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High-Field ^{1}H and ^{13}C NMR Spectroscopic Study of the 2-Norbornyl Cation[1a]

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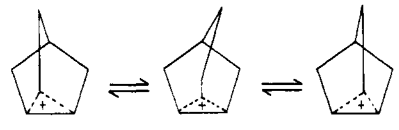
Abstract: The high-field (395-MHz ^{1}H and 50-MHz ^{13}C) NMR spectroscopic study of the 2-norbornyl cation (**1**) between −80 and −160 °C is reported. The completely resolved ^{1}H and ^{13}C spectra are discussed with regard to chemical shifts and coupling constants. Besides these data the lack of observation of any significant line broadening in the ^{1}H NMR spectrum at −158 °C at 395 MHz, compared to that at 100 MHz, indicates that ion **1** at this temperature has a symmetrically bridged structure. Alternatively, if the cation still would undergo undetectable rapid Wagner–Meerwein-like shifts, these must be between unsymmetrically bridged (nonclassical) ions with a very low energy barrier ($\leq$3 kcal/mol). The single energy minumum vs. double minima problem thus is of little consequence concerning the bridged nature of the ion **1**.

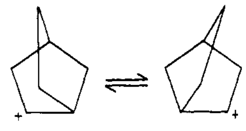
The structural elucidation of the 2-norbornyl cation **1** has aroused much interest in the last two decades.[2] The structure of the 2-norbornyl cation**1** has also been the focal point of the so-called nonclassical ion controversy.[2c] The structure of the 2-norbornyl cation **1** under long-lived stable ion conditions was studied by a variety of spectroscopic techniques[3,4] such as ^{1}H and ^{13}C NMR, Raman, and X-ray photoelectron[7] spectroscopy. Recently Saunders and co-workers[8] have applied their isotopic perturbation of resonance technique[5] to the 2-norbornyl cation.[6] Yannoni and Myhre have studied the ion by solid-state ^{13}C NMR spectroscopy using cross polarization magic angle spinning techniques at very low temperatures.[7] The rapid advances made in NMR spectroscopic techniques, particularly the availability of high-field superconducting magnet spectrometers led us to restudy the low-temperature ^{1}H and ^{13}C NMR spectra of the 2-norbornyl cation **1** at high fields.

Results and Discussion

From ^{1}H NMR investigations at 60 and 100 MHz at various temperatures (room temperature to −154 °C), Olah and coworkers in the early 1970s determined the barriers for the 2,3 hydrogen shift as well as the 6,1,2 hydrogen shift by line-shape analysis and found to be 10.8 ± 0.6 and 5.9 ± 0.2 kcal/mol, respectively.[3] However, the ^{1}H NMR spectrum of the 2-norbornyl cation obtained in the $SbF_5/SO_2ClF/SO_2F_2$ solvent system at −154 °C (at 100 MHz) still showed unresolved peaks at the upfield methylene proton region.

The ^{1}H NMR spectrum of the 2-norbornyl cation at room temperature shows a single peak at δ^1H 3.10 for all the protons indicating fast 2,3 hydrogen, 6,1,2 hydrogen, and Wagner–Meerwein shifts.[8] Cooling a solution of the 2-norbornyl cation in the $SbF_5/SO_2ClF/SO_2F_2$ solvent system down to −100 °C at 395 MHz (Figure 1) results in three peaks at δ^1H 4.92 (4 protons), 2.82 (1 proton), and 1.93 (6 protons), indicating that the 2,3 hydrogen shift is fully frozen, whereas the 6,1,2 hydrogen and Wagner–Meerwein shifts are still fast on the NMR time scale. Cooling the solution down further to −158 °C results in significant changes in the spectrum. The peak at δ^1H 4.92 decoalesces into two peaks at δ^1H 6.75 and 3.17 with a ratio of 2:2. The high-field peak broadens and splits into two peaks at δ^1H 2.13 and 1.37 in the ratio 4:2. The peak at δ^1H 2.82 remains unchanged. The assignments and the comparison of chemical shifts at −100 and −158 °C are shown in Table I. The chemical shifts compare remarkably well within the experimental error. The line width ($\approx$60 Hz) observed at 395 mHz is rather small as compared to the one obtained at 100 MHz[3]($\approx$30 Hz). This has important implications. If there was any slow exchange process occurring at this temperature, the line should have broadened 15.6 times at 395 MHz over the one observed at 100 MHz. The observation of comparably narrow line widths at 395 MHz indicates that either the 6,1,2 hydrogen shift and the Wagner–Meerwein shift (σ-bond shift) are completely frozen and the 2-norbornyl cation has a symmetrically bridged structure **1a** or the 6,1,2 hydrogen shift is frozen and the so-called Wagner–Meerwein shift is still fast on the NMR time scale with a very shallow activation energy barrier (barrier less than 3 kcal/mol). The second possibility raises the question as to the nature of the ion undergoing equilibration through an extremely low activation energy barrier. If such a process occurs, it must be exclusively between unsymmetrically σ-bridged ions **1b** equilibrating through the intermediacy of the symmetrically bridged species **1a**. For all practical purposes the unsymmetrically bridged ions **1b** would be indistinguishable from the symmetrically bridged system **1a**. It is important to recognize that the open classical norbornyl cations **2** cannot be involved as populated species.


1b 1a 1b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We also have obtained the 50-MHz ^{13}C NMR spectrum of the 2-norbornyl cation **1** in mixed $SbF_5/SO_2ClF/SO_2F_2$ solvent system

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[1] (a) Stable Carbocations. 241. For part 240, see: Goldstein, M. J.; Dinnocenzo, J. P.; Ahlberg, P.; Engdahl, C.; Paquette, L. A.; Olah, G. A. *J. Org. Chem.* **1981**, *46*, 3751. (b) University of Southern California. (c) University of California.

[2] (a) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41–52 and references cited therein. (b) Brown, H. C. *Tetrahedron* **1976**, *32*, 179–204. (c) Brown, H. C. (with Comments by P. v. R. Schleyer) "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

[3] Olah, G. A.; White, A. M.; DeMember, J. R.; Commeyras, A.; Lui, C. Y. *J. Am. Chem. Soc.* **1970**, *92*, 4627–4640.

[4] Olah, G. A.; Liang, G.; Mateescu, G. D.; Riemenschneider, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8698–8702.

[5] Saunders, M.; Jaffe, M. H; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558–2561.

[6] Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 6867–6868.

[7] Myhre, P. C.; Yannoni, C. S., presented at IUPAC meeting on Physical Organic Chemistry at Santa Cruz, CA, August 1981. Also see: Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 907–909. Myhre, P. C., private communication.

[8] Saunders, M.; Schleyer, P. v. R.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 5679–5680.

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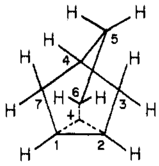
Table I. ^{1}H NMR Data[a] of 2-Norbornyl Cation



temp, °C	tot av	H_1	H_2	H_3	H_4	H_5	H_6	H_7
room temp, (60 MHz)	3.10				3.10 (br)			
−100 (395 MHz)	3.10	4.92	4.92	1.93	2.82	1.93	4.92	1.93
−158 (395 MHz)	3.08	6.75	6.75	2.13	2.82	1.37	3.17	2.13

Comparison of ^{1}H NMR Chemical Shifts at −100 and −158 °C

	calcd obsd dev
$\frac{H_1 + H_2 + 2H_6}{4} = \frac{6.75 + 6.75 + 2(3.17)}{4} =$	$4.96 - 4.92 = +0.04$
$\frac{2H_3 + 2H_5 + 2H_7}{6} = \frac{2(2.13) + 2(1.37) + 2(2.13)}{6}$	$= 1.88 - 1.93 = -0.05$

[a] Chemical shifts are in ppm from external Me_4Si.

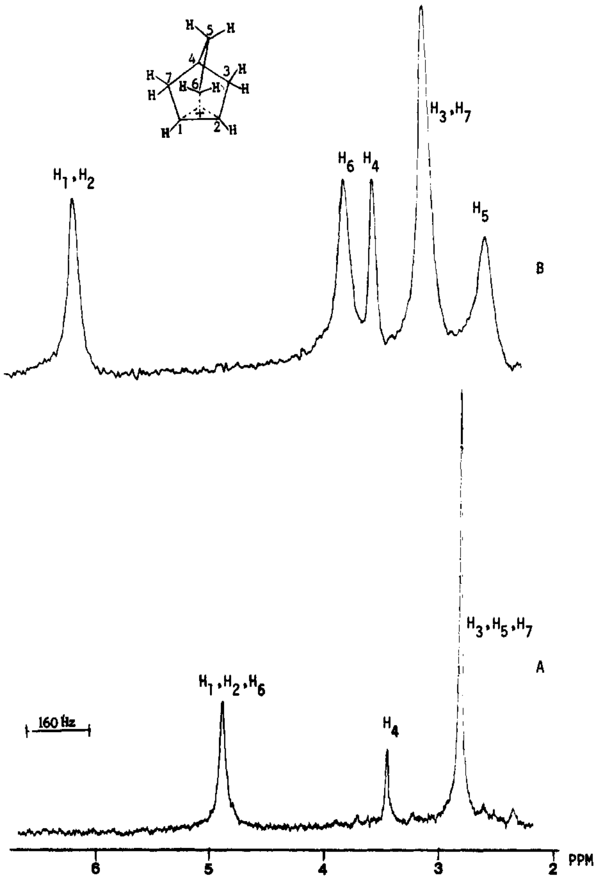


Figure 1. 395-MHz ^{1}H NMR spectra of the 2-norbornyl cation in $SbF_5/SO_2ClF/SO_2F_2$ solution: (A) at −100 °C, (B) at −158 °C.

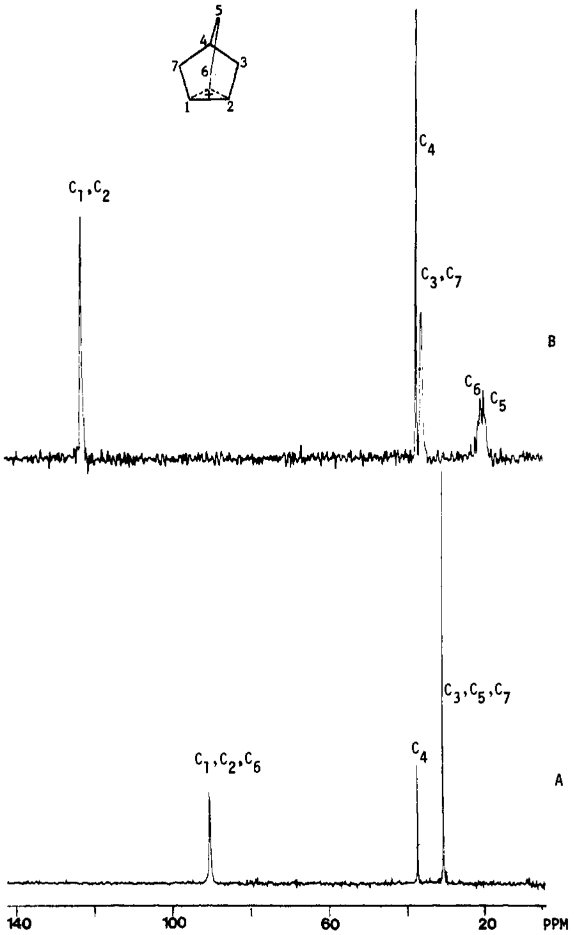
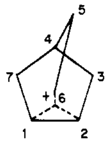


Figure 2. 50-MHz Proton-decoupled ^{13}C NMR spectra of the ^{13}C-enriched 2-norbornyl cation in $SbF_5/SO_2ClF/SO_2F_2$ solution: (A) at −80 °C, (B) at −159 °C.

at −159 °C. For a well-resolved ^{13}C NMR spectrum, the cation **1** was generated from 95% ^{13}C-enriched *exo*-2-chloronorbornane (the label present corresponds to one carbon per molecule randomly distributed over the C_1, C_2, and C_6 centers). The ionization of the ^{13}C-enriched *exo*-2-chloronorbornane in $SbF_5/SO_2ClF/SO_2F_2$ solution at −78 °C results in the 2-norbornyl cation wherein the ^{13}C label is distributed evenly over all the seven carbons as a result of slow 2,3 hydrogen and fast 6,1,2 hydrogen and Wagner–Meerwein shifts.

At −80 °C, the 50-MHz ^{13}C NMR spectrum of the cation **1** (Figure 2) shows three absorptions at δ^{13}C 91.7 (q, J_{C-H} = 55.1 Hz), 37.7 (d, J_{C-H} = 153.1 Hz), and 30.8 (t, J_{C-H} = 139.1 Hz), indicating that the 2,3 hydrogen shift is frozen, but the 6,1,2 hydrogen and the Wagner-Meerwein shift is still fast on the NMR time scale. Cooling the solution down results in broadening and slow merger into the base line of the peaks at δ^{13}C 91.7 and 30.8, but the peak at δ^{13}C 37.7 remains relatively sharp. At −159 °C, the peaks at δ^{13}C 91.7 and 30.8 decoalesce into two sets of two peaks at δ^{13}C 124.5 (d, J_{C-H} = 187.7 Hz), 21.2 (t, J_{C-H} = 147.1 Hz), and δ^{13}C 36.3 (t, J_{C-H} = 131.2 Hz), 20.4 (t, J_{C-H} = 153.2 Hz), respectively. The peak assignments as well as detailed chemical shift and coupling constant correlations are shown in Table II.[9] The observed chemical shifts and coupling constants

Table II. ^{13}C NMR Data[a] of the 2-Norbornyl Cation at 50 MHz



temp, °C	tot av	C_1	C_2	C_3	C_4	C_5	C_6	C_7
room temp	59.8				59.8 (s, br)			
−80	57.8	91.7 (q, 55.1 Hz)	91.7	30.8 (t, 139.1 Hz)	37.7 (d, 153.1 Hz)	30.8	91.7	30.8
−159	57.3	124.5 (d, 187.7 Hz)	124.5	36.3 (t, 131.2 Hz)	37.7 (d, 150.9 Hz)	20.4[b] (t, 153.2 Hz)	21.2[b] (t, 147.1 Hz)	36.3

Comparison of ^{13}C NMR Chemical Shifts at −80 and −159 °C

				calcd		obsd		dev
$\frac{C_1 + C_2 + C_6}{3}$	=	$\frac{124.5 + 124.5 + 21.2}{3}$	=	90.06	−	91.7	=	−1.64
$\frac{C_3 + C_5 + C_7}{3}$	=	$\frac{36.3 + 20.4 + 36.3}{3}$	=	31.0	−	30.8	=	+0.2

Comparison of Coupling Constants

				calcd		obsd		dev
$\frac{C_1 + C_2 + C_3}{12}$	=	$\frac{187.7 + 187.7 + 2 \times 147.1}{12}$	=	55.8	−	55.1	=	+0.7
$\frac{C_3 + C_5 + C_7}{3}$	=	$\frac{131.2 + 153.2 + 131.2}{3}$	=	137.8	−	139.1	=	−1.9

[a] Chemical shifts are in ppm from external Me_4Si. [b] There is uncertainty in the coupling constant measurement by at least ±5 Hz; s = singlet, q = quintet, d = doublet, t = triplet, br = broad.

at −159 °C match very well with the average data obtained at −80 °C. Going from room temperature to −159 °C (in Table II), the total average chemical shifts of all the seven carbons of the 2-norbornyl skeleton is gradually shielded by (+2.5 ppm) indicating some contribution of the more localized structures to the NMR parameters at higher temperature. The observed ^{13}C NMR spectral data at −159 °C complements well with the 395 MHz ^{1}H NMR data at −158 °C. The observation of the C_1 and C_2 carbons at δ^{13}C 124.5 and the C_6 carbon at δ^{13}C 21.2 clearly supports the bridged structure for the ion. Five-(or higher) coordinate carbons generally show shielded (upfield) ^{13}C NMR shifts. In fact, the higher coordinate carbons in the 7-norbornenyl,[10] tris(homocyclopropenyl),[11] and 9-pentacyclononyl[12] (Coates system) cations are observed at δ^{13}C 34.0, 4.9, and 29.6, respectively. Applying the additivity of the chemical shift analysis[13] to the 2-norbornyl cation **1** also supports the bridged nature of the ion. A chemical shift difference of 168.0 ppm is observed between the ion **1** and its parent hydrocarbon, i.e., norbornane, whereas ordinary trivalent carbocations such as the cyclopentyl cation reveal a chemical shift difference of ≈360 ppm.[13]

As mentioned earlier Yannoni and Myhre[7a] have obtained magic angle cross polarization ^{13}C NMR spectra of the ^{13}C-enriched 2-norbornyl cation **1** in SbF_5 solid matrix down to −190 °C. Their solid-state chemical shifts correlate well with our solution data except for their lack of resolution in the upfield methylene region. Furthermore, they observed no change in the spectrum from −150 to −190 °C, indicating that the barrier for a rapid Wagner–Meerwein-like shift, if it still exists, must be less than 2 kcal/mol. In a more recent study the same authors[7b] have obtained solid-state ^{13}C NMR spectrum at −269 °C with no change in the relative peak positions, indicating the barrier to be less than 0.2 kcal/mol. In fact a recent calculation by Scheafer and co-workers[14a] at 4.21G/4.21G level puts the energy difference between the unsymmetrically delocalized structure **1b** and the symmetrically delocalized structure **1a** to be 0.2 kcal/mol. The classical cation **2**, however, is estimated[14b] to be less stable by as much as 20 kcal/mol compared to the bridged structures.

Conclusions

The present high-field 395-MHz ^{1}H and 50-MHz ^{13}C NMR spectroscopic study of the 2-norbornyl cation provides further conclusive evidence for its σ-bridged nature under long-lived stable ion conditions. The data are consistent with the previous lower field NMR studies.[3,4,9]

Experimental Section

The 95% ^{13}C-enriched *exo*-2-chloronorbornane (label present on one carbon per molecule randomly distributed over C_1, C_2, and C_6 centers) was prepared from *exo*-2-norborneol (one 95% ^{13}C label present randomly distributed over C_1, C_2, and C_6 carbons) by use of $SOCl_2$. The 95% ^{13}C-enriched *exo*-2-norborneol was prepared from 95% ^{13}C-enriched β-3-cyclopenteneethanol (95% ^{13}C enrichment at the hydroxymethylene group) following the procedure of Bartlett and co-workers.[15] The 95% ^{13}C-enriched β-3-cyclopenteneethanol was prepared in five steps starting from 3-cyclopentenecarboxylic acid.[16]

3-Cyclopentenemethanol. 3-Cyclopentenecarboxylic acid[15] (20.2 g, 0.179 mol) in 60 mL of ether was slowly added to 7.6 g of lithium aluminum hydride dispersed in 250 mL of diethyl ether so as to maintain a gentle reflux. After the addition was complete, the mixture was refluxed for an additional 6 h under a nitrogen atmosphere. After the reaction was complete the mixture was allowed to cool down and was carefully quenched with 5 mL of water followed by 20 mL of 40% sodium hydroxide solution. The precipitated hydroxides were filtered. The clear ether layer was dried over anhydrous $MgSO_4$ and evaporated to provide pure 3-cyclopentenemethanol: 17 g (97% yield); bp 71 °C (21 mm); ^{13}C

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(9) The currently reported data closely resemble the data obtained at 25 MHz[4] in the low-field region. However, there were some ambiguities in the previously reported spectrum[4] in the upfield methylene region.

(10) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 6803–6806.

(11) (a) Masamune, S.; Sakai, M.; Jones, A. V. K.; Nakashima, T. *Can. J. Chem.* **1974**, *52*, 855–857. (b) Masamune, S.; Sakai, M.; Jones, A. V. K. *Ibid.* **1974**, *52*, 858–860. (c) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N.; Whittaker, D.; Rees, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3935–3939.

(12) Coates, R. M.; Fretz, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 2538–2540.

(13) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683–691.

(14) (a) Goddard, G. J.; Osamura, W.; Schaefer, H. F. *J. Am. Chem. Soc.* **1982**, *104*, 3258–3262. (b) Schaefer, H. F., private communication.

(15) (a) Bartlett, P. D.; Bank, S. *J. Am. Chem. Soc.* **1961**, *83*, 2591–2592. (b) Bartlett, P. D.; Bank, S.; Crawford, R. J.; Schmid, G. H. *Ibid.* **1965**, *87*, 1288–1297.

(16) Murdock K. C.; Angier, R. *J. Org. Chem.* **1962**, *27*, 2395–2398.

NMR ($CDCl_3$) $\delta^{13}C$ 132.1 (d), 68.8 (t), 41.9 (d), and 38.3 (t).

3-Cyclopentenemethyl Tosylate. To 14.6 g of 3-cyclopentenemethanol (0.149 mol) dissolved in 40 mL of dry pyridine at 0 °C was added dry *p*-toluenesulfonyl chloride (28.69 g, 0.15 mol) in several portions. After the addition was complete the mixture was stirred for 10 h at 0 °C. Then the reaction mixture was poured into 100 mL of ice water, and the product tosylate was extracted in chloroform (3 × 150 mL). The chloroform extract was washed several times with cold water to get rid of any trace of pyridine. The washed chloroform layer was dried over anhydrous $MgSO_4$ and evaporated to give almost pure 3-cyclopentenemethyl tosylate. Attempted distillation of the tosylate, however, resulted in substantial decomposition. The crude tosylate was used for the next reaction without any further purification; ^{13}C NMR ($CDCl_3$), $\delta^{13}C$ 147.7 (s), 136.1 (s), 132.8 (t), 132.0 (d), 130.6 (d), 76.7 (t), 38.9 (d), 38.1 (t), and 24.0 (q).

3-Cyclopentenemethyl Iodide. To the crude 3-cyclopentenemethyl tosylate (34 g, 0.135 mol) dissolved in 300 mL of acetone was added 39.6 g (0.136 mol) of dry sodium iodide with stirring. The whole mixture was refluxed for 36 h under a nitrogen atmosphere. After the reaction was complete, the precipitated sodium tosylate was filtered, the pale yellow acetone layer was evaporated, and the crude residue was distilled to obtain 24.7 g of pure 3-cyclopentenemethyl iodide (88% yield): bp 54 °C (1.2 mm); ^{13}C NMR ($CDCl_3$) $\delta^{13}C$ 128.2 (d), 39.3 (d), 39.0 (t), and 13.9 (t).

3-Cyclopenteneacetic Acid (95% ^{13}C Enriched at the Carboxylic Carbon). About 4.4 g of 95% ^{13}C-enriched carbon dioxide generated form 20 g of 95% ^{13}C-enriched barium carbonate and 30 mL of 30% sulfuric acid was condensed into a cooled solution of 3-cyclopentenemethylmagnesium iodide in 200 mL of dry ether (prepared from 24.7 g of 3-cyclopentenemethyl iodide and 3.6 g of magnesium turnings) under argon at −120 °C (with liquid nitrogen/ethanol slush). The reaction mixture was slowly warmed to room temperature followed by gentle reflux for 4 h. The reaction mixture was quenched with 100 mL of ice-cold 10% ammonium chloride solution. The ether layer was evaporated and the crude 95% ^{13}C-enriched 3-cyclopenteneacetic acid was further purified by base extraction: 7 g (50% yield based on CO_2); ^{13}C NMR ($CDCl_3$) $\delta^{13}C$ 178.4 (s), 128.9 (d), 39.9 (t of d, $J_{^{13}C-^{13}C} = 54.9$ Hz), 38.1 (t), and 32.9 (d).

β-3-Cyclopenteneethanol (95% ^{13}C Enriched at the Hydroxymethylene Position). A total of 6.10 g of 95% ^{13}C-enriched β-3-cyclopenteneacetic acid (0.044 mol) dissolved in 50 mL of ether was slowly added to a slurry of 3.7 g of lithium aluminum hydride in 150 mL of ether dropwise so as to maintain a gentle reflux. After the addition was complete the mixture was refluxed for 5 h under a nitrogen atmosphere. After the reflux the mixture was allowed to cool down and was carefully quenched with 3 mL of water followed by 10 mL of 40% sodium hydroxide solution. The precipitated hydroxides were filtered, and the clear ether layer was dried over anhydrous magnesium sulfate. The ether layer on evaporation gave pure 95% ^{13}C-enriched β-3-cyclopenteneethanol: 5.3 g (97% yield); bp 92 °C (20 mm) [lit. bp[15] 90–95 °C (20 mm)]; ^{13}C NMR ($CDCl_3$) δ ^{13}C 129.4 (d), 60.6 (t), 38.8 (t), 37.8 (d), 35.2 (t of d, $J_{^{13}C-^{13}C} = 50.2$ Hz).

Preparation of the Carbocation. The 2-norbornyl cation was prepared by addition of the precursor *exo*-2-chloronorbornane in SO_2ClF solution to excess $SbF_5/SO_2ClF/SO_2F_2$ solution at −78 °C so as to obtain roughly 5% of the ion in solution. These solutions were then transferred into precooled NMR tubes for the spectroscopic studies.

^1H NMR spectra were obtained on a 395-MHz superconducting NMR spectrometer equipped with a low-temperature probe (built at UCLA).

^{13}C NMR spectra (50 MHz) were obtained on a Varian Associates Model XL-200 NMR spectrometer equipped with a broad-band variable-temperature probe. The chemical shifts are referenced from external capillary tetramethylsilane. Both ^1H and ^{13}C NMR spectra were taken in the Fourier transform mode without any field lock. The ^1H NMR spectra depicted in Figure 1 were obtained with a line broadening function of 8 Hz. The ^{13}C NMR spectrum recorded at −159 °C was resolution enhanced by the convolution difference method with a convolution difference (CD) of 0.7 and constant of convolution difference (CCD) of 0.99.

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Registry No. 1, 24321-81-1; 3-cyclopentenecarboxylic acid, 7686-77-3; 3-cyclopentenemethyl tosylate, 25125-22-8; 3-cyclopentenemethanol, 25125-21-7; 3-cyclopentenemethyl iodide, 83528-59-0; 3-cyclopentene-acetic-*1*-^{13}C acid, 83528-60-3; β-3-cyclopenteneethanol-α-^{13}C, 83528-61-4; *exo*-2-chloronorbornane-^{13}C, 83572-19-4; *exo*-2-norborneol-^{13}C, 83572-20-7.

Betylates. 3. Preparative Nucleophilic Substitution by Way of [2]-, [3]-, and [4]Betylates. Stoichiometric Phase Transfer and Substrate–Reagent Ion-Pair (SRIP) Reactions of Betylates

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Abstract: The preparation of [2]-, [3]-, and [4]betylates ((trialkylammonio)alkanesulfonates) and the corresponding norbetylates ((dialkylammonio)alkanesulfonates) is described, and their use as intermediates in the transformation of the hydroxyl group of primary and secondary alcohols is illustrated by examples involving 36 different nucleophiles and 10 different alkyl groups; for a number of products these procedures provide what appears to be the best, or only, access. The reactions generally take place under mild conditions, are easily worked up giving good to excellent yields, and may be carried out in solvents ranging from water to hydrocarbons. Clean inversion is generally found in reactions at chiral secondary centers; a substrate–reagent ion-pair (SRIP) procedure provides a method for preparing both the *R* and *S* series of derivatives from a single enantiomer of the chiral alcohol. The notable ease of these reactions is discussed in terms of generally applicable stoichiometric phase-transfer processes, especially substrate phase transfer into the aqueous phase, and SRIP reactions in nonpolar solvents.

A particularly useful functional group interchange in organic synthesis is the conversion of an alcohol, ROH, into a product, RZ, using a nucleophile (e.g., Z^-) as a source of the Z grouping. Since hydroxide itself is a feeble nucleofuge in bimolecular nucleophilic displacements, the transformation requires the conversion of the alcohol to an intermediate in which the leaving tendency of the oxygen is enhanced. Ideally such an intermediate should be formed easily and cheaply and react readily with a wide array of nucleophiles in a variety of solvents to give a high yield of product in a readily purified form. It may be too much to expect that a single intermediate species will show all of these properties under all circumstances, but a synthetic chemist may reasonably