

95066-13-0; **5g**, 95066-20-9; **6a**, 95066-10-7; **6b**, 95066-26-5; **6c**, 95066-11-8; **6d**, 95066-19-6; **6e**, 95066-24-3; **6f**, 95066-15-2; **6g**, 95066-21-0; **7a**, 96728-24-4; **7b**, 96728-25-5; **8a**, 96728-26-6; **8b**, 96728-27-7; **9**, 95066-28-7; **10**, 71204-43-8; L-leucine methyl ester,

2666-93-5; *N*-(benzyloxycarbonyl)lysine benzyl ester, 24458-14-8; L-alanine methyl ester, 10065-72-2; L-methionine methyl ester, 10332-17-9; L-glutamic acid dibenzyl ester, 2768-50-5; L-phenylalanine methyl ester, 2577-90-4; L-proline methyl ester, 2577-48-2.

Solvolysis of 2-Adamantyl Trifluoromethanesulfonate: A Y_{OTf} Scale¹

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The solvolysis of 2-adamantyl trifluoromethanesulfonate proceeds at a convenient rate at temperatures below ambient in a wide variety of pure and aqueous organic solvents and in ethanol-2,2,2-trifluoroethanol mixtures. A scale of Grunwald-Winstein Y values (Y_{OTf}) is developed for 26 solvents and it is found to much more closely resemble the corresponding Y_{OCIO_3} scale than the corresponding scale of Y_{OTs} values. In aqueous ethanol, there is a preference for product formation by interaction with water molecules by a factor of ca. 1.5, essentially independent of solvent composition (96-50% ethanol).

Because of their extremely high nucleofugality, about 10^4 - 10^5 times higher than that for the *p*-toluenesulfonate (tosylate) ion,²⁻⁴ the trifluoromethanesulfonate (triflate) and other perfluoroalkanesulfonate ions have found extensive use in both synthetic and mechanistic studies.⁵ Their ability to depart from esters with formation of relatively unstable carbenium ions has been utilized in the generation of carbocations from cyclopropyl triflates,⁶ of α -keto cations,⁷ of carbenium ions destabilized by one or more α -trifluoromethyl groups or by a α -cyano group,⁸ of disubstituted carbenium ions (vinyl cations),^{4,9,10} and of carbocations from polycyclic structures.^{6,11-13} The solvolysis of 7-norbornyl triflate has recently been used to establish Y_{OTf} values for eight solvents.¹³ These are recommended for use within the Grunwald-Winstein equation (eq. 1) for solvolyses of triflate esters. In eq 1, k and k_0

$$\log \left(\frac{k}{k_0} \right)_{\text{ROTF}} = m Y_{\text{OTf}} \quad (1)$$

represent the specific rates of solvolysis in the solvent

under consideration and in the standard solvent (80% ethanol), Y represents the solvent ionizing power of the solvent under consideration, and m represents the sensitivity of the rate of solvolysis of the substrate to changes in solvent ionizing power.

Attempts to correlate the rates of solvolysis of triflate esters against Y values (based on *tert*-butyl chloride solvolysis) or Y_{OTs} values (based on adamantyl tosylate solvolysis^{14,15}) have met with varying success. In aqueous-ethanol mixtures, vinyl,^{4,9,16-19} cyclopropyl,²⁰ and bridgehead¹² triflates have been correlated against Y values with reasonable m values. Correlations of cyclopropyl and bridgehead triflates against Y values in aqueous-acetone mixtures led⁶ to lower m values, reminiscent of the behavior of 2-adamantyl perchlorate.¹⁵ However, when a more extensive range of solvents was incorporated into a study of α -trifluoromethyl-destabilized carbocations, plots of specific solvolysis rates against Y_{OTs} values showed both dispersion and variable m values for different mixed-solvent systems,^{8a} again reminiscent of 2-adamantyl perchlorate solvolysis,¹⁵ and the need for a thorough study of the solvent dependence of triflate reactivities was emphasized. The rates of solvolyses of 7-norbornyl triflate also correlated rather poorly with Y_{OTs} values.¹³ The rates of solvolysis of several vinyl triflates have also been correlated²¹ by using the extended Grunwald-Winstein equation with N_{OTs} and Y_{OTs} scales^{14a} (eq 1, with the addition of a lN term, which is governed by solvent nucleophilicity and the sensitivity of the solvolysis rate of a given substrate toward changes in solvent nucleophilicity).

The extremely slow solvolyses of 7-norbornyl triflate, except in solvents of high ionizing power,¹³ limit the range

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Table I. First-Order Rate Coefficients for the Solvolysis of 2-Adamantyl Trifluoromethanesulfonate^{a,b} and Y_{OTf} Values

| temp, °C | $10^6k, s^{-1}$ | | | | | |
|-------------|----------------------|--------|--------|----------------------|----------------------|-------------------------------------|
| | 80% EtOH | MeOH | EtOH | <i>i</i> -PrOH | <i>t</i> -BuOH | C ¹⁴ H ₃ COOH |
| -20.0 | 19.4 | 2.57 | 0.281 | (0.079) ^c | (0.048) ^c | (0.407) ^c |
| -9.9 | 110 | | | | | |
| 0.1 | 654 | 72.4 | 9.22 | | | |
| 10.0 | 2478 | 358 | 42.5 | 12.0 | | |
| 18.0 | | | | | | 205 |
| 25.0 | (21300) ^c | 2822 | 372 | 118 | (37.0) ^c | 462 |
| 27.2 | | | | | 48.6 | |
| 34.8 | | | | 352 | 123 | 1986 |
| 45.1 | | | | 1403 | 385 | 6364 |
| 55.0 | | | | | 1133 | |
| Y_{OTf}^d | 0.000 | -0.880 | -1.841 | -2.389 | -2.606 | -1.679 |
| Y_{OTf}^e | 0.000 | -0.878 | -1.756 | -2.256 | -2.760 | -1.664 |

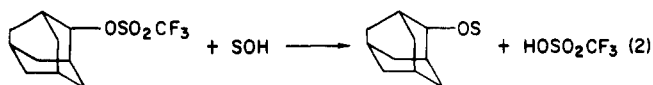
^a Solvolysis of ca. 0.004 M 2-AdOTf in a solvent consisting of 98% of the indicated composition plus 2% dioxane; all runs performed in duplicate. ^b Standard deviations for k were within 6% of reported values. ^c Calculated by using the Arrhenius equation. ^d $\log(k/k_0)_{2AdOTf}$ at -20.0 °C, where k_0 refers to the specific rate in 80% ethanol. ^e Calculated as in footnote *d* but using values at 25.0 °C.

Table II. Enthalpies (ΔH^\ddagger) and Entropies (ΔS^\ddagger) of Activation for Solvolysis of 2-Adamantyl Trifluoromethanesulfonate^a

| solvent | $\Delta H^\ddagger_{298} \text{ °C, kcal/mol}$ | $\Delta S^\ddagger_{298} \text{ °C, eu}$ |
|----------------------------|--|--|
| 80% ethanol ^b | 22.7 ± 0.3 | +10.0 ± 1.1 |
| methanol | 22.8 ± 0.1 | +6.3 ± 0.5 |
| ethanol | 23.4 ± 0.1 | +4.1 ± 0.2 |
| 2-propanol | 23.4 ± 0.4 | +2.0 ± 1.3 |
| <i>tert</i> -butyl alcohol | 21.5 ± 0.1 | -6.6 ± 0.2 |
| acetic acid | 23.2 ± 0.5 | +4.0 ± 1.7 |

^a Calculated by using the data of Table I, with associated standard errors. ^b On a volume-volume basis at 25.0 °C.

of solvents for which it can be used to establish Y_{OTf} values. Use of 2-adamantyl triflate (eq 2) will have the advantage



both of allowing a study in solvents of lower ionizing power and of allowing a more direct comparison with scales developed for other nucleofuges, which have been based on solvolyses of their adamantyl derivatives. Possibly, Y_{OTf} values in low ionizing power solvents could be used in conjunction with the 7-norbornyl triflate values to give an extended range. The isomeric 1-adamantyl triflate has been prepared²² but it was found to be extremely reactive, even extracting hydride ion quite rapidly from continuous chain alkanes.

It will be of interest to see whether Y_{OTf} values, established in the present study for 26 pure and binary solvents, resemble more closely Y_{OTs} values, based on the (superficially at least) structurally similar but much less reactive tosylate, or Y_{OClO_3} values, based on the structurally different but only slightly less reactive²³ perchlorate.

Results

Solvolyses in Dry Alcohols, Acetic Acid, and 80% Ethanol. Rates of solvolysis were determined at four temperatures in the -20 to +55 °C range. Constant integrated values for the first-order rate coefficients were obtained throughout each run. All of the values for duplicate runs were averaged and these averages are reported in Table I, together with four values for temperatures below the freezing points of the solvents and a value for 80% ethanol at 25.0 °C, calculated by using the appro-

Table III. First-Order Rate Coefficients for the Solvolysis of 2-Adamantyl Trifluoromethanesulfonate^a in Aqueous-Organic Solvents, at -20.0 °C, and Y_{OTf} Values^b

| solvent ^{c-e} | $10^6k, s^{-1/f}$ | Y_{OTf}^g | solvent ^{c-e} | $10^6k, s^{-1/f}$ | Y_{OTf}^g |
|------------------------|-------------------|-------------|--------------------------|-------------------|-------------|
| 90% EtOH | 4.32 | -0.653 | 95% acetone | 3.17 ^j | -0.788 |
| 70% EtOH | 66.3 | 0.533 | 90% acetone | 8.76 | -0.346 |
| 60% EtOH | 168 | 0.936 | 80% acetone | 34.0 | 0.243 |
| 90% MeOH | 15.5 | -0.098 | 70% acetone | 116 | 0.777 |
| 80% MeOH | 156 | 0.905 | 60% acetone | 386 | 1.298 |
| 70% MeOH | 353 | 1.260 | 50% acetone | 1465 | 1.877 |
| 60% MeOH | 2112 | 2.036 | 80% T-20% E ^h | 35.0 | 0.255 |
| 100% TFE ^h | 328 ⁱ | 1.227 | 60% T-40% E | 9.42 | -0.314 |
| 97% TFE | 441 | 1.355 | 40% T-60% E | 1.88 | -1.016 |
| 90% TFE | 793 | 1.611 | 20% T-80% E | 0.640 | -1.483 |

^a Concentration ca. 0.004 M. ^b For additional values, see Table I. ^c On a volume-volume basis, at 25.0 °C, except for TFE-H₂O mixtures which are on a weight percentage basis. ^d With water as the other component, except for TFE-EtOH (T-E) mixtures. ^e Actual solvent composition is 98% of the composition indicated plus 2% dioxane (volume-volume); all runs performed in duplicate. ^f Standard deviations for k within 6% of reported value. ^g For definition, see footnote *d* of Table I. ^h 2,2,2-Trifluoroethanol. ⁱ In the presence of 0.005 M pyridine. ^j At 24.7 °C, a value of $1.31 \times 10^{-3} s^{-1}$ was obtained (lit.⁶ $1.27 \times 10^{-3} s^{-1}$ at 25.4 °C). ^k 2,2,2-Trifluoroethanol-ethanol mixtures.

appropriate Arrhenius parameters of Table II. Solvent ionizing power values (Y_{OTf}) based on 2-adamantyl triflate as substrate and calculated at both -20 and 25 °C are also reported within Table I.

Solvolyses in Solvents of Varying Ionizing Power. A study has been made at -20 °C in the following aqueous-organic mixtures: 100-60% ethanol (five compositions), 100-60% methanol (five compositions), 100-90% 2,2,2-trifluoroethanol (TFE) (three compositions), and 95-50% acetone (six compositions). A study was also made over the full range of TFE-ethanol mixtures (six compositions). With the exception of those values already reported in Table I, averages of all of the values for the integrated first-order rate coefficients from duplicate runs and Y_{OTf} values are reported in Table III.

Product Studies. The products from the reactions in aqueous-ethanol mixtures were studied at 24.9 °C for the same solvent compositions as used in the kinetic studies. A 10% excess of pyridine was added to prevent any acid-catalyzed equilibration of the alcohol and the ethyl ether products.^{24,25} The 3.8% of 2-adamantanol found after solvolysis in 100% ethanol was virtually identical with the 3.5% found after ethanolysis of 2-adamantyl perchlorate¹⁵

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Table IV. Percentage of Product Present^a as 2-Adamantanol after the Solvolysis of 2-Adamantyl Trifluoromethanesulfonate^b in Aqueous Ethanol, at 24.9 °C, and Selectivity Values (*S*)^c

| % EtOH ^d | 100 | 96 | 90 | 85 | 80 | 70 | 65 | 60 | 50 |
|---------------------|------------------|------|------|------|------|------|------|------|------|
| % AdOH | 3.8 ^e | 20.3 | 39.8 | 48.6 | 56.6 | 68.9 | 72.7 | 75.2 | 83.7 |
| <i>S</i> | | 1.55 | 1.68 | 1.54 | 1.51 | 1.52 | 1.46 | 1.34 | 1.53 |

^a Only 2-adamantanol and 2-adamantyl ethyl ether detected as products. ^b Concentration ca. 0.01 M and a 10% excess of pyridine was present. ^c Ratio of specific rate constants for reaction of intermediate ionic species with water and ethanol, respectively (see text). ^d On volume-volume basis and overall composition is 95% the solvent of indicated composition plus 5% dioxane. ^e Corresponds to percentage of 2-adamantanol impurity in the 2-adamantyl trifluoromethanesulfonate stock solution.

Table V. Calculated Slopes (*m*) and Intercepts (*c*) for Plots of Y_{OTf} against Y_{OTs} or Y_{OCIO_3}

| | aq EtOH ^a | aq MeOH ^a | aq acetone ^b |
|----------------|----------------------|----------------------|-------------------------|
| m_{OTs} | 1.05 | 1.20 | 0.63 |
| c_{OTs} | -0.06 | 0.18 | 0.97 |
| r_{OTs}^c | 0.999 | 0.994 | 0.994 |
| m_{OCIO_3} | 0.93 | 1.02 | 1.08 |
| c_{OCIO_3} | -0.06 | -0.01 | -0.56 |
| $r_{OCIO_3}^c$ | 0.996 | 0.997 | 0.997 |

^a 100–60% alcohol (5 compositions). ^b 95–50% acetone (6 compositions). ^c Correlation coefficient.

and it is similarly ascribed as being due to adventitious moisture present during the preparation of the ester from 2-adamantyl bromide and the silver salt.

Selectivity values (*S*) were calculated according to eq 3 and they are reported in Table IV. The percentages of 2-adamantanol within the product were corrected for the 3.8% found after solvolysis in 100% ethanol before insertion into eq 3.

$$S = \frac{[2\text{-adamantanol}]}{[\text{ethanol}]/[2\text{-adamantyl ethyl ether}][\text{water}]} \quad (3)$$

Discussion

At 25.0 °C, values comparing the specific rates of 2-adamantyl perchlorate solvolysis to those of slower reacting 2-adamantyl derivatives have previously been reported.¹⁵ These ratios can be extended by incorporation of data for the triflate ester. The OTf:OCIO₃ ratio of solvolysis rates is 14.3 in 80% ethanol, 12.2 in ethanol, and 9.6 in acetic acid. The reactivity relative to the previously reported¹³ 7-norbornyl triflate can also be considered; at 25.0 °C, the rate ratios favoring 2-adamantyl triflate are 1.9×10^5 in ethanol, 3.3×10^5 in 80% ethanol, and 3.4×10^5 in acetic acid. For the acetolyses of the much slower reacting tosylate esters, a very similar ratio of 6.6×10^5 was reported.²⁶

In any comparison of *Y* scales established at different temperatures, caution must be exerted because of possible temperature dependence of the *Y* values. The present Y_{OTf} values have been determined for five pure solvents at -20 and at 25 °C (Table I) and very little variation is observed between the values at the two temperatures; this could have been anticipated from the very similar activation energies for these solvents and 80% ethanol, reported within Table II. While variations for binary solvent systems could possibly be larger, the studies with pure solvents do suggest that Y_{OTf} values are not very temperature dependent.

The logarithmic variations in the first-order rate coefficient for the solvolysis of 2-adamantyl triflate, at -20 °C, has been considered in terms of three different *Y* scales. The plot against traditional Grunwald-Winstein *Y* values,²⁷ supplemented by more recent values for TFE-containing solvents,²⁸ leads to a *m* value (26 solvents) of 0.876

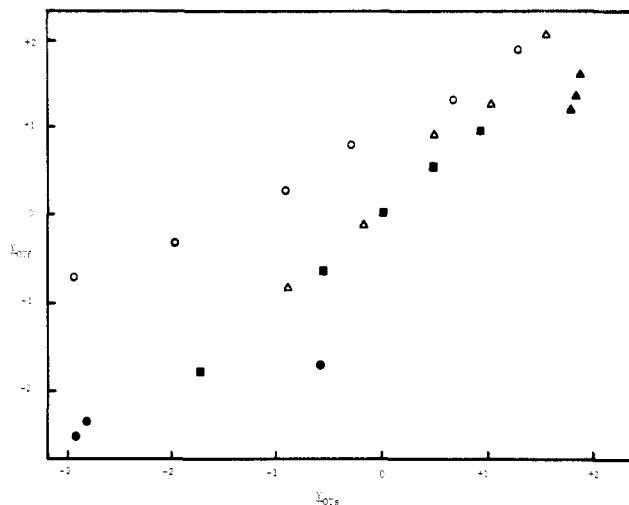


Figure 1. Grunwald-Winstein solvent ionizing power: plot of Y_{OTf} against Y_{OTs} : (open circles) aqueous acetone; (open triangles) aqueous MeOH; (closed triangles) aqueous TFE; (closed squares) aqueous EtOH; (closed circles) (from left to right) *t*-BuOH, *i*-PrOH, and CH₃COOH.

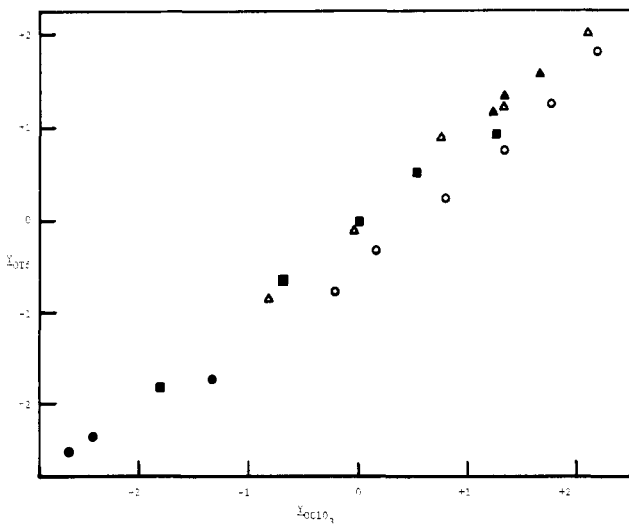


Figure 2. Grunwald-Winstein solvent ionizing power: plot of Y_{OTf} against Y_{OCIO_3} . Designation of solvents is as for Figure 1.

($r = 0.936$). For correlations with Y_{OTs} ^{14,15} and Y_{OCIO_3} ¹⁵ values, values for the four TFE-ethanol mixtures are not available and *m* values (22 solvents) of 0.782 ($r = 0.879$) for a plot against Y_{OTs} values and of 0.961 ($r = 0.986$) for a plot against Y_{OCIO_3} values are obtained. The plots of Y_{OTf} against Y_{OTs} and Y_{OCIO_3} are presented in Figures 1 and 2. Individual mixed solvent systems give good correlations ($r > 0.994$) of Y_{OTf} against either Y_{OTs} or Y_{OCIO_3} (Table V).

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In the two aqueous-alcohol mixtures, the slopes are close to unity and the intercepts have small values. For aqueous acetone, correlation against Y_{OTs} gives a relatively low slope²⁹ of 0.63 and a large positive intercept, indicating (as for 2-adamantyl perchlorate solvolysis¹⁵) faster solvolyses than one would predict based upon Y_{OTs} values. Correlations, for aqueous acetone, against Y_{OCIO_3} values give a slope of close to unity but an appreciable negative intercept, consistent with 2-adamantyl triflate solvolysis being subject to accelerative effects in aqueous acetone intermediate between those for 2-adamantyl tosylate and 2-adamantyl perchlorate.

It is interesting that the 2-adamantyl triflate solvolysis rates correlate much better with 2-adamantyl perchlorate solvolysis rates than with the rates of solvolysis of 2-adamantyl tosylate, despite triflates and tosylates both being sulfonate esters. The non-fluorinated equivalent, 2-adamantyl methanesulfonate, has previously^{14b} been shown to correlate very well with Y_{OTs} values. One factor may be the extensive delocalization of charge into the CF_3 group, a delocalization which is essentially absent in sulfonate ions incorporating either $C_6H_5CH_2$ or CH_3 groups. It is possible that hydrogen bonding interaction of solvent molecules with the fluorines of the CF_3 group³⁰ may be a factor, but the observation of relatively positive entropies of activation (Table II) for the 2-adamantyl triflate solvolyses would appear to argue against increased solvation of the incipient anion.^{15,31} The results of the present investigation give strong support to the viewpoint^{14,32} that each leaving group requires a separate consideration of the influence of solvent variation upon its leaving-group ability.

The difference in reactivities of 10^5 to 10^6 between 2-adamantyl and 7-norbornyl triflates is similar to the difference between 1-adamantyl and 2-adamantyl tosylates^{33,34} and, since it has been found that Y_{OTs} values established with both of the adamantyl tosylates can be used in conjunction, it may well be that an extended range of Y_{OTf} values can be obtained by using the two bridgehead triflates in tandem. For four solvents, Y_{OTf} values are available from solvolyses of both substrates. For ethanol, values are -1.50 from 7-norbornyl triflate solvolysis¹³ and -1.85 from the present investigation. Corresponding values are 0.88 and 0.94 for 60% ethanol, -1.78 and -1.68 for acetic acid, and 0.40 and 1.23 for TFE. Two Y_{OTf} values, based on cyclic vinyl triflate solvolyses, had previously been reported:²¹ -1.64 for acetic acid and 0.93 for 97% TFE. Agreement between the Y_{OTf} values is very good except for 100% and 97% TFE solvents. Rappoport and Kaspi³⁵ have demonstrated previously that Y scales in TFE-H₂O mixtures can vary appreciably for different probes; investigation of other S_N1 -solvolyzing triflates would be worthwhile.

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Tidwell^{8a} in his study of 1-phenyl-2,2,2-trifluoroethyl triflate solvolysis found, in correlations against Y_{OTs} values, m values of less than unity in aqueous ethanol and considerably greater than unity in aqueous TFE. He resisted the temptation to ascribe these effects³⁶ as being due to nucleophilic solvent assistance and he described the results as "inconclusive". His caution is clearly justified by the present finding for S_N1 solvolyses³⁷ of 2-adamantyl triflate of a m_{OTs} value of essentially unity in aqueous ethanol coupled with a logarithmic rate difference between 100% and 90% TFE of 0.4 units, despite essentially constant Y_{OTs} values over this TFE-H₂O range (difference of only 0.07 units). His prediction that triflate solvolysis rates would be less sensitive to solvent ionizing power than corresponding tosylate solvolysis rates is supported by the present investigation.

The selectivity values (Table IV) show the usual pattern for solvolyses of adamantyl derivatives; that is, an essentially constant selectivity, independent of the ethanol to water ratio in the solvent, and a slight preference for reaction with the less nucleophilic water.^{24,25} The average S value of 1.52 ± 0.09 (standard deviation) is very similar to the value of 1.75 ± 0.14 found for the corresponding solvolysis of the perchlorate ester.

Experimental Section

Materials. Silver trifluoromethanesulfonate (Aldrich) was used as received. The purification of solvents and of 2-adamantyl bromide was carried out as previously outlined.¹⁵

2-Adamantyl Trifluoromethanesulfonate. The preparation of a pentane solution and the transfer to dioxane paralleled the preparations of 2-adamantyl perchlorate solutions,¹⁵ except for a doubling of the reaction time. Experiments were also carried out in which the 2-adamantyl triflate was isolated as a pale amber oil by evaporation of the pentane under vacuum. The oil solidified on standing at ca. 0 °C to give a 96% yield of white crystals, mp 24–26 °C. The ¹H NMR spectrum (in CDCl₃) was consistent with that previously reported.⁶ The infrared spectrum (neat) included peaks at 2920, 2860, 1455, 1420, 1280, 1240, 1190, 1150, 1055, 920, 900 cm⁻¹. Anal. Calcd for C₁₁H₁₅F₃SO₃: C, 46.47; H, 5.32. Found: C, 46.42; H, 5.68.

Pentane solutions were stable at ca. 0 °C for up to three weeks. Two identical portions of a freshly prepared pentane solution were taken. Acetone, at -78 °C, was added to one and the other was treated with 60% ethanol for 2 h (to allow complete solvolysis) prior to acetone addition. Titration of the two solutions, against methanolic sodium methoxide to a Lacmoid (resorcinol blue) endpoint, indicated 2.8% initial acid to be present, this is in good agreement with the initial 3.5% 2-adamantanol indicated by GLC.

Kinetic and Product Studies. These were carried out as previously reported¹⁵ for experiments with a stock solution of 2-adamantyl perchlorate in dioxane.

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