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Preparation and ^{13}C NMR Spectroscopic Study of the 2-(Adamantylidenemethyl)-2-adamantyl and 2-Adamantylidene-1,1-dicyclopropylethyl Cations[1a]

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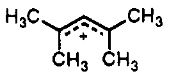
2-(Adamantylidenemethyl)-2-adamantyl cation (**5**) was prepared by ionization of 2-(adamantylidenemethyl)-2-adamantanol (**9**) in FSO_3H/SO_2ClF or neat FSO_3H at −78 °C. In spite of its high inherent steric strain, carbocation **5** is stable up to 80 °C. Its rotational barrier was estimated to be 16.8 kcal/mol on the basis of the coalescence temperature of the ^{13}C NMR signals of its diastereomeric β-methylene carbons, which is in agreement with a $\Delta H^{\ddagger}$ value of 16.5 kcal/mol calculated by MNDO. Similarly, 2-adamantylidene-1,1-dicyclopropylethyl cation (**6**) was prepared by the ionization of 1,1-dicyclopropyl-2-(2-hydroxy-2-adamantyl)ethanol (**12**) in SbF_5–FSO/SO_2ClF or FSO_3H/SO_2ClF. Carbocation **6** shows a rotational barrier of less than 5 kcal/mol. The small rotational barrier in **6** is interpreted as due to the positive charge stabilizing influence of the adjacent cyclopropyl groups resulting in an unsymmetrically charge-delocalized allylic cation.

Introduction

The existence of the allyl cations as reactive intermediates was originally inferred from solvolytic studies. Subsequently, several substituted allyl cations have been prepared and studied in superacid media under stable ion conditions.[2-4] Several of these carbocations were found to be extremely stable even at elevated temperatures or in relatively nucleophilic media, such as neat sulfuric acid. On the basis of the observed ^1H and ^{13}C NMR chemical shifts symmetrical structures, i.e., structures having equivalent charge distribution on the Cl and C3 carbons, were proposed for these carbocations. The symmetrical structures were also supported by deuterium isotopic perturbation studies by Saunders and Kates.[4] In contrast, on the basis of the regioselectivity of the allyl carbocations toward nucleophiles[5] or dienes,[6] Nordlander, Gassman, and their co-workers proposed unequally charge distributed structures involving unsymmetrically associated gegenions. Such a discrepancy may be attributed to the high ionizing power of the solvent and the relatively nonnucleophilic nature of the counterions of the superacid medium, which disfavors contact ion pairs.

The rotational barriers for allyl cations were also determined by ^1H NMR spectroscopy. From the temperatures required for the coalescence of the absorptions for the methyl groups, rotational barriers of 15.8 and 13.8 kcal/mol were estimated for the 1,1,3,3-tetramethyl- and 1,1,2,3,3-pentamethylallyl cations (**1** and **2**), respectively.[2b,c,3a] The relatively low value for the rotational barrier of the latter carbocation implies weakening of the allylic C–C bond with increased steric crowding. In other words, the steric strain inherent in **2** causes relative weakening of the allylic π-bond by increasing the p–p π inter orbital angle. Schleyer and co-workers[7a] calculated the values for the rotational barriers for **1** and **2** as 27.7 and 25.3 kcal/mol, respectively, which, although larger in magnitude than the experimental values show the same relative order. The large discrepancy in magnitude between the theoretically calculated and experimental values was interpreted as due to solvation and counterion effect on the stabilization of the carbocation in the condensed phase, where the rotational barriers were measured. The rotation of the allyl cation involves the perpendicular conformation which lacks π delocalization as the transition state. The decreased electronic stabilization results in relatively more solvation of the perpendicular conformer, compared to that of the planar conformer. The differential solvation of the planar and the perpendicular conformers results in the reduced rotational barrier. In accordance, the rotational barrier for the yet unobserved parent allyl cation was calculated to be 21 ± 6 kcal/mol when solvated by HF, about 13 kcal/mol less than in the gas phase.[8]



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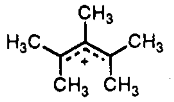

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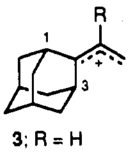

3; R = H
4; R = SiMe3

We have recently prepared the 2-vinyl-2-adamantyl cation (**3**) and 2-[1-(trimethylsilyl)vinyl]-2-adamantyl cation (**4**).[9] Diastereotopic C1 and C3 carbons of **3** showed nonequivalent chemical shifts (Δδ = 8.5 ppm) due to hindered rotation about the allylic π bond. The rotational barrier could not be measured since the carbocation decomposed above −90 °C. Carbocation **4**, on the other hand showed equivalent chemical shift values for C1 and C3 carbons even at −120 °C, indicating extremely low activation barriers for the rotation about the π bond. This was interpreted as due to the hyperconjugative β-silyl stabilization of the perpendicular conformation (transition

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[1] (a) Stable Carbocations, 289. For 288, see: Olah, G. A.; Bausch, J.; Rasul, G.; George, H.; Prakash, G. K. S. *J. Am. Chem. Soc.*, submitted for publication. (b) California State University.

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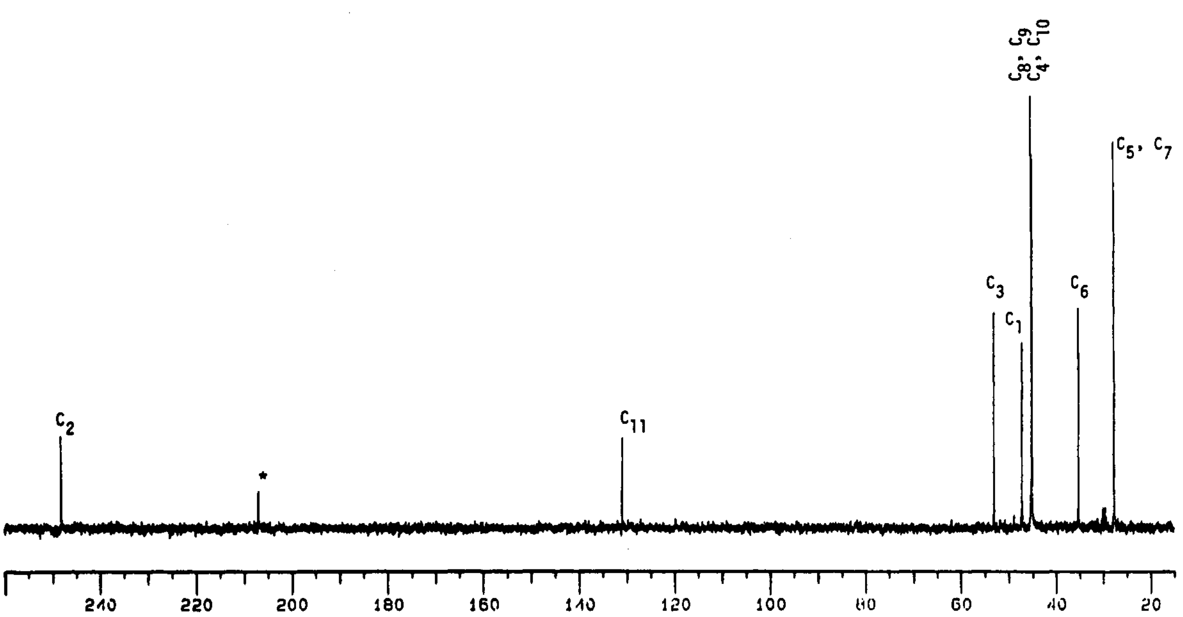


Figure 1. ^{13}C NMR spectrum (90.6 MHz, proton decoupled) of 2-(adamantylidenemethyl)-2-adamantyl carbocation (5). Absorptions due to acetone-d_6 are indicated by asterisks.

state for the rotation) of the carbocation.

We now report the preparation and NMR study of two highly sterically hindered allyl cations, 2-(adamantylidenemethyl)-2-adamantyl cation (5) and 2-adamantylidene-1,1-dicyclopropylethyl cation (6). Their rotational barriers were also estimated based on NMR studies and MNDO calculations.

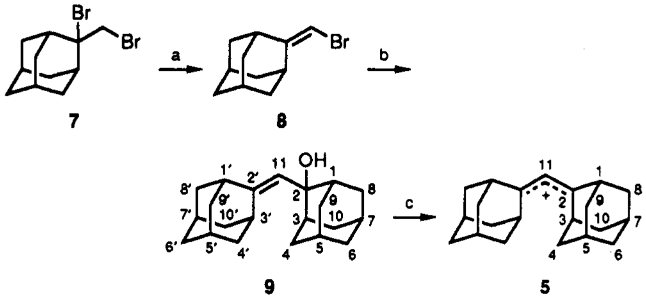
Results and Discussion

Allyl cations are usually prepared by the ionization of the corresponding allyl alcohols or halides. Ionization of the 1,3-diols or their derivatives also provides in suitable cases the corresponding allyl cations.[10] More recently, allyl cations have been prepared by the ionization of the α-spirocyclopropyl-substituted alcohols, which involve the rearrangement of the initially formed α-spirocyclopropyl-substituted carbocations.[11]

In our studies the ionization of allyl alcohol 9 seemed to be the best approach to carbocation 5. We synthesized allyl alcohol 9 by the reaction of adamantylidenemethyllithium with 2-adamantanone. For preparing ion 6, however, 1,3-diol 12 was considered the most convenient precursor.

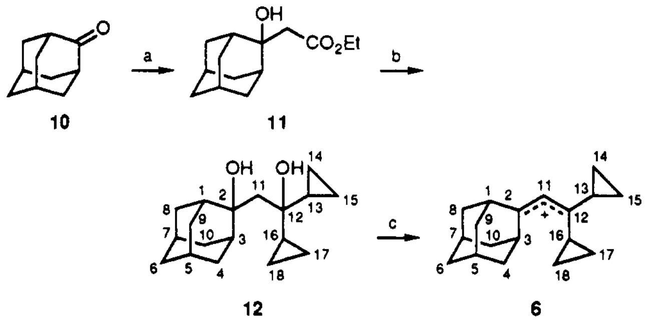
Dehydrohalogenation of 2-(bromomethyl)-2-bromoadamantane (7) with potassium *tert*-butoxide in diethyl ether provided 2-(bromomethylene)adamantane (8).[12] Vinyl bromide 8 was treated with *tert*-butyllithium at −78 °C, and the resulting lithio derivative was reacted with 2-adamantanone in refluxing ether to obtain the allyl alcohol 9. Ionization of alcohol 9 in either FSO_3H/SO_2ClF, or in neat FSO_3H at −78 °C gave allyl cation 5 as a clear yellow solution (Scheme I). Ethyl (2-hydroxy-2-adamantyl)acetate (11), prepared by a modified Reformatsky reaction[13] of 2-adamantanone with ethyl bromoacetate using Zn/Cu couple, was reacted with cyclopropyllithium to obtain the diol, 1,1-dicyclopropyl-2-(2-hydroxy-2-adamantyl)ethanol (12). Ionization of the diol 12 with FSO_3H/SO_2ClF or SbF_5SO_2ClF at −78 °C provided the allyl cation 6. The hydroxyl-protonated dication 13 was also obtained by ionization of 12 at −120 °C (Scheme II). However, the expected 1,3-carbodication 14 could not be observed. If such 1,3-carbodication were a possible intermediate for the formation of allyl cation 6, it must have an extremely short life time under these conditions. We made similar observations in attempts to prepare other

Scheme I[a]



[a] (a) KOBu^t, ether, RT, 30 min. (b) (i) t-BuLi, ether, −78 °C; (ii) 2-adamantanone. (c) FSO_3H/SO_2ClF, or neat FSO_3H, −78 °C.

Scheme II[a]



[a] (a) CH_2BrCO_2Et/Zn-Cu, ether, 4 h/reflux. (b) C_3H_5Li/ether; 0 °C to RT, 1 h. (c) FSO_3H/SO_2ClF, −78 °C or SbF_5/SO_2ClF, −78 °C.

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related 1,3-carbodications.[10]

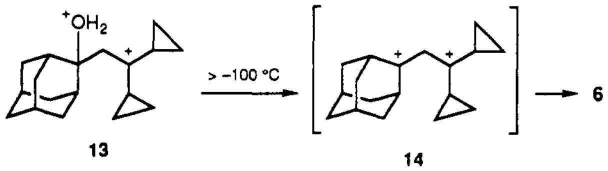
Allyl cation 5, in SO_2ClF solution, showed essentially unchanged ^1H and ^{13}C NMR spectra over a wide range of temperature, from −78 to 0 °C. The ^1H NMR showed two distinct α-bridgehead allylic hydrogens (C1-H and C3-H) at δ^1H 3.24 and 2.57, while showing a characteristic olefinic absorption at δ^1H 6.89. ^{13}C NMR spectrum (Figure 1) complemented ^1H NMR spectrum showing nonequivalent chemical shifts for the α-bridgehead carbons (C1 and C3) at $\delta^{13}C$ 53.0 and 47.1 ($\Delta\delta^{13}C$ = 44.5 Hz at 75.429 MHz). The cis- and trans-α-bridgehead carbons are thus in dissimilar environments. The ^{13}C NMR, in addition, showed two distinct absorptions for the β-methylene carbons at $\delta^{13}C$ 45.1 (C8, C9) and 44.9 (C4, C10) ($\Delta\delta^{13}C$ = 13 Hz at 75.429 MHz). These observations clearly point out that the two adamantyl moieties do not rotate about the allylic C–C bond in this temperature range. The rotation around the π bonds is restricted due to the steric hindrance provided by the bulky adamantyl groups. The ^{13}C NMR spectrum of the carbocation in neat FSO_3H was unchanged even when warmed to room temperature. Upon heating to 50 °C (in neat FSO_3H), the *cis-* and *trans-β*-methylene signals (C4,C10 and C8,C9) coalesced to give a single sharp signal, and the intensity of C1 and C3 signals was significantly reduced. On further warming, the C1 and C3 carbon signals continued decreasing in intensity and merged into the base line at 80 °C. Coalescence of these signals could not be observed since the carbocation decomposed above 80 °C.

The larger the separation of the diastereotopic carbons' signals ($\Delta\delta$), the higher will be the temperatures needed for their coalescence. The C1 and C3 carbons have a $\Delta\delta$ of 445 Hz, while C4,C10 and C8,C9 carbons have a $\Delta\delta$ of 13 Hz, requiring a much higher temperature for the coalescence of C1 and C3 absorptions than that for the latter β-methylene carbons. A more accurate value for $\Delta G^\ddagger$ would be expected from the coalescence temperature of C1 and C3 absorptions which have a larger chemical shift separation. However, they only merged into the base line (disappeared) at 80 °C, the maximum temperature at which the carbocation was stable to be observed. On the basis of the coalescence temperature of 50 °C for the absorptions of C4,C10 and C8,C9 carbons, a rate constant of 28.8 s^{-1} and a $\Delta G^\ddagger$ of 16.8 kcal/mol was estimated for the rotation around the allylic bonds.[14]

The MNDO-optimized minimum energy structure of carbocation 5 shows it to have C_{2v} symmetry about the C11–H bond with an allyl p–p π inter orbital angle of 18.2°.[15] This angle significantly reduces the nonbonded steric interaction between C3-hydrogens of the two adamantyl groups, while slightly decreasing the π-orbital overlap. Using a rigid-rotor model on the MNDO-optimized structure, a minimum value for the barrier to rotation around the allylic π bond was calculated to be 16.5 kcal/mol. This value agrees with the experimental rotational barrier obtained. Semiempirical MNDO provides data on the activation enthalpies rather than the activation free energies; i.e., the barrier obtained is $\Delta H^\ddagger$. However, the entropies of activation, $\Delta S^\ddagger$, for the rotation of the allyl cations are expected to be very low because of minimum structural reorganization, so that $\Delta G^\ddagger$ and $\Delta H^\ddagger$ can be compared. Indeed, rotational barriers for several simple allyl cations were calculated by semiempirical methods and were shown to be in good agreement with the experimentally obtained $\Delta G^\ddagger$ values.[7b–d]

Ionization of the diol 12 at −120 °C gave a mixture of the allylic cation 6 and dication 13. There were ^{13}C NMR absorptions at $\delta^{13}C$ 268.5 (C^+) and 99.9 (COH_2^+) attributable to 13, besides those for the cabocation 6. After warming to −80 °C, the absorptions due to dication 13 disappeared, and a single carbocation 6 was obtained. The allylic carbocation 6 showed absorptions in the ^1H NMR spectrum at δ^1H 5.77 and 3.07 for the olefinic and α-bridgehead allylic hydrogens. The ^{13}C NMR spectrum showed a well-resolved 11-line spectrum. The spectrum remained unchanged even after warming to as high as −50 °C, but upon cooling below −80 °C, the absorption for C13 and C16 at $\delta^{13}C$ 31.6 gradually broadened and disappeared at −90 °C. New absorptions could not be seen even at −110 °C. Since the coalescence temperature is at −90 °C, the barrier for the allylic π-bond rotation in this carbocation is probably less than 5 kcal/mol. The exact determination of the barrier was not possible as separate signals for C13 and C16 could not be observed even at −110 °C. Such low rotational barrier around the C11 and C12 bond of 6 can be explained as due to the weakening of the C11–C12 π bond, a consequence of the cyclopropyl group participation. The stronger π bond for C2–C11 is also reflected in the distinct ^{13}C NMR signals for the cis- and trans-α-bridgehead, and the β-methylene carbons of the adamantyl ring. Thus, carbocation 6 exists as an unsymmetrically delocalized species.

The formation of the carbocation 6 can take place through dehydration of the hydroxyl-protonated dication 13, or through the incipient formation of the 1,3-carbodication 14. The existence of the 1,3-carbodication 14 as a higher energy intermediate, however, seems to be more likely.



In summary the 2-(adamantylidenemethyl)-2-adamantyl cation (5) was obtained in spite of its high inherent steric strain, and its rotation barrier is only slightly higher than the related 1,1,3,3-tetramethylallyl cation (1). 2-Adamantylidene-1,1-dicyclopropylethyl cation (6), on the other hand, shows a low rotational barrier around the C11–C12 allylic bond, in part, due to the stabilization of the positive charge by the adjacent cyclopropyl groups resulting in the increased π localization on C2–C11 bond.

Experimental Section

Diethyl ether was distilled from sodium–benzophenone ketyl immediately before use. Lithium metal, cyclopropyl bromide, and 2-adamantanone were obtained from Aldrich and used as received. GC/MS analyses were carried out on a Finnigan-Mat/Incos-50 mass spectrometer, equipped with a Varian 3400 gas chromatograph, or a Hewlett-Packard 5971 mass spectrometer, equipped with a Hewlett-Packard 5890 series II gas chromatograph. Melting points were determined using a Mettler FP1 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-200 or a Bruker-360 instrument equipped with a variable-temperature probe. The ^1H and ^{13}C NMR chemical shifts for the carbocations were referenced with respect to the external capillary tetramethylsilane.

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(14) The rate constant was obtained from the equation: $k = (\pi/\sqrt{2})\Delta\delta$, where k is the rate constant, and $\Delta\delta$ is the separation of the signals in hertz. $\Delta G^\ddagger$ was obtained from Eyring equation ($k = (\kappa T/h)e^{-\Delta G^\ddagger/RT}$) (Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* 1971, 656–657 and references cited therein). Olah, G. A.; Prakash, G. K. S.; William, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley-Interscience: New York, 1987; pp 143–144.

(15) MNDO calculations were carried out using version 4.00, from Frank J. Seiler Research Laboratory, U. S. Air Force Academy, Colorado Springs, CO 80840. Single point calculations without optimization were carried out at 10-deg increments of rotation about the C11–C2 bond.

2-(Bromomethylene)adamantane (8). 2-(Bromomethyl)-2-bromoadamantane (7, 1.8 g, 5.8 mmol) in 50 mL of anhydrous ether was treated with potassium *tert*-butoxide (1.3 g, 11.6 mmol), and the resulting suspension was stirred at room temperature for 30 min. The contents were filtered and dried over $MgSO_4$, and the solvent was removed by evaporation under reduced pressure. 2-(Bromomethylene)adamantane[12] (1.3 g, 99%) was obtained as a colorless liquid: MS (*m/z*, %) 228 (M^+, ^{81}Br, 73), 227 (4), 226 (M^+, ^{79}Br, 75), 147 (43), 119 (30.5), 105 (53), 91 (100); ^1H NMR δ 5.81 (s, 1 H), 3.1 (s, 1 H, allylic-H), 2.57 (s, 1 H, allylic H), 1.7–1.93 (m, 12 H); ^{13}C NMR δ 128.3 (CHBr), 92.9 (C2), 39.7 (C1,C3), 39.3 and 38.0 (C4,C9 and C8,C10), 36.8 (C6), 34.5 and 28.1 (C5 and C7).

2-(Adamantylidenemethyl)-2-adamantanol (9). A solution of 2-(bromomethylene)adamantane (8, 1.3 g, 5.8 mmol) in 20 mL of dry ether was placed in a three-necked round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, a nitrogen inlet, and an addition funnel. The flask was cooled to −78 °C, and *tert*-butyllithium (5.1 mL, 8.7 mmol, 1.5 equiv) was added dropwise through the addition funnel. The reaction mixture became light yellow after the addition. The contents were warmed to 0 °C for 30 min and recooled to −78 °C, a solution of 2-adamantanone (0.87 g, 5.8 mmol) in 10 mL of dry ether was added to the contents, and the resulting mixture was warmed to room temperature. After stirring for 30 min, the contents were heated under reflux for 3 h, cooled to room temperature, poured into 100 mL of 10% ammonium sulfate, and extracted with diethyl ether (3 × 50 mL). The combined organic layer were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. Compound 9 (0.85 g, 49%) was obtained as a white crystalline solid after two recrystallizations from dichloromethane at −78 °C: mp 179 °C; MS (*m/z*, %) 299 ($M^+ + 1$, 2.6), 298 (M^+, 12), 280 (78), 237 (6.4), 175 (100), 135 (11); ^1H NMR δ 5.48 (s, 1 H, olefinic H), 3.38 (s, 1 H), 2.28 (br, s, 2 H), 2.21 (s, 1 H), 2.0 (s, 1 H), 1.1–1.93 (24 H); ^{13}C NMR δ 151.9 (C2′), 124.0 (C11), 74.9 (C2), 41.2 (C1′), 40.0 and 38.8 (C8′,C9′ and C4′,C10′), 39.0 (C1, C3), 38.0 (C6′), 37.2 (C6), 35.2 and 32.7 (C4,C9 and C8,C10), 33.2 (C3′), 28.2 (C5′ and C7′), 27.1 and 26.9 (C5 and C7).

Ethyl (2-Hydroxy-2-adamantyl)acetate (11). A 250-mL three-necked round-bottomed flask equipped with a magnetic stirrer, an addition funnel, a nitrogen inlet, and a reflux condenser was charged with zinc (4.35 g, 66.6 mmol), Cu_2Cl_2 (0.66 g, 6.65 mmol), and 10 mL of ether. The contents were refluxed for 30 min and cooled to room temperature, and a solution of 2-adamantanone (5 g, 33.3 mmol) and ethyl bromoacetate (6.66 g, 39.9 mmol) in 10 mL of ether was added dropwise. The reaction mixture was refluxed for 1 h, cooled to room temperature, acidified with 10% HCl, and extracted with ether (3 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. Compound 11 (6.2 g, 78%) was obtained as white crystalline material after recrystallization from 10% toluene in hexane: mp 48.8 °C; MS (*m/z*, %) 238 (M^+, 2.2), 220 (100), 219 (82), 193 (20), 164 (24), 151 (75), 105 (51); ^1H NMR δ 4.15 (q, $J = 7.1$ Hz, 2 H, OCH_2), 2.7 (s, 2 H, CH_2), 2.28 (apparent d, $J = 12.3$ Hz, 2 H), 1.76 (br s, 10 H), 1.67 (s, 1 H), 1.49 (apparent d, $J = 12.8$ Hz, 2 H), 1.25 (t, $J = 7.1$ Hz, 3 H, CH_3); ^{13}C NMR δ 173.3 ($>C{=}O$), 73.9 (C2), 60.6 (CH_2 α to $C{=}O$), 42.2 (OCH_2), 38.2 (C6), 37.2 (C1, C3), 34.5 and 32.6 (C4,C9 and C8,C10), 27.2 and 27.1 (C5 and C7), 14.2 (CH_3).

1,1-Dicyclopropyl-2-(2-hydroxy-2-adamantyl)ethanol (12). Lithium wire (sodium content 1%, 0.35 g, 50.4 mmol) was hammered into shiny plates and was suspended in 20 mL of ether in a three-necked round-bottomed flask equipped with a reflux condenser, an addition funnel, a magnetic stirrer, and a nitrogen inlet. The flask was cooled to 0 °C, and a solution of cyclopropyl bromide (2.0 g, 16.8 mmol) in 5 mL of ether was added dropwise to the contents at such a rate as to maintain a gentle reflux, and the contents were stirred for 30 min. A solution of ethyl (2-hydroxy-2-adamantyl)acetate (1 g, 4.2 mmol) in 10 mL of dry ether was added to the contents dropwise, warmed to room temperature, and stirred for 2 h. The reaction mixture was quenched with 100 mL of ice-cold water and extracted with ether (2 × 50 mL), the combined organic layers were washed with saturated sodium bicarbonate solution (50 mL), dried ($MgSO_4$), and filtered, and the solvent was removed under reduced pressure. The compound 12 (0.8 g, 69%) was obtained as white crystalline material after two recrystallizations from 10% toluene in hexane: mp 152 °C; CIMS (methane), (*m/z*, %), 276 (M^+, 0.28), 275 (4), 259 (11), 230 (6), 217 (21), 149 (44), 148 (98), 135 (4), 111 (100), 109 (95); ^1H NMR δ 3.2 (s, 2 H, OH), 1.44–2.26 (m, 16 H), 0.22–0.59 (m, 2 H, cyclopropyl CH), 0.8–0.95 (m, 8 H, cyclopropyl CH_2); ^{13}C NMR δ 77.1 and 72.2 (C2 and C12), 46.9 (C11), 38.7 (C1,C3), 38.3 (C6), 34.7 and 32.8 (C4,C9 and C8,C10), 27.2 and 26.8 (C5 and C7), 20.8 (C13, C16), 1.54 and 0.76 (C14, C15 and C17, C18).

Preparation of Carbocations. SbF_5 and FSO_3H were freshly distilled before use. A 5-fold excess of magic acid (1:1 SbF_5 and FSO_3H) or FSO_3H in SO_2ClF was added to a suspension of the precursor alcohols in SO_2ClF contained in 5-mm NMR tubes at 78 °C in a dry ice/acetone bath, or at −120 °C (pentane/liquid nitrogen slush), resulting in an approximately 10% solution of the ions. Efficient mixing of the solution was effected using a vortex stirrer.

2-(Adamantylidenemethyl)-2-adamantyl cation (5) was prepared by the reaction of 9 with FSO_3H in SO_2ClF at −78 °C: ^1H NMR (−53 °C) δ 6.89 (s, 1 H, olefinic), 3.24 (s, 2 H, C1-H), 2.57 (s, 2 H, C3-H), 1.36–1.88 (24 H); ^{13}C NMR (−53 °C) δ 248.2 (s, C2), 130.8 (d, $J = 164$ Hz, C11), 53.0 (d, $J = 138$ Hz, C1), 47.1 (d, $J = 132$ Hz, C3), 45.1 (t, $J = 121$ Hz, C8, C9), 44.9 (t, $J = 121$ Hz, C4, C10), 35.2 (t, $J = 123$ Hz, C6), 27.7 (d, $J = 136$ Hz, C5, C7). For higher temperature studies, 5 was prepared in neat FSO_3H.

2-Adamantylidene-1,1-dicyclopropylethyl cation (6) was prepared by the reaction of 12 with magic acid in SO_2ClF at −78 °C: ^1H NMR (−80 °C) δ 5.77 (s, olefinic), 3.07 (s, bridgehead allylic), 1.2–2.2 (overlapping multiplets); ^{13}C NMR (−80 °C) δ 47.2 (d, $J = 137.5$ Hz, C1), 207.9 (s, C2), 39.8 (d, $J = 138.8$ Hz, C3), 40.9 (t, $J = 133.7$ Hz, C4, C10), 27.3 (d, $J = 134.8$ Hz, C5, C7), 35.3 (t, $J = 131.9$ Hz, C6), 41.6 (t, $J = 131.9$ Hz, C8, C9), 121.5 (d, $J = 155.4$ Hz, C11), 244.3 (s, C12), 31.6 (d, $J = 174.7$ Hz, C13, C16), 29.6 (t, $J = 169.3$ Hz, C14, C15, C17, C18). Ionization of the alcohol 12 at −120 °C resulted in the formation of the carbocation 13 ($\delta^{13}C$, 268.5 and 99.9 for C^+ and COH_2^+, respectively), which was fully ionized to the allyl cation 6 above −100 °C.

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Supplementary Material Available: NMR spectra of carbocation 6 and compounds 8, 9, 11, and 12 (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.