctly the energies of these cations.

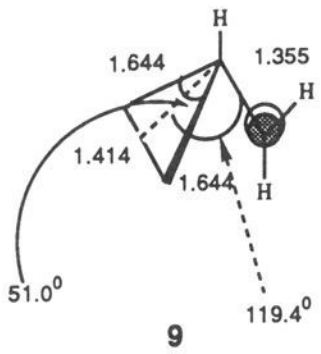
The potential energy surface in the $C_4H_7^+$ cations proved to be too complex to give any unequivocal answer. Earlier semiempirical MINDO/3 calculations by Dewar and co-workers indicated that both the bicyclobutonium and the bisected cyclopropylcarbinyl cation structures were minima, the latter being 5.6 kcal/mol less stable than the bicyclobutonium ion.[19a] They, however, pointed out that MINDO/3 underestimates strain energies in small rings, and hence the calculated heats of formation for the bicyclobutonium ions might be too negative. Assuming both the bisected cyclopropylcarbinyl cation and bicyclobutonium ion to be similar in energy, they obtained a realistic estimate of the barrier to their interconversion as 7–8 kcal/mol. The C1–C3 bond distance in the bicyclobutonium ion was calculated to be 1.714 Å, implying a relatively strong 1,3-transannular bond in this structure, resembling the protonated bicyclobutonium ion. The bisected cyclopropylcarbinyl cation was also formulated as equivalent to a π-complex formed by ethylene, as the π-donor, and the vinyl cation as the acceptor. The structure is further stabilized by back-donation of π-electrons from the vinyl cation into the antibonding orbital of ethylene. The planar cyclobutyl cation was calculated to be higher in energy than the bicyclobutonium ion by 9.6 kcal/mol and was proposed to act as a transition state connecting two mirror-image bicyclobutonium ions. Hehre's ab initio calculations show that the bisected cyclopropylcarbinyl cation is the lowest minimum, and the puckered cyclobutyl cation is a transition state connecting the equivalent bisected cyclopropylcarbinyl cations.[19b-d] At 6-31G*//4-31G level of calculations, they found[19e] two more minima (**9a** and **9b**) higher in energy by 0.5–1.0 kcal/mol than the most stable bisected cyclopropylcarbinyl cation (**9**). The puckered cyclobutyl cation was found to be 3.7 kcal/mol higher in energy than the bisected cyclopropylcarbinyl cation.[19c] The unsymmetrical bisected structures (**9a** and **9b**) have unequal C1–C2 and C1–C3 bond lengths, resembling the original bicyclobutonium ion proposed by Roberts.[3]



9a **9** **9b**

Recent ab initio calculations at very high levels of theory by McKee,[18] Saunders and Schleyer,[12] and Koch[17] also fail to agree with one another in providing a clear-cut potential energy surface, yet they all lead to the conclusion that inclusion of correlation in these

CHART 1



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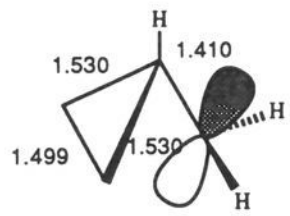
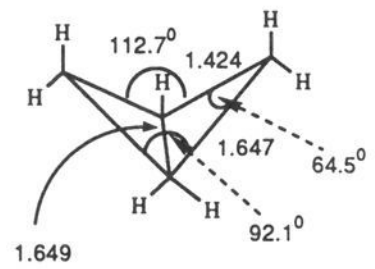
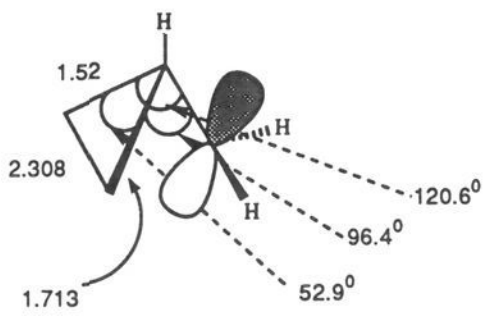


10
(at MP2/6-31G*)[12a]



10a



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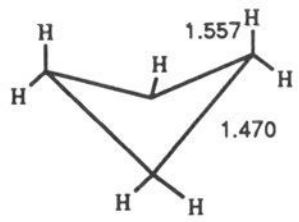
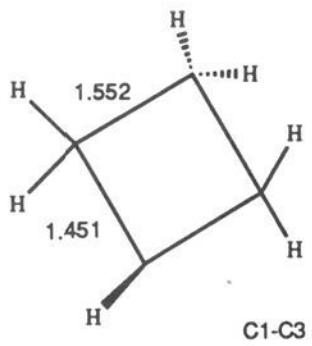


C1-C3 = 2.105 Å

11a
(at HF/6-31G*)[12a]



C1-C3 = 2.107 Å

11b
(at MP2/6-31G*)[12a]

calculations is essential to distinctly characterize the intermediates. At uncorrelated levels of theory, the bicyclobutonium ion was predicted to be higher in energy, acting as a transition state connecting the bisected cyclopropylcarbinyl cations. Inclusion of correlation at MP4(SDQ)/6-31G*//MP2/6-31G* showed the bicyclobutonium ion as the more favored structure by 0.7 kcal/mol.[18] At even higher level of theory at MP4(SDTQ)/6-311G**//MP2/6-31G** + ZPVE, both the bicyclobutonium ion and the bisected cyclopropylcarbinyl structures were shown to be similar in energy and above the global minimum, the 1-methylallyl cation, by 9.0 kcal/mol.[17] Harmonic frequencies and IR intensities for these isomers were also calculated at the MP2/6-31G* level. Selected MP2/6-31G** optimized[17] bond lengths (Å) and bond angles (deg) for the bisected and perpendicular cyclopropylcarbinyl cations (**9** and **10**), the bicyclobutonium ion (**10a**), cation **11** (the transition structure for **9** to **10**), puckered cyclobutyl cation (C_s, **11a**), and planar cyclobutyl cation (C_{2v}, **11b**) are as shown in Chart 1.

At the MP3(FC)/6-31G* level, it was found that the perpendicular structure (**10**) was less stable than the bisected structure (**9**) by 35.68 kcal/mol.[12a] Planar cyclobutyl cation of C_{2v} symmetry, **11b**, was found to be even less stable (by 36.93 kcal/mol than the bicyclobutonium ion at MP2(Full)/6-31G*). Saunders and co-workers also calculated[12a] the barriers for 1,2- and 1,3-hydrogen shifts. The transition structure for 1,2-hydrogen shift was found to be 19.6 kcal/mol less stable than the bisected cyclopropylcarbinyl cation and that for the 1,3-hydrogen shift by 43.9 kcal/mol.[12a] These activation parameters are within the experimentally obtainable limits.

Puckered cyclobutyl cation, **11a**, was found[12a] to collapse without activation barrier to the bicyclobutonium ion at MP2/6-31G* level, showing that this structure is not a minimum on the potential energy surface connecting **9** and **10a**. The 1,3-distance in this structure is 2.105 Å, while the corresponding distance in the bicyclobutonium ion, **10a**, is 1.649 Å, indicating that the more puckered structure of the bicyclobutonium ion involves additional stabilization of the cationic center by 1,3-transannular interaction. In conclusion one can say that the bicyclobutonium ion and σ-delocalized cyclopropylcarbinyl cation are of similar energies.

3. (1-Methylcyclopropyl)carbinyl Cation (1-Methylcyclobutyl Cation)

Ionization of 1-methylcyclobutyl chloride or (1-methylcyclopropyl)carbinyl chloride with SbF_5–SO_2ClF at −80 °C gave the same ^1H NMR spectrum.[20] The ion at −80 °C showed two singlets at δ 3.87 (CH_2) and 2.87 (CH_3) in a ratio of 2:1. Thus all the ring protons are rapidly equilibrated. The trideuteriomethyl analogue prepared from 1-(trideuteriomethyl)cyclobutyl chloride shows only one absorption at δ 3.89, and no proton–deuterium exchange occurred. Saunders and Rosenfeld proposed[20] equilibrating classical 1-methylcyclobutyl

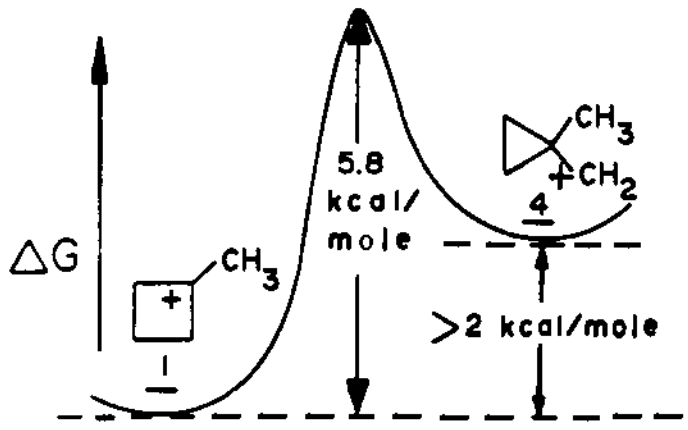
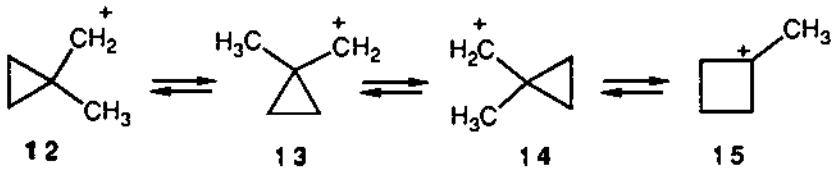


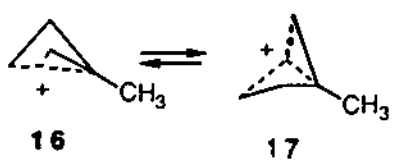
Figure 2. Potential energy diagram for the interconversion of 1-methylcyclobutyl cation (**15**) with 1-(α-methylcyclopropyl)-carbinyl cation (**12** or **13** or **14**) (reprinted from ref 16; copyright 1977 American Chemical Society).

and (1-methylcyclopropyl)carbinyl cations to account for these observations. At −25 °C, the ^{1}H NMR spectrum showed a quartet for the methylene and a septet for the methyl absorptions with a coupling constant of 0.9 Hz. At this temperature, the ion slowly rearranged to the static (cyclopropylmethyl)carbinyl cation with an activation energy of about 20 kcal/mol (^{1}H NMR δ 9.51 (m, 1 H), 4.4 (m, 5 H), 3.37 (3 H, d, J = 6.3 Hz).

Olah and co-workers obtained a ^{13}C NMR spectrum of 1-methylcyclobutyl cation at −80 °C.[21] It showed three absorptions at δ 163.1 (s), 48.7 (t), and 25.4 (q). The observation of a single average absorption for the methylenes was rationalized by the incorporation of rapidly equilibrating bisected σ-delocalized (1-methylcyclopropyl)carbinyl cations (**12**–**14**) exchanging with classical 1-methylcyclobutyl cation **15**. Involvement of equilibrating bicyclobutonium ions (**16** and **17**) was also considered.



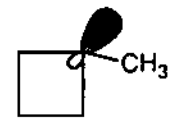
12 **13** **14** **15**



16 **17**

Sorensen and Kirchen[16] found that at −156 °C, the methylene peaks were no longer equivalent, but split into two peaks at δ 72.72 and −2.83 in a ratio of 2:1. Quaternary carbon at δ 163.1 and the methyl group at δ 25.4 remained relatively unchanged. From the temperature-affected line-broadening changes, they calculated the rate of exchange for the 1-methylcyclobutyl cation with the (1-methylcyclopropyl)carbinyl cation as 2.2×10^{-5} s^{-1} at −100 °C, with a free energy of activation of 5.8 kcal/mol. Figure 2 shows the free energy diagram for this interconversion process. The reverse barrier, i.e., the $\Delta G^{\ddagger}$ for (1-methylcyclopropyl)carbinyl cation to 1-methylcyclobutyl cation was estimated to be less than 3.8 kcal/mol, thus providing a rationale for the exclusive formation of 1-methylcyclobutyl products from the solvolysis of (1-methylcyclopropyl)carbinyl systems. On the basis of these observations, especially the high-field methylene absorption at δ −2.83, they postulated a classical, but sp^3-hybridized, static 1-methylcyclobutyl cationic structure (**18**).

The highly shielded peak at δ −2.83, however, suggests definite involvement of a bridged species. Also, a strained sp^3-hybridized trivalent carbocationic center

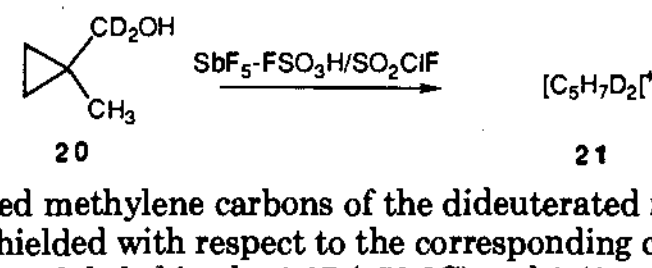


18

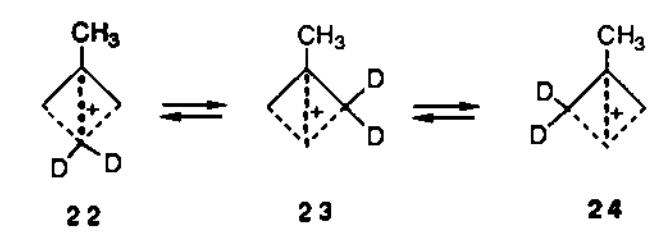
would be expected to show absorptions at much lower field than the observed value of δ(^{13}C) 163.1, based on comparison with nonplanar carbocations such as the 1-adamantyl (δ(^{13}C) 299) and 1-bicyclo[3.3.3]undecyl cation (δ(^{13}C) 356.3). Consequently Olah and co-workers interpreted the results at low temperatures as involving a degenerate set of σ-delocalized bicyclobutonium ions (**16** and **17**) rapidly interconverting through a symmetrical σ-delocalized species (**19**), or static ion, **19**, itself.[22]

19

Olah and co-workers subsequently studied deuterium isotope effects on the ^{13}C NMR behavior of the cation.[23] α,α-Dideuterio-1-methylcyclobutyl cation (**21**) was prepared from α,α-dideuterio(1-methylcyclopropyl)-carbinol (**20**) at −78 °C. At this temperature the unlabeled methylene carbons of the dideuterated ion, **21**, are shielded with respect to the corresponding carbons of the unlabeled ion by 1.27 (−50 °C) and 1.41 ppm (−90 °C), indicating involvement of an equilibrium isotope effect. The deuterium-labeled methylene carbon of ion **21** (quintet, J_{CD} = 27.4 Hz) was deshielded from the undeuteriated methylene by 2.91 ppm at −50 °C. Small temperature-dependent changes of ∼0.14 ppm were observed between −50 to −90 °C. Equilibration of σ-delocalized cyclopropylcarbinyl cations, by exchange of the methylene carbons, can account for these results. The observation that the deuteriated methylenes are deshielded from the undeuteriated methylenes indicates that in the equilibrium, which averages the methylenes, structure **22**, which contains deuterium on the pentacoordinated carbon, is less preferred over structures **23** and **24**.



20 **21**



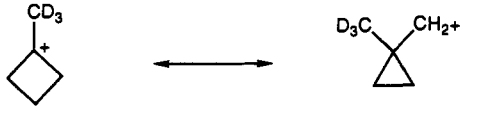
22 **23** **24**

At −154 °C, undeuteriated methylenes of ion **21** split into absorptions at δ 71.3 and −2.14, whereas the quaternary and the methyl carbons are observed at δ(^{13}C) 161.72 and 25.06, respectively. These chemical shifts are virtually identical with those of corresponding unlabeled ions, except for small intrinsic deuterium induced isotopic shifts. Thus, at −154 °C, the ion is not equilibrating σ-delocalized cyclopropylcarbinyl cations (**12**–**14**) but an asymmetrically delocalized bicyclobutonium ion (**19**). This ion, alternatively, can be thought of as a resonance hybrid of unsymmetrically

delocalized bicyclobutonium ions (16 and 17). Schindler theoretically calculated the ^{13}C NMR chemical shifts of the 1-methylbicyclobutonium ion, and they showed good agreement with the experimental values.[12b]

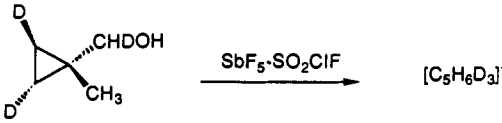
Siehl confirmed the above equilibrium isotope effect in the α,α-dideuterio-1-methylcyclobutyl cation and also studied the α-monodeuterio analogue.[24] The ^{13}C NMR spectrum of a mixture of monodeuterio and unlabeled 1-methylcyclobutyl cation showed more clearly the effect of the equilibrium isotope effect. The triplet (J_{CD} = 25.3 Hz) due to the deuteriated carbon in the monodeuterio cation is deshielded by 0.898 (−80 °C) and 0.536 (−46 °C) compared to the unlabeled ion. These results are in accordance with the conclusion reached by Olah and co-workers,[23] namely, in the equilibrium which averages the methylenes, structures having a pentacoordinated carbon with a deuterium attached to it are less preferred over structures that contain deuterium on the tricoordinated carbon.

Servis and Shue[25] examined the β-deuterium kinetic isotope effects on carbocationic carbon chemical shifts for several cations and their data for 1-(trideuteriomethyl)cyclobutyl cation shows that the carbocationic chemical shift of the former ($\delta(^{13}C)$ 161.3) is more shielded than that of the unlabeled ion ($\delta(^{13}C)$ 162.4). Such shieldings due to deuterium substitution were interpreted to be due to the involvement of nonclassical σ-delocalization in the cation. By the same criterion, classical static carbocations showed deshielding for the deuteriated ions compared to the unlabeled ions. In the classical ions, the positive charge on the cationic center is stabilized by inductive and hyperconjugative effects of the neighboring methyl group. Since the hyperconjugative stabilization by the CD_3 group is smaller than that of CH_3, the cationic center is more deshielded for the deuterio analogue. In the nonclassical ions, on the other hand, the cationic center is stabilized by neighboring σ- or π-participation, and additional stabilization from the adjacent methyl groups is not required. The small observed shielding was interpreted as due to the perturbation of resonance by the CD_3 substituent, resulting in the decreased contribution of 1-(trideuteriomethyl)cyclobutyl cation (25) to the resonance hybrid.



25 25a

The nonplanarity of the 1-methylcyclobutyl cation was finally demonstrated by Saunders and Krause.[26] They prepared α,β,α'-trideuteriated-1-methylcyclobutyl cation (27) from the stereospecifically deuterium-labeled precursor, (*trans*-2,3-dideuterio-1-methylcyclopropyl)-deuteriomethanol (26) by ionization with SbF_5–SO_2ClF.



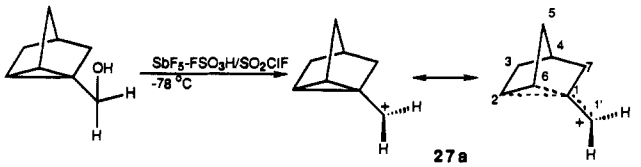
26 27

The ^1H NMR spectrum showed two peaks in a ratio of 2:1 for the methylene protons of α,β,α'-trideuterio ion 27 deshielded from the methylene protons of the unlabeled ion. The downfield shifts were also slightly temperature dependent. The high intensity peak shifted by between 0.065 (−100 °C) to 0.045 ppm (−30 °C). The methyl group's absorption remained unchanged. The splitting of the methylene group absorptions was interpreted as due to the isotopic perturbation to the inversion of the nonplanar structure. If the structure were planar, one would have expected to observe just one absorption for all the methylene hydrogens, since the geminal hydrogens are equivalent in the planar structure. The deshielding of the absorptions due to deuteriated methylenes compared to the corresponding hydrogens of the unlabeled ion was interpreted by invoking the presence of a minor species in equilibrium with the major isomer. The nature of the minor species, however, is not yet clear. On the basis of the above discussion it is safe to conclude that the methylbicyclobutonium structure is the ground-state structure for the species obtained by the ionization of 1-methylcyclobutyl or (α-methylcyclopropyl)carbinyl derivatives.

B. Static Cations

1. Nortricyclylcarbinyl Cation

Sorensen and co-workers prepared the primary nortricyclylcarbinyl cation (27a) by ionizing the corresponding nortricyclylcarbinol with SbF_5–SO_2ClF.[27]



27a

The ion was stable up to −20 °C. ^1H NMR spectrum showed the anti and syn C1′-H at δ 7.83 and 7.61, respectively. The difference in chemical shifts, $\Delta\delta$ = 0.22 ppm, is similar in magnitude to those of other typical bisected cyclopropylcarbinyl cations. The other ^1H absorptions included δ 5.95 (C2-H, C6-H), 1.91 and 1.82 (C3-H, C5-H), 2.62 (C4-H), 1.63 (C7-H). A ^{13}C NMR spectrum showed peaks at δ 113.5 (C1), 191.4 (C1′), 112.9 (C2, C6), 39.8 (C3, C5), 36.5 (C4), 31.0 (C7). This ion represents the only known example of a primary, static bisected cyclopropylcarbinyl cation. C_1–$C_{1'}$ bond rotational barrier in this cation is also unusually high, as there was no sign of any rotation on the NMR time scale up to −20 °C. The high stability of the cation, and the high rotational barrier was postulated to be due to the contribution of a vinyl-bridged 2-norbornyl cation structure to the resonance hybrid. By using isodesmic reaction analysis, the relative ratio of the contributions of the vinyl bridged species and the cyclopropyl–carbinyl cations was calculated as 57:43. This contributing ratio is considerably higher than that in the analogous (α,β,β-trimethylcyclopropyl)carbinyl cation, where it was found to be approximately equal.[28]

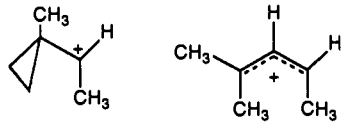
III. Secondary Cyclopropylcarbinyl Cations

A. Equilibrating (Degenerate) Cations

1. 1-(1-Methylcyclopropyl)ethyl Cation

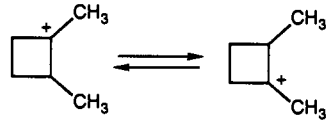
1-(1-Methylcyclopropyl)ethanol was ionized with SbF_5 in SO_2ClF solution at −78 °C to give the cation 28.[29] The cation at the lowest temperature studied (−119 °C) shows five absorptions in the ^{13}C NMR

spectrum: $\delta(^{13}C)$ 210.5 (C^+), 88.9 (quaternary C), 55.6 (CH_2), 23.8 (C^+-CH_3), 16.2 (CH_3). These chemical shifts stay relatively unchanged up to −98 °C. Thus, the ion is a static classical species below −98 °C. On warming, the signals for the two methyl groups coalesce. At −73 °C, they appear as a single peak at $\delta(^{13}C)$ 20.8, indicating a degenerate equilibrium at higher temperatures. Consistent with this proposal, the cationic center and the quaternary carbon absorptions broaden into the base line. Above −39 °C, the ion irreversibly rearranges to the 1,1,3-trimethylallyl cation (**29**).



28 **29**

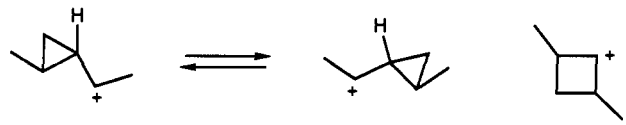
The equilibration at higher temperatures may involve the equilibrating enantiomeric 1,2-dimethylcyclobutyl cations, **30** and **31**, as intermediates. Since the latter species could not be observed by NMR, the 1-(1-methylcyclopropyl)ethyl cation (**28**) must be at least 2 kcal/mol more stable than the cyclobutyl intermediates. The absorptions for the methyl groups of **28** coalesce at −80 °C, in the ^{13}C NMR spectrum, and at −95 °C, in ^1H NMR spectrum, respectively. On the basis of these coalescence temperatures (T_c), an approximate energy barrier of 8.9 ± 0.5 kcal/mol (by ^{13}C NMR), or 8.6 ± 0.5 kcal/mol (by ^1H NMR) was estimated for the 1,2-hydride shift in the intermediate 1,2-dimethylcyclobutyl cation. Assuming the symmetrically 1,2-hydrogen-bridged species as the transition state for the rearrangement, Schleyer and Chandrashekhar calculated[30] an activation barrier of 7.9 kcal/mol (STO-3G) for the 1,2-hydride migration for the cyclobutyl cation. This value closely resembles the estimated barrier for **30** to **31**.



30 **31**

2. 1-(2-Methylcyclopropyl)ethyl Cation

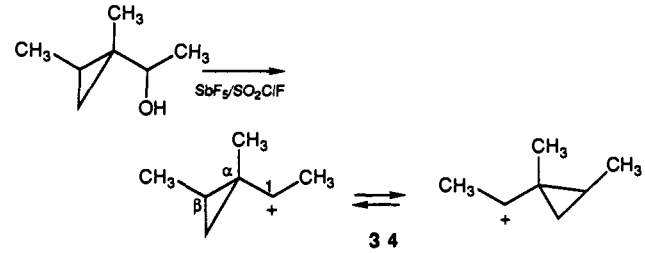
Ionization of (*E*)-1-(2-methylcyclopropyl)ethanol in SbF_5–SO_2ClF solution at −78 °C provided the secondary cyclopropylcarbinyl cation (**32**).[31] A ^{13}C NMR spectrum showed four absorptions at $\delta(^{13}C)$ 167.4 (d, J_{CH} = 177.6 Hz, C^+, and β-CH)), 81.2 (d, J_{CH} = 192.1 Hz, α-CH), 55.9 (t, CH_2), and 25.9 (q, CH_3). The equivalence of the methyl absorptions and the C^+ and β-CH absorptions show that the ion is undergoing a fast 2-fold degenerate rearrangement on the NMR time scale. At −108 °C, the averaged cationic center peak $\delta(^{13}C)$ 167.4) merged into the base line, indicating that the equilibration is occurring with an activation barrier of less than 5 kcal/mol. The equilibration may proceed through an unpopulated secondary 2,4-dimethylcyclobutyl cation intermediate or transition state (**33**).



32 **33**

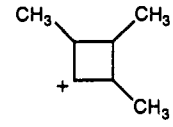
3. 1-(cis-1,2-Dimethylcyclopropyl)ethyl Cation

1-(*cis*-1,2-Dimethylcyclopropyl)ethanol on ionization with SbF_5–SO_2ClF at −78 °C provided the cation **34**, which also showed 2-fold degenerate equilibration on the NMR time scale.[31]



34

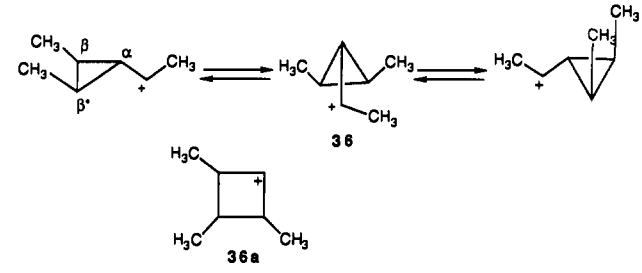
It gave ^{13}C NMR absorptions at δ 160.7 (d, J_{CH} = 173.3 Hz, C^+, β-CH), 90.1 (s, C_α), 56.2 (t, CH_2), 21.6 (q, Cl-CH_3 and β-CH_3), and 14.6 (q, α-CH_3). The β- and 1-methyl signals are averaged (δ 21.6), as are also the cationic center and β-methine carbons (δ 160.7). Attempts to freeze out the equilibrium were not successful even at −130 °C, although the averaged cationic center and β-methyne signals merge into the base line at −100 °C, indicating an activation barrier of less than 5 kcal/mol. A puckered, 1,2,4-trimethylcyclobutyl cation (**35**) may be a transition state or an unpopulated intermediate in the equilibration process.



35

4. 1-(cis-2,3-Dimethylcyclopropyl)ethyl Cation

Ionization of 1-(*cis*-2,3-dimethylcyclopropyl)ethanol in SbF_5–SO_2ClF solution at −78 °C provided the cation **36**, whose ^{13}C NMR spectrum showed three signals at $\delta(^{13}C)$ 137.3 (J_{CH} = 163.7 Hz, C^+, β-CH, and β′-CH)), 89.1 (J_{CH} = 181.2 Hz, α-CH), and 19.8 (q, CH_3).[31] Observation of only three signals indicates that the ion exists as a 3-fold degenerate species. A very low barrier for the interconversion was indicated by the inability to freeze the equilibrium process even at −140 °C. Puckered 2,3,4-trimethylcyclobutyl cation (**36a**) was postulated as an intermediate or a transition state.



36 **36a**

5. 8,9-Dehydro-2-adamantyl Cation

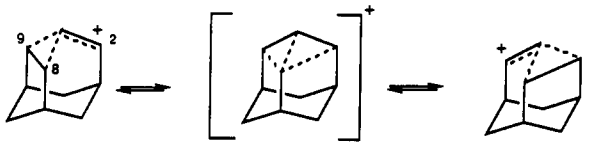
From the unusual rate acceleration observed for the solvolysis of 8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate (10^6 times more reactive than the cyclopropylcarbinyl dinitrobenzoate, and the corresponding extrapolated value for the tosylate was 4×10^8 times higher than for 2-adamantyl tosylate), Baldwin and

TABLE 3. ^{13}C Chemical Shifts for 2,4-Dehydro-5-homoadamantyl Cation (43)

	T, °C	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
static	-110	29.3	127.8	86.5	82.9	239.3	42.3	27.9	24.1	23.4	30.7	61.1
degenerate	-45	35.4	(183.6)	88.4	83.5	(183.6)	35.4	26.5	24.5	26.5	31.3	61.1

Foglesong proposed equilibrating bridged nonclassical structures **37** and **38** for the charge delocalized 8,9-dehydro-2-adamantyl cation[32] (Scheme 3). The ion

SCHEME 3



37 39 38

linking the degenerate cyclopropylcarbinyl cations (**37** and **38**) was represented as a bicyclobutonium-type ion (**39**). The 2-deuterio and 2-tritio analogues of 8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate, on solvolysis, gave the 8,9-dehydro-2-adamantanol, in which the label was scrambled nearly equally between carbons 2, 8, and 9. This complete scrambling of the deuterium label was interpreted as due to 3-fold degenerate rearrangement involving structures **37** and **38**, by the migration of the C8–C9 bond to the cationic center. The involvement of a transitory intermediate, C_s symmetric ion (**39**), was also supported by extended Hückel molecular orbital calculations.[33]

The 8,9-dehydro-2-adamantyl cation was subsequently synthesized under stable ion conditions, and characterized by NMR spectroscopy by Olah, Murray, and co-workers.[34] It was obtained by reacting 2-hydroxy-8,9-dehydroadamantane with FSO_3H in SO_2ClF at −120 °C, and from 4-*endo*-hydroxy-2,5-dehydroprotoadamantane or 4-*endo*-chloro-2,5-dehydroprotoadamantane by reacting with SbF_5–SO_2ClF at −120 °C.

Ionization of 2-*exo*-hydroxyprotoadamantane with SbF_5–SO_2ClF solution at −120 °C also gave the dehydroadamantyl cation (about 25%), along with polymerized material. The ^1H and ^{13}C NMR spectra for the ion are shown in Figure 3.

The ^1H NMR spectrum shows a highly deshielded doublet of doublets at δ 7.96 (3 H) due to hydrogens on C2, C8, and C9 carbons, a quartet at δ 4.92 (1 H) due to the proton on C1, and two broad peaks at δ 3.20 (3 H) and 2.60 (6 H) for the remaining bridgehead, and methylene protons, respectively. From these data it was inferred that the ion is undergoing a facile 3-fold degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement, fast on the NMR time scale even at −120 °C. Consistent with the above interpretation, the ^{13}C NMR spectrum of the ion also shows only four signals: δ(^{13}C) 157.0 (δ, J = 177.7 Hz, C2, C8, C9), 85.1 (δ, J = 186.2, C1), 49.3 (t, J = 134.2 Hz, C4, C6, C10), and 38.2 (δ, J = 143.2 Hz, C3, C5, C7).

The degenerate rearrangement of **40** and **41** was postulated to proceed through the 2,5-dehydro-4-protoadamantyl cation (**42**), formed by C_1–C_9 bond migration to the cationic center. This explanation is also substantiated by the fact that the same cation was also formed from 2,5-dehydro-4-protoadamantyl derivatives.

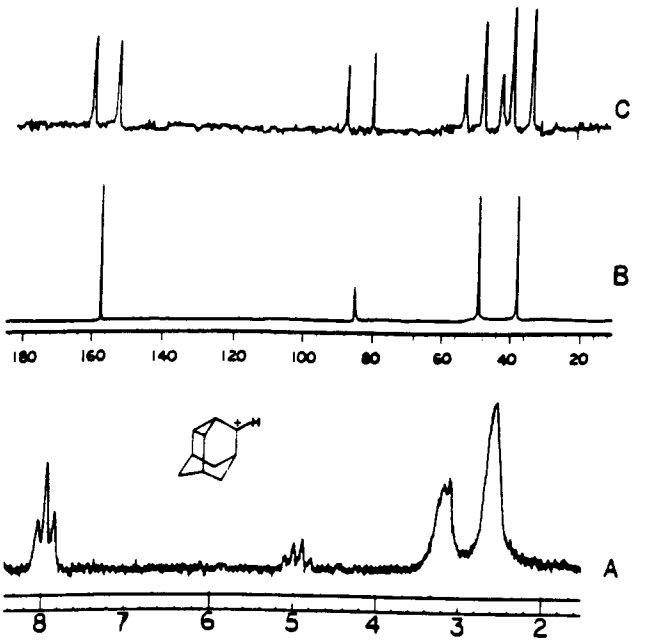
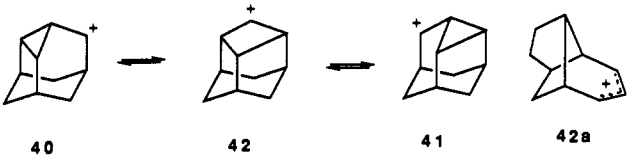


Figure 3. NMR spectra for 8,9-didehydro-2-adamantyl cation (**40** or **41**): (A) ^1H NMR (60 MHz) spectrum of in FSO_3H–SO_2ClF at −120 °C; (B) proton-decoupled ^{13}C NMR spectrum; (C) proton-coupled ^{13}C NMR spectrum (reprinted from ref 34; copyright 1978 American Chemical Society).

Upon warming to −78 °C, the ion rearranged into the allylic cation **42a** by a sequence of Wagner–Meerwein and hydride shifts.

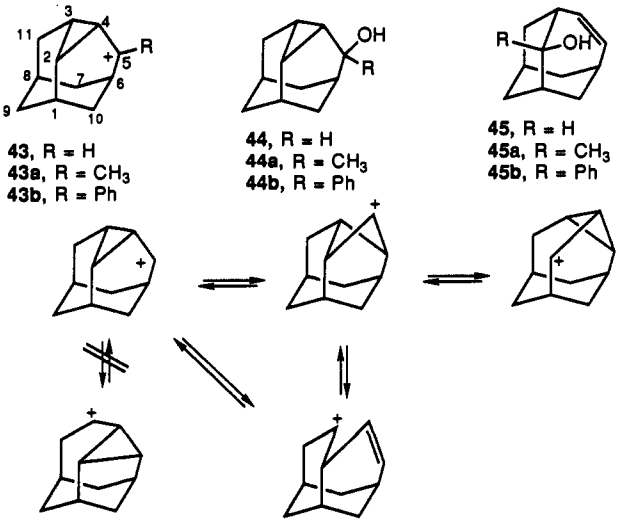


40 42 41 42a

6. 2,4-Dehydro-5-homoadamantyl Cation

2,4-Dehydro-5-homoadamantyl cation (**43**, Scheme 4) was prepared from the corresponding 2,4-dehydro-5-

SCHEME 4



43, R = H
43a, R = CH_3
43b, R = Ph

44, R = H
44a, R = CH_3
44b, R = Ph

45, R = H
45a, R = CH_3
45b, R = Ph

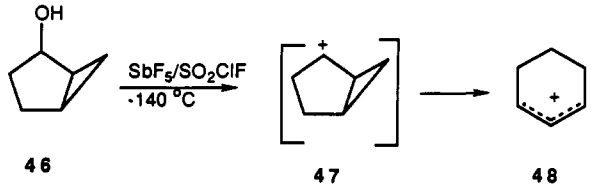
homoadamantanol (44) or the 2-homoadamant-4-enyl alcohol (45) by reacting with FSO_3H in SO_2ClF at −120 °C.[35] The ion showed ^{13}C and ^1H NMR spectral characteristics similar to 3-nortricyclyl cations (vide infra), indicating it to be a classical ion with charge delocalization into the cyclopropane ring. The ion is static at −110 °C and shows 11 ^{13}C NMR signals. At −45 °C, the ^{13}C NMR spectrum has only eight signals (Table 3). C2, C5 carbons, C1, C6 carbons, and C7, C9 carbons can be equivalent if the ion undergoes degenerate equilibration by initial cleavage of the C_3–C_4 bond to form the puckered cyclobutyl cation or the homoallyl cation, followed by ring closure to give the enantiomeric cation. Participation of the C2–C3 bond would be expected to give a nondegenerate ion, which, however, could not be detected by NMR. This is an indication that the C3–C4 bond is better aligned with the empty p orbital on the cationic center than the C2–C3 or C2–C4 bonds.

The degenerate rearrangement in the cation has a much higher activation energy than that of the parent 8,9-dehydro-2-adamantyl cation (24), whose 3-fold degenerate equilibria could not be frozen out even at −120 °C.

7. Bicyclo[n.1.0]alkyl Cations and Their Degenerate Rearrangements

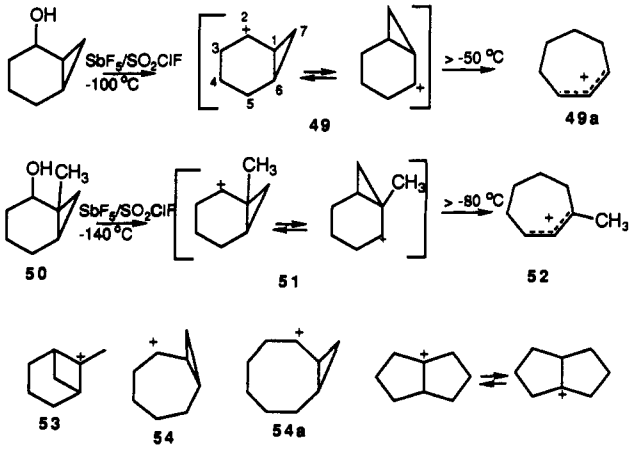
Several bicyclo[*n*.1.0]alkyl cations were prepared and their facile degenerate rearrangements were studied by Olah and co-workers.[36] The ^{13}C NMR chemical shift data are provided in Table 4.

Ionization of bicyclo[3.1.0]hexan-2-ol (46) in SbF_5–SO_2ClF at −140 °C gave cyclohexenyl cation 48 presumably through initially formed unstable bicyclo[3.1.0]hex-2-yl cation (47).



a. Bicyclo[4.1.0]hept-2-yl Cation (49). Ionization of bicyclo[4.1.0]heptan-2-ol in SbF_5–SO_2ClF at −100 °C gave bicyclo[4.1.0]hept-2-yl cation (49, Scheme 5) which showed seven signals in the ^{13}C NMR, indicating it as a static ion at this temperature. As the solution was warmed to −50 °C, signals due to C2, C6 and C3, C5 averaged out at $\delta(^{13}C)$ 179.8 and 32.3, respectively, indicating that the cation is undergoing degenerate equilibration at higher temperatures, presumably through the unpopulated bicyclo[3.1.1]hept-2-yl cation. Above −50 °C, the cation, irreversibly rearranges to the cycloheptenyl cation 49a.

SCHEME 5



b. 2-Methylbicyclo[4.1.0]hept-2-yl Cation (51). Ionization of 2-methylbicyclo[4.1.0]heptan-2-ol (50) in SbF_5–SO_2ClF at −140 °C gave the degenerate 2-methylbicyclo[4.1.0]hept-2-yl cation (51) whose ^{13}C NMR spectrum showed equivalence of the C2, C6 and C3, C5 carbons. The ion is stable up to −80 °C, above which it rearranges rapidly to the 3-methyl-3-cycloheptenyl cation (52). As the degeneracy of the ion could not be frozen out even at −140 °C, an activation barrier of less than 6.0 kcal/mol was predicted for this rearrangement. The degenerate equilibration may proceed through 2-methylbicyclo[3.1.1]hept-2-yl cation (53).

c. Bicyclo[5.1.0]oct-2-yl Cation (54). Bicyclo[5.1.0]octan-2-ol upon ionization in SbF_5–SO_2ClF at −139 °C gave stable bicyclo[5.1.0]oct-2-yl cation (54) which rearranged to the thermodynamically more stable bicyclo[3.3.0]oct-1-yl cation at temperatures above −100 °C.

d. Attempted Preparation of Bicyclo[6.1.0]non-2-yl Cation (54a). Bicyclo[6.1.0]nonan-2-ol (103) upon ionization in FSO_3H–SO_2ClF or SbF_5–SO_2ClF at −140 °C gave only the rearranged 1-cyclopropyl-1-cyclohexyl cation (100, Table 4), which may have formed through a series of hydride and Wagner–Meerwein shifts from the incipient bicyclo[6.1.0]non-2-yl cation (54a) (vide infra).[36]

9. 3-Tricyclo[3.2.1.0^{2,7}]octyl (3-Homonortricyclyl) Cation

Bicyclo[3.2.1]oct-3-en-2-ol (55) was transformed to 3-homonortricyclyl cation (57) by treating it with SbF_5–SO_2ClF at −78 °C, and subsequent warming of the intermediate bicyclo[3.2.1]oct-3-en-2-yl cation (56) to 20 °C[37] (Scheme 6). Homonortricyclanol (57a), under the same conditions, also gave the same cation. The formation of homonortricyclyl cation 57 from 56 was

SCHEME 6

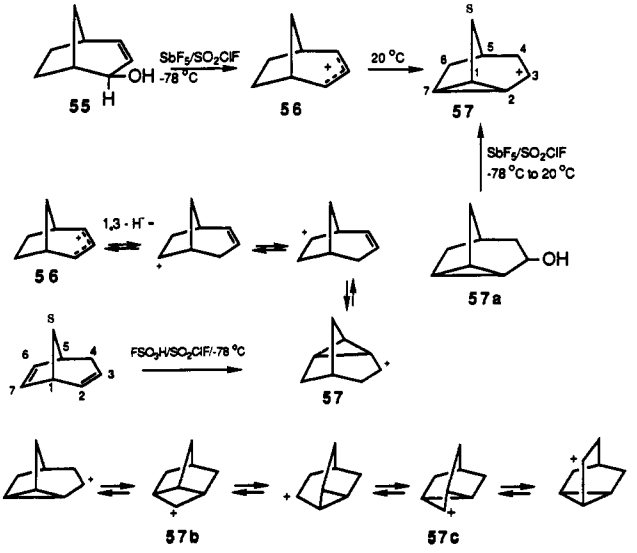


TABLE 4. ^{13}C NMR Data for Some Bicyclo[n.1.0]alkyls and Their Rearranged Cations

cation	T, °C	C1	C2	C3	C4	C5	C6	C7	others
49	-50	76.60	179.8	32.30	23.50	32.30	179.80	55.60	
	-110	76.50	238.9	38.1	23.50	25.80	109.6	55.40	
99	-80	80.1	271.8	42.60	23.30	21.20	65.50	53.50	37.1 (Me)
51	-90	89.0	178.30	32.10	25.80	32.10	178.30	59.00	23.9 (Me)
54	-139	69.5	215.30	br	br	br	74.1	60.20	
100	-80	287.5	51.0	35.3	25.9	35.3	40.1	-	54.5 (a), 52.3 (b)

TABLE 5. ^{13}C NMR Data for 3-Homonortricyclyl Cation (57)

	T, °C	C1	C2	C3	C4	C5	C6	C7	C8
static	-85	85.64	81.26	234.1	43.62	31.56	31.56	85.64	31.56
degenerate	20	(135.8)	82.28	(135.18)	36.19	32.47	36.19	(135.18)	36.19

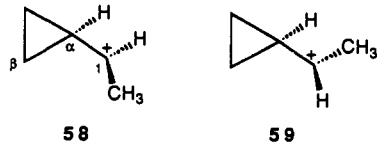
postulated to involve initial 1,3-hydride shift from C7 to C2, followed by a 1,2-hydride shift from C6 to C7 and a subsequent homoallylic rearrangement. This mechanism was also consistent with the fact that the cation could also be generated from bicyclo[3.2.1]octa-2,6-diene by fluorosulfuric acid. The latter process involves protonation of the C6–C7 bond rather than the C2–C3 bond, giving the same postulated intermediates as for **56** to **57**. Once formed, the cation shows temperature-dependent degenerate rearrangement between −100 °C to 20 °C. Below −80 °C, it is a static cation. At 20 °C, signals due to C4, C6, and C8 were averaged out to a single peak at $\delta(^{13}C)$ 36.19, signals due to C1, C3, and C7 at $\delta(^{13}C)$ 135.8, merged into the base line and the signals due to C2 and C5 remained unchanged. Complete ^{13}C NMR data with assignments are summarized in Table 5. The degenerate equilibration may proceed through the intermediate puckered cyclobutyl cations, **57b** and **57c**.

B. Static Cations

Several secondary cyclopropylcarbinyl cations, including the parent (α-methylcyclopropyl)carbinyl cation, the dicyclopropylmethyl cation, and other related secondary cations were reviewed earlier.[1b] Hence these previously discussed ions are not included in the current discussion.

1. (α-Methylcyclopropyl)carbinyl Cation

Of the two stereoisomers possible for the ion, the thermodynamically more stable trans isomer **59**, was formed on reaction of the cyclopropylmethylcarbinol with SbF_5–SO_2ClF at low temperatures.[5] Preparation of the cis isomer **58** was achieved by ionizing *cis*-2-



58 59 60

chloro-1-methylcyclobutane or *cis*-3-chloro-1-methylcyclobutane in SbF_5–SO_2ClF at −135 °C, and the NMR spectra were recorded at −125 °C.[38] On warming to −80 °C, it cleanly transformed to the trans isomer. That the equilibrium does not involve simple rotation of C_1–C_α bond, but involves an intermediate (*E*)-1-ethylallyl cation **60**, was shown by following the rearrangement of **58** by NMR spectroscopy. The spectral data for these three ions are provided in Table 6. The

TABLE 6. ^1H and ^{13}C NMR Chemical Shifts for 58–60[a]

	H_1	H_α	H_β(cis)	H_β(trans)	CH_3
58	10.07	3.75	3.75	3.87	2.23
59	8.78	3.75	3.51	3.73	2.57

	C_1	C_α	C_β	CH_3
58	257.5	65.3	66.1	26.4
59	252.2	66.7	59.9	32.7

	H_1	H_2	H_3(syn)	H_3(anti)	CH_2	CH_3
60	10.14	7.81	8.19	8.46	3.45	1.07

	C_1	C_2	C_3	CH_2	CH_3
60	258.0	146.5	199.6	46.4	9.0

[a] Taken from ref 38.

kinetics of this equilibrium were calculated yielding the following parameters at −100 °C.

$$\mathbf{58} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{60} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{59}$$

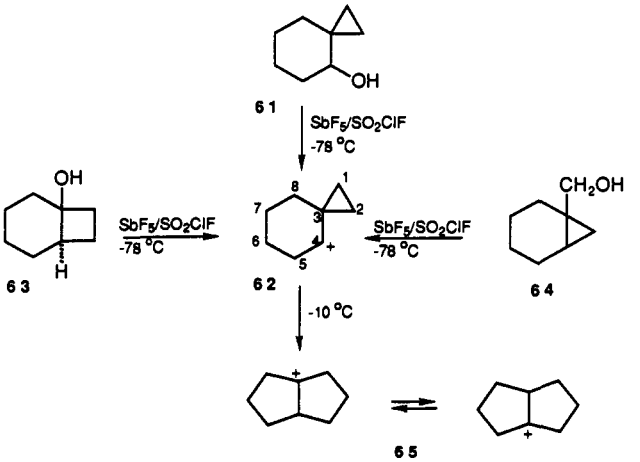
$$K(\mathbf{59}/\mathbf{58}) = 50$$

$$k_1 = 7 \times 10^{-4}\ s^{-1}\ \Delta G^\ddagger = 12.5\ kcal/mol$$
$$k^{-1} = 9 \times 10^{-4}\ s^{-1}\ \Delta G^\ddagger = 12.4\ kcal/mol$$
$$k_2 = 3.5 \times 10^{-4}\ s^{-1}\ \Delta G^\ddagger = 12.7\ kcal/mol$$

2. Spiro[2.5]oct-4-yl Cation

Spiro-fused cyclopropyl groups stabilize the adjacent cation center, making possible the observation of hitherto unobserved secondary cyclohexyl cations.[39] Spiro[2.5]octan-4-ol (**61**) was ionized with SbF_5–SO_2ClF at −78 °C to provide cation **62** (Scheme 7) which showed

SCHEME 7



^{13}C absorptions at $\delta(^{13}C)$ 201.1 (d, J_{CH} = 170.5 Hz, C4), 95.0 (s, C3), 51.5 (t, J_{CH} = 178.1 Hz, C1, C2), 34.9 (t, C5), 29.3 (t, C8), 21.0 (t, C6), 19.2 (t, C7) (Figure 4).

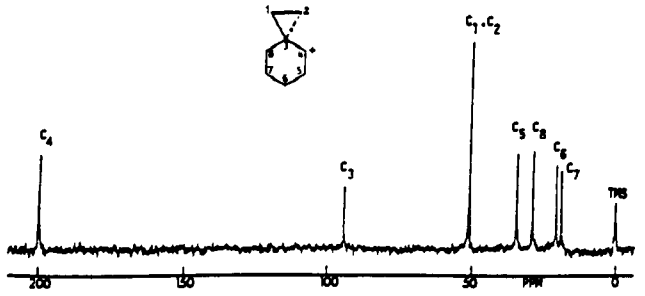
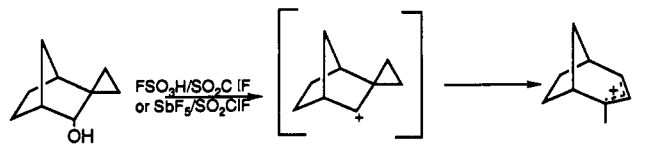


Figure 4. Proton-decoupled ^{13}C NMR spectrum of the spiro-[2.5]oct-4-yl cation in SbF_5–SO_2ClF at −80 °C (reprinted from ref 39; copyright 1981 American Chemical Society).

The same ion was also obtained by ionization of *trans*-bicyclo[4.2.0]octan-1-ol (**63**) or bicyclo[4.1.0]-hept-1-ylmethanol (**64**) in SbF_5–SO_2ClF at −78 °C. The equivalence of the cyclopropyl methylene signals is in accordance with a bisected geometry of the cyclopropane ring with respect to the empty p orbital of the cationic center. The secondary cation upon warming to −10 °C, irreversibly rearranges to the thermodynamically more stable rapidly equilibrating bicyclo[3.3.0]-oct-1-yl cation **65**. Involvement of this cation as an intermediate in solvolysis reactions was postulated earlier.[40a,b]

3. 3-Spirocyclopropyl-2-norbornyl and Related Cations

Spirocyclopropyl stabilization of the carbenium centers in 2-bicyclo[2.1.1]heptyl systems was anticipated from previous solvolysis data.[41a,b] However, 3-spirocyclopropyl-2-norbornanol upon ionization under stable ion conditions did not yield the expected 3-spirocyclopropyl-2-norbornyl cation (**66**); instead, the rearranged 2-methylbicyclo[3.2.1]oct-3-en-2-yl cation (**67**) was the only observed cation.[41c] The participation of the cyclopropyl group in the incipient cation **66** leads to the more stable allylic ion **67**.

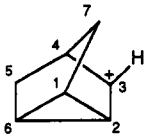


Tertiary 2-methyl-, 2-phenyl-, and 2-cyclopropyl-3-spirocyclopropyl-2-norbornyl cations (2-R-**66**) were prepared from the corresponding alcohols in SbF_5 + SO_2ClF/SO_2ClF.[41d] From the observed ^{13}C NMR chemical shifts of these cations it was evident that the 3-spirocyclopropyl group effectively dominates the norbornyl C1–C6 bond in the charge dispersal. Whereas the 2-cyclopropyl-3-spirocyclopropyl-2-norbornyl cation was stable up to −20 °C, the former two cations rearranged at higher temperatures to 2,4-dimethylbicyclo-[3.2.1]oct-3-en-2-yl cation (4-Me-**67**), and 2-methyl-4-phenylbicyclo[3.2.1]oct-3-en-2-yl cation (4-Ph-**67**), respectively.

Attempted preparation of the homologous 3-spirocyclopropyl-2-bicyclo[2.2.2]octyl cation also resulted in the ring opening rearrangement to give 2-methylbicyclo[3.2.2]non-3-en-2-yl cation.[41e]

4. 3-Nortricyclyl Cation (Tricyclo[2.2.1.0^{2,6}]hept-3-yl) Cation

The cyclopropyl ring in 3-nortricyclyl cations is oriented in the bisected conformation with respect to the cation center. Maximum charge delocalization is therefore expected in this cation. The parent 3-nortricyclyl cation (**68**) was generated from 3-nortricyclanol



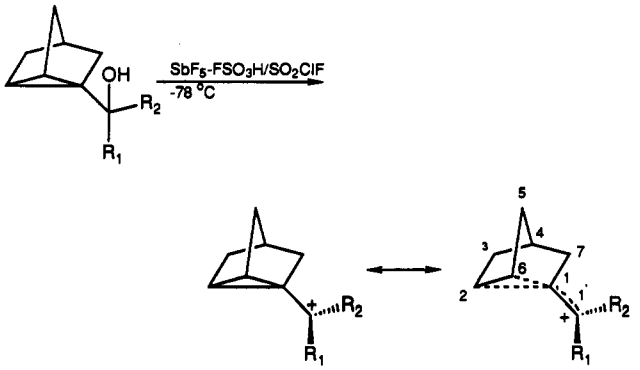
68

and characterized by ^1H and ^{13}C NMR spectroscopy[42] [^{13}C NMR: $\delta(^{13}C)$ 258.5 (C3), 116.6 (C1, C6), 86.3 (C2), 46.6 (C5, C7), 42.4 (C4)]. The carbocationic carbon peak ($\delta(^{13}C)$ 258.5) is highly deshielded, as are the cyclopropane ring carbons, suggesting that the cation is a classical type of carbenium ion with significant charge delocalization into the cyclopropane ring. The two equivalent cyclopropyl carbons (C1 and C6) are deshielded by 25 ppm from the (C2) carbon. The difference in chemical shift ($\Delta\delta$ C1(C6) − C2) is highest for this parent cation and varies with the degree of charge delocalization into the cyclopropane ring, in the corresponding tertiary systems. The same trend was also observed in the ^1H NMR and is indicative of the highest charge delocalization into the cyclopropane ring in ion **68**.

Comparison of the carbenium center's chemical shift of the 3-nortricyclyl cation with those of the cyclopropylcarbinyl cation, or didehydroadamantyl cation shows that the carbenium ion center (C3) in 3-nortricyclyl cation is more deshielded, contrary to expectation based on the ideal bisected geometry which can be explained by steric inhibition of hyperconjugation. Inspite of considerable charge delocalization into the cyclopropane ring, the limiting nonclassical ion structure was not attained in this system.

5. Nortricyclylmethylcarbinyl Cation

Sorensen and co-workers prepared the secondary nortricyclylmethylcarbinyl cations **69** and **70** by ionizing the corresponding alcohols with SbF_5–SO_2ClF.[27] The ions were stable even at room temperature. Ion **70** was



69, R_1 = H, R_2 = CH_3
70, R_1 = CH_3, R2 = H

only observed as a minor populated isomer and was basically characterized by ^1H NMR. The ^{13}C NMR spectrum of **69** consists of peaks at δ 97.0 (C1), 220.8 (C1′), 95.4 (C2, C6), 38.4 (C3, C5), 34.1 (C4), 29.2 (C7), 27.1 (CH_3). These ions, like the primary nortricyclylcarbinyl cation showed no sign of rotation around the C1–C1′ bonds, even at the highest temperatures attainable, before their decomposition sets in. The high

TABLE 7. ^{13}C NMR Data for Benzonortricyclyl Cations

cation	C1, C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	CH_3
71	96.1	51.2	39.1	131.8	152.6	125.2	165.5	51.2	193.8	84.1	
72	86.0	49.7	38.8	133.5	172.6	126.8	164.8	49.7	194.1	75.6	24.2
73	70.5	47.2	38.9	127.4	177.2	110.5	159.3	47.2	189.2	61.3	60.2
74	93.6	50.3	39.4	133.0	163.1	126.8	165.1	50.3	193.4	80.9	
74a	89.3	47.5	45.5	133.7	165.3	126.9	156.1	64.9	188.1	80.9	
74b	88.3	47.3	45.8	134.7	166.8	128.0	158.7	78.9	186.3	76.6	

TABLE 8. ^{13}C Chemical Shifts for 2,4-Dehydro-5-homoadamantyl Cations

cation	T, °C	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
43a	−60	25.6	95.3	85.4	71.4	267.2	48.2	29.7	24.4	23.0	31.1	51.8
43b	−60	25.0	80.2	73.4	59.9	244.4	42.5	30.1	24.7	25.5	30.99	45.3

TABLE 9. ^{13}C NMR Spectral Data for Tertiary 3-Nortricyclyl Cations

cation	C1, C6	C2	C3	C4	C5, C7	others
102	83.7	67.5	293.2	47.0	43.7	33.7 (CH_3)
103	82.6	64.4	295.2	46.2	43.5	42.7 (CH_2), 10.0 (CH_3)
104	72.8	50.8	275.8	38.5	44.5	phenyl[a]
105	74.1	47.7	258.0	40.2	42.0	
106	84.1	69.0	267.8	49.4	43.6	

[a] 136.7 (C_o), 135.8 (C_o), 132 (C_m), 142.4 (C_p), 130.5 (C_i).

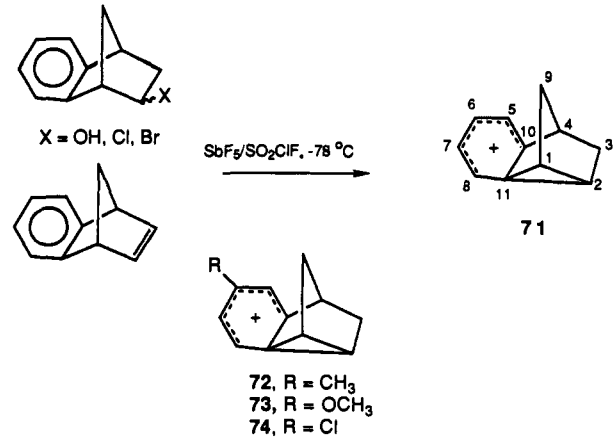
stability and the large rotational barriers in these ions were postulated as due to the partial contribution of vinyl-bridged 2-norbornyl cation structure to the resonance hybrids.

6. Benzo-2-nortricyclyl Cations

Benzo-2-nortricyclyl cation (71) was prepared by treating benzo-2-norbornene, 2-chlorobenzonorbornane, 2-bromobenzonorbornane, or 2-hydroxybenzonorbornane with SbF_5–SO_2ClF at −78 °C.[43] The ion was stable from −120 to 10 °C. A proton NMR spectrum of the ion showed an AB quartet at δ 3.52 (J = 12.5 Hz) due to C3 and C9 protons, a broad one-proton singlet at δ 3.7 due to C4 proton, a two-proton singlet at δ 6.5 (C1, C2-H), and three sets of multiplets centered at δ 8.02, 8.5, and 8.78 due to aromatic protons. The spectrum is similar to those of 3-nortricyclyl or 3-methyl-3-nortricyclyl cations. The ^{13}C NMR spectrum of the cation has nine peaks, instead of 11 peaks, indicating that it must be symmetrical in nature (Table 7). The homo-ortho (C8 and C10) and homo-para (C6) ring positions experience substantial deshielding effects caused by significant charge delocalization into the aromatic ring. This points to a static classical ion and rules out rapidly equilbrating pairs of classical 2-benzonorbornenyl cations, as this would not allow much positive charge delocalization into the ring. The chemical shift difference between the spiro carbon (C1) and ortho carbon (C2) of ethylenebenzenium ion (**119**, Δδ 110, vide infra) is almost of the same magnitude as that between C11 (spiro) and C10 (ortho) of **71** (Δδ 109.1), indicating the aliphatic nature of this carbon. The aromatic carbons are slightly more deshielded than those of ethylenebenzenium ion, showing more positive charge delocalization into the ring. The cation thus shows similarity to the ethylenebenzenium ion (vide infra) and the 3-nortricyclyl cations, but not to the 2-norbornyl cation. Therefore, it is indicated that a nonclassical benzonortricyclyl cation is not involved.

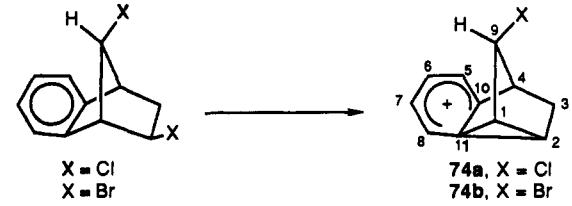
6-Methyl-, 6-methoxy-, and 6-chlorobenzo-2-nortricyclyl cations (**72–74**) were prepared from their respective 2-benzonorbornenyl chloride precursors in either SbF_5–SO_2ClF or FSO_3H–SbF_5–SO_2ClF solution at −78 °C (Scheme 8). The ^{13}C NMR spectral data of these cations are summarized in Table 7. The positive charge of the cation is shared to varying extents by the cyclopropyl ring in the 6-substituted ions, since the electron-donating properties of the C6 substituents are varied. The cyclopropyl carbons are most deshielded in the unsubstituted ion, and least in the methoxy derivative. The charge delocalization into the cyclopropyl ring follows the decreasing order: **71** > **74** > **72** > **73**.

SCHEME 8



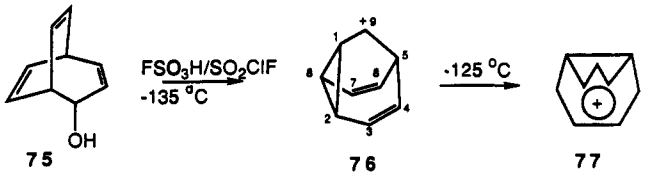
All the spectral data again indicate that the substituted ions formed are also of the benzonortricyclyl cation type, resembling ethylenebenzenium ions containing tetrahedral spiro carbon atoms (vide infra), and nonclassical 2-benzonorbornyl cations are not involved. Thus the cationic vacant p orbital is extensively stabilized by π-interaction with the aromatic π-system.

C_9-halo (Cl and Br) benzonortricyclyl cations (**74a** and **74b**) were also prepared by ionization of *exo*-2-*anti*-7-dihalobenzonorbornanes in SbF_5–SO_2ClF or FSO_3H–SbF_5 solution at −78 °C.[43] The NMR data are summarized in Table 7 along with other substituted benzonortricyclyl cations. It is important in this connection that the C9–X bond was not ionized, since the corresponding cation would be expected to have similar C10 and C11 carbon-13 chemical shifts, contrary to their observed differences of δ(^{13}C) 107.2 and 109.7 for **74a** and **74b**, respectively.



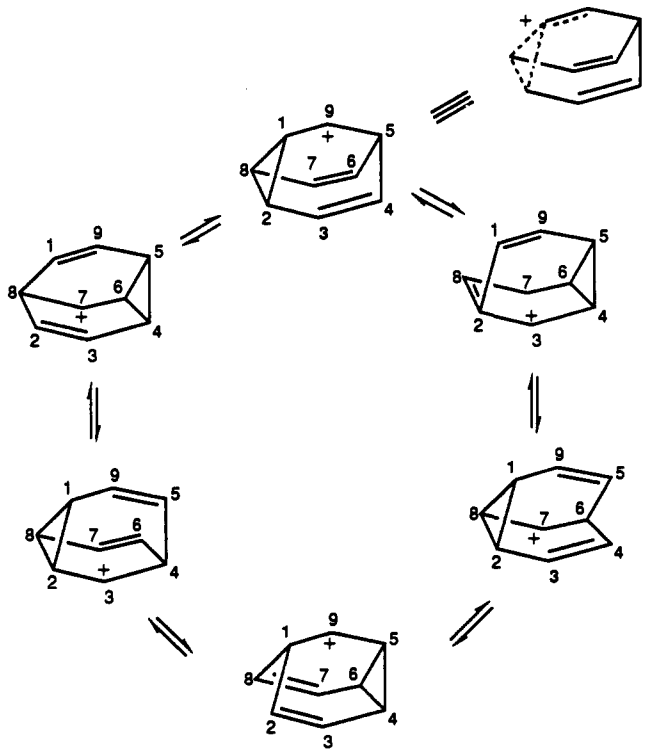
7. 9-Barbaralyl (Bicyclo[3.2.2]nona-2,6,8-trien-4-yl) Cation

Ahlberg and co-workers have demonstrated by ^{13}C and ^{2}H labeling studies that the ion $C_9H_9^+$, generated from bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**75**), by fluorosulfuric acid, has the 9-barbaralyl cation structure (**76**).[44,1f] This cation is stable only at −135 °C, and on warming to −125 °C, it irreversibly rearranged to 1,4-dihomotropylium ion (**77**). The ion **76** undergoes a



6-fold partially degenerate equilibration involving a divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl cation mechanism with an activation barrier of ~3.8 kcal/mol (Scheme 9).

SCHEME 9. Degenerate Rearrangements in 9-Barbaralyl Cation (76)



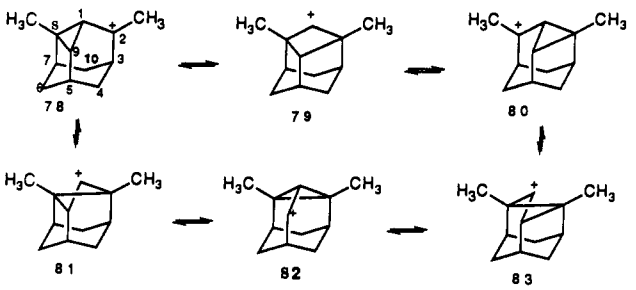
IV. Tertiary Cyclopropylcarbinyl Cations

A. Degenerate Cations

1. 2,8-Dimethyl-8,9-dehydro-2-adamantyl Cation

In order to explore the possibility of degenerate rearrangement in tertiary dehydroadamantyl systems, 2,8-dimethyl-8,9-dehydro-2-adamantyl cation (**78**) was prepared by dissolution of the corresponding alcohol precursor in sulfuryl chloride fluoride and excess fluorosulfuric acid at −78 °C[45] (Scheme 10). The ion, interestingly, shows reversible temperature dependence between −26 and −128 °C. At −26 °C, the ^{1}H NMR spectrum showed equivalence of two methyls (δ 2.78), C3 and C5, C7 bridgehead protons (δ 3.3–2.8), and C4, C6, C10 protons (δ 2.3). C1 and C9 protons appeared

SCHEME 10

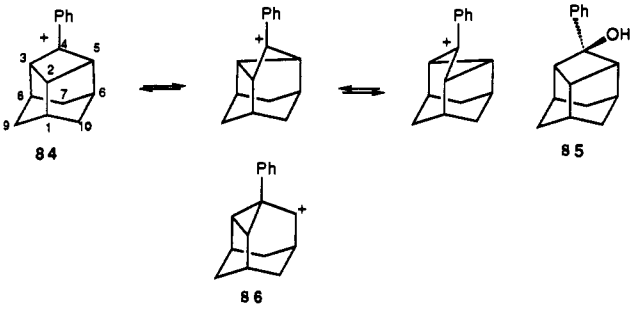


at δ 4.37 and 5.2, respectively. A ^{13}C NMR spectrum similarly showed only eight carbon resonances at δ(^{13}C) 202.7 (C2, C8), 88.4 (C9), 85.6 (C1), 55.3 (C10), 45.1 (C3, C7), 42.2 (C4, C6), 35.8 (C5), and 29.7 (CH_3). As the temperature was lowered to −128 °C, a static 2,8-dimethyl-8,9-dehydro-2-adamantyl cation resulted. Formerly equivalent methyl signals split into two peaks at δ(^{13}C) 32.8 and 26.5. The resonances for C2 and C8 appear at δ 253.9 and 151.0, respectively. The degenerate equilibrium was explained to proceed by the intermediacy of protoadamantyl cations, **79**, **81**, and **83**. An approximate activation energy barrier ($\Delta G^{\ddagger}$) of 7.4 ± 0.5 kcal/mol was calculated for **78** to **79**, using the coalescence temperature of −112 °C for the merging of methyl signals.

2. 4-Phenyl-2,5-dehydro-4-protoadamantyl Cation

Cation **84** also shows temperature-dependent behavior between −40 and −135 °C.[45] The cation was prepared by adding 4-*endo*-hydroxy-4-*exo*-phenyl-2,5-dehydroprotoadamantane (**85**) to a solution of fluorosulfuric acid in sulfuryl chloride fluoride at −78 °C. The ^{13}C NMR spectrum showed a 3-fold axis of symmetry for the cation as (C2, C3, C5), (C1, C6, C8), and (C7, C9, C10) were equivalent. ^{13}C NMR data observed were δ(^{13}C) 222.4 (C4), 146.8 (C_p), 137.1 (C_o), 132.0 (C_m), 131.5 (C_i), 72.7 (C2, C3, C5), 58.3 (C1, C6, C8), and 43.0 (C7, C9, C10). At −135 °C, a static structure was evident. Thus, formerly equivalent C2, C3, and C5 carbons are resolved into δ 46.8 (C2) and 85.2 (C3, C5). C4 appeared at δ(^{13}C) 222.0 The degenerate rearrangement was rationalized as proceeding through 1-phenyl-8,9-dehydro-2-adamantyl cation (**86**) as an intermediate (Scheme 11). From the coalescence temperature of

SCHEME 11

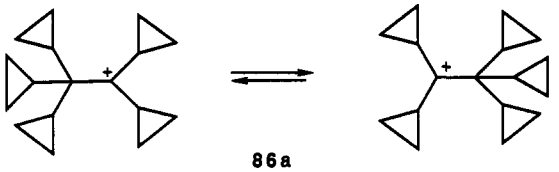


−110 °C for merging C2, C3, and C5 resonances, an approximate activation energy barrier of 6.9 ± 0.5 kcal/mol was estimated for the degenerate rearrangement.[45]

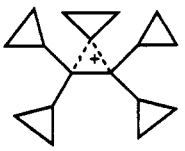
3. 1,1,2,2,2-Pentacyclopropylethyl Cation

Jun and Timberlake prepared the pentacyclopropylethyl cation (**86a**) by ionizing 1,1,2,2,2-penta-

cyclopropylethan-1-ol in FSO_3H–SO_2ClF at −85 °C.[46]



86a



86b

The ^{13}C NMR spectrum of the ion showed only three signals at $\delta(^{13}C)$ 125.6 (C^+ and quaternary), 81.7 (tertiary), and 13.1 (secondary) up to −100 °C. The proton NMR spectrum also showed only a broad absorption at δ 3.4 ppm for all α-protons and at δ 0.3 ppm for all β-protons. The equivalence of all the cyclopropyl groups was explained as due to the degenerate equilibration of two classical carbenium ions. The classical carbenium ion nature was also supported by application of Schleyer and Olah's chemical shift additivity criterion.[47] Thus, the sum of the chemical shifts of the cation was greater by about 511 ppm compared with the estimated value for the corresponding hydrocarbon, pentacyclopropylethane, ruling out the bridged structure **86b**. Such chemical shift additivity comparisons were successfully applied to distinguish several classical from nonclassical cations.[47]

B. Static Cations

A number of dicyclopropylalkyl and dicyclopropylaryl cations were prepared and characterized by ^1H or ^{13}C NMR, and the data were comprehensively reviewed earlier.[1b] Thus, these are not included in the present review.

1. Tricyclopropylcarbinyl Cation

Historically the tricyclopropylcarbinyl cation has been one of the earliest stable carbocation to be prepared and studied. It shows an UV absorption at λ_{max} 270 nm with an extinction coefficient exceeding 20 000.[48a] The cation could be even generated in sulfuric acid solution. It was also obtained as a crystalline hydroxytrifluoroborate salt. Low-field ^1H NMR spectra of the cation showed only one broad absorption for all the methylene and methine protons, but at 300 MHz,[48b] they were well resolved and appear at δ 3.0 (br s, CH_2) and 2.6 (m, CH). The ^{13}C NMR spectrum had absorptions at $\delta(^{13}C)$ 280.5 (C^+), 32.5 (CH), and 30.8 (CH_2).

2. α,α-Dimethylcyclopropylcarbinyl Cation

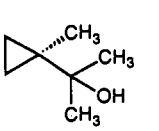
α,α-Dimethylcyclopropylcarbinyl cation was prepared by Olah et al. by ionizing 1-cyclopropyl-1-methylethanol in SbF_5–SO_2ClF at −78 °C.[48] The cation was also prepared by hydride abstraction from the 1-cyclopropyl-1-methylethane in FSO_3H–SbF_5–SO_2ClF.[49] The ^1H NMR spectrum shows absorptions at δ 2.7 (CH_2), 3.18 (CH_2), 3.83 (CH), 3.57 (endo-CH_3), 3.68 (exo-CH_3) [^{13}C NMR: δ 279.9 (C^+), 59.1 (CH), 53.1 (CH_2), 39.1 (exo-CH_3), 30.1 (endo-CH_3)]. Thus, the *cis*- and *trans*-methyl carbons differ by 9 ppm in ^{13}C NMR spectrum. The different absorptions for the methyl groups indicate that the cation exists in the bisected conformation, and rotation around the C^+–CH bond is slow on the NMR time scale. The *cis*-methyl group experiences diamagnetic anisotropy of the ring and appears at higher field than the *trans*-methyl group. Free rotation of the cyclopropyl ring was not observed up to −35 °C, and hence the barrier was estimated to be at least 8–10 kcal/mol.

Kabakoff and Namanworth[50] first measured the rates of rotation of the dimethylcyclopropylcarbenium ion by the double resonance method to be 0.05 s^{-1} at −49 °C and 2.14 s^{-1} at −21 °C, with E_a = 13.7 kcal/mol and log A = 12.2. They observed a low coupling constant between the cationic center and the methyl hydrogens, $J_{(C^+-CH_3)}$, of 1.2 Hz, indicating charge delocalization into the cyclopropane ring (compare $J_{C^+-CH_3}$ of isopropyl = 6.0 Hz).

The energy difference between the bisected and perpendicular conformers of dimethylcyclopropylcarbinyl cation was theoretically estimated to be 9 kcal/mol (EHMO), 25 kcal/mol (CNDO), 13.21 (STO-3G), and 18 kcal/mol (3-21G).[51]

3. 2-(1-Methylcyclopropyl)propyl Cation

2-(1-Methylcyclopropyl)propan-2-ol (**87**) was cleanly ionized in SbF_5–SO_2ClF at −78 °C to give the tertiary cation **88**.[52] The ^1H NMR spectrum of the ion at −75 °C shows absorptions at δ 3.80 (m) due to the ring hydrogens, 1.86 for the C1-CH_3, and 2.77 and 3.11 ppm for the α-CH_3 groups. ^{13}C NMR spectrum has the following absorptions: $\delta(^{13}C)$ 64.7 (C1), 276.6 (C^+), 61.7 (J = 174.9, C2, C3), 20.4 (J = 130.8, C1-CH_3), 36.2 (quartets, J = 130 Hz, α-CH_3), 38.7 and 28.8 (q, J = 132 Hz, α-CH_3). Comparing the ^{13}C absorptions with those of the α,α-dimethylcyclopropylcarbinyl cation, it is evident that ion **88** is also a static cation in the bisected conformation. There are also two distinct CH_3 absorptions in ^1H and ^{13}C NMR spectrum. The more deshielded NMR chemical shifts for the cyclopropyl carbons indicate that 1-methylcyclopropyl group is a better electron-releasing group than the unsubstituted cyclopropyl group, also consistent with the solvolytic results.



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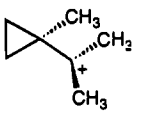
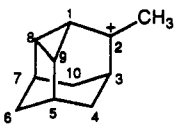


88

4. 2-Methyl-8,9-dehydro-2-adamantyl Cation

2-Hydroxy-2-methyl-8,9-dehydroadamantane or 2-hydroxy-8-methyl-8,9-dehydroadamantane on reaction with FSO_3H–SO_2ClF or SbF_5–SO_2ClF at −78 °C gave ion **89**.[34] This cation is stable up to 10 °C, and de-

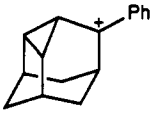


89

composes at room temperature. The proton NMR spectrum shows absorptions at δ 5.69 (br m) due to C8, C9-H and δ 4.52 (t, J = 5.8 Hz) due to the hydrogens on C1 and the methyl group(s) at 3.35 ppm. The rest of the proton shifts are spread over δ 2 to 3.5. ^{13}C NMR spectrum shows the following data: δ(^{13}C) 71.8 (d, J = 186.9 Hz, C1), 274.4 (s, C2), 47.3 (d, J = 142.4 Hz, C3), 47.3 (t, J = 134.3 Hz, C4, C6, C10), 34.5 (d, J = 144.1 Hz, C5, C7), 100.7 (d, J = 181.5 Hz, C8, C9), 33.5 (q, J = 127.7 Hz, CH_3). The ion, thus, has a plane of symmetry.

5. 2-Phenyl-8,9-dehydro-2-adamantyl Cation

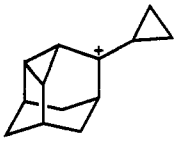
2-Hydroxy-2-phenyl-8,9-dehydroadamantane was ionized with FSO_3H–SO_2ClF at −78 °C to give the tertiary cation **90**.[34] The proton NMR spectrum showed the following chemical shifts: δ 4.45 (C1-H), 4.22 (C3-H), 2.60 (C4-H, exo-C6-H, C10-H), 2.95 (C5, C7-H), 2.10 (endo-C6-H), 5.2 (C8, C9-H), 7.8–8.6 (C_6H_5). The data are in agreement with a static carbenium ion with some charge delocalization into the cyclopropane ring.



90

6. 2-Cyclopropyl-8,9-dehydro-2-adamantyl Cation

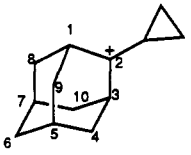
2-Hydroxy-2-cyclopropyl-8,9-dehydroadamantane in FSO_3H–SO_2ClF at −78 °C gave the tertiary cyclopropyl substituted ion **91**:[34] ^1H NMR δ 3.72 (C1-H), 2.42 (C3-H), 2.42 (C4, C5, C7, C10-H), 1.92 (endo-C6-H), 4.6 (C8, C9-H), 3.42 (cyclopropyl CH), 2.75 (cyclopropyl CH_2).



91

7. 2-Cyclopropyl-2-adamantyl Cation

2-Cyclopropyl-2-adamantanol upon ionization in 1:1 FSO_3H–SbF_5/SO_2 at −80 °C gave the 2-cyclopropyl-2-adamantyl cation (**91a**).[53] The ion could not be pre-



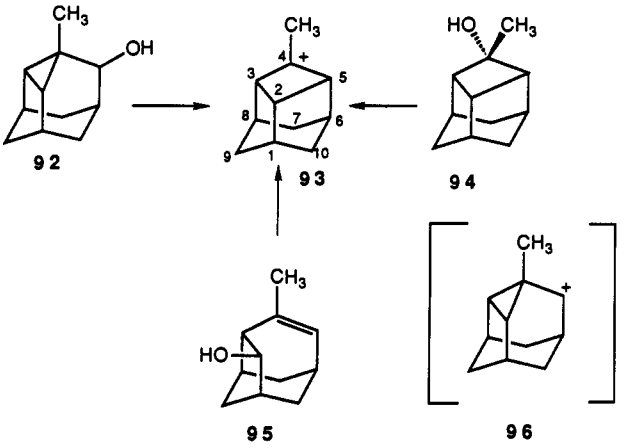
91a

pared in less nucleophilic solvents, such as SO_2ClF, where it rearranged into the allylic cation, 2-(2′-propenyl)adamantyl cation. A ^{13}C NMR spectrum of **91a** displayed absorptions at δ(^{13}C) 294.3 (C^+), 56.4 (C1), 49.5 (C3), 45.9 (C4, C10), 45.7 (C8, C9), 35.6 (C6), 28.0 (C5, C7) for the adamantane ring and at δ 48.9 (CH_2), and 45.4 (CH) for the cyclopropane ring. Cyclopropyl conjugation makes the C1 and C3 bridgehead carbons and the β-methylene carbons (C4, C10, and C8, C9) nonequivalent.[54]

8. 4-Methyl-2,5-dehydro-4-protoadamantyl Cation

Ionization of 2-hydroxy-1-methyl-8,9-dehydroadamantane (**92**) in SbF_5–SO_2ClF solution at −120 °C did not give the 1-methyl-8,9-dehydro-2-adamantyl cation (**96**, Scheme 12). Instead it rearranged to the

SCHEME 12



4-methyl-2,5-dehydro-4-protoadamantyl cation (**93**) which was stable up to −45 °C.[34] The same ion was also obtained upon ionization of 4-*endo*-hydroxy-4-methyl-2,5-dehydroprotoadamant-4-ene (**95**). The ^{13}C NMR spectrum of the ion shows only five peaks at δ(^{13}C) 187.0 (C4), 83.3 (C2, C3, C5), 50.5 (C1, C6, C8), 42.1 (C7, C9, C10), and 26.2 (CH_3), indicating that the ion is undergoing a 3-fold degenerate rearrangement, fast on the NMR time scale even at −120 °C. This rearrangement may proceed through the intermediacy of the 1-methyl-8,9-didehydro-2-adamantyl cation (**96**).

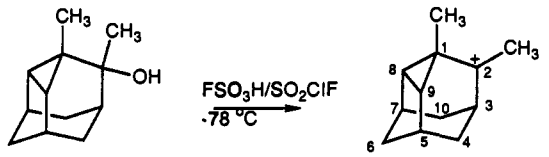
9. Tertiary 2,4-Dehydro-5-homoadamantyl Cations

5-Methyl- and 5-phenyl-2,4-dehydro-5-homoadamantyl cations (**43a** and **43b**) were prepared from their precursor alcohols (**44a** and **44b**)[35] by reacting with fluorosulfuric acid in sulfuryl chloride fluoride solution at −120 °C. The ions were also prepared from 2-*endo*-hydroxy-2-*exo*-methylhomoadamant-4-ene (**45a**) and 2-*endo*-hydroxy-2-*exo*-phenylhomoadamant-4-ene (**45b**), respectively in FSO_3H–SO_2ClF at −110 °C. The ^{13}C NMR data for these ions are summarized in Table 8.

It is apparent from the highly deshielded C^+ chemical shifts that the ions are classical cations, involving charge delocalization into the ring. The difference in the chemical shifts of C2 and C3 are particularly indicative of relative charge delocalization into the ring. Thus Δδ for **43a** (9.9 ppm) is larger than that for **43b** (6.8 ppm), indicating more charge delocalization into the cyclopropane ring of the methyl derivative, **43a**. The corresponding Δδ for the parent ion, **43**, is 41.32 ppm, indicating that such charge delocalization is highest in the parent system.

10. 1,2-Dimethyl-8,9-dehydro-2-adamantyl Cation

1,2-Dimethyl-8,9-dehydro-2-adamantyl cation (**98**) was prepared from 1,2-dimethyl-2-hydroxy-8,9-dehydroadamantane (**97**) in FSO_3H–SO_2ClF solution at −78 °C.[34] The ^1H and ^{13}C NMR spectra of this cation also showed it to be a static classical carbenium ion [^{13}C NMR: δ 266.3 (C2), 108.6 (C8, C9), 82.0 (C1),

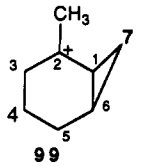


97 98

47.5 (C3), 47.1 (C4, C6, C10), 36.2 (C5, C7), 19.5 (C1-CH_3), 31.7 (C2-CH_3)].

11. 2-Methylbicyclo[4.1.0]hept-2-yl Cation

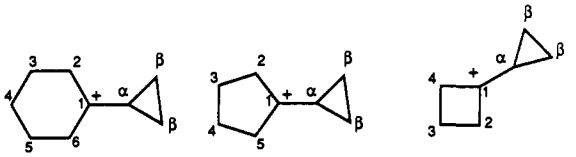
The tertiary 2-methylbicyclo[4.1.0]hept-2-yl cation (**99**) is static from −140 to 0 °C, as its ^{13}C NMR spectrum (Table 4) shows for all eight signals throughout this temperature range.[36]



99

12. 1-Cyclopropyl-1-cycloalkyl Cations

The 1-cyclopropyl-1-cyclohexyl cation (**100**) is formed from either 1-cyclopropylcyclohexanol, or bicyclo-[6.1.0]nonan-2-ol (vide supra) upon ionization in FSO_3H–SO_2ClF.[36] The ^{13}C NMR data for this cation are summarized in Table 4. The cation is a typical bisected cyclopropylcarbinyl cation, consequently, the C2 and C6 carbons of the cyclohexyl rings experience significant anisotropy and their chemical shifts differ by 10 ppm.

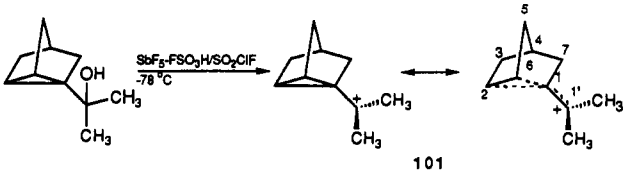


100 100a 100b

Sorensen and Kirchen[16] prepared the 1-cyclopropyl-1-cyclopentyl (**100a**) and 1-cyclopropyl-1-cyclobutyl (**100b**) cations by ionizing the corresponding alcohols in SbF_5–$FSO_3H/CFCl_3$. Cation **100a** shows ^{13}C NMR absorptions at $\delta(^{13}C)$ 298.3 (C^+), 49.5 (C2), 44.2 (C5), 25.6 (C3, C4), 44.2 (C5), and 53.4 (Cα and Cβ). Cation **100b** has the following ^{13}C NMR absorptions: $\delta(^{13}C)$ 297.1 (C^+), 49.9 (C2), 42.4 (C4), 16.3 (C3), 55.5 (Cβ), 54.4 (Cα). Cations **100a** and **100b** are also bisected cyclopropylcarbinyl cations as the C2 and C5 carbons in **100a** and C2 and C4 carbons in **100b** have different chemical shifts. Cation **100b** is extremely unstable and rearranges to the cyclopentylallyl cation at −100 °C ($t_{1/2}$ = 600 s at −93.5 °C, $\Delta G^{\ddagger}$ = 12.7 kcal/mol). To explain the relatively unstable nature of this cation, Sorensen and Kirchen[16] suggested equilibration of the sp^2-hybridized cation **100b** with a minor sp^3-hybridized 1-cyclopropyl-1-cyclobutyl cation, which lacks cyclopropyl participation.

13. Nortricyclyldimethylcarbinyl Cation

The tertiary ion **101** was prepared from the corresponding alcohol, by ionizing with SbF_5–SO_2ClF. The ion is extremely stable, up to nearly 100 °C.[27] At 80

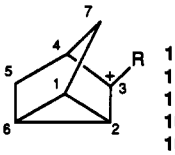


101

°C, a slight broadening of the methyl absorptions is observed. From the line broadening, a rotational barrier of at least 18 kcal/mol was estimated. STO-3G calculations gave a value of 17.7 kcal/mol for this rotational barrier. The high observed rotational barrier was also interpreted as due to partial contribution of a vinyl-bridged 2-norbornyl cation structure to the overall ion structure. ^{13}C NMR: $\delta(^{13}C)$ 84.2 (C1), 249.6 (C1′), 86.1 (C2, C6), 38.1 (C3, C5), 33.0 (C4), 31.4 (C7), 33.7 (anti-CH_3), 30.2 (syn-CH_3).

14. Tertiary 3-Nortricyclyl Cations

Tertiary 3-nortricyclyl cations **102–104** were prepared from the corresponding alcohols, in FSO_3H–SbF_5–SO_2ClF or SbF_5–SO_2ClF, at −78 °C. The corresponding



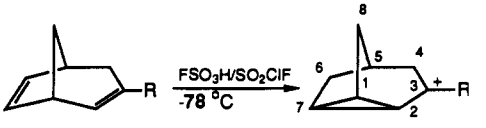
102, R = CH3,
103, R = Et,
104, R = Ph,
105, R = F,
106, R = Cl

3-halo-3-nortricyclyl cations (**105** and **106**) were prepared from the corresponding dihalonortricyclanes in SbF_5–SO_2ClF solution at −78 °C.[42] 3-Fluoronortricyclyl cation (**105**) is the most stable of these cations, sufficiently stable even at −20 °C. The ions were characterized by ^1H and ^{13}C NMR spectral analysis. The ^{13}C NMR spectral data are summarized in Table 9.

The difference in chemical shifts of C1 and C2 reflect the extent of charge delocalization into the cyclopropane ring. This difference is largest in the primary ion (25.3 ppm) and is typically small in tertiary alkyl systems. The fluorine substituent is more effective in the dispersal of charge than chlorine, as indicated by the lesser deshielded chemical shifts of the nortricyclyl ring carbons in cation **105**. The fluorocarbenium ion, **105**, also shows a $>C^+$–F doublet with an unusually large coupling constant of 420 Hz, indicating a strong p-π back-conjugation with the cationic center.

15. 3-Halo- and 3-Methyl-3-tricyclo[3.2.1.0^{2,7}]octyl (3-Homonortricyclyl) Cations

3-Methyl-, 3-chloro-, and 3-bromohomonortricyclyl cations (**107–109**) were prepared from the 3-substituted bicyclo[3.2.1]octa-2,6-dienes by protonation by fluorosulfuric acid.[37] The ^{13}C NMR data are tabulated in Table 10.



107, R = CH_3
108, R = Br
109, R = Cl

The cationic centers in these cations are much less deshielded than those of typical tertiary cations, indi-

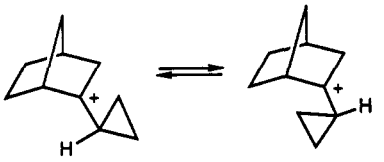
TABLE 10. ^{13}C NMR Data for Tertiary Homonortricyclyl Cations

cation	T, °C	C1	C2	C3	C4	C5	C6	C7	C8
107	-85	72.6	70.8	260.5	46.9	29.7	30.7	72.6	30.7
108	-85	81.5	81.5	229.8	51.9	32.9	31.4	81.5	31.4
109	-60	79.13	7.94	234.01	48.91	31.23	31.49	79.13	31.49

cating significant charge delocalization into the cyclopropane ring.

16. 2-Cyclopropyl-2-norbornyl Cation

Ionization of 2-cyclopropyl-2-norbornanol in FSO_3H–SbF_5/SO_2ClF at −90 °C gave the tertiary 2-cyclopropyl-2-norbornyl cation (110). Ion 110 appears to

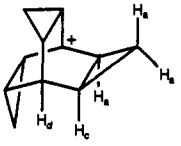


110

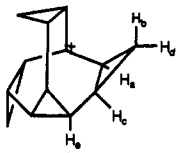
be an equilibrating set of two cations. The cationic chemical shift of the major and the minor isomers were at δ 289.4 and 288.1, respectively. The remaining carbons of the major isomer appeared at δ 55.0 (C1), 49.4 (C3), 38.2 (C4), 23.9 (C5), 30.1 (C6), 39.5 (C7), and 65.3 (cyclopropyl CH), 43.0, and 56.0 (cyclopropyl CH_2). The rotational barrier for these isomers could not be measured as the cation decomposes above −70 °C. The relatively moderately deshielded C1 chemical shift in the ion indicates considerable charge delocalization into the cyclopropane ring.[54]

17. 1-Trishomobarrelyl and 1-Trishomobullvalyl Cations

1-Trishomobarrelyl and 1-trishomobullvalyl cations (111 and 112) were prepared from the corresponding bridgehead chloride precursors with SbF_5–SO_2ClF at −78 °C.[55]



111



112

Trishomobarrelyl cation was stable up to −10 °C and shows four absorptions in the ^1H NMR spectrum at δ 2.34 (q, H_e), 3.14 (q, $H_c + H_d$) 3.47 (q, H_b), 3.72 (q, H_a). 1-Trishomobullvalyl cation (112) was stable up to −40 °C and showed the following ^1H NMR: δ 1.66 (br s, H_e), 2.09 (br s, H_d), 3.18 (br s, $H_b + H_c$), 3.58 (m, H_a). Thus, the positive charge is about uniformly delocalized at all centers of the adjacent cyclopropyl groups.

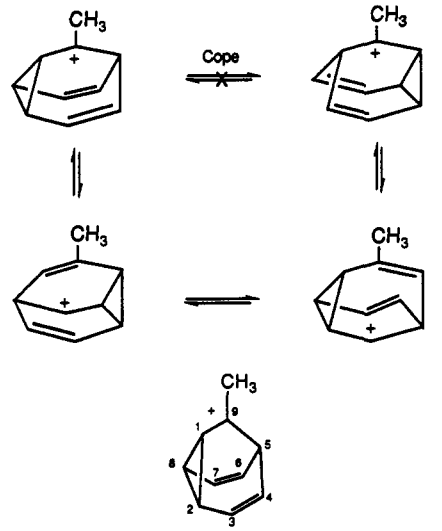
Ionization of 1,5-dichlorotrishomobarrelene (113) with SbF_5–SO_2ClF gave the suggested 5-chlorotrishomobarrelyl mono cation (114) in which the chlorine substituent was proposed to undergo a rapid intermolecular exchange. The expected 1,5-dication could not be observed.[56]

113 114

18. 9-Methylbarbaralyl Cation

Tertiary, 9-methylbarbaralyl cation (115) also shows low barrier (7.63 kcal/mol at −129 °C) to proposed degenerate divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl rearrangement (Scheme 13).[44]

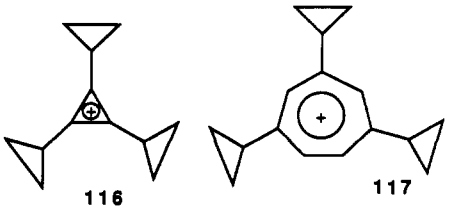
SCHEME 13. Degenerate Rearrangements in 9-Methylbarbaralyl Cation (115) through the Secondary Cationic Intermediates



115

19. Tricyclopropylcyclopropenium and TricyclopropylTropylium Ions

The tricyclopropylcyclopropenium (116), and tricyclopropyltropylium cations (117) were prepared with a hydrocarbon counter anion (Kuhn's anion, $C_{67}H_{39}^-$).[57] These salts exist as ionic species in polar solvents such as dimethyl sulfoxide, but in nonpolar solvents such as chloroform, they form covalent hydrocarbons. Upon redissolution in DMSO, ionic species are again formed. Tricyclopropyltropylium ion exists as an equilibrium mixture of ionic, radical, and covalent species in THF. This indicates single electron transfer (SET) from Kuhn's anion to the tropylium ion.



116 117

V. Phenonium (Spirocyclopropylarenium) Ions

Cram's pioneering studies on the solvolysis of 3-phenyl-2-butyl tosylates clearly implicated the intermediate formation of symmetrically bridged phenonium ions.[58] The optically active *threo*-tosylate gave almost completely racemized product, and the *erythro*-tosylate gave almost complete retention of configuration. The

phenonium ion from the *threo*-tosylate is meso and hence gives racemic product, whereas the phenonium ion from the *erythro*-tosylate is dissymetric, and hence retention is expected, as found experimentally. Brown challenged the phenonium ion concept on the basis of the relatively small rate-enhancing effect of the phenyl group.[59] He favored equilibrating classical, or partially π-complexed cations, depending on the substrate and solvents.

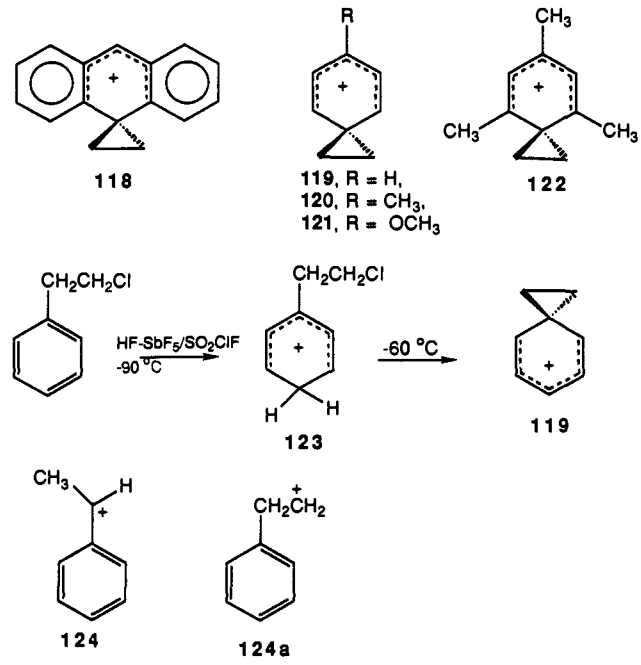
The work of Nordlander and Kelly[60a] in particular established the importance of solvent assisted pathway (k_s) in these systems, in determining the relative rates of these substrates. Trifluoroacetolysis of 2-phenylethyl tosylate, proceeded 3000 times faster than that of the ethyl tosylate, whereas in conventional media, such as acetic acid, the former was slightly less reactive. Similarly, 1-phenyl-2-propyl tosylate was 564 times as reactive as 2-propyl tosylate (after correction for the inductive effect of the phenyl group).[60b] In weakly nucleophilic trifluoroacetic acid, the solvent assisted pathway (k_s) is minimal, and great demand is exerted on neighboring phenyl group participation. Complete retention of configuration was also observed in this solvent. Brown subsequently recognized the competing solvent assistance and acknowledged the importance of phenonium ions in these solvolyses reactions.[61] The topic of phenonium ions has been thoroughly reviewed and no further discussion is needed here.[2d]

The direct observation of phenonium ions was achieved under superacidic, stable ion conditions. The symmetrical nature of these bridged species was well established by comparing the ^{13}C NMR chemical shifts of the aromatic carbons with those of typical benzenium ions, and of the cyclopropyl carbons with the cyclopropylcarbinyl cations. The study was also extended to ethylenenaphthalenium ions, ethyleneanthracenium ions, and haloarenium ions.

A. Ethylenebenzenium Ions (Spiro[2.5]octa-5,7-dien-4-yl Cations)

Phenonium ions (or ethylenearenium ions) are indeed spirocyclopropylarenium ions, which owe their substantial stabilization to the spirocyclic cylopropyl group. They can also be regarded as cyclopropylcarbinyl cations, as significant positive charge is delocalized into the cyclopropane ring. Winstein and Eberson first prepared such a stable cation, i.e., the 9,9-ethyleneanthracenium ion (**118**), by ionizing the corresponding alcohol.[62] The ^1H NMR spectrum of this ion consisted of a sharp singlet at δ 3.44 (CH_2CH_2) and two triplets and one singlet at δ 7.73, 8.20, and 9.64, respectively. Subsequently, Olah and co-workers prepared the parent unsubstituted ethylenebenzenium ion (**119**) ethylene-4-methyl benzenium (**120**), ethylene-2,4,6-trimethylbenzenium ion (**122**), and ethylene-4-methoxybenzenium ion (**121**) by ionizing the β-phenylethyl chloride precursors with SbF_5–SO_2ClF at –78 °C. They were characterized by ^{13}C NMR spectroscopy.[63] As the 4-substituent is varied from hydrogen to methyl to methoxy, the cyclopropyl methylenic carbons were progressively shielded, reflecting the decreasing demand on the cyclopropyl group for the stabilization of the cations as more electron-donating groups are attached to the aromatic ring. Later, an improved procedure for the preparation of the parent ion was developed.[64] (2-Chloroethyl)benzene in HF–SbF_5/SO_2ClF at –90 °C initially formed the (2-chloroethyl)benzenium ion (**123**) whose ^{13}C NMR spectrum was similar to the monoalkylbenzenium ions (Scheme 14). After several hours

SCHEME 14

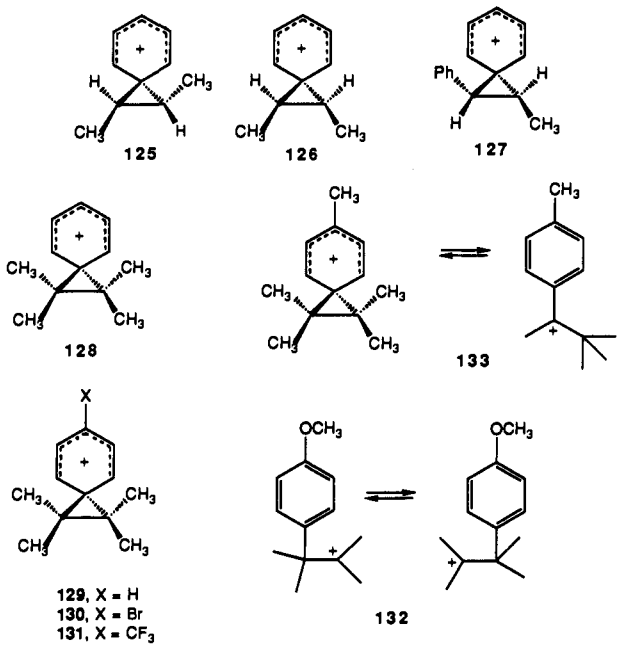


at –60 °C, the ion was converted to the ethylenebenzenium ion. The ion, thus prepared, had only small impurities. This ion was further converted to the α-styryl cation (**124**) after keeping several hours above –30 °C.

The small concentration of α-styryl cation, formed at –60 °C, was shown to arise from the α-ethylenebenzenium ion, rather than directly from the (chloroethyl)benzenium ion by hydride shift. The latter was ruled out as ionization of α-^{13}C-labeled phenylethyl chloride resulted in the equal distribution of ^{13}C label among C^+ and CH_3. This can arise only through involvement of the phenonium ion. The kinetics of transformation of the ethylenebenzenium ion to α-styryl cation was followed by ^1H NMR and was found to proceed with an E_a of 13 kcal/mol and log A of 13.6. Assuming 2-phenylethyl cation (**124a**) to be a local minimum near the transition state leading to the α-styryl cation, an upper limit of 13 kcal/mol was placed on the energy difference between the ethylenebenzenium ion and 2-phenylethyl cations. Hehre's STO-3G calculations showed the energy difference between the open chain and bridged forms to be 35.4 kcal/mol. He indicated, however, that higher level calculations should decrease the energy difference.[65]

(Dimethylethylene)benzenium ions (**125** and **126**) and (methylphenylethylene)benzenium ion (**127**), *p*-methoxyethylenebenzenium ion, and (tetramethylethylene)benzenium ion (**128**) were also prepared from the corresponding β-phenylethyl chlorides (Scheme 15), and characterized by ^1H NMR spectroscopy.[66] Ionization of 3-(*p*-X-phenyl)-2,3-dimethyl-2-butyl chloride or 2-(*p*-X-phenyl)-3,3-dimethylbutyl chloride yielded identical cations. These cations were characterized as ethylenearenium ions (**129**–**131**), equilibrating classical ion (**132**), or equilibrating ethylenearenium ions with the classical ion (**133**) depending on the nature of X.[67]

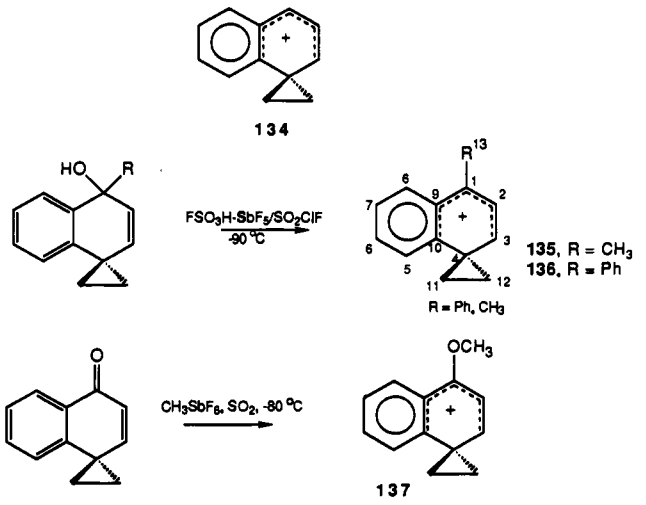
SCHEME 15



B. Ethylenenaphthalenium Ions

The unsubstituted α-ethylenenaphthalenium ion (**134**) is still elusive to preparation.[68a] However, 1-methyl-, 1-phenyl-, and 1-methoxyethylene-naphthalenium ions (**135–137**; Scheme 16) were pre-

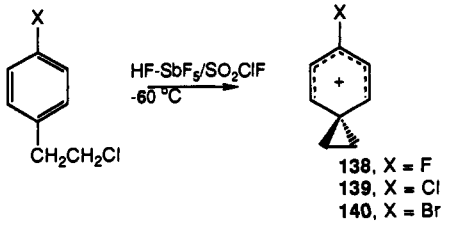
SCHEME 16



pared by previously indicated methods. The ^{13}C NMR chemical shifts for ions **135–137** are listed in Table 11.

C. α-Ethylenehaloarenium Ions

Halogens stabilize electron-deficient centers through back-donation of nonbonded electron pairs. In order to see the effect of the halogens on the stability of α-ethylenearenium ions, 4-halophenylethyl chlorides (X = F, Cl, or Br) were ionized with HF–SbF_5/SO_2ClF at –60 °C, to obtain the 4-halo-α-ethylenebenzenium ions (**138–140**).[68b] Based on the difference in the chemical shifts of the C4 carbon of these cations compared with their neutral precursors (Δδ 19.8, 35.2, 38.0 ppm for **138**, **139**, and **140**, respectively), it was concluded that there is strong back-donation by fluorine atoms, less back-

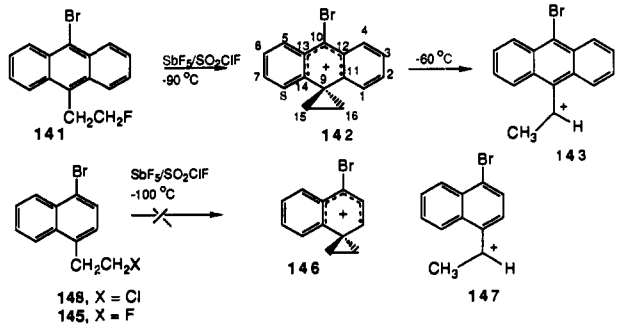


donation by chlorine, and a negligible back-donation by bromine in these cations.

D. 9-(α-Ethylene)-10-bromoanthracenium Ion

9-(α-Ethylene)-10-bromoanthracenium (**142**) was prepared by ionization of 9-(β-fluoroethyl)-10-bromoanthracene (**141**) in a solution of SbF_5 in SO_2ClF at –90 °C[68b] (Scheme 17) [^{13}C NMR: δ(^{13}C) 166.5 (C10), 157.0

SCHEME 17

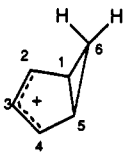


(C11, C14), 142.6 (C2, C7), 136.6 (C4, C5), 133.1 (C12, C13), 130.0 (C3, C6), 122.5 (C1, and C8), 45.9 (C15, C16), 40.8 (C9)]. Upon warming to –60 °C, ion **142** rearranged to the benzylic cation **143**.

Attempted preparation of 1-bromo-α-ethylene-naphthalenium ion (**146**) from 1-(2-haloethyl)-4-bromonaphthalenes (**144** and **145**) in SbF_5–SO_2ClF gave only the rearranged benzylic ion **147**.

VI. Allylic Cyclopropylcarbinyl Cations

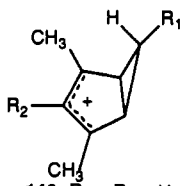
Berson and co-workers prepared the bicyclo[3.1.0]-hexenyl cation (**148**) and characterized it by ^1H NMR.[69]



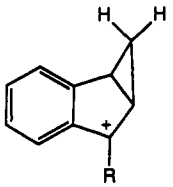
148

The C6-*endo*-hydrogen was found to be slightly more deshielded than the C6-*exo*-hydrogen (Δδ = 0.30 ppm), in sharp contrast to the homotropylium ion (bicyclo-[5.1.0]octa-2,4-dienyl cation), in which a value of $\delta_{endo} - \delta_{exo} = -5.8$ ppm was observed. This was interpreted as due to opposing ring current effects in the carbocations. Ion **148** was found to undergo degenerate circumambulatory migration with an activation barrier of 15.1 kcal/mol, as determined from the deuterium labeled analogue. However, there was no line broadening in the NMR spectra between –96 to –15 °C.

Olah and co-workers[70] subsequently prepared several substituted bicyclo[3.1.0]hexenyl cations (**149–151**) and benzobicyclo[3.1.0]hexenyl cations (**152–155**) and characterized them by ^1H and ^{13}C NMR spectroscopy.



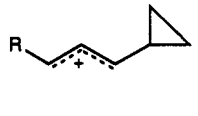
149, $R_1 = R_2 = H$
150, $R_1 = H$, $R_2 = CH_3$
151, $R_1 = R_2 = CH_3$



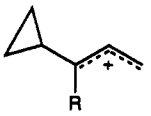
152, R = H
153, R = CH_3
154, R = Et
155, R = $(CH_3)_2CH$

In all these carbocations, the differences in the chemical shifts of the endo and exo methylene hydrogens of the cyclopropyl group are in the same order (0.3 to 0.6 ppm). The ^{13}C NMR spectra revealed significant charge delocalization into the cyclopropane ring, as the cyclopropyl methylene carbons are strongly deshielded (δ-(^{13}C) 105–124 in bicyclo[3.1.0]hexenyl cations, and $\delta(^{13}C)$ 89–103 in benzobicyclo[3.1.0]hexenyl cations).[70]

Several cyclopropyl-substituted allyl cations (156–160) were also prepared by the ionization of the corresponding alcohols in FSO_3H–SO_2 or FSO_3H–SO_2ClF at −78 or −120 °C.[71a] 1,3-Dicyclopropylallyl cation (157) adopts a trans,trans conformation, as the C1 and C3 carbons show identical NMR characteristics. In 1,1-dicyclopropyl-, and 1-cyclopropyl-1-phenyl-, and 1-cyclopropyl-1-methylallyl cations (158–160), the cat-



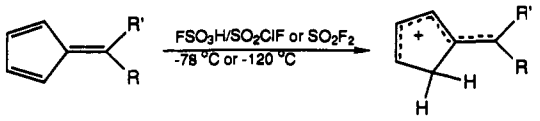
156, R = CH_3,
157, R = Cyclopropyl



158, R = CH_3
159, R = Cyclopropyl
160, R = Phenyl

ionic charge is localized on the C1 carbon almost exclusively. The conformational mobility of cyclopropyl group in allylic cations have been studied by Sorensen and co-workers.[71b,c]

6,6-Disubstituted fulvenes undergo protonation at the C2 carbon in FSO_3H–SO_2ClF at low temperatures to give the dienylic cations 161 and 162.[72] In all these carbocations, the cyclopropyl group was found to delocalize the charge better than phenyl or methyl groups.

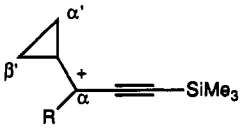


161, R = Cyclopropyl, R' = Phenyl
162, R = R'= Cyclopropyl

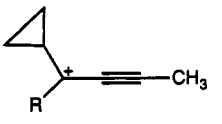
VII. Alkynylcyclopropylcarbinyl Cations

Several alkynylcyclopropylcarbinyl cations (163–168) were prepared by ionizing the corresponding alcohols in FSO_3H or SbF_5–SO_2ClF at −78 °C.[73] In these cations, the cyclopropyl group was more effective than the phenyl or methyl group in stabilizing the carbocationic centers. The mesomeric vinyl cationic contribution is decreased in these cyclopropyl-stabilized alkynyl cations.

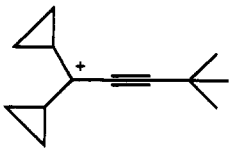
γ-Trimethylsilyl-substituted cations (163–165) did not have any noticeable effect on the chemical shifts of cationic centers. However, the cyclopropyl carbons are slightly deshielded with respect to the γ-*tert*-butyl-substituted cation (168), indicating slight destabilizing effect of the γ-silicon substituent (Table 12).



163, R = Cyclopropyl
164, R = Phenyl
165, R = Methyl



166, R = Cyclopropyl
167, R = Phenyl



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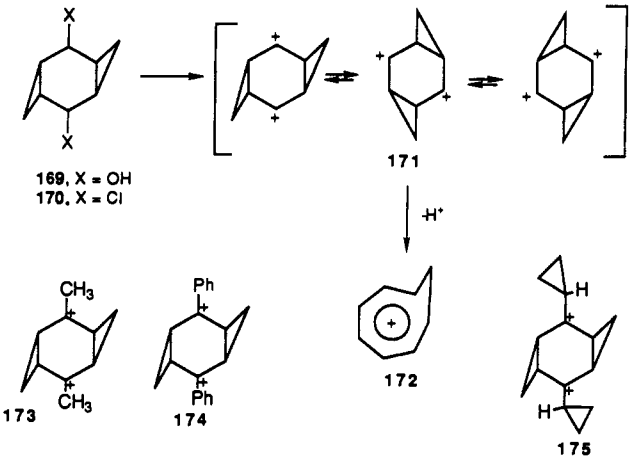
VIII. Cyclopropyl-Stabilized Carbodications

A. *anti*-Tricyclo[5.1.0.0^{3,5}]octa-2,6-diyl Dications

In an attempt to extend the observation of bicyclo-[4.1.0]hept-2-yl cations to the corresponding symmetrical dicyclopropylcarbinyl dications, *anti*-tricyclo-[5.1.0.0^{3,5}]octane-2,5-diol (169) and 2,5-dichloro-*anti*-tricyclo[5.1.0.0^{3,5}]octane (170) were ionized in SbF_5–SO_2ClF or SbF_5–SO_2ClF at −120 to −130 °C[74] (Scheme 18). The expected circumambulation could not be

SCHEME 18



observed in the resulting cation, 171, as it immediately rearranges into homotropylium cation 172.[74] The 2,6-dimethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octa-2,6-diyl dication (173) prepared from the corresponding diol in SbF_5–SO_2ClF at −120 °C showed four signals in the ^{13}C NMR spectrum, indicating expected symmetry (Table 13). The C4 and C8 carbons in the dication 173 are highly deshielded ($\delta(^{13}C)$ 55.9), indicating significant delocalization of the positive charge into the cyclopropane rings.

B. 2,6-Diphenyl-*anti*-tricyclo[5.1.0.0^{3,5}]octa-2,6-diyl Dication

The 2,6-diphenyl-*anti*-tricyclo[5.1.0.0^{3,5}]octa-2,6-diyl dication (174), prepared from the corresponding diol in SbF_5–FSO_3H/SO_2ClF showed seven absorptions in the ^{13}C NMR (Table 13).[74] The para carbon ($\delta(^{13}C)$ 155.5) and cyclopropane methylenes ($\delta(^{13}C)$ 46.3) are deshielded, showing the dispersal of positive charge into both the phenyl and cyclopropane rings.

TABLE 11. ^{13}C NMR Chemical Shifts of α-Ethylenenaphthalenium Ions

cation	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
135	178.1	132.3	180.4	52.6	121.6	137.4	128.2	130.3	132.9	151.9	48.5	48.5	22.6
136	175.5	133.5	179.7	53.7	122.5	137.9	129.9	131.3	134.6	154.4	50.7	50.7	
137	181.6	128.1	178.9	40.5	119.0	137.5	121.8	127.3	124.1	152.3	37.9	37.9	70.2

TABLE 12. Comparison of ^{13}C Chemical Shift δ(^{13}C) Values for Selected Cations

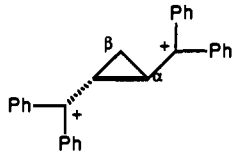
cation	$C_a(C^+)$	$C_{a'}$	$C_{b'}$
163	242.7	47.6	42.1
168	242.4	44.9	45.5
166	243.3	45.5	39.1

C. 2,6-Dicyclopropyl-*anti*-tricyclo[5.1.0.0^{3,5}]octa-2,6-diyl Dication

The dication (175), obtained from the 2,6-dicyclopropyl-*anti*-tricyclo[5.1.0.0^{3,5}]octa-2,6-diol in SbF_5–SO_2ClF at −78 °C showed eight ^{13}C NMR absorptions, indicating conformationally induced asymmetry into the tricyclic ring carbons (Table 13).[74] The strongly deshielded absorptions for the free cyclopropyl [δ(^{13}C) 54.9 (d), 53.8 (t), 52.5 (t)] and annulated cyclopropyl [δ 37.9 (t), 35.5 (t), and 29.6 (d), 27.3 (d)] rings show that substantial delocalization of the charge into the cyclopropane rings occurs.

D. *trans*-Cyclopropane-1,2-bis(diphenylmethylium) Dication

trans-1,2-Bis(diphenylhydroxymethyl)cyclopropane was ionized in FSO_3H–SO_2ClF or FSO_3H/SbF5–SO_2ClF to give the *trans*-cyclopropane-1,2-bis(diphenylmethylium) dication (176).[75] The proton NMR



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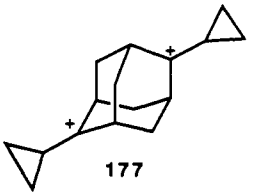
spectrum showed absorptions at δ 8.17 for ortho and meta hydrogens, δ 8.5 for para hydrogens, a triplet at δ 4.66 (J = 8.5 Hz) for α-cyclopropyl hydrogens, and a triplet at δ 3.54 (J = 8.5 Hz) for β-cyclopropane hydrogens. ^{13}C NMR spectrum also showed a symmetrical structure: δ(^{13}C) 220.9 (C^+), 139.1 (C_{ipso}), 141.5 (C_{ortho}), 131.7 (C_{meta}), 147.4 (C_{para}), 42.4 (J = 172.5 Hz, C_α), 29.9 (J = 173.6, C_β). A comparison of the ^{13}C chemical shifts with those of diphenylcyclopropylmethyl cation show that the β-carbon in 176 is more shielded than that in the latter, indicating that charge is predominantly delocalized into the aromatic rings. However, some charge is also delocalized into the cyclopropane ring, as the α-carbon is slightly deshielded compared to that of the diphenylmethyl cation.

E. 2,6-Dicyclopropyl-2,6-adamantanediyl Dication

2,6-Dicyclopropyl-2,6-adamantanediyl dication (177) was prepared by ionizing the corresponding ditertiary alcohol in 1:1 FSO_3H–SbF_5/SO_2 at −80 °C.[53] The ^{13}C



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NMR spectrum of this dication shows absorptions at δ(^{13}C) 277.1 (C^+), 50.5 (C1, C5), 47.5 (C4, C8, C9, C10), 40.8 (C3, C7), 60.4 (cyclopropyl CH_2), 58.1 (cyclopropyl CH). It is interesting to note that in this dication, the cationic centers are shielded by 17 ppm compared to that of the monocyclopropyl-2-adamantyl cation. This is an indication that in 177, due to the intervening charge–charge repulsion, there is more stabilization from the adjacent cyclopropyl groups. Supporting this suggestion, the cyclopropyl carbons are also more deshielded in dication 177 than in the monocation.

IX. Protonated Cyclopropyl Ketones (Cyclopropylhydroxycarbenium Ions)

Protonated cyclopropylcarbonyl compounds (hydroxycyclopropylcarbenium ions) show the cationic ^{13}C NMR chemical shifts at much higher field than those in the related alkyl- or arylcyclopropyl carbenium ions. Although the cationic charge is delocalized to some extent in these cations into the cyclopropyl rings, there remains appreciable C–O double bond character; i.e., the carbocationic center is extensively stabilized by electron donation from the oxygen atom.[1b] Data of NMR studies of two typical protonated cyclopropylalkyl ketones are representatives.

A. 1-(1-Methylcyclopropyl)-1-hydroxyethyl Cation

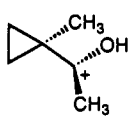
Methyl 1-methylcyclopropyl ketone on dissolution in FSO_3H–SO_2ClF at −78 °C gave an NMR spectra corresponding to the protonated ketone structure and showed only two singlets for methyl groups: AAX'X' pattern for the cyclopropyl ring protons and the deshielded hydroxyl resonance.[52] At −100 °C the deshielded methyl absorption (^1H NMR) at δ 2.55 split into δ 2.45 and δ 2.99 in a ratio of 4:1. The major isomer was assigned to 178, and the minor one to the 179. On warming the solution to −15 °C, sharp spectral lines

TABLE 13. ^{13}C NMR Chemical Shifts for *anti*-Tricyclo[5.1.0.0^{2,5}]octa-2,6-diyl Dications

cation	C1	C2	C3	C4	C5	C6	C7	C8	others
173	43.3	293.4	43.0	55.9	43.0	293.4	43.0	55.9	48.4 (Me)
174	35.8	235.4	35.3	46.3	35.3	235.4	35.3	46.3	phenyl[a]
175	29.6	260.8	27.3	37.9	27.3	260.8	29.6	35.5	cyclopropyl[b]

[a] 155.5 (C_p), 133.9 (C_m), 140.8 (C_o), 130.1 (C_i). [b] 54.9 (C_α), 53.8 and 52.5 (C_β).

were observed, indicating that rotation about C1–Cα bond was fast on the NMR time scale. **178**: ^{1}H NMR δ 2.22, 2.45 (H2, H3), 1.50 (C1-CH_3), 2.45 (Cα-CH_3); ^{13}C NMR δ(^{13}C) 36.2 (C1), 236.15 (C^+), 32.5 (C2,C3), 16.0 (C1-CH_3), 21.65 (Cα-CH_3). **179**: ^{1}H NMR δ 2.22, 2.45 (H2, H3), 1.50 (C1-CH_3), 2.99 (Cα-CH_3); ^{13}C NMR δ(^{13}C) 33.5 (C1), 241.85 (C^+), 38.9 (C2, C3), 17.4 (C1-CH_3), 28.65 (Cα-CH_3).



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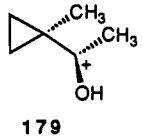

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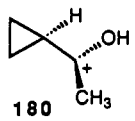
B. 1-Cyclopropyl-1-hydroxyethyl Cation

Cyclopropyl methyl ketone in FSO_3H–SO_2ClF at −90 °C showed the presence of two isomers (cis and trans) in a ratio of 4:1 with a temperature dependence similar as for the 1-methyl analogue.[52] Cis isomer (**180**): ^{13}C NMR δ(^{13}C) 29.75 (C1), 240.7 (C^+), 30.75 (C2, C3), 27.6 (Cα-CH_3). Trans isomer (**181**): ^{13}C NMR δ(^{13}C) 20.2 (C1), 237.75 (C^+), 25.2 (C2, C3), 27.6 (Cα-CH_3).



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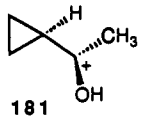


181

Comparison of these chemical shifts with those of the 1-methyl analogue again shows that the 1-methylcyclopropyl group is better electron donating than the cyclopropyl group.

The 3-hydroxy-3-nortricyclyl cation[42] illustrates a hydroxycyclopropylcarbinyl cation, where the cyclopropyl group is part of a strained ring.

X. Relative Charge-Delocalizing Abilities of Cyclopropyl and Phenyl Groups

Assuming that the ^{13}C chemical shifts vary linearly with the carbon charge densities, Olah and White, in 1969, concluded that the stabilizing effects of both cyclopropyl and phenyl groups are substantially higher than that of hydrogen but less than that of hydroxyl.[63b] Table 14 compares the chemical shifts of the carbocation centers for the cyclopropyl- and phenyl-substituted carbocations with hydroxy-, hydrogen-, and methyl-substituted analogues. The cationic center of the phenyldimethylcarbenium ion (δ(^{13}C) 254.2) is considerably more shielded than that of cyclopropyldimethylcarbenium ion (δ^{13}C) 279.9). Neglecting the minimal contribution of neighboring group anisotropies and phenyl ring current effects on chemical shifts, these results prompted the suggestion that the phenyl group may be more stabilizing than the cyclopropyl.

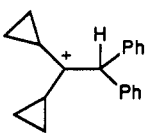
Deno and co-workers, on the other hand, on the basis of thermodynamic and gas-phase stabilities, concluded that cyclopropyl group is more electron delocalizing than the phenyl.[76] Thus, the equilibrium constant for the formation of the tricyclopropylmethyl cation from the alcohol is much higher than that for the triphenylmethyl cation. The superior stabilizing ability of the cyclopropyl group was also reflected in the gas phase by comparing the relative appearance potentials for the cyclopropyl- and phenyl-substituted cations. The appearance potentials for the carbocations from the respective alkanes, relative to R = H (0) are R = CH_3 (36 kcal/mol), R = Ph (55 kcal/mol), and R = cyclopropyl (58 kcal/mol). Tertiary 1-cyclopropyl-1-

$$RCH_3 + e^- \rightarrow RCH_2^+ + 2e^- + H^\bullet \quad (1)$$

methylethyl cation is more stable than the 1-phenyl-1-methylethyl cation by 0.8 kcal/mol, while the secondary 1-cyclopropylethyl cation is less stable than the 1-phenylethyl cation by 4.8 kcal/mol, as determined by their gas-phase heats of formation.[77] This trend of diminishing stabilizing effect of the phenyl group over cyclopropyl group from primary to secondary to tertiary cations was also substantiated by theoretical calculations at STO-3G level.

However, the data related to kinetics or equilibrium constants provide only an indication of energy differences between the ion and precursors.[78,79] Since ^{13}C chemical shifts are more reliable for estimating the relative charge density on the cationic carbon, they could provide more direct information on the properties of the carbocationic center. The data in Table 14 show that the cationic center of the phenyl-substituted cations are more shielded than those of cyclopropyl-substituted cations, which in turn are more shielded than the methyl analogues. Thus, the apparent stabilizing effects of the phenyl, cyclopropyl, and methyl groups would seem to be in the order: phenyl > cyclopropyl > methyl on the basis of the assumption that the charge densities on cationic carbons are directly related to the ^{13}C chemical shift values. However, effects other than charge density also can affect chemical shifts.[80]

When phenyl and cyclopropyl groups compete with each other intramolecularly for the positive charge, as in **182** and **183**, indication on the stabilizing effect



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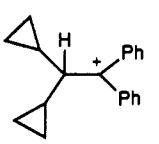


183

should be revealed. However, it was found that the activation energy for the hydride migration in these cyclopropyl-substituted cations is much higher, thus effectively preventing their interconversions.[78,79]

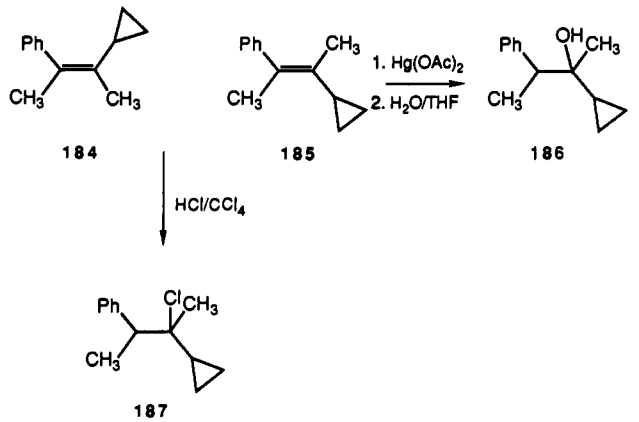
TABLE 14. ^{13}C NMR Chemical Shifts of Some Methyl-, Cyclopropyl-, Phenyl-, and Hydroxy-Substituted Carbocation Centers[a]

cation	chemical shift (δ)
$(CH_3)_2CH^+$	318.1
$(CH_3)_3C^+$	328.5
$[(CH_3)_2C{=}OH)_2]^+$	248.8
$[CH_3C(OH)_2]^+$	194.7
$[CH(OH)_2]^+$	176.1
$[C(OH)_3]^+$	165.1
$(c\text{-}Pr)_2CH^+$	253.0
c-PrCH$^+$Ph	225.7
c-PrCH$^+$$CH_3$	252.2
$(c\text{-}Pr)_3C^+$	270.9
c-PrC$^+$$(CH_3)_2$	279.9
$Ph_2(c\text{-}Pr)C^+$	234.4
$Ph(c\text{-}Pr)_2C^+$	260.4
PhC$^+$$(CH_3)_2$	254.2
Ph_2CH^+	198.7
Ph_3C^+	211.2

[a] Chemical shift values are calculated with reference to δ CS_2 = 193.1 ppm. The ions were prepared in SbF_5–SO_2ClF or FSO_3H–SbF_5–SO_2ClF at −20 to −90 °C.[63b,81]

Electrophilic addition reactions to olefins involve formation of carbocations and should give evidence complimentary to the solvolytic studies. Oxymercuration and hydrochlorination of olefins 184 and 185 gave the alcoholic and chlorinated products 186 and 187 with OH and Cl groups attached to the same carbons having the cyclopropyl groups (Scheme 19). This

SCHEME 19



shows that the cyclopropyl group stabilizes the carbocationic intermediates more effectively than the phenyl group.[78] These results parallel the rate-accelerating effect observed for the cyclopropyl group in solvolysis reactions and show that the cyclopropyl group is the better participating group.

Although chemical shifts cannot be quantitatively correlated to charge densities, they provide qualitative indicators for the charge densities at the carbons of similar structures. Subsequent detailed study involving the correlation of σ^+-substituent constants with the ^{13}C cationic shifts of several cyclopropylphenylcarbinyl cations showed that phenyl and cyclopropyl groups are about comparable in their stabilizing abilities.[81] Kerber[82] and Moss[83a] and co-workers determined the relative stabilizing effects of cyclopropyl and phenyl groups on cyclopropenyl cations by their pK_{R^+} determinations. The pK_{R^+} values for $Ph_3C_3^+$, $CyPh_2C_3^+$, $Cy_2PhC_3^+$, and $Cy_3C_3^+$ were found to be 3.4, 5.04, 7.09, and 9.4 respectively. Thus, replacing each phenyl group by a cyclopropyl group results in approximately a gain of two pK units of stabilization on the pK_{R^+} scale. Arnett and co-workers[83b,c] from thermochemical carbocation stability studies using solution calorimetry found surprising dependence of the orders for the stabilization by cyclopropyl and phenyl with the experimental conditions of ionization. Thus, ionization of the tertiary alcohols in SbF_5–SO_2ClF at low temperatures gave a relative order of cyclopropyl > phenyl > methyl, whereas ionization in SbF_5–FSO_3H–SO_2ClF provided an order of phenyl > cyclopropyl > methyl. It can be concluded from the existing divergent results that the cyclopropyl is slightly more effective in dispersing cationic charge than phenyl, although steric and electronic demands on specific substrates and solvation of the ions may change the relative order.[71,72]

XI. Relative Stabilities of Allyl and Cyclopropylcarbinyl Cations

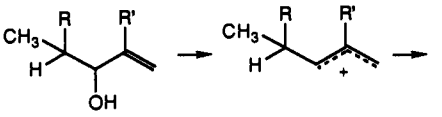
It was observed that allyl alcohols (188–190) form the cyclopropylcarbinyl cations (194–196) when treated with FSO_3H–SO_2ClF at −78 and −120 °C.[84] These

TABLE 15. Summary of Bond Distances (Å) of Selected Cations[a]

cation	av cyclopropyl	distal (C3–C4)	C1–C2
205	1.483	1.418	1.405
206	1.507	1.448	1.461
207	1.509	1.433	1.403
200	1.506	1.448	1.417
201	1.509	1.468	1.430
202	1.52	1.501	1.474

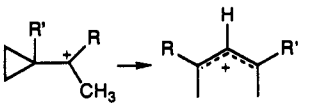
[a] Taken from ref 85.

cations were presumably arising through initially formed allyl cations (191–193). Thus the cyclo-



188, R = CH_3, R' = H
189, R = R' = CH_3
190, R = R' = H

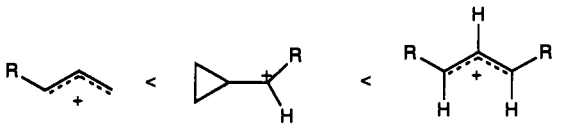
191, R = CH_3, R' = H
192, R = R' = CH_3
193, R = R' = H



194, R = CH_3, ROH
195, R = R' = CH_3
196, R = R' = H

197, R = CH_3, R' = H
198, R = R' = CH_3
199, R = R' = H

propylcarbinyl cations (194–196) are more stable than the allyl cations (191–193). On further warming to more elevated temperatures, they rearranged to the more stable allyl cations, 197–199, respectively. Thus the relative stabilizing effects of vinyl and cyclopropyl groups are in the following order:



R = alkyl

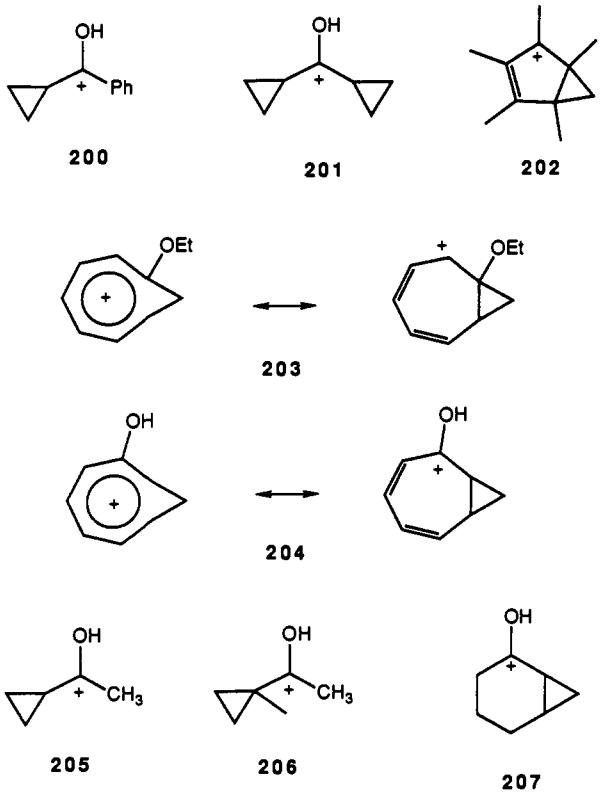
The cyclopropyl group was estimated to be more stabilizing than the vinyl group by 11–17 kcal/mol.

XII. X-ray Studies

Direct structural information on hydroxycyclopropyl cations, which closely resemble the cyclopropylcarbinyl cations in their NMR behavior, was obtained by Childs and co-workers.[85] They obtained the structures of cations 200–207 (Scheme 20) as their hexafluoroantimonate salts by single-crystal X-ray diffraction. The salts were obtained by treatment of the corresponding ketones with HF–SbF_5 in dichloromethane solution at −78 °C. The structure of these cations, as compared with their precursors show lengthened vicinal bonds, shortened distal bonds, and C(=O)—C(apex) bonds. The structures adopt a bisected geometry (200, 201, 205), or closely related geometry (206, 207).

Introduction of an α-methyl group such as in 206 was expected to increase the charge delocalization into the cyclopropane ring, compared to 205, as reflected in NMR chemical shift changes. However, structurally, there were no significant changes in the bond lengths of C2–C3 or C2–C4 bonds. The C1–C2 bond in 206 (1.461 Å) is, on the other hand, much larger than that in 205 (1.405 Å). The bond length data for these carbocations are given in Table 15.

SCHEME 20



XIII. Acknowledgment

Support of our work over the years by the National Institutes of Health is gratefully acknowledged.

Registry No. Cyclopropylmethylium, 14973-56-9.

XIV. References

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