Protonation studies on epimeric homoallylic adamantylidene-adamantyl alcohols, 4-methyleneadamantylideneadamantane, adamantylideneadamantane (Ad=Ad) and sesquihomoadamantene, and reaction of Ad=Ad and sesquihomoadamantene with $NO_2^+BF_4^-$ and PhI(OH)OTs: a stable-ion NMR and theoretical (GIAO-NMR) study †

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Under stable-ion conditions, the "*pseudo-axial*" homoallylic alcohol **1-ax** is protonated at the Ad=Ad double-bond and the resulting carbocation undergoes rapid cyclization to produce the oxonium ion **9H**$^+$ as the only observable species, which on quenching furnishes the cyclic ether **9**. In contrast, protonation of the "*pseudo-equatorial*" homoallylic alcohol **1-eq** gave a persistent homoallylic cation **1a**$^+$. Protonation of the methylene-substituted derivative **8** gave a 5 : 1 mixture of two carbocations, in which the minor ion is homoallylic **8aH**$^+$. Adamantylideneadamantane Ad=Ad **5** reacts with FSO_3H–CH_2Cl_2 to give the previously observed **5H**$^+$ (as a rapidly equilibrating pair of carbocations), together with the oxonium ion **6H**$^+$. The outcome of the reaction of Ad=Ad with NO_2BF_4, $NOBF_4$ and with PhI(OH)OTs is the same, in all cases producing the spirocyclic ketone **6**. Sesquihomoadamantene **7** is protonated in FSO_3H–SO_2ClF and the initially formed carbocation (not observed) rapidly rearranges to **5H**$^+$. Compound **7** also reacts with NO_2BF_4, and TFA–CH_2Cl_2 to produce the spirocyclic ketone **6** and **5**, after quenching. With PhI(OH)OTs the recovered material is **7** itself plus PhI. For comparison, the homoallylic carbocations **1a**$^+$, **8aH**$^+$, their skeletally rearranged allylic cations **1b**$^+$, **8cH**$^+$, and the oxonium ions **9H**$^+$ and **6H**$^+$ were studied computationally by GIAO-NMR at the BLYP/6-31G(d)//BLYP/6-31G(d) level.

Introduction

A dramatic rate enhancement (between 2×10^5 and 4×10^6) was observed by Bennet and associates[1–5] in the room temperature solvolysis of the "pseudo-equatorial" homoallylic adamantylideneadamantyl tosylate (toluene-4-sulfonate) **1-eq(OTs)** (Scheme 1) relative to 2-adamantyl tosylate, whereas the "pseudo-axial" epimer **1-ax(OTs)** showed only a modest rate increase (*ca.* 4 fold). The reactions exhibited reduced sensitivity to solvent ionizing power, indicative of either σ- or π-participation during ionization. The *m* value for **1-ax(OTs)** was larger than that for **1-eq(OTs)**, implying that there is less charge dispersion in the transition state for solvolysis of **1-ax(OTs)**. Therefore, σ-participation in the solvolysis of **1-ax(OTs)** is less effective in stabilizing the developing carbocation than π-participation in the solvolysis of **1-eq(OTs)**. Steric crowding prevents nucleophile trapping at the olefinic carbons of the homoallylic carbocation **1a**$^+$. The skeleton remains intact and the resulting products exhibit complete retention of configuration (**2**). In contrast, solvolysis of **1-ax(OTs)** gives skeletally rearranged products (**3**). Takeuchi and associates[6,7] studied the solvolysis of 4-methylene-2_{ax}- and 4-methylene-2_{eq}-adamantyl tosylates (**4-eq** and **4-ax**) (Scheme 1) and found that the rate for **4-eq** was higher than that for **4-ax**. This rate enhancement was attributed to π-bridging in **4-eq** to give **4a**$^+$, which gives rise to the observed products, whereas the products formed *via* **4-ax** arise from an equilibrium between **4b**$^+$ and **4c**$^+$ (Scheme 1).

As part of a broader study of electrophilic reactions at multiple bonds, Olah and associates[8] reported in 1974 on the low-temperature protonation of parent Ad=Ad **5**, forming a rapidly equilibrating pair of carbocations. Quenching returned intact **5**. Introduction of Cl_2 into the solution of **5H**$^+$ gave a 3-membered cyclic chloronium species (**5-Cl**$^+$). The reaction of **5** with NO_2^+ and NO^+ was also studied by Olah *et al.*[8] leading to the spirocyclic ketone **6** (Scheme 2). The availability of **1-eq** and **1-ax** alcohols and the 4-methylene derivative **8** (Fig. 1)

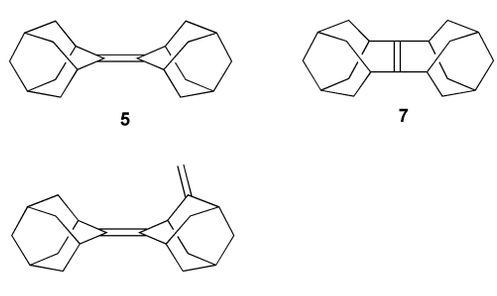
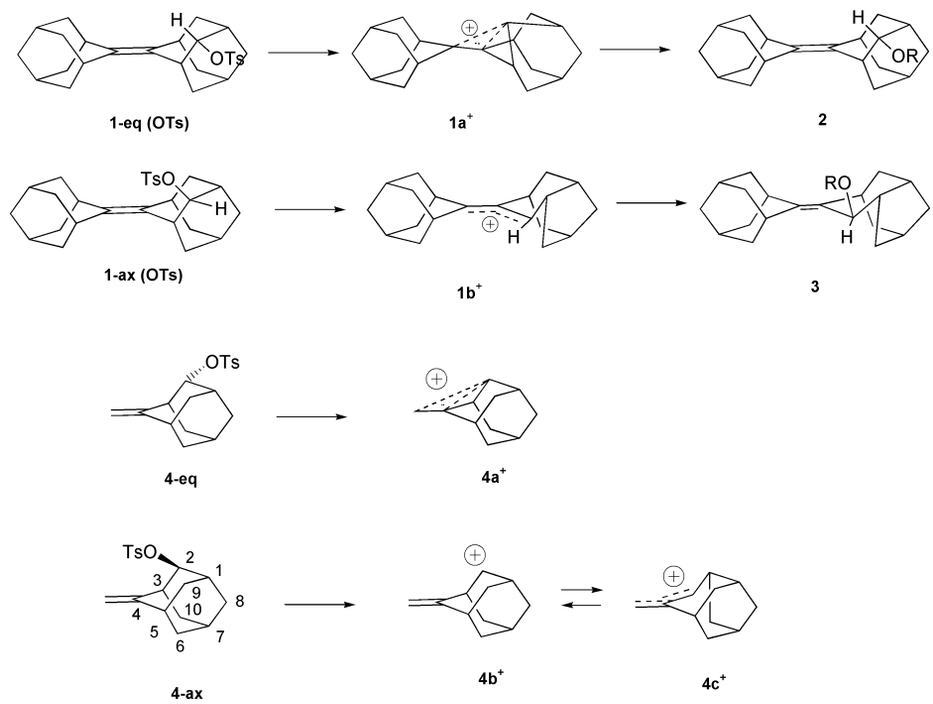
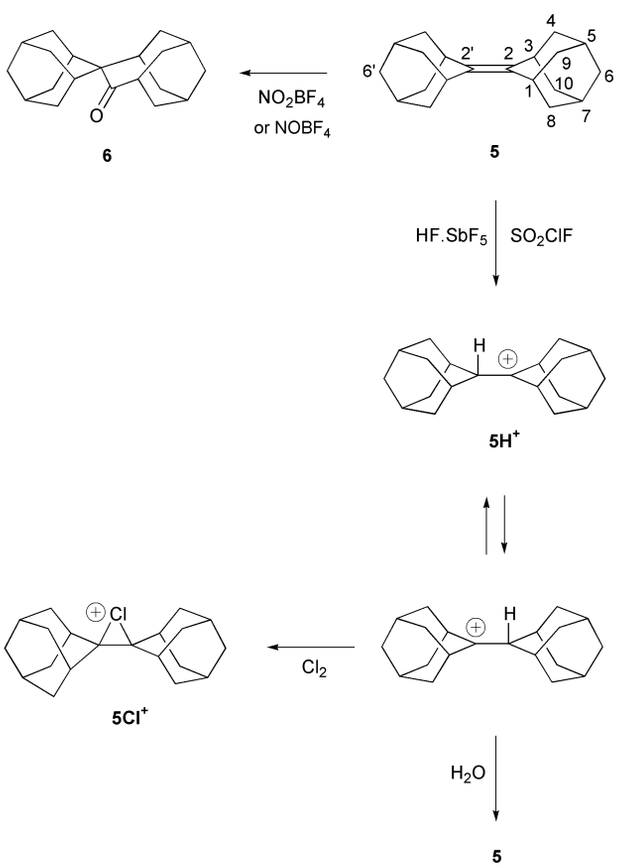


Fig. 1 Structures of compounds **5**, **7** and **8**.

† Electronic supplementary information (ESI) available: representative 1D-NMR spectra and tables of cartesian coordinates. See http://www.rsc.org/suppdata/p2/b2/b201660e/



Scheme 1 Proposed carbocations *via* solvolysis of **1-eq(OTs)**, **1-ax(OTs)**, **4-eq** and **4-ax**.



Scheme 2 Previous studies with **5**.

provided the opportunity to search for their derived persistent carbocations for comparison with the solvolytic data.

In addition, we have also studied the protonation of **5** and sesquihomoadamantene **7** under various conditions, and examined the reaction of **5** and **7** with NO_2BF_4 and with Koser's reagent PhI(OH)OTs. To augment the NMR assignments and for comparison, a number of model carbocations and their precursors were probed theoretically by GIAO-NMR at the BLYP/6-31G(d)//BLYP/6-31G(d) level.

Results and discussion

NMR assignments

Detailed NMR assignments for the observed carbocations, their precursors and products were based on ^{1}H, ^{13}C, COSY, HMQC (or HETCOR), NOED and DEPT spectra. Coupling constants $^1J_{CH}$ were determined *via* non-decoupled ^{13}C or INEPT spectra (data are summarized in Charts 1 and 2).

Protonation of the homoallylic pseudo-axial alcohol (1-ax). Low-temperature protonation of **1-ax** in FSO_3H–SO_2ClF gave the protonated cyclic ether **9H**$^+$ as the only persistent species (a colorless solution) (Scheme 3). The resulting oxonium ion exhibits a distinct low field proton resonance at 9.09 ppm which is broadened by exchange with FSO_3H at −70 °C. In the ^{13}C NMR spectrum, the lowest field resonances are those of C-2′ and C-2 at 126.3 and 97.4 ppm respectively (for detailed assignments see Chart 1) (representative 1D-NMR spectra are included in the electronic supplementary information).

Quenching of the superacid solution with ice–bicarbonate furnished the corresponding ether **9** whose CI-MS and NMR spectral data (in Chart 2) agree with the structure. The cyclic ether **9** was obtained by Bennet *et al.*[4] as a minor product in the solvolysis of a 1 : 1 mixture of **1-ax(OTs)**–**1-eq(OTs)** in aqueous H_2SO_4–HOAc solvent. Protonation of **1-ax** with FSO_3H–SbF_5 (4 : 1)–SO_2ClF was not clean and resulted in a complex mixture in which **9H**$^+$ is a major component. The low-temperature stable-ion study illustrated that the double-bond is preferentially protonated and anchimeric assistance results in an oxonium ion which gives a stable cyclic ether upon quenching. Clearly, the stable-ion data differ from those under solvolytic conditions where **1b**$^+$ is formed and trapped to give rearranged products (Scheme 1).

Protonation of the homoallylic pseudo-equatorial alcohol (1-eq). Low-temperature reaction of **1-eq** in FSO_3H–SO_2ClF produced a colorless solution, whose NMR spectral data are consistent with the formation of the homoallylic cation **1a**$^+$ (Scheme 3). The most downfield shifted carbon resonance is the adamantylidene quaternary carbon at 252.1 ppm, with the C-2, C-3, and C-4 carbons observed at 103.6, 81.9, and 89.2 ppm respectively (Chart 1 and electronic supplementary inform-

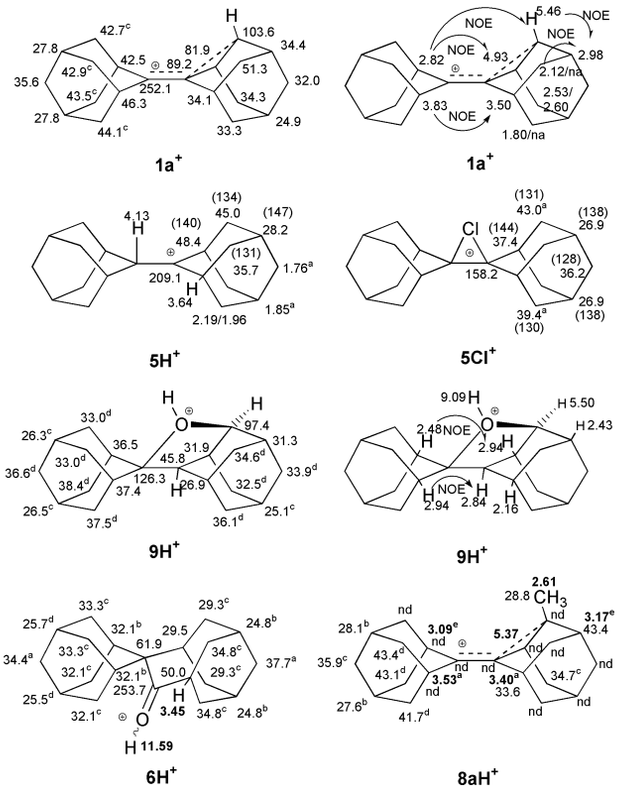


Chart 1 Summary of the NMR data for the carbocations. The letters a–e denote interchangeable assignments. $^{1}J_{CH}$ (Hz) in parentheses. For **6H**$^{+}$ and **8aH**$^{+}$ characteristic and specifically assigned proton resonances are shown in bold; nd = either not detected or could not be specifically assigned.

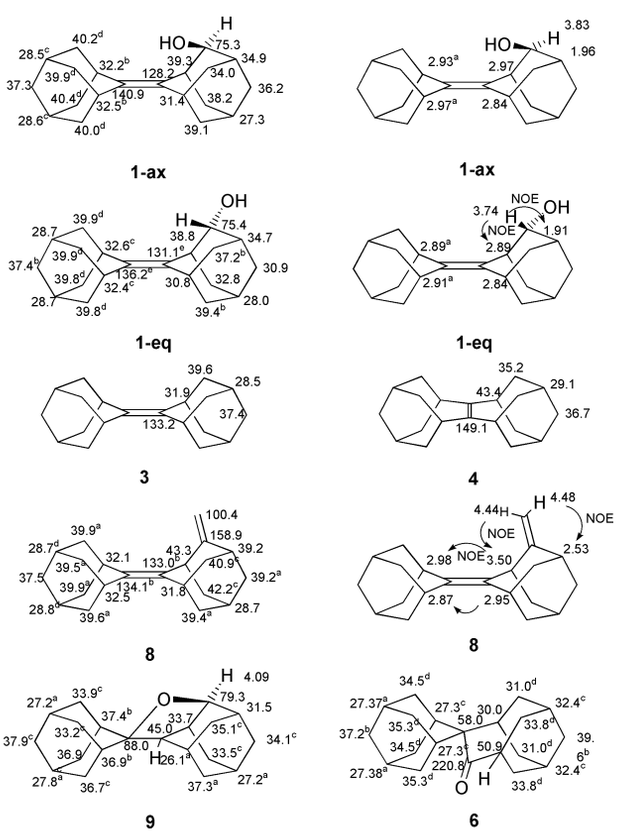


Chart 2 Summary of the NMR data for the precursors. The letters a–e denote interchangeable assignments.

ation). The magnitude of the deshielding at C-2 and C-4 is significantly less relative to "regular" allyl cations.[9] Deshielding at C-3 and C-9 (at δ 51.3) suggests some degree of charge delocalization into these sites. The observed charge delocalization pattern for **1a**$^{+}$ compares rather well with the homoallylic cations generated by Russian workers from the benzocyclene skeleton (see Fig. 2).[10] In the proton spectrum, the most downfield signal is due to H-2 (δ 5.46); the bridgehead protons H-1, H-3, H-5, H-1′, and H-3′, are also significantly deshielded relative to other protons.

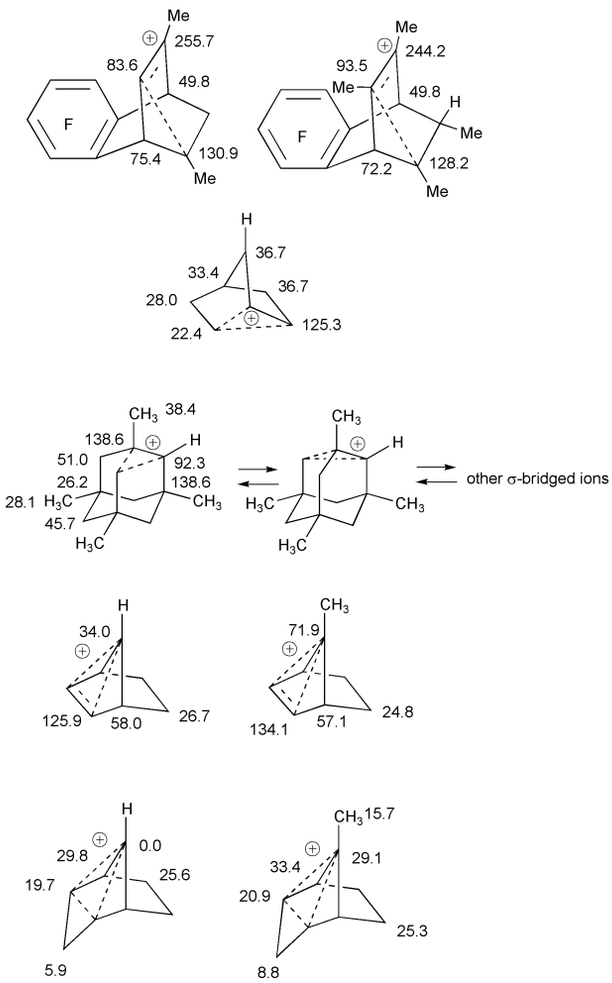
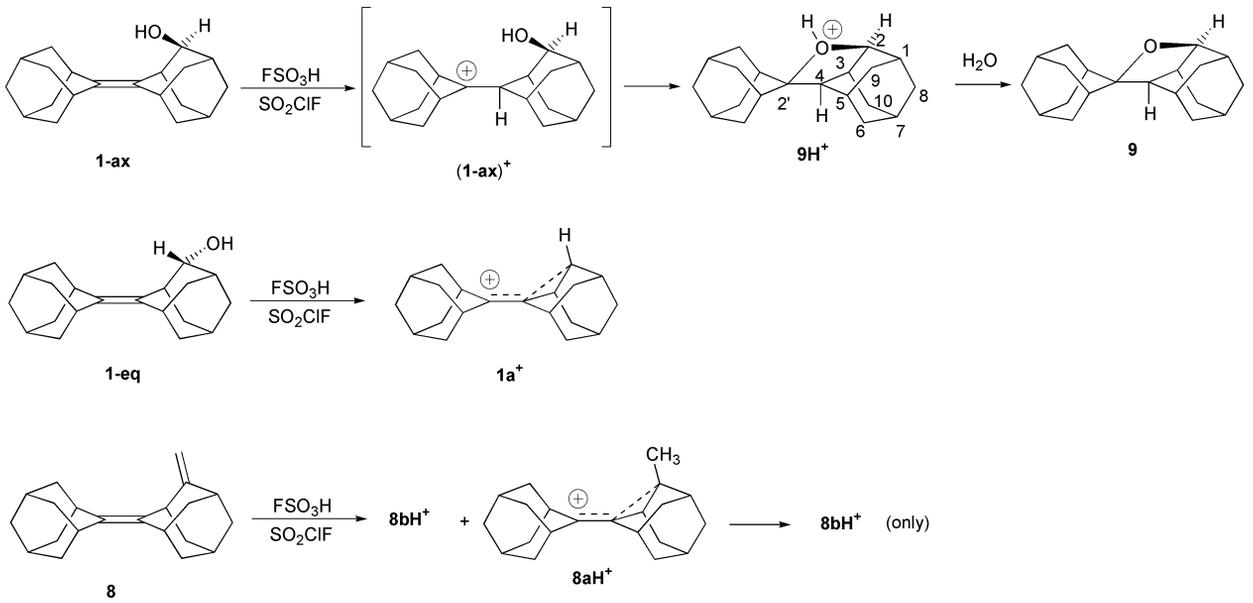


Fig. 2 Model carbocations (homoallylic, nonclassical, equilibrium and trishomoallylic).

Protonation of 2-(2-adamantylidene)-4-methyleneadamantane (8). We had anticipated that compound **8**[11] would serve as an ideal precursor to **8aH**$^{+}$ (Scheme 3), a tertiary homoallylic carbocation, but the situation proved to be more complex! Low-temperature protonation with FSO_3H–SO_2ClF gave a colorless solution at −78 °C. The NMR spectra (recorded at −70 °C) indicated clean formation of a single species (**8bH**$^{+}$) whose NMR spectral data are listed in the Experimental section. The low-field proton resonance at 6.13 ppm exhibits NOE with the peak at 2.95 ppm. The three most downfield carbon resonances (120.5, 110.1 and 104.0 ppm) are too shielded in comparison to usual cationic carbons (typical spectra in electronic supplementary information). Comparison with the reported values for model systems such as norbornyl cation,[12a] 2-adamantyl cation,[12b] nonbornen-7-yl cations[12c] and trishomocyclopropenium cations[12d] (Fig. 2) suggests that its structure could be nonclassical, equilibrium or of the bis-homoallylic type. In the hope of narrowing down the possibilities, the sample was cooled to −100 °C, but the spectra remained unchanged. Finally, the ^{19}F NMR spectrum of the reaction mixture exhibited, apart from the signals for FSO_3H



Scheme 3 Stable-ion study of **1-ax**, **1-eq** and **8**.

and SO_2ClF, a small peak at 63.0 ppm (in the range for an $–SO_2F$ derivative rather than an $–OSO_2F$ derivative). Subsequent quenching with ice–bicarbonate resulted in a complex mixture whose components could not be separated cleanly to allow positive identification. When the protonation experiment was repeated under more carefully controlled conditions to reduce local overheating, initial spectra were consistent with the formation of a mixture of two carbocations (in a 5 : 1 ratio) where the major ion was **8bH**$^+$. The minor carbocation **8aH**$^+$ converted to **8bH**$^+$ fairly quickly during NMR data collection. Therefore only partial assignment of the ^{13}C spectrum could be made for **8aH**$^+$ (in Chart 1). Since the minor **8aH**$^+$ had a chemical shift pattern similar to **1a**$^+$ it is most probably homoallylic. The available data do not rule out the possibility that **8bH**$^+$ may in fact be a neutral **8**–SO_2F derivative!

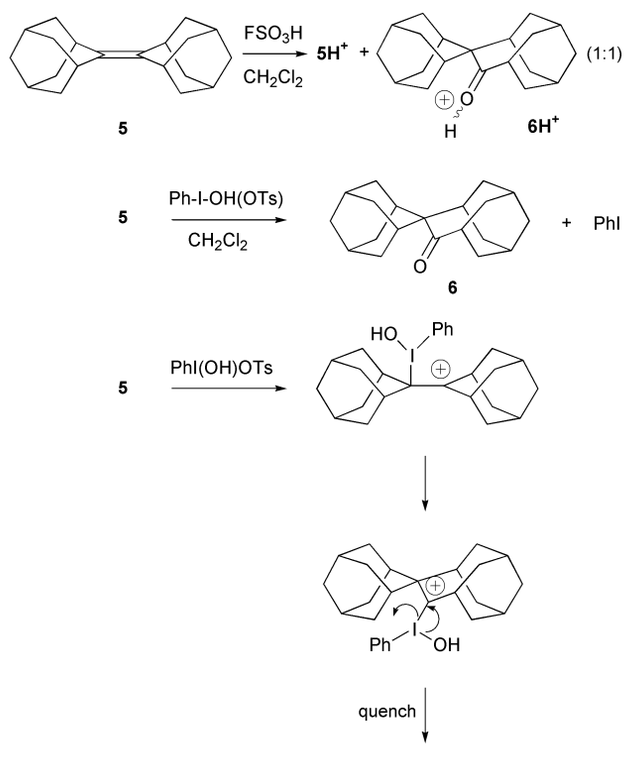
Reaction of Ad=Ad (5) with FSO_3H, NO_2BF_4 and PhI(OH)OTs

When **5** was reacted with FSO_3H in dry CH_2Cl_2 at −78 °C and the sample was stored at −20 °C for 2 days, NMR analysis at low temperature indicated the formation of **5H**$^+$ as a rapidly equilibrating carbocation as previously reported,[8] and the protonated spirocyclic ketone (**6H**$^+$) formed by *in situ* reaction with trace amounts of water in CH_2Cl_2 (Scheme 4) in 1 : 1 ratio.

The NMR data for **6H**$^+$ are included in Chart 1. Reaction of **5** with NO_2BF_4 gave the spirocyclic ketone **6**, as found by Olah *et al*.[8] The same ketone was also obtained when **5** was reacted with Koser's reagent PhI(OH)OTs (complete NMR data for **6** are included in Chart 2). Formation of **6** by reaction of electrophilic PhI(OH)OTs can be understood as addition to the double-bond, formation of a tertiary carbocation, skeletal rearrangement by Wagner–Meerwein shift, trapping with OH, cleavage of PhI, and deprotonation on quenching of the carboxonium ion (Scheme 4).

Reactions of sesquihomoadamantene (7) with FSO_3H–SO_2ClF, CF_3COOH, NO_2BF_4 and PhI(OH)OTs

Low-temperature reaction of **7** with FSO_3H–SO_2ClF gave a colorless solution, which was analyzed by NMR at −50 °C (Scheme 5). The spectral data were those of **5H**$^+$. When the sample was stored at −20 °C for 2 days, a new cation appeared (*ca.* 50%), whose NMR spectral data agreed with those reported by Olah *et al.* for **5Cl**$^+$.[8] Since no Cl_2 had been introduced into the sample, the SO_2Cl_2 impurity in SO_2ClF is a



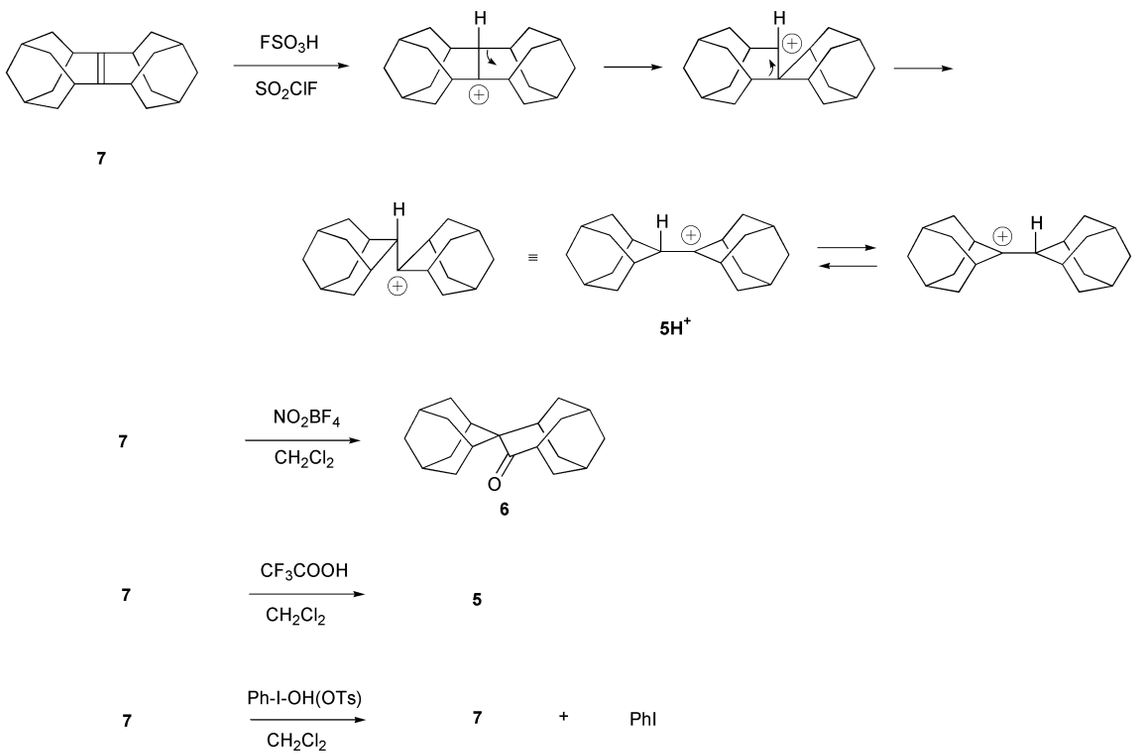
Scheme 4 Protonation of **5** with FSO_3H–CH_2Cl_2 and its reaction with PhI(OH)OTs.

logical candidate to bring about this transformation. The C–H coupling constants for the rapidly hydride-rearranged cation (**5H**$^+$) are close to those of static **5Cl**$^+$ (see Chart 1). Quenching of the sample with water afforded Ad=Ad (NMR assay). Reaction of **7** in CF_3COOH–CH_2Cl_2 at rt gave **5** quantitatively after quenching. Monitoring the reaction by NMR indicated that complete conversion to **5** had occurred after 10 minutes of mixing at room temperature. No persistent carbocations could be observed in TFA. Formation of **5H**$^+$ from **7** can be readily visualized by protonation of the double bond and subsequent skeletal rearrangement. Reaction of **7** with NO_2BF_4–CH_2Cl_2 gave the spirocyclic ketone **6**. Reaction of **7** with PhI(OH)OTs did give PhI, but surprisingly the recovered compound was **7** itself.

Table 1 Electronic energies (E), zero point energies (ZPE) and Gibbs free energies (G) obtained from DFT calculations

Cations	E/hartree	ZPE/hartree	G/hartree	ΔG/kcal mol^{-1}
1a$^+$	−777.6879005	0.421078	−777.307047	0
1c$^+$	−777.6940278	0.420453	−777.314774	−4.6
8aH$^+$	−816.9802929	0.448231	−816.573590	0
8cH$^+$	−816.9816113	0.440722	−816.577190	−2.3
6aH$^{+\,a}$	−854.0962393	0.449356	−853.687338	0
6bH$^{+\,b}$	−854.0931083	0.449317	−853.684701	1.64

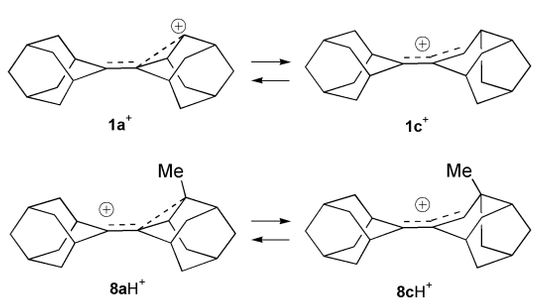
^{a} OH pointing towards nonrearranged Ad. ^{b} OH pointing towards rearranged Ad.



Scheme 5 Protonation of **7** and its reaction with NO_2BF_4, TFA and PhI(OH)OTS.

DFT calculations

In an effort to augment the NMR assignments and for comparison with experiment, the secondary and tertiary homoallylic carbocations **1a**$^+$ and **8aH**$^+$ and their corresponding rearranged allylic carbocations **1c**$^+$ and **8cH**$^+$ were studied computationally by GIAO-NMR at the BLYP/6-31G(d)//BLYP/6-31G(d) level. The oxonium ions **9H**$^+$ and **6H**$^+$ (**6aH**$^+$, **6bH**$^+$), and the neutral cyclic ether **9** were also examined. For **9**, the GIAO chemical shifts obtained at the BLYP/6-31G//AM1 and at the BLYP/6-31G(d)//BLYP/6-31G(d) levels were very similar. For **9H**$^+$ attempted geometry optimization at the BLYP/6-31G(d) level led to ring opening. Therefore the GIAO chemical shifts were computed using the structures minimized by the AM1 method. The results are summarized in Chart 3 (relative energies for the carbocations and oxonium ions are gathered in Table 1). Whereas the overall correspondence between the experimental and theoretical chemical shifts is quite reasonable, the key GIAO shifts are somewhat underestimated. The rearranged allylic carbocations (**1c**$^+$ and **8aH**$^+$) (see Scheme 6) are predicted to be more stable relative to their homoallylic counterparts (by 4.6 and 2.3 kcal mol^{-1}, respectively). A notable feature in the minimized structures is that the C-2–C-4 bond distance in the secondary homoallylic carbocation **1a**$^+$ is shorter (1.723 Å) than in the tertiary cation **8aH**$^+$(2.099 Å), suggesting that homoallylic delocalization is less effective in the tertiary system (the C-2–C-4 distance is 2.49 Å in neutral Ad=Ad).[1] Finally, for **6H**$^+$ two regioisomeric oxonium ions (**6aH**$^+$, **6bH**$^+$) are possible. DFT calculations predict



Scheme 6 Homoallylic–allylic carbocation rearrangements *via* a Wagner–Meerwein shift.

that the isomer in which the OH group is pointing towards the non-rearranged adamantyl ring is 1.64 kcal mol^{-1} lower in energy. The optimized structures are not symmetrical and the C_s symmetrical structures (*i.e.* zero dihedral angle for the ethano bridge) were found to be transition states (one imaginary frequency).

Conclusion

The homoallylic carbocation **1a**$^+$, whose involvement was previously proposed by Bennet *et al. via* solvolysis of **1-eq(OTs)**, has been directly observed in the present study. Solvolysis of the *pseudo-axial* tosylate **1-ax(OTs)** suggested σ-participation and **1b**$^+$ was recognized as a key intermediate. Under stable-ion conditions, rapid initial protonation at the double bond is

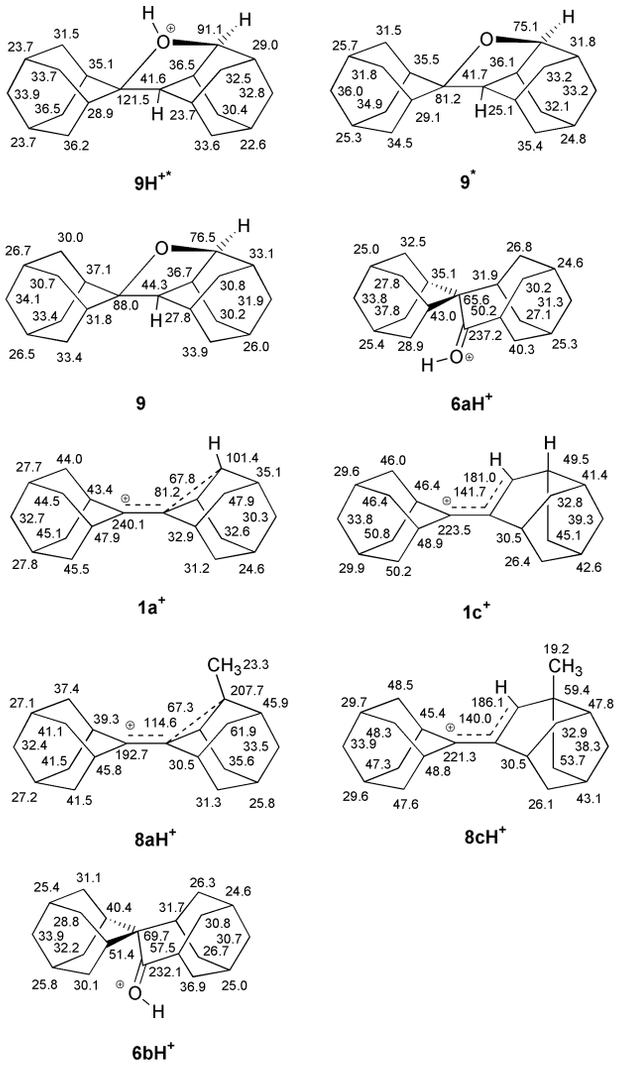


Chart 3 Calculated (GIAO-NMR) chemical shifts, all at the BLYP/6-31G(d)//BLYP/6–31 G(d) level except those marked with *, which were computed by BLYP/6-31G(d)//AM1.

followed by anchimeric assistance leading to a persistent oxonium ion which gives the cyclic ether on quenching. The cyclic ether was previously detected as a minor product *via* the solvolytically formed carbocation. The situation with the methylene derivative **8** is less clear-cut. Whereas the expected tertiary homoallylic cation **8aH**$^+$ is involved and was observed as a minor species, it converted quickly to another species (either another carbocation **8bH**$^+$ or a fluorosulfonylated derivative **8**–SO_2F). The GIAO-NMR calculations give good overall correspondence with the experimental values but somewhat underestimate the key chemical shifts. Theory predicts that the rearranged allylic carbocations **1c**$^+$ and **8cH**$^+$ are somewhat more stable than their homoallylic precursors **1a**$^+$ and **8aH**$^+$. Carbocation **5H**$^+$ can be generated not only from Ad=Ad but also from sesquihomoadamantene **7**. Conversion of **7** into **5** occurs rapidly even in TFA. The spirocyclic ketone **6** is the key end-product which is produced in a variety of ways from both **5** and **7**.

Experimental

Compounds **1-ax**, **1-eq**, **5**, **7**, and **8** were available from previously published studies from the Bennet laboratory.[1–4] Complete NMR analysis of these was made in the present study prior to the protonation experiments (data are gathered in Chart 2).

FSO_3H (Allied and Aldrich) was freshly distilled in an all-glass distillation unit under a dry-nitrogen atmosphere and stored under nitrogen in Nalgene bottles with Teflon seals. SO_2ClF was prepared from SO_2Cl_2, NH_4F and CF_3COOH according to a modified procedure of Prakash *et al.*[13] Several distillations provided pure SO_2ClF (evidence for SO_2Cl_2 impurity acting as chlorinating agent was nevertheless found on one occasion in the present study; see Results and discussion).

CH_2Cl_2 was distilled over P_2O_5. Other chemicals and reagents were commercially available and were used as received.

NMR spectra were recorded on Varian INOVA 500 MHz (at KSU) and on JEOL 400 and 270 MHz instruments (at Kyoto-U). Those of neutral precursors were recorded in $CDCl_3$ at room temperature. Carbocations were studied between −70 and −50 °C. NMR analyses included ^{1}H, ^{13}C, DEPT, H–H COSY, HMQC (or HETCOR), and NOED experiments. CI-mass spectra (isobutane) were recorded on a Shimadzu GC-MS instrument.

Calculations

AM1 calculations were carried out utilizing MOPAC version 6.01 program[14] (tables of internal coordinates for **9H**$^+$ and **9** are included in the electronic supplementary information). DFT calculations was performed using the GAUSSIAN 98 A.9 package.[15] Geometry optimizations were verified by frequency calculations. Additionally, global minima were checked by manually changing initial geometries and by comparing the resulting optimized structures and their energies (tables of cartesian coordinates are provided as electronic supplementary information).

General procedure for stable-ion generation

SO_2ClF (*ca.* 0.4 mL) was distilled into a 5 mm NMR tube containing the substrate (15–20 mg) cooled to dry ice–acetone temperature. To the resulting suspension cold FSO_3H (2–3 drops) was added with efficient mixing until homogeneous (vortex). Subsequently, 2 drops of CD_2Cl_2 were added on top of the cold solution and the mixture was thoroughly mixed. The resulting carbocation/carboxonium ion solutions were all colorless (NMR data are summarized in Chart 1, except those for **8bH**$^+$ which are listed below).

Ion 8bH$^+$

^{1}H δ 6.13 (d, 1H, J = 7.5 Hz), 2.95 (br s, 2H), 2.60–1.70 (m, 25H), 1.90 (s, 3H), 1.53 (d, 1H, J = 14.0 Hz), ^{13}C δ 120.5 (C), 110.1 (C), 104.0 (CH), 55.2 (C), 45.2 (CH), 42.2 (CH_2), 40.9 (CH_2), 40.2 (CH), 38.0 (CH), 37.5 (CH_2), 37.2 (CH), 34.9 (CH_2), 34.8 (CH_2), 34.3 (CH_2), 33.4 (CH_2), 33.1 (CH_2), 31.0 (CH_2), 28.5 (CH), 25.8 (CH), 25.6 (CH), 22.9 (CH_3).

Quenching experiments

The superacid solution was carefully poured into ice–bicarbonate and the mixture was extracted with CH_2Cl_2. The organic extract was washed (10% NaCl) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Quenching of **5H**$^+$ gave intact **5**. Quenching of **9H**$^+$ gave **9** [CI-MS: 285 (M^+ + H), 284 (M^+ for $C_{20}H_{28}O$), 283 (M^+ − H), 267 (M^+ − H − O)]. Quenching of **7H**$^+$ gave **5** and unreacted **7**. Reactions of both **7** and **5** with NO_2BF_4 and reaction of **7** with TFA produced the spirocyclic ketone **6**.

Compound 6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.71 (br t, J = 5.5 Hz, 1H), 2.53 (m, 3H), 2.12 (br s, 2H), 2.02–1.54 (m, 22H); ^{13}C NMR (125 MHz) δ 220.8 (C=O), 58.0 (C), 50.9 (CH), 39.6 (CH_2), 37.2 (CH_2), 35.3 ($2CH_2$), 34.5 ($2CH_2$), 33.8 ($2CH_2$), 32.4 (2CH), 31.0 ($2CH_2$), 30.0 (CH), 27.38 (CH), 27.37 (CH), 27.3 (2CH).

Reaction of sesquihomoadamantene 7 with Koser's reagent[16]

A mixture of sesquihomoadamantene (10 mg, 0.037 mmol) and PhI(OH)OTs (30 mg, 0.076 mmol) in dry CH_2Cl_2 (0.20 mL) was stirred for 19 h at rt. After addition of water, the resulting mixture was extracted with CH_2Cl_2 and the organic layer was dried ($MgSO_4$). Removal of solvent gave a colorless oil (15 mg), which was identified by NMR analysis as PhI and **7**.

Reaction of sesquihomoadamantene with the nitronium salt

NO_2BF_4 (6 mg, 0.05 mmol) was mixed with a solution of sesquihomoadamantene (6 mg, 0.02 mmol) in dry CH_2Cl_2 (0.5 mL). After 16 h, NMR analysis of the mixture indicated conversion to the spirocyclic ketone **6**. The mixture was poured into water, extracted with CH_2Cl_2 and dried ($MgSO_4$). Removal of the solvent gave a colorless oil (4 mg), SiO_2 column chromatography of which (hexane–ether = 19 : 1) afforded pure **6** (4 mg) as colorless crystals (yield 60%).

Reaction of 7 with CF_3COOH–CH_2Cl_2

CF_3COOH (0.06 mL, 0.8 mmol) was mixed with a solution of **7** (5 mg, 0.02 mmol) in dry CH_2Cl_2 (0.5 mL). After 10 minutes the mixture was poured into water, extracted with CH_2Cl_2 and dried ($MgSO_4$). Removal of the solvent gave almost pure Ad=Ad as colorless crystals (5 mg).

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