Acknowledgments. The authors are very grateful to Professor Yoshida of Kyoto University for his helpful discussions. The authors are also grateful to du Pont de Nemours and Co. for their kind supply of adamantane.

Registry No.—1,3-Dimethyladamantane, 702-79-4; ethylene, 74-85-1; 1-ethyl-3,5-dimethyladamantane, 1687-35-0; 1-*n*-butyl-3,5-dimethyladamantane, 52826-28-5; 1-*n*-hexyl-3,5-dimethyladamantane, 52873-50-4; 1-*n*-octyl-3,5-dimethyladamantane, 52855-93-3; 1-cyclohexyl-3,5-dimethyladamantane, 19385-91-2; 1-cyclooctyl-3,5-dimethyladamantane, 52826-29-6; adamantane, 281-23-2.

References and Notes

(1) Fragmentation is one of the common fates of an intermediate from a chain aliphatic compound.

(2) Even for free-radical reactions, some intramolecular rearrangement was observed. See, *e.g.*, W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N.Y., 1966 p 13, for the 1,2-chlorine shift. But the 1,2-hydrogen shift on the adamantyl radical was not observed although the following indirect intermolecular process was sometimes observed which

$$\mathrm{Ad}\cdot^{(2)} \xrightarrow{\mathrm{SH}} \mathrm{AdH} \xrightarrow{\mathrm{R}\cdot} \mathrm{Ad}\cdot^{(1)} \xrightarrow{\mathrm{Y-X}} \mathrm{Ad}^{(1)}\text{–}\mathrm{X}$$

was confirmed in the perester decomposition in biacetyl (I. Tabushi, K. Fukunishi, and S. Kojo, manuscript in preparation).

(3) Unselective chlorination and autooxidation; G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26,** 2207 (1961).

(4) Chlorocarbonylation; I. Tabushi, J. Hamuro, and R. Oda, *J. Org. Chem.*, **33,** 2108 (1968); I. Tabushi, T. Okada, Y. Aoyama, and R. Oda, *Tetrahedron Lett.*, 4069 (1969).

(5) Regiospecific photoacetylation; I. Tabushi, S. Kojo, and Z. Yoshida, *Tetrahedron Lett.*, 2329 (1973).

(6) Radical bromination or chlorination with various halogenating reagents; I. Tabushi, J. Hamuro, and R. Oda, *J. Amer. Chem. Soc.*, **89,** 7127 (1967). See also I. Tabushi, Y. Aoyama, S. Kojo, I. Hamuro, and Z. Yoshida, *J. Amer. Chem. Soc.*, **94,** 1177 (1972), and I. Tabushi, Y. Aoyama, and Z. Yoshida, *ibid.*, **93,** 2077 (1971).

(7) This compound is a liquid under the reaction conditions and reaction proceeds much more smoothly by using this than parent adamantane.

(8) S. Landa, *et al.*, *Chem. Listy*, **51,** 2325 (1957).

(9) E. Osawa, Z. Majerski, and P. v. R. Schleyer, *J. Org. Chem.*, **36,** 205 (1971).

(10) 1-Adamantyl bromide and an olefin in the presence of a Lewis acid; E. C. Capaldi, U.S. Patent, 3,437,701 (1969); *Chem. Abstr.*, **70,** 114713 (1969).

(11) Adamantane and an olefin with a Lewis acid; B. A. Kazanskii, E. A. Shokova, and T. V. Koroteleva, *Izv. Akad. Nauk SSSR,* 2161 (1968); B. A. Kazanskii *et al.*, *Dokl. Akad. Nauk SSSR,* 188 (1969); 191 (1970).

(12) An adamantane and an alcohol with sulfuric acid; A. Schneider, U.S. Patent, 3,382,288 (1968); *Chem. Abstr.*, **69,** 35584 (1968); *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.*, 15 (1970); *Chem. Abstr.*, **75,** 109936 (1971).

(13) Dimethyladamantane with boron trifluoride–ether complex and sulfuric acid; R. E. Moore, U.S. Patent, 3,671,600 (1972); *Chem. Abstr.*, **77,** 100938 (1972).

(14) Adamantyl bromide and thiophene with stannic chloride followed by Raney Ni desulfurization; W. Hoek, *et al.*, *Recl. Trav. Chim. Pays-Bas*, **85,** 1045 (1966).

(15) In the case of 1,3-dimethyladamantane, the substituent effect seems to be operative also.

(16) (a) The results of systematic analyses of the reactivities will be published soon. A part of the work was presented; I, Tabushi, Y. Aoyama, and Z. Yoshida, 12th Symposium on Organic Free Radicals, Nagoya, 1971, Abstracts of Papers, p 75; 26th Annual Meeting of Japan Chemical Society, Hiratsuka, 1972, Abstracts of Papers, III, p 1333. (b) The statistically corrected reactivity ratio of bridgehead to bridge position for the chlorocarbonylation of 1-substituted adamantanes amounted to 2.3 for methyl, 5.7 for methoxyl, and 4.4 for carbomethoxy (considerably larger than 1.2 for the unsubstituted); I. Tabushi, T. Okada, Y. Aoyama, and R. Oda, *Tetrahedron Lett.*, 4069 (1969). Similarly, the reactivity ratios for the $BrCCl_3$ bromination were 26.8 for methyl and 22.8 for methoxyl (18.3 for the unsubstituted); P. H. Owens, G. J. Gleicher, and L. M. Smith, Jr., *J. Amer. Chem. Soc.*, **90,** 4122 (1968). However, in the above results, differentiations between 2 and 4 positions were not made.

Stable Carbocations. CLXXII.[1] 2-Adamantyl Cations

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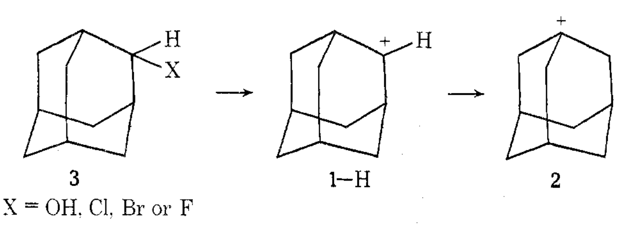
A series of 2-alkyl-, 2-phenyl-, and 2-halo-substituted 2-adamantyl cations were obtained in FSO_3H, $FSO_3H \cdot SbF_5$, and SbF_5 (SO_2ClF or SO_2) solutions at −78° and their ^1H and ^{13}C nmr spectra were studied. Tertiary 2-adamantyl cations, unlike the parent secondary 2-adamantyl cation which immediately undergoes intermolecular rearrangement to the bridgehead 1-adamantyl cation, show no skeletal rearrangement in superacidic media. 2p–π conjugation between the phenyl π system and the empty 2p orbital at the carbenium center in 2-phenyl-2-adamantyl cation was found important. Halogen back donation (n–2p conjugation) induced by the halogen unshared electron pairs in 2-halo-2-adamantyl cations was found to increase in accordance with the increasing order of halogen electronegativity Br < Cl < F.

The observation and study of 1-adamantyl cations[2] in strongly acidic media in our laboratory prompted interest in the study of 2-adamantyl cations. These ions have similar rigidity but bear positive charge at the secondary, nonbridgehead position of the adamantane system. The parent 2-adamantyl cation 1–H has thus far not been directly observed. The reason is that fast intermolecular hydride shift takes place immediately after the relatively unstable secondary ion 1–H is formed, giving the more stable tertiary bridgehead 1-adamantyl cation **2**.[3,4]



3 1–H 2

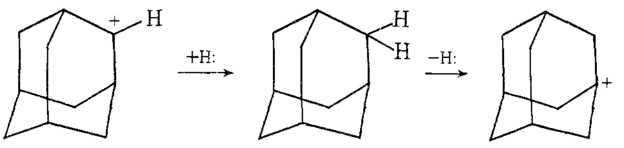
X = OH, Cl, Br or F

2-Methyl-2-adamantyl cation is, however, stable in strong acid solutions (in H_2SO_4, FSO_3H, or $FSO_3H–SbF_5$) and shows no tendency to interconvert.[5] Many rearrangements involving apparent 1,2-hydride shifts in adamantane systems are now known to take place intermolecularly.[3,4,6] The interconversion of 2-methyl- and 1-methyladamantane, however, was shown to proceed intramolecularly involving rearrangement of 2-methyl-2-adamantyl cation to the 4-protoadamantyl cation followed by a rearrangement back to the adamantyl skeleton.[4b]

Although a series of 1-adamantyl cations have been prepared and characterized,[2] 2-substituted-2-adamantyl cations have not yet been reported in the literature. We, therefore, undertook the preparation of a series of 2-substituted-2-adamantyl cations and the study of their structure and stability in superacidic media. Proton and carbon-13 nmr spectra of 2-adamantyl cations including 2-alkyl-, 2-phenyl-, and 2-halo-substituted ions were obtained.

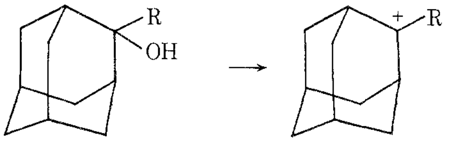
Results and Discussion

2-Adamantyl Cation 1-H. Attempts to prepare the parent secondary 2-adamantyl cation 1-H from various precursors 3 (X = OH, Cl, Br, F) at different temperatures (−78 and −120°) were unsuccessful.[2] The initially formed ion 1-H in SbF_5SO_2ClF solution even at −120° immediately rearranged into the more stable tertiary ion **2**. The solvolysis of 2-adamantyl esters gave 2-adamantanol as the sole product after saponification,[4a,6,7] indicating the potential stability of ion 1-H under nucleophilic substitution conditions. The secondary ion 1-H formed under nonnucleophilic, stable ion conditions must undergo facile intermolecular hydrogen transfer to give ion 2 (intramolecular 1,2-hydrogen shift is impossible, because the orientation of the empty p orbital relating to the tertiary C–H bonds prevents it). A possible pathway might be visualized in the following manner.

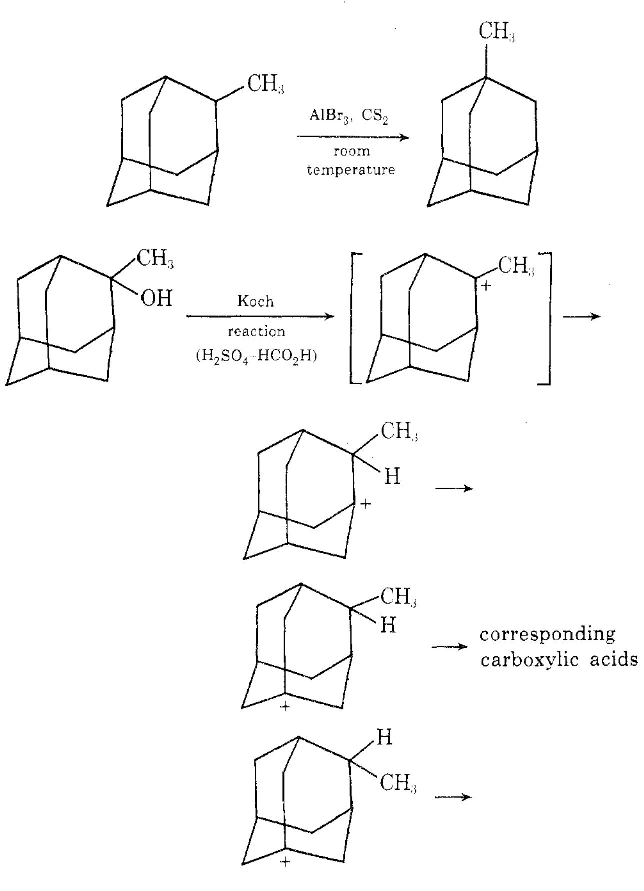


1–H 3 (X = H) 2

2-Methyl- and 2-Ethyl-2-adamantyl Cations. (1-CH_3 and 1-CH_2CH_3). These two ions are formed in fluorosulfuric acid–antimony pentafluoride sulfuryl chloride fluoride solution at −78° from their respective alcohols, 4. Both ions are stable and show no rearrangement in the temperature range studied (−78–+25°). Under the conditions of the Koch reaction,[8] 2-methyl-2-adamantanol is known to give a mixture of isomeric methyladamantylcarboxylic acids, while 2-methyladamantane is known to isomerize to 1-methyladamantane.[8-10] However, under stable ion conditions the 2-methyl-2-adamantyl cation 1-CH_3 is stable and apparently no isomerization takes place. Likewise, ion 1-CH_2CH_3 is also sufficiently stable under these conditions, to be observed as the stable, nonrearranging ion.



4, R = CH_3 or CH_2CH_3 1-R



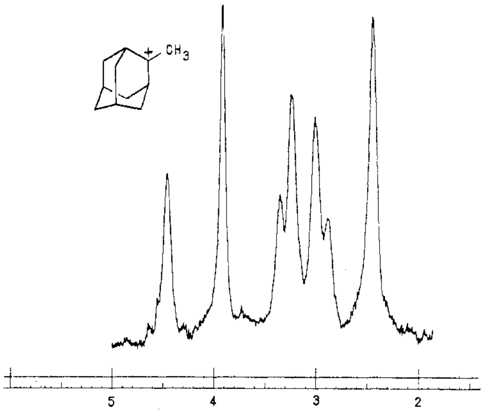


Figure 1. Pmr spectrum (100 MHz) of 2-methyl-2-adamantyl cation.

Pmr spectra of 2-methyl- and 2-ethyl-2-adamantyl cations (1-CH_3 and 1-CH_2CH_3) are very similar and considerably different from that of the 1-adamantyl cation[2a,b,g] (Figure 1). Pmr spectra of 2-substituted-2-adamantyl cations are summarized in Table I. Four basic proton resonances are observed in all 2-adamantyl cations. The two bridgehead protons resonances in the β positions to the empty p orbital (H_1 and H_3) are observed at δ 4.5 as a singlet; the four equivalent methylene protons show an AB quartet centered at δ 3.12 and 3.08 for 1-CH_3 and 1-CH_2CH_3, respectively; the additional two bridgehead protons (H_5 and H_7) are found at about δ 2.3–2.4; and the C_6 methylene protons usually are overlapping with the H_5 and H_7 signals.

Fourier transform (FT) ^{13}C nmr spectra of 1-CH_3 and 1-CH_2CH_3 are also completely different from that of 1-adamantyl cation.[2c,d] We have now obtained the complete FT ^{13}C nmr spectra for these ions and have summarized cmr parameters in Table II. The carbenium carbon shifts for both ions are found at $\delta_{^{13}C}$ 323.0 and 322.7 (from external capillary TMS), respectively. These values are very close to those found in the *tert*-butyl- ($\delta_{^{13}C}$ 329.1) and 1-methylcyclohexyl ($\delta_{^{13}C}$ 331.5) cations, indicating only a slight shielding due to the electron-releasing alkyl groups attached to the sp^2 center. The two equivalent bridghead carbons (C_1 and C_3) and the four equivalent methylene carbons (C_4, C_8, C_9, and C_{10}) all show normal deshielded carbon shifts (Table II) experiencing the inductive effect at α and β positions to the positive charge, respectively. One noticeable point is that the two bridgehead carbons (C_5 and C_7) are found to be more shielded (by about 7–8 ppm) than the methylene carbon (C_6) which is the furthest away from the carbenium center. This observation is striking, since carbons γ to the carbenium center are generally more deshielded than those at the δ position. In the parent adamantane molecule, the bridgehead methine carbon atoms are less deshielded ($\delta_{^{13}C}$ 38) than the methylene ones ($\delta_{^{13}C}$ 27). We believe a contributing factor to the deshielding is the strain induced by ionization. If so, the same reasoning can be applied to the unusual observations of cmr shifts of 2-adamantyl cations.

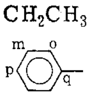
Protonated 2-adamantanone 1-OH has previously been reported and characterized by pmr.[11] Ion 1-OH (in

Table I
Pmr Parameters of 2-Adamantyl Cations[a]

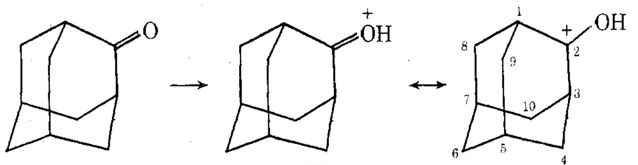
R	Registry no.	H_1, H_3	H_4, H_8, H_9, H_{10}	H_5, H_7	H_6	CH_3	$CH_2{*}CH_3$	Other
CH_3	27411-03-6	4.45, s	3.12, ABq	2.45, s	2.45, s	3.90		
CH_2CH_3	52873-72-0	4.48, s	3.08, ABq	2.48, s	2.30, s	1.80, t	4.25, q	
C_6H_5	52873-73-1	4.82, s	3.00 ABq	2.58, s	2.58, s			o: 9.12, d[b] p: 8.96, t m: 8.35, d-d
Br	52873-74-2	5.02, s	3.35, s	2.60, s	2.60, s			
Cl	52873-75-3	4.82, s	3.56, ABq	2.78, s	2.78, s			
F	51608-57-2	4.20, d	3.45, ABq	2.70, s	2.70, s			
OH	52873-76-4	3.50	2.73	2.40	2.30			13.85

[a] Pmr shifts (δ) are relative to external TMS; s = singlet; ABq = AB quartet; t = triplet; d = doublet; d-d = doublet of doublet. [b] Aromatic protons: o = ortho; p = para; m = meta.

Table II
^{13}Cmr Nmr Shifts of 2-Adamantyl Cations[a]

R	C^+	C_1, C_3	C_4, C_8, C_9, C_{10}	C_5, C_7	C_6	CH_3	$*CH_2CH_3$	Other
CH_3	323.0	66.3	52.6	29.1	36.6	41.2		
CH_2CH_3	322.7	62.5	51.3	28.7	36.0	7.8	49.4	
	271.3	51.4	49.3	29.5	36.3			o: 138.1[b] m: 132.9 p: 154.2 q: 137.1
OH	267.1	47.5	44.2	27.4	35.3			
Br	316.1	76.2	56.2	30.4	37.0			
Cl	313.7	71.6	56.5	30.4	36.9			
F	297.2[c] 286.0	56.1	53.9	29.3	36.4			

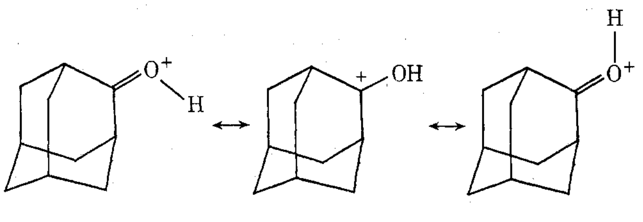
[a] Carbon-13 shifts are in parts per million from external TMS (capillary). [b] Aromatic carbons: o = ortho; m = meta; p = para; q = quaternary. [c] A doublet is observed for **1**-F with J_{CF} = 422.6 Hz, and the average carbon shift is 291.6; ^{19}F shift for this ion is −126.4 (triplet, J_{HF} = 17 Hz). ^{19}F chemical shift is in parts per million from external CCl_3F (capillary).

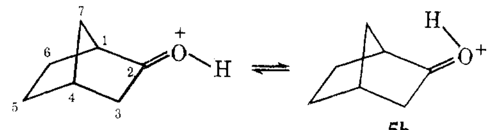


1–OH

FSO_3H-SO_2 or SO_2ClF) is extremely stable and only one OH absorption is observed (Table I) between −125 and 25°. The FTC C nmr spectrum of 1-OH shows five carbon absorptions characteristic to all the 2-adamantyl cations. Again, C_6 is more deshielded than C_5 and C_7.

Protonation of ketones normally gives isomeric species and the energy barrier for interconversion between isomers varies with different systems. The energy barrier for 1-OH seems generally to be low and the interconversion between the two oxonium ion forms must be fast since both ^{1}H and ^{13}C spectra indicate that the ion is symmetrical. If only one of the isomers would be present at low temperature, the two bridgehead carbons (C_1 and C_3) apparently should be different and a more complicated cmr spectrum should be obtained. An example is seen in the C nmr spectrum of the protonated 2-norbornanone **5**.[1b,10] At low temperature, two isomeric protonated 2-norbornanones are observed in FSO_3H-SO_2ClF. The bridgehead carbon C_1 in **5a** has a different carbon shift than that of C_1 in **5b**, and the C_3 carbon shift in **5a** is different than that in **5b**. At higher temperature (+10°), **5a** and **5b** equilibrate.

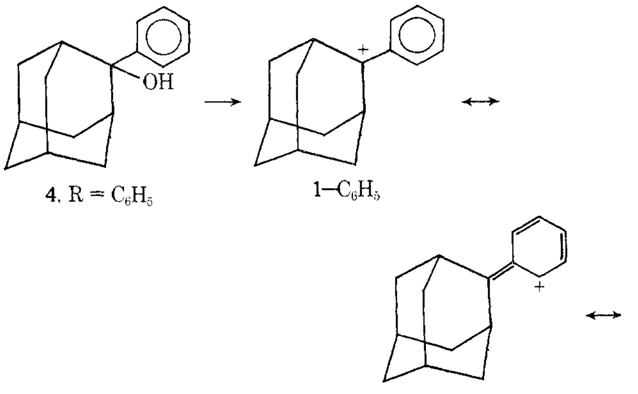




5a **5b**

It is surprising that rotation along the C–O bond is very fast in the case of 1-OH. This behavior is quite different from other protonated bicyclic ketones.[10] There must be some yet not understood special factors which enable 1-OH to undergo interconversion through a very low barrier.

The 2-phenyl-2-adamantyl cation 1-C_6H_5 has not been previously obtained. When the corresponding alcohol



4, R = C_6H_5

1–C_6H_5

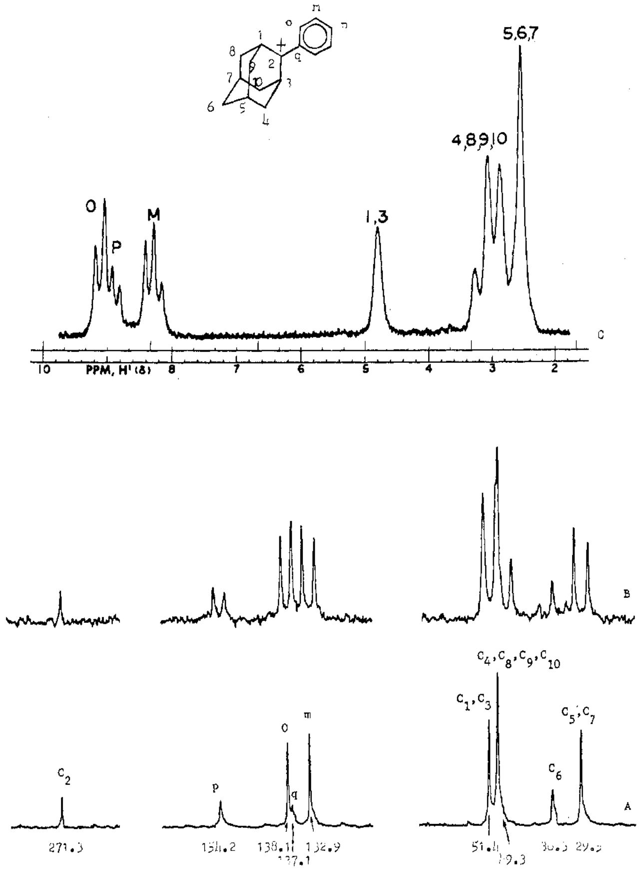
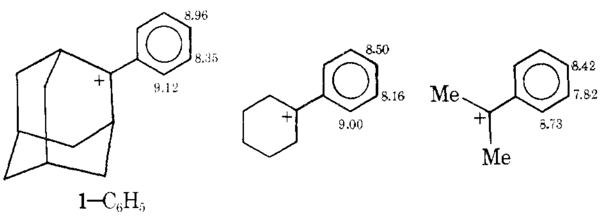
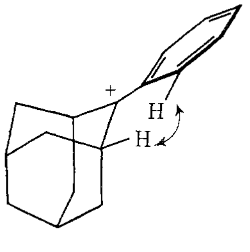


Figure 2. Proton-decoupled ^{13}C nmr (A), off-resonance ^{13}C nmr (B), and ^1H nmr (C) spectra of **1**-C_6H_5.

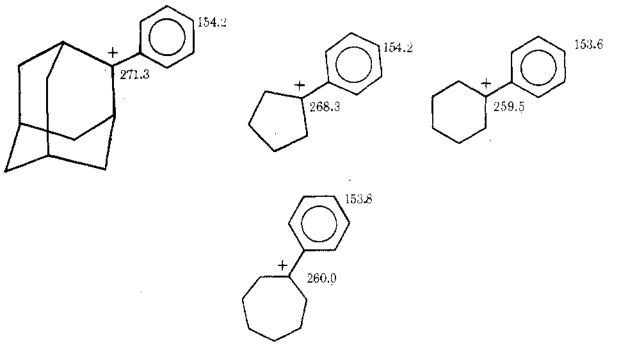
4-C_6H_5 is added to FSO_3H–SO_2ClF at −78°, a light colored solution of 1-C_6H_5 is formed, the pmr (60 MHz) spectrum of which (Figure 2) was obtained. Ion 1-C_6H_5 shows the characteristics of classical tertiary phenylcarbenium ion. Both ortho and para protons are deshielded (δ 9.12 and 8.96, respectively) along with the other four proton resonances which are characteristic of a 2-substituted adamantyl cation. The two bridgehead protons (H_1 and H_3) are furthermore more deshielded than those of 1-CH_3 and 1-CH_2CH_3.



1–C_6H_5

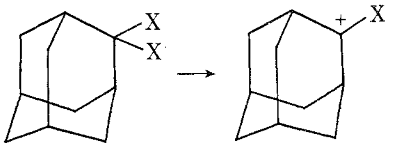


The Fourier-transform C nmr spectrum (Table II) of 1-C_6H_5 also clearly indicates that extensive charge delocalization exists between the adamantyl nucleus and the phenyl ring. The carbon-13 chemical shift of the carbenium center is observed at $\delta_{^{13}C}$ 271.3, which is very close to those of tertiary phenyl carbenium ions.



That the positive charge is extensively delocalized into the phenyl ring is further indicated by the observation of the deshielded para carbon in 1-C_6H_5 ($\delta_{^{13}C}$ = 154.2) whose shift is very similar to those in the model ions shown.[1b] This is also supported by the fact that 2-phenyl-2-adamantanol can be recovered unchanged when this alcohol is treated with 98% sulfuric acid at 0° for 1 hr.[10a] 2-Methyl-2-adamantanol, on the contrary, undergoes extensive rearrangement under the same condition.[3,4,10]

2-Halo-2-adamantyl Cations. In SbF_5–SO_2ClF or FSO_3H–SbF_5–SO_2ClF solutions, 2-halo-2-adamantyl cations 1-Br, 1-Cl, and 1-F were found stable at −78°. They are formed directly from the respective 2,2-dihaloadamantanes **6**. Among the three ions, the 2-bromo-2-adamantyl cation 1-Br is less stable than the other two cations.



6   1–X, X = F, Cl, Br

In the pmr spectra of ions 1-Br, 1-Cl, and 1-F (see data summarized in Table I) the two bridgehead protons (H_1 and H_3) are found most deshielded in 1-Br, and least deshielded in 1-F, while those in 1-Cl fall in between. Two important factors should be considered to interpret the results: (a) different anisotropic effects of the halogen atoms, (b) decreasing n-p conjugation between the halogen atom and the empty p orbital in the order F > Cl > Br. We consider that the shielding of the two bridgehead carbons (H_1 and H_3) in 1-F is caused by effective n-p conjugation between the fluorine lone pairs of electrons and the empty p orbital of the carbenium center. C_2 in 1-F apparently bears less positive charge than those in 1-Br and 1-Cl.

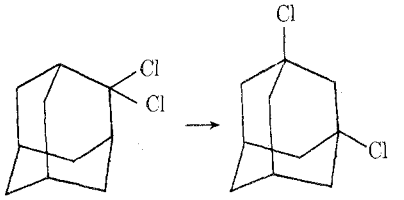
The anistropy effect of halogen atoms in the halocarbenium ions apparently has direct effect toward the deshielding of the neighboring protons. The methylene protons (H_4, H_8, H_9, and H_{10}) in both 1-Cl and 1-F exhibit AB quartets with coupling constants smaller than those of 2-alkyl- (1-CH_3, 1-CH_2CH_3) and 2-phenyl- (1-C_6H_5) 2-adamantyl cations; and those in 1-Br exhibit a singlet absorption (Table I). The difference can, therefore, be attributed to the fact that the size of a bromine atom is considerably larger than those of chlorine and fluorine atoms.

The Fourier transform C nmr spectra of 2-halo-2-adamantyl cations, the cmr parameters, and assignments are summarized in Table II. A consideration of the cmr data reveals several interesting points. (a) The magnitude of the deshielding of the carbenium carbon increases in the order of 1-F < 1-Cl < 1-Br. (b) The two bridgehead carbons (C_1 and C_3) show increasing shielding effect according to the order 1-Br < 1-Cl < 1-F. (c) The methylene carbons (C_6)

fathest from the positive charge are more deshielded than the bridgehead carbons (C_5 and C_7) which are closer to the positive charge.

We have previously discussed the effect of halogen substitution toward the carbenium carbon shifts in halocarbenium ions.[12,13] Fluorocycloalkyl cations show less deshielded carbenium ion centers than those in chloro- and bromocyclocarbenium ions,[12,13] due to the presence of strong fluorine "back-donation." We find this is also true in the case of 2-halo-2-adamantyl cations. The n–p conjugation between the empty p orbital and the fluorine unshared 2p electrons not only places less positive charge on the carbenium center in 1–F but also makes the bridgehead carbons α to the carbenium center less deshielded (see Table II).

2,2-Dichloro- and 2,2-dibromoadamantane (**6,** X = Cl and Br) have recently been found to undergo Lewis acid halide catalyzed rearrangement,[10] similar to the case of 2-methyl-2-adamantanol, when a solution of the dichloride (**6,** X = Cl) in carbon tetrachloride is stirred in the presence of aluminum chloride for 3 days at room temperature. 1,3-Dichloroadamantane is obtained in 70% yield.[10a] The 2,2-dibromide (**6,** X = Br) rearranges much more readily than does the dichloride; after 1 hr in carbon disulfide–aluminum chloride the product contains 75% 1,3-dibromoadamantane.[10a] Although the 1-adamantyl and 2-halo-2-adamantyl cations do not show any rearrangement in antimony pentafluoride based superacids, their behavior in general Friedel-Crafts catalyzed systems may be different and tend to show rearrangements.



6, X = Cl 70%

Experimental Section:

Materials. 2-Methyl-,[7a] 2-ethyl-, and 2-phenyl-2-adamantanols[10a] were prepared from the reaction of 2-adamantanone (Aldrich) with methyl-, ethyl-, and phenylmagnesium bromides, respectively.

2,2-Dichloro- and 2,2-dibromoadamantanes (**6,** X = Cl and Br) were prepared by reaction of 2-adamantanone with the appropriate $PX_5 \cdot PX_3$ mixture.[10a,14] 2,2-Difluoroadamantane (**6,** X = F) was obtained from the reaction of 2-adamantanone with SF_4 at room temperature, mp 195.9°.

Formation of 2-Adamantyl Cations. A cold solution of the 2-adamantane precursors in SO_2ClF (SO_2) was added dropwise, with vigorous stirring, to a solution of FSO_3H, FSO_3H–SbF_5, or SbF_5 in SO_2ClF (SO_2) at −78°.

Proton and Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Pmr spectra were obtained using Varian Associates Model A-56/60A and HA-100 spectrometers, equipped with a variable temperature probe. Tetramethylsilane (external capillary) was used as reference. ^{12}C nmr spectra were obtained using a Varian VFT, XL-100-15 spectrometer equipped with a broad-band proton noise decoupler and a variable temperature probe. The instrument was operated in the pulse Fourier transform mode. Typically 500–2000 (~30°) pulses were needed for the accumulation of satisfactory spectra. No pulse delay was employed. Carbon chemical shifts were measured from the ^{13}C signal of capillary TMS (5% ^{13}C enriched).

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References and Notes

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