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Trifluoromethyl Triflate: Synthesis and Reactions[1a]

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A new and convenient synthesis of trifluoromethyl trifluoromethanesulfonate (trifluoromethyl triflate, TFMT) has been devised. The addition of triflic anhydride to a catalytic amount of antimony pentafluoride at 25 °C produces TFMT in 94% yield, utilizing a new and stronger Lewis acid catalyst produced in the reaction, $F_4SbOSO_2CF_3$. This reaction makes pure TFMT conveniently and economically available in large quantities. A mechanism is presented that accounts for the substitution of a triflate ligand for a fluorine ligand on antimony, as well as for the formation of TFMT. Trifluoromethyl triflate does not trifluoromethylate nucleophiles (pyridine, triethylamine, iodide, phenyllithium, phenylmagnesium bromide, lithium thiophenolate, or sodium napththalenide) but gives products that result from an initial attack of the nucleophile at sulfur. Fluoride ion, which is formed by fragmentation of the trifluoromethoxide ion displaced from sulfur, is a chain carrier in the rapid decomposition of TFMT to give trifluoromethanesulfonyl fluoride and fluorophosgene. This limits the synthetic utility of trifluoromethyl triflate.

Methods for introducing the CF_3 moiety into molecules are of considerable synthetic and commercial importance. While many of the direct methods involve the use of the trifluoromethyl radical,[2a–c] or in a few cases a trifluoromethyl anion equivalent,[2d,e] there are few examples[3] that may involve a trifluoromethyl cation. A new method for introducing the CF_3 moiety by electrophilic trifluoromethylation would therefore be of considerable interest. Trifluoromethyl trifluoromethanesulfonate (trifluoromethyl triflate, TFMT) has been known since its preparation by Noftle and Cady[4a] in 1965, but very few reports dealing with its reactions have appeared, even though alkyl triflates are among the most powerful alkylating reagents known. This paucity of chemical studies on TFMT may be attributed to its relative inaccessibility until very recently. A number of syntheses of TFMT have been reported[4] but most suffer from one or more of the following difficulties: low yields,[4b,c] the handling of dangerously reactive reagents,[4a,e] the need for specialized equipment,[4a,e] high cost of reagents,[4d] or unwieldy procedures for isolation and purification of TFMT.[4b,c] The most convenient previously published method[4g] (method 6) appears to be an acid-catalyzed decomposition of triflic anhydride (Tf_2O). Engelbrecht and Tschager[4f] (method 5) have also reported the formation of TFMT in the decomposition of concentrated solutions of $B(OTf)_3$ in triflic acid (TfOH).

$$CF_3SO_2OSO_2CF_3 \xrightarrow{10°C} \underset{67\%}{CF_3SO_3CF_3} + CF_3CF_3 + SO_3 \quad \text{(Method 1)}^{4a}$$

$$CF_3SO_3H + FSO_3H \xrightarrow{165°C} \underset{19\%}{CF_3SO_3CF_3} + FSO_3CF_3 \quad \text{(Method 2)}^{4b,c}$$

$$CF_3I + AgOSO_2CF_3 \xrightarrow[200°C]{C_6H_6} \underset{86\%}{CF_3SO_3CF_3} + AgI \quad \text{(Method 3)}^{4d}$$

$$ClOSO_2CF_3 + BrCF_3 \xrightarrow{-111°C} \underset{95\%}{CF_3SO_3CF_3} + BrCl \quad \text{(Method 4)}^{4e}$$

$$B(OSO_2CF_3)_3 + CF_3SO_3H \longrightarrow CF_3SO_3CF_3 + BF_3 \quad \text{(Method 5)}^{4f}$$

$$CF_3SO_3H + P_2O_5 \xrightarrow{\Delta} \underset{70\%}{CF_3SO_3CF_3} + H_3PO_4 \quad \text{(Method 6)}^{4g}$$

The first preparation and the characterization of TFMT by Noftle and Cady[4a] occurred in 1965. They reported

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[1] (a) Presented in part at the 18th National Meeting of the American Chemical Society, Washington, DC; August 28–September 2, 1983; American Chemical Society: Washington, D.C., 1983, FLUO 21. (b) Current address: Vanderbilt University, Box 1822, Station B, Nashville, TN 37235.

[2] See, for example: (a) Cowell, A. B.; Tamborski, C. *J. Fluorine Chem.* **1981**, *17*, 345. (b) Kobayashi, Y.; Kumadaki, I. *Tetrahedron Lett.* **1979**, 4071. (c) Golitz, P.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 854. (d) Kitazume, T.; Ishikawa, N. *Chem. Lett.* **1981**, 1679. (e) Hartkopf, U.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 443. (f) Burton, D. J.; Wiemers, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 5014. (g) Wiemers, D. M.; Burton, D. J. *ibid.* **1986**, *108*, 832.

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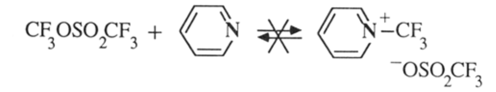
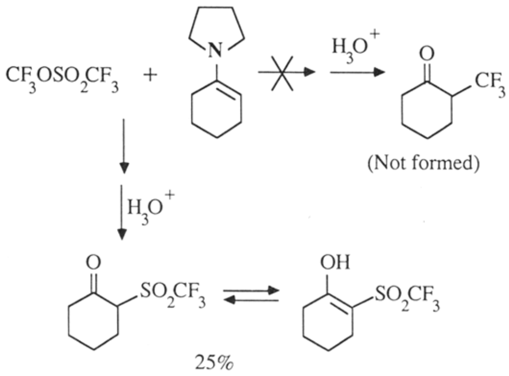
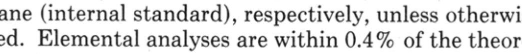
TFMT to be unreactive toward water at room temperature for 16 h but to be hydrolyzed by 0.1 N sodium hydroxide at 100 °C. The TFMT did contain the peroxide $(CF_3SO_2)_2O_2$ as an impurity, which made the TFMT reactivity a bit difficult to establish. Olah and Ohayama[4b] described observations that were interpreted in terms of a reversible trifluoromethylation of pyridine and triethylamine (Et_3N) with TFMT to give quaternary ammonium salts. Trace amounts of benzotrifluoride and iodine were detected in the synthesis of TFMT by method 3, but in view of the severe reaction conditions used, it is possible that CF_3I was the trifluoromethylating reagent, not TFMT. In contrast to the report of Olah and Ohayama, it was reported[4d] by Kobayashi et al. that TFMT reacted with an enamine via S–O bond cleavage, rather than by C–O bond cleavage, to give trifluoromethanesulfonylation.





Nucleophiles have been reported to react with 1,1-H_2-perfluoroalkyltriflates (R_FCH_2OTf) to give both C–O and S–O bond cleavage products.[5] Soft nucleophiles such as amines and iodide ion attack only at carbon[5a,b] while hard nucleophiles such as alkoxides attack predominantly at sulfur. Nucleophiles have been reported[6] to react at the sulfur, the nitrogen, and a carbon (N–C) of *N*,*N*-bis(trifluoromethyl)amino triflate. These results suggested to us that reaction of various nucleophiles with TFMT might give either trifluoromethylation (path a) or trifluoromethanesulfonylation (path b), depending on the nature of the nucleophile.



$$\mathrm{Nuc{-}CF_3} \xleftarrow[\mathrm{Nuc}]{a} \mathrm{CF_3} \overset{a}{\vdots} \mathrm{O} \overset{b}{\vdots} \mathrm{SO_2CF_3} \xrightarrow[\mathrm{Nuc}]{b} \mathrm{Nuc{-}SO_2CF_3}$$

We here report a convenient and economical method for the large-scale synthesis of TFMT and a reinvestigation of its reported reactions.

Experimental Section

General. Antimony pentafluoride (SbF_5) was distilled before use. The ^1H and ^{19}F NMR chemical shifts are reported downfield from tetramethylsilane (internal standard) and chlorotrifluoromethane (internal standard), respectively, unless otherwise indicated. Elemental analyses are within 0.4% of the theoretical values calculated for each listed element unless otherwise noted.

Preparation of Triflic Anhydride (Tf_2O). Triflic anhydride was economically prepared from TfOH[7] by using literature methods[8] modified by thoroughly mixing an equal volume of fine, dried sand with P_2O_5 before addition of the TfOH. The sand gives better mixing of the TfOH and P_2O_5 and also breaks up the hydrated P_2O_5 surface to allow easier distillation of the Tf_2O.

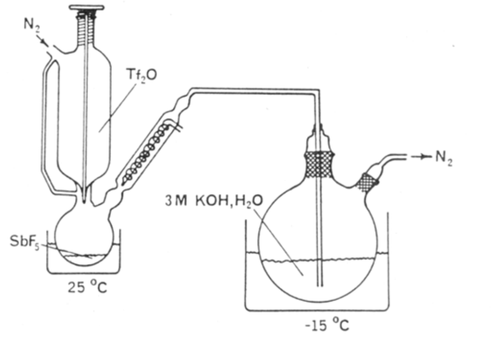


Figure 1. Apparatus used for the preparation and purification of trifluoromethyl triflate.

Preparation of TFMT. In the apparatus shown in Figure 1, 120 g (0.43 mol) of Tf_2O was slowly added to 0.60 g (2.8 mmol) of SbF_5 with stirring. The temperature of the bath was kept near 25 °C. The volatile products produced in the rapid and exothermic reaction were carried by a slow stream of N_2 through the water-cooled condenser and bubbled through a rapidly stirred 3 M aqueous KOH solution in a −15 °C bath. After addition of Tf_2O, the reaction flask was heated to 60 °C for 15 min. The TFMT (bottom layer) was then separated from the KOH solution in the receiver, dried (P_2O_5), and distilled to give 75 g (0.34 mol, 80%) of pure TFMT: ^{19}F NMR ($CFCl_3$) δ −74.0 (q, 3, SCF_3, $^5J_{FF}$ = 3.5 Hz), −53.3 (q, 3, OCF_3, $^5J_{FF}$ = 3.5 Hz) (lit.[4a] −76.22 and −55.61). The infrared spectrum gave peaks at frequencies published previously.[4a]

Sequential Addition of Triflic Anhydride to SbF_5. The Tf_2O (0.37 mL, 2.2 mmol) was slowly added to SbF_5 (0.49 g, 2.3 mmol) under a N_2 atmosphere with stirring. Volatile products were trapped at −196 °C. The viscous solution was stirred for 5 min at 25 °C and then for 10 min at 55 °C to expel residual volatile products. These products were transferred to an NMR tube containing $CFCl_3$, sealed, and quantitatively integrated relative to internal standard $PhCF_3$. Four more additions of 1 equiv of Tf_2O were carried out by using the same procedure. Twenty-four hours later, two more equivalents of Tf_2O were added sequentially. The products were identified (Table II) as TFMT, CF_4 [^{19}F NMR ($CFCl_3$) δ −62.5 (s); IR (gas, 10 Torr) 2188 (m), 1269 (s) cm^{-1} (lit.[9] 2187 (m), 1283 (s) cm^{-1})], and CF_3SO_2F [^{19}F NMR ($CFCl_3$) δ −37.7 (q, 1, SO_2F, $^3J_{F-F}$ = 19.5 Hz), −73.2 (d, 3, CF_3, $^3J_{F-F}$ = 19.5 Hz)]. While the first 2 equiv of Tf_2O reacted rapidly upon addition to the SbF_5 at 25 °C, subsequent additions required a temperature ca. of 35 °C for rapid reaction.

$SbF_4(OSO_2CF_3)$ (1). Triflic anhydride (60 mL, 0.36 mol) was slowly added to 16.3 g (0.075 mol) of SbF_5 at 25 °C. Volatile products were trapped at −196 °C. Distillation of the remaining reaction mixture gave 17.1 g of a clear, very viscous liquid collected at 70–84 °C (0.2 Torr). Redistillation gave 11.9 g (0.0343 mol, 46%) of pure **1**: bp 80–90 °C (3 Torr); ^{19}F NMR (external $CFCl_3$) δ −71.5 (s with shoulders, 76, $SbOSO_2CF_3$), −86.0 (m, 42, cis Sb–F), −93.3 (s, 16, trans, Sb–F), −118.8 (t, 42, cis Sb–F, J = 126 Hz). Anal. (CF_7O_3SSb) C, S, Sb. Calcd: F, 38.35. Found: F, 38.9.

Reaction of Triflic Anhydride. (a) With $SbF_4(OSO_2CF_3)$ (1). The Tf_2O (1.60 mL, 9.68 mmol) was slowly added to 0.33 g (0.95 mmol) of **1** at 25 °C and the volatile products were trapped at −196 °C. Residual volatile products were transferred to the trap by heating the reaction mixture to 55 °C for ca. 10 min. Trapped products were quantitatively identified by ^{19}F NMR using $PhCF_3$ as an internal standard: TFMT (7.3 mmol, 76%), CF_4 (0.017 mml, 0.18%), COF_2 (1.0 mmol, 11%), and Tf_2O (0.96 mmol, 10%). Further addition of 1.6 mL of Tf_2O gave TFMT

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(7) Available in bulk quantities from 3-M at relatively low cost.

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(8.6 mmol, 90%), CF_4 (0.045 mmol, 0.47%), COF_2 (0.19 mmol, 12.0%), and Tf_2O (1.3 mmol, 13%). The combined yield of TFMT, based on unrecovered starting material, was 94%.

(b) With $AlCl_3$, $FeCl_3$, $SnCl_4$ and SbF_3. A sample of Tf_2O (0.45 mL, 2.7 mmol) was sealed in an NMR tube with the requisite amount of Lewis acid (Table III) and heated at 75 °C. The ^{19}F NMR spectra, taken periodically, showed no products being formed over 20 days.

(c) With BF_3 or AsF_5. The specified amount of BF_3 or AsF_5 (Table III) and Tf_2O (0.50 mL, 3.0 mmol) was sealed in an NMR tube, heated at 75 °C, and monitored periodically by ^{19}F NMR. No reaction with BF_3 was detected after 6 days. With AsF_5, no Tf_2O was detected after 5 days at 75 °C. Products determined by ^{19}F NMR were as follows (relative molar ratios): TFMT (55), CF_3SO_2F (6), CF_4 (8), and COF_2 (31).

(d) With $TiCl_4$. A mixture of Tf_2O (0.45 mL, 2.7 mmol) and $TiCl_4$ (0.034 mL, 0.38 mmol) was sealed in an NMR tube, heated to 75 °C, and monitored periodically by ^{19}F NMR. No reaction had occurred after 6 days. An orange-yellow solid had formed after 20 days; however, and at that time the ^{19}F NMR spectrum showed that no Tf_2O remained. Products detected by ^{19}F NMR (relative molar ratios): TFMT (72), CF_3SO_2F (4), COF_2 (10), and CF_3SO_2Cl (15) [^{19}F NMR δ -76.3 (s); IR (gas) 1433, 1239, 1126 cm^{-1}, (lit.[10] 1439, 1239, 1124 cm^{-1})].

(e) With $TiCl_2(OSO_2CF_3)_2$. A mixture of Tf_2O (2.2 mL, 13 mmol) and $TiCl_2(OSO_2CF_3)_2$ (0.28 g, 0.68 mmol), prepared by the method of Noftle and Cady,[11] was heated at 85 °C. The reaction converted a portion of the yellow solid, $TiCl_2(OSO_2CF_3)_2$, to a brown foam after 1 h. More Tf_2O (1.27 mL, 7.61 mmol), added in three portions at 85 °C, converted the remaining yellow solid to foam. The volatile products, trapped at -196 °C, were quantitatively identified by ^{19}F NMR using $PhCF_3$ as an internal standard: TFMT (9.1 mol, 69%), Tf_2O (0.59 mmol, 4.5%), and COF_2 (0.71 mmol, 5.4%). Removal of volatile products in the foam by vacuum gave a light brown transparent solid. Anal. ($C_4F_{12}O_{12}S_4Ti$) C, H, Cl, S, Ti.

Reaction of TFMT. (a) With Pyridine. The reaction of TFMT (0.12 g, 0.53 mmol) and pyridine (0.29 g, 3.7 mmol) in THF (0.5 mL) in a sealed NMR tube gave slow formation of transparent crystals. The ^{19}F NMR spectrum of the supernatant liquid showed only CF_3SO_2F.

The reaction of TFMT (0.23 g, 1.0 mmol) and pyridine (0.08 mL, 0.78 g, 1.0 mmol) in acetonitrile (0.5 mL) in a sealed NMR tube also gave a solid but ^1H and ^{19}F spectra showed the supernatant liquid to contain CF_3SO_2F and 8, a complex of COF_2 with pyridine: ^{19}F NMR (CH_3CN) δ -26 (br s, $-CF_2O-$); ^1H NMR (CH_3CN) δ 7.5–7.6 (m, 2, H-3,5), 7.9–8.1 (m, 1, H-4), 8.8–8.9 (m, 2, H-2,6). Pyridine (0.08 mL, 1.0 mmol) in acetonitrile (0.5 mL) gave the following: ^1H NMR (CH_3CN) δ 7.2–7.3 (m, 2, H-3,5), 7.6–7.8 (m, 1, -4), 8.5–8.6 (m, 2, H-2,6).

A mixture of TFMT (0.41 g, 1.9 mmol) and pyridine (0.15 mL, 1.9 mmol) in a sealed tube gave a solid plus a small amount of liquid after 10 min at 25 °C. The solid slowly decomposed at atmospheric pressure when the tube was opened to give a mixture of gases, CF_3SO_2F and COF_2 (by ^{19}F NMR), and a liquid, pyridine (by ^1H NMR). No TFMT was detected.

(b) With Triethylamine (Et_3N). A solution of TFMT (0.26 mL, 1.2 mmol) and Et_3N (0.050 g, 0.49 mmol) in THF (0.5 mL) at 25 °C in a sealed tube reacted exothermically with vigorous bubbling to give CF_3SO_2F and COF_2 (by ^{19}F NMR). No TFMT remained. No solid was produced and there was no evidence (^1H and ^{19}F NMR) for a $Et_3N–COF_2$ complex in solution at 25 °C.

(c) With Cesium Fluoride. When TFMT (0.11 g, 0.51 mmol) was heated with CsF (0.016 g, 0.10 mmol) in THF (0.5 mL) at 55 °C for 20 h in a sealed NMR tube, ^{19}F NMR showed the only products to be CF_3SO_2F and COF_2. Neither $CsOCF_3$ nor CF_4 was observed and no TFMT remained.

(d) With Pyridine and Hexamethyldisilazane (HMDS). The reaction of TFMT (0.049 g, 0.23 mmol) and pyridine (0.005 mL, 0.0 mmol) in THF (0.4 mL), HMDS (0.25 mL, 1.2 mmol), and $PhCF_3$ (0.103 g, 0.705 mmol) at 25 °C for 1 h in a sealed NMR tube produced no solids. Using $PhCF_3$ as the internal standard, ^{19}F NMR gave (mmol) the following: CF_3SO_2F (0.023); 5 (0.54) and 6 (0.17) [^{19}F NMR (THF) δ -80.3 (s)]. The hydrolysis product of 6 was isolated by adding the product mixture to water and ether. The ether layer was separated and the solvent removed to give $CF_3SO_2NH_2$: mp 118–119 °C (lit.[12] mp 119 °C); ^{19}F NMR (CD_3CN) δ -79.3 (s); ^1H NMR (CD_3CN) δ 6.45 (br s). Anal. ($CH_2F_3NO_2S$) C, H, N.

(e) With Phenyllithium. To a solution of TFMT (2.0 g, 9.2 mmol) in ether (10 mL) was added 6.6 mL of 1.4 M PhLi (9.2 mmol) in benzene/ether (70/30). After 1 h at -78 °C and 1 h at 25 °C, the reaction mixture was poured onto cracked ice. The products were extracted into ether and the ether was removed. The ^{19}F NMR spectrum (benzene) showed no $PhCF_3$ but a peak at -79.1 ppm corresponds closely to the reported chemical shift of $PhSO_2CF_3$ (-79.2 ppm).[13] Benzene was removed by distillation. Addition of pentane to the residue gave a pentane layer, an immiscible oil, and a solid. The solid was washed with ether and recrystallized ($CHCl_3$/pentane) to give 0.06 g of diphenyl sulfone: mp 123–125 °C (lit[14] mp 125.5–126 °C); ^1H NMR ($CDCl_3$) δ 7.42–7.53 (m, 3, Ar H), 7.85–8.00 (m, 2, Ar H); mass spectrum (70 eV), *m/e* (relative intensity)8 (23, M^+), 125 (100, $C_6H_5SO^+$). The pentane solution was separated into three fractions, which were mixtures of compounds, by preparative TLC (alumina with ether/pentane). A major component of the 0.13-g third fraction appears to be Ph_2CO by ^1H NMR and mass spectrometry (70 eV): *m/e* (relative intensity)2 (27, M^+), 105 (1 0, $C_6H_5CO^+$), 77 (61, $C_6H_5^+$), 51 (16, $C_4H_3^+$).

(f) With Iodide. A solution of (n-$C_7H_{15})_4N^+I^-$) (0.30 g, 0.56 mmol) in CH_2Cl_2 (0.6 mL) at 25 °C was treated with TFMT (0.077 g, 0.35 mmol) and sealed in an NMR tube. The ^{19}F NMR spectrum after 10 min indicated quantitative conversion to CF_3SO_2F and COF_2. Starch–KI paper was used to confirm the absence of I_2.

(g) With Sodium Naphthalenide. To a 25 °C solution of sodium naphthalenide, prepared by the addition of naphthalene (2.3 g, 0.018 mol) to sodium metal (0.3 g, 10 mmol) in THF (125 mL) for 4 h at 25 °C, was added a solution of TFMT (3.9 g, 18 mmol) in THF (50 mL) at 0 °C. The mixture was kept for 35 min at 25 °C and then at 70 °C for 75 min. Volatile products trapped at -196 °C were shown by ^{19}F NMR to be TFMT (0.2 mmol), CF_3SO_2F (4.4 mmol), and COF_2 (1.1 mmol). The THF solution contained only CF_3SO_2F and COF_2 (by ^{19}F NMR), and CF_3SO_2F was the only fluorine-containing compound detected after most of the THF was removed by distillation. Inverse addition of the reactants gave the same products.

Superacid Measurements. (a) General. The ^1H NMR chemical shifts are reported in ppm downfield from tetramethylsilane in acetone-d_6 (external standard). Commercial samples of SbF_5, triflic acid, and 4-methoxybenzaldehyde were distilled before use. The $SbF_4(OSO_2CF_3)$ was twice distilled before use and SO_2ClF was twice distilled from P_2O_5. The NMR samples were prepared under a nitrogen atmosphere in a drybox and on a vacuum line.

(b) Preparation of a Typical SbF_5 Sample. A solution of 4-methoxybenzaldehyde (10.0 mL, 0.083 mmol) in triflic acid (0.295 mL, 3.33 mmol) was added at -5 °C to 0.180 g (0.83 mmol) of SbF_5 with thorough stirring. The solution was added to a 3-mm o.d. quartz NMR tube insert, an approximate equal volume of SO_2ClF was added by distillation, and the tube was sealed. The sample was kept at -196 °C until the NMR spectrum was run.

(c) Preparation of a Typical $SbF_4(OSO_2CF_3)$ Sample. A solution of 4-methoxybenzaldehyde (5.5 mL, 0.0452 mmol) in triflic acid (0.125 mL, 1.40 mmol) was added at -5 °C with 0.090 mL of a standard $SbF_4(OSO_2CF_3)$/triflic acid solution (3.736 M and 5.764 M, respectively). The solution was added to a 3-mm o.d. quartz NMR tube insert, an approximately equal volume of SO_2ClF was added by distillation, and the tube was sealed.

(d) Determination of Acidity. The acidities of the superacid solutions were determined by using the NMR method of Sommer, Canivet, Schwartz, and Rimmelin.[15] The ^1H NMR spectra were run at -55 °C (200 MHz) and the peaks referenced to external

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Table I. ^{19}F NMR of Perfluoroalkanesulfonic Acids and Symmetrical Anhydrides

	δ		*J* (Hz)	
	X = OH	X = OSO$_2$RF	X = OH	X = OSO$_2$R$_F$
SO$_2$X				
CF$_2$	−112.49	−107.30	15.2, 3.4	14.5
CF$_2$	−121.70	−121.03	13.3, 3.4	
CF$_2$	−123.20	−123.20	15.2	14.5
CF$_2$	−124.29	−124.29	13.3, 10.2	10.2
CF$_2$	−128.02	−128.02	2.5	2.5
CF$_3$	−83.31	−83.31	10.2, 2.5	10.2, 2.5
SO$_2$X				
CF$_3$	−78.80	−74.65		

tetramethylsilane (see Results).

Equilibration of Perfluoroalkanesulfonic Acids and Anhydrides. Triflic anhydride (0.037 mL, 0.22 mmol) was added to perfluorohexanesulfonic acid (0.088 g, 0.22 mmol) that contained approximately 0.3 to 0.4 equiv of water (by elemental analysis) in a coaxial NMR tube insert with $CFCl_3/CDCl_3$ used as an external reference. The equilibration, followed by ^{19}F NMR (84.6 MHz), was complete after 3 days. Peaks assigned to both acids and both symmetrical anhydrides were observed at 84.6 MHz (Table I).

At higher field (338 MHz), however, the singlet at −74.65 ppm is resolved into two resonances in a ratio of 1.0/1.5, the former being 0.016 ppm (5.5 Hz) downfield of the other resonance. We assign the peak at lower field to the unsymmetrical anhydride and that at higher field to triflic anhydride.

A sample of perfluorohexanesulfonic anhydride, prepared by reaction of the acid with 1.2 equiv of P_2O_5, contained ca. 25% of the starting acid. When this material was mixed with triflic acid in a 1.0/1.2 ratio, equilibration also produced the two peaks near −74.65 ppm, consistent with the formation of the unsymmetrical anhydride.

Results

Reaction of Triflic Anhydride with SbF$_5$. When Tf_2O is slowly added at room temperature to a catalytic amount of SbF_5, a vigorous and exothermic reaction produces TFMT and sulfur dioxide as the major products. As Noftle and Cady[4a] have pointed out, it is difficult to separate TFMT (bp 18 °C) and sulfur dioxide (bp −10 °C) by the use of gas–liquid chromatography or by repeated bulb-to-bulb distillation. Because TFMT is essentially unreactive toward water and reacts only very slowly with aqueous KOH,[4a] it is possible to wash a TFMT–sulfur dioxide mixture with aqueous KOH in a −15 °C bath to extract the sulfur dioxide as sulfite ion. The TFMT, which is immiscible with water, is then easily separated from the less dense aqueous layer to give TFMT free of sulfur dioxide. The presence of sulfite ion in the water was confirmed by the slow addition of bromine to the aqueous phase until it was no longer decolorized and oxidation of the sulfite to sulfate ion, which was subsequently precipitated by the addition of barium chloride. The very low reactivity of TFMT toward KOH appears to be a manifestation of its very low solubility in aqueous KOH. When TFMT is added to KOH in 95% ethanol at room temperature, it reacts immediately.

This method provides TFMT easily and economically in a one-step procedure. By the slow addition of 120 g of Tf_2O to 0.60 g of SbF_5, 75 g (80%) of pure TFMT was isolated. The greater than 87% yields of TFMT found for the addition of Tf_2O to $SbF_4(OSO_2CF_3)$ (see Experimental Section and Table II) suggest that in this large-scale preparation, unreacted Tf_2O is being carried over in the gas stream and hydrolyzed in the KOH solution to make the yield and the conversion equal at 80%.

Table II. Sequential Additions of 1-Equiv Samples of Tf$_2$O to a Retained Catalyst Derived from SbF$_5$ (2.26 mmol)

addn	Tf$_2$O (mmol)	volatile products detected (mmol)			
		TFMT	CF$_4$	CF$_3$SO$_2$F	Tf$_2$O[a]
1	2.22	0.37	0.21	0.07	0.08
2	2.22	1.05	0.35	0.13	0.13
3	2.31	2.11	0.11	0.02	0.11
4	2.28	1.89	0.04	*b*	0.07
5	2.31	3.09	0.02	*b*	0.17
6	2.28	2.44	0.04	*b*	0.09
7	2.34	2.26	0.02	*b*	0.14

[a] Some of the Tf_2O was swept into the cold trap without reaction. [b] Product was not detected by ^{19}F NMR.

Side Products of the Reaction. In addition to TFMT and sulfur dioxide, minor amounts of CF_4, CF_3SO_2F, and COF_2 are also produced in the reaction of Tf_2O with SbF_5. A careful incremental addition was carried out in which successive, approximately 1-equiv portions of Tf_2O were added to SbF_5, followed by warming to 55 °C in a standard manner, to study the production of these minor products. The volatile products were trapped after addition of each portion and were then quantitatively measured by ^{19}F NMR, using an internal standard. A total of seven additions were made. Care was taken to keep reaction temperatures and times consistent. Additions 6 and 7, carried out 24 h after the reaction of addition 5 was completed, show that the catalyst is stable over this time span. Results are listed in Table II. It is obvious that as the first 2 equiv are added, not all of the products are trapped. By visual inspection, there appears to be a corresponding increase in the volume of the SbF_5 reaction mixture solution as the first 2 equiv of Tf_2O are added. This may be due to complexation of some of the products with SbF_5. A number of sulfonyl compounds have been shown to give complexes with SbF_5 with formation of a Sb–O bond.[16] This would account for the small amount of products trapped in runs 1 and 2. It is significant to note that the amounts of CF_4 and CF_3SO_2F are higher during earlier additions and become insignificant in amount for later additions of Tf_2O.

Nature of the Catalyst. The major Sb–F peaks in the ^{19}F NMR (250 MHz, −100 °C) spectrum of the reaction from the addition of 10 equiv of Tf_2O to SbF_5, after removal of volatile products (50 °C, 1 Torr), are consistent with a mixture of cis and trans linked polymers of $TfOSbF_4$. When the triflate groups are cis to each other, the two F_1 fluorines and the two F_2 fluorines split each other into triplets at −86.8 and −120.4 ppm. (J = 129 Hz). However, when they are trans to each other, all four fluorine atoms (F_3) are equivalent and a singlet at −99.0 ppm is observed. There are also small peaks in the Sb–F region that may be attributed to polymers of $(TfO)_2SbF_3$ such as **2** and **3**. These assignments are consistent with the observations made in studies of $SbF_4(OSO_2F)$,[17a] of solutions containing $SbF_4(OSO_2F)_2^-$ species,[17] and of SbF_5/triflic acid solutions.[18] Triplets at 92 and −123 ppm and a singlet at −98 ppm are observed for neat SbF$_4$(OS-

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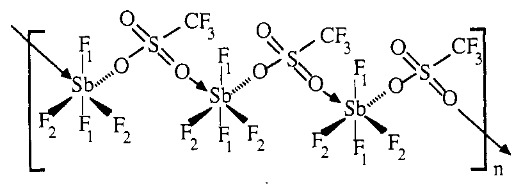
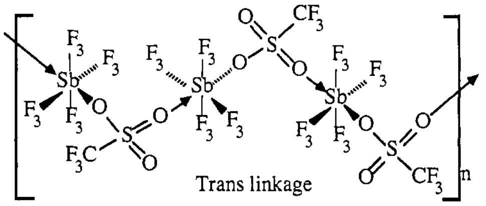
[16] (a) Moore, J. W.; Baird, H. W.; Miller, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 1358. (b) Dean, P. A. W.; Gillespie, R. J. *ibid.* **1969**, *91*, 7260. (c) Dean, P. A. W.; Gillespie, R. J. *ibid.* **1969**, *91*, 7264.

[17] (a) Thompson, R. C.; Barr, J.; Gillespie, R. J.; Milne, J. B.; Rothenbury, R. A. *Inorg. Chem.* **1965**, *4*, 1641. (b) Gillespie, R. J.; Rothenbury, R. A. *Can. J. Chem.* **1964**, *42*, 416.

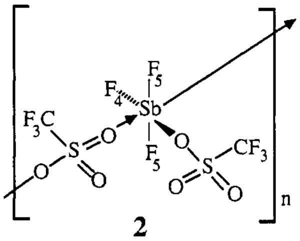
[18] Brunel, D.; Germain, A.; Commeyras, A. *Nouv. J. Chim.* **1978**, *2*, 275.



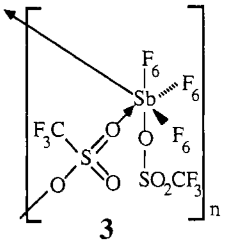
Cis linkage



Trans linkage



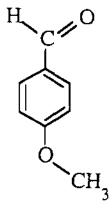
2



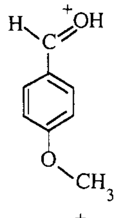
3

O_2F). The ^{19}F NMR spectrum of solvent-free, pure 1 gives a complex multiplet (at both 84.6 and 338 MHz) at −86.0 ppm and a triplet at −118.8 ppm (J = 126 Hz) for the cis linkage and a singlet at −93.3 ppm for the trans linkage with a cis to trans ratio at ca. 5.4 to 1. In each case, the Sb–F peaks for 1 are at lower fields than those for $SbF_4(OSO_2F)$, which may suggest a greater electron-withdrawing ability of OSO_2CF_3 relative to that of OSO_2F.

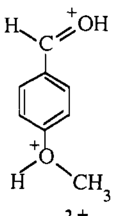
Relative Acidities of SbF_5 and $SbF_4(OSO_2CF_3)$. In marginal superacid media (e.g., triflic acid), 4-methoxybenzaldehyde is monoprotonated but, in sufficiently strong superacid media, it is diprotonated. It has been shown[15] that protonated 4-methoxybenzaldehyde can be used as a Hammett base indicator for the comparison of relative acidities of superacid systems using NMR techniques (rather than UV) to determine ionization ratios, **I**. The following expression was used to determine the ionization ratio **I** where δ_{obsd} is the observed $C{=}OH^+$ chemical shift of the respectively diprotonated and monoprotonated forms of 4-methoxybenzaldehyde.



B



BH⁺



BH_2^{2+}

$$I = \frac{\delta_{BH^+} - \delta_{obs}}{\delta_{obs} - \delta_{BH_2^{2+}}}$$

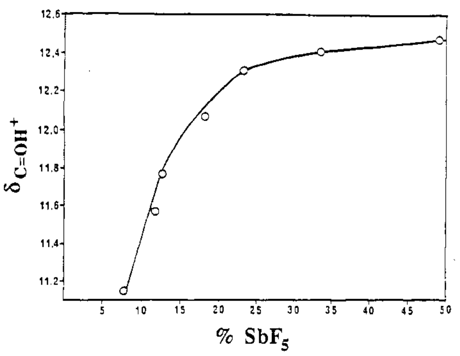


Figure 2. Dependence of the $C{=}OH^+$ ^1H NMR chemical shift of carbonyl protonated 4-methoxybenzaldehyde (2%) on the SbF_5 content in CF_3SO_3H.

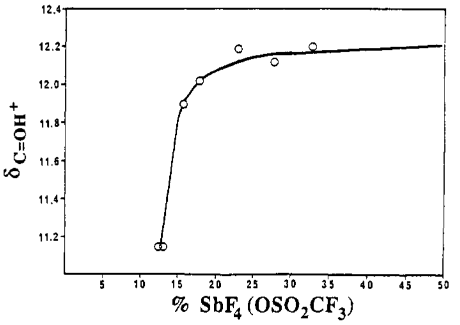


Figure 3. Dependence of the $C{=}OH^+$ ^1H NMR chemical shift of carbonyl protonated 4-methoxybenzaldehyde (2%) on the $SbF_4(OSO_2CF_3)$ content in CF_3SO_3H.

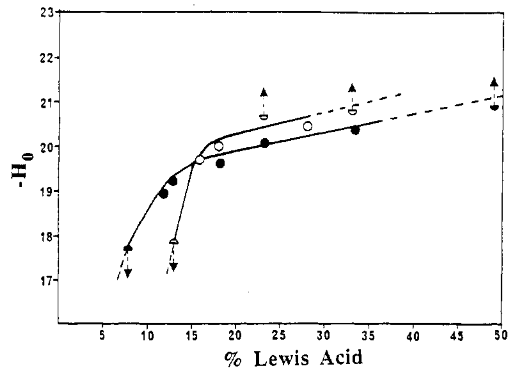


Figure 4. Dependence of H_0 on the SbF_5 (●) and the $SbF_4(OSO_2CF_3)$ (○) content in CF_3SO_3H (2% base). Upper and lower limits are indicated when the values for I exceed the limits of $0.5 < I < 20$.

The limiting values δ_{BH^+} and $\delta_{BH_2^{2+}}$ were measured in triflic acid with 0 and >40 mol % Lewis acid, respectively.[15] Figures 2 and 3 show the dependence of δ_{obsd}[15] on the Lewis acid content in triflic acid. Both are similar in shape to that observed for SbF_5 in fluorosulfuric acid.[15] Since the indicator base and any spurious water act as strong bases in these media and 1 equiv of acid is used to protonate these bases, the true Lewis acid content was calculated from the amount of added Lewis acid by subtracting the amount of added indicator base,[19] and the amount of water present (determined by integration of the H_3O^+ peak). The percentage of Lewis acid was then calculated from the Lewis acid content and the total amount of acid present.

Figure 4 compares the relative acidities of SbF_5 and $SbF_4(OSO_2CF_3)$ in triflic acid as related by the following Hammett acidity function: A value of −19.3 was used for

$$H_0 = -pK_{BH_2^{2+}} - \log I$$

$pK_{BH_2^{2+}}$.[27] These results show that triflic acid with $SbF_4(OSO_2CF_3)$ is a slightly stronger acid (ca. 0.5 H_0 unit) than is triflic acid with SbF_5.

Reaction of Triflic Anhydride with Lewis Acids. The reactivity of a number of Lewis acids toward Tf_2O was investigated. Results are given in Table III. Although $TiCl_4$ gave no evidence of reaction with Tf_2O after several days, TFMT was detected after 20 days when an orange-yellow solid had formed in the NMR tube. Since the

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[19] In each case 2% of indicator base was used.

Table III. Reaction of Tf_2O with Lewis Acids[a]

Lewis acid	Lewis acid	temp, °C	time	% yield of TFMT[c]
$AlCl_3$	3	75	20 days	N.R.[f]
AsF_5	7	75	5 days[b]	55
BF_3	3	75	6 days	N.R.
$FeCl_3$	9	75	20 days	N.R.
$SnCl_4$	13	75	26 days	N.R.
SbF_3	10	75	20 days	N.R.
SbF_5[d]	14	25	*e*	87
$SbF_4(OSO_2CF_3)$[d]	5	25		94
$TiCl_4$	14	75	20 days[b]	75
$TiCl_2(OSO_2CF_3)_2$[d]	5	85	30 min[b]	73
$TiCl_3(OSO_2CF_3)$[d]	10	85	3 h	N.R.

[a] Unless otherwise specified, the reaction was carried out in a sealed NMR tube. [b] All Tf_2O has reacted. [c] Determined by ^{19}F NMR. [d] Reaction was not run in a sealed tube. [e] Data from Table I. [f] N.R. = no reaction.

Table IV. Reactions of Nucleophiles with Excess TFMT

nucleophile	temp, °C	time	% TFMT reacted
C_6H_5N	25	15 min	100
Et_3N	25	5 min	100
THF	75	90 min	0
Ph_2S	65	3 days	0
Ph_3P	65	3 days	0

compounds $TiCl_{4-n}(OSO_2CF_3)_n$ (n = 1, 2, 3) are known to be yellow solids,[11,20] it appears that $TiCl_4$ is probably not the reactive catalyst. This suggests the following reaction sequence:

$$n\ Tf_2O + TiCl_4 \xrightarrow{slow} \underset{(solid)}{TiCl_{4-n}(OSO_2CF_3)_n} + n\ CF_3SO_2Cl$$

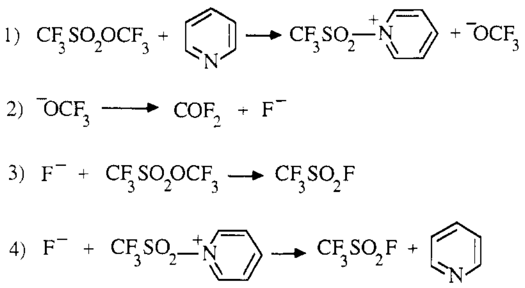
$$Tf_2O \xrightarrow[fast]{TiCl_{4-n}(OSO_2CF_3)_n} SO_2 + TFMT$$

The addition of excess Tf_2O to $TiCl_2(OSO_2CF_3)_2$ under conditions similar to those used for $TiCl_4$ gave complete reaction after only 30 min (Table III). During the course of the reaction, the crystalline $TiCl_2(OSO_2CF_3)_2$ was converted to a brittle, apparently polymeric foam. While $TiCl_2(OSO_2CF_3)_2$ reacts with Tf_2O only at temperatures of 85 °C or greater, the polymeric substance reacts to give TFMT at 45 °C. No reaction of Tf_2O with $TiCl_3(OSO_2CF_3)$ had occurred after 3 h at 85 °C. Attempts to identify the polymeric substance by ^{19}F NMR and mass spectrometry were inconclusive but elemental analyses are within 0.4% compatible with a Ti/C/S ratio of 1/4/4, as expected for $Ti(OSO_2CF_3)_4$. While the mono-, di-, and tritriflates of $TiCl_4$ have been characterized, $Ti(OSO_2CF_3)_4$ has not been reported. These results point to a significant Lewis acidity enhancement by substitution of halogen with the triflate group.

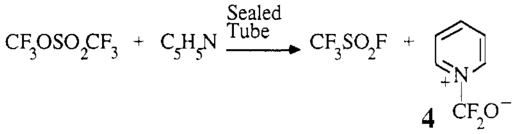
The only other Lewis acid that has been shown to react with Tf_2O is AsF_5. It is assumed that AsF_5 reacts in a manner similar to that of SbF_5. The rate of reaction is, however, much slower. Of the Lewis acids used, SbF_5 is the reagent of choice because milder conditions can be used and it appears to give a higher yield of TFMT.

Reactions of TFMT with Neutral Nucleophiles. Results are listed in Table IV. It had been reported that TFMT transfers a trifluoromethyl cation to pyridine or triethylamine at room temperature in a sealed tube to give quaternary ammonium triflates that readily decompose at atmospheric pressure to regenerate TFMT.[4b] Although the reaction of ordinary alkyl triflates with pyridine give pyridinium triflates,[21] the reverse reactions requiring the very weakly nucleophilic triflate anion to displace pyridine are not facile. We have reinvestigated this reaction of TFMT and pyridine and find no evidence for trifluoromethylation.

Scheme I



The following reaction takes place in excess pyridine:


4

$$\mathbf{4} \xrightarrow[1\ atm]{25°C} COF_2 + C_5H_5N$$

No TFMT is is detected. At atmospheric pressure, 4 decomposes to give pyridine and COF_2. Compound 4 is observed by NMR when the reaction is run in acetonitrile in which 4 is partially soluble. The ^{19}F NMR at 25 °C of 4 shows an expected 4 ppm upfield shift from that of uncomplexed COF_2 and the ^1H NMR spectrum shows three multiplets, each shifted ca. 0.3 ppm downfield, for a complex of pyridine with COF_2. These changes in chemical shifts are analogous to the ones observed for complexes of tertiary amines such as 1,4-diaza[2.2.2]bicyclooctane and triethylamine with trifluoroacetophenone.[22] When triethylamine was added to excess TFMT in THF in a sealed tube, no solid was produced, nor was there any NMR evidence for any remaining TFMT. The TFMT was quantitatively converted to CF_3SO_2F and COF_2.

We propose a fluoride ion chain (Scheme I) to account for this observed quantitative reaction of excess TFMT. Step 1 involves nucleophilic attack of pyridine on sulfur to displace trifluoromethoxide, which rapidly loses fluoride to form COF_2. It has recently been reported[23] that pyridine or triethylamine reacts with fluoroalkyl fluorosulfates at 20 °C to give perfluoroacyl fluorides in good yield. This can also be envisioned as a nucleophilic displacement by fluoride at the sulfur of the fluorosulfate group, giving a fluoroalkoxide. Loss of fluoride from the fluoroalkoxide gives the acyl fluoride. The rapid and quantitative reaction of TFMT with a catalytic amount of cesium fluoride to give CF_3SO_2F and COF_2 supports the importance of the chain-propagating step 3 when fluoride ion is present. An attempt was made to stop the chain carrier in the chain decomposition of TFMT by adding hexamethyldisilazane (HMDS) to trap fluoride as Me_3SiF (5). Instead of stopping the chain decomposition of TFMT, the addition of HMDS formed a second chain carrier, amide anion 8. The products obtained can be explained by the reaction sequence shown in Scheme II. Fluoride ion is initially produced by nucleophilic attack of pyridine on TFMT. The HMDS scavenges most of the fluoride ion but a small

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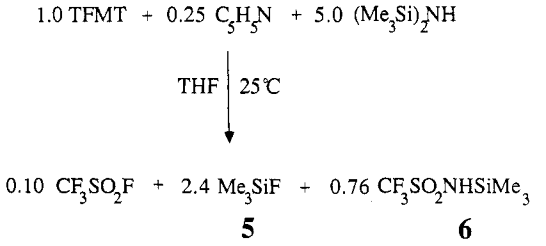
(20) (a) Dalziel, J. R.; Klett, R. D.; Yeats, P. A.; Aubke, F. *Can. J. Chem.* **1974**, *52*, 231. (b) Schmeisser, M.; Sartori, P.; Lippsmeier, B. *Chem. Ber.* **1970**, *103*, 868.

(21) Burdon, J.; McLoughlin, V. C. R. *Tetrahedron* **1965**, *21*, 1.

(22) Schilling, M. L. M.; Roth, H. D. *J. Am. Chem. Soc.* **1980**, *102*, 4271.

(23) Fokin, A. V.; Studnev, Y. N.; Ragulin, L. I.; Krotovich, I. N. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1982**, *8*, 1906.



$$1.0\,\text{TFMT} + 0.25\,C_5H_5N + 5.0\,(Me_3Si)_2NH \xrightarrow[\text{THF}]{25\,^\circ C} 0.10\,CF_3SO_2F + 2.4\,\underset{\mathbf{5}}{Me_3SiF} + 0.76\,\underset{\mathbf{6}}{CF_3SO_2NHSiMe_3}$$

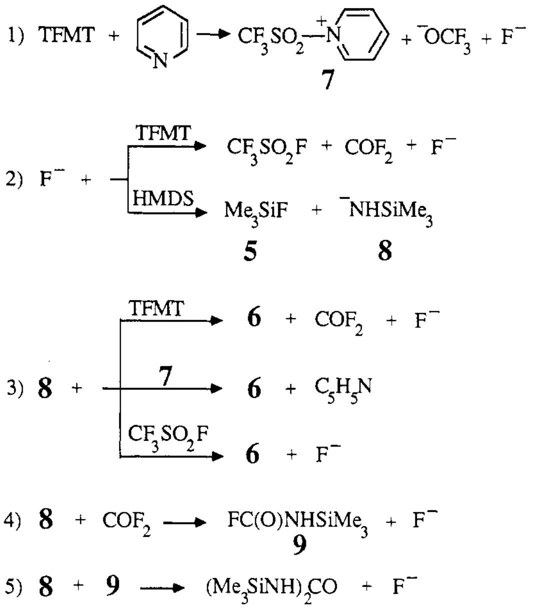
amount still reacts with TFMT to produce CF_3SO_2F. The formation of triflamide **6**, isolated as its hydrolysis product, $CF_3SO_2NH_2$, shows that amide anion **8** competes effectively with pyridine and fluoride ion in reaction with TFMT. The production of 3 equiv of **5**, explained by steps 2, 4, and 5, suggests that COF_2 competes effectively with TFMT for reaction with nucleophiles that are present. While TFMT is readily decomposed by pyridine or triethylamine, it is stable toward other nucleophiles such as triphenylphosphine and diphenyl sulfide. TFMT is unreactive toward THF at 75 °C and toward ether, acetic acid, and ethyl acetate at room temperature. It reacts readily with dimethylformamide and dimethyl sulfoxide and slowly with ethanol at room temperature.

Reaction of TFMT with Anionic Nucleophiles. The reaction of TFMT with *n*-butyllithium, phenyllithium, phenylmagnesium bromide, and lithium thiophenolate gave complex mixtures of products. However, no products arising from trifluoromethylation of the added nucleophiles were detected by ^{19}F NMR. The fluorine chemical shifts of these desired products are far enough removed from the observed products that their presence would have easily been detected. The products detected in the reaction with phenyllithium in ether illustrate some of the complications in these reactions (Scheme III). Not all of the TFMT reacted when it was present in excess. Participation of lithium fluoride from the reaction mixture may have kept the fluoride ion chain from operating efficiently.

Excess TFMT reacts quantitatively and rapidly in the presence of $(C_7H_{15})_4N^+\ I^-$ at room temperature to give CF_3SO_2F and COF_2. An attempt to reduce TFMT by reaction with sodium naphthalenide to provide a possible source of trifluoromethyl radical gave only CF_3SO_2F and COF_2, presumably formed by the fluoride chain. If there were any products arising from the reduction of TFMT to $CF_3^\bullet$ and $CF_3SO_3^-$, they were not produced in large enough quantity to be detected by ^{19}F NMR.

Attempted Friedel–Crafts Reactions of TFMT. In an attempt to further activate TFMT to nucleophilic attack, TFMT was added to aromatic compounds in the presence of Lewis acids. It had been reported[4b] that TFMT failed to react with benzene at room temperature with SbF_5 as a catalyst. Since SbF_5 reacts rapidly to oxidize benzene itself,[24] other Lewis acids were used in attempts to catalyze the reaction of TFMT with benzene. Neither $AlCl_3$ nor BF_3 catalyzed a reaction over 3 days at 70 °C. The TFMT is unreactive toward benzene, either as a trifluoromethylating or a trifluoromethanesulfonylating reagent. The stronger Lewis acid $TiCl_2(OSO_2CF_3)_2$, (as suggested by the results of Table III) also fails to catalyze such a reaction but does react directly with the benzene.

Scheme II



Scheme III

$$CF_3SO_2OCF_3 + PhLi \longrightarrow CF_3SO_2Ph + COF_2 + LiF$$

$$CF_3SO_2Ph + PhLi \longrightarrow PhSO_2Ph + CF_3Li$$

$$COF_2 + 2\,PhLi \longrightarrow PhCOPh + 2\,LiF$$

Discussion

We found initially that in preparation of Tf_2O by distillation of TfOH with 1 equiv of P_2O_5, trace amounts of TFMT were produced. During the course of our studies, a TFMT synthesis was published[4g] that involved the slow distillation of TfOH in the presence of small amounts of P_2O_5. The TFMT was postulated[4g] to result from a protonic acid catalyzed decomposition of the Tf_2O formed in situ from TfOH and P_2O_5. A slow rate of distillation was needed to keep the Tf_2O in contact with the TfOH. We found that boiling pure Tf_2O in the presence of P_2O_5 over a period of 18 days converted up to 25% of the Tf_2O to TFMT. This initially suggested to us that P_2O_5 was acting as a Lewis acid to promote ionization of the Tf_2O to the unstable trifluoromethanesulfonyl cation ($CF_3SO_2^+$). Loss of sulfur dioxide from $CF_3SO_2^+$ yields the reactive trifluoromethyl cation (CF_3^+), which reacts with triflate anion to produce the observed TFMT. It is also possible, however, that a protonic acid catalyzed decomposition of Tf_2O is also operative here because of the probable existence of trace amounts of TfOH in equilibrium with the Tf_2O and P_2O_5. Our initial postulate of Lewis acid catalysis led us to use catalytic amounts of stronger Lewis acids. We found that Tf_2O reacts rapidly with catalytic amounts of SbF_5 or $SbF_4(OSO_2CF_3)$ under very mild conditions to give sulfur dioxide and TFMT in high yield. The reaction procedure we have developed using these catalysts produces TFMT from Tf_2O rapidly and conveniently on any scale.

Mechanism. In addition to TFMT and sulfur dioxide, small amounts of other products are produced as noted in Table II. It is noteworthy that significant amounts of CF_4 and CF_3SO_2F are formed during earlier stages of the reaction and then decrease to an insignificant level during later stages of the reaction. To explain these observations, we propose a mechanism (Scheme IV) that involves competing reactions a and b at several branch points in the reaction pathway. Ionization of Tf_2O by SbF_5 (path 1) produces (trifluoromethanesulfonyloxy)pentafluoroantimonate ion (**10**) and the trifluoromethanesulfonyl

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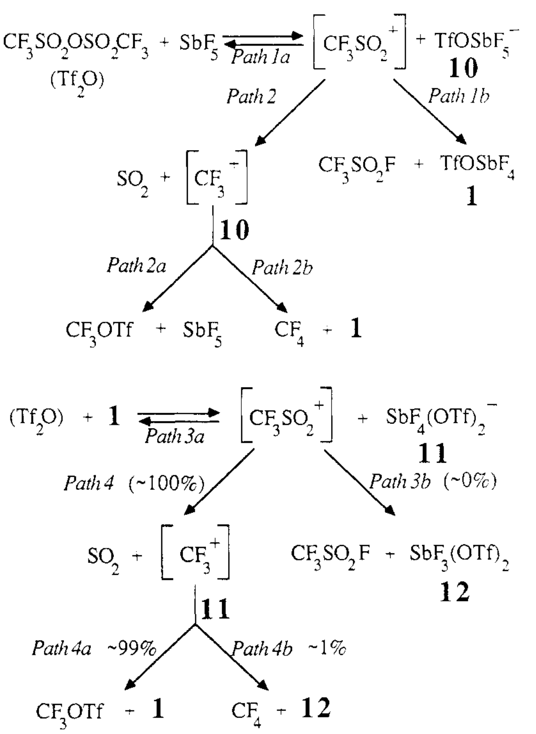
[24] Olah, G. A.; Schilling, P.; Gross, I. M. *J. Am. Chem. Soc.* **1974**, *96*, 876.

Scheme IV



cation, $CF_3SO_2^+$. Antimonate **10**, a 12-Sb-6 species,[25] is analogous to **13**, one of the species observed[16c,17b] in SbF$_5$–FSO$_3$H solutions.

$$2\ FSO_3H + SbF_5 \rightleftharpoons F_5Sb(OSO_2F) + FSO_3H_2^+$$

13

Subsequent reaction of the reactive $CF_3SO_2^+$ with **10** occurs by two paths: electrophilic attack at a fluoride ligand of **10** (path 1a) to produce CF_3SO_2F and a new antimony Lewis acid catalyst (**1**), and abstraction of triflate ($CF_3SO_3^-$) (path 1b), in a reversal of the initial ionization, to regenerate Tf_2O and SbF_5. Alternatively, $CF_3SO_2^+$ can lose sulfur dioxide to form the reactive CF_3^+. It then reacts with **10** either by abstraction of fluoride to give CF_4 and the new 10-Sb-5 catalyst (**1**) (path 2b) or by abstraction of triflate (path 2a) to give TFMT and regenerate SbF_5. Reaction of Tf_2O with the new catalyst, **1**, gives a new 12-Sb-6 species, **11**, plus $CF_3SO_2^+$. Reaction of $CF_3SO_2^+$ or the CF_3^+ generated from it involves another branch point similar to that involving **10**. Reaction with **11** produces CF_3SO_2F, Tf_2O, CF_4, and TFMT and either regenerates**1** or produces still another 10-Sb-5 species with two triflate ligands, a new catalyst, **12**. Similar reactions, which involve ionization of Tf_2O by higher members of the series of 10-Sb-5 catalysts $[SbF_{5-n}(OSO_2CF_3)_n]$, are not needed to explain the results of Table II.

The initially substantial production of CF_3SO_2F and CF_4, and their vanishingly small level of production later in the reaction, is explained by this reaction scheme. As the ratio of **1** to SbF_5 increases during the initially rapid formation of CF_3SO_2F and CF_4 (paths 1b and 2b), Tf_2O begins to react preferentially with **1** via paths 3 and 4. Antimonate **11** contains one more triflate ligand and one less fluorine than **10**. It is therefore reasonable to expect, simply on statistical grounds, that reaction of **11** with the electrophiles $CF_3SO_2^+$ and CF_3^+ should give less attack at fluorine (path a) and more at the triflate ligands (path b) than was the case for the analogous reactions of **10**.

Another factor in the decreased production of CF_3SO_2F and CF_4 as the reaction progresses is the slightly stronger Lewis acidity of $TfOSbF_4$ (**1**) vs. SbF_5 as suggested by our measurement of their relative acidities (see Results). The Tf_2O would therefore be expected to react preferentially with **1** (path 3), rather than with SbF_5 (path 1). Table II indicates (by the amount of CF_3SO_2F and CF_4 trapped) that when an amount approaching one-half of the original amount of SbF_5 has been converted to **1**, the production of TFMT has become nearly quantitative and the production of CF_3SO_2F and CF_4 is very small. The greater acidity of **1** vs. SbF_5 in triflic acid implies a greater delocalization of negative charge on the triflate ligands relative to the fluorine ligands of **11** than is the case in **10**. The resulting lower rate of fluoride ionization or abstraction (path b) in path 4 relative to path 2 is confirmed by the addition of 10 equiv of Tf_2O to pure **1**. Reaction gives only 0.02 equiv of CF_4 and no detectable amounts of CF_3SO_2F as compared to ca. 0.5 equiv of CF_4 and CF_3SO_2F in the reaction of 7 equiv of Tf_2O to SbF_5 (Table II). As the relative concentration of **1** increases, further aliquots of Tf_2O react via path 4a to produce decreasing amounts of CF_3SO_2F and CF_4.

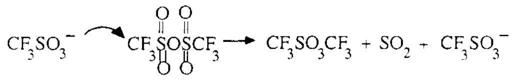
The formation of the other observed side product, COF_2, is most simply explained by the reaction of CF_3^+ with spurious water.[4e] Even under stringently anhydrous conditions, significant amounts of COF_2 formation is often observed. The addition of 10 equiv of Tf_2O to**1** gave 1.1 equiv of COF_2, far more than could reasonably be attributed to reaction with water. The catalyst was also found to contain CF_3SO_3H at the end of the reaction. When the reaction is carried out in a Teflon-brand vessel only 0.3 equiv of COF_2 were produced. The water responsible for the hydrolysis products seen in this reaction carried out in a glass vessel is therefore almost certainly formed by the reaction of HF with glass. The HF is regenerated in the subsequent hydrolysis of CF_3^+. A consequence of the production of TfOH and HF is that during the course of a reaction carried out in a glass vessel the catalyst of the reaction may change from one involving a Lewis acid to a Brønsted acid catalyzed decomposition of Tf_2O. There was no noticeable difference in the rate of reaction in a glass vessel and a Teflon-brand vessel. In any event, the rate of reaction is much faster than that reported[4g] for the triflic acid catalyzed conversion of Tf_2O to TFMT.

$$4\,HF + SiO_2 \longrightarrow SiF_4 + 2\,H_2O$$

$$H_2O + CF_3^+ \longrightarrow COF_2 + HF + H^+$$

$$H_2O + CF_3SO_2^- \longrightarrow CF_3SO_3H + H^+$$

Germain and co-workers have postulated[4h] a Brønsted acid catalyzed decomposition of triflic anhydride by an ionic bimolecular mechanism. They postulate nucleophilic attack of triflate anion on the protonated triflic anhydride to give TFMT and sulfur dioxide. Nucleophilic attack of the highly nonnucleophilic triflate anion at CF_3 would, however, be very surprising in view of the absence of reaction of nucleophiles at the CF_3 of TFMT observed in our work, even in the presence of Lewis acids.



$$CF_3SO_3^- + CF_3SO_2SO_2CF_3 \longrightarrow CF_3SO_3CF_3 + SO_2 + CF_3SO_3^-$$

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(25) The N-X-L classification scheme characterizes species in terms of the number (N) of formal valence shell electrons about an atom X and the number of ligands (L) bonded to X: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Algeria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

A dissociative mechanism involving $CF_3SO_2^+$ and CF_3^+ was considered unlikely by the authors,[4h] since species such as CF_3^+ have not been observed in solution. Failure to observe CF_3^+ directly suggests that it is a very reactive species but does not rule it out as a short-lived intermediate.

A mixture of a perfluoroalkanesulfonic acid and triflic anhydride or a mixture of triflic acid and a perfluoroalkanesulfonic anhydride was reported to give, upon equilibration, only symmetrical anhydrides.[4g,h] This was considered to be evidence against a dissociative mechanism. This would be true if the acid-catalyzed ionization of a symmetrical anhydride produced only the symmetrical ester, but this is unlikely since protonation of the anhydride generates a molecule of the conjugate base of the protonic acid catalyst in the vicinity of the ionizing anhydrides.

Equilibration of an acid and the anhydride of a different acid to give only symmetrical anhydrides is unexpected. We added perfluorohexanesulfonic acid to triflic anhydride and allowed the mixture to reach equilibrium at ambient temperature (to preclude decomposition to give esters). Over a 3-day period, new peaks appeared in the ^{19}F NMR spectra at 84.6 MHz that were consistent (see Table I) with perfluorohexanesulfonic anhydride and triflic acid. The ^{19}F NMR spectra at 338 MHz, however, showed two peaks in the triflic anhydride region separated by 0.016 ppm (5.5 Hz) in a 1.0/1.5 ratio, consistent with the presence of both triflic anhydride and the unsymmetrical anhydride. The peaks for the perfluorohexane group of the unsymmetrical anhydride are not resolved from those of the acid under these conditions. It therefore appears that chemical shift near-degeneracy could explain the reported failure to see the unsymmetrical anhydride in a mixture of a sulfonic acid with the anhydride of a different sulfonic acid.

Reactions of mixtures of triflic and other perfluoroalkanesulfonic anhydrides in the presence of the related sulfonic acids preferentially form trifluoromethyl esters during the early stages of the reaction. This is consistent with a dissociative mechanism since trifluoromethyl cation is more easily formed than analogues in which one of the CF_3 fluorines is replaced by a perfluoroalkyl group.[26] As the relative amount of the triflyl group diminishes during the reaction, the perfluoroalkyl ester is formed in greater amounts.

Acidity Measurements. Our determination that a solution of $TfOSbF_4$ (1) in triflic acid yields a stronger Brønsted acid than SbF_5 in triflic acid, which implies that 1 is a stronger Lewis acid than SbF_5, is consistent with the studies of fluorosulfuric superacid systems. Conductometric, cryoscopic, and fluorine nuclear magnetic resonance studies[17b] on solutions of SbF_5, $SbF_4(OSO_2F)$, and SbF_5–SO_3 mixtures in fluorosulfonic acid show that there exists a series of increasingly stronger acids with the general formula $H[SbF_{5-n}(OSO_2F)_{1+n}]$ where $n = 0, 1, 2, 3$. Each successive replacement of fluorine by OSO_2F better stabilizes the negative charge of the conjugate base by withdrawing negative charge to the OSO_2F group. From the results of conductivity measurements, the following relative acid strengths in fluorosulfuric acid have been reported:[27] $PF_5 < AsF_5 < AsF_4(OSO_2F) < SbF_5 < AsF_2(OSO_2F_3 < SbF_2(OSO_2F)_3$. In both studies, replacement of fluorine by fluorosulfate gave a stronger acid.

In addition to our study of $TfOSbF_4$ (1), we have observed a great enhancement of the Lewis acid reactivity of titanium tetrachloride almost to the level of that of SbF_5 in reaction with Tf_2O (Table III) by replacing two chlorines with triflate groups. Engelbrecht and Tschager have reported[4f] the synthesis of $B(OSO_2CF_3)_3$ and its acidity measurements in CF_3SO_3H. It is comparable to the SbF_5–$3SO_3$–FSO_3H superacid system, one of the most acidic systems known. These show that there is a marked enhancement of acidity upon replacement of halides with triflate groups.

The general trend observed in fluorosulfonic acid superacid media suggests that $Sb(OSO_2F)_5$ would give the strongest acid system possible in fluorosulfuric acid. These higher fluorosulfate species do not, however, appear to be stable since ^{19}F NMR measurements indicate that $SbF_2(OSO_2F)_3$ in fluorosulfuric acid is appreciably dissociated to give sulfur trioxide and $SbF_3(OSO_2F)_2$. Dissociations or decompositions of this type are observed for a number of fluorosulfates.[28] Since triflates cannot undergo the same

$$SbF_2(OSO_2F)_3 \rightleftarrows SbF_3(OSO_2F)_2 + SO_3$$

type of decomposition seen for fluorosulfates, involving loss of SO_3, it would appear that replacement of fluoride by triflate ligands could produce superior superacid media.

Limitations of TFMT Utility. Our investigation of the use of TFMT as a possible CF_3^+ equivalent was successful only in that we observed the apparent in situ trapping of CF_3^+, produced during the synthesis of the TFMT from Tf_2O in the presence of $TfOSbF_4$. The possibilities for synthetically useful trapping of this postulated CF_3^+ intermediate are, however, severely limited by the extreme reactivity of the reaction medium in which CF_3^+ is produced. It is difficult to conceive of nucleophiles, which might compete with the catalyst-bound triflate in the trapping of the CF_3^+ intermediate, that would exist for any appreciable time in the reaction medium. Benzene, for example, is rapidly oxidized in SbF_5.[24] Trifluoromethyl halides react with SbF_5 at −78 °C to form CF_4, in a reaction analogous to the one we have observed.[29]

The reactions of TFMT with nucleophiles in the absence of Lewis acids also fail to trifluoromethylate the nucleophiles. A wide range of soft and hard nucleophiles react with TFMT via nucleophilic displacement only at sulfur. This suggests the use of TFMT as a possible trifluoromethanesulfonylating reagent. There are two other major complications that also make the use of this reagent unattractive. First, reaction of TFMT with any nucleophile produces trifluoromethoxy anion, a source of fluoride ion, a nucleophile much more reactive toward TFMT than those added as desired reactants. This gives a fluoride ion chain reaction that destroys the TFMT (Scheme I). The efficiency of the fluoride ion chain decomposition is evidenced by the formation of CF_3SO_2F even in the presence of large amounts of fluoride scavengers such as hexamethyldisilazane. Secondly, fluorophosgene produced in this reaction competes effectively with TFMT in reaction of nucleophiles. The competitive reaction of fluorophosgene vs. TFMT with nucleophiles is demonstrated by Scheme III in which nucleophiles are consumed by reaction with fluorophosgene.

The attempted Friedel–Craft reactions show that even in the presence of Lewis acids, TFMT is unreactive toward benzene, either as a trifluoromethylating or trifluoromethanesulfonylating reagent. Since Hendrickson and Bair[30] have reported the trifluoromethanesulfonylation of

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benzene in 61% yield with Tf$_2$O and AlCl$_3$ at room temperature, it is clear that TFMT is less effective as a sulfonylating agent than is Tf$_2$O.

Conclusion

We have found that TFMT is conveniently and economically prepared in high yield by the reaction of Tf$_2$O with strong Lewis acids such as TfOSbF$_4$, which is formed in the reaction of Tf$_2$O with SbF$_5$. Although TFMT is readily accessible as a result of this reaction, we have found no examples of trifluoromethylation by this reagent, contrary to published reports.[4b] Initial reaction with a wide range of nucleophiles occurs at sulfur to displace trifluoromethoxide to give trifluoromethanesulfonylation of the nucleophile. The synthetic utility of TFMT as a trifluoromethanesulfonylating reagent is severely limited, however, because the reagent is rapidly destroyed by a fluoride ion chain reaction in the presence of other nucleophiles. Fluorophosgene, a product of the decomposition, reacts with many of the added nucleophiles to make them less accessible for reaction with TFMT.

Although we suggest that CF$_3^+$ may be an intermediate in the formation of TFMT, the strongly electrophilic nature of the reaction medium makes trapping of the CF$_3^+$ with added nucleophiles difficult. We have not been able to devise a suitable system to carry out trifluoromethylations by trapping the CF$_3^+$.

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Registry No. **1**, 109084-87-9; **5**, 420-56-4; **6**, 28920-31-2; **8**, 88035-99-8; TFMT, 3582-05-6; Tf$_2$O, 358-23-6; HMDS, 999-97-3; THF, 109-99-9; SbF$_5$, 7783-70-2; TiCl$_4$, 7550-45-0; AsF$_5$, 7784-36-3; TiCl$_2$(OSO$_2$CF$_3$)$_2$, 15001-53-3; Et$_3$N, 121-44-8; PhSO$_2$CF$_3$, 426-58-4; Ph$_2$CO, 119-61-9; (*n*-C$_7$H$_{15}$)$_4$N$^+$I$^-$, 3535-83-9; Ph$_2$S, 139-66-2; Ph$_3$P, 603-35-0; pyridine, 110-86-1; cesium fluoride, 13400-13-0; phenyllithium, 591-51-5; diphenyl sulfone, 127-63-9; sodium naphthalenide, 3481-12-7; perfluorohexanesulfonic acid, 355-46-4; perfluorohexanesulfonic anhydride, 109065-55-6.

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Reactions of the Readily Accessible Electrophile, Trifluoroacetyl Triflate: A Very Reactive Agent for Trifluoroacetylations at Oxygen, Nitrogen, Carbon, or Halogen Centers

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Trifluoroacetyl triflate (TFAT) is readily prepared in 82% yield by the dehydration (phosphorus pentoxide) of a 2:1 mixture of trifluoroacetic acid and trifluoromethanesulfonic (triflic) acid. Reactions of this highly electrophilic trifluoroacetylating reagent with alcohols, ketones, ethers, amines, and pyridines give esters, enol esters, ether cleavage, amides, and acylpyridinium ions, respectively. Reactions with ionic or easily ionizable alkyl halides give the very volatile trifluoroacetyl halides and the ionic triflate. Triphenylmethyl chloride, for example, is quantitatively converted to triphenylcarbenium triflate in a very convenient synthetic procedure. Trifluoroacetyl triflate is used in the synthesis of the first member of a new class of pyrylium salts, 2,6-dimethoxypyrylium triflate.

Compounds that contain the trifluoromethanesulfonate (triflate) moiety[2] are potent electrophilic reagents because the triflate (OTf) group is one of the best electrofugal leaving groups known[3] and is a powerful electron-withdrawing group. This is illustrated by the marked electrophilicity observed for alkyl,[4] acyl,[5] and halogen[6] triflates. Of the many trifluoroacetylating reagents that have been reported, trifluoroacetyl triflate (TFAT) is probably the most powerful and useful, as evidenced here and in an earlier paper,[7a] by virtue of its reactivity toward several types of nucleophiles under mild conditions. Although evidence for salts of the trifluoroacetylium cation, which would be expected to be a more powerful trifluoroacetylating reagent, have been claimed,[8] further work[9] showed them to be covalent acyl fluoride complexes, not acylium salts. We here report the convenient synthesis of TFAT and survey its reaction with a variety of nu-

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