by suction filtration, washed twice with 2-mL portions of cold water, and dried in air. Weight of the free acid 10 was 0.035 g (79%): mp 176 °C (lit.[3] mp 177 °C); TLC, IR, ^{1}H NMR, and EIMS were identical with those of an authentic standard.[3]

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Registry No. 1, 603-83-8; 2, 115118-93-9; 3, 4769-97-5; 4, 7150-46-1; 5, 115118-94-0; 6a, 90947-20-9; 6b, 115118-95-1; 6c, 91974-30-0; 7, 115118-96-2; 8, 115118-97-3; 9, 115118-98-4; 10, 79473-09-9; H_2CO, 50-00-0; $NH(CH_3)_2$, 124-40-3; Eschenmoser's salt, 33797-51-2; 1,2-ethanedithiol, 540-63-6.

Synthesis of 2-(((*p*-Nitrophenyl)sulfonyl)oxy) Esters from Ketene Silyl Acetals and Bis((*p*-nitrophenyl)sulfonyl) Peroxide

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We recently reported that the reactions of enol derivatives of ketones (enol acetates, silyl enol ethers, and enamines) with bis(arylsulfonyl) peroxides provide a very efficient and regiospecific route to 2-((arylsulfonyl)oxy) ketones.[1] These analogues of 2-halo ketones have a much simpler and more selective reactivity pattern than the 2-halo ketones, and they can be readily converted to 2-hydroxy ketals and acetals and 2-amino ketones in high yields.[2]

Since 2-oxygenated carboxylic acids and esters have a great deal of utility in synthesis,[3] it seemed that 2-((arylsulfonyl)oxy) esters might likewise provide useful starting materials for the synthesis of 2-substituted esters and acids. Only a few reports of 2-(sulfonyloxy) esters can be found in the literature. Creary has prepared a few 2-mesyl and 2-triflyl esters as solvolysis substrates.[4] Several reports have appeared that show that 2-triflyl esters are reactive alkylating agents toward nucleophiles.[5] While it has been stated that 2-(mesyloxy) and 2-(tosyloxy) esters are much less useful than the triflates,[5d] to our knowledge no specific compounds or data are available in the literature relevant to this claim.

2-(Sulfonyloxy) esters are invariably made by reaction of the 2-hydroxy ester with a sulfonylating agent. While this route provides high yields and can be used for the preparation of optically active 2-(sulfonyloxy) esters, the 2-hydroxyl group must be already present in the starting material. We wish to report that 2-(((*p*-nitrophenyl)sulfonyl)oxy) (nosyl) esters can be prepared directly from esters by conversion to ketene silyl acetals and reaction with bis((*p*-nitrophenyl)sulfonyl)) peroxide (pNBSP).

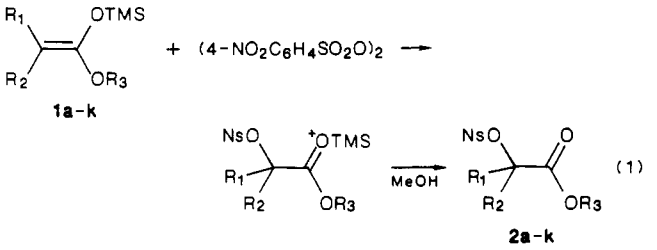
Table I. Preparation of 2-(((*p*-Nitrophenyl)sulfonyl)oxy) Esters from *O*-Trimethylsilyl Ketene Acetals and pNBSP

		yield,[a] %	
ketene acetal	product	method A	method B
1a	**2a**	75	88
1b	**2b**	77	79
1c	**2c**	low	82
1d	**2d**	54	84[b]
1e	**2e**	67	
1f	**2f**	78	79[c]
1g	**2g**	68	
1h	**2h**		67
1i	**2i**		69
1j	**2j**	low	73
1k	**2k**	very low	61

[a] Yields are isolated yields of pure products. [b] This experiment utilized 1.0 equiv of the *O*-trimethylsilyl ketene acetal. [c] The yield with 1.0 equiv of *O*-trimethylsilyl ketene acetal is 79%.

Results and Discussion

A series of *O*-trimethylsilyl ketene acetals, **1a–k**,[6] was reacted with pNBSP (1.0 equiv) and methanol (5 equiv) in ethyl acetate solution at 0 °C (method A). Simple aqueous workup gave the 2-nosyl esters, **2a–k**, isolated by flash chromatography in good to high yields (Table I). The methanol was needed to trap the oxonium ion produced from the electrophilic addition of pNBSP to the silyl ketene acetal double bond (eq 1).[1] If methanol is omitted,



a, R_1 = H; R_2, R_3 = Me
b, R_1 = H; R_2 = Me; R_3 = Et
c, R_1 = H; R_2 = Me; R_3 = *t*-Bu
d, R_1 = H; R_2 = Et; R_3 = Et
e, R_1 = H; R_2 = Et; R_3 = *i*-Bu
f, R_1 = H; R_2 = C_6H_5; R_3 = Me
g, R_1, R_2 = H; R_3 = *i*-Pr
h, R_1, R_2, R_3 = Me
i, R_1, R_2 = $-(CH_2)_5-$; R_3 = Me
j, R_1 = H; R_2, R_3 = $-(CH_2)_3-$
k, R_1 = H; R_2, R_3 = $-(CH_2)_2-$

the product mixtures are much more complex. Too much methanol (>20 equiv) also gave reduced yields because the silyl ketene acetal begins to degrade noticeably. While the stoichiometry of eq 1 indicates a 1:1 ratio of trimethylsilyl ketene acetal to pNBSP, in practice an excess (1.2–1.5 equiv) of the ketene acetal was normally used to ensure complete reaction of the peroxide. Comparable yields were obtained, however, when a 1:1 ratio of reactants was employed for several examples (Table I).

Several *O*-trimethylsilyl ketene acetals failed to give products under these conditions or gave low yields of products that were components of a complex product mixture. It was surmised that the high acidity of the *p*-nitrobenzenesulfonic acid byproduct was causing hydrolysis and/or degradation of the ester function. A simple change (method B) was to use sodium methoxide (1.5

(1) (a) Hoffman, R. V. *Synthesis* **1985**, 760. (b) Hoffman, R. V.; Carr, C. S.; Jankowski, B. J. *J. Org. Chem.* **1985**, *50*, 5148. (c) Hoffman, R. V.; Carr, C. S. *Tetrahedron Lett.* **1986**, *27*, 5811.
(2) Hoffman, R. V.; Jankowski, B. J.; Carr, C. S. *J. Org. Chem.* **1986**, *51*, 130. See also: Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3.
(3) (a) Evans, D. A.; Morrissey, M. M.; Dorow, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 4346. (b) For example: Oppolzer, W.; Dudfield, P. *Helv. Chim. Acta* **1985**, *68*, 216.
(4) (a) Creary, X. *J. Am. Chem. Soc.* **1984**, *106*, 5568. (b) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 4151.
(5) (a) Flynn, G. A.; Giroux, E. L.; Dage, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 7914. (b) Urbach, H.; Henning, R. *Tetrahedron Lett.* **1984**, *25*, 1143. (c) Effenberger, F.; Burkard, U.; Willfahrt, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 65. (d) Shiosaki, K.; Fels, G.; Rapoport, H. *J. Org. Chem.* **1981**, *46*, 3230. (e) Vedejs, E.; Engler, D. A.; Mullins, M. J. *J. Org. Chem.* **1977**, *42*, 3109.
(6) (a) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 59. (b) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.

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equiv) suspended in the reaction mixture in place of methanol. The sodium methoxide served to neutralize the sulfonic acid produced in the electrophilic addition and, at the same time, was a source of methanol to trap the oxonium ion. With this modification, quite good yields were obtained for all the substrates examined, even *tert*-butyl ester **2c** and lactones **2i** and **2k**, which were particularly sensitive to the acidic conditions of method A. As a general rule method B is the preferred method to use, although in many cases comparable yields were obtained with method A.

While the 2-nosyl esters were generally of good purity by NMR spectroscopy of the crude products, they are easily purified by flash chromatography using hexane–ethyl acetate to deliver the reported yields of analytically pure products. The electrophilic addition does not appear to be particularly sensitive to steric effects since methyl, ethyl, isopropyl, isobutyl, and *tert*-butyl esters all give good results (Table I). Furthermore, good yields were obtained for substrates with primary (**1g**), secondary (e.g., **1a,e**), or tertiary (**1h,i**) carbons at the 2-position. The method thus constitutes a versatile route to 2-nosyl esters without the need of a 2-oxygenated precursor.

Experimental Section

All esters used as starting materials were obtained commercially (Aldrich or Sigma) and were used as received. Ethyl acetate was reagent grade material and was used without further purification. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian XL 200 spectrometer. Infrared (IR) spectra were obtained on a Perkin-Elmer 1310 IR spectrometer. Melting points were recorded on a MelTemp apparatus and are uncorrected. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Analytical TLC was performed on Whatman silica gel on glass TLC plates. Flash chromatography was carried out by Still's method.[7] pNBSP was prepared by the method of Dannley.[8]

General Procedure for the Preparation of 2-Nosyl Esters. Method A. To a cooled (0 °C), stirred solution of trimethylsilyl ketene acetal (1.2–1.5 equiv)[9] in ethyl acetate (30 mL) was added bis((*p*-nitrophenyl)sulfonyl) peroxide[8] (1.2–2.0 mmol) followed by methanol (2–10 equiv). After 2 h of stirring at the same temperature, the reaction mixture was stirred at room temperature overnight. The resulting milky solution was diluted with ethyl acetate (30 mL), washed with 2.5 M HCl (3 × 30 mL) and water (50 mL), passed through a short pad of anhydrous $MgSO_4$ and silica gel 60, and concentrated by rotary evaporation to provide the 2-nosyl ester as a pale yellow oil or solid. TLC analysis (hexane/ethyl acetate) showed a single major component was obtained in most cases. Further purification to analytical purity was accomplished by flash chromatography (hexane/ethyl acetate (90:10)).

Method B. To a cooled (0 °C), stirred solution of trimethylsilyl ketene acetal (1.2–1.5 equiv)[9] in ethyl acetate (30 mL) was added bis((*p*-nitrophenyl)sulfonyl) peroxide[8] (1.2–2.0 mmol) followed by sodium methoxide (1.5–1.6 equiv). After 2 h of stirring at 0 °C, the reaction mixture was stirred at room temperature overnight. Workup and product purification were carried out as in method A.

Methyl 2-(((*p*-nitrophenyl)sulfonyl)oxy)propionate (2a) was prepared by method A from 1-(trimethylsiloxy)-1-methoxypropene (**1a**) (1.5 mmol), pNBSP (1.25 mmol), and MeOH (7.5 mmol) as a colorless oil (75%) after purification by flash chromatography (hexane/ethyl acetate (90:10 to 80:20)): NMR ($CDCl_3$) δ 1.60 (d, 3 H, J = 7.0 Hz, $CHCH_3$), 3.71 (s, 3 H, OCH_3), 5.13 (q, 1 H, J = 6.8 Hz, $CHCH_3$), 8.41 and 8.44 (two d, 4 H, aromatic *H*'s); IR (neat) 3100, 2960, 1760, 1530, 1370 cm^{-1}. Anal. Calcd for $C_{10}H_{11}NO_7S$: C, 41.52; H, 3.81; N, 4.84. Found: C, 41.33; H, 3.72; N, 4.68. Method B gave **2a** in 88% yield.

Ethyl 2-(((*p*-nitrophenyl)sulfonyl)oxy)propionate (2b) was prepared by method A from 1-(trimethylsiloxy)-1-ethoxypropene (**1b**) (1.5 mmol), pNBSP (1.3 mmol), and MeOH (3.0 mmol) as a colorless oil (77%) after purification by flash chromatography (hexane/ethyl acetate (90:10 to 80:20)): NMR ($CDCl_3$) δ 1.23 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 1.60 (d, 3 H, J = 7.0 Hz, $CHCH_3$), 4.16 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 5.10 (q, 1 H, J = 7.0 Hz, $CHCH_3$), 8.17 and 8.42 (two d, 4 H, aromatic H's); IR (neat) 3100, 2980, 1750, 1530, 1370, 1180 cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO_7S$: C, 43.56; H, 4.29; N, 4.62. Found: C, 43.53; H, 4.22; N, 4.63. Method B gave **2b** in 79% yield.

***tert*-Butyl 2-(((*p*-nitrophenyl)sulfonyl)oxy)propionate (2c)** was prepared by method B from 1-(trimethylsiloxy)-1-*tert*-butoxy-1-propene (**1c**) (1.6 mmol), pNBSP (1.0 mmol), and NaOMe (1.7 mmol) as white needles (82%) after purification on flash chromatography (hexane/ethyl acetate (90:10)): mp 111–112 °C: NMR ($CDCl_3$) δ 1.42 (s, 9 H, $C(CH_3)_3$), 1.55 (d, 3 H, J = 7.0 Hz, $CHCH_3$), 5.00 (m, 1 H, $CHCH_3$), 8.16 and 8.41 (two d, 4 H, aromatic H's); IR (KBr) 3100, 2990, 1740, 1530, 1360, 1190 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO_7S$: C, 47.13; H, 5.14; N, 4.23. Found: C, 47.15; H, 5.15; N, 4.16. Use of method A gave a complex product mixture in which **2c** was present in low yield.

Ethyl 2-(((*p*-nitrophenyl)sulfonyl)oxy)butyrate (2d) was prepared by method A from 1-(trimethylsiloxy)-1-ethoxy-1-butene (**1d**) (1.5 mmol), pNBSP (1.0 mmol), and MeOH (15 mmol) as a colorless oil (54%) after purification by flash chromatography (hexane/ethyl acetate (90:10 to 80:20)): NMR ($CDCl_3$) δ 0.98 (t, 3 H, J = 7.4 Hz, $CHCH_2CH_3$), 1.23 (t, 3 H, OCH_2CH_3), 1.94 (m, 2 H, $CHCH_2CH_3$), 4.15 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 4.96 (two d, 1 H, $CHCH_2$), 8.30 and 8.42 (two d, 4 H, aromatic H's); IR (neat) 3100, 2980, 1750, 1525, 1370, 1350, 1160 cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO_7S$: C, 45.42; H, 4.73; N, 4.42. Found: C, 45.63; H, 4.69; N, 4.13. Use of method B with **1d** (3.0 mmol), pNBSP (2.0 mmol), and NaOMe (3.3 mmol) gave **2d** in 84% yield. Use of method B with 1 equiv of **1d** gave **2d** in 79% yield.

Isobutyl 2-(((*p*-nitrophenyl)sulfonyl)oxy)butyrate (2e) was prepared by method A from 1-(trimethylsiloxy)-1-isobutoxy-1-butene (**1e**) (1.5 mmol), pNBSP (1.0 mmol), and MeOH (15 mmol) as a colorless oil (67%) after purification by flash chromatography (hexane/ethyl acetate (95:5 to 90:10)): NMR ($CDCl_3$) δ 0.91 (d, 6 H, J = 6.8 Hz, $CH(CH_3)_2$), 0.98 (t, 3 H, J = 7.2 Hz, CH_2,cH_3), 1.90 (m, 3 H, CH_2CH_3, $CH(CH_3)_2$), 3.89 (d, 2 H, J = 6.6 Hz, OCH_2), 4.95 (t, 1 H, OCH), 8.16 and 8.41 (two d, 4 H, aromatic H's); IR (neat) 3100, 2960, 1750, 1600, 1525, 1370, 1340, 1180 cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO_7S$: C, 48.70; H, 5.51; N, 4.06. Found: C, 48.92; H, 5.48; N, 4.04.

Methyl 2-phenyl-2-(((*p*-nitrophenyl)sulfonyl)oxy)acetate (2f) was prepared by method A from 1-(trimethylsiloxy)-1-methoxy-2-phenylethylene (**1f**) (1.5 mmol), pNBSP (1.2 mmol), and MeOH (7.5 mmol) as a white solid (78%) after purification by flash chromatography (hexane/ethyl acetate (90:10)): mp 107.5–108.5 °C; NMR ($CDCl_3$) δ 3.72 (s, 3 H, OCH_3), 5.95 (s, 1 H, PhC*H*), 7.33 (s, 5 H, phenyl H's), 8.27 and 8.32 (two d, 4 H, *p*-NO_2Ph); IR (CH_2Cl_2) 3100, 2950, 1740, 1600, 1530 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_7S$: C, 51.28; H, 3.70; N, 3.99. Found: C, 51.48; H, 3.72; N, 3.72. Use of method B with 1 equiv of **1f** gave **2f** in 79% yield.

Isopropyl (((*p*-nitrophenyl)sulfonyl)oxy)acetate (2g) was prepared by method A from a mixture (~1:1) of 1-(trimethylsiloxy)-1-isopropoxyethylene (**1g**) (3.0 mmol) and isopropyl (trimethylsilyl)acetate, pNBSP (2.0 mmol), and MeOH (30 mmol) as a white solid (68%) after purification by flash chromatography (hexane/ethyl acetate (90:10)): mp 46–48 °C; NMR ($CDCl_3$) δ 1.24 (d, 6 H, J = 6.2 Hz, $CH(CH_3)_2$), 4.72 (s, 2 H, CH_2), 5.03 (m, 1 H, J = 6.2 Hz, CH), 8.19 and 8.43 (two d, 4 H, aromatic H's); IR ($CDCl_3$, NaCl) 3100, 2980, 1750, 1530, 1370, 1180 cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO_7S$: C, 43.56; H, 4.29; N, 4.62. Found: C, 43.90; H, 4.39; N, 4.64.

Methyl 2-methyl-2-(((*p*-nitrophenyl)sulfonyl)oxy)-propionate (2h) was prepared by method B from 1-(trimethylsiloxy)-1-methoxy-2-methyl-1-propene (**1h**) (3.0 mmol), pNBSP (2.0 mmol), and NaOMe (3.0 mmol) as white needles (67%) after purification by flash chromatography (hexane/ethyl acetate (90:10)): mp 88–89 °C; NMR ($CDCl_3$) δ 1.76 (s, 6 H, $C(CH_3)_2$), 3.84 (s, 3 H, OCH_3), 8.18 and 8.41 (two d, 4 H, aromatic

(7) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(8) Dannley, R. L.; Gagen, J. E.; Stewart, O. J. *J. Org. Chem.* **1970**, *35*, 3076.
(9) The trimethylsilyl ketene acetals were prepared by ref 6 and distilled in vacuo just before use.

H's); IR (KBr) 3110, 2950, 1750, 1530, 1350, 1180 cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO_7S$: C, 43.56; H, 4.29; N, 4.62. Found: C, 43.69; H, 4.26; N, 4.55.

Methyl 2-cyclohexyl-2-(((*p*-nitrophenyl)sulfonyl)oxy)-acetate (2i) was prepared by method B from 1-(trimethylsiloxy)-1-methoxy-2-cyclohexylethylene (1i) (2.1 mmol), pNBSP (2.0 mmol), and MeOH (10 mmol) as a colorless oil (69%) after purification by flash chromatography (hexane/ethyl acetate (90:10 to 80:20)): NMR ($CDCl_3$) δ 1.2–2.4 (set of m, cyclohexyl H's), 3.19 (s, 3 H, CH_3), 8.21 and 8.40 (two d, 4 H, aromatic H's); IR (neat) 3100, 2940, 1740, 1530, 1350, 1160 cm^{-1}. Anal. Calcd for $C_{14}H_{17}NO_7S$: C, 49.00; H, 4.96; N, 4.08. Found: C, 49.56; H, 5.05; N, 3.97.

2-(((*p*-Nitrophenyl)sulfonyl)oxy)valerolactone (2j) was prepared by method A from 2-(trimethylsiloxy)-1-oxacyclohex-2-ene (1j) (1.5 mmol), pNBSP (1.0 mmol), and NaOMe (1.6 mmol) as a white solid (73%) after purification by flash chromatography (hexane/ethyl acetate (60:40 to 50:50)): mp 97–98 °C; NMR ($CDCl_3$) δ 2.02–2.70 (m, 4 H, CH_2CH_2), 2.38 (m, 2 H, OCH_2), 5.20 (t, 1 H, OCH), 8.18 and 8.42 (two d, 4 H, aromatic H's); IR (CH_2Cl_2, NaCl) 3050, 2970, 1760, 1530, 1350 1190 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_7S$: C, 43.85; H, 3.65; N, 4.66. Found: C, 44.24; H, 3.77; N, 4.61. Use of method A gave a low yield (15%) of **2j**.

2-(((*p*-Nitrophenyl)sulfonyl)oxy)butyrolactone (2k) was prepared by method B from 2-(trimethylsiloxy)-1-oxacyclopent-2-ene (1k) (3.0 mmol), pNBSP (2.0 mmol), and NaOMe (3.1 mmol) as a white solid (61%) after purification by flash chromatography (hexane/ethyl acetate (60:40)): mp 136 °C; NMR (acetone-d_6) δ 2.50 (m, 1 H, $-CH_2CH_2O-$), 2.80 (m, 1 H, $-CH_2CH_2O-$), 4.46 (m, 2 H, $-CH_2CH_2O-$), 5.64 (t, 1 H, OCHCH$_2$–), 8.38 and 8.58 (two d, 4 H, aromatic H's); IR (KBr) 3100, 2920, 1790, 1565, 1350, 1180 cm^{-1}. Anal. Calcd for $C_{10}H_9NO_7S$: C, 41.81; H, 3.14; N, 4.88. Found: C, 41.98; H, 3.15; N, 4.66.

Studies of the Solvolysis of 2-Adamantyl Pentafluorobenzenesulfonate: A Y_{PFBS} Scale[1]

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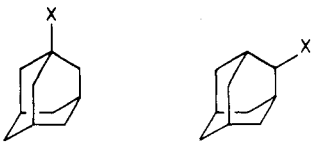
The original Grunwald–Winstein equation (eq 1) defines a scale of solvent ionizing power (Y) based on the specific rates of solvolysis of *tert*-butyl chloride at 25 °C. In eq

$$\log (k/k_0) = mY \quad (1)$$

1, k/k_0 represents the specific rate of solvolysis in the solvent under consideration (k) relative to that in 80% ethanol (k_0), the standard solvent. For *tert*-butyl chloride, m, which represents the sensitivity of the solvolysis to solvent ionizing power, is defined as unity. Though intended as a model for solvolysis by a limiting mechanism, *tert*-butyl chloride has since been shown to solvolyze with some degree of nucleophilic participation, which results in inclusion of a small nucleophilic solvation component in the *tert*-butyl chloride Y scale.[2,3]

In 1-adamantyl substrates (I), backside nucleophilic attack is sterically prohibited by the rigid, caged structure of the adamantyl skeleton.[4] The 2-adamantyl system (II)



I II

has also been shown to lack sensitivity to solvent nucleophilicity,[5,6] It has been demonstrated that solvent effects on the reactivity of 1-adamantyl *p*-toluenesulfonate (tosylate) (I, X = OTs) are virtually identical with those of 2-adamantyl tosylate (II, X = OTs).[7] Consequently, both 1-adamantyl and 2-adamantyl substrates are excellent compounds for defining scales of solvent ionizing power.

Recent investigations[8,9] have given strong support to the viewpoint[3,7,10,11] that each leaving group requires a separate consideration of the influence of solvent variation upon its leaving-group ability. Y_X scales of solvent ionizing power have been developed for a number of nucleofuges based on the solvolyses of 1-adamantyl and 2-adamantyl derivatives (I, X = Cl,[3] Br,[3] I,[12] and picrate;[13] II, X = OTs,[7,10,11] OTf,[9,13] and $OClO_3$[8,13]). In this paper we present an additional scale of solvent ionizing power for pentafluorobenzenesulfonates (Y_{PFBS}) based on the solvolysis of 2-adamantyl pentafluorobenzenesulfonate (II, X = PFBS). This new scale of solvent ionizing power, for a sulfonate leaving group bridging the 10^5–10^6-fold nucleofugality gap between tosylate and trifluoromethanesulfonate (triflate),[14] will be compared with presently existing scales.

Results

Solvolyses in Ethanol, Methanol, Acetic Acid, and 80% Ethanol. Specific rates of solvolysis were determined at four temperatures in the 16–55 °C range. Constant integrated first-order rate coefficients were obtained throughout each kinetic run. The averages of all of the values for the integrated first-order rate coefficients for duplicate runs are reported in Table I. Solvent ionizing power values (Y_{PFBS}) based on 2-adamantyl pentafluorobenzenesulfonate as the standard substrate at 25.0 °C are also presented in Table I. Activation parameters (ΔH^*, ΔS^*) calculated with the data of Table I are listed in Table II.

Solvolyses in Solvents of Varying Ionizing Power. A study has been made at 25.0 °C in the following aqueous organic solvents: 100–70% ethanol (four compositions), 100–80% methanol (three compositions), 95–60% acetone (five compositions), 95–70% dioxane (four compositions), and 100–80% 2,2,2-trifluoroethanol (TFE) (four compositions). A study was also made over a full range of TFE–ethanol mixtures (six compositions). Table III lists the averages of all of the integrated first-order rate coefficients for duplicate runs in each of the solvent mixtures studied, with the exception of those already listed in Table I. Calculated Y_{PFBS} values are also listed within Table III.

(1) Presented in part at the 3rd Chemical Congress of the North American Continent, Toronto, Canada, June 5–11, 1988.
(2) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635.
(3) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.
(4) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977.
(5) 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.
(6) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540.
(7) Bentley, T. W.; Carter, G. E. *J. Org. Chem.* **1983**, *48*, 579.
(8) Kevill, D. N.; Bahari, M. S.; Anderson, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 2895.
(9) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1985**, *50*, 3330.
(10) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.
(11) Bentley, T. W.; Bowen, C. T.; Brown, H. C.; Chloupek, F. J. *J. Org. Chem.* **1981**, *46*, 38.
(12) Bentley, T. W.; Carter G. E.; Roberts, K. *J. Org. Chem.* **1984**, *49*, 5183.
(13) Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 4821.

0022-3263/88/1953-3857$01.50/0