Solvolysis of 2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate. Evidence for the Formation of Classical Carbocation Intermediates

Takao Okazaki,* Eiichi Terakawa, Toshikazu Kitagawa,* and Ken'ichi Takeuchi

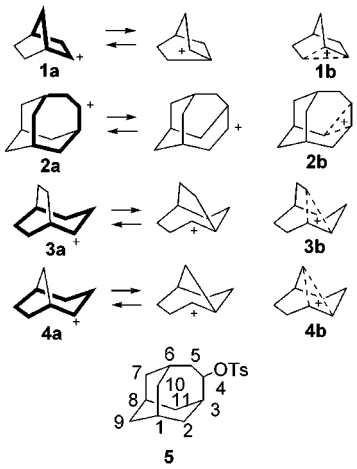
Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Received September 7, 1999

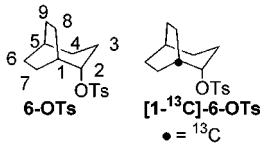
The solvolysis rate of 2-bicyclo[3.2.2]nonyl *p*-toluenesulfonate (**6-OTs**) was nearly equal to that of cycloheptyl *p*-toluenesulfonate in 2,2,2-trifluoroethanol (TFE). This indicates that the ethylene bridge in **6-OTs** does not significantly enhance the rate and that **6-OTs** ionizes without anchimeric assistance. The solvolysis of [1-^{13}C]-2-bicyclo[3.2.2]nonyl *p*-toluenesulfonate in methanol or TFE gave 2-substituted bicyclo[3.2.2]nonane, *exo*-2-substituted bicyclo[3.3.1]nonane, 2-bicyclo[3.2.2]-nonene (**10**), and 2-bicyclo[3.3.1]nonene (**11**), whose distributions of ^{13}C labels were determined by quantitative ^{13}C NMR analysis using a relaxation reagent. The ^{13}C labels were exclusively placed at only two positions, the ratios of them were not unity, and the labels in **10** were less extensively scrambled than those in other products. These results indicate that the 2-bicyclo[3.2.2]nonyl cation is classical and that **10** is formed at a former ionization stage than 2-substituted bicyclo[3.2.2]-nonane. The ^{13}C redistributions for both *exo*-2-substituted bicyclo[3.3.1]nonane and **11**, which are yielded via 1,3-hydride shift, were similar to that of 2-substituted bicyclo[3.2.2]nonane, suggesting that 1,3-hydride shift occurs mainly at the solvent-separated ion pair.

Introduction

The 2-norbornyl cation is believed to be nonclassical (**1b**) in the gas phase and under stable ion conditions.[1−3] However, the distinction between the nature of the cation under solvolytic conditions and that under gas-phase conditions remains controversial.[4] The 2-norbornyl cation can be regarded as a substituted secondary cyclopentyl cation. On the other hand, the 4-homoadamantyl cation (**2**),[5,6] 2-bicyclo[3.2.2]nonyl cation (**3**),[7] and 2-bicyclo[3.2.1]-octyl cation (**4**)[8] can be regarded as substituted secondary cycloheptyl cations. Many of these cations were suggested to have classical structures in solvolysis. Nordlander et al. suggested that the 4-homoadamantyl cation should to be classical (**2a**) from the results of the solvolysis of deuterium-labeled 4-homoadamantyl *p*-toluenesulfonate (**5**).[5] We confirmed the validity of their conclusion by using ^{13}C isotope labels, whose isotope effect on the product pattern should be less than that of deuterium.[6] Goering and Sloan reported that the solvolysis of optically active *endo*-2-bicyclo[3.2.1]octyl brosylate gave racemic substitution products and suggested that the 2-bicyclo-[3.2.1]octyl cation is nonclassical (**4b**).[8] However, there are only a few reports about **3**.



Schaefer et al. reported that the acetolysis of 2-bicyclo-[3.2.2]nonyl *p*-toluenesulfonate (**6-OTs**) gave (after Li-



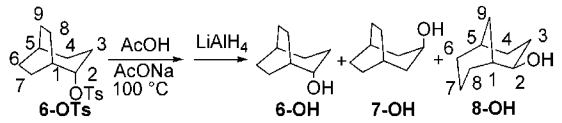
AlH_4 reduction) 2-bicyclo[3.2.2]nonanol (**6-OH**), 3-bicyclo-[3.2.2]nonanol (**7-OH**), and *exo*-2-bicyclo[3.3.1]nonanol (**8-OH**) (Scheme 1).[9] There was no information about elimination products. Berson et al. reported the behavior of the 2-bicyclo[3.2.2]nonyl cation generated by the deamination of tritiated 1-(2-bicyclo[2.2.2]octyl)methyl-amine (**9-T**) (Scheme 2).[7] The tritium label in **9-T** was

* Address correspondence to T. Okazaki. Tel: +81-75-753-5714. Fax: +81-75-753-3350. e-mail: okazaki@scl.kyoto-u.ac.jp.

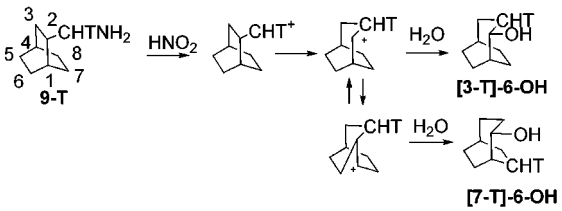
(1) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1393.
(2) (a) Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Org. Chem.* **1997**, *62*, 4216. (b) Schreiner, P. R.; Severance, D. L.; Jorgensen, W. L.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 2663.
(3) It was recently reported that an atoms in molecules (AIM) study indicated that the norbornyl cation is not a nonclassical, σ-bridged cation but a π-complex: Werstiuk, N. H.; Muchall, H. M. *J. Mol. Struct. (THEOCHEM)* **1999**, *463*, 225.
(4) Brown, H. C. *Nonclassical Ion Problem*; (with comments by Schleyer, P. v. R.); Plenum Press: New York, 1977.
(5) Nordlander, J. E.; Hamilton, J. B., Jr.; Wu, F. Y.-H.; Jindal, S. P.; Gruetzmacher, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 6658.
(6) Kitagawa, T.; Okazaki, T.; Komatsu, K.; Takeuchi, K. *J. Org. Chem.* **1993**, *58*, 7891.
(7) Berson, J. A.; Luibrand, R. T.; Kundu, N. G.; Morris, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 3075.
(8) Goering, H. L.; Sloan, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 1397.
(9) Schaefer, J. P.; Endres, L. S.; Moran, M. D. *J. Org. Chem.* **1967**, *32*, 3963.

10.1021/jo9914061 CCC: $19.00
Published on Web 03/02/2000

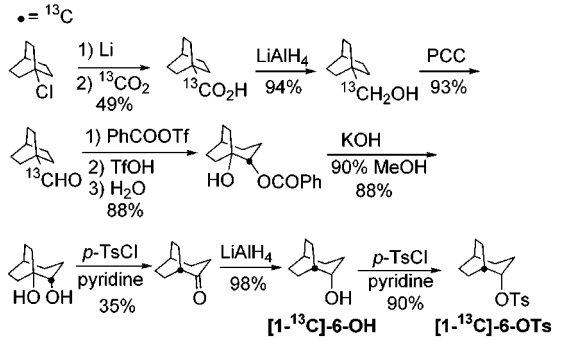
Scheme 1



Scheme 2



Scheme 3



scrambled at two positions by the Wagner−Meerwein rearrangement, and the distribution ratio of the labels in the products (**[3-T]-6-OH** and **[7-T]-6-OH**) was not 1:1. They suggested that the cation was not a nonclassical ion (**3b**), but a classical one (**3a**).

However, cations generated by deamination are called "hot cations" and are different in reactivity and selectivity from cations in solvolysis.[10,11] Therefore, the reaction mechanism and structure of **3** under solvolytic conditions is of particular interest.

We now report the solvolysis of 2-bicyclo[3.2.2]nonyl *p*-toluenesulfonate (**6-OTs**) and [1-^{13}C]-2-bicyclo[3.2.2]-nonyl *p*-toluenesulfonate (**[1-^{13}C]-6-OTs**), prepared by the acylative ring expansion[12] from 1-bicyclo[3.2.2]nonane-[^{13}C]carbaldehyde. The ^{13}C labels were exclusively scrambled into two carbons of the solvolysis products, and the redistribution ratio suggested that the 2-bicyclo[3.2.2]-nonyl cation under the solvolytic conditions is a classical ion (**3a**).

Results and Discussion

Synthesis of 2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate (6-OTs) and [1-^{13}C]-2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate ([1-^{13}C]-6-OTs). The synthesis of [1-^{13}C]-2-bicyclo[3.2.2]nonyl *p*-toluenesulfonate (**[1-^{13}C]-6-OTs**) is shown in Scheme 3. 1-Bicyclo[2.2.2]octane[^{13}C]-carboxylic acid[13,14] was synthesized by the reaction of $^{13}CO_2$ and 1-bicyclo[2.2.2]octyllithium.[13,15] The $LiAlH_4$ reduction of 1-bicyclo[2.2.2]octane[^{13}C]carboxylic acid and the subsequent pyridinium chlorochromate (PCC) oxidation gave 1-bicyclo[2.2.2]octane[^{13}C]carbaldehyde. The acylative ring expansion and the hydrolysis of the aldehyde by a method similar to that previously reported[12] yielded [2-^{13}C]-1,2-bicyclo[3.2.2]nonanediol. The reaction of the diol with *p*-toluenesulfonyl chloride in pyridine yielded [1-^{13}C]-2-bicyclo[3.2.2]nonanone, which was converted to [1-^{13}C]-2-bicyclo[3.2.2]nonanol (**[1-^{13}C]-6-OH**) by the $LiAlH_4$ reduction.[9,16] **[1-^{13}C]-6-OH** was converted to **[1-^{13}C]-6-OTs** by the standard method. Quantitative ^{13}C NMR with a relaxation reagent[6,17] indicated that ^{13}C label (98.5%) in **[1-^{13}C]-6-OH** was exclusively placed at the bridgehead position C(1).

Unlabeled 2-bicyclo[3.2.2]nonyl *p*-toluenesulfonate (**6-OTs**)[9] was synthesized from 1-bicyclo[2.2.2]octanemethanol[12] by a method similar to that described above.

Table 1. Rate Constants for the Solvolysis of 2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate (6-OTs) in Methanol and 2,2,2-Trifluoroethanol (TFE)

solvent	2,6-lutidine, M	temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
MeOH	1.00×10^{-2}	50.0	$2.39\ (\pm 0.03) \times 10^{-5}$ [a]		
	1.33×10^{-2}	25.0	$7.33\ (\pm 0.09) \times 10^{-7}$ [a]	26.1	1.0
TFE	4.00×10^{-2}	40.0	$5.99\ (\pm 0.03) \times 10^{-4}$ [b]		
	2.50×10^{-2}	25.0	$1.02\ (\pm 0.02) \times 10^{-4}$ [a]	21.4	−5.2

[a] Determined titrimetrically. [b] Determined conductometrically.

Solvolysis Rates and Products in Methanol and 2,2,2-Trifluoroethanol. Solvolysis rates of **6-OTs** in methanol and 2,2,2-trifluoroethanol (TFE) buffered with 2,6-lutidine were determined and are shown in Table 1. The activation free energy ($\Delta G^{\ddagger}$) for the solvolysis of **6-OTs** in TFE at 25 °C is calculated to be 23.0 kcal mol^{-1}, and $\Delta G^{\ddagger}$ for cycloheptyl *p*-toluenesulfonate in TFE was reported to be smaller by only 0.2-0.3 kcal mol^{-1}.[18] The nearly identical $\Delta G^{\ddagger}$'s suggest that the ethylene bridge in **6-OTs** has essentially no effect on the S_N1 solvolysis rates and that **6-OTs** ionizes without significant anchimeric assistance.

For a product study, **6-OTs** was solvolyzed in methanol and TFE buffered with 2,6-lutidine. Gas chromatography indicated that the products were 2-bicyclo[3.2.2]nonene (**10**),[19] 2-bicyclo[3.3.1]nonene (**11**),[9,20,21] tricyclo[3.3.1.0^{2,8}]-nonane (**12**),[22] 2-R-bicyclo[3.2.2]nonane [**6-R**: **6-OMe** (R = OMe), **6-OTFE** (R = OCH_2CF_3)], *exo*-2-R-bicyclo-[3.3.1]nonane [**8-R**: **8-OMe** (R = OMe), **8-OTFE** (R = OCH_2CF_3)], and a small amount of an unidentified ether (Scheme 4). The yields of the products are shown in Table 2. **10**, **11**, and **6-OMe**[16] were identified by comparison with authentic samples. **8-OMe**[16] was determined by the

(10) Okazaki, T.; Isobe, H.; Kitagawa, T.; Takeuchi, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2053.
(11) (a) Keating, J. T.; Skell, P. S. In *Carbonium Ions*; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. 2, pp 573−653. (b) Friedman, L. In *Carbonium Ions*; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. 2, pp 655−713.
(12) Takeuchi, K.; Kitagawa, I.; Akiyama, F.; Shibata, T.; Kato, M.; Okamoto, K. *Synthesis* **1987**, 612.
(13) Della, E. W.; Pigou, P. E.; Taylor, D. K.; Krivdin, L. B.; Contreras, R. H. *Aust. J. Chem.* **1993**, *46*, 63.
(14) Della, E. W.; Pigou, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 1085.
(15) Wang, S. S.; Sukenik, C. N. *J. Org. Chem.* **1985**, *50*, 653.
(16) Kirmse, W.; Feldmann, G. *Chem. Ber.* **1989**, *122*, 1531.
(17) Martin, M. L.; Martin, G. J.; Delpuech, J.-J. *Practical NMR Spectroscopy*; Heyden and Sons: London, 1980; Chapter 10, Section 3. (18) Schneider, H.-J.; Thomas, F. *J. Am. Chem. Soc.* **1980**, *102*, 1424.
(19) (a) Goldstein, M. J.; Natowsky, S. *J. Am. Chem. Soc.* **1973**, *95*, 6451. (b) Goldstein. M. J.; Natowsky, S.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1973**, *56*, 294.
(20) Rademacher, P.; Wiesmann, R. F. *Chem. Ber.* **1994**, *127*, 509.
(21) Schaefer, J. P.; Lark, J. C.; Flegal, C. A.; Honig, L. M. *J. Org. Chem.* **1967**, *32*, 1372.
(22) (a) Biethan, U.; Cuntze, U.; Musso, H. *Chem. Ber.* **1977**, *110*, 3649. (b) Musso, H.; Klusacek, H. *Chem. Ber.* **1970**, *103*, 3076. (c) Musso, H.; Klusacek, H. *Chem. Ber.* **1970**, *103*, 3066. (d) Biethan, V. U.; Klusacek, H.; Musso, H. *Angew. Chem.* **1967**, *79*, 152.

Scheme 4

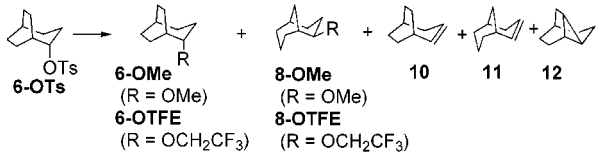


Table 2. Solvolysis Products of 2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate (6-OTs) and [1-^{13}C]-2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate ([1-^{13}C]-6-OTs) in Methanol or 2,2,2-Trifluoroethanol (TFE) Buffered with 0.05 M 2,6-Lutidine

		yield, %[a]					
substrate	solvent	**6-R**	**8-R**	**10**	**11**	**12**	unknown
6-OTs[b]	MeOH	18[c]	21[c]	36	18	4	3
	TFE	10[d]	12[d]	26	47	<1	5
[1-^{13}C]-6-OTs[e]	MeOH	22[c]	23[c]	33	15	5	2
	TFE	16[d]	13[d]	24	44	<1	3

[a] Determined by gas chromatography. [b] At 50 °C for 10 half-lives. [c] R = OMe. [d] R = OTFE. [e] At 40 °C for 20 half-lives.

Table 3. ^{13}C Redistribution in the Products of the Solvolysis of [1-^{13}C]-2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate ([1-^{13}C]-6-OTs) in Methanol or 2,2,2-Trifluoroethanol (TFE) at 40 °C

		^{13}C redistribution, %[a]		
compound	solvent	C(1)	C(2)	C(8)
6-OMe	MeOH	72	28	
6-OTFE	TFE	60	40	
8-OMe	MeOH		72	28
8-OTFE	TFE		62	38
10	MeOH	81	19	
10	TFE	69	31	
11	MeOH		70	30
11	TFE		59	41

[a] Determined by quantitative ^{13}C NMR analysis with a relaxation reagent, Fe(acac)$_3$. The ^{13}C redistribution at the other positions was negligible. Assignment of the ^{13}C NMR signals is shown in Table 4.

comparison of its NMR data with the reported data. **6-OTFE** and **8-OTFE** were identified on the basis of their NMR and the results of acetolysis of **6-OTs** reported by Schaefer et al.[9] The structure of **12** was deduced on the basis of the ^{13}C NMR data that indicate the existence of cyclopropane ring (δ ^{13}C = 12.1 ppm) and its retention time, which is near to those of **10** and **11**, in gas chromatography.

^{13}C Redistribution in the Products and Mechanism for the Solvolysis of [1-^{13}C]-2-Bicyclo[3.2.2]-nonyl *p*-Toluenesulfonate. The ^{13}C distributions in the solvolysis products (**6-OMe**, **6-OTFE**, **8-OMe**, **8-OTFE**, **10**, and **11**) from **[1-^{13}C]-6-OTs** were analyzed by the quantitative ^{13}C NMR measurement with the aid of a relaxation reagent, and calculated ^{13}C redistributions are shown in Table 3. The ^{13}C labels were exclusively placed at two positions of each of the products, and the labels in the bicyclo[3.2.2]nonyl derivatives were located predominantly at the original position. The redistribution ratios C(8)/C(2) in **11** are nearly equal to C(2)/C(1) in **6-R** and C(8)/C(2) in **8-R**, while the ratios C(2)/C(1) in **10** are smaller than the redistribution ratios in the other products. Furthermore, the ^{13}C label was more extensively scrambled by Wagner−Meerwein rearrangement in TFE than that in methanol.

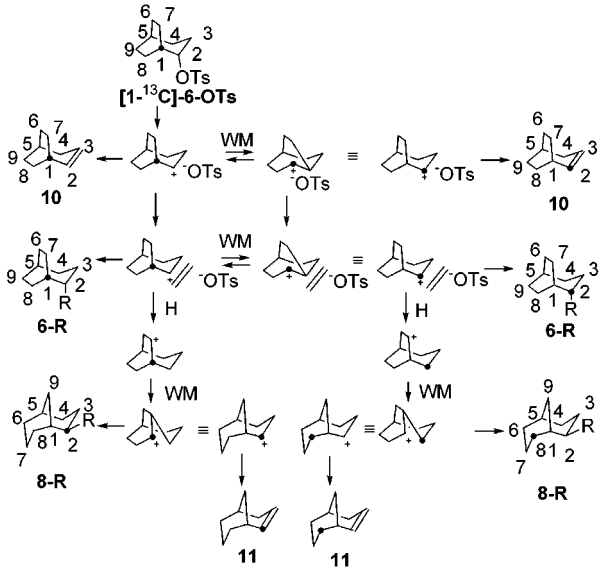
A probable solvolysis mechanism is shown in Scheme 5. The degree of scrambling for **10** was smaller than that

Table 4. Selected Assignment of the Signals in ^{13}C NMR Spectra of 2-R-Bicyclo[3.2.2]nonanes [6-OMe (R = OMe), 6-OTFE (R = Och$_2$CF$_3$)], 2-R-Bicyclo[3.3.1]nonanes [8-OMe (R = OMe), 8-OTFE (R = Och$_2$CF$_3$)], 2-Bicyclo[3.2.2]nonene (10), and 2-Bicyclo[3.3.1]-nonene (11)

	δ, ppm[a]		
compound	C(1)	C(2)	C(8)
6-OMe	33.1	86.9	
6-OTFE	33.7	87.4	
8-OMe		81.0	28.2
8-OTFE		81.4	27.8
10	30.1	135.6	
11		130.5	29.2

[a] Determined by ^{13}C NMR analysis in CDCl$_3$.

Scheme 5



for **6-R** in both solvents. This indicates that at least two kinds of ion pairs of equilibrating cationic intermediates, tight ion pair and solvent-separated ion pair, exist and that elimination product **10** is formed from the former ion pair.

If the 2-bicyclo[3.2.2]nonyl cation were a nonclassical ion (**3b**), the ^{13}C label should be equally distributed at the two positions in the substitution and the elimination products. In actuality, all the products were found to have different amounts of ^{13}C label at the two positions. Clearly, the cation is asymmetric and gives the products by the nucleophilic attachment of solvents or hydride elimination before the Wagner−Meerwein rearrangement achieve complete equilibrium.

The ^{13}C label can be scrambled between C(1) and C(2) by the Wagner−Meerwein rearrangement in the 2-bicyclo-[3.2.2]nonyl cation (**3a**). The formation of **11** and **8-R** involves 1,3-hydride shift in **3a**. If the hydride shift occurred at the stages of both the tight ion pairs and the solvent-separated ion pairs, the redistribution ratios C(8)/C(2) for **11** and **8-R** should be smaller than the ratio C(2)/C(1) for **6-R**. However, the label scrambling in **11** and **8-R** are nearly identical to that in **6-R**, and more progressed than in **10**. Therefore, the 1,3-hydride shift occurs only at the stage of the solvent-separated ion pair.

The rate ratio k_{TFE}/k_{MeOH} for the solvolysis of **6-OTs** is 140 at 25 °C. This number is considerably smaller than

that for the solvolysis of 2-adamantyl tosylate (k_{TFE} = 1.51×10^{-6} s^{-1} and $k_{MeOH} = 2.9 \times 10^{-9}$ s^{-1}; k_{TFE}/k_{MeOH} = 520 at 25 °C).[23] This might indicate possible acceleration of methanolysis of **6-OTs** due to the k_s process. However, this process would be unimportant because the ^{13}C redistribution in **6-R** was almost identical to that in **8-R** in both solvents. If the k_s process were significant, the label should remain in greater amount at C(1) of **6-R** than at C(2) of **8-R**.

The difference in the product distribution in the two solvents (Table 2) is in accord with the above mechanism. The decreased yield of **10** in TFE can be explained by the weakening of the basicity of the tightly paired tosylate anion, which is considered an effective base for elimination, by electrophilic solvation.[5,6] The ratio (**8-R** + **11**)/**6-R**, which corresponds to the extent of the 1,3-hydride shift, is significantly higher in TFE (5.9) than in MeOH (2.2), owing to the low nucleophilicity of TFE.

In conclusion, the above solvolytic data indicate that the 2-bicyclo[3.2.2]nonyl cation is classical under solvolytic conditions. This agrees with Berson's conclusion derived from the behavior of the "hot cation" generated by the deamination of **9-T**.

Experimental Section

General. Melting points are uncorrected. ^{13}C NMR spectra (67.8 or 100 MHz) were recorded in $CDCl_3$. Solvolyses were carried out in anhydrous MeOH and TFE which had been obtained by distillation over MeONa and P_2O_5, respectively. All the anhydrous solvents used for synthetic work were purified by standard procedures. Other commercially available reagents were used as received. 1,2-Bicyclo[3.2.2]nonanediol was synthesized by the literature method.[12] 1-Bicyclo[2.2.2]-octane[^{13}C]methanol was prepared by the literature method[14] by using $Ba^{13}CO_3$ (98% ^{13}C) purchased from Aldlich Chemical Co., Inc.

2-Bicyclo[3.2.2]nonanone. To a solution of 1,2-bicyclo-[3.2.2]nonanediol (1.6 g, 9.9 mmol) in pyridine (20 mL) was added *p*-toluenesulfonyl chloride (2.0 g, 10 mmol). The mixture was stirred for 6 days under nitrogen and refluxed for 2 h. The mixture was poured into 10% HCl and extracted with ether. The combined organic layer was washed with water, 5% $NaHCO_3$, and 10% NaCl and dried ($MgSO_4$). Removal of the solvent gave colorless crystals, purification of which by column chromatography (SiO_2, 9:1 hexane−ether) yielded 2-bicyclo[3.2.2]nonanone[9,24] as colorless crystals (570 mg) in 42% yield.

2-Bicyclo[3.2.2]nonanol (6-OH). 6-OH[9,16] was obtained by the reduction of 2-bicyclo[3.2.2]nonanone with $LiAlH_4$ in ether in 66% yield. ^{13}C NMR (100 MHz) δ 76.6 (CH), 37.0 (CH), 30.0 (CH_2), 29.2 (CH_2), 27.3 (CH), 26.7 (CH_2), 23.4 (CH_2), 23.0 (CH_2), 18.4 (CH_2).

2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate (6-OTs). The reaction of **6-OH** (430 mg, 3.1 mmol) with *p*-toluenesulfonyl chloride (700 mg, 37 mmol) in pyridine (4.3 mL) yielded colorless crystals. Recrystallization from pentane at −40 °C gave **6-OTs** as colorless crystals (630 mg) in 69% yield: mp 48.0−51.0 °C (lit.[9] 46−48 °C).

[2-^{13}C]-1,2-Bicyclo[3.2.2]nonanediol. [2-^{13}C]-1,2-Bicyclo-[3.2.2]nonanediol was synthesized by a method similar to that reported for the preparation of unlabeled 1,2-bicyclo[3.2.2]-nonanediol.[12] 1-Bicyclo[2.2.2]nonane[^{13}C]methanol (880 mg, 6.24 mmol) was oxidized to 1-bicyclo[2.2.2]nonane[^{13}C]carbaldehyde (807 mg, 93%) by using pyridinium chlorochromate in dry CH_2Cl_2 in 93% yield. A solution of 1-bicyclo[2.2.2]-nonane[^{13}C]carbaldehyde (807 mg, 5.80 mmol) in dry CCl_4 (10 mL) was dropwise added to a solution of benzoic trifluoromethanesulfonic anhydride (1.20 mL, 1.81 g, 7.13 mmol) in dry CCl_4 (8 mL). After the mixture had been stirred for 0.5 h, trifluoromethanesulfonic acid (1.26 mL, 2.14 g, 14.2 mmol) was dropwise added, and the mixture was stirred for 0.1 h. To the mixture was dropwise added water (4 mL). The resulting mixture was poured into water, and the product was extracted with ether. The combined organic phase was washed with saturated $NaHCO_3$ and saturated NaCl and dried ($MgSO_4$). Removal of the solvent gave a pale yellow oil. Recrystallization and MPLC (SiO_2, 1:1 hexane−ether) gave pure [2-^{13}C]-1-hydroxy-2-bicyclo[3.2.2]nonyl benzoate as colorless crystals in 88% yield.

[2-^{13}C]-1-Hydroxy-2-bicyclo[3.2.2]nonyl benzoate (1.27 g, 4.85 mmol) was added to a solution of KOH (1.06 g, 16 mmol) in 90% methanol (30 mL), and the mixture was refluxed for 3 h. After evaporation of most of the methanol, to the resulting mixture was added water, and the product was extracted with $CHCl_3$. The combined organic phase was washed with 10% NaCl and dried ($MgSO_4$). Removal of the solvent gave a colorless crystals, which was purified by recrystallization and MPLC (SiO_2, 1:1 hexane−ether) to give [2-^{13}C]-1,2-bicyclo-[3.2.2]nonanediol as colorless crystals in 88% yield.

[1-^{13}C]-2-Bicyclo[3.2.2]nonanone. The reaction of [2-^{13}C]-1,2-bicyclo[3.2.2]nonanediol (600 mg, 3.8 mmol) and *p*-toluenesulfonyl chloride (730 mg, 3.8 mmol) in pyridine (7.6 mL) gave [1-^{13}C]-2-bicyclo[3.2.2]nonanone (180 mg) as colorless crystals in 35% yield.

[1-^{13}C]-2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate ([1-^{13}C]-6-OTs). The reduction of [1-^{13}C]-2-bicyclo[3.2.2]nonanone (211 mg, 1.51 mmol) with $LiAlH_4$ in ether gave **[1-^{13}C]-6-OH** (209 mg) in 98% yield. The reaction of **[1-^{13}C]-6-OH** (192 mg, 1.36 mmol) with *p*-toluenesulfonyl chloride (337 mg, 1.77 mmol) in pyridine (2.1 mL) yielded **[1-^{13}C]-6-OTs** (362 mg) as colorless crystals in 90% yield: mp 50.5−52.0 °C.

Authentic 2-Methoxybicyclo[3.2.2]nonane (6-OMe). To a solution of **6-OH** (60 mg, 0.43 mmol) in dry THF under nitrogen atmosphere was dropwise added a solution of butyllithium in hexane (1.47 M, 0.32 mL, 0.47 mmol). The mixture was stirred for 10 min, and iodomethane (0.11 mL, 0.25 g, 1.8 mmol) was dropwise added to the mixture. After stirring overnight, ether was added to the solution, and the resulting mixture was filtered. The removal of the solvent gave a colorless oil. Purification by chromatography (SiO_2, pentane) gave **6-OMe**[16] (29 mg, 43%) as a colorless oil: ^{13}C NMR (67.8 MHz) δ 86.9 (CH), 56.1 (CH_3), 33.1 (CH), 29.7 (CH_2), 27.9 (CH), 27.8 (CH_2), 26.9 (CH_2), 24.2 (CH_2), 23.6 (CH_2), 19.3 (CH_2).

Authentic 2-Bicyclo[3.2.2]nonene (10). A solution of **6-OH** (308 mg, 2.20 mmol) in HMPA (10.0 mL) was heated at 200 °C for 2 h. The cooled solution was poured into water and the product was extracted with ether. The combined organic layer was washed with water and dried ($MgSO_4$). The removal of the solvent gave a brown oil. Purification by chromatography (SiO_2, pentane) gave **10**[19] (150 mg, 56%) as a pale yellow oil: ^{13}C NMR (100 MHz) δ 135.6 (CH), 128.6 (CH), 40.0 (CH_2), 30.1 (CH), 28.9 (CH), 28.7 ($2CH_2$), 25.8 ($2CH_2$).

Authentic 2-Bicyclo[3.3.1]nonene (11). 11 was prepared by a method similar to that reported in the literature.[20,21,25] In the reported ^{13}C NMR data[20] one carbon signal was missing. The complete data follow: ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 130.5 (CH), 129.4 (CH), 34.2 (CH_2), 32.4 (CH_2), 31.8 (CH_2), 29.6 (CH), 29.2 (CH_2), 27.2 (CH), 18.2 (CH_2).

Solvolysis of 2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate (6-OTs) in MeOH. A solution of **6-OTs** (130 mg, 0.46 mmol) in MeOH (23 mL) containing 0.05 M 2,6-lutidine was heated at 50 °C for 10 half-lives. The product distribution was determined by GLC, which indicated that products were 2-methoxybicyclo[3.2.2]nonane (**6-OMe**), *exo*-2-methoxybicyclo-[3.3.1]nonane (**8-OMe**),[16] 2-bicyclo[3.2.2]nonene (**10**), 2-bicyclo-[3.3.1]nonene (**11**), tricyclo[3.3.1.0^{2,8}]nonane (**12**),[22] and an unidentified ether (Table 2). Most of the solvent was removed

(23) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

(24) Smith, K.; Pelter, A.; Jin, Z. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 851.

(25) Hanack, M.; Kraus, W.; Rothenwöhrer, W.; Kaiser, W.; Wentrup, G. *Liebigs Ann. Chem.* **1967**, *703*, 44.

by distillation and to the residue was added ether. The solution was washed with 10% NaCl, cold 5% HCl, 10% NaCl, 5% $NaHCO_3$, and saturated NaCl and dried ($MgSO_4$). Solvent removal gave a pale yellow oil (160 mg). Column chromatography (SiO_2, pentane) gave a mixture of **6-OMe** and **8-OMe** as a colorless oil (12 mg). **8-OMe**: ^{13}C NMR (67.8 MHz) δ 81.0 (CH), 55.9 (CH_3), 31.4 (CH), 31.5 (CH_2), 28.3 (CH_2), 27.1 (CH), 28.2 (CH_2), 26.8 ($2CH_2$), 20.8 (CH_2).

Solvolysis of 2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate (6-OTs) in CF_3CH_2OH. A solution of **6-OTs** (110 mg, 0.36 mmol) in CF_3CH_2OH (18 mL) containing 0.05 M 2,6-lutidine was heated at 50 °C for 10 half-lives. The product distribution was determined by GLC, which indicated that products were 2-(2,2,2-trifluoroethoxy)bicyclo[3.2.2]nonane (**6-OTFE**), *exo*-2-(2,2,2-trifluoroethoxy)bicyclo[3.3.1]nonane (**8-OTFE**), **10**, **11**, and an unidentified ether (Table 2). Most of the solvent was removed by distillation, and to the residue was added ether. The solution was worked up as described for the methanolysis of **6-OTs** to give a pale yellow oil (28 mg). Column chromatography (SiO_2, pentane) gave almost pure **8-OTFE** as a colorless oil (2 mg) and a mixture of **6-OTFE** and **8-OTFE** as a colorless oil (3 mg). **6-OTFE**: ^{13}C NMR (100 MHz) δ 87.4 (CH), 33.7 (CH), 29.3 (CH_2), 27.8 (CH), 27.7 (CH_2), 26.8 (CH_2), 24.1 (CH_2), 23.4 (CH_2), 19.1 (CH_2). **8-OTFE**: ^{13}C NMR (100 MHz) δ 81.4 (CH), 31.9 (CH), 31.4 (CH_2), 28.0 (CH_2), 27.8 (CH_2), 27.2 (CH_2), 27.1 (CH), 26.6 (CH_2), 20.7 (CH_2).

Solvolysis of [1-^{13}C]-2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate ([1-^{13}C]-6-OTs) in MeOH. A solution of **[1-^{13}C]-6-OTs** (305 mg, 1.03 mmol) in MeOH (52 mL) containing 0.05 M 2,6-lutidine was heated at 40 °C for 20 half-lives. GLC analysis showed the formation of **6-OMe**, **8-OMe**, **10**, **11**, **12**, and an unidentified ether (Table 2). The mixture was washed with 10% NaCl, 5% $NaHCO_3$, and saturated NaCl, and dried ($MgSO_4$). Solvent removal gave a pale yellow oil (125 mg). Column chromatography (SiO_2, pentane) gave a mixture of **10**, **11**, and **12** as colorless crystals (27 mg) and a mixture of **6-OMe** and **8-OMe** as a colorless oil (47 mg). The ^{13}C distributions for the obtained products were determined by a quantitative ^{13}C NMR analysis using a relaxation reagent, 0.05 M $Fe(acac)_3$, in $CDCl_3$.

Solvolysis of [1-^{13}C]-2-Bicyclo[3.2.2]nonyl *p*-Toluenesulfonate ([1-^{13}C]-6-OTs) in CF_3CH_2OH. A solution of **[1-^{13}C]-6-OTs** (43 mg, 0.15 mmol) in CF_3CH_2OH (7.3 mL) containing 0.05 M 2,6-lutidine was heated at 40 °C for 20 half-lives. The product distribution was determined by GLC, which indicated the formation of **6-OTFE**, **8-OTFE**, **10**, **11**, and an unidentified ether (Table 2). Column chromatography (SiO_2, pentane) gave a mixture of **10** and **11** as colorless crystals (27 mg) and a mixture of **6-OTFE** and **8-OTFE** as a colorless oil (47 mg). The ^{13}C distributions for the obtained products were determined by a quantitative ^{13}C NMR analysis with a relaxation reagent, 0.05 M $Fe(acac)_3$, in $CDCl_3$.

Kinetics. Rate constants of the solvolysis of **6-OTs** in MeOH or TFE were determined by the previously reported methods.[6]

Quantitative ^{13}C NMR Analysis. Redistribution of ^{13}C label in solvolysis products was determined by the quantitative ^{13}C NMR analysis, the method of which was previously reported.[6,17] $Fe(acac)_3$ was used as the relaxation reagent.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 10440188) from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: ^1H NMR and ^{13}C NMR spectra for **8-OTFE** and for the mixture of **6-OTFE** and **8-OTFE**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9914061