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Response of Triflates to Solvent Ionizing Power. A Y_{OTf} Scale Based on 7-Norbornyl Triflate

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A solvent effect study on rates of solvolysis of 7-norbornyl triflate (1) showed a relatively small overall response to solvent ionizing power parameters. A poor correlation with Y_{OTs} values was observed despite the involvement of a cationic intermediate. Triflate **1**, which is very resistant to S_N2-type reactions, has been used to define a new set of solvent ionizing power values, Y_{OTf}. The triflate derivative of pivaloin (**2**), 1-methylcyclopropyl triflate (**3**), and 6,6-(ethylenedioxy)-*endo*-bicyclo[2.2.1]hept-2-yl triflate (**5**) all gave poor rate correlations with Y_{OTs} values, despite the involvement of cationic intermediates in solvolysis. Greatly improved correlations with Y_{OTf} values were observed. *endo*-2-Methyl-*exo*-bicyclo[3.1.0]hex-2-yl triflate (**4**) gave an m_{OTf} value which was more indicative of a cationic intermediate than the m_{OTs} value. Previously reported data for α-phenyltrifluoroethyl triflate (**13**) and (*E*)- and (*Z*)-butenyl triflates **17** and **18** showed improved correlations when rates were plotted against Y_{OTf} values. These studies all suggest that the solvation requirements of the developing, relatively stable trifluoromethanesulfonate anion are somewhat different from tosylate or chloride ion. Low rate responses to increasing solvent polarity in triflate solvolyses are not inconsistent with involvement of cationic intermediates.

One of the primary mechanistic criteria employed to establish the intermediacy of carbocationic intermediates in solvolysis processes is a large increase in rate with increasing solvent polarity. Winstein and Grunwald[1] expressed this rate increase quantitatively. A linear free energy relationship (eq 1) was developed where k is the

$$\log (k/k_0) = mY \tag{1}$$

solvolysis rate at a given substrate in a given solvent, k_0 is the rate in the standard solvent, 80% aqueous ethanol, Y is a solvent parameter called the solvent ionizing power, and m is a substrate parameter which gives the response of a substrate to changes in solvent ionizing power. The substrate used by Winstein and Grunwald to define Y values was *tert*-butyl chloride. Over the years, variations of the original Winstein–Grunwald equation have appeared. The importance of the nucleophilic character of a solvent in determining solvolysis rates of certain substrates was recognized quite early. This led to the introduction of a four-parameter equation (eq 2)[2] which at-

$$\log (k/k_0) = lN + mY \tag{2}$$

tempts to express rates as a function of solvent ionizing power and solvent nucleophilicity N. Another variation used by Schleyer, Bentley, and Schadt[3] is a three-parameter equation (eq 3) which contains the adjustable param-

$$\log (k/k_0) = (1 - Q) \log (k/k_0)_{\text{CH}_3\text{OTs}} + Q \log (k/k_0)_{\text{2-AdOTs}} \tag{3}$$

eter Q. This equation allows one to determine to what extend a substrate's reactivity resembles methyl tosylate ($Q = 0$) or 2-adamantyl tosylate ($Q = 1$). For a completely limiting case (a k_c process), eq 3 reduces to eq 4 which has

$$\log (k/k_0) = mY_{\text{OTs}} \tag{4}$$

the same form as the original Winstein–Grunwald equation where Q and m are equivalent. Equation 4 uses a set of Y values which is based on the defining substrate, 2-adamantyl tosylate.[3] This secondary substrate was used to define Y values since it solvolyzes by a k_c mechanism; i.e., there is negligable nucleophilic solvent assistance in a range of solvents.[4] This simple equation has retained popularity and has recently been used to correlate a number of substrates solvolyzing by cationic processes.[5-7]

Over the years, we have been interested in solvolytic reactions of substrates containing the triflate leaving group. We reported[8a] in a limited study (two solvents) that cyclopropyl triflates gave a fairly small rate response to increasing solvent ionizing power in an aqueous acetone solvent. Schiavelli and Stang[9] have also observed decreased solvent responses in solvolyses of certain vinyl triflates in aqueous ethanol systems. We also found[8b] that the triflate derivative of pivaloin gave a relatively small rate response. However, we were confident, based on the rearrangements observed, that these substrates were solvolyzing via cationic intermediates. It therefore appears that the m value criterion fails to confirm the presence of cationic intermediates for certain triflates when Y values based on *tert*-butyl chloride and 2-adamantyl tosylate are employed. We have therefore carried out a detailed examination of the response of triflates **1**–**5** to changing solvent ionizing power. These substrates all solvolyze, giving cationic intermediates of widely differing structure. How do these substrates response? Answers to this question are reported herein.

Solvolysis of 7-Norbornyl Triflate (1). The rate behavior of 7-norbornyl triflate (**1**) has been examined in a variety of solvents. This substrate reacts via a cationic intermediate, **6**, which has been suggested by recent studies

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(1) (a) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846–854. (b) Winstein, S.; Grunwald, E.; Jones, H. W. *Ibid.* **1951**, *73*, 2700–2707.

(2) Winstein, S.; Fainberg, A. H.; Grunwald, E. *J. Am. Chem. Soc.* **1957**, 79, 4146–4155.

(3) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674.

(4) (a) Fry, J. L.; Lancelot, C. J.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2538–2540. (b) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *Ibid.* **1970**, *92*, 2540–2542. (c) Schleyer, P. v. R.; Fry, J. L.; Lam, L. K. M.; Lancelot, C. J. *Ibid.* **1970**, *92*, 2542–2544.

(5) (a) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *J. Am. Chem. Soc.* **1982**, *104*, 207–211. (b) Allen, A. D.; Ambridge, I. C.; Che, C.; Michael, H.; Muir, R. J.; Tidwell, T. T. *Ibid* **1983**, *105*, 2343–2350.

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(7) (a) Bentley, T. W.; Carter, G. E. *J. Org. Chem.* **1983**, *48*, 579–584. (b) Brown, H. C.; Ravindranathan, M.; Chloupek, F. J.; Rothberg, I. *J. Am. Chem. Soc.* **1978** *100*, 3143–3149.

(8) (a) Creary, X. *J. Am. Chem. Soc.* **1976**, *98*, 6608–6613. (b) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1983**, *105*, 7123–7129.

(9) Schiavelli, M. D.; Jung, D. M.; Vaden, A. K.; Stang, P. J.; Fisk, T.; Morrison, D. S. *J. Org. Chem.* **1981**, *46*, 92–95.

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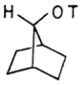
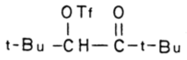
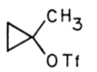


1



$$t\text{-Bu}-\overset{\text{OTf}}{\overset{|}{\text{C}}}\text{H}-\overset{\text{O}}{\overset{\|}{\text{C}}}-t\text{-Bu}$$

2



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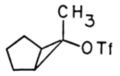

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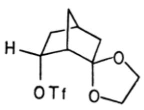

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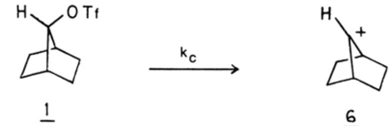
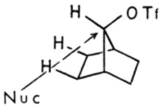


of Sunko[10] to be bent. Rate data are given in Table I and presented graphically as a function of Y_{OTs} in Figure 1. While there are generally rate increases with solvent ionizing power, there is a relatively poor correlation ($r = 0.92$) with Y_{OTs} (or $Y_{t\text{-BuCl}}$) values over the entire range of solvents studied. The overall m value (0.58) is also rather small. While a linear relationship is observed in aqueous ethanol solvents, rates are faster in these solvents than those expected on the basis of Y_{OTs} values relative to other solvents.[11] The rate in trifluoroacetic acid is also considerably slower than that expected on the basis of its Y_{OTs} value.

Triflate 1 has been chosen as a model k_c substrate for triflate solvolyses since it reacts at convenient rates in a variety of solvents.[12] Additionally, as suggested for 2-adamantyl systems, the solvolysis of 1 is not susceptible to nucleophilic solvent assistance. This has been verified by the previous observation[13] that 7-norbornyl tosylate does not give S_N2-type displacement of tosylate even when treated with methoxide or cyanide in methanol at 200 °C. Additionally our studies show that potassium thiophenoxide reacts with 7-norbornyl triflate *less readily* than with cyclohexyl mesylate despite the fact that the triflate leaving group is a substantially better leaving group (approximately 10^5 times more reactive)[10b] than the mesylate nucleofuge.

Examination of molecular models shows that the reluctance of triflate 1 to give S_N2-type reactions is due in part to the C_2C_3 hydrogens of 1 which hinder the preferred approach of a nucleophile. Since nucleophilic solvent assistance in solvolysis of 1 is presumably negligible the rate data in Table I has been used to define a Y_{OTf} scale. Values are given in Table II.



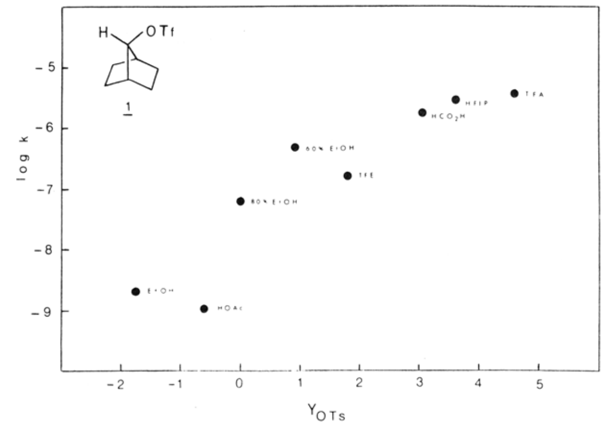


Figure 1. Plot of log k for solvolysis of 1 vs. Y_{OTs}.

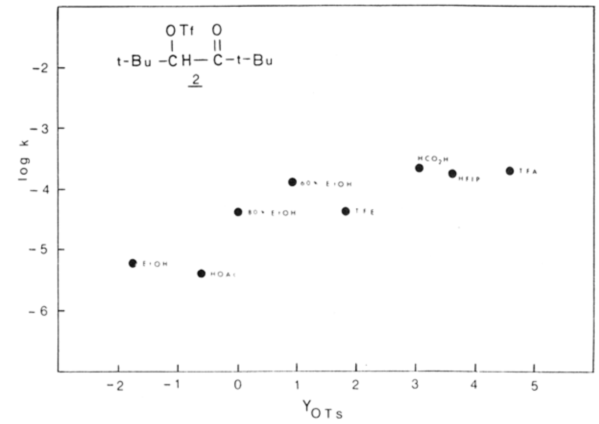


Figure 2. Plot of log k for solvolysis of 2 vs. Y_{OTs}.

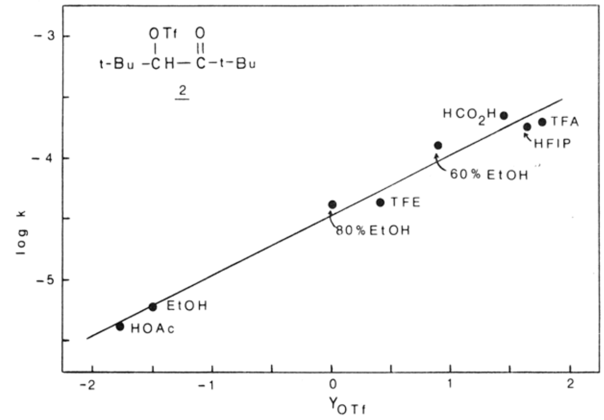
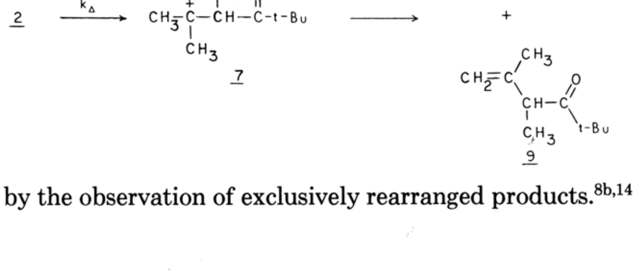


Figure 3. Plot of log k for solvolysis of 2 vs. Y_{OTf}.

Solvent Effects on Reactivity of Triflates 2–5. The reactivity of triflates 2–5 has been examined in a variety of solvents. Triflate 2 solvoylzes by a k_Δ route as evidenced by the observation of exclusively rearranged products.[8b,14]



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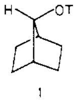
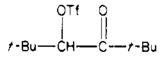
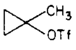
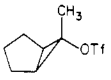
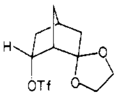
[10] Cation 6 is the structure suggested by MINDO/3 calculations. A somewhat different bent cation is suggested by MINDO/2 calculations. See: Sunko, D. E.; Vancik, H.; Deljac, V.; Milun, M. *J. Am. Chem. Soc.* **1983**, *105*, 5364–5368. For previous studies on 7-norbornyl triflate, see ref 8. See also: (b) Su, T. A.; Sliwinski, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 5386–5388. For studies on 7-norbornyl tosylate, see: (c) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183. (d) Gassman, P. G.; Hornback, J. M. *Ibid.* **1967**, *89*, 2487–2488. (e) Gassman, P. G.; Hornback, J. M.; Marshall, J. L. *Ibid.* **1968**, *90*, 6238–6239. (f) Miles, F. B. *Ibid.* **1967**, *89*, 2488–2489. (g) Miles, F. B. *Ibid.* **1968**, *90*, 1265–1628.

[11] There are instances where aqueous ethanol data gives linear mY correlations and other aqueous solvents give different (but linear) correlations. This type of dispersion is often observed when Y values based on *tert*-butyl chloride are used. Ideally one would not see such dispersions if completely analogous mechanisms operated. For typical examples, see ref 2.

[12] 2-Adamantyl triflate[8] was not chosen as a model triflate since it has extremely high reactivity in more highly ionizing solvents.

[13] Gassman, P. G.; Hornback, J. M.; Pascone, J. M. *Tetrahedron Lett.* **1971**, 1415–1416.

Table I. Solvolysis Rates of Triflates

compound	solvent^a	T, °C	k, s^{-1}
 1	EtOH	114.9	1.46×10^{-4}
		95.0	1.96×10^{-5}
		25.0^b	2.01×10^{-9}
	HOAc	125.0	5.25×10^{-4}
		100.0	3.81×10^{-5}
		25.0^b	1.07×10^{-9}
		25.0^{b,c}	1.37×10^{-9}
	80% EtOH	95.0	4.89×10^{-4}
		75.0	5.46×10^{-4}
		25.0^b	6.41×10^{-8}
	60% EtOH	80.0	6.50×10^{-4}
		60.0	6.32×10^{-5}
		25.0^b	4.88×10^{-7}
	TFE	80.0	1.38×10^{-4}
		60.0	1.53×10^{-5}
		25.0^b	1.62×10^{-7}
	HCO_2H	60.0	2.08×10^{-4}
		40.0	1.57×10^{-5}
		25.0^b	1.80×10^{-6}
	97% HF1P	60.0	1.19×10^{-4}
		35.0	9.10×10^{-6}
		25.0^b	2.89×10^{-6}
	TFA	25.0	3.72×10^{-6}
 2	EtOH	25.0	5.98×10^{-6}
	80% EtOH	25.0	4.15×10^{-5}
	60% EtOH	25.0	1.28×10^{-4}
	HOAc	25.0	4.15×10^{-6}
	TFE	25.0	4.36×10^{-5}
	HCO_2H	25.0	2.22×10^{-4}
	97% HF1P	25.0	1.82×10^{-4}
	TFA	25.0	2.0×10^{-4}
 3	EtOH	25.0	4.03×10^{-5}
	HOAc	25.0	5.52×10^{-5}
	80% EtOH	25.0	6.53×10^{-4}
	60% EtOH	25.0	2.71×10^{-3}
	TFE	25.0	9.24×10^{-4}
	HCO_2H	25.0	5.07×10^{-3}
	97% HF1P	25.0	6.41×10^{-3}
	TFA	25.0	5.9×10^{-3}
 4	EtOH	25.0	4.44×10^{-5}
	80% EtOH	25.0	6.42×10^{-4}
	60% EtOH	25.0	2.86×10^{-3}
	HOAc	25.0	5.82×10^{-5}
	TFE	25.0	5.47×10^{-3}
	HCO_2H	25.0	1.14×10^{-2}
	97% HF1P	25.0	7.11×10^{-2}
 5	EtOH	25.0	1.00×10^{-4}
	HOAc	25.0	7.53×10^{-5}
	80% EtOH	25.0	8.05×10^{-4}
	60% EtOH	25.0	2.21×10^{-3}
	TFE	25.0	1.29×10^{-3}
	HCO_2H	25.0	4.18×10^{-3}
	97% HF1P	25.0	4.51×10^{-3}

[a] EtOH contains 0.025 M 2,6-lutidine; 80% EtOH contains 20% (by volume) water; 60% EtOH contains 40% (by volume) water; HOAc contains 1% acetic anhydride and 0.1 or 0.05 M NaOAc; TFE, 0.025 M 2,6-lutidine in trifluoroethanol; HCO_2H contains 0.05 M sodium formate; 97% HF1P contains 3% (by weight) water in hexafluoroisopropyl alcohol and 0.05 M 2,6-lutidine; TFA contains 0.5% trifluoroacetic anhydride and 0.2 M sodium trifluoroacetate. [b] Extrapolated value. [c] Reference 10b.

Table II. Solvent Ionizing Power Values

solvent	Y_{OTf}	Y_{OTs}
EtOH	−1.50	−1.75
80% EtOH	0.00	0.00
60% EtOH	0.88	0.92
HOAc	−1.78	−0.61
TFE	0.40	1.80
HCO_2H	1.49	3.04
97% HF1P	1.65	3.61
TFA	1.76	4.57

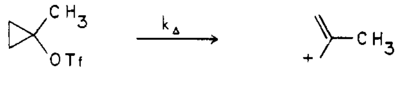
Table III. Correlation of Triflate Solvolysis Rates with Y Values

cmpd	m_{OTs} (r; $S_{y\cdot x}$; n)^a	m_{OTf} (r; $S_{y\cdot x}$; n)^a
1	0.58 (0.921; 0.50; 8)	1.00 (definition)
2	0.27 (0.869; 0.32; 8)	0.49 (0.990; 0.09; 8)
3	0.36 (0.905; 0.35; 8)	0.64 (0.992; 0.10; 8)
4	0.59 (0.969; 0.27; 7)	0.85 (0.966; 0.29; 7)
5	0.34 (0.903; 0.29; 7)	0.54 (0.998; 0.05; 7)
13	0.46 (0.830; 0.63; 8)	0.84 (0.961; 0.31; 8)
13 (omit TFA)	0.60 (0.908; 0.50; 7)	0.94 (0.993; 0.14; 7)
17	0.27 (0.688; 0.52; 5)	0.59 (0.969; 0.18; 5)
18	0.08 (0.171; 0.88; 5)	0.51 (0.671; 0.66; 5)

[a] r = correlation coefficient; $S_{y\cdot x}$ = standard error of estimate; n = number of data points.

Despite the intermediacy of cation **7**, the entire rate spread in the solvents examined is only a factor of 53. A poor correlation ($r = 0.869$) is observed (Figure 2 and Table III) when rates are plotted vs. Y_{OTs}. However, deviations are, in a qualitative sense, similar to those seen for 7-norbornyl triflate. When rate data are plotted vs. Y_{OTf} values (Figure 3), triflate **2** gave a fairly good correlation ($r = 0.990$). The m value of 0.49 is still substantially lower than that for the defining substrate, 7-norbornyl triflate. This suggests that the "small" solvent response in **2** is due not only to the triflate leaving group but also to some other factor. This other factor may well be charge delocalization in the transition state for solvolysis of this k_Δ substrate.

Triflate **3** solvolyzes by a concerted ionization–ring-opening mechanism, giving the allyl cation **10** as the initial intermediate.[15] As in the case of **2**, a poor correlation is obtained when rates are plotted vs. Y_{OTs} values (Table III). When plotted against Y_{OTf} values (Figure 4), a much better correlation ($r = 0.992$) is obtained. The m_{OTf} value of 0.64 is substantially less than 1.0, and, as in the case of **2**, may be due to transition-state charge delocalization or less than "normal" transition-state charge development.



3 10

Triflate **4** solvolyzes by a stepwise ionization to an unopened cyclopropyl cation **11** (a k_c process) which then rapidly opens to an allylic cation **12**.[15a,b] The exo orientation of the triflate group in this ring system precludes the concerted ionization–ring-opening process.[16] The high

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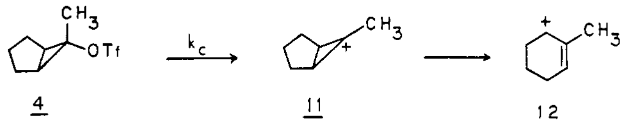
[14] Creary, X. *J. Org. Chem.* **1979**, *44*, 3938–3945.

[15] (a) Creary, X. *J. Org. Chem.* **1976**, *41*, 3734–3739; (b) 3740–3743. For studies on the corresponding tosylate, see: (c) Schleyer, P. v. R.; Sliwinski, W. F.; Van Dine, G. W.; Schöllkopf, U.; Paust, J.; Fellenberger, K. *J. Am. Chem. Soc.* **1972**, *94*, 125–133.

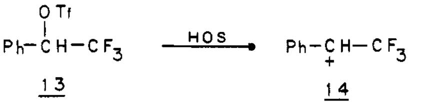


4 11 12

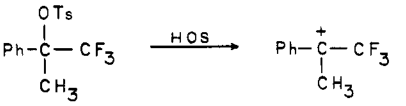
reactivity of **4** in trifluoroacetic acid, which generally gives the largest deviation in Y_{OTs} plots, prevented measurement of rates in this solvent. The m_{OTs} value obtained from the other solvents was 0.59 and the correlation was fair. A rate plot vs. Y_{OTf} values does not significantly change the correlation. However, the m_{OTf} value is 0.85, a value more indicative of a k_c process.

Triflate **5**, which is expected to be substantially less reactive than *endo*-2-norbornyl triflate due to the inductive effect of the ketal functionality,[17] showed trends similar to those of **2** and **3**. The poor correlation seen with Y_{OTs} was substantially improved when rates were plotted vs. Y_{OTf} (Figure 5). For unknown reasons, the m_{OTf} value (0.54) remains substantially smaller than unity.

Correlation of Triflates 13 and 17 with Y_{OTf} Values. Tidwell[5b] has done a detailed study of the reactivity of triflate **13** and concluded that this substrate solvolyzes via a cationic process, generating the "electron deficient cation" **14**. A puzzling feature was the lack of correlation of rate with Y_{OTs} values. This contrasted with the behavior of the tertiary analogue **15**,[5] which gave a good correlation with Y_{OTs} values. We have now plotted rate data for **13** vs. Y_{OTf} values (Figure 6), and a significantly improved correlation (r = 0.961) is seen. The trifluoroacetic acid data still deviates from the line defined by the other solvents, and omission of this data gave a correlation coefficient of 0.993 and an m_{OTf} value of 0.94. Clearly, the behavior of **13** is more analogous to 7-norbornyl triflate than to 2-adamantyl tosylate and supports the suggested intermediacy of cation **14**.

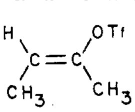

$$\mathrm{Ph{-}\overset{OTf}{C}H{-}CF_3} \xrightarrow{\mathrm{HOS}} \mathrm{Ph{-}\overset{}{\underset{+}{C}}H{-}CF_3}$$

13 14


$$\mathrm{Ph{-}\overset{OTs}{\underset{CH_3}{C}}{-}CF_3} \xrightarrow{\mathrm{HOS}} \mathrm{Ph{-}\overset{+}{\underset{CH_3}{C}}{-}CF_3}$$

15 16

Attention was next turned to vinyl triflates **17** and **18**. It had been previously noted[18] that these triflates gave a poor correlation with $Y_{t\text{-BuCl}}$ values, with rates in acetic acid, TFE, and TFA showing substantial deviations (lower reactivity) from the line defined by aqueous ethanol solvents. Our attempt (Table III) to correlate the date for triflates **17** and **18** with Y_{OTf} values gave only limited success. With use of the five solvents for which data are available, an improved correlation is seen for **17** (m_{OTf} = 0.59; r = 0.969), while a poor correlation is seen for **18**. Rates of solvolysis of **18** in TFE and TFA still fall substantially below the line defined by acetic acid and aqueous ethanol solvents. The reason for the poor correlation for **18** with Y_{OTf} values is uncertain but may be indicative of the importance of solvent nucleophilicity and/or basicity in solvolysis of **18**.



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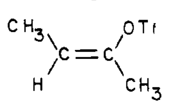

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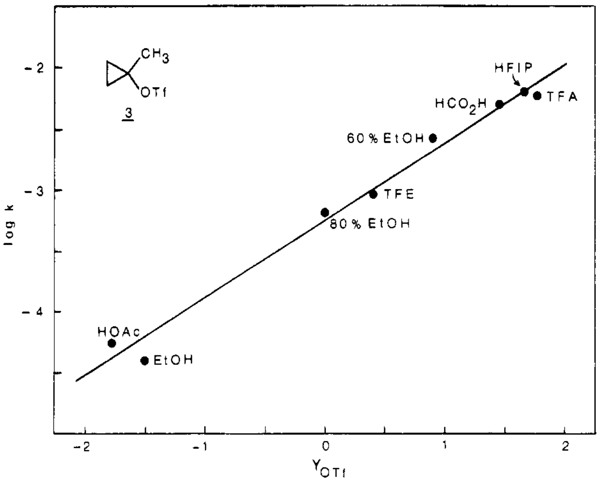

Figure 4. Plot of log k for solvolysis of **3** vs. Y_{OTf}.

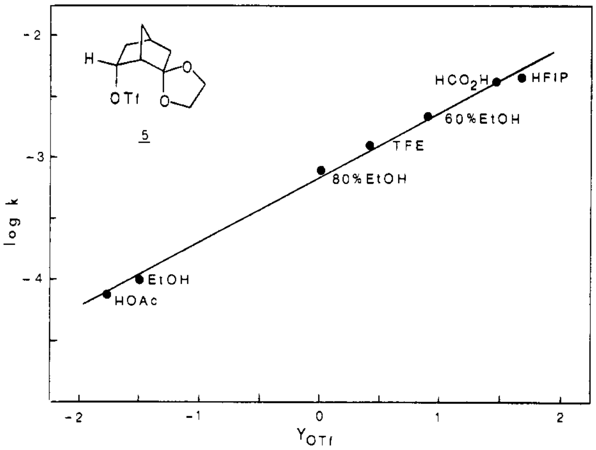

Figure 5. Plot of log k for solvolysis of **5** vs. Y_{OTf}.

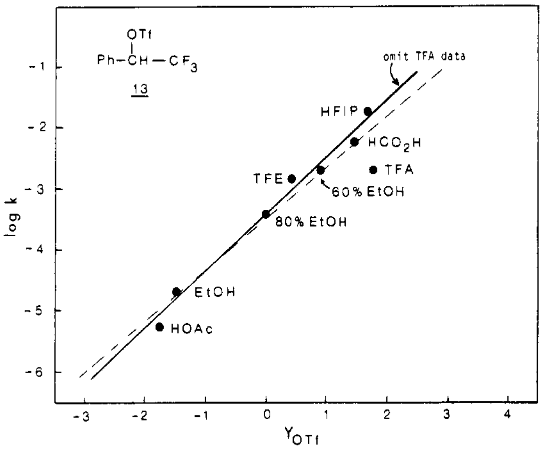

Figure 6. Plot of log k for solvolysis of **13** vs. Y_{OTf}. The solid line excludes data in TFA.

Summary and Conclusions

In general, triflates solvolyze with less than "normal" rate increases with increasing solvent polarity. This overall

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trend is thought to be partially due to the decreased solvation demands of the developing trifluoromethanesulfonate anion which should require less stabilization by hydrogen bonding than chloride or *p*-toluenesulfonate anions. Over a large range of solvents, poor correlations of rate data with Y_{OTs} values were observed. Rates in trifluoroacetic acid were considerably slower than expected on the basis of Y_{OTs} values and rates in ethanol–water mixtures were somewhat faster than expected. The decreased rates of triflate solvolysis in trifluoroacetic acid may be reflecting reduced electrophilic catalysis in loss of the triflate group due to the low basicity of the trifluoromethanesulfonate moiety.

7-Norbornyl triflate has been used to define a set of solvent ionizing power values, Y_{OTf}. In general, triflate solvolysis rates gave superior correlations with these Y_{OTf} values than with Y_{OTs} or $Y_{t\text{-BuCl}}$ values. This also suggests that the solvation requirements of the developing trifluoromethanesulfonate anion are somewhat different from tosylate or chloride. Lack of large rate increases with solvent polarity in solvolysis of triflates therefore does not rule out the involvement of cationic intermediates.

Experimental Section

Triflates 1,[19] 2,[14], 3,[15a] and 4,[15a] were prepared as previously described.

Preparation of 6,6-(Ethylenedioxy)-*exo*-bicyclo[2.2.1]heptan-2-ol. The previous procedure[20] for preparation of this alcohol involved reaction of lithium aluminum hydride in *N*-ethylmorpholine with *exo*-2,3-epoxy-6,6-(ethylenedioxy)bicyclo[2.2.1]heptane. The present procedure uses lithium triethylborohydride (Aldrich Chemical Co.) in di-*n*-butyl ether to open the epoxy ketal.

Three-hundred milliliters of 1.0 M lithium triethylborohydride in tetrahydrofuran was added to 30 g of *exo*-2,3-epoxy-6,6-(ethylenedioxy)bicyclo[2.2.1]heptane in a 1-L flask under nitrogen. The tetrahydrofuran was removed by evacuation of the flask using a water aspirator until a viscous oil remained. The atmosphere in the evacuated flask was replaced with nitrogen, and 200 mL of dry butyl ether was added. The mixture was heated and the temperature in the flask was maintained at 120–125 °C for 10 h. The mixture was cooled to room temperature and about 200 mL of 10% aqueous sodium hydroxide was carefully added. The mixture was transferred to a separatory funnel and extracted with two portions of ether. The combined ether extracts were washed with water and saturated sodium chloride solution and dried over Na_2SO_4. The solvent was removed by rotary evaporator and the residue was distilled to give 22.5 g (74%) of 6,6-(ethylenedioxy)-*exo*-bicyclo[2.2.1]heptan-2-ol,[20] bp 73–75 °C (0.03 mm).

Preparation of 6,6-(Ethylenedioxy)bicyclo[2.2.1]heptan-2-one. Dimethyl sulfoxide (6.3 mL) was dissolved in 50 mL of methylene chloride and the mixture was cooled to −70 °C. Trifluoroacetic anhydride (9.3 g) was added slowly dropwise to the mixture at −70 °C. The hydroxy ketal obtained above (5.0 g) was dissolved in 5 mL of Me_2SO and 5 mL of CH_2Cl_2, and the solution was added dropwise to the −70 °C solution. The mixture was then stirred at −70 °C for 30 min and 12.3 mL of triethylamine was added. The mixture was allowed to warm to room temperature and ether was added, and the organic phase was extracted with three small portions of water. The organic phase was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was removed on a steam bath, and the residue was distilled to give 4.7 g of 6,6-(ethylenedioxy)bicyclo[2.2.1]heptan-2-one: bp 75–83 °C (0.16 mm); IR $\nu_{\mathrm{C=O}}$ 1750 cm^{-1}; NMR (CCl_4) δ 4.2–3.7 (4 H, m), 2.73 (1 H, m), 2.48 (1 H, m), 2.35–1.55 (6 H, m). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.34; H, 7.23.

Preparation of 6,6-(Ethylenedioxy)-*endo*-bicyclo[2.2.1]heptan-2-ol. A solution of 1.31 g of 6,6-(ethylenedioxy)bicyclo[2.2.1]heptan-2-one in 8 mL of ether was added dropwise to a mixture of 0.26 g of $LiAlH_4$ in 30 mL of ether. After being stirred for 30 min at room temperature, a solution of 0.10 g of NaOH in 0.9 g of water was carefully added dropwise. The mixture was stirred for 8 h and $MgSO_4$ was added. After filtration, the solvent was removed on a rotary evaporator. The entire product was chromatographed on 30 g of silica gel and eluted with increasing amounts of ether in Skelly solve F. The product eluted with 20–25% ether. After solvent removal on a rotary evaporator, the residue was distilled to give 0.94 g (71%) of 6,6-(ethylenedioxy)-*endo*-bicyclo[2.2.1]heptan-2-ol: bp 90–93 °C (1.9 mm); NMR ($CDCl_3$) δ 4.4–3.5 (6 H, m), 2.4–0.8 (8 H, M). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.86; H 8.36.

Preparation of Triflate 5. A solution of 0.50 g of the hydroxy ketal obtained above in 5 mL of CH_2Cl_2 was cooled to −50 °C and 0.38 g of 2,6-lutidine was added. To the stirred solution under nitrogen was added 0.92 g of triflic anhydride, and the mixture was then allowed to warm to 0 °C. The mixture was then taken up into ether, washed rapidly with cold water, dilute HCl solution, and saturated NaCl solution, and dried over $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator, leaving 0.86 (97%) of crude triflate **5**. Triflate **5** decomposes readily on standing in the absence of solvent at room temperature. Even at −20 °C, decomposition is substantial after 1 day. A $CDCl_3$ solution also slowly decomposes: NMR ($CDCl_3$) δ 5.21 (1 H, m), 4.2–3.6 (4 H, m), 2.8–1.2 (8 H, m).

Reaction of 7-Norbornyl Triflate with Thiophenoxide in Isopropyl Alcohol. A solution of potassium thiophenoxide in isopropyl alcohol (0.45 M) was prepared under nitrogen by dissolving 1.76 g of potassium metal in isopropyl alcohol, adding 5.0 g of thiophenol, and diluting to 100 mL. A solution of 0.428 g of triflate **1** in 7.8 mL of this solution was sealed under nitrogen in four tubes. After 23 h at room temperature, the contents of the first tube were taken up into ether and water, washed with dilute KOH solution and saturated NaCl solution, and dried over $MgSO_4$. Gas chromatography showed a trace of 7-norbornyl phenyl sulfide. After solvent removal on a rotary evaporator, the residue was analyzed by 300-MHz NMR which showed 96% unreacted 7-norbornyl triflate and 4% 7-norbornyl phenyl sulfide. An analogous reaction of cyclohexyl mesylate for 23 h at room temperature gave 14% unreacted cyclohexyl mesylate and 86% cyclohexyl phenyl sulfide.

The second tube was heated at 70 °C for 290 min and a similar workup followed. Analysis by 300-MHz NMR showed 22% unreacted 7-norbornyl triflate and 78% 7-norbornyl phenyl sulfide. Under the same conditions, cyclohexyl mesylate was completely consumed.

The remaining two tubes were heated at 100 °C for 5 h and a similar workup followed. Gas chromatography showed no unreacted **1**. After solvent removal on a rotary evaporator, 0.177 g (99%) of crude 7-norbornyl phenyl sulfide was obtained: NMR ($CDCl_3$) δ 7.7–7.0 (5 H, m) 3.23 (1 H, br s), 2.5–1.0 (10 H, m).

Kinetics Procedures. Rates of solvolysis of triflates **1**–**5** in acetic acid, ethanol, trifluoroethanol, formic acid, and 97% hexafluoroisopropanol were determined by using the titrimetric method previously described.[6] Sealed ampules were not used for runs at 25 °C. For rapid rates, samples were quenched in acetic acid at about 16 °C, cooled in an ice bath, and titrated as rapidly as possible as previously described. Reactions of **1**–**4** in 80% ethanol and 60% ethanol were monitored by quenching 2-mL aliquots in 4 mL of absolute ethanol and titrating the liberated triflic acid with 0.01 M Et_3N in ethanol. Reactions of **5** in 80% ethanol and 60% ethanol were buffered with 0.025M Et_3N, and the unreacted Et_3N was titrated with 0.01M $HClO_4$ in ethanol.

Solvolysis of **1** in trifluoroacetic acid was monitored by 300-MHz NMR by following the decrease in intensity of the C-7 hydrogen at δ 3.97. The corresponding hydrogen in the product appears 0.07 ppm upfield in TFA. The reaction was monitored for 70 h and the NMR tube was maintained at 25 °C between measurements.

Solvolysis of **3** in TFA was monitored by quenching samples in cold $CDCl_3$ and following the appearance of the olefinic methylene hydrogens or the methylene hydrogens on the carbon bonded to the trifluoroacetoxy group of the product by 300-MHz NMR. Analyses were carried out rapidly since reaction continues to occur (but at a greatly decreased rate) after quenching in $CDCl_3$.

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Note Added in Proof: Professor D. N. Kevill has examined 2-adamantyl triflate and has developed a Y_{OTf} scale based on this substrate. We thank Professor Kevill for informing us of his results prior to publication.

Registry No. 1, 25354-43-2; 2, 71341-17-8; 3, 60153-74-4; 4, 60153-71-1; 5, 94110-61-9; 13, 84877-46-3; 17, 24576-95-2; 18, 24577-69-3; *exo*-2,3-epoxy-5,5-(ethylenedioxy)bicyclo[2.2.1]heptane, 61557-99-1; 6,6-(ethylenedioxy)-*exo*-bicyclo[2.2.1]heptan-2-ol, 61524-55-8; 6,6-(ethylenedioxy)bicyclo[2.2.1]heptan-2-one, 67594-65-4; 6,6-(ethylenedioxy)-*endo*-bicyclo[2.2.1]heptan-2-ol, 94160-56-2; potassium thiophenoxide, 3111-52-2; 7-norbornyl phenyl sulfide, 94110-62-0; triflic anhydride, 358-23-6.

A Novel Dissociative Mechanism in Acyl Group Transfer from Aryl 4-Hydroxybenzoates in Aqueous Solvents[†]

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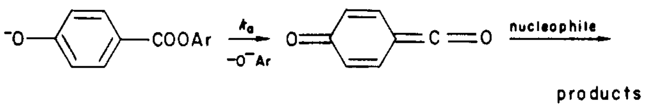
The hydrolysis of aryl 4-hydroxybenzoate esters exhibits the kinetic rate law $k_{\mathrm{obsd}} = (k_a + k_b[\mathrm{OH}^-])/(1 + [\mathrm{H}^+]/K_a)$ where k_b is the second-order rate constant for hydroxide ion attack on the ionized ester and K_a is the ionization constant. The apparent second-order rate constant for the hydrolysis of the 2,4-dinitrophenyl ester (k_aK_a/K_w) is some 340-fold larger than that determined from the Hammett correlation for the alkaline hydrolysis of substituted 2,4-dinitrophenyl benzoates known to possess a $\mathrm{B_{Ac}2}$ mechanism. A slightly positive entropy of activation for k_a and aniline trapping experiments for the 2,4-dinitrophenyl ester are consistent with a mechanism where a *p*-oxo ketene intermediate takes the reaction flux.



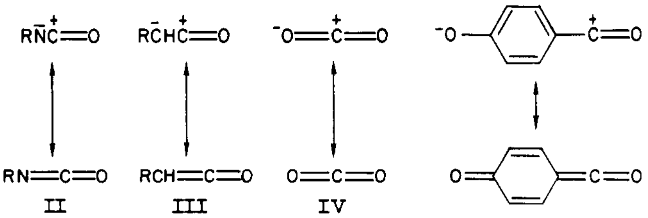
Correlation of k_aK_a/K_w with the pK of the leaving phenol fits the equation $k_aK_a/K_w = 10^{(-1.33\mathrm{p}K+9.57)} + 10^{(-0.35\mathrm{p}K+3.51)}$ which favors the $\mathrm{B_{Ac}2}$ mechanism for poor leaving groups and the E1cB pathway for good leaving groups. There is no reason to postulate a borderline concerted displacement process in this case.

Introduction

We are interested in the factors causing change in mechanisms of acyl group transfer in aqueous solution from associative paths such as the $\mathrm{B_{Ac}2}$ process to dissociative mechanisms for example E1cB or $\mathrm{S_N1}$.[1] Whereas the $\mathrm{S_N1}$ route for acyl group transfer (eq 1) is rare in

$$\mathrm{RCOX} \xrightarrow{-\mathrm{X}^-} \underset{\mathrm{I}}{\mathrm{RCO}^+} \xrightarrow{+\mathrm{Y}^-} \mathrm{RCOY} \qquad (1)$$

aqueous solution because the acylium ion I is unstable, the pathway can be favored if electron-donating features are included in the structure of R which could be RN^-,[2] $\mathrm{RC}^-\mathrm{H}$,[3] or O^-.[4] The acylium ion is thus effectively neutralized as isocyanate (II), ketene (III), or carbon dioxide (IV), respectively. One can conceive of many other ways in which



II III IV V

the $\mathrm{S_N1}$ intermediate could be stabilized to yield a species not normally thought of as an acylium ion.[1] We investigate here the possibility that the *p*-oxo ketene V is an E1cB intermediate. Species similar to V have been discussed in the literature and there is matrix isolation trapping evidence that the *o*-oxo ketene has been isolated.[5] A nitrogen analogue (an *o*-imino ketene) has been observed in the mass spectrometer[6] and similar species have been postulated to explain the formation of novel reaction products.[7] Ketenes and thioketenes fused into aromatic rings have been reported.[8] The species are related to quinones and quinone methides which are well-known compounds; they are liable to be much more reactive than these species however because nucleophilic attack at the

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[†] Dedicated to Professor Giuseppe Leandri on the occasion of his 70th birthday.

[‡] Instituto di Chimica Organica dell'Università.

[§] University Chemical Laboratory.

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