H), 3.67 (dd, J = 10.9, 4.5 Hz, 1 H), 3.60 (dd, J = 10.7, 5.9 Hz, 1 H), 2.87 (q, J = 5.1 Hz, 1 H), 2.04 (q, J = 7.0 Hz, 2 H), 1.95 (br s, 4 H, exchanged with D_2O), 1.24 (br s, 22 H), 0.86 (t, J = 6.7 Hz, 3 H). This NMR spectrum matched one obtained for a sample of naturally derived material (Sigma Chem. Co.): HRMS (FAB, glycerol matrix), m/z 300.2927 (calcd for $C_{18}H_{38}NO_2$ (M + H^+), 300.2902).

Method B. The remaining acetylide addition reaction mixture described above (120 mL) was added directly to a −78 °C blue solution of Li^0 (0.482 g, 0.0695 mol) in $EtNH_2$ (75 mL) via cannula using positive N_2 pressure. After stirring at −78 °C for 4 h the TLC in 4:1:1 n-BuOH–H_2O–HOAc showed the complete formation of sphingosine **5a** at the expense of starting alkyne **3a** and the intermediate alkene **4a**. The reaction was allowed to warm to ambient temperature overnight and then quenched with 8.8 g of solid NH_4Cl. The remaining ethylamine and solvent were removed on a rotory evaporator and the resulting white solid was partitioned between 300 mL of H_2O and 2 × 300 mL of Et_2O. The combined Et_2O layers were washed with brine (300 mL), dried with Na_2SO_4, filtered, and concentrated to give crude **5a** as a waxy solid (2.4364 g). Trituration of this crude material with cold pentane (10 mL) left 1.450 g of an off-white solid which was recrystallized from 1:1 hexanes–EtOAc to give 1.339 g of **5a** as a TLC and NMR homogeneous white solid in 68% overall yield, mp 68–70 °C. This product was spectroscopically indistinguishable from the synthetic **5a** prepared by hydrolysis of **4a**. Further recrystallization from 1:1 hexanes–EtOAc afforded 0.865 g of **5a**: mp 72–75 °C (shr at 70°); $[\alpha]_D$ −0.78° (c 2.02, $CHCl_3$).

D-*threo*-Sphingosine (5b) and D-*erythro*-Sphingosine (5a) via Alane Addition. A solution of 1-pentadecyne (1.00 g, 4.82 mmol) in dry hexanes (6.5 mL–distilled from Na^0) was treated with a solution of 1.5 M DIBAL in toluene (3.25 mL, 4.88 mmol) and the mixture heated at 60 °C for 2 h under N_2. At this time, the TLC in hexanes showed the disappearance of starting alkyne at R_f 0.66 (char A) and the clean formation of (presumed) alane-derived 1-pentadecene at R_f 0.92. The vinylalane solution was cooled to −78 °C (a suspension formed) and to it was added a −78 °C solution of aldehyde 1 (0.850 g, 3.71 mmol) in dry toluene (3.3 mL–distilled from Na^0) via cannula over 5 min. The resulting suspension was stirred for 2 h during which time the mixture was allowed to warm to −60 °C, whereupon a colorless solution formed. The TLC in 3:1 hexanes–EtOAc showed the clean formation of two products, $R_{f_{major}}$ 0.44 (char B) and $R_{f_{minor}}$ 0.47, at the expense of starting material at R_f 0.42. The mixture was poured into ice–water (80 mL), acidified to pH 1 with 1 N HCl (15 mL), and extracted with 3 × 150 mL of Et_2O. The combined extracts were washed with brine (80 mL), dried with $MgSO_4$, filtered, and concentrated to give 1.855 g of crude product as a colorless oil which was shown by NMR analysis to contain a 2:1 mixture of diastereomers **4b** and **4a**. An enriched sample (**4b**:**4a** = 7:1) was obtained separately by careful flash chromatography of the crude mixture on silica gel, eluting with 12:1 hexanes–EtOAc: $[\alpha]_D$ −39° (c 0.25, $CHCl_3$); IR (neat) 3470, 1700, 1670 cm^{-1}; ^1H NMR data for **4b** (400 MHz, C_6D_6, 60 °C) δ 5.70 (dt, J = 15.6, 6.8 Hz, 1 H), 5.52 (dd, J = 15.5, 7.1 Hz, 1 H), 4.40 (t, J = 7.2 Hz, 1 H), 3.95 (pseudo t, J = 6.3 Hz, 1 H), 3.89 (br d, J = 9.1 Hz, 1 H), 3.67 (dd, J = 6.4, 4.9 Hz, 1 H), 1.99 (q, J = 6.8 Hz, 2 H), 1.65 (br s, 3 H), 1.46 (br s, 3 H), 1.39 (br s, 9 H), 1.31 (br s, 22 H), 0.91 (t, J = 6.9 Hz, 3 H), 0.55 (br s, H, exchanged with D_2O); HRMS (FAB, glycerol matrix), m/z 440.3732 (calcd for $C_{26}H_{50}NO_4$ (M + H^+), 440.3740).

The crude 2:1 mixture of **4b** and **4a** described above was combined with 1 N HCl (80 mL) and THF (80 mL) and heated at 70–80 °C with stirring for 16 h under N_2 when the TLC in 3:1 hexanes–EtOAc no longer showed any starting material at R_f 0.46. After cooling and removal of the THF with a rotary evaporator, the reaction mixture was extracted with 3 × 150 mL of 1:1 Et_2O–hexanes to remove any neutral byproducts, basified to pH 10 with 1 N NaOH (85 mL), and then extracted with 3 × 200 mL of CH_2Cl_2. The combined extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to give 770 mg (69% yield) of a pale yellow waxy solid. This material was shown to consist of a 2:1 mixture of **5b** and **5a** by ^1H NMR analysis. A sample of analytically pure **5b** was prepared by deprotection of chromatographically enriched **4b** (vide supra) followed by two recrystallizations from hexanes–CH_2Cl_2: mp 86–87 °C [lit.[4g] mp 88.0–88.5 °C]; $[\alpha]_D$ −2.65° (c 1.13, $CHCl_3$); IR (KBr) 3350, 1590 cm^{-1}; ^1H NMR (400 MHz, 1.9 mg/0.5 mL $CDCl_3$, room temperature) δ 5.72 (dt, J = 15.5, 6.5 Hz, 1 H), 5.44 (dd, J = 15.6, 6.8 Hz, 1 H), 3.97 (t, J = 6.0 Hz, 1 H), 3.66 (dd, J = 10.8, 4.5 Hz, 1 H), 3.53 (dd, J = 10.7, 6.43 Hz, 1 H), 2.77 (q, J = 4.7 Hz, 1 H), 2.03 (q, J = 6.9 Hz, 2 H), 1.96 (br s, 4 H, exchanged with D_2O), 1.24 (br s, 22 H), 0.86 (t, J = 6.7 Hz, 3 H); HRMS (FAB, glycerol matrix), m/z 300.2895 (calcd for $C_{18}H_{38}NO_2$ (M + H^+), 300.2902).

***N,O,O*-Triacetyl-D-*erythro*-sphingosine (6a) and *N,O,O*-Triacetyl-D-*threo*-sphingosine (6b).** In each case a 0.08 M solution of synthetic sphingosine (**5a** or **5b**) was treated with an equal volume of acetic anhydride and pyridine and then stirred at ambient temperature for 2 h. The volatiles were removed in vacuo, leaving the respective triacetates as a white solids in essentially quantitative yield. Triacetate **6a** was purified by recrystallization from hexanes–CH_2Cl_2: R_f 0.41 in 1:1 EtOAc–hexanes (developed 3 times); mp 102.5–103.5 °C [lit.[3c] mp 103.5–104.5 °C, lit.[4a] mp 103 °C, lit.[4b,e] mp 101–102 °C]; $[\alpha]_D$ −13.0° (c 1.08, $CHCl_3$) [lit.[3c] −12.9° ($CHCl_3$), lit.[4a] −12.2° (c 1, $CHCl_3$), lit.[4b] −13.3° (c 1.4, $CHCl_3$), lit.[4e] −12.8° (c 1, $CHCl_3$)]; IR (KBr) 3293, 1741, 1657, 1555 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, room temperature) δ 5.77 (dt, J = 15.3, 6.8 Hz, 1 H), 5.61 (d, J = 9.2 Hz, 1 H), 5.37 (dd, J = 15.4, 7.4 Hz, 1 H), 5.26 (pseudo t, J = 6.5 Hz, 1 H), 4.40 (m, 1 H), 4.28 (dd, J = 11.5, 6.1 Hz, 1 H), 4.03 (dd, J = 11.5, 3.4 Hz, 1 H), 2.06–1.96 (m, 11 H, contains three singlets at 2.15, 2.05, and 1.96), 1.25 (br s, 22 H), 0.86 (t, J = 6.7 Hz, 3 H). Anal. Calcd for $C_{24}H_{43}NO_5$: C, 67.73; H, 10.18; N, 3.29. Found: C, 67.36; H, 10.18; N, 3.18. **6b** was purified by selectively crystallizing out **6a** from a hexanes–CH_2Cl_2 solution as described above followed by evaporation of the filtrate: R_f 0.35 in 1:1 EtOAc–hexanes (developed 3 times); mp 42–44 °C [lit.[3c] mp 43–43.5 °C (from CH_2Cl_2–light petroleum ether)]; $[\alpha]_D$ +7.02° (c 2.05, $CHCl_3$) [lit.[3c] +8.43° ($CHCl_3$), lit.[4a] +8.78° (c 1.2, $CHCl_3$)]; IR (KBr) 3290, 1745, 1650, 1550 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, room temperature) δ 5.75 (dt, J = 13.9, 7.0 Hz, 1 H), 5.62 (d, J = 9.2 Hz, 1 H), 5.38 (m, 2 H), 4.38 (m, 1 H), 4.06 (m, 2 H), 2.06–1.96 (m, 11 H, contains three singlets at 2.06, 2.05, and 1.98), 1.25 (br s, 22 H), 0.86 (t, J = 6.8 Hz, 3 H). Anal. Calcd for $C_{24}H_{43}NO_5$: C, 67.73; H, 10.18; N, 3.29. Found: C, 67.73; H, 10.18; N, 3.29.

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Note Added in Proof: After submission of this manuscript, we became aware of two other sphingosine syntheses based on stereocontrolled additions to the oxazolidine aldehyde 1: Herold, P. *Helv. Chim. Acta* **1988**, *71*, 354. Nimkar, S.; Menaldino, D.; Merrill, A. H.; Liotta, D. *Tetrahedron Lett.* **1988**, *29*, 3037.

Registry No. 1, 102308-32-7; 2, 105563-08-4; **3a**, 115464-01-2; **3b**, 115464-02-3; **4a**, 115464-03-4; **4b**, 115464-04-5; **5a**, 123-78-4; **5b**, 25695-95-8; **6a**, 2482-37-3; **6b**, 78779-96-1; 7, 41765-25-7; Br-$(CH_2)_{12}$Me, 765-09-3; NaC≡CH, 1066-26-8; HC≡C$(CH_2)_{12}$Me, 765-13-9.

Potassium Fluoride Catalyzed Fluorodesulfonylations of Aryl Sulfonyl Fluorides

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Although the conversion of aryl sulfonyl chlorides or bromides to the corresponding aryl halide proceeds in good yield upon the action of light[1] or metallic catalysts,[2,3]

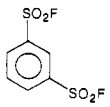
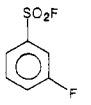
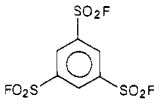
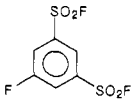
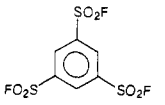
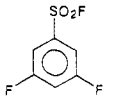
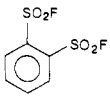
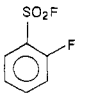
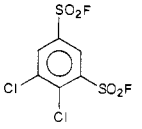
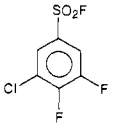
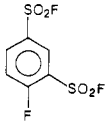
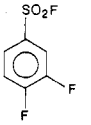
similar conditions fail entirely or give poor yields for aryl sulfonyl fluorides. Consequently, while the conversion of aromatic sulfonyl fluorides to aryl fluorides is known, the reaction is not generally recognized as being synthetically useful. McCall and Cummings[2] reported the formation of fluorobenzene in 31% yield by passing benzenesulfonyl fluoride over Cu on charcoal at 360 °C. This appears to be the best yield reported for a fluorodesulfonylation reaction. Blum and Scharf[3] studied the conversion of aryl sulfonyl fluorides to aryl fluorides with RhCl $(PPh_3)_3$ as catalyst at 330 °C, but the best yield obtained was only 10%. Yakobson et al.[4] also found that aryl sulfonyl chlorides, when heated with KF at temperatures up to 330 °C, gave only small amounts (2–10%) of aryl fluorides. With each method, however, yields of aryl chlorides from sulfonyl chlorides were much higher. Yakobson et al. concluded that chlorodesulfonylation (ArCl from KCl and $ArSO_2Cl$) takes place more readily than fluorodesulfonylation (ArF from KF and $ArSO_2F$).

It may be noted that in the literature cited, conditions favorable for SNAR reactions, including the presence of strong electron withdrawing groups, were generally not employed. The fluorosulfonyl (SO_2F) group should be a good leaving group in such reactions, however. This is suggested by previous work on SNAR reactions of related functionalities, such as the reaction of nucleophiles with nitroaryl alkyl sulfones (loss of RSO_2^-).[5,6] These studies demonstrated that the SO_2R group was not only a good leaving group, but also a good activating group for SNAR reactions. Consequently, it seemed reasonable to expect fluorodesulfonylations to be synthetically useful for compounds bearing groups that facilitate SNAR reactions. A study was therefore undertaken to determine the potential of these reactions where an activating group (SO_2F) was present, i.e. fluorodesulfonylations of di- and tribenzenesulfonyl fluorides catalyzed by KF.

Results and Discussion

Initial experiments were conducted on desulfonylations activated by a nitro group. *p*-Nitrobenzenesulfonyl chloride, on treatment with KF in sulfolane gave *p*-fluorobenzenesulfonyl fluoride (fluorodenitration) and *p*-fluoronitrobenzene (fluorodesulfonylation) in a ratio of about 7:2. This result can be compared with those of Loudon and Shulman,[5] who found that NO_2^- and RSO_2^- can be competitive leaving groups, although the nucleofluge was quite dependent on the nature of the attacking nucleophile. Similar treatment of 2-fluoro-5-nitrobenzenesulfonyl fluoride with KF gave a 7:1 mixture of 3,4-difluoronitrobenzene and 2,5-difluorobenzenesulfonyl fluoride, indicating in this case a preference for fluorodesulfonylation. Notably, the leaving group in either case was meta to the primary activating group. This result was encouraging from a practical standpoint. Since the SO_2F group is meta directing in electrophilic substitutions, starting materials in which the SO_2F group is meta to any strongly electron withdrawing group are more readily accessible than those where the activating group is ortho or para to SO_2F. In fact, a single *m*-SO_2F group is sufficiently activating for fluorodesulfonylation to occur. Heating 1,3-benzenedisulfonyl fluoride with KF in sulfolane proceeded smoothly with gas evolution at 235 °C to give *m*-fluorobenzenesulfonyl fluoride in 45% distilled yield.

Table I. Fluorodesulfonylations of Aryl Sulfonyl Fluorides

no.	starting material	product	yield,[a] %	conditions
1			45	4.75 h, 235–242 °C, KF/org = 2.2, sulfolane
2			65	20 min, 200 °C, KF/org = 0.68, 18-Crown-6
3			49	1.25 h, 190–210 °C, KF/org = 2.0, sulfolane
4			80	0.75 h, 200–215 °C, KF/org = 1.3, sulfolane
5			53[b,c]	0.75 h, 150 °C, KF/org = 2.9, DMF
6			50	1.33 h, 225–230 °C, KF/org = 1.9, sulfolane

[a] Isolated, distilled yields. [b] Yield from 4,5-dichloro-1,3-benzenedisulfonyl chloride. See the Experimental Section. [c] Containing 5–10% 3,4,5-trifluorobenzenesulfonyl fluoride.

Further examples are shown in Table I. Both dimethylformamide and sulfolane have been used as solvents with satisfactory results. The reaction can also be conducted in the absence of solvent with the use of a crown ether as phase-transfer catalyst. Good stirring and the presence of the crown ether appear essential under these conditions.

Although in principle only a catalytic amount of KF should be required, it was observed that reactions that employed substantially less than stoichiometric KF tended to stop before completion but resumed upon the addition of more KF. For this reason, at least 1 mol of KF per mole of SO_2F group replaced was typically used. The KF/organic ratio could in fact be used to control the extent of fluorodesulfonylation of 1,3,5-benzenetrisulfonyl fluoride. Thus, with 0.66 equiv of KF, only one SO_2F group was replaced by fluorine (65% yield). With 2 equiv KF, two SO_2F groups were replaced by fluorine (49%). Analysis of the effluent gas by GC–MS indicated that it consisted primarily of SO_2 and lesser amounts (2–10%) of thionyl fluoride. The formation of a fluorine-containing volatile product explains the inability to obtain complete conversions at low KF/SO_2F ratios.[7]

Evidence that these are nuclephilic aromatic substitution reactions includes the following facts. First, in the absence of KF and solvent, the starting materials are thermally stable at the reaction temperatures. For example, 1,3,5-benzenetrisulfonyl fluoride, heated alone for 2 h at 200–210 °C, was recovered unchanged, but on the addition of KF and crown ether, rapid gas evolution began and ceased in

(1) Miller, B.; Walling, C. *J. Am. Chem. Soc.* **1957**, *79*, 4187.
(2) McCall, E. B.; Cummings, W. U. S. Patent 3 256 343, 1966.
(3) Blum, J.; Scharf, G. *J. Org. Chem.* **1970**, *35*, 1895.
(4) Yakobson, G. G.; Vlasov, V. M.; Vorozhtsov, N. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1967**, *37*, 149.
(5) Loudon, J. D.; Shulman, N. *J. Chem. Soc.* **1941**, 722.
(6) Suhr, H. *Chem. Ber.* **1964**, *97*, 3268.

(7) The formation of SOF_2 is also believed to contribute to yield loss since it is likely formed by the following sequence of reactions. $ArSO_2F + KF \rightarrow ArF + FSO_2K$; $ArSO_2F + FSO_2K \rightarrow ArSO_2OSOF + KF \rightarrow ArSO_3K + SOF_2$.

10 min. After 20-min reaction time, 5-fluoro-1,3-benzenedisulfonyl fluoride was isolated in 65% yield. Second, benzyne intermediates can be excluded since *o*-benzenedisulfonyl fluoride gave only *o*-fluorobenzenesulfonyl fluoride (80%) and no meta isomer expected for cine substitution. Third, where nonequivalent SO_2F groups are present, the one that departs is that predicted on the basis of the σ^- values of the nondeparting groups. Thus, 4-fluoro-1,3-benzenedisulfonyl fluoride gave only 3,4-difluorobenzenesulfonyl fluoride.

Evidence for the excellent leaving group ability of FSO_2^- was clearly demonstrated in the reaction of KF with 4,5-dichloro-1,3-benzenedisulfonyl fluoride. In DMF, the reaction was quite rapid; the onset of gas evolution being less than 100 °C. The product was 3,4-difluoro-5-chlorobenzenesulfonyl fluoride. GC analysis indicated that at longer reaction times this further reacted to give 3,4,5-trifluorobenzenesulfonyl fluoride, although the formation of the latter could not be completely avoided. Regardless of the relative rate of exchange of the chlorine at C-4, the SO_2F group at C-3 reacted faster than the chlorine at C-5. This result is somewhat surprising, since Cl–F exchange at C-5 in the intermediate 4-X-5-chloro-1,3-benzenedisulfonyl fluoride (X = Cl or F) is activated by one halogen and two strongly activating SO_2F groups. Fluorodesulfonylation of the SO_2F group at C-3, however, is assisted by two halogens and only one SO_2F group. Nonetheless, it is the SO_2F group that cleaves first.

Fluorine NMR was particularly useful in assigning product structures. Fluorine in the SO_2F group was generally observed at 63–66 ppm downfield from $CFCl_3$. *o*-Chlorine, however, caused a downfield shift to 57.3 ppm in 4,5-dichloro-1,3-benzenedisulfonyl fluoride. A fluorosulfonyl group ortho to fluorine was assigned by a coupling constant of 12 Hz.

The results of Table I demonstrate that fluorodesulfonylations catalyzed by KF are useful transformations for the preparation of fluorinated aryl sulfonyl fluorides. As the fluorosulfonyl group can be displaced by fluoride when activated by meta electron-withdrawing groups, the fluorodesulfonylation reaction also holds potential for the synthesis of a variety of fluorinated aromatics which may be difficult to obtain by other procedures.

Experimental Section

KF was dried under vacuum at 120 °C. Sulfolane was vacuum distilled, while reagent grade acetonitrile and dimethylformamide were dried over 4-Å molecular sieves. NMR spectra were recorded on a Varian EM-390 spectrometer; ^{19}F spectra were recorded in $CDCl_3$ with internal $CFCl_3$. Melting points are uncorrected. Elemental analyses were performed by this department.

1,3,5-Benzenetrisulfonyl Fluoride. 1,3,5-Benzenetrisulfonyl chloride (18.9 g, 0.051 mol) was added portionwise over 15 min to 63.3 g of dry pyridine and 16.0 g (0.155 mol) of anhydrous ZnF_2 with ice-bath cooling. The mixture was stirred for 0.5 h at ice-bath temperature and for 1.5 h at room temperature and then poured slowly into a mixture of 80 mL of concentrated HCl in 320 mL of ice–water. The product was filtered, washed with water, and dried to give 9.1 g of solid (55% yield), mp 166–8 °C (lit.[8] mp 166–7 °C). Its proton NMR consisted of a singlet at δ 9.1 while the ^{19}F NMR displayed a singlet 65.8 ppm downfield from $CFCl_3$.

3,5-Difluorobenzenesulfonyl Fluoride. 1,3,5-Benzenetrisulfonyl fluoride (8.2 g, 25 mmol), 3.0 g (52 mmol) of KF, and 10 mL of sulfolane were heated under N_2 for 1.25 h at 190–210 °C in a flask fitted with a short path distillation take-off head. During this time gas was evolved. The product was distilled directly at 20 mmHg to give 2.4 g (49%) of a colorless liquid boiling at 78–80 °C: ^1H NMR ($CDCl_3$) δ 7.6 (m, 2 H), 7.25 (tt, 1 H); ^{19}F NMR ϕ^* –64.5 (s, 1 F), 103.7 (m, 2 F); IR 3105, 1610, 1450, 1420, 1310, 1215, 1135, 1090, 995, 900, 870, 775, 665, and 610 cm^{-1}; MS, *m/e* 196 (parent), 113 (base). Anal. Calcd for $C_6H_3F_3O_2S$: C, 36.74; H, 1.54. Found: C, 36.55; H, 1.66.

5-Fluoro-1,3-benzenedisulfonyl Fluoride. A mixture of 1.60 g (4.9 mmol) of 1,3,5-benzenetrisulfonyl fluoride, 0.19 g (3.3 mmol) of KF, and 0.05 g of dibenzo-18-crown-6 were heated under N_2 for 20 min at 200 °C. During this time gas evolution was rapid during the first 10 min. The product was distilled directly from this mixture: bp 88 °C (0.45 mmHg) (0.82 g, 65%); ^1H NMR ($CDCl_3$) δ 8.43 (s, 1 H), 8.1 (dd, 2 H); ^{19}F NMR ϕ^* –65.3 (s, 2 F), 101.3 (t, 1 F); IR (neat) medium and strong bands at 3100, 1610, 1450, 1425, 1272, 1215, 845, 790, 770, 665, and 620 cm^{-1}. Anal. Calcd for $C_6H_3F_3O_4S_2$: C, 27.70; H, 1.17. Found: C, 28.04; H, 1.25.

1,3-Benzenedisulfonyl Fluoride. A mixture of 25 g of 3-(fluorosulfonyl)benzenesulfonyl chloride (0.097 mol), 0.2 g of 18-crown-6, and 10 g (0.172 mol) of KF in 75 mL of acetonitrile was stirred under N_2 overnight at room temperture. The slurry was filtered, and the filtrate was evaporated under vacuum. Distillation of the residue gave 21.9 g (94%) of a white solid, mp 39–40 °C (bp 98–104 °C at 0.5 mm) (lit.[8] mp 38–39 °C).

3-Fluorobenzenesulfonyl Fluoride. 1,3-Benzenedisulfonyl fluoride (14.5 g, 0.06 mol), 7.8 g (0.134 mol) of KF, and 10 mL of sulfolane were heated under N_2 for 4.75 h at 235–242 °C. The mixture was cooled and diluted with 100 mL of CH_2Cl_2 and 100 mL of water. The organic layer was separated, and the aqueous portion was extracted with CH_2Cl_2. The combined organic layers were distilled, the product being collected at 92–101 °C (20 mm) (lit.[9] bp 26–33 °C at 0.6 mm): yield 4.8 g (45%); ^{19}F NMR ϕ^* –64.5 (s, 1 F), 107.7 ppm (dt, 1 F). Sulfonamide, mp 129–131 °C (lit.[10] mp 129–130 °C).

1,2-Benzenedisulfonyl Fluoride. *o*-Benzenedisulfonyl chloride (prepared from the dipotassium salt)[11] was converted to the corresponding difluoride in 88% yield by stirring 11 g (0.04 mol) of the disulfonyl chloride, 12.5 g (0.22 mol) of KF, and 0.4 g of dibenzo-18-crown-6 in 110 mL of CH_3CN for 0.5 h at room temperature. Recrystallization from 60:40 $CHCl_3$/hexanes gave colorless crystals, mp 130–1 °C: ^{19}F NMR ϕ^* –64.5; ^1H NMR AA'BB' pattern at δ 8.1 and 8.5; IR 1215 cm^{-1} (SO_2F). Anal. Calcd for $C_6H_4F_2O_4S_2$: C, 29.75; H, 1.66. Found: C, 29.79; H, 1.63.

2-Fluorobenzenesulfonyl Fluoride. *o*-Benzenedisulfonyl fluoride (6.3 g, 26 mmol), 2.0 g (34 mmol) of KF, and 6 mL of sulfolane were heated under N_2 for 45 min at 200–215 °C. The condenser was replaced with a short vigreaux column, and the product was distilled directly from the reaction mixture, yielding 3.7 g (80%) of a colorless liquid, bp 90–94 (10 mm) (lit.[9] bp 35–40 °C at 0.2 mm): ^{19}F NMR ϕ^* –63.3 (d, J = 12 Hz, 1 F), 106.7 (m, 1 F); MS, *m/e* 178 (parent and base).

4-Fluoro-1,3-benzenedisulfonyl Fluoride. 4-Fluoro-1,3-benzenedisulfonyl chloride[12] (24 g, 0.082 mol), 40 g (0.69 mol) of KF, and 0.3 g of dibenzo-18-crown-6 were refluxed in 200 mL of CH_3CN overnight. The mixture was cooled and filtered, and solvent was removed by rotary evaporation to give an oil, which was distilled under vacuum to give 18.1 g (85%) of the corresponding disulfonyl fluoride, bp 98–102 °C (0.05 mm Hg): ^1H NMR δ 8.6 (dd, 1 H), 8.47 (ddd, 1 H), 7.7 (t, 1 H); ^{19}F NMR ϕ^* –66.0 (s), –63.8 (d), 93.3 (m). Anal. Calcd for $C_6H_3F_3O_4S_2$: C, 27.70; H, 1.16. Found: C, 28.03; H, 1.16.

3,4-Difluorobenzenesulfonyl Fluoride. This material was prepared from 4-fluoro-1,3-benzenedisulfonyl fluoride in a manner similar to that described above for 3-fluorobenzenesulfonyl fluoride (50% yield): bp 72 °C (8 mm); ^1H NMR δ 7.3–7.6 (1 H), 7.7–8.0 (2 H); ^{19}F NMR ϕ^* –65.5, 123.7, and 131.3. The infrared spectrum of this material was identical with that of material obtained from chlorosulfonylation of authentic *o*-difluorobenzene, followed by Cl–F exchange. There was no evidence of 2,5-difluorobenzene-

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sulfonyl fluoride[13] as a reaction product.

4,5-Dichloro-1,3-benzenedisulfonyl Chloride. *o*-Dichlorobenzene (19.5 g, 0.133 mol) and chlorosulfonic acid (180 mL, 2.7 mol) were refluxed for 40 h. Workup gave 29.3 g of crude product, which was recrystallized from hexanes/benzene (100/40) to give pure material (20.5 g), mp 114–5 °C (lit.[14] mp 110–111 °C): IR (Nujol) 1190 and 1172 cm^{-1} (SO_2Cl); ^1H NMR δ 8.65 (d, 1 H, J = 2 Hz), 8.4 (d, 1 H). Anal. Calcd for $C_6H_2Cl_4S_2O_4$: C, 20.95; H, 0.59. Found: C, 20.76; H, 0.55.

4,5-Dichloro-1,3-benzenedisulfonyl Fluoride. The above disulfonyl chloride (19.1 g, 56 mmol), 19.1 g (0.33 mol) of dry KF, 0.3 g of 18-crown-6, and 125 mL of CH_3CN were refluxed for 7.5 h. The cooled mixture was filtered, and the solvent was removed by rotary evaporation. ^{19}F NMR indicated that no ring chlorines had exchanged (singlets at 66.0 and 57.3 ppm downfield from $CFCl_3$). Crude material, containing some residual crown ether, was used in the fluorodesulfonylation described below.

3-Chloro-4,5-difluorobenzenesulfonyl Fluoride. Crude 4,5-dichloro-1,3-benzenedisulfonyl fluoride (19.0 g, 0.06 mol) was heated in 65 mL of DMF containing 10 g (0.17 mol) of KF to reflux over a period of 30 min and held at reflux for an additional 45 min. The mixture was cooled, poured into 400 mL of water, and extracted with ether. The combined ether extracts were washed with water and brine and dried over $MgSO_4$. After removing the ether, the residue (10.4 g) was distilled under vacuum. The fraction boiling at 71–86 °C (7.2 g) contained 5–10% 3,4,5-trifluorobenzenesulfonyl fluoride (GC–MS, m/e 214 (parent); ^{19}F NMR showed aromatic fluorine at ϕ^* 127.2 (dd) and 146 (dtt)). Pure (97%) 3-chloro-4,5-difluorobenzenesulfonyl fluoride was obtained by redistillation (bp 78–80 °C at 4 mmHg): GC–MS, m/e 230 (P), P + 2 ca. 30% of P, 135 (base); ^{19}F NMR ϕ^* −65.8 (s), 124.1, 128.2. Anal. Calcd for $C_6H_2ClF_3O_2S$: C, 31.25; H, 0.87. Found: C, 30.88; H, 0.87.

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Selectivity in the Solvolysis in Binary Solvents of 1-Adamantyl Derivatives Bearing Leaving Groups That Depart as Neutral Molecules

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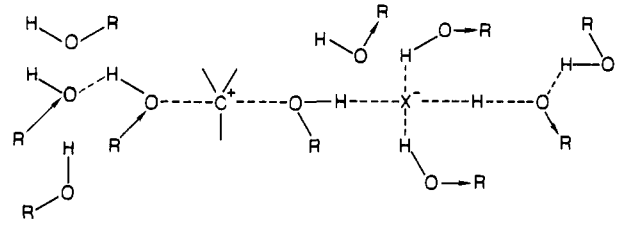
In solvolysis of alkyl halides or tosylates which can undergo backside solvolytic displacement, ethanol (EtOH) is found to be 2–3 orders of magnitude more nucleophilic than trifluoroethanol (TFE).[1] However, with 1-adamantyl derivatives where only front-side displacement occurs, EtOH and TFE have been found to exhibit similar reactivities as measured by product studies and using eq 1 to calculate relative reactivities or selectivities (S).[2–7]

$$S = k_{TFE}/k_{EtOH} = ([1\text{-AdOTFE}]/[1\text{-AdOEt}])([EtOH]/[TFE]) \quad (1)$$

Previous studies of the selectivity of substitution of 1-adamantyl derivatives in binary solvents have failed to agree on the factors leading to the abnormal nucleophilicity orders.[2–7] Since solvent-separated ion pairs are thought to be involved in these solvolytic reactions, it has generally been assumed that the selectivities reflect the relative stabilities of the two solvent-separated ion pairs.[8] Other factors, however, have not been rigorously excluded. McManus and Zutaut[2] recently concluded that solvent bulk and electrophilicity are significant in solvolytic displacements involving 1-adamantyl derivatives and that intrinsic nucleophilicity[1] is of lesser significance. That study dealt with solvolytic substitution of 1-adamantyl derivatives in binary solvents of varying nucleophilicities and electrophilicities including fluorinated solvents. A complementary study by Allard and Casadevall has appeared.[3] Together these reports extend the previous work of Ando,[4] Pross,[5] Rappoport,[6] and Whiting.[7] A puzzling aspect of the earlier reports was the finding of an unusual selectivity for water and for trifluoroethanol (TFE) in water–ethanol (EtOH) and water–TFE binary solvent mixtures, respectively. Since these reactions only involve front-side solvent attack (i.e. reaction with retention of stereochemistry), quite clearly, solvent electrophilicity may be responsible for the unusual selectivities observed.

If it were important, solvent sorting or organization around the substrate in order to provide the lowest energy solvated form is a factor that could affect selectivities. There is, however, no concrete evidence for solvent sorting around intermediates or transition states. Nevertheless, in an EtOH–TFE solvent mixture, it is reasonable to suggest that there would be a favorable enthalpy change (but not necessarily a favorable entropy change) for solvation of the leaving group by the more electrophilic TFE molecules and for solvation of the developing carbocation by the more nucleophilic EtOH molecules. This view is depicted below.



By the above line of reasoning, solvolysis should lead to the more electrophilic TFE molecules being preferentially incorporated by front-side attack while ethanol molecules should be preferentially incorporated by back-side attack. Of course, with 1-adamantyl substrates there is no backside solvation; hence, one may expect to see an abnormal selectivity with this substrate if solvent sorting is important in these reactions. Thus, one could argue that the unusual selectivities reported for TFE–water and EtOH–TFE may be accounted for by solvent sorting. This theory can be tested by using an adamantyl derivative that contains a positively charged leaving group at C-1. In such cases the

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