2-nitrobenzyl bromide (**1j**; 432 mg, 2 mmol), **2** (315 mg, 2.4 mmol), and THF (5 mL) was heated at 50 °C for 2 h. Then, HMPA (10 mL) and CsF (1.5 g, 10 mmol) were added and the mixture was stirred for 24 h at room temperature. The reaction mixture was mixed with 2% Na_2CO_3 (200 mL) and extracted with ether (100 mL × 4). The ethereal extract was washed with water (100 mL × 2), dried ($MgSO_4$), and concentrated. Distillation of the residue gave 311 mg (80%) of **8j**. The spectral data are summarized in Table V.

Reaction of (4-Nitrobenzyl)dimethyl[(trimethylsilyl)methyl]ammonium Bromide (3k) with CsF. In a manner similar to that described for **3j**, 4-nitrobenzyl bromide (**1k**; 432 mg, 2 mmol), **2** (315 mg, 2.4 mmol), and CsF (1.5 g, 10 mmol) were allowed to react to give 299 mg (77%) of a mixture of **7k** and **8k**: bp 130 °C (20 mmHg). A part of the mixture (244 mg) was separated on a silica gel column (ether:triethylamine = 20:1) to give **7k** (23 mg) and **8k** (172 mg).

***N,N*-Dimethyl-3-amino-4-methylbenzamide (11).** A mixture of *N,N*-dimethyl-3-nitro-4-methylbenzamide[10] (20.82 g, 0.1 mol) and 5% Pd/C (950 mg) in EtOH (200 mL) was shaken with hydrogen until no more hydrogen was absorbed. The catalyst was filtered off, and the filtrate was concentrated. The residue was taken up in chloroform and 10% HCl. The acidic layer was neutralized with aqueous Na_2CO_3 and extracted with chloroform. The extract was dried over $MgSO_4$ and concentrated, and the residue was recrystallized from hexane to give 15.65 g (88%) of **11**: mp 98–99 °C; ^1H NMR ($CDCl_3$) δ 2.16 (3 H, s, $PhCH_3$), 3.05 (6 H, s, NCH_3), 3.75 (2 H, s, NH), 6.77 (1 H, dd, J = 8 and 2 Hz), 6.82 (1 H, d, J = 2 Hz), 7.11 (1 H, d, J = 8 Hz, aromatic H); IR (Nujol) 3320, 3400 (NH), 1650 (CO) cm^{-1}. Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.39; H, 7.92; N, 15.71.

***N,N*-Dimethyl-3-amino-4-methylbenzylamine (12).** A mixture of **11** (3.57 g, 20 mmol), $LiAlH_4$ (1.14 g, 30 mmol), and THF (60 mL) was stirred for 48 h at room temperature. The mixture was treated with AcOEt (1 mL) and 10% NaOH (4 mL) and then was filtered. The filtrate and washings of the precipitate were dried ($MgSO_4$) and concentrated. The residue was recrystallized from hexane to give 2.38 g (72%) of **12**: mp 73–76 °C; ^1H NMR ($CDCl_3$) δ 2.15 (3 H, s), 2.24 (6 H, s), 3.35 (2 H, s), 3.66 (2 H, br s), 6.72 (1 H, dd, J = 8 and 2 Hz), 6.75 (1 H, d, J = 2 Hz), 7.06 (1 H, d, J = 8). Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.13; H, 9.82; N, 17.06. Found: C, 73.02; H, 9.64; N, 16.92.

***N,N*-Dimethyl-3-cyano-4-methylbenzylamine (9).** To an ice-cooled mixture of **12** (821 mg, 5 mmol), 35% HCl (1.5 mL), and water (5 mL) was added dropwise a solution of $NaNO_2$ (345 mg, 5 mmol) in water (2 mL), and stirring was continued for 2 h. The mixture was neutralized to pH 7 with aqueous Na_2CO_3, and then it was added to an ice-cooled suspension of CuCN (896 mg, 10 mmol) in water (6 mL). After 2 h of stirring, the reaction mixture was made basic with aqueous Na_2CO_3 and extracted with ether. The ether layer was extracted with 10% HCl. The acidic extract was neutralized, and then it was extracted with ether. The ethereal extract was dried ($MgSO_4$) and concentrated. Distillation of the residue gave 261 mg of a colorless oil [bp 135 °C (17 mmHg)], which was chromatographed on a preparative TLC (Merck, Kieselgel 60 F_{254}, AcOEt bubbled with NH_3 gas). A separated oil (61 mg) was distilled to give 39 mg (5%) of **9**, bp 100 °C (17 mmHg) (Kugelrohr). The spectral data showed good agreement with that of the sample isolated from the reaction mixture of **3h** with CsF.

(10) Scherpenzeel, V. *Recl. Trav. Chim. Pays-Bas* **1901**, *20*, 159.

Ring-Opening Rearrangements of Sesquinorbornyl Cations

Paul D. Bartlett,* Michael D. Ravenscroft, and Antonius A. M. Roof

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

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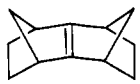
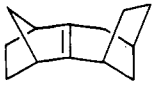
In superacid media, *anti*-sesquinorbornene (**2**) is protonated to yield the directly related carbocation 2^+ at −78 °C. On raising the temperature the cation rearranges irreversibly with ring opening to the 1-(2-norbornyl)-2-cyclopentenyl allylic cation 3^+. This rearrangement does not occur with *syn*-sesquinorbornene, within the temperature range studied, but is observed in the syn isomer **7** whose double bond is not shared between the norbornene ring systems. These observations permit the formulation of a general mechanism for the formation of the allylic cation.

Introduction

Of the five isomeric octahydro-1,4,5,8-dimethanonaphthalenes, the name "sesquinorbornenes" has been applied to those two isomers in which the norbornene units share a common double bond: *syn*- (**1**, SSNB)[1] and *anti*-sesquinorbornene (**2**, ASNB).[2] These two molecules possess some interesting structural and chemical features.[3,4]



SSNB (1)



ASNB (2)

Table I. ^{13}C NMR Chemical Shifts[a] for 2^+ at −75 °C and for the Species 3^+ Obtained at −25 °C

2^+	3^+	2^+	3^+
312.9 (s)	266.8 (s)	44.7 (t)	45.1 (t)
76.0 (d)	219.9 (d)	40.7 (t)	40.8 (t)
69.8 (d)	145.1 (d)	33.8 (d)	37.4 (d)
55.7 (d)	56.5 (d)	27.8 (t)	37.3 (t)
53.6 (d)	47.6 (t)	23.1 (t)	30.4 (t)
48.9 (t)	46.5 (d)	20.8 (t)	27.4 (t)

[a] ppm, CD_2Cl_2 (at 53.1 ppm) as internal standard.

X-ray crystallographic studies on ASNB[7] and on derivatives of SSNB[5a] show a planar double bond for the former

(1) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186, 7218.

(2) Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

(3) (a) Bartlett, P. D.; Roof, A. A. M.; Winter, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6520. (b) Roof, A. A. M.; Winter, W. J.; Bartlett, P. D. *J. Org. Chem.* **1985**, *50*, 4093. (c) Paquette, L. A. In *Stereochemistry and Reactivity of Systems Containing π-electrons*; Watson, W. H., Ed.; Verlag Chemie: Gainesville, FL, 1983; Chapter 2.

(4) (a) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, *23*, 927. (b) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron* **1983**, *39*, 3345. (c) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980. (d) Johnson, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1135. (e) Jørgensen, F. S. *Tetrahedron Lett.* **1983**, *24*, 5289.

(5) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022. (b) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553. (c) Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.* **1983**, *48*, 1250.

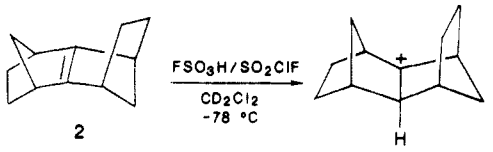
0022-3263/87/1952-1847$01.50/0

and a bent double bond for the latter with a dihedral angle of about 162°. (Thus far, theoretical force field calculations are not able to derive this generalization.[8]) Thermal additions to the double bond of 1 occur exclusively on the unhindered exo face, but photoexcited 1 undergoes endo,endo hydrogenation.[3a] Related to this structural difference, there are some contrasting chemical responses of SSNB and ASNB to various reagents.[3b,9]

We report here on the ^{13}C NMR spectra obtained upon protonation of ASNB and some related compounds. The study shows that there is quite a different picture emerging with ASNB from that with SSNB. Irreversible rearrangements take place with **2** and some isomers, and the structure of the rearranged carbocation has been established.

Results and Discussion

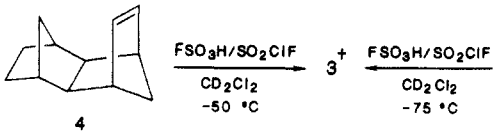
***anti*-Sesquinorbornyl Cation.** Treatment of a CD_2Cl_2 solution of ASNB with FSO_3H in SO_2ClF at −78 °C gave an orange solution. The ^{13}C NMR spectrum at −75 °C displayed 12 lines. Pertinent data have been collected in Table I.



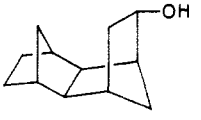
2 2^+

After standing at −78 °C for 2 days, the spectrum of this sample was rerecorded at −75 °C. Signals due to 2^+ were still present, but extra lines had appeared. The ^{13}C NMR spectrum was then recorded sequentially at −65 °C, −50 °C, and −25 °C (allowing time for thermal equilibration before recording the spectra), resulting in the complete disappearance of the signals due to 2^+. The spectrum consisted of 12 major lines. Off-resonance decoupling was carried out; data for the chemical shifts of the new species are shown in Table I.

Carbocations Generated from Related Compounds. When 4[13] was treated under similar conditions as described for **2**, a spectrum identical with that of 3^+ was obtained, even at −75 °C. The spectrum of 3^+ persisted at −30 °C but slowly disappeared at temperatures above 0 °C. No evidence was found for the existence of the cation directly derived from **4** for the temperature range studied. In



4

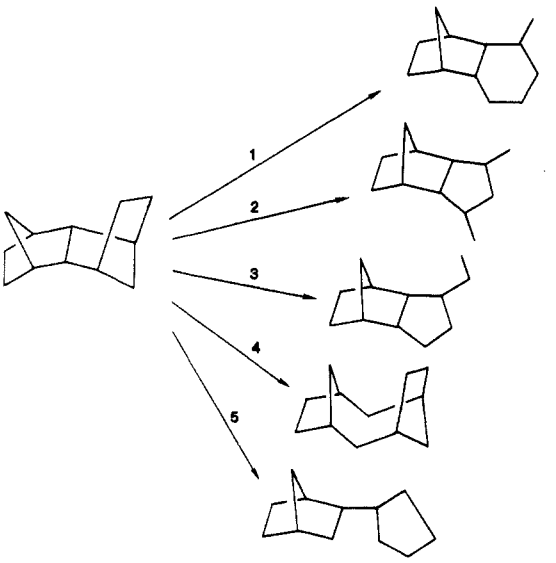


5

addition, some broadening of the signal suggested that some polymerization may have taken place.

On treatment of the alcohol **5** with FSO_3H/SO_2ClF in CD_2Cl_2 at −75 °C, the spectrum of 3^+ was again obtained,

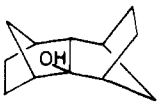
Scheme I. Ring Opening Modes for the *anti*-Sesquinorbornene Structure



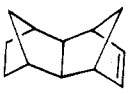
9

but not to the exclusion of minor signals.

Alcohol **6** and olefin **7** also gave the same spectrum as 3^+ upon treatment with FSO_3H/SO_2ClF in CD_2Cl_2. The

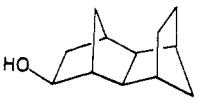


6



7

alcohol **8** at −50 °C gave a spectrum with its lowest field signal at 89.9 ppm (s), but upon warming to −5 °C the spectrum of 3^+ emerged.



8

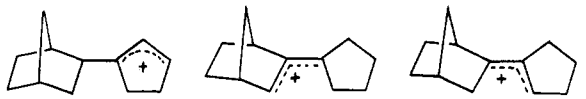
Identity of the Cation 3^+. The common feature of the ^{13}C NMR spectra obtained upon protonation of *anti*-sesquinorbornene (**2**) and related olefins and alcohols is a distinctive set of signals. The three low field absorptions are typically those of an allylic carbocation, a singlet at lowest field (267 ppm) and two doublets at 220 and 145 ppm. This pattern can be found in several studies dealing with allylic carbocations.[11]

In order to form an allylic carbocation from a sesquinorbornyl cation, ring opening must occur. The various possibilities are shown in Scheme I (neglecting for the moment the precise location of the allylic group within these basic structures). Of the five possible modes of ring opening, modes 1, 2, and 3 all result in products with CH_3 groups, shown to be absent by the NMR data. Route 4

(6) Hagenbuch, J. P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1819.
(7) Gajhede, M.; Jørgensen, F. S.; Kopecky, K. R.; Watson, W. H.; Kashyap, R. P. *J. Org.* Chem. **1985**, *50*, 4395.
(8) Ermer, O.; Bödecker, C.-D. *Helv. Chim. Acta* **1983**, *66*, 943.
(9) Bartlett, P. D.; Roof, A. A. M.; Subramanyam, R.; Winter, W. J. *J. Org. Chem.* **1984**, *4*, 1875.
(10) Paquette, L. A.; Ohkata, K.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 3303.
(11) Wu, C.; Bartlett, P. D. *J. Org. Chem.* **1985**, *50*, 733 and references cited therein.
(12) Deno, N. C.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 1744.
(13) Soloway, S. B. *J. Am. Chem. Soc.* **1952**, *74*, 1027.
(14) Stille, J. K.; Witherell, D. R. *J. Am. Chem. Soc.* **1964**, *86*, 2188.
(15) Cau, D. D.; Paddon-Row, M. N.; Patney, H. K. *Aust. J. Chem.* **1983**, *36*, 2423.
(16) Winstein, S.; Carter, P.; Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1965**, *87*, 5247.

is interesting, but the product has to accommodate either the charge or the double bond at a bridgehead, which is not likely to happen. Route 5 is the most promising to accommodate an allylic group.

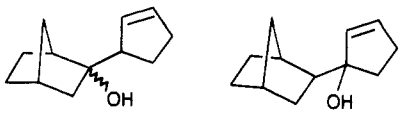
The NMR data suggest that one terminal carbon atom of the allylic fragment is tertiary (which might have been predicted, on the basis of the known 3° > 2° > 1° order of carbocation stability) with the other two carbon atoms being secondary. Structure **9** contains four tertiary carbon atoms, of which only two (C-2, C-1′) can bear the charge, since the other two (C-1, C-4) are bridgeheads. Placing the double bond in conjugation with the charge center leads to allylic structures **10a–c**, of which structures **10b**



10a **10b** **10c**

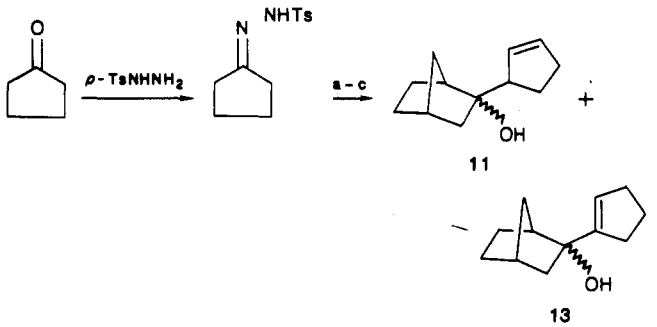
and **10c** can be ruled out by the observed off-resonance multiplicities of the allylic carbon atoms (**10b** and **10c** would give two singlets and a doublet, whereas the observed spectrum displays one singlet and two doublets). The structure **10a** is compatible with the observed spectrum.

To substantiate the evidence in favor of structure **10a**, it was desired to generate the spectrum independently from a precursor that would have a closer structural similarity to **10a**. Compound **11** was chosen for this purpose,



11 **12**

since the synthetic scheme to get to the isomer **12**, the most obvious choice, failed. **11** was prepared according to the following scheme:[17a]



(a) 2BuLi; -78 °C; (b) norcamphor, -78 °C; (c) 2MeLi, room temperature.

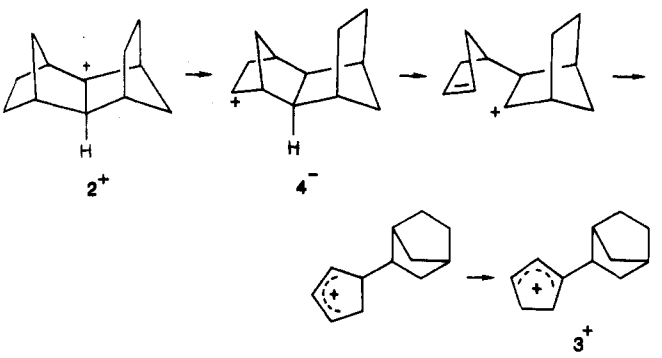
A mixture of **11** and **13** was formed, from which pure **11** could be obtained by repeated column chromatography. ^{13}C NMR showed this to be a mixture of stereoisomers.

A preparation employing lithium diisopropylamide as a sterically hindered, nonnucleophilic base gave mainly **11**.

A ^{13}C NMR spectrum obtained from a sample containing 98% of **11** (FSO_3H, SO_2ClF, CD_2Cl_2, -75 °C) gave 12 peaks that were identical with those of 3^+. In addition, a set of minor peaks was present, indicating the presence of another carbocation.

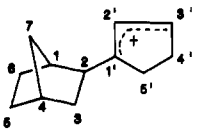
(17) (a) Lipton, M. F.; Shapiro, R. H. *J. Org. Chem.* **1978**, *43*, 1409. (b) Shapiro, R. H. *Org. React. (N.Y.)* **1975**, *23*, 405.

Scheme II



2^+ 4^- 3^+

The following assignment seems reasonable for the chemical shifts observed with 3^+:



assignments

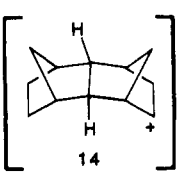
1	46.5	1′	266.8
2	56.5	2′	145.1
3	40.8	3′	219.9
4	37.4	4′	45.1
5	27.4	5′	47.6
6	30.4		
7	37.3		

Although no direct formation of 3^+ from **11** can occur, an exothermic 1,3-hydride shift can convert the cation of **11** into 3^+.

3^+

In all cases the ready protonation of the sesquinorbornenes, while associated with easy access to the double bond, is not due to any special stabilization of the initially formed carbocation. The ease of rearrangement—an overall exothermic process in all cases—is a matter of overcoming the obstacles to the conversion of one cation to the next.

SSNB does not readily undergo the ring opening leading to an allylic cation. Of the cases studied here, the only syn structure showing the reaction is the olefin **7**, whose related norbornyl-type cation would be secondary rather than tertiary. It appears that the ring opening of a sesquinorbornene to the allylic structure 3^+ proceeds well only after a transannular hydride shift has moved the charge in $SSNB^+$ or $ASNB^+$ to one of the outer ethylene bridges. The required hydride shift occurs more easily in $ASNB^+$ than in $SSNB^+$; in the latter case, the initial configurations being what they are, a hydride shift from C-2 to C-8a or from C-3 to C-4a could lead only to the prohibitively strained cation **14**, with hydrogens trans to each other at the critical central bond. This explains why the only *syn*-dimethanooctahydronaphthalene undergoing the allylic ring opening is the isomer **7** with the unshared double bond.



14

Scheme II depicts the necessary steps to arrive at 3^+, of which the final hydride shift is an energetically favorable step that has precedents in the literature.[12] The moving of the charge from the norbornyl ring to the cyclopentenyl ring could occur by successive 1,2-hydride shifts; it is also a type of reaction that could occur between a norbornyl cation and a cyclopentene molecule in a solvent cage, a state approximated by the bonding between these two units.

Experimental Section

General. Melting and boiling points are uncorrected. NMR spectra (^1H and ^{13}C) were recorded on a Varian Associates XL-300 spectrometer operating at 300 MHz (^1H) and 75.4 MHz (^{13}C). The solvent was $CDCl_3$ unless stated otherwise. IR spectra were obtained on a Perkin-Elmer 197 instrument, using thin films (liquids) or KBr disks (solids). Spectra were calibrated with polystyrene film. GC analyses were carried out on a Perkin-Elmer 2000 gas chromatograph coupled with a Hewlett-Packard 3370A integrator. A 25-m Carbowax 20M capillary column was installed. GC/MS analyses were conducted on a Finnigan OWA 1020 GC-MS-DS instrument equipped with an SE 30 capillary column and employing EI (70 eV).

High resolution MS analyses were carried out at the Midwest Center for Mass Spectrometry at the University of Nebraska at Lincoln, to whom we are grateful.

Solvents and Reagents. THF was distilled from sodium/benzophenone. CH_2Cl_2 was distilled from CaH_2. CD_2Cl_2 was 99.8 atom % D (MSD. Isotopes). FSO_3H (Aldrich) was distilled under argon and had bp 162–164 °C. SO_2ClF was spectroscopic grade from Cationics (via Aldrich).

Syntheses. The compounds **2**,[2] **4**,[13] **5**,[14] **6**,[9] **7**,[15] and **8**[16] were prepared according to literature procedures.

Cyclopentanone tosylhydrazone was prepared in a 92% yield by treating (*p*-toluenesulfonyl)hydrazide with cyclopentanone in ethanol containing a trace of concentrated HCl, mp 179–182 °C dec (lit.[17] mp 180–184 °C dec).

2-(2-Cyclopentenyl)bicyclo[2.2.1]heptan-2-ol (11). The procedure described by Shapiro[17] was used on a 12-mmol scale. To a suspension of cyclopentanone tosylhydrazone in THF at −78 °C was added *n*-BuLi. After 30 min at this temperature the deep red solution was quenched by the addition of norcamphor in THF during ca. 5 min. After warming to room temperature, the suspension was treated dropwise with MeLi and the resulting solution was stirred overnight at room temperature. Workup was by aqueous NH_4Cl decomposition and extraction with THF. The crude product was chromatographed on silica gel (50 g), eluting with petroleum ether/methylene chloride (2:1, v/v, 100 mL; 1:1, 100 mL; 1:2, 100 mL) and methylene chloride. One fraction consisted of three components, and further treatment of this fraction on silica gel with CH_2Cl_2 gave pure homoallylic alcohol **11**: ^1H NMR δ 5.65 (m, 1 H), 5.59 (m, 1 H) 2.90 (br d, partially resolved m, 1 H), 2.50–1.00 (series of m, 15 H); ^{13}C NMR δ 135.5 (d), 134.7 (d), 130.3 (d), 129.5 (d), 80.9 (s), 80.4 (s), 56.0 (d), 55.2 (d), 45.9 (t), 45.8 (t), 45.1 (d), 44.4 (d), 38.8 (t), 38.0 (d), 37.4 (t), 37.1 (t), 32.7 (t), 32.1 (t), 28.4 (t, 2C), 24.4 (t), 23.4 (t), 22.4 (t), 22.3 (t); IR 3540 (m), 3450 (m), 3030 (m), 2940 (s), 2850 (s), 1605 (w), 1480 (m), 1450 (s), 1360 (m), 1350 (s), 1305 (s), 1280 (s), 1260 (m), 1235 (m), 1180 (w), 1170 (m), 1160 (w), 1140 (w), 1120 (w), 1100 (w), 1050 (m), 1035 (s), 995 (s), 940 (m), 910 (m), 810 (m), 755 (s), 715 (m); GC/MS, *m/e* (relative intensity) 111 (100), 93 (35), 91 (18), 83 (15), 77 (13), 67 (96), 66 (18), 65 (18), 55 (40), 53 (13), 43 (14), 41 (81), 39 (71).

A later fraction from the chromatographic treatment consisted mainly of the allylic alcohol **13**, **2-(1-cyclopentenyl)bicyclo-[2.2.1]heptan-2-ol (ca. 60%)** and **2-*n*-butylbicyclo[2.2.1]heptan-2-ol (ca. 22%).**

13: ^{13}C NMR δ 150.1 (s), 123.9 (d), 78.8 (s), 45.8 (d), 44.5 (d), 38.7 (t), 37.0 (d), 32.4 (t), 31.3 (t), 29.0 (t), 23.7 (t), 21.9 (t); ^1H NMR δ 5.50 (m, 1 H), 2.50–0.85 (series of m, 18 H); MS, *m/e* (relative intensity) 178 (M^+, 6), 160 (18), 132 (37), 131 (47), 117 (36), 115 (17), 111 (13), 110 (16), 104 (13), 95 (54), 93 (11), 91 (58), 79 (23), 77 (27), 68 (10), 67 (75), 66 (29), 65 (31), 55 (21), 53 (20), 51 (14), 43 (13), 41 (88), 39 (100); high resolution MS, calcd for $C_{12}H_{18}O$ 178.1361, found 178.1364.

Low-Temperature NMR Spectroscopy. All NMR spectra were recorded on a Varian Associates XL-300 instrument, operating in the FT mode at 300 MHz (^1H) and 75.4 MHz (^{13}C). The probe was cooled to the desired temperature by circulating cold N_2 and calibrated before use by using the temperature-dependence of the methyl and hydroxyl chemical shift difference of methanol.[20] The thus-measured temperature was in all cases exactly that displayed digitally on the front panel of the instrument.

For carbon, the samples were not spun, line-broadening being unimportant. The sweep width employed was 26 000 Hz with a transmitter offset of 5000 Hz, corresponding to a spectral width of ca. −6 to +344 ppm. Chemical shifts are referenced to CD_2Cl_2 (53.1 ppm).[21] No pulse delays were employed. Good quality spectra were usually obtained after 250–600 transients. Line-broadening of 3–5 Hz was occasionally applied during processing to improve S/N ratios (particularly for off-resonance decoupled spectra). Fully decoupled spectra were obtained on a Waltz-16 and off-resonance decoupling employed a decoupler frequency offset of −2500 Hz.

General Procedure for Carbocation Generation. FSO_3H (typically 200–360 mg, 2.0 to 3.6 mmol) was placed in a dry, argon-flushed 5-mm NMR tube, previously tared. The tube was capped and placed in an acetone–dry ice bath. After allowing the tube and contents to cool, ca. 300–400 μL of SO_2ClF was condensed into the NMR tube via a double-ended needle (24 in., 18 gauge) and with standard inert atmosphere transfer techniques.[22] A solution of precursor (typically 60–95 mg, ca. 5×10^{-4} mol) in CD_2Cl_2 (ca. 180 μL) was carefully added by syringe as an upper layer to the contents of the NMR tube. Some color often developed at the interface. After allowing time for the solutions to cool again to −78 °C (frequently resulting in precipitation of the precursor from solution), the contents of the tube were mechanically mixed by gentle agitation using a Pasteur pipette that had been drawn out in a Bunsen flame for this purpose. The NMR tube was maintained in the cold bath during this operation, which usually required ca. 15–25 s. After mixing, the solutions were homogeneous and red-orange, the exact color and the intensity varying from sample to sample. The tube was then sealed in an oxygen flame and stored at −78 °C until use. The probe of the instrument was always pre-cooled to the desired temperature before insertion of samples. This method was found to give good results for alcohols, alkenes, and unsaturated alcohols.

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Registry No. **2**, 73679-39-7; 2^+, 107171-80-2; 3^+, 107037-78-5; **4**, 15914-93-9; **5**, 107133-43-7; **6**, 89824-46-4; **7**, 1076-12-6; **8**, 107133-44-8; **11**, 107081-99-2; **12**, 107082-00-8; **13**, 107082-01-9; 2-*n*-butylbicyclo[2.2.1]heptan-2-ol, 37710-44-4; cyclopentanone tosylhydrazone, 17529-98-5; norcamphor, 497-38-1; *exo*-2-bromonorbornane, 2534-77-2.

Supplementary Material Available: ^{13}C NMR spectra of 2^+ at −75 °C, 3^+ at −25 °C, and 2^+ undergoing conversion to 3^+; off-resonance and fully decoupled spectra (5 pages). Ordering information is given on any current masthead page.

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