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Solvolyses of 4-Oxo-2_{eq}- and -2_{ax}-adamantyl Triflates: Significant Through-Bond Interaction of the β-Carbonyl Lone Pair with the Cationic p Orbital in Equatorial Solvolyses

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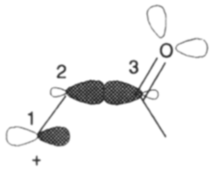
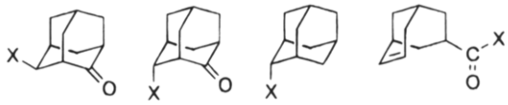
The rates of solvolysis in ethanol, methanol, 2,2,2-trifluoroethanol (TFE), and aqueous ethanols at 25 °C have been determined for 4-oxo-2_{eq}- and -2_{ax}-adamantyl trifluoromethanesulfonates (triflates) (**1_{eq}-OTf** and **1_{ax}-OTf**, respectively). **1_{eq}-OTf** solvolyzed faster than **1_{ax}-OTf** by a factor of 15−24 in the solvents examined, supporting the idea of through-bond stabilization of the transition state in the ionization of **1_{eq}-OTf**. In trifluoroethanolysis, both **1_{eq}-OTf** and **1_{ax}-OTf** gave the equatorial substitution products **1_{eq}-OTFE** and **3-OTFE** (by fragmentation) as major products, indicating that through-bond interaction is at work not only in the ionization step but also in the product-forming step. On the other hand, in methanolysis, both triflates afforded the corresponding inverted methyl ethers as major product. The intervention of a nucleophilically solvated ion pair intermediate has been suggested.

Introduction

The through-bond interaction of a β-carbonyl lone pair with a cationic p orbital was proposed by Vogel and coworkers as $pC(1)^+ \leftrightarrow \sigma C(2)C(3) \leftrightarrow n(CO)$ hyperconjugative interaction in a $C(1)^+{-}C(2){-}C(3){=}O$ species.[1] This concept was successfully used in rationalizing the effect of the carbonyl group in regiospecific electrophilic additions to the double bond of olefinic ketones.[1,2] Recently, we used the solvolyses of the 3-oxobicyclo[2.2.2]oct-1-yl system to quantitatively evaluate the through-bond stabilization of the bridgehead cation and showed that the cation would be more stable by 4−5 kcal/mol than expected from the electron-withdrawing effect of the carbonyl group.[3]



In order that such an interaction develops, the orbitals have to overlap properly. The 3-oxobicyclo[2.2.2]oct-1-yl system has a nice geometry that permits an almost complete overlapping arrangement of the carbonyl lone-pair, C(2)−C(3) σ bond, and the cationic p orbital. However, this system has a drawback in that we cannot control the degree of orbital overlap. For such a purpose, the 4-oxo-2-adamantyl system appeared to be suitable since the direction of the developing p orbital of the 4-oxo-2-adamantyl cation can be controlled by using the equatorial and axial isomers. It was expected that the equatorial triflate (**1_{eq}-OTf**) has a favorable geometry for an overlap arrangement of orbitals, but it is not the case with the axial triflate (**1_{ax}-OTf**). The solvolysis rate study revealed the stabilization of the equatorial transition state by through-bond interaction.[4] The product study in TFE showed that the through-bond interaction is at work not only in the ionization step, but also in the product-forming step. On the other hand, the results of methanolysis were interpreted by postulating an S_N2 (intermediate) mechanism.



X = OH	**1_{eq}-OH**	**1_{ax}-OH**	**2-OH**	**3-OH**
X = OTf	**1_{eq}-OTf**	**1_{ax}-OTf**	**2-OTf**	
X = OCH_2CF_3	**1_{eq}-OTFE**	**1_{ax}-OTFE**		**3-OTFE**
X = OCH_3	**1_{eq}-OMe**	**1_{ax}-OMe**		**3-OMe**

Results

Synthesis of Solvolysis Substrates. 4-Oxo-2_{eq}- and -2_{ax}-adamantanols (**1_{eq}-OH** and **1_{ax}-OH**, respectively) were prepared by previously reported methods[5] and converted to the corresponding triflates (**1_{eq}-OTf** and **1_{ax}-OTf**) by treatment with triflic anhydride in CH_2Cl_2 in the presence of pyridine. The triflates were too unstable to isolate at room temperature; therefore, the worked-up CH_2Cl_2 solution was stabilized by adding 20 mol % of 2,6-lutidine, concentrated to approximately 30 v/v %, and then subjected to solvolysis studies. The ^{13}C NMR spectra of the triflate solutions showed that the triflates were essentially pure (≥97%).

Solvolysis Rates. The solvolyses were conducted in the presence of 2,6-lutidine and the rates determined conductimetrically. Although the solvolyses of 2-ada-

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Table 1. Rate Data of Solvolysis of 1_{eq}-OTf, 1_{ax}-OTf, and 2-OTf in Various Solvents[a]

compound	solvent	temp (°C)	k_1 (s^{-1})[b]	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
1_{eq}-OTf	EtOH	25.0	$1.87 \times 10^{-3\,c}$		
	80% EtOH	25.0	$1.82 \times 10^{-2\,c}$	18.4	−4.8
		5.2	$1.86 \times 10^{-3\,c}$		
	60% EtOH	25.0	$6.86 \times 10^{-2\,c}$		
	MeOH	25.0	$6.93 \times 10^{-3\,c}$		
	TFE	25.0	$1.10 \times 10^{-2\,c,d}$	20.6	1.5
		3.7	$7.03 \times 10^{-4\,c,d}$		
1_{ax}-OTf	EtOH	25.0	$1.08 \times 10^{-4\,c}$		
	80% EtOH	25.0	$1.19 \times 10^{-3\,c}$	21.1	−1.2
		40.0	$6.87 \times 10^{-3\,c}$		
	60% EtOH	25.0	$4.56 \times 10^{-3\,c}$		
	MeOH	25.0	$3.24 \times 10^{-4\,c}$		
	TFE	25.0	$4.60 \times 10^{-4\,c,d}$	21.8	−0.7
		40.0	$2.81 \times 10^{-3\,c,d}$		
2-OTf	EtOH	25.0	$3.72 \times 10^{-4\,e}$		
	80% EtOH	25.0	$2.13 \times 10^{-2\,e}$		
	MeOH	25.0	$2.82 \times 10^{-3\,e}$		
	TFE	25.0	$1.30 \times 10^{-1\,f}$	18.7	0.3
		4.2	$1.12 \times 10^{-2\,c}$		
		−14.0	$9.52 \times 10^{-4\,c}$		

[a] Buffered with 0.025 M 2,6-lutidine except in TFE. [b] Determined by a single run. In all cases the correlation coefficient for the first-order plot was greater than 0.999. [c] Determined conductimetrically within an experimental error of ±0.5% by using 2×10^{-4} M of the substrate. [d] Buffered with 1.2×10^{-3} M 2,6-lutidine. [e] See ref 6a. [f] Extrapolated from data at other temperatures.

Table 2. Various Rate Ratios of Solvolysis in Various Solvents at 25 °C

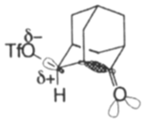
	rate ratio		
solvent	**1_{eq}-OTf/1_{ax}-OTf**	**1_{eq}-OTf/2-OTf**	**1_{ax}-OTf/2-OTf**
EtOH	17	5.0	0.29
80% EtOH	15	0.85	0.056
60% EtOH	15		
MeOH	21	2.5	0.11
TFE	24	0.085	0.0035

mantyl triflate (**2-OTf**) had been extensively studied,[6] its rate in 100% TFE at 25 °C had not been reported:[7] therefore, we determined the rate at 25 °C by extrapolation from data at lower temperatures. All the substrates followed good first-order kinetics ($r > 0.999$) over 80–90% reactions. The rate data and activation parameters in various solvents are summarized in Table 1. In Table 2 are shown the rate ratios **1_{eq}-OTf**:**1_{ax}-OTf**, **1_{eq}-OTf**:**2-OTf**, and **1_{ax}-OTf**:**2-OTf**.

Solvolysis Products. The solvolyses of **1_{eq}-OTf** and **1_{ax}-OTf** were conducted in TFE and methanol on 0.040 M substrate solutions containing 0.050 M 2,6-lutidine at 25 °C for a period longer than 10 half-lives. The product distribution was directly determined by GLC for the reaction mixture. In all cases, the product consisted of equatorial substitution product (**1_{eq}-OR**), axial substitution product (**1_{ax}-OR**), and fragmentation product (**3-OR**). The results are summarized in Tables 3 and 4.

Discussion

The Effect of the 4-Oxo Substituent on Solvolysis Rates. In all the solvents used, **1_{eq}-OTf** solvolyzed faster than **1_{ax}-OTf** by a factor of 15–24. Although small, this factor would be attributed to the presence of the through-bond stabilization of the transition state of ionization in **1_{eq}-OTf** and its unimportance in **1_{ax}-OTf**. As illustrated by **4** and **5**, although **1_{eq}-OTf** has a favorable geometry to assume overlap arrangement of the carbonyl lone-pair, C-C σ bond, and cationic p orbital, it is not the case with **1_{ax}-OTf**. However, this factor of 15–24 is much smaller than 10^3–10^4 that was estimated as the rate enhancement factor in the solvolysis of 3-oxobicyclo[2.2.2]oct-1-yl triflate.[3] This large discrepancy shows that efficient through-bond interaction is effected only when antiperiplanar arrangement can be attained. In the transition state from **1_{eq}-OTf** the cationic p orbital is tilted from the C−C=O plane by about 60°. By assuming that the orbital interaction is proportional to $\cos^2 \phi$ in energy scale,[8] the rate enhancement is predicted as $10^{0.75}$ (≈6)–10, which is fairly close to the value 15–24 obtained for **1_{eq}-OTf**:**1_{ax}-OTf**.



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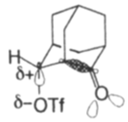

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The insignificance of the difference between their ground state energies in determining the rate ratio was supported by MM2(87) calculations.[9] From lack of the parameters for sulfonates, the calculations were performed on their corresponding alcohols to show that **1_{eq}-OH** is only 0.2 kcal/mol less stable than **1_{ax}-OH** with respect to their steric energies (24.0 and 23.8 kcal/mol, respectively). Consequently, the experimental **1_{eq}-OTf**:**1_{ax}-OTf** rate ratio of 15–24 would be reasonably attributed to the presence of stabilization in the incipient carbocation from **1_{eq}-OTf** and its absence for **1_{ax}-OTf**.

Table 3. Product Distributions in the Trifluoroethanolysis of 1_{eq}-OTf and 1_{ax}-OTf at 25 °C[a]

	product distribution (%)[b]		
compd	equatorial product **1_{eq}-OTFE**	axial product **1_{ax}-OTFE**	fragmentation product **3-OTFE**
1_{eq}-OTf[c]	35	10	52
1_{ax}-OTf[d]	51	3.2	44

[a] For reaction conditions, see text. [b] Determined by GLC within an experimental error of ±0.5%. [c] An unidentified product of 3% was detected. [d] An unidentified product of 2% was detected.

Table 4. Product Distributions in the Methanolysis of 1_{eq}-OTf and 1_{ax}-OTf at 25 °C[a]

	product distribution (%)[b]		
compd	equatorial product **1_{eq}-OMe**	axial product **1_{ax}-OMe**	fragmentation product **3-OMe**
1_{eq}-OTf	3	54	43
1_{ax}-OTf[c]	82	2	14

[a] For reaction conditions, see text. [b] Determined by GLC within an experimental error of ±0.5%. [c] An unidentified product of 2% was detected.

Solvolysis Intermediates in Trifluoroethanol. The most notable feature of trifluoroethanolysis of **1_{eq}-OTf** and **1_{ax}-OTf** is that they gave the equatorial substitution product **1_{eq}-OTFE** in greater amounts than the axial product **1_{ax}-OTFE** with the **1_{eq}-OTFE**:**1_{ax}-OTFE** ratio 35:10 from **1_{eq}-OTf** and 51:3.2 from **1_{ax}-OTf** (Table 3). The results may be explained by assuming that the equatorial ion pair is in equilibrium with the axial ion

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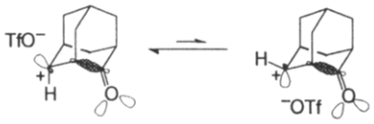
[6] (a) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1985**, *50*, 3330. (b) Bentley, T. W.; Roberts, K. *Ibid.* **1985**, *50*, 4821.

[7] The rate of **2-OTf** in 97% TFE at 25 °C has been determined[6b] but that in 100% TFE has been reported only for −20 °C.[6a]

[8] DeFrees, D. J.; Hehre, W. J.; Sunko, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 2323.

[9] The MM2(87) program was obtained from QCPE.

Scheme 1



pair and that the former is favored, being stabilized by the through-bond orbital interaction between the carbonyl lone pair and the cationic p orbital (Scheme 1). The assumption of the presence of the two equilibrating ion pairs is based on the recently reported ab initio calculations on the 2-adamantyl cation which suggest that the cation may exist as a pair of rapidly equilibrating ion pairs having nonplanarity at the cation center.[10] The formation of **1$_{ax}$-OTFE** in a greater amount from **1$_{eq}$-OTf** than from **1$_{ax}$-OTf** appears to be explained in terms of an S$_N$2 (intermediate) mechanism[11] though it should be less important than in methanolysis (vide infra).

Solvolysis Intermediates in Methanol. In contrast to trifluoroethanolysis, the most notable feature of methanolysis of **1$_{eq}$-OTf** and **1$_{ax}$-OTf** is that it gives the inversion product in greater amounts than the retention product with the **1$_{eq}$-OMe**:**1$_{ax}$-OMe** ratio 3:54 from **1$_{eq}$-OTf** and 82:2 from **1$_{ax}$-OTf** (Table 4). Such characteristic behavior was actually utilized in the synthesis of **1$_{eq}$-OH** and **1$_{eq}$-OMe** from relatively easily available **1$_{ax}$-OTf**.[5b] These results suggest that the nucleophilic solvent attack from the rear side of the leaving group can happen even in a 2-adamantyl system in spite of the typical k_c character of the parent 2-adamantyl system.[11a,b] Probably, this would be ascribed to retarded rates of solvolysis and development of slight positive charge at the reaction center in the ground state owing to the presence of the electron-withdrawing 4-oxo group. There might be slight deformation of the adamantyl structure that would make the k_s process easier. Despite significant rear-side attack by methanol, considerable amounts of fragmentation product **3-OMe** (43% from **1$_{eq}$-OTf** and 14% from **1$_{ax}$-OTf**) was produced, although in smaller amounts than **3-OTFE** (52% from **1$_{eq}$-OTf** and 44% from **1$_{ax}$-OTf**) (Tables 3 and 4). The formation of these methanolysis products may be rationalized by an S$_N$2 (intermediate) mechanism[11] which involves the nucleophilically solvated ion pair intermediates as shown in Scheme 2. The amount of **3-OMe** from **1$_{eq}$-OTf** (43%) is greater than that from **1$_{ax}$-OTf** (14%), suggesting the greater through-bond interaction in the solvated equatorial ion pair intermediate than in the solvated axial one. The predominant inversion of configuration in the methanolysis of **1$_{eq}$-OTf** and **1$_{ax}$-OTf** is in striking contrast to the solvolysis of 2-adamantyl substrates having an electron-withdrawing substituent on the 4- or 5-position, which generally give a greater amount of *syn* substitution product than *anti* one.[12]

The Effect of Solvent on Solvolysis Rates. The mY relations provide useful information about solvolysis mechanism. In Figure 1 are shown the mY relations of **1$_{eq}$-OTf** and **1$_{ax}$-OTf** in ethanol, methanol, TFE, and aqueous ethanols at 25 °C by the use of $Y_{2-\mathrm{AdOTf}}$.[6] The previously reported mY relation for 3-oxobicyclo[2.2.2]oct-1-yl triflate (**6-OTf**)[3b] is also reproduced in Figure 1 for a comparative purpose.

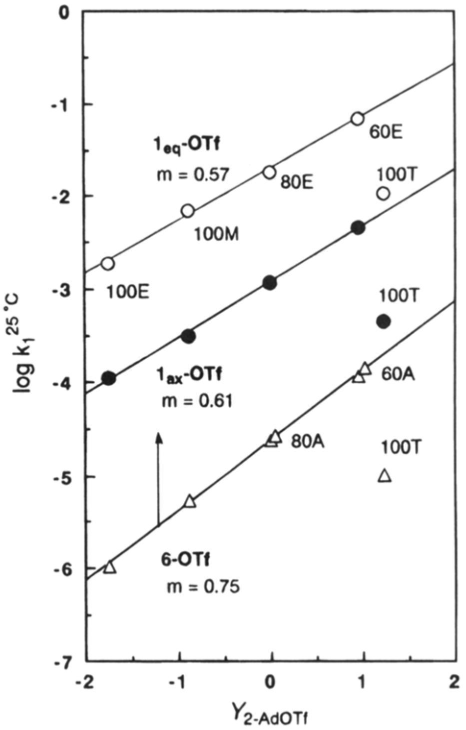


Figure 1. Plots of log k_1 for solvolyses of **1$_{eq}$-OTf**, **1$_{ax}$-OTf**, and **6-OTf** vs $Y_{2-\mathrm{AdOTf}}$ at 25 °C. Open and closed circles, and triangles are for **1$_{eq}$-OTf** ($r = 0.999$), **1$_{ax}$-OTf** ($r = 0.999$), and **6-OTf** ($r = 1.000$), respectively. The data for **6-OTf** were taken from ref 3b and shifted downward by 2 units. E, M, T, and A stand for ethanol, methanol, TFE, and acetone, respectively, and the attached numbers mean their vol percentages in aqueous solutions. The 100T points are not included in the correlations.

6-OTf

Similarly to 3-oxobicyclo[2.2.2]oct-1-yl triflate (**6-OTf**), both **1$_{eq}$-OTf** and **1$_{ax}$-OTf** give nicely linear $mY_{2\text{-AdOTf}}$ relations ($r = 0.999$ for both triflates) (excluding the TFE data) with very small m values (0.57 for **1$_{eq}$-OTf** and 0.61 for **1$_{ax}$-OTf**). Notably, these m values are even smaller than that for 3-oxobicyclo[2.2.2]oct-1-yl triflate (**6-OTf**) (m = 0.75).[3b] These smaller m values in the 4-oxo-2-adamantyl system would be attributed not only to the through-bond interaction, but also to the nucleophilic assistance by the solvents with high nucleophilicity.[13] It is also noted that the TFE point for each substrate deviates from its correlation line. Similarly to the case of 3-oxobicyclo[2.2.2]oct-1-yl triflate,[3b] this deviation is probably ascribed to destabilization of the intermediate carbocation by a hydrogen-bonding interaction between

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[10] Dutler, R.; Rauk, A.; Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* **1989**, *111*, 9024.

[11] (a) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658. (b) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7667. (c) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5466. (d) Bentley, T. W.; Carter, G. E. *Ibid.* **1982**, *104*, 5741.

[12] (a) Grob, C. A.; Wittwer, G.; Rao, K. R. *Helv. Chim. Acta* **1985**, *68*, 760. (b) Nordlander, J. E.; Haky, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 1518. (c) Cheung, C. K.; Tseng, L. T.; Lin, M.-H.; Srivastava, S.; le Noble, W. J. *Ibid.* **1986**, *108*, 1598.

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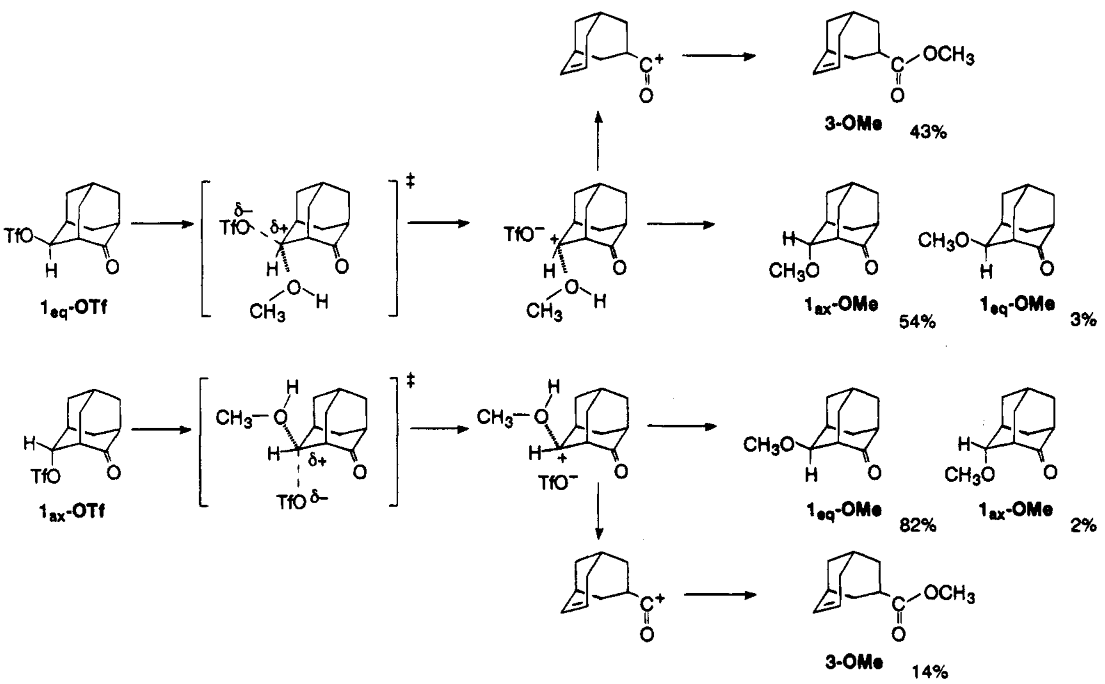
Scheme 2



the carbonyl oxygen and TFE (pK_a 12.37[14]). Such an interaction of a highly acidic solvent with a carbonyl oxygen has been shown by the IR absorption shift for the carbonyl stretching vibration of camphor in hexafluoro-2-propanol.[15] Similar hydrogen-bonding interactions with ether oxygen,[16] sulfur,[17] and amino nitrogen[17] have also been reported to cause deviations in mY relations.

Through-Bond Stabilization of 4-Oxo-2-adamantyl Radical. More than two decades ago, Tabushi, Aoyama, and Yoshida studied the radical bromination of adamantanone with $BrCCl_3$, NBS, and CH_2Br_2 and found that the equatorial:axial selectivity ratio at the radical-transfer step of 4-oxo-2-adamantyl radical to give $\mathbf{1_{eq}}$**-Br** and $\mathbf{1_{ax}}$**-Br** was 2.3–4.3.[18] They interpreted the greater equatorial selectivity in terms of a dipolar effect and/or a steric factor. However, it now appears more reasonable to explain the greater equatorial selectivity in terms of the through-bond orbital interaction between the carbonyl lone pair and the p orbital of the radical center in the radical-transfer transition state. This kind of orbital interaction even in neutral molecules has been observed by photoelectron spectroscopy.[19]

Experimental Section

Melting points are uncorrected. IR spectra were recorded on Hitachi 215 and Perkin-Elmer 1640 spectrophotometers. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX90A spectrometer by using TMS as an internal standard. The 4_{eq}- and 4_{ax}-hydroxy-2-adamantanones ($\mathbf{1_{eq}}$**-OH** and $\mathbf{1_{ax}}$**-OH**, respectively)[5] and 4-oxo-2_{ax}-adamantyl triflate ($\mathbf{1_{ax}}$**-OTf**)[5b] were prepared as described previously. The methanolysis and hydrolysis of $\mathbf{1_{ax}}$**-OTf** have been reported.[5b] 2-Adamantyl triflate (**2-OTf**) was synthesized following a literature procedure.[6] Ethanol and methanol were refluxed over the corresponding magnesium alkoxides and distilled. Acetone and 2,2,2-trifluoroethanol were stored over 4- and 5-Å sieves, respectively, and distilled. Methylene chloride was refluxed over P_2O_5 and distilled. Triflic anhydride was prepared by dehydration of triflic acid with P_2O_5. Pyridine and 2,6-lutidine were dried over KOH and distilled. The other reagents were of a reagent grade quality and used as received. Medium pressure liquid chromatography (MPLC) was conducted on Merck silica gel 60 (230-400 mesh).

4-Oxo-2$_{eq}$-adamantyl Triflate ($\mathbf{1_{eq}}$-OTf). To a stirred solution of 4_{eq}-hydroxy-2-adamantanone ($\mathbf{1_{eq}}$**-OH**) (0.052 g, 0.313 mmol) and pyridine (0.052 g, 0.657 mmol) in CH_2Cl_2 (2 mL) was added a solution of triflic anhydride (0.106 g, 0.376 mmol) in CH_2Cl_2 (2 mL) at 0 °C over 10 min, and then stirring was continued for 2 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL), washed at 0 °C with H_2O (3 × 10 mL), 5% HCl (4 × 10 mL), H_2O (2 × 10 mL), and dried ($MgSO_4$). Since a preliminary experiment revealed that $\mathbf{1_{eq}}$**-OTf** was too unstable a liquid to isolate at room temperature, the above CH_2Cl_2 solution was stabilized by adding 2,6-lutidine (0.007 g, 0.065 mmol), concentrated to approximately 2 mL with a rotary evaporator and then subjected to solvolysis studies: ^{13}C NMR (22.5 MHz, CD_2Cl_2) δ 26.3, 32.4, 44.9, 52.4, 89.5 (CH), 29.6, 31.2, 33.7, 38.7 (CH_2), 210.3 (C=O).

Product of Solvolysis of $\mathbf{1_{eq}}$-OTf in 2,2,2-Trifluoroethanol: A Typical Procedure. To a CH_2Cl_2 solution (ca. 2 mL) of $\mathbf{1_{eq}}$**-OTf** prepared from $\mathbf{1_{eq}}$**-OH** (0.184 g, 1.11 mmol) was added a solution of 0.050 M 2,6-lutidine in TFE (22.2 mL) and the resulting solution kept at 25 °C for 1.7 h (97 half-lives). GLC (PEG 20 M) analyses of the reaction mixture exhibited the formation of 4_{eq}-(2,2,2-trifluoroethoxy)adamantan-2-one ($\mathbf{1_{eq}}$**-OTFE**) (35%), 4_{ax}-(2,2,2-trifluoroethoxy)adamantan-2-one ($\mathbf{1_{ax}}$**-OTFE**) (10%), and 2,2,2-trifluoroethyl bicyclo[3.3.1]non-2-ene-7-carboxylate (**3-OTFE**) (52%). After most of the TFE had been removed with a rotary evaporator, the residue was dissolved in CH_2Cl_2 (50 mL) and the solution washed with 10% NaCl (30 mL), 5% HCl (3 × 30 mL), 10% NaCl (30 mL), saturated $NaHCO_3$ (30 mL), and dried ($MgSO_4$). Evaporation of solvent afforded a pale yellow liquid, which on MPLC (SiO_2, hexane–ether (9:1, 8:2)) gave **3-OTFE** (0.091 g, 33%), $\mathbf{1_{eq}}$**-OTFE** (0.071 g, 26%), and a mixture (0.051 g) of $\mathbf{1_{ax}}$**-OTFE** and an unknown compound (ca. 5%) (74:26 in mol), all as pale yellow liquids, in this sequence. The low yields of the

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products were due to their high volatility. **1_{eq}-OTFE**: ^{1}H NMR (89.55 MHz, $CDCl_3$) δ 1.5–2.8 (m, 12 H), 3.65 (br, 1 H), 3.89 (q, 2 H, J = 8.6 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 26.2, 30.7, 45.0, 50.7, 81.2 (CH), 29.4, 32.0, 32.7, 38.2 (CH_2), 65.6 (q, CF_3CH_2, J = 34 Hz), 123.6 (q, CF_3, J = 279 Hz), 213.3 (C=O). **1_{ax}-OTFE**: ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 26.3, 31.4, 46.1, 50.7, 86.4 (CH), 32.7, 34.9, 37.7, 38.7 (CH_2), 65.3 (q, CF_3CH_2, J = 34 Hz), 123.8 (q, CF_3, J = 279 Hz), 214.9 (C=O). **3-OTFE**: ^{1}H NMR (89.55 MHz, $CDCl_3$) δ 1.5–2.8 (m, 11 H), 4.34 (q, 2 H, J = 8.6 Hz), 5.57 (br, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 26.2, 28.3, 35.7, 128.9, 130.3 (CH), 29.6, 31.2, 31.4, 31.7 (CH_2), 60.2 (q, CF_3CH_2, J = 36 Hz), 123.3 (q, CF_3, J = 277 Hz), 173.7 (C=O).

Product of Solvolysis of 1_{ax}-OTf in 2,2,2-Trifluoroethanol. From a CH_2Cl_2 solution (ca. 2 mL) of **1_{ax}-OTf**, which had been prepared from **1_{ax}-OH** (0.400 g, 2.41 mmol), in 0.050 M 2,6-lutidine in TFE (48.2 mL) at 25 °C for 5.1 h (12.2 half-lives) was obtained a pale yellow liquid, which on MPLC (SiO_2, hexane–ether (9.5:0.5, 7:3)) afforded **3-OTFE** (0.189 g, 32%), **1_{eq}-OTFE** (0.243 g, 41%), and a mixture (0.032 g) of **1_{ax}-OTFE** and an unknown compound (2:1 mol ratio), all as pale yellow oils, in this sequence.

Product of Solvolysis of 1_{eq}-OTf in Methanol: A Typical Procedure. To a CH_2Cl_2 solution (ca. 2 mL) of **1_{eq}-OTf** prepared from **1_{eq}-OH** (0.140 g, 0.842 mmol) was added a solution of 0.050 M 2,6-lutidine in methanol (16.8 mL) and the resulting solution kept at 25 °C for 19 h (684 half-lives). GLC (PEG 20 M) analyses of the reaction mixture exhibited the formation of 4_{eq}-methoxy-2-adamantanone (**1_{eq}-OMe**) (3%), 4_{ax}-methoxy-2-adamantanone (**1_{ax}-OMe**) (54%), and methyl bicyclo[3.3.1]non-2-ene-7-carboxylate (**3-OMe**) (43%). After most of the methanol had been removed with a rotary evaporator, the residue was dissolved in CH_2Cl_2 (25 mL) and the solution washed with 10% NaCl (30 mL), 5% HCl (4 × 15 mL), 10% NaCl (15 mL), saturated $NaHCO_3$ (15 mL), and dried ($MgSO_4$). Evaporation of solvent afforded a pale yellow liquid, which on MPLC (SiO_2, hexane–ether (9:1, 8:2)) gave **3-OMe** (0.040 g, 26%) and **1_{ax}-OMe** (0.061 g, 40%), both as colorless liquids, in this sequence. The low yields of the products were due to their high volatility. Although the amount of **1_{eq}-OMe** (3%) was too low to isolate, it was identified by GLC whose retention time agreed with that of **1_{eq}-OMe** obtained in the methanolysis of **1_{ax}-OTf**.[5b] The ^{13}C NMR data of **3-OMe**[5b] and **1_{ax}-OMe**[20] agreed with reported data.

Kinetic Studies. The preparation of solvents and kinetic methods were described previously.[21] Conductimetric measurements were carried out in the presence of 2,6-lutidine (1.2×10^{-3} M in TFE and 0.025 M in the other solvents) with 2×10^{-4} M substrate concentration.

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Supplementary Material Available: ^{13}C NMR spectra for new compounds **1_{eq}-X** and **1_{ax}-X** (X = OTf, OTFE) and **3-X** (X = OMe, OTFE) (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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