bp 84-85 (3.0)]; *p*-F, 56 (0.2); *p*-Cl, 70 (0.1); *m*-$CH_3$, 60 (0.2); *m*-F, 54 (0.1); *m*-Cl, 66 (0.1); *m*-$CF_3$, 58 (0.2); 3,5-$Cl_2$, 84 (0.1). The *p*-$OCH_3$, H, *p*-$CF_3$, and 3,5-$(CF_3)_2$ derivatives were available from earlier work in our laboratories.[18] Satisfactory analytical data (C ± 0.2, H ± 0.2, F ± 0.1, and Cl ± 0.2) were obtained for all of the new compounds. All of these precursors gave $^{13}C$ NMR spectral data in accordance with their structures.

**Carbocations.** The ions were prepared by slow addition of a solution of the precursor in $SO_2ClF$ at -78 °C to a solution of $SbF_5/FSO_3H/SO_2ClF$ at -78 °C with rapid vortex mixing. The acid ($SbF_5/FSO_3H$ 1:1 M) concentration in the solution was 3 M. The concentration of the ion based on the precursor added was ~0.5 M. Transfer of the solution under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended syringe, as described previously.[19]

**NMR Spectra.** $^{13}C$ NMR spectra were recorded at -80 °C or at -30 °C on a Varian CFT-20 spectrometer with 8-mm tubes containing a concentric 3-mm (o.d.) capillary tube of acetone-$d_6$ and $Me_4Si$, 8192 data points, a spectral width of 6500 Hz, and a pulse angle of 45°. Chemical shifts are in parts per million downfield from external $Me_4Si$.

**Registry No. 1** (Z = *p*-$OCH_3$), 53600-66-1; **1** (Z = *p*-$CH_3$), 53600-69-4; **1** (Z = *p*-F), 51823-56-4; **1** (Z = *p*-Cl), 53600-70-7; **1** (Z = *m*-$CH_3$), 64618-83-3; **1** (Z = H), 18026-67-0; **1** (Z = *m*-F), 81390-38-7; **1** (Z = *m*-Cl), 53600-74-1; **1** (Z = *m*-$CF_3$), 81390-39-8; **1** (Z = 3,5-$Cl_2$), 81390-40-1; **1** (Z = *p*-$CF_3$), 53600-75-2; **1** (Z = 3,5-$(CF_3)_2$), 53600-76-3; **8** (Z = *p*-$OCH_3$), 35144-47-9; **8** (Z = *p*-$CH_3$), 36043-28-4; **8** (Z = *p*-F), 51804-42-3; **8** (Z = *p*-Cl), 41912-30-5; **8** (Z = *m*-$CH_3$), 84074-03-3; **8** (Z = H), 36043-29-5; **8** (Z = *m*-F), 84074-04-4; **8** (Z = *m*-Cl), 84074-05-5; **8** (Z = *m*-$CF_3$), 84074-06-6; **8** (Z = 3,5-$Cl_2$), 84074-07-7; **8** (Z = *p*-$CF_3$), 84074-08-8; **8** (Z = 3,5-$(CF_3)_2$), 84074-09-9; **10**, 84074-10-2.

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[18] Brown, H. C.; Peters, E. N.; Ravindranathan, M. *J. Am. Chem. Soc.* **1977**, *99*, 505.

[19] Brown, H. C.; Kelly, D. P. *Aust. J. Chem.* **1976**, *29*, 957.

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# Carbocationic Rearrangements Originating from the 2-*tert*-Butyl-2-adamantyl System[1]

**James A. Saba and James L. Fry***

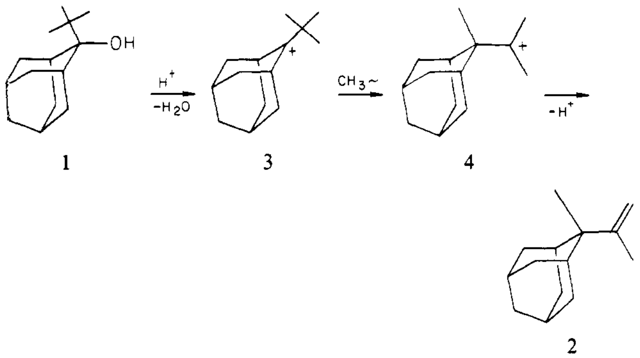
*Contribution from Bowman-Oddy Laboratories, Department of Chemistry, The University of Toledo, Toledo, Ohio 43606. Received March 8, 1982*

**Abstract:** The nature of carbocationic species ($C_{14}H_{23}^+$) related to the 2-*tert*-butyl-2-adamantyl cation (**3**) has been explored by trapping and isotope-labeling experiments and by spectroscopic studies under stable ion conditions. Treatment of either 2-*tert*-butyl-2-adamantanol (**1**) or 2-isopropenyl-2-methyladamantane (**2**) with acid in the presence of a reducing agent (HI or tri-*n*-hexylsilane) yielded 2-*tert*-butyladamantane (**5**) as the major or exclusive product. Deuterium exchange experiments established the rapid interconversion of the 2-(2-methyl-2-adamantyl)-2-propyl cation (**4**) with ion **3** under these conditions. In hydrogen chloride saturated media ($Et_2O$, $CH_2Cl_2$, or $CHCl_3$) at 100 °C, alkene **2** formed within 4 h a mixture containing 5% of the isomeric compound 2,2-dimethylspiro[cyclopropane-1,2'-tricyclo[3.3.1.$1^{3,7}$]decane] (**7**). Each of the compounds **1**, **2**, and **7** gave a single carbocationic species in the temperature range of -78 to -20 °C in $FSO_3H-SbF_5-SO_2ClF$ that was identified by $^1H$ and $^{13}C$ NMR spectroscopy as ion **3**. At extended times or temperatures of 150-200 °C, **2** and **7** in HCl-saturated $CHCl_3$ solution were consumed and replaced by a mixture of products consisting of 2-isobutylideneadamantane (**8**, 30-40%), 1-(2-adamantyl)-2-methylprop-1-ene (**9**, 60-70%), and methyleneadamantane (**10**, 0-10%). Pure **8** and **9** formed a 40:60 equilibrium mixture in the presence of acid at 150 °C. Deuterium labeling established a single 1,3-hydride shift connecting isomeric carbocations as the pathway between **8** and **9**. The formation of **10** is suggested to arise from the $\alpha$ expulsion of dimethylcarbene from ion **4**.

2-*tert*-Butyl-2-adamantanol (**1**) and its derivatives undergo carbocation-forming reactions extremely rapidly.[2] For example, 2-*tert*-butyl-2-adamantyl *p*-nitrobenzoate quickly reacts in aqueous solvolytic media to give the methyl-shifted alkene 2-isopropenyl-2-methyladamantane (**2**) as the major product along with minor amounts of the unrearranged parent alcohol **1**.[2,3] Treatment of alcohol **1** with traces of acid causes a fast conversion to alkene **2**.[2,4] These results have been understood in terms depicted in Scheme I.

The driving force for the dehydration of **1** as well as the solvolytic behavior of its ester derivative is believed to be the formation of the relatively unstrained 2-*tert*-butyl-2-adamantyl cation (**3**) from sterically strained **1**.[2-4] Since direct loss of a $\beta$ proton from ion **3** would result in the formation of an extremely strained bridgehead alkene, a methyl rearrangement to produce ion **4** which can then undergo proton loss to yield the observed alkene **2** seems to be a more favorable reaction pathway. That ion **3** is a discrete precursor to the methyl-shifted ion **4** was indicated by the disparity of the deuterium kinetic isotope effects on the overall rate of solvolysis (1.11) vs. methyl migration (1.25) during the solvolysis of the *p*-nitrobenzoate ester which was deuterated at all *tert*-butyl methyl groups.[3]

Scheme I



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[1] Portions of this work have been communicated in preliminary form: Fry, J. L.; Saba, J. A. *Tetrahedron Lett.* **1982**, *23*, 1743; "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 28-April 2, 1982; American Chemical Society: Washington, D.C, 1982; ORGN 56.

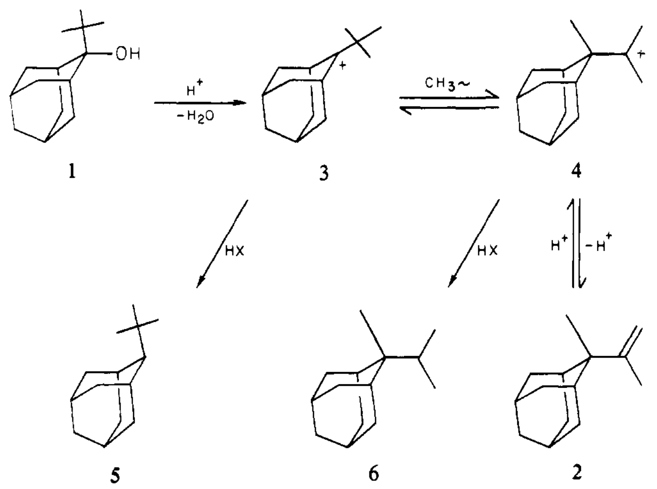
[2] Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 4628.

[3] Badger, R. C.; Fry, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 1680.

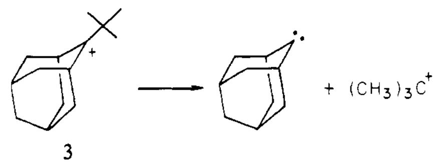
[4] Lomas, J. S.; Luong, P. K.; Dubois, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 5478; *J. Org. Chem.* **1979**, *44*, 1647.

0002-7863/83/1505-0533$01.50/0

Scheme II



Because of the unique steric and stereoelectronic restraints placed on the reaction pathways available to ion **3**, we considered it a possibility that ion **3** might undergo spontaneous $\alpha$ expulsion of *tert*-butyl cation to form adamantylidene, a reaction not previously documented for simple alkyl cations in solution (eq 1).[5]



(1)

This prompted an exploratory study in which we treated alcohol **1** with various hydrogen halides in nonnucleophilic, nonbasic media with the hope of finding simple products derived from adamantylidene. Although these studies did not reveal evidence to support the occurrence of the fragmentation shown in eq 1, the results that we report in this paper indicate some interesting and unexpected chemistry in the 2-adamantyl system.

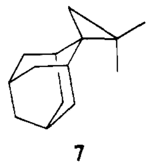
## Results

**Studies at 25 °C.** The behavior of alcohol **1** toward various hydrogen halide saturated solvents such as dichloromethane, chloroform, and carbon tetrachloride was studied in some preliminary experiments. In all cases, the dehydration rearrangement to alkene **2** was found to occur almost at once at room temperature. In one case, however, that in which hydrogen iodide was used to saturate a carbon tetrachloride solution of **1**, alkene **2** was consumed and replaced by a major and a minor new product. This conversion varied somewhat, but in most cases it was complete within about 1 h at room temperature. With dichloromethane or chloroform as solvent, the reaction was slower by at least a factor of 2. In a particular experiment, after 1 h at 25 °C, a solution of **1** in carbon tetrachloride was found by GC analysis to consist of 4% of alkene **2**, 93% of a major product, and 3% of a minor product.

The major product had spectral properties identical with those of previously reported 2-*tert*-butyladamantane (**5**).[6,7] The minor product had spectral properties identical with those of a known sample of 2-isopropyl-2-methyladamantane (**6**) which was prepared by hydrogenation of 2-isopropenyl-2-methyladamantane (**2**). When alcohol **1** was treated with tri-*n*-hexylsilane and trifluoroacetic acid in dichloromethane,[8] only **5** was formed in 90% isolated yield.

The results of these experiments may be understood in terms of the mechanism presented in Scheme II. Proof of the reversible nature of the methide shift connecting ions **3** and **4** was given by a deuterium exchange study. Treatment of a chloroform solution of alkene **2** with deuterium chloride for 5 min at 25 °C resulted in the recovery of **2** which had incorporated deuterium into it. The $^1$H NMR spectrum of this product had diminished height and reduced integration for the signals for the 2-methyl group ($\delta$ 1.10), allylic methyl group ($\delta$ 1.70), and vinylic hydrogens ($\delta$ 4.79, 4.87). The proton-decoupled $^2$H NMR spectrum further verified the incorporation of deuterium by showing signals at $\delta$ 1.10, 1.70, 4.79, and 4.89. The proton-decoupled $^{13}$C NMR spectrum showed the loss of three signals ($\delta$ 109.7, 26.0, and 19.0) which were replaced by small diffuse humps. The fact that deuterium was found on the 2-methyl group of **2** indicates that ions **3** and **4** are interconvertible under these conditions.

**Studies at 100 °C.** When solutions of either alcohol **1** or alkene **2** in dichloromethane, diethyl ether, or chloroform were saturated with hydrogen chloride and held in a sealed vessel at 100 °C for 4 h, a mixture was formed that consisted of 95% of alkene **2** and 5% of a new hydrocarbon (**7**).[9] Isolation of **7** by GC showed it to be extremely sensitive to traces of acid. In ordinary solutions of $DCCl_3$ at room temperature it completely reverted to alkene **2** within 24 h unless a small amount of ammonia was first added to the solvent. The identity of compound **7** was established by comparison of its physical and spectral properties with those of a sample of 2,2-dimethylspiro[cyclopropane-1,2′-tricyclo-[3.3.1.1$^{3,7}$]decane][10] which was synthesized by an independent route.



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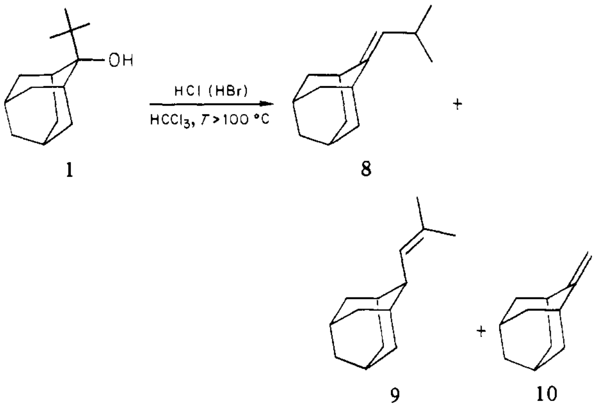
**Studies above 100 °C.** When hydrogen bromide or hydrogen chloride saturated solutions of **1** in chloroform were either held at 100 °C for a longer time than that needed for the formation of **7** or raised to 150–200 °C, two new major products (**8** and **9**) and a new minor product (**10**) began to accumulate. Eventually, **2** and **7** were completely consumed and **8** and **9** accounted for about 30–40% and 60–70% of the reaction mixture, respectively (eq 2). A minor product, **10**, was formed in amounts varying between 0% and 10%, with the larger amount seen at 200 °C.

Isolation of the three products by GC and consideration of their spectral properties led to the structural assignments of 2-isobutylideneadamantane[11] for **8**, 1-(2-adamantyl)-2-methylpropene for **9**, and methyleneadamantane[12] for **10**.



(2)

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[5] Base-induced $\alpha$ deprotonation of some dialkoxyl carbocations and their thio analogues to produce carbenes is a known process: Olofson, R. A.; Walinski, S. W.; Marino, J. P.; Jernow, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 6554.

[6] Woodworth, C. W.; Buss, V.; Schleyer, P. v. R. *Chem. Commun.* **1968**, 569.

[7] Woodworth, C. W. Ph.D. Dissertation, Princeton University, 1969.

[8] Carey, F. A.; Tremper, H. S. *J. Org. Chem.* **1971**, *36*, 758.

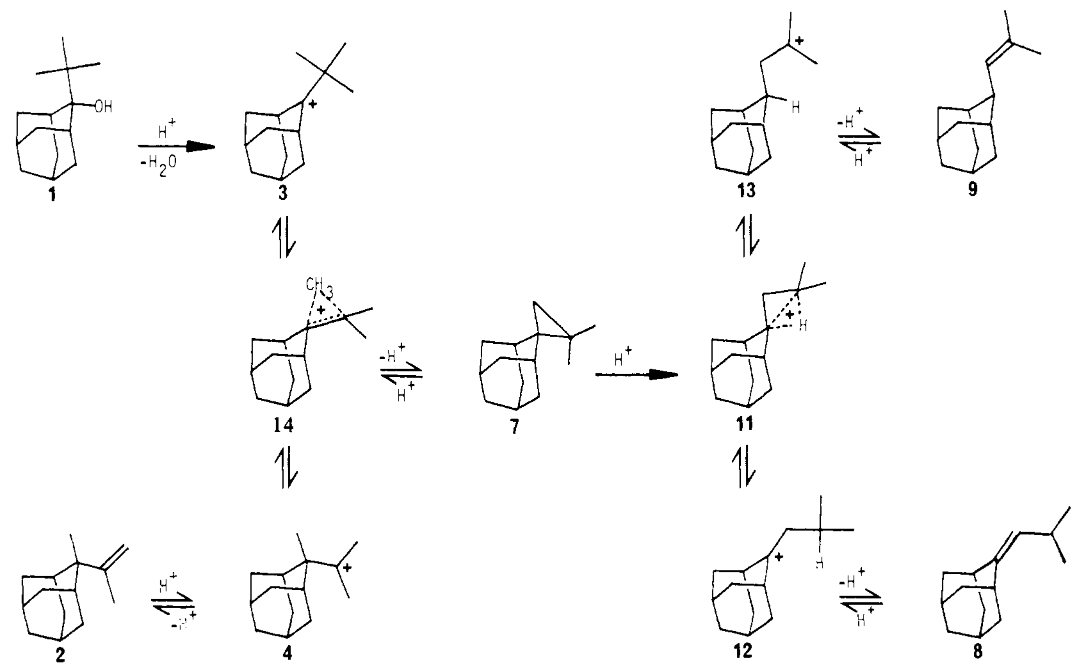
[9] Compound **7** was not formed from either **1** or **2** under these conditions in carbon tetrachloride solvent.

[10] Moss, R. A.; Chang, M. J. *Tetrahedron Lett.* **1981**, *22*, 3749.

[11] Landa, S.; Vais, J.; Burkhard, J. *Collect. Czech. Chem. Commun.* **1967**, *32*, 570; "Nuclear Magnetic Resonance Spectra", Sadtler Research Laboratories, Inc., Philadelphia; Vol. 9, spectrum no. 5943M.

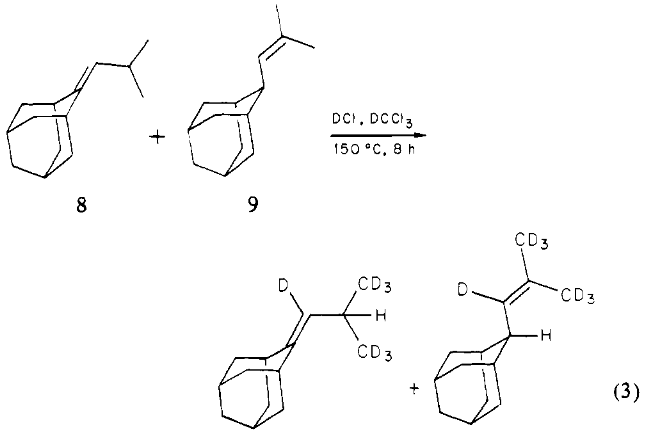
[12] Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 182.

Scheme III

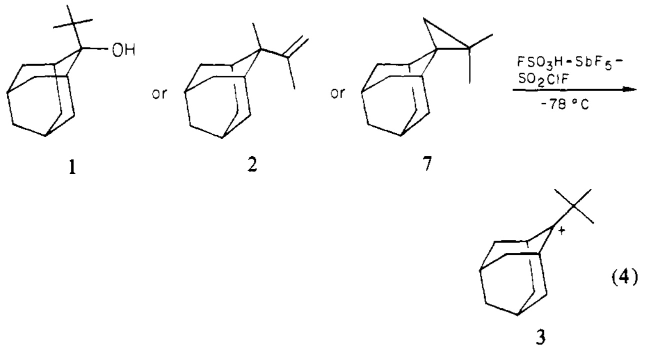


An equilibrium mixture consisting of 40% **8** and 60% **9** was obtained when a hydrogen chloride saturated chloroform solution of either pure **8** or **9** was held at 150 °C for 4 h. This interconversion took place at temperatures as low as 100 °C, but not in the absence of acid. No formation of compounds **2** or **7** from **8** or **9** was observed. If any **10** was formed during the equilibrations, it was in amounts at the limits of GC detection.

A mixture of **8** (30%) and **9** (70%) was dissolved in deuterium chloride saturated deuteriochloroform and held at 150 °C for 8 h in order to study the mechanism of this interconversion in greater detail. At the end of this time, the equilibrated mixture of **8** (40%) and **9** (60%) was separated by GC and each of the pure components was examined by proton-decoupled $^2$H NMR spectroscopy. The results were quite unexpected. Deuterium was found to have been incorporated into **8** at both the side chain methyl groups and the vinyl position, but *not* at the side chain allylic hydrogen site. Isomer **9** had incorporated deuterium into it at both of the side chain methyl groups and the vinyl hydrogen, but *not* at the allylic ring hydrogen site (eq 3). These results are only consistent with a very stereospecific mode of isotopic exchange and isomerization.



**Stable Ion Studies.** Stable carbocation solutions from compounds **1**, **2**, and **7** were prepared in $FSO_3H$–$SbF_5$–$SO_2ClF$ at −78 °C and were examined by $^1$H and $^{13}$C NMR spectroscopy. All of the solutions produced the same spectra. These solutions were stable for at least 24 h at −78 °C and did not undergo any appreciable spectral changes in the temperature range of −78 to −20 °C.[13] Both the $^1$H and $^{13}$C NMR spectra obtained were very similar to those reported for the 2-methyl-2-adamantyl and 2-ethyl-2-adamantyl cations[14] and were quite consistent with the structure of a stable 2-*tert*-butyl-2-adamantyl cation, **3** (eq 4). There was no evidence of any appreciable amount of ion **4** in these solutions.



## Discussion

The results of these experiments clearly establish that a manifold of interconverting isomeric ions and hydrocarbons exists which originates from the 2-*tert*-butyl-2-adamantyl system. Taken together, the reductive trapping and deuterium exchange experiments performed at room temperature and the spectral studies of the stable ions at subambient temperatures indicate that ions **3** and **4** are in a state of rapid equilibrium and that ion **4** must have a free energy at least several kcal/mol more than that of ion **3**. This is most likely a reflection of the lesser steric strain energy inherent in ion **3** compared with ion **4**.[15]

Scheme III depicts what we believe is a concise representation of the interconnections of the species studied in this work. The corner- and edge-protonated cyclopropanes **14** and **11**, respectively, are suggested as reasonable connecting links for ions **3** and **4**, on the one hand, and **12** and **13**, on the other, with spirocyclopropane

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(13) Ion **3** has been independently studied in stable ion media at −102 to −128 °C: Saunders, M.; Loyd, J. R.; Schleyer, P.v. R.; Chang, L. W.-K., to be published. Loyd, J. R. Ph.D. Dissertation, Yale University, 1978.

(14) Olah, G. A.; Liang, G.; Mateescu, G. D. *J. Org. Chem.* **1974**, *39*, 3750.

(15) Molecular mechanics calculations indicate that ion **4** has 6.7 kcal mol$^{-1}$ more strain energy than does ion **3** and hydrocarbon **6** has 3.3 kcal mol$^{-1}$ more strain energy than does even the relatively strained compound **5**: Schleyer, P. v. R., private communication of Chang, L. W.-K. Ph.D. Disseration, Princeton University, 1977.

**7**. It may be that they do not have discrete existences as reaction intermediates. Other elaborations of Scheme III are, of course, possible.

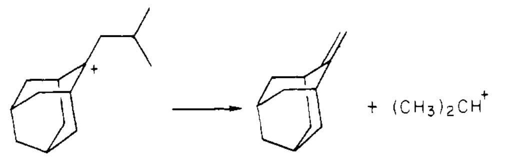
Our results indicate a rather large kinetic and thermodynamic barrier separating species related directly to ion **14** with those structurally related more directly to ion **11**. At higher than ambient temperatures species represented on the left side of Scheme III were transformed slowly and essentially irreversibly into species on the right side. It seems reasonable that this barrier has steric strain differences as its primary origin.

One very interesting result from this study concerns the mode of interconversion of alkenes **8** and **9**. The deuterium labeling experiments showed that only one hydrogen on the side chain, that depicted explicitly on ions **11**, **12**, and **13** of Scheme III, did *not* exchange with the medium. This indicates that a single 1,3-hydride shift connecting ions **12** and **13** must be the key step in the interconversion of **8** and **9**.[16]

Species **11** is undoubtedly of higher energy than ions **12** or **13** and very likely represents the transition state connecting ions **12** and **13** rather than a discrete edge-protonated cyclopropane intermediate.[17] A similar 1,3-hydride shift has been observed in the formally analogous 2,4-dimethyl-2-pentyl cation.[18,19] The relative inaccessibility of species related to **11** compared with species related more directly to **14** is shown by the fact that direct protonation of spirocyclopropane **7** produced only ion **3** with the exclusion of **12** and **13** under stable ion conditions.

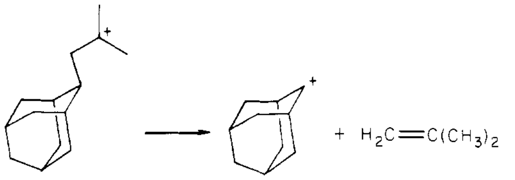
It should be noted that the deuterium exchange studies not only indicate a direct 1,3-hydride shift in the acid-catalyzed interconversion of alkenes **8** and **9** but also offer further evidence of the substantial energy barrier separating ions to the left of **7** from those to the right. If ions **12** and **13** were to "cross over" to ions **3** and **4**, then *all* of the side chain hydrogen sites in species **8** and **9** would undergo protium–deuterium exchange, an observation *not* made.

The formation of methyleneadamantane (**10**) from **2** must occur by a fragmentation route. One possibility is that it arises from $\beta$ expulsion of the 2-propyl cation from ion **12** (eq 5). However, several lines of reasoning cast doubt on that. First, at best, no more than a trace of **10** was observed during the interconversion of olefins **8** and **9**. Second, if conditions were conducive for ion **12** to undergo the fragmentation shown in eq 5, it is difficult to imagine that isomeric ion **13** would not have an even greater propensity to undergo an analogous cleavage to form 2-methylpropene and the 2-adamantyl cation (eq 6). Yet in none of the experiments were even traces of any simple products derived from the 2-adamantyl cation observed.



12 10

(5)



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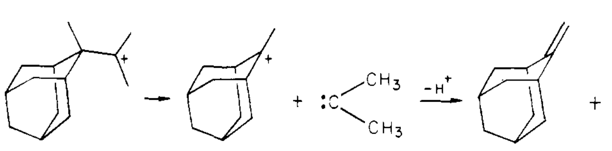
(6)

Another possibility that must be considered is the $\alpha$ expulsion of dimethylcarbene from ion **4** to produce the 2-methyl-2-adamantyl cation which then undergoes deprotonation to yield **10** (eq 7). Such an $\alpha$ fragmentation of a carbocation has a precedent in mass spectral fragmentation.[20] In this case it would lead to products of considerably lower steric energy than that of the reactant. Further work will be required to precisely define the origin of **10**.



4 10

$CH_3CH{=}CH_2$ (7)

## Experimental Section

Nuclear magnetic resonance spectra were obtained by using a JEOL FX-90Q Fourier transform spectrometer. Unless otherwise indicated, the solvent used was $DCCl_3$ and chemical shifts were related to $Me_4Si$. Infrared spectra were obtained on a Pye Unicam SP3-200 instrument with $CCl_4$ solutions in 0.1-mm NaCl cells. Mass spectra were run on a Nuclide 12-90G mass spectrometer. Gas chromatographic analyses were conducted either on a Varian Aerograph 90-P instrument or on a Hewlett-Packard 5722A instrument equipped with an electronic integrating recorder. Unless otherwise noted, both analytical and preparative GC work were performed on 6.4-mm × 2-m columns. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

**Synthesis of 2-*tert*-Butyl-2-adamantanol (1).** Compound **1** was synthesized as previously reported by addition of 2-adamantanone to *tert*-butyllithium.[2] The crude product obtained after workup was then purified by flash column chromatography on a 4 × 20-cm column of 230–400 mesh silica gel with 15% diethyl ether in hexane as the eluting solvent.[21] Pure **1** was the first compound to be eluted (80%). Physical and $^1$H NMR spectral properties were as previously described.[2] The $^{13}$C NMR spectrum displayed signals at $\delta$ 77.5, 39.8, 35.8, 35.2, 35.0, 29.0, and 27.4.

**Preparation of 2-Isopropenyl-2-methyladamantane (2).** One gram of 2-*tert*-butyl-2-adamantanol (**1**) was dissolved in 10 mL of HCl(g)-saturated $HCCl_3$ and placed in an open-ended 25-mL flask containing a stirring bar. After the mixture was stirred for 1 min it was neutralized with a saturated aqueous solution of $NaHCO_3$. The organic layer was dried ($MgSO_4$) and the solvent removed and the residue was subjected to Kugelrohr distillation [95 °C (0.1 torr)] to yield 0.9 g of product whose physical and $^1$H NMR spectral features were as previously reported.[2] Its $^{13}$C NMR spectrum showed signals positioned as expected at $\delta$ 152.8, 109.7, 44.4, 39.0, 34.4, 34.1, 33.3, 27.9, 26.0, and 19.0.

**Production of 2-*tert*-Butyladamantane (5) and 2-Isopropyl-2-methyladamantane (6) from 1.** Into a 25-mL flask were placed 0.1 g of **1**, 10 mL of $CCl_4$, and a stirring bar. With vigorous stirring HI(g) was bubbled in (50 mL/min) at room temperature. As time progressed the solution became dark purple, indicating oxidation of iodide ion to iodine. After 25 min, the flask was sealed and its contents were vigorously stirred for an additional 30 min. The resulting acidic solution was neutralized with a saturated aqueous solution of $NaHCO_3$. Removal of solvent yielded an oil. GC analysis (20% SE-30, 180 °C, 30 mL/min He flow) of the oil showed three peaks. The first peak (7.0 min, 93%) had the same $^1$H NMR spectrum as previously reported for 2-*tert*-butyladamantane.[6,7] The $^{13}$C NMR spectrum showed signals at $\delta$ 54.6, 42.2, 39.0, 34.1, 33.4, 30.7, 29.9, 29.2, and 28.1. Mass spectrum: $m/z$ 135 (base), 192 ($M^+$). Peak two (8.2 min, 4%) was identified as alkene **2**. Collection of peak three (8.65 min, 3%) gave a compound identical with a known sample of 2-isopropyl-2-methyladamantane (**6**), which was prepared by hydrogenation of a solution of alkene **2** in glacial acetic acid using Adams catalyst in a low-pressure Parr apparatus.[6] The $^1$H NMR spectrum of compound **6** consisted of signals at $\delta$ 0.75 (6 H, d, $J$ = 6.8 Hz), 0.82 (3 H, s), 1.3–2.2 (14 H, br m), 2.4 (1 H, sept, $J$ = 6.8 Hz); $^{13}$C NMR $\delta$ 15.78, 15.81, 27.91, 28.18, 29.28, 32.56, 33.98, 34.05, 39.25, 40.11.

**Silane Reduction of 1.** Into a 50-mL round-bottomed flask equipped with a stirring bar were placed 20 mL of dichloromethane and 0.25 g of alcohol **1**. With rapid stirring, first 2.5 mL of trifluoroacetic acid and then 0.5 mL of tri-*n*-hexylsilane (PCR) were added to the reaction solution. After 10 min, 2.5 mL of water was added. The organic layer was

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[16] Fry, J. L.; Karabatsos, G. J. In "Carbonium Ions"; Olah, G. A.; Schleyer, P. v. R., Ed.; Wiley-Interscience: New York, 1970; Vol. II, Chapter 4.

[17] Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53.

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neutralized with aqueous sodium bicarbonate, dried ($MgSO_4$), and reduced in volume on a rotary evaporator. The oily residue was then subjected to Kugelrohr distillation [95 °C (0.06 torr)] to yield 0.21 g (90%) of hydrocarbon **5**.

**Deuteration of Alkene 2.** DCl was admitted into a solution of 50 mmol of **2** in 1 mL of chloroform at 25 °C for 5 min. $^1H$ NMR spectroscopy showed diminished height and reduced integration at the 2-methyl group at $\delta$ 1.10 along with the vinylic hydrogens and allylic methyl group at $\delta$ 4.87, 4.79 and $\delta$ 1.70, respectively. The $^{13}C$ NMR spectrum showed the loss of three signals ($\delta$ 109.7, 26.0, and 19.0) which were replaced by small diffuse humps. The proton-decoupled $^2H$ NMR spectrum (13.7 MHz, $HCCl_3$ solvent with $DCCl_3$ internal reference taken as $\delta$ 7.24) showed signals at $\delta$ 4.89, 4.79, 1.70, and 1.10.

**Formation of 7 from 2.** A solution of 1.0 g of **2** in 15 mL of HCl(g)-saturated $HCCl_3$ was sealed in a glass tube and held at 100 °C for 4 h. The reaction tube was then allowed to cool to room temperature and its contents, consisting of unreacted **2** and a new product in about 5% yield, was removed and neutralized with a saturated aqueous solution of $NaHCO_3$. Purification of the desired product (15% FFAP on 60–80 Chromosorb W, 160 °C, 20 mL/min He flow, retention time 16 min) yielded a colorless oil. The $^1H$ NMR spectrum showed signals at $\delta$ 0.05 (2 H, s), 1.10 (6 H, s), 1.40 (2 H, br s), and a conglomerate between $\delta$ 1.65 and 2.00 (12 H). The $^{13}C$ NMR spectrum showed signals at $\delta$ 37.5, 37.3, 36.7, 34.4, 33.9, 28.1, 26.1, 21.1, and 20.8; mass spectrum, $m/z$ (rel intensity) 190 (73), 175 (100), 161.2 (metastable); IR 3050, 1440, 1370, 1013, 979, 905 $cm^{-1}$. Anal. Calcd for $C_{14}H_{22}$: C, 88.35, H, 11.65. Found: C, 88.24; H, 11.72.

**Synthesis of 7 from Isopropylideneadamantane.** An alternate synthesis of 7 was conducted by a Simmons–Smith procedure.[22] Into a nitrogen-purged 100-mL flask fitted with a condenser and stirring bar were placed 25-mL of anhydrous diethyl ether, 10 g of Zn dust, and 1.6 g of finely ground CuCl. The mixture was held at reflux with vigorous stirring for 0.5 h to form the Zn–Cu couple before 6 mL of diiodomethane, 5.4 g (0.031 mol) of isopropylideneadamantane,[23] 6 mL of diethyl ether, and 0.24 g of iodine were added. The reaction mixture was held at reflux with vigorous stirring for 24 h. At this time, GC analysis indicated a 95% conversion to product. The mixture was filtered through a fritted glass funnel, the solvent was evaporated, and the oily residue was subjected to Kugelrohr distillation [90 °C (0.06 torr)] to yield 4.1 g (70%) of 7, identical in all respects with that obtained from **2**.

**Study of Stable Carbocations Derived from 1, 2, and 7.** Solutions were prepared by adding ca. 60 mg of **1**, **2**, or 7 into ca. 1 mL of a rapidly stirred mixture of $FSO_3H$–$SbF_5$–$SO_2ClF$ (1:1:8 v/v/v, Aldrich) at −78 °C. The clear solutions were examined by both $^1H$ and $^{13}C$ NMR spectroscopy. The chemical shifts were determined from $Me_4Si$ which was mixed with acetone-$d_6$ (1:1 v/v) and sealed in a capillary tube which was inserted into the sample tube. The solutions were stable for at least 24 h at −78 °C and all gave the same spectra. The spectra did not undergo any significant changes in the temperature range of −78 °C to −20 °C. $^1H$ NMR $\delta$ 2.04 (9 H, s), 2.57 (4 H, s), 3.10 (8 H, ABq), 4.60 (2 H, s); $^{13}C$ NMR $\delta$ 26.2 (q), 28.3 (d), 35.5 (t), 50.4 (t), 57.5 (d), 59.4 (s), 317.8 (s). These spectra are both consistent with that for the structure of ion **3** but not for that of ion **4**. The spectral assignments follow directly from those made on other 2-alkyl-2-adamantyl cations.[14]

**Formation of 8, 9, and 10 from 1 above 100 °C.** A solution of 1.0 g of **1** in 15 mL of chloroform which was saturated with either HBr(g) or HCl(g) was sealed in a glass tube and heated either at 200 °C for 2.5 h or at 150 °C for 48 h. The reaction tube was then cooled and its contents were neutralized with saturated aqueous sodium bicarbonate solution. Three products were isolated by preparative GC (15% FFAP on 60–80 Chromosorb W, 160 °C, 20 mL/min He flow). They had retention times of 7, 13, and 24 min and were formed in relative amounts of 0–10%, 30–40%, and 60–70%, respectively.

The compound with the shortest retention time had physical and $^1H$ NMR spectral features identical with those of methyleneadamantane (**10**).[12] The $^{13}C$ NMR spectrum of **10** consisted of signals at $\delta$ 158.4, 100.6, 39.9, 39.4, 37.6, and 28.6. The compound of intermediate retention time had properties identical with those of isobutylideneadamantane (**8**).[11] Its $^{13}C$ NMR spectrum had signals at $\delta$ 145, 125, 40.7, 40.1, 39.3, 37.6, 32.8, 29.0, 25.9, and 23.9.

The compound of longest retention time (an oil) had a $^1H$ NMR spectrum consisting of signals at $\delta$ 5.5 (1 vinyl H, d, $J$ = 8.57 Hz, septets, $J$ = 1.32 Hz), 2.55 (1 allylic H, d, $J$ = 8.57 Hz), 1.9 (14 H, br s), 1.7 (3 methyl H, d, $J$ = 1.32 Hz), and 1.6 (3 methyl H, d, J = 1.32 Hz). Decoupling experiments showed that (1) irradiation at $\delta$ 5.5 caused the two doublet methyl signals to become singlets and the doublet at $\delta$ 2.55 to become a singlet, (2) irradiation at $\delta$ 2.55 caused the doublet at $\delta$ 5.5 to become a singlet, and (3) irradiation at either methyl doublet resulted in loss of the septets at $\delta$ 5.5. Mass spectrum, $m/z$ (rel intensity) 190 (76), 175 (100), 161.2 (metastable); IR 845, 890, 1100, 1375, 1450, 1640, and 3050 $cm^{-1}$. Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.27; H, 11.76. These properties are consistent with those for the structure of 1-(2-adamantyl)-2-methylpropene (**9**).

**Deuterium Exchange and Equilibration of 8 and 9.** A 1.0-g mixture of **8** (30%) and **9** (70%) was dissolved in 15 mL of DCl-saturated $DCCl_3$. The solution was sealed in a glass tube and held at 150 °C for 8 h. At the end of this time the cooled reaction mixture was neutralized with saturated aqueous sodium bicarbonate solution. After removal of solvent, the residual mixture of **8** (40%) and **9** (60%) was separated by preparative GC. The proton-decoupled $^2H$ NMR spectrum of **8** showed signals at $\delta$ 4.90 and 0.94, whereas that of **9** showed signals at $\delta$ 5.5, 1.7, and 1.6, but not at $\delta$ 2.55.

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