Articles

Alkyl 2,2,2-Trifluoroethanesulfonates (Tresylates): Elimination−Addition vs Bimolecular Nucleophilic Substitution in Reactions with Nucleophiles in Aqueous Media[1]

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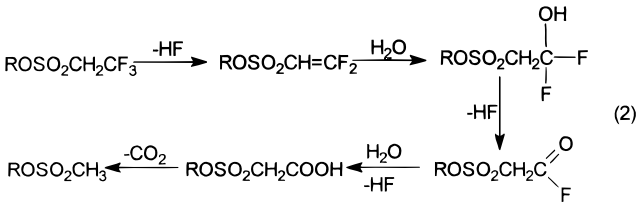
Alkyl 2,2,2-trifluoroethanesulfonate esters (tresylates), $ROSO_2CH_2CF_3$, react with aqueous base (pH ≥ 9) to give the (alkoxysulfonyl)acetic acid, $ROSO_2CH_2COOH$; with the further addition of either a primary or secondary amine or of an alkanethiol, the product is the either the corresponding amide, $ROSO_2CH_2C(O)NR^1R^2$, or a mixture in which the ketene dithioacetal, $ROSO_2CH{=}C(SR^1)_2$, or the thioorthoester, $ROSO_2CH_2C(SR^1)_3$, may predominate. Kinetic and product studies are consistent with the following: (a) the reaction of tresylates with water is the normal sulfonic ester hydrolysis and (b) reaction with hydroxide is an $(E1cB)_{rev}$ process with loss of HF to yield the alkyl 2,2-difluoroethenesulfonate, $ROSO_2CH{=}CF_2$, which rapidly yields the observed products. Benzyl 2,2,2-trifluoroethyl sulfone reacts analogously. The relationship between these observation with small molecules and those of earlier workers with tresyl agarose is discussed.

Esters of sulfonic acids have a long history as useful intermediates enabling the replacement of a hydroxyl group by a wide array of nucleophiles, as in eq 1. Among

$$ROH \longrightarrow ROSO_2R' \xrightarrow{Nu^-} RNu + R'SO_3^- \qquad (1)$$

the most extensively used are *p*-toluenesulfonates (tosylates, R′ = *p*-Tol) and methanesulfonates (mesylates, R′ = CH_3), and, where high reactivity is a particular advantage, trifluoromethanesulfonates (triflates, R′ = CF_3). In 1971 Crossland, Wells, and Shiner[3] introduced 2,2,2-trifluoroethanesulfonates (tresylates, R′ = CF_3CH_2) as "an easily synthesized reactive new leaving group" typically 100 times more reactive than tosylates and 400 times less reactive than triflates in solvolytic reactions. Tresylates have found use in solvolytic studies[4] and to a limited extent in S_N2 reactions with nucleophiles such as azide,[5] thiourea,[5] or thiolate anion.[6]

Relatively recently evidence has emerged suggesting that tresylates do not always react simply by the familiar C−O cleavage process associated with sulfonic esters. In 1993 Choe and Katzenellenbogen[7a] reported that a steroid tresylate reacted at room temperature with tetrabutylammonium fluoride to form the corresponding mesylate ester, perhaps via the pathway shown in eq 2.



(2)

More recently still, Jennissen and co-workers[8] showed that some products derived from treatment of agarose with tresyl chloride followed by reaction with a nucleophile could not have structures of the kind proposed by their original discoverers.[9] Rather than the simple S_N2 displacement products suggested by Nilsson and Mosbach[9] (see eqs 3 and 4), Jennissen and co-workers[8]

$$\text{Agarose}{-}CH_2OSO_2CH_2CF_3 + H_2N{-}L \longrightarrow \text{Agarose}{-}CH_2NH{-}L + HOSO_2CH_2CF_3 \qquad (3)$$

$$\text{Agarose}{-}CH_2OSO_2CH_2CF_3 + HS{-}L \longrightarrow \text{Agarose}{-}CH_2S{-}L + HOSO_2CH_2CF_3 \qquad (4)$$

(L = ligand or enzyme)

proposed a displacement at sulfur with cleavage of the S−C bond (eqs 5−7).

$$\text{Agarose}{-}CH_2OSO_2CH_2CF_3 + 3\ NaOH \longrightarrow \text{Agarose}{-}CH_2OSO_3H + CH_3COOH + 3\ NaF \qquad (5)$$

$$\text{Agarose}{-}CH_2OSO_2CH_2CF_3 + RSH + 3\ NaOH \longrightarrow \text{Agarose}{-}CH_2OSO_2SR + CH_3COOH + 3\ NaF + H_2O \qquad (6)$$

$$\text{Agarose}{-}CH_2OSO_2CH_2CF_3 + RNH_2 + 3\ NaOH \longrightarrow \text{Agarose}{-}CH_2OSO_2NHR + CH_3COOH + 3\ NaF + H_2O \qquad (7)$$

⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Organic Sulfur Mechanisms. 40. For part 39, see ref 2. Presented in part at the 78th Canadian Society for Chemistry Conference, Guelph, Ontario, May 1995.

(2) King, J. F.; Guo, Z. R.; Lock, J. D. *Phosphorus Sulfur Silicon* **1994**, *97*, 191−197.

(3) Crossland, R. K.; Wells, W. E.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4217−4219.

(4) See, for example: Shiner, V. J., Jr.; Fisher, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2553−2554. Shiner, V. J., Jr.; Seib, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 862−864. McDonald, R. N.; Curi, C. A. *J. Am. Chem. Soc.* **1979**, *101*, 7116−7118.

(5) King, J. F.; Loosmore, S. M.; Aslam, M.; Lock, J. D.; McGarrity, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 7108−7122.

(6) McManus, S. P.; Karaman, R. M.; Sedaghat-Herati, R.; Hovanes, B. A.; Ding, X.-T.; Harris, J. M. *J. Org. Chem.* **1993**, *58*, 6466−6469.

(7) (a) Choe, Y. S.; Katzenellenbogen, J. A. *Tetrahedron Lett.* **1993**, *34*, 1579−1580. (b) Golding, B. T.; Griffin, A. L.; Robinson, D. H. *Tetrahedron Lett.* **1993**, *34*, 6459−6462.

(8) Demiroglou, A.; Bandel-Schlesselmann, C.; Jennissen, H. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 120−123.

(9) Nilsson, K.; Mosbach, K. *Biochem. Biophys. Res. Commun.* **1981**, *102*, 449−457.

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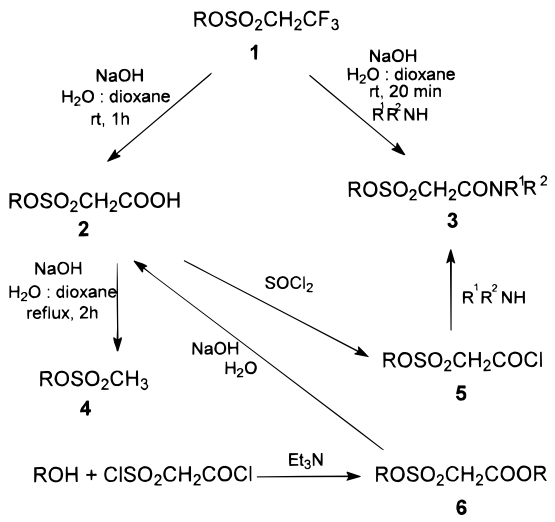
Scheme 1[a]



[a] (**a**) R = Me_3CCH_2; (**b**) R = Me_2CHCH_2; (**c**) R = Et; (**d**) R = $Me(CH_2)_7$.

The suggested reactions of Jennissen and co-workers, however, have no parallel that we are aware of in the chemistry of sulfonic esters, nor there is any known or readily imagined mechanism that would satisfactorily account for the formation of acetic acid and sulfuric, thiosulfuric, or sulfamic esters under these conditions. It therefore seemed to us that another reaction pathway would be much more likely. In our view such a route might be an elimination−addition process following the pattern demonstrated initially for substitution β to a sulfonyl group by Stirling and co-workers[10] and closely related to that suggested for the reactions of tresylates with fluoride or acetate[7] ions, and also for transformations observed by Eleev, Sokol'skii, and Knunyants with tresyl fluoride.[11] To obtain information on the matter, we have carried out a study of the reactions of some simple alkyl tresylates with aqueous sodium hydroxide in the presence of some simple amines and thiols, and now report our results. A preliminary report describing some of these experiments has appeared;[12] essentially the same conclusion for the reaction of butylamine in a related model system has been independently reported by Gais and Ruppert.[13]

Results and Discussion

Reactions and Products. Neopentyl tresylate (**1a**) was chosen as the substrate for our first experiments, because it would be expected to show minimal rates of simple alkyl transfer resulting from attack of nucleophiles with C−O cleavage, while at the same time being well setup to undergo reactions at the trifluoroethyl group. The reactions of **1a** and other esters with hydroxide and amines are summarized in Scheme 1. With 0.5 M NaOH in 1:1 H_2O−dioxane **1a** gave ((neopentyloxy)sulfonyl)acetic acid (**2a**) in 90% yield. The structure of **2a** follows from (a) its conversion (in 60% yield) to neopentyl mesylate (**4a**) on refluxing with aqueous base and (b) its synthesis by partial hydrolysis of dineopentyl sulfoacetate (**6a**) which was in turn prepared from (chlorosulfonyl)acetyl chloride and neopentyl alcohol.[14] Also shown in Scheme 1 are the reactions of **1a** with butylamine to give **3a** (R^1 = Bu, R^2 = H), and with diethylamine to form the corresponding diethylamide (**3a**, $R^1 = R^2$ = Et) in 30% and 80% yields, respectively. The structures follow from spectra and their syntheses from **2a** via the acid chloride (**5a**). These results and those recently reported by Gais and Ruppert[13] are in complete accord.

Shown in Scheme 2 are the reactions of **1** with sodium hydroxide with added phenylmethanethiol. With equimolar amounts of **1a** and thiol, a 3:4:3:1 mixture of **2a**, the stereoisomeric fluoro monosulfides (**7a**), the ketene dithioacetal (**8a**), and the benzyl thioester (**9a**) was obtained; with a 3-fold excess of the thiol the product was entirely **8a** (80% yield). The structure of **8a** is assigned from spectra, mode of synthesis, and its conversion into a mixture of **4a** and 1,1,2-tris((phenylmethyl)thio)ethene (**11**), on refluxing with 4.5 M NaOH in H_2O:dioxane for 39 h.[15] The trisulfide (**11**) was synthesized independently from phenylmethanethiol, sodium ethoxide, and trichloroethene, following the general procedure of Truce and Kassinger.[16] The structures of the fluoro sulfides (**7a**) followed also from their spectra, mode of synthesis, and further reactions; the latter included (a) conversion of one isomer to **8a** with aqueous sodium hydroxide and phenylmethanethiol under mild conditions and (b) transformation of the other isomer slowly with aqueous NaOH into a mixture of **2a** and **8a** containing a small amount of the thioester (**9a**). The geometry of the fluoro sulfides (**7a**) was deduced from the hydrogen−fluorine coupling constants; that with the 28.6 Hz coupling was assigned the *trans* H−F arrangement as in *E*-**7a**, and the isomer with the 16.5 Hz coupling the *cis* H−F geometry as in *Z*-**7a**. The thioester (**9a**) was not isolated in pure form from either of the reaction products above; its presence in the mixture was deduced from the observation of characteristic ^{1}H NMR signals at δ 3.90, 4.22, and 4.25 found with an authentic **9a** prepared from the acid chloride (**6a**) and phenylmethanethiol. Interestingly, treatment of a sample of **9a** under conditions comparable to those that yield **8a** and **10a** led only to partial (10%) hydrolysis to **2a**, with most (90%) of the **9a** recovered unchanged.

Replacement of the neopentyl group in **1a** with other alkyl groups (**1b**−**1d**) led to relatively small changes in the reactions in Schemes 1 and 2. With isobutyl tresylate (**1b**) the reaction with 3 equivs of phenylmethanethiol (and reaction time of 40 min) gave principally the ketene dithioacetal (**8b**) along with a smaller amount of the thioorthoester (**10b**) (ratio 4:1). With 7 equivs of thiol (reaction time 260 min) or 20 equivs (reaction time 75 min) the thioorthoester was the major product (3:1 ratio of **10b** to **8b**). The formation of **8a** from **1a** without any sign of any **10a** would appear to arise at least partly from the low solubility of **8a** which leads to its spontaneous precipitation from the reaction mixture. This does not occur with the isobutyl and ethyl esters, and the corre-

(10) Stirling, C. J. M. *Chem. Ind. (London)* **1960**, 933. Kader, A. T.; Stirling, C. J. M. *J. Chem. Soc.* **1962**, 3686−3692 and later papers in this series.

(11) Eleev, A. F.; Sokol'skii, G. A.; Knunyants, I. L. *Izv. Akad. Nauk SSSR Ser. Khim.* **1978**, 2084−2090 (Engl. Transl. 1837−1842).

(12) King, J. F.; Gill, M. S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1612−1613.

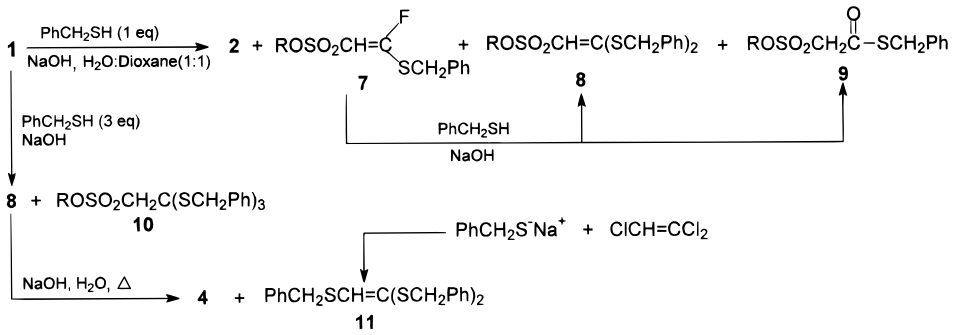
(13) Gais, H.-J.; Ruppert, S. *Tetrahedron Lett.* **1995**, *36*, 3837−3838.

(14) *Cf.* R. Vieillefosse, *Bull. Soc.Chim. Fr.* **1947**, 351−356.

(15) The survival under these conditions of (a considerable portion of) the neopentyl mesylate (**4a**) formed emphasizes the slowness of the S_N2 reactions of neopentyl sulfonic esters.

(16) Truce, W. E.; Kassinger, R. *J. Am. Chem. Soc.* **1958**, *80*, 1916−1919.

Scheme 2[a]



[a] (**a**) R = Me_3CCH_2; (**b**) R = Me_2CHCH_2; (**c**) R = Et; (**d**) R = $Me(CH_2)_7$.

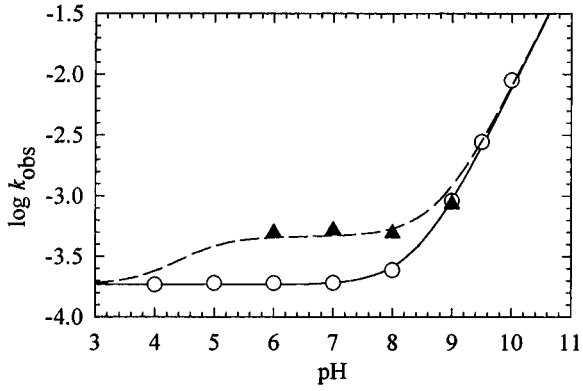
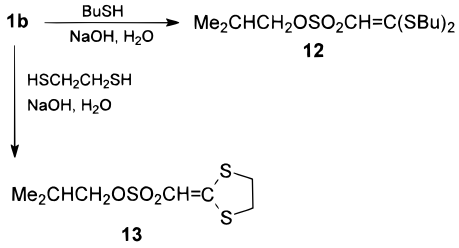


Figure 1. pH−rate profile for the hydrolysis of ethyl tresylate (**1c**) (circles) and for the reaction of **1c** with aniline (0.05 M) in water, at 25.0 °C. The lines are calculated from the equations $k_{obs} = k_w + k_{OH}[OH^-]$ (solid line) and $k_{obs} = k_w + k_{OH}[OH^-] + k_N[PhNH_2]$ (dashed line) using $k_w = 1.85 \times 10^{-4}$ s^{-1}, $k_{OH} = 75$ M^{-1} s^{-1}, and $k_N = 5.5 \times 10^{-3}$ M^{-1} s^{-1}; the points are experimental.

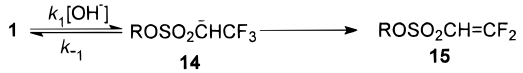
sponding thioorthoesters (**10b** and **10c**) are formed in the reactions with the relatively higher proportions of phenylmethanethiol. Butanethiol (3 equiv, 15 min) gave the ketene dithioacetal (**12**) with no sign of the thioorthoester; ethane-1,2-dithiol also yielded only the dithioacetal (**13**).



An unexpected feature of the reactions of the ethyl and octyl esters (**1c** and **1d**) is the comparative insignificance of the direct S_N2 reaction at carbon with loss of the tresylate anion. Our limited study of the octyl ester (**1d**) showed no sign of any S_N2 reaction, while the ^1H NMR spectrum of the products of the reaction of the ethyl ester (**1c**) with $PhCH_2SH$ indicated the presence of perhaps 5% of the S_N2 product, $PhCH_2SEt$. In another experiment using less phenylmethanethiol (2.2 equiv, 15 min) the ratio of **8d**:**10d**:$PhCH_2SEt$ was found to be 77:22:1. The ^{19}F NMR spectrum of the aqueous phase showed the fluorine to be present almost entirely as fluoride anion (≥99.5%) with only a trace of tresylate anion (≤0.5%); it would appear that the benzyl ethyl sulfide probably arises more from reaction of the thiolate anion with **8d** and (or) **10d** than with **1d**.

Rate Studies. The pH−rate profile of the hydrolysis of **1c** was obtained by the pH−stat method and is shown in Figure 1 (circles); this yields the rate law $k_{obs} = k_w + k_{OH}[OH^-]$. The ^1H NMR spectrum of the products of the deuterolysis at pD ≤ 8.0 showed the presence of CH_3CH_2OD and $CF_3CH_2SO_3^-$, but at pD 13.7 the product consisted of $CH_3CH_2OSO_2CD_2COO^-$ along with a small amount of the monodeuterated material, $CH_3CH_2OSO_2CHDCOO^-$. In an experiment in which NaOD in D_2O was added to a solution of **1a** in CD_3CN:D_2O, the ^{19}F NMR signal due to neopentyl 2,2,2-trifluoroethanesulfonate changed from a triplet to mixtures of a triplet, doublet, and singlet (due to a mixture of the CH_2, CHD, and CD_2 isotopomers) and finally to a product consisting mostly of $CF_3CD_2SO_2OCH_2CMe_3$ along with some of the solvolysis product (chiefly $CF_3CD_2SO_3^-$). It would appear that the reaction of water (k_w term) is exclusively the conventional solvolysis usual with sulfonic esters, whereas the reaction of hydroxide anion is clearly consistent with the reversible E1cB reaction shown below. The subsequent Michael-type reactions of **15** with amines or phenylmethanethiolate anion would appear to be fast since there is no sign of any buildup of **15** in the reaction mixture.

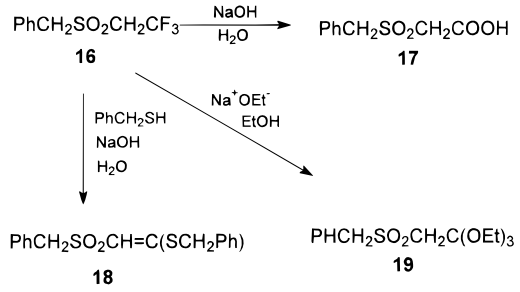
The pH−rate profile for the reaction of **1c** with aqueous aniline is also shown in Figure 1 (triangles) and corresponds to the rate expression $k_{obs} = k_w + k_{OH}[OH^-] + k_N[PhNH_2]$. Examination of the product of the reaction at pH 6 showed the presence of *N*-ethylaniline (21% yield), as expected if the k_N term is a simple S_N2 displacement at carbon by aniline. At the high pH end of the reaction range studied, $k_{OH}[OH^-] \gg k_N[PhNH_2]$ and the formation of **15** and its subsequent reactions become the major processes.



A reversible E1cB process is specific base catalyzed and is therefore not expected to show any acceleration with added amines, provided they act only as bases and not as nucleophiles. With dibutylamine (0.01 M total amine concentration, at pH 9.5) the pseudo-first-order rate constant was found to be 2.5×10^{-3} s^{-1} as compared to 2.8×10^{-3} s^{-1} without the amine; analogously, diethylamine (0.1 M, pH 9.0) gave $k_{obs} = 12.2 \times 10^{-4}$ s^{-1} vs 9.1×10^{-4} s^{-1} for the reaction at pH 9.0 without the amine. These results are thus in good agreement with an $(E1cB)_{rev}$ mechanism with very little or no direct nucleo-

philic attack of the amine on the ester (**1c**). The reaction of the thiolate anion is presumably similar.

Reactions of Benzyl 2,2,2-Trifluoroethyl Sulfone. Virtually all of the reactions shown in Schemes 1 and 2 do not require the sulfonic ester function and would be expected to appear in appropriately modified form in the reactions of other substrates bearing the 2,2,2-trifluoroethylsulfonyl group. Accordingly benzyl 2,2,2-trifluoroethyl sulfone (**16**) was found to react with aqueous NaOH with and without phenylmethanethiol to yield **18** and **17**, respectively; also shown is the formation of the orthoester (**19**) by the reaction of sodium ethoxide in ethanol.



Reactions of Tresyl Agarose. As is noted in the introduction, the present study was prompted by the report by Jennissen and co-workers[8] putting forward what appeared to us to be highly suspect structures for the products of the solid phase reactions of tresyl agarose with nucleophiles in the presence of base. It is our view that the study of solid phase polymer reactions should be informed by a thorough knowledge of the analogous solution phase chemistry, and hence we set out to do the experiments described in this paper. In our communication[12] we suggested that our model studies and the evidence of Jennissen *et al*. published at that point were consistent with the products being not those shown in eqs 5−7 but rather, respectively, agarose−$CH_2OSO_2CH_2$-COOH (**20**), agarose−$CH_2OSO_2CH_2C(O)NHBu$ (**21**), and a mixture of **20** and agarose−$CH_2OSO_2CH{=}C(SBu)_2$ (**22**). In reviewing our paper Professor Jennissen provided some unpublished information (notably a set of CP/MAS ^{13}C NMR spectra) from which one might conclude that butyl-*SS*-agarose (the product from the reaction with butanethiol) could well be more complex than we had indicated. Accordingly we simply suggested that in view of the complexity of the products from **1,** butyl-*SS*-agarose could well have a complex composition, with components corresponding to any (or all) of the (seven) structures encountered in our model studies, i.e., in addition to **20** and **22**, $ROSO_2CH{=}CFSBu$ (*E* and *Z* isomers), $ROSO_2CH_2C(SBu)_3$, $ROSO_2CH_2CO$-SBu, and even RSBu. In addition there are the further possibilities of (a) simple hydrolysis to give back the agarose unit and (b) a reaction of the analogue of **15** with one or more of the hydroxyl groups of the carbohydrate; the formation of the orthoester (**19**) from **16** suggests one possible mode.

In a Comment on our paper, Jennissen[17a] announced his conclusion that he concurred with our structures **20** and **21**, but took issue with our initial suggestion for the structure for butyl-*S*,*S*-agarose. In our Reply we reiterated[17b] our proposal that butyl-*S*,*S*-agarose may have a complex structure, as previously mentioned; we regard this picture, perhaps with further modifications as noted in the paragraph above, as sufficient to account for the available information.

In our view it is unlikely that our model reactions and those of the solid phase system will be either (a) qualitatively very different or (b) quantitatively identical. The local environment (especially steric aspects) of any tresylate ester in tresyl agarose will differ one from another depending on its location in the solid phase polymer, and it is unlikely that many of these will have environments identical to those of the alkyl tresylate models (**1a** to **1d**). In the reaction of alkyl tresylates with a thiolate anion, the model system is clearly complex and it is unreasonable to expect the solid phase reactions to show the same subtle balance of competing influences leading to the same balance of products—even though the products are in all likelihood derived from fundamentally the same chemistry.

Experimental Section

Instrumentation and general procedures are the same as described elsewhere,[18] except as noted below. ^{19}F chemical shifts are relative to $CFCl_3$; IR spectra were obtained using a Perkin Elmer 2000 FT-IR spectrometer. Melting points were determined using either a Kofler Hot Stage or a Gallenkamp melting point apparatus and are uncorrected. Kieselgel, silica gel for TLC (containing 5% $CaSO_4$, purchased from Inter Science, Markham, Ontario), was used for thin-layer chromatography and thick-layer preparative plates. Workup refers to (a) addition of 1 M H_2SO_4 to pH 1−2, (b) extraction with dichloromethane, (c) drying of the organic extract with anhydrous magnesium sulfate, and (d) evaporation of the solvent using a Büchi rotary evaporator connected to a water aspirator. (Chlorosulfonyl)acetyl chloride was prepared by the procedure of Hinman *et al*.[19] in 30% yield, as a clear liquid, ^1H NMR δ 5.07 (s); reported ^1H NMR δ 5.06 (s).[20] Dichloromethane was distilled from calcium hydride prior to use; otherwise reagent grade chemical and solvents were used as received. pD = pH meter reading + 0.37.

Preparation of, spectrometric data for, and interconversions among **1a**, **2a**, **3a**, **5a**, *E*-**7a**, *Z*-**7a**, **8a**, and **11** are given elsewhere.[12]

Materials and Authentic Specimens. Tresylates (1b−1d) were obtained by the procedure of Crossland *et al*.[3] **Isobutyl 2,2,2-trifluoroethanesulfonate (1b):** clear liquid, 74% yield; IR ($CHCl_3$) ν_{max} 2967 (w), 1387 (s), 1325 (s), 1275 (s), 1259 (s), 1186 (s), 1138 (s), 1081 (s), 960 (s), 947 (s) cm^{-1}; ^1H NMR δ 1.00 (d, J = 7 Hz, 6H), 2.07 (nonet, 1H), 3.90 (q, J = 8.8 Hz, 2H), 4.12 (d, J = 7 Hz, 2H); ^{13}C NMR δ 18.3, 28.2, 53.4 (q, J = 32.2 Hz), 78.0, 121.0 (q, J = 277.5 Hz); ^{19}F NMR δ −62.64 (t, J = 8.4 Hz). **Ethyl 2,2,2-trifluoroethanesulfonate (1c):** clear liquid, 55% yield; IR ($CHCl_3$) ν_{max} 1384 (s), 1326 (s), 1275 (s), 1259 (s), 1185 (vs), 1139 (s), 1090 (s), 997 (s), 929 (vs) cm^{-1}; ^1H NMR δ 1.46 (t, J = 7 Hz, 3H), 3.89 (q, J = 8.8 Hz, 2H), 4.43 (q, J = 7 Hz, 2H); ^{13}C NMR δ 14.9, 52.6 (q, J = 33 Hz), 69.0, 121.0 (q, J = 277.5 Hz); ^{19}F NMR δ −63.67 (t, J = 9 Hz), reported ^1H NMR δ 1.40 (t, J = 7 Hz, 3H), 3.90 (q, J = 9 Hz, 2H), 4.40 (q, J = 7 Hz, 2H) and ^{19}F NMR (CF_3COOH) δ 16.0 (t, J = 9 Hz).[21] **Octyl 2,2,2-trifluoroethanesulfonate (1d)**: clear liquid, 80% yield; ^1H NMR δ 0.88 (t, 3H), 1.28 (br s, 10H), 1.78 (m, 2H), 3.88 (q, J = 8.7 Hz, 2H), 4.35 (t, J = 7 Hz, 2H). Authentic **4** was

(17) (a) Jennissen, H. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2495. (b) King, J. F.; Gill, M. S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2495.

(18) King, J. F.; Rathore, R.; Lam, J. Y. L.; Guo, Z. R.; Klassen. D. F. *J. Am. Chem. Soc.* **1992**, *114*, 3028−3033.

(19) Hinman, R. L.; Locatell, L., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 5655−5658.

(20) Pouchert, C. J.; Behnke, J. *Aldrich Library of ^{13}C and ^1H FT NMR Spectra.* **1** (1), 1415C.

(21) Ohta, Y.; Kohda, K.; Kimoto, H.; Okano, T.; Kawazoe, Y. *Chem. Pharm. Bull.* **1988**, *36*, 2410−2416.

prepared from neopentyl alcohol and MsCl[22] (84% yield): IR (neat) ν_{max} 1480 (m), 1354 (vs), 1176 (vs), 967 (vs), 846 (s) cm^{-1}; ^1H NMR δ 0.99 (s, 9H), 3.00 (s, 3H), 3.87 (s, 2H); ^{13}C NMR δ 25.8, 31.5, 36.7, 78.9; reported ^1H NMR δ 0.98 (s, 9H), 2.98 (s, 3H), 3.82 (s, 2H).[23]

Neopentyl ((Neopentyloxy)sulfonyl)acetate (6a). A solution of neopentyl alcohol (194 μL, 2.2 mmol) and (chlorosulfonyl)acetyl chloride (214 mg, 1.2 mmol) in dichloromethane (7 mL) was stirred at rt for 30 min and then cooled in an ice bath; triethylamine (87 μL, 1.2 mmol) was added and the mixture stirred for 15 min in ice bath and for 30 min at rt. Workup gave **6a** (214 mg, 69.5%) as an oil purified on a thick-layer preparative plate by eluting with toluene:diethyl ether (10:1) and extracting with dichloromethane (112 mg, 36.4%): IR ($CHCl_3$) ν_{max} 2965 (s), 1742 (s), 1497 (s), 1370 (vs), 1292 (s), 1178 (s), 1119 (s), 962 (vs) cm^{-1}; ^1H NMR δ 0.98 (s, 9H), 1.0 (s, 9H), 3.92 (s, 2H), 4.0 (s, 2H), 4.12 (s, 2H); ^{13}C NMR δ 25.9, 26.2, 31.4, 31.8, 54.6, 75.8, 80.9, 162.1. **6a** (18.9 mg, 0.07 mmol) in 1 M NaOH (1 mL, 1 mmol) was stirred at rt for 18 h. Workup gave **2a** (8.8 mg, 62%) as a clear liquid with ^1H and ^{13}C NMR spectra identical to those of the previously prepared **2a**.[12]

Benzyl ((Neopentyloxy)sulfonyl)thioacetate (9a). **5a** (20 mg, 0.087 mmol) was treated with excess phenylmethanethiol in an NMR tube in $CDCl_3$; after a week **9** was isolated and purified on a thick-layer preparative plates eluting with ethyl acetate:petroleum ether (35−60 °C) to give a white solid (21 mg, 75%), which was recrystallized from diethyl ether:petroleum ether (bp 35−60 °C), mp 47−48 °C: IR ($CHCl_3$) ν_{max} 3032 (w), 2966 (w), 1688 (s), 1368 (w), 1177 (s), 1020 (w), 957 (vs), 893 (w), 839 (w) cm^{-1}; ^1H NMR δ 0.96 (s, 9H), 3.90 (s, 2H), 4.22 (s, 2H), 4.25 (s, 2H), 7.25−7.31 (m, 5H); ^{13}C NMR δ 25.9, 31.9, 34.3, 60.7, 81.1, 127.7, 128.7, 128.9, 135.9, 185.8. **9** (19 mg, 0.6 mmol) was dissolved in 1 M NaOH (0.2 mL, 0.2 mmol) and dioxane (0.25 mL) and stirred at rt for 25 min. Workup gave a clear liquid, the ^1H NMR spectrum of which showed signals due to **2a** (10%) and unreacted **9a** (90%).

Reaction of 1a with NaOD/D_2O. To a solution of **1a** (20 mg, 0.09 mmol) in CD_3CN (0.3 mL) in an NMR tube was added an NaOD/D_2O solution (pD 12.07) dropwise, and the reaction was monitored by ^{19}F NMR. In a series of five spectra over an 80 min interval the initial triplet at −62.20 ppm due to **1a** was replaced by (an initially larger) a doublet at −62.29 and a singlet at −62.38 ppm due to the CHD and CD_2 isotopomers, respectively; the final trace showed the doublet and the singlet (ratio ~1:10) along with signals at −62.73 (d) and −62.51 (s) ppm assigned to the CHD and CD_2 isotopomers of the tresylate anion.

((Isobutyloxy)sulfonyl)acetic Acid (2b). **1b** (32 mg, 0.01 mmol) in 1 M NaOH (0.5 mL, 0.5 mmol) and dioxane (0.25 mL), reacted at rt for 30 min and then made acidic and extracted with $CDCl_3$ (1 mL), gave **2b** (17 mg, 60%), as a clear liquid: IR ($CHCl_3$) ν_{max} 3031 (w), 2968 (s), 1741 (s), 1370 (vs), 1175 (s), 972 (s), 949 (s), 912 (W) cm^{-1}; ^1H NMR δ 0.99 (d, 6H), 2.07 (1H), 4.14 (d, 2H), 4.16 (s, 2H), 8.55 (br s, 1H); ^{13}C NMR δ 18.5, 28.3, 54.2, 78.1, 165.8. **((Octyloxy)sulfonyl)-acetic Acid (2d).** **1d** (49 mg, 0.18 mmol) similarly gave **2d** (27 mg, 60%) as a clear liquid: ^1H NMR δ 0.88 (t, 2H), 1.28 (br s, 10H), 1.77 (m, 2H), 4.15 (s, 2H), 4.36 (t, J = 6.5 Hz, 2H). **(Ethoxysulfonyl)acetic Acid (2c).** **1c** (20 mg, 0.1 mmol) similarly gave **2c** (10 mg, 57%) as a clear liquid: ^1H NMR δ 1.45 (t, 3H), 4.14 (s, 2H), 4.44 (q, 2H), 5.12 (br s, 1H); ^{13}C NMR δ 15.1, 54.5, 68.9, 165.1.

Reaction of 1b with Excess Phenylmethanethiol and Aqueous NaOH. (i) 1b (58.8 mg, 0.27 mmol) in dioxane (0.3 mL) and phenylmethanethiol (94 μL, 0.8 mmol) in 1 M NaOH (0.67 mL, 0.67 mmol) at rt for 40 min gave an oil, shown by ^1H NMR to be a mixture of 1-((isobutyloxy)sulfonyl)-2,2-bis-((phenylmethyl)thio)ethene (**8b**), 1-((isobutyloxy)sulfonyl)-2,2,2-tris((phenylmethyl)thio)ethane (**10b**) (4:1 ratio), and unreacted phenylmethanethiol. The product mixture was separated on a thick-layer preparative plate, eluting with ethyl acetate:petroleum ether (35−60 °C) (1:8), to give **8b** (white solid, 65 mg, 50.5%) as the lower band and **10b** (liquid, 21 mg, 15%) as the upper band. **8b**: mp 69−70 °C; IR ($CHCl_3$) ν_{max} 3032 (w), 2969 (w), 1496 (s), 1355 (vs), 1179 (vs), 976 (s), 943 (s), 852 (w) cm^{-1}; ^1H NMR δ 0.90 (d, J = 9 Hz, 6H), 1.90 (nonet, 1H), 3.67 (d, J = 7 Hz, 2H), 4.06 (s, 2H), 4.27 (s, 2H), 6.02 (s, 1H), 7.25−7.38 (m, 10H); ^{13}C NMR δ 18.7, 28.0, 37.5, 39.0, 76.1, 113.9, 127.7, 128.1, 128.6, 128.9, 128.93, 129.2, 133.6, 135.5, 156.8. **10b**: IR ($CHCl_3$) ν_{max} 3032 (w), 2966 (w), 1602 (w), 1495 (s), 1454 (s), 1368 (vs), 1175 (vs), 1162 (vs), 971 (vs), 947 (vs), 818 (w) cm^{-1}; ^1H NMR δ 0.93 (d, J = 7 Hz, 6H), 1.96 (sept, 1H), 3.78 (s, 2H), 3.91 (d, J = 7 Hz, 2H), 4.08 (s, 6H), 7.21−7.38 (m, 15H); ^{13}C NMR δ 18.6, 28.3, 36.5, 60.2, 65.2, 76.6, 127.5, 128.7, 129.4, 135.8. **(ii) 1b** (130 mg, 0.6 mmol) in dioxane (5 mL) and phenylmethanethiol (485 μL, 4.13 mmol) in 1 M NaOH (5 mL, 5 mmol) at rt showed a precipitate after 5 min; 2 mL of dioxane was added and worked up after 260 min at rt to give an oil, TLC of which showed **10b** and **8b** present in a 3:1 ratio. Further purification on thick-layer preparative plates as above gave **10b** (150 mg, 48%) and **8b** (36 mg, 15%). **(iii) 1b** (46.6 mg, 0.21 mmol) in THF (0.5 mL) and phenylmethanethiol (497 μL, 4.2 mmol) in 1 M NaOH (4.5 mL, 4.5 mmol), under nitrogen when stirred at rt for 75 min, gave an oil, the ^1H NMR spectrum of which showed signals due to **10b** and **8b** (3:1 ratio) and unreacted phenylmethanethiol.

Reaction of 1b with Excess Ethane-1,2-dithiol and Aqueous NaOH. 1b (106 mg, 0.5 mmol) dissolved in dioxane (0.5 mL) was added to a solution of ethane-1,2-dithiol (121 μL, 0.14 mmol) in 1 M NaOH (1.5 mL, 1.5 mmol); the flask was flushed with nitrogen and the reaction mixture was stirred at rt for 25 min. Workup gave a yellowish oil, which was purified on a thick-layer preparative plate, eluting with ethyl acetate: petroleum ether (bp 35−60 °C) (1:8) and extracting with dichloromethane to give 2-(((isobutyloxy)sulfonyl)methylene)-1,3-dithiolane **(13)** (62 mg, 50%), as a light yellow liquid: IR ($CHCl_3$) ν_{max} 3030 (w), 2996 (w), 1530 (s), 1345 (s), 1161 (vs), 978 (s), 928 (w), 858 (s) cm^{-1}; ^1H NMR δ 0.94 (d, J = 6.5 Hz, 6H), 1.99 (nonet, 1H), 3.43−3.55 (m, 4H), 3.85 (d, J = 6.5 Hz, 2H), 6.23 (s, 1H); ^{13}C NMR δ 18.7, 28.1, 37.0, 39.5, 76.0, 105.1, 164.3; exact mass calcd for $C_8H_{14}O_3S_3$ 254.0105, found 254.0093.

Reaction of 1b with Excess Butanethiol and Aqueous NaOH. 1b (56.8 mg, 0.26 mmol) in THF (0.5 mL) was added to a solution of butanethiol (83 μL, 0.77 mmol) in 1 M NaOH (1 mL, 1 mmol), the reaction flask was flushed with nitrogen, and the reaction mixture was stirred at rt for 15 min. Workup gave a yellowish liquid (67.6 mg), the ^1H NMR spectrum of which showed signals appropriate to 1-((isobutyloxy)sulfonyl)-2,2-bis(butylthio)ethene **(12)**. Purification of the reaction mixture on a thick-layer preparative plate, eluting with ethyl acetate:petroleum ether (35−60 °C) (1:9), and extracting with dichloromethane gave **12** (32 mg, 37%) as a clear liquid: ^1H NMR δ 0.94 (m, 6H), 0.99 (d, J = 7 Hz, 6H), 1.46 (sept, 4H), 1.61−1.74 (m, 4H), 2.04 (sept, 1H), 2.85 (t, J = 7 Hz, 2H), 3.04 (t, J = 7 Hz, 2H), 3.91 (d, J = 7Hz, 2H), 5.93 (s, 1H); ^{13}C NMR δ 13.5, 18.8, 21.8, 22.0, 28.2, 29.4, 31.5, 32.4, 33.8, 76.0, 110.0, 159.4.

Reaction of 1d with Excess Phenylmethanethiol and Aqueous NaOH. 1d (51.7 mg, 0.19 mmol) in dioxane (0.5 mL) and phenylmethanethiol (66 μL, 0.56 mmol) in 1 M NaOH (0.47 mL, 0.47 mmol) at rt for 20 min gave an oil (75.5 mg), the ^1H NMR spectrum of which showed **8d** as the only major product; chromatography on a thick-layer preparative plate eluting with ethyl acetate:petroleum ether (35−60 °C) (1:8) gave **8d** (56 mg, 64%) as a broad band: ^1H NMR δ 0.90 (t, 3H), 1.28 (br s, 10H), 1.55−1.65 (m, 1H), 3.89 (t, 2H), 4.60 (s, 2H), 4.27 (s, 2H), 6.03 (s, 1H), 7.23−7.40 (m, 10H).

Reaction of 1d with Diethylamine and Aqueous NaOH. Diethylamine (73 μL, 0.7 mmol) and 1 M NaOH (0.59 mL, 0.59 mmol) and **1d** (65 mg, 0.24 mmol) in dioxane (0.5 mL) at rt for 15 min gave *N*,*N*-diethyl((octyloxy)sulfonyl)acetamide (**3d**, R^1,R^2 = Et) (54 mg, 75%), as a low-melting solid: ^1H NMR δ

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0.88 (t, $J = 7$ Hz, 3H), 1.39−1.50 (m, 16H), 1.71−1.82 (m, 1H), 3.37−3.52 (m, 2H), 4.18(s, 2H), 4.36 (t, $J = 7$ Hz, 2H).

Reaction of 1c with Excess Phenylmethanethiol and Aqueous NaOH. 1c (37.2 mg, 0.19 mmol) in THF (0.5 ML) and phenylmethanethiol (70 μL, 0.6 mmol) in 1 M NaOH (0.5 mL, 0.5 mmol) under N_2 at for 15 min gave an oil (82.5 mg), the ^{1}H NMR spectrum of which showed signals due to 1-(ethoxysulfonyl)-2,2,2-tris((phenylmethyl)thio)ethane **(10c)** and 1-(ethoxysulfonyl)-2,2-bis((phenylmethyl)thio)ethene **(8c)** and signals at δ 1.23 (t, $J =$ Hz, 3H), 2.44 (q, $J =$ Hz, 2H), and 3.72 (s, 2H) assigned to benzyl ethyl sulfide (reported ^{1}H NMR δ 1.23 (t, $J =$ Hz, 3H), 2.44 (q, $J =$ Hz, 2H), 3.72 (s, 2H), 7.21−7.33 (m, 5H),[24] in a 53:41:6 ratio. The reaction mixture was purified on a thick-layer plate, eluting with ethyl acetate: petroleum ether (bp 35−60 °C) (1:7), to give **10c** (44 mg, 45%) as a white solid and **8c** (22 mg, 30%) as a clear liquid. **10c**: ^{1}H NMR δ 1.35 (t, $J = 7.1$ Hz, 3H), 3.81 (s, 2H), 4.09 (s, 6H), 4.25 (q, $J = 7.1$ Hz, 2H), 7.23−7.38 (m, 15H); ^{13}C NMR δ 15.2, 36.5, 60.3, 65.3, 67.5, 127.5, 128.7, 129.5, 135.8. Anal. Calcd for $C_{25}H_{28}O_3S_4$: C, 59.51; H, 5.60; S, 25.37. Found: C, 59.70; H, 5.73; S, 25.15. **8c**: ^{1}H NMR δ 1.26 (t, $J = 7.1$ Hz, 3H), 3.97 (q, $J = 7.1$ Hz, 2H), 4.07 (s, 2H), 4.28 (s,2H), 6.03 (s, 1H), 7.24−7.40 (m, 10H); ^{13}C NMR δ 14.8, 37.6, 39.0, 66.6, 114.2, 127.7, 128.1, 128.6, 128.9, 129.2, 133.6, 135.5, 156.8; exact mass calcd for $C_{18}H_{20}O_3S_3$ 380.0575, found: 380.0580.

Reactions of 1c with NaOD/D_2O. Below pD 8. 1c (10 mg, 0.05 mmol) was dissolved in CD_3CN (0.2 mL) in an NMR tube, and to this was added D_2O (0.5 mL). The reaction was followed by ^{1}H NMR and after 9 days it showed signals due to ethanol-*d* and trifluoroethanesulfonate anion (1:1 ratio) and traces of unreacted **1c** (4%). NMR spectra run after addition of authentic specimens of ethanol and $CF_3CH_2SO_3^-$ confirmed the identity of the products ethanol-*d* (^{1}H NMR (D_2O/CD_3CN/DSS) δ 1.14 (t, 3H), 3.59 (q, 2H); ^{13}C NMR δ 19.6, 59.8) and trifluoroethanesulfonate (^{1}H NMR δ 3.75 (q, $J = 10$ Hz, 2H); ^{13}C NMR δ 55.0 (q, $J = 30$ Hz), 125.5 (q, $J = 275.7$ Hz)). **Above pD 10. 1c** (7 mg, 0.036 mmol) was dissolved in 0.48 N NaOD/D_2O solution (0.5 mL). The ^{19}F NMR spectrum after 10 min showed signals only due to fluoride anion (−122.0 ppm); the ^{1}H NMR spectrum after 20 min showed signals due to ethanol-*d* and (ethoxysulfonyl)acetate anion-d_2 in a 3:97 ratio. **(Ethoxysulfonyl)acetate**: ^{1}H NMR (D_2O/DSS) δ 1.39 (t, 3H), 4.41 (q, 2H).

Reaction of 1c with Aniline at pH 6. 1c (22.8 mg, 0.12 mmol) in THF (100 μL) and aniline (230 μL, 2.52 mmol) in water (50 mL), set at pH 6 with addition of dilute NaOH and HCl, at rt for 270 min with the pH was maintained at pH 6 by adding NaOH (0.1 M), was extracted with $CDCl_3$ (1 mL). ^{1}H NMR showed weak signals ascribable to *N*-ethylaniline; an authentic sample of *N*-ethylaniline (1 μL) was added to the NMR tube and the spectrum was run again to confirm the identity of product and estimate the amount originally present (21%).

Kinetic Studies with Ethyl Tresylate (1c). General Procedure. The rate of hydrolysis of **1c** and kinetics of reaction of **1c** with amines were determined using the pH−stat technique as previously described.[18] **Hydrolysis**: A solution of **1c** (50 μL) (0.013−0.024 mmol) in THF was injected into water (50 mL) at 25 °C, which had been previously adjusted to the desired pH value with aqueous sodium hydroxide (1 M) or aqueous hydrochloric acid (1 M). The reaction mixture was vigorously stirred and the pH of the solution kept constant with a sodium hydroxide solution (0.1 M). The rate of hydrolysis was monitored by recording the volume (mL) of the titrant (sodium hydroxide) added with time. Plots of $-\ln(v_\infty - v_t)$ vs time were constructed from the volume of sodium hydroxide titrant added. The pseudo-first-order rate constants were then obtained from the slopes of straight lines; the results are listed in Table 1 (supporting information). **Hydrolysis−Aminolysis.** A solution of 40 or 50 μL of **1c** in THF was injected into a solution of the amine in water (50 mL) set at the desired pH and the reaction was followed as above: the quantities of the amines were, respectively, (i) aniline, 230 μL (0.252 mmol); (ii) butylamine, 490 μL (4.96 mmol); (iii) diethylamine, 520 μL (5.03 mmol); and (iv) morpholine, 220 μL (2.52 mmol).

Benzyl 2,2,2-Trifluoroethyl Sulfone (16). Benzyl 2,2,2-trifluoroethyl sulfide[25] (3.03 g, 14.7 mmol) was dissolved in glacial acetic acid (15 mL) in a 100 mL flask placed in a water bath and stirred. To the above stirred solution was added 30% hydrogen peroxide (10 mL) dropwise over a period of 1 h. The reaction mixture was stirred for 67 h. The precipitate was filtered and washed with a small amount of water. Recrystallization from methanol gave **16** (2.32 g, 67%) as a white solid: mp 150 °C; IR ($CHCl_3$) ν_{max} 3034 (w), 1495 (w), 1457 (w), 1401 (w), 1348 (vs), 1313 (s), 1272 (s), 1238 (w), 1159 (w), 1129 (vs), 1079 (w) cm^{-1}; ^{1}H NMR δ 3.58 (q, $J = 9.3$ Hz, 2H), 4.40 (s, 2H), 7.26−7.46 (m, 5H); ^{13}C NMR δ 52.6 (q, $J = 31.8$ Hz), 61.2, 121.3 (q, $J = 277.4$ Hz), 126.7, 129.4, 129.7, 130.7; ^{19}F NMR δ −61.12 (t, $J = 8.8$ Hz).

((Phenylmethyl)sulfonyl)acetic Acid (17). 16 (100 mg, 0.42 mmol) was dissolved in 1 M NaOH (2 mL, 2 mmol) and dioxane (2 mL). The reaction mixture was stirred at rt for 30 min. Workup gave **17** (84 mg, 93%) as a white solid, which was recrystallized from dichloromethane: mp 134−136 °C; IR ($CHCl_3$) ν_{max} 3027 (s), 1735 (s), 1603 (w), 1331 (vs), 1156 (w), 1125 (s), 904 (w), 874 (w) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 4.02 (s, 2H), 4.62 (s, 2H), 7.36−7.54 (m, 5H); ^{13}C NMR (acetone-d_6) δ 56.4, 59.8, 129.3, 129.5, 129.6, 132.1, 164.9.

1-((Phenylmethyl)sulfonyl)-2,2-bis(phenylmethylthio)-ethene (18). 16 (72 mg, 0.3 mmol) dissolved in dioxane (1 mL) was added to a solution of phenylmethanethiol (89 μL, 0.76 mmol) and 1 M NaOH (1 mL, 1 mmol), and the reaction mixture was stirred at rt for 40 min. Workup gave **18** (91 mg, 70%), as a white solid, which was recrystallized from dichloromethane:diethyl ether: mp 108.5−109 °C; IR ($CHCl_3$) ν_{max} 3025 (s), 1603 (w), 1495 (s), 1455 (w), 1314 (s), 1141 (w), 1115 (vs), 934 (w), 882 (w), 828 (w) cm^{-1}; ^{1}H NMR δ 3.89 (s, 2H), 4.26 (s, 2H), 4.27 (s, 2H), 5.82 (s, 1H), 7.04−7.44 (m, 10H); ^{13}C NMR δ 37.8, 39.1, 60.5, 118.5, 127.9, 128.2, 128.4, 128.5, 128.8, 129.3, 130.9, 133.6, 136.2, 157.1.

2-((Phenylmethyl)sulfonyl)-1,1,1-triethoxyethane (19). To a solution of sodium ethoxide (2.17 mmol, 0.87 M) in dry ethanol (1.5 mL) was added a solution of **16** (93.6 mg, 0.4 mmol) in dry ethanol (1 mL), and the reaction mixture was stirred at rt for 15 min. Excess ethanol was removed on rotary evaporator and under vacuum to give a white solid which upon extraction with anhydrous diethyl ether gave **19** (solid, 108 mg, 86%): IR ($CHCl_3$) ν_{max} 3024 (w), 2984 (w), 2934 (w), 2904 (w), 1597 (w), 1456 (w), 1323 (vs), 1279 (w), 1235 (s), 1122 (s), 1072 (s), 1041 (w) cm^{-1}; ^{1}H NMR δ 1.25 (t, $J = 7.1$ Hz, 9H), 3.37 (s, 2H), 3.65 (q, $J = 7.1$ Hz, 6H), 4.41 (s, 2H), 7.37−7.48 (m, 5H); ^{13}C NMR δ 14.9, 53.9, 58.3, 59.9, 110.7, 127.9, 128.6, 128.7, 131.1.

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Supporting Information Available: NMR spectra of new compounds and of reaction products characterized primarily by NMR and a table of pseudo-first-order rate constants for hydrolysis and aminolysis of ethyl tresylate (**1c**) at 25 °C (67 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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