Trifluoromethanesulfonic Acid and Derivatives

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Contents

I. Introduction

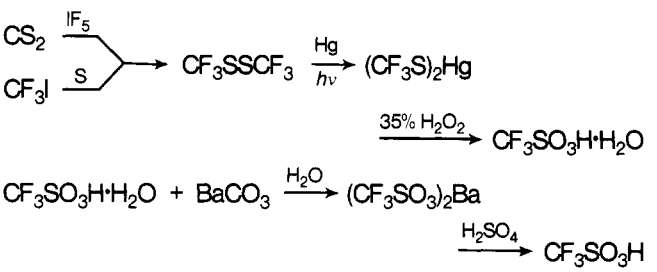
Trifluoromethanesulfonic acid† has often been acclaimed as the strongest of all known monoprotic organic acids. Fluorosulfonic acid has also been given the same status. The actual order is of relatively little consequence for several reasons. First, current evidence indicates that the ordering of acidities of these and other strong acids is highly dependent upon the solvent media in which they are compared. Secondly, the difference in acidity between trifluoromethanesulfonic and fluorosulfonic acids in any given reaction medium is so small as to be generally outweighed by other considerations in the selection of one of these strong acids for a particular application. Trifluoromethanesulfonic acid and its conjugate base have extreme thermal stability and resistance to both reductive and oxidative cleavage. They do not provide a source of fluoride ions even in the presence of strong nucleophiles. The nonoxidizing nature of trifluoromethanesulfonic acid can be beneficial in minimizing or eliminating side reactions in some instances, and it obviously reduces the hazards associated with strong oxidizing acids such as perchloric acid. These uncommon properties have been a great stimulus to extensive research efforts directed toward trifluoromethanesulfonic acid and its derivatives. The plethora of information published on this subject in the last two decades has prompted the authors to review in a systematic manner the preparation and reactions of the acid and its most studied derivatives. A review by Senning[1] includes salient features of the pre-1965 literature on trifluoromethanesulfonic acid and derivatives.

† Trifluoromethanesulfonic acid has been given the common name "triflic acid",[127] and its esters and salts are commonly known as "triflates". In this review the more formal names will be used.

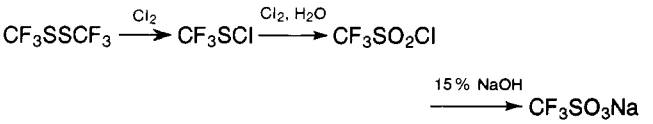
II. Trifluoromethanesulfonic Acid

A. Preparation and Physical Properties

The first reported syntheses of trifluoromethanesulfonic acid appeared in 1954.[2,3] Haszeldine and Kidd[2] obtained the acid by oxidation of bis(trifluoromethylthio)mercury with aqueous hydrogen peroxide.

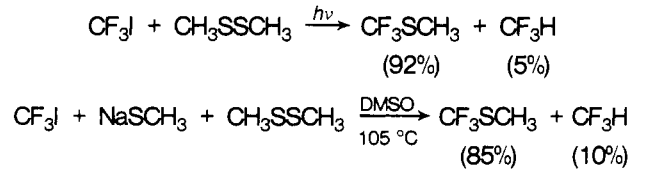


This process was later modified by the direct formation of bis(trifluoromethylthio)mercury from carbon disulfide and mercuric fluoride.[4] An alternate route to the acid via trifluoromethanesulfenyl chloride has also been described by Haszeldine and Kidd.[5]



Commonly, the hygroscopic salts of trifluoromethanesulfonic acid are dehydrated at about 100 °C under vacuum prior to the addition of sulfuric acid.

Methyltrifluoromethyl sulfide is another intermediate that has been employed in the synthesis of trifluoromethanesulfonic acid.[6] The sulfide is most conveniently prepared by the reaction of trifluoroiodomethane with sodium methanethiolate, but even higher yields are obtained from a photochemical reaction.



$$CF_3SCH_3 \xrightarrow[HOAc]{KMnO_4\ (or\ H_2O_2)}$$

$$CF_3SO_2CH_3 \xrightarrow[aq\ KMnO_4]{1.\ NaOCl\ \ 2.\ OH^-} CF_3SO_3^-$$

The oxidation of methyltrifluoromethyl sulfide to the sulfonate salt was successfully carried out under a variety of conditions.[6,7]

The disclosure that trifluoromethanesulfonic acid, as well as higher homologous perfluoroalkanesulfonic acids, can be prepared by electrochemical fluorination (ECF) of alkanesulfonyl fluorides (or chlorides) was also made in 1954.[3]

$$CH_3SO_2F \xrightarrow[ECF,\ -3H_2]{3HF} CF_3SO_2F \xrightarrow{aq\ KOH} CF_3SO_3K \xrightarrow{100\%\ H_2SO_4} CF_3SO_3H$$

In contrast to methanesulfonyl fluoride, trifluoromethanesulfonyl fluoride cannot be conveniently hydrolyzed directly to the acid. Therefore, the pure acid is usually obtained by distillation from a mixture of either the anhydrous sodium, potassium, or barium salts combined with sulfuric acid.[3,8] The salts must be thoroughly dried by heating under vacuum prior to the addition of sulfuric acid since trifluoromethanesulfonic acid forms a stable monohydrate which can also be distilled from the sulfuric acid mixture. The ECF method results in a very high yield of trifluoromethanesulfonic acid, and this procedure has also been described by Gramstad and Haszeldine.[9,10] They noted that methanesulfonic acid itself is an unsuitable raw material for the ECF process due to discharge of hydroxyl ions at the anodes. The oxygen difluoride which is formed may then result in oxidative attack on either methanesulfonic acid or the fluoride.

Pure trifluoromethanesulfonic acid is a clear, colorless liquid which boils at 162 °C (760 Torr).[2] By comparison, methanesulfonic acid boils at 165 °C (8.5 Torr) reflecting a much higher degree of intermolecular association. Trifluoromethanesulfonic acid fumes in moist air until it is converted to the stable monohydrate which is a solid at room temperature (mp 34 °C).[11] The monohydrate is more correctly termed hydronium trifluoromethanesulfonate since water is quite a good base in the presence of such a strong acid. Like the analogous hydronium perchlorate, this salt is very hygroscopic and will liquify upon contact with moist atmosphere. An x-ray crystallographic study showed that its structure is comprised of oxonium ions which are hydrogen-bonded to three sulfonate groups in a pyramidal arrangement.[12]

In addition to being miscible with water in all proportions, trifluoromethanesulfonic acid is soluble in many polar organic solvents such as dimethylformamide, sulfolane, dimethyl sulfoxide, dimethyl sulfone, and acetonitrile. The acid is also soluble in alcohols, ketones, ethers, and esters; however, these are generally not suitable inert solvents. Trifluoromethanesulfonic acid is completely dissociated in dimethyl sulfoxide, whereas some other strong acids such as methanesulfonic, trifluoroacetic, and sulfuric acid are not.[13] Indeed, trifluoromethanesulfonic acid is one of the strongest of all known acids. Conductivity studies of strong acids in anhydrous acetic acid have shown that in this medium trifluoromethanesulfonic acid is a stronger acid than perchloric or fluorosulfonic acid.[14,15] However, based on the greater electron withdrawal when fluorine is attached to the sulfonyl group, it was predicted that fluorosulfonic acid would be the stronger acid.[16] Russell and Senior[17] have recently reported the specific conductances for trifluoromethanesulfonic and fluorosulfonic acids in anhydrous sulfuric acid. The former was found to be the weaker acid in this system. Ion-pair formation was negligible in sulfuric acid, but the value, $K_a = 8 \times 10^{-4}$ mol·kg^{-1}, reflects the ability of trifluoromethanesulfonic acid to donate a proton to the sulfuric acid solvent. Actually, K_a is given by $K_I K_D/(1 + K_I)$ where K_I is the ionization constant and K_D is the ion-pair dissociation constant. In the much more basic solvent, acetic acid, the K_a would largely be determined by K_D, since $K_I \gg 1$.

TABLE I. Kramer Selectivity Parameter and H_0 Values for Some Strong Acid Systems

Acid	K_{iso}, h^{-1}	K_{ex}, h^{-1}	I/E	$-H_0$
HF	0	0.03	0	11.2–11.7
2 M SbF_5–HF	2.42	0.69	3.50	15.3
2 M TaF_5–HF	0.58	0.07	8.29	13.5
HSO_3F	1.42	>3.34	0.42	14.5–15
2 M SbF_5–HSO_3F	1.42	0.79	1.80	>18
2 M TaF_5–HSO_3F	0.72	0.62	1.16	16.7
CF_3SO_3H	0	>5.92	0	13
2 M SbF_5–CF_3SO_3H	2.68	0.62	4.25	>18
2 M TaF_5–CF_3SO_3H	4.89	4.76	1.03	16.5

In another comparison of acid strength, trifluoromethanesulfonic acid functioned as the proton donor in binary systems with sulfuric, acetic, chloroacetic, dichloroacetic, trichloroacetic, or trifluoroacetic acid.[18–20] Plots of mole fraction vs. the deviation of molar volume from additivity or mole fraction vs. the relative temperature coefficients of conductivity and viscosity indicated that 1:1 addition products were predominant since maxima occurred at or near 0.5 mol fraction. Prudence is warranted in judging relative acid strengths by such measurements on dissimilar acid types since these correlations would suggest that trifluoromethanesulfonic acid is of lesser strength than perchloric acid, and this order has not been borne out by any of the previously mentioned studies.

The rate of aromatic hydrogen exchange in the presence of a Brønsted acid is also a measure of the proton-donating abilities of such acids. It has been reported that the rate of hydrogen exchange in benzene with trifluoromethanesulfonic acid was 2.2×10^{11} times faster than with trifluoroacetic acid.[21] Kramer[22,23] has devised a method of ranking strong acids by an empirical kinetic means which reflects the inherent ability of an acid to promote carbonium ion rearrangements. Ideally, the "better" acid should give a higher ratio of isomerization to exchange (I/E). Specifically, the rate of isomerization at 23 °C of an equilibrium methylpentane mixture to 2,2-dimethylpentane and *n*-hexane divided by the rate of proton exchange with isopentane or methylcyclopentane was defined as the selectivity parameter. Perhaps a direct correlation could be found with acid strength by this method. However, as is obvious from the limited data presented in Table I, the Hammett acidity function values, H_0, are not a simple function of I/E. The H_0 values were determined by the method proposed by Gillespie and Peel,[24] and they represent the first such comparison between trifluoromethanesulfonic acid and other strong acids.

The exceptional strength of trifluoromethanesulfonic acid has also been demonstrated by nonaqueous titrimetry. Lane[25] found that titration of selected tertiary amines with trifluoromethanesulfonic acid in glacial acetic acid compared favorably in instrument response and visual endpoint detection with the standard perchloric acid/glacial acetic acid titrant. Unlike the situation in many perchloric acid titrations, there was no trace of precipitation or gel formation with trifluoromethanesulfonic acid. The nonoxidizing character of the latter acid represents another potential advantage to its use as a nonaqueous titrant.

Other properties of trifluoromethanesulfonic acid such as a relatively low freezing point and viscosity when compared with sulfuric acid have made it a highly useful solvent for the generation of some cation radicals for ESR spectral studies.[26]

The following values have been reported[19,27] for the density, index of refraction, viscosity, and electrical conductivity at 25

°C for the pure acid: $d = 1.6980$, $n^{25}D$ 1.325, $\eta = 2.87$ cP, and $\chi = 2 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$.

B. Reactions and Uses of Trifluoromethanesulfonic Acid

1. Salt Formation

Trifluoromethanesulfonic acid reacts exothermally with aqueous metal hydroxide or metal carbonate solutions to give salts. In some cases, metal oxides are directly added to the neat acid. Many of these salts possess excellent thermal stability, especially in the anhydrous state. Pure sodium, potassium, barium, and silver trifluoromethanesulfonates all require temperatures in excess of 350 °C for thermal decomposition.[8,9] They have been recrystallized from various organic solvents such as acetone, ethanol, and ethyl ether/carbon tetrachloride. The barium salt can easily be obtained in a high degree of purity without recrystallization since excess barium can be effectively precipitated from aqueous solution as the sulfate.

A less common method of sulfonate salt formation was discovered during early attempts to obtain infrared spectra of the acid using conventional sodium chloride plates.[2] Hydrogen chloride fumes were evolved, and sodium trifluoromethanesulfonate was formed. Dalziel and Aubke[28] have prepared the cesium salt in this manner.

$$CF_3SO_3H + CsCl \rightarrow CF_3SO_3Cs + HCl$$

The infrared spectrum of the acid can be successfully recorded with silver chloride plates[29] which indicates that only a very slow reaction (if any) occurs with silver chloride.

Cuprous and cupric trifluoromethanesulfonates have been prepared under nonaqueous conditions from cuprous oxide[30-32] or cupric carbonate.[32,33] In the former case, a complexing agent (L) was employed, and the stable complex rather than the free salt was isolated.

$$2CF_3SO_3H + Cu_2O \xrightarrow[\Delta]{L} 2CF_3SO_3Cu \cdot L + H_2O$$

Typical complexing agents included compounds from the following classes: aromatic hydrocarbons, olefinic hydrocarbons, nitriles, nitroalkyls, nitroaryls, and sulfones (see also section III.A). Uncomplexed cuprous trifluoromethanesulfonate is a maroon powder. It is somewhat unstable when exposed to the atmosphere and decomposes above 300 °C in a sealed capillary.[32] It has been prepared from cuprous oxide in a noncomplexing solvent such as *n*-octane, and it was obtained by reduction of the anhydrous cupric salt with copper metal in the presence of trifluoromethanesulfonic acid[32,33] or a complexing agent.[30,31]

$$2CF_3SO_3H + CuCO_3 \xrightarrow[-CO_2,-H_2O]{CH_3CN} (CF_3SO_3)_2Cu \xrightarrow[CF_3SO_3H]{Cu} 2CF_3SO_3Cu$$

Cupric acetate was nearly as effective as cupric carbonate in the above reaction sequence.[33]

A 2,2′-bipyridyl complex of argentous trifluoromethanesulfonate was obtained from the reaction of either argentous carbonate or oxide with excess aqueous trifluoromethanesulfonic acid–2,2′-bipyridyl mixture.[34] Conversion to the argentic complex was accomplished by an electrolytic procedure using dilute trifluoromethanesulfonic acid.

Salts of the general formula $(CF_3SO_3)_3M \cdot xH_2O$, where M is a rare earth metal, have been prepared by the reaction of rare earth metal oxides with trifluoromethanesulfonic acid.[35-38] The trivalent rare earth metals can be extracted from various ores, such as bastnasite and monazite by this method. These trifluoromethanesulfonates in the hydrated form are much more soluble in organic solvents than the corresponding fluorosulfonates which recommends the former as potentially useful homogeneous catalysts. Uranium oxide can be converted into an oxyuranium trifluoromethanesulfonate upon reaction with the appropriate stoichiometric amount of the acid.[39]

$$UO_3 + 2CF_3SO_3H \rightarrow UO_2(OSO_2CF_3)_2 + H_2O$$

$$UO_2(OSO_2CF_3)_2 \xrightarrow[100\ °C]{10^{-4}\ Torr}$$

Ammonium trifluoromethanesulfonate has been prepared by neutralization of the aqueous acid with ammonia.[40] The crude salt was easily purified by vacuum sublimation, and it was only mildly hygroscopic in the pure state. A crystal structure determination of this salt was recently completed.[41]

Grakauskas[42] observed a somewhat similar degree of hygroscopicity for fluorammonium trifluoromethanesulfonate which could be isolated without the exclusion of atmospheric moisture. In solution it did not etch glass. Also, this salt was more thermally stable and more soluble in organic solvents than the analogous perchlorate or methanesulfonate salts.

$$NHFCO_2CH(CH_3)_2 + 2CF_3SO_3H \xrightarrow[25\ °C,\ -CO_2]{CH_2Cl_2} NH_3F^+CF_3SO_3^- + CF_3SO_3CH(CH_3)_2$$

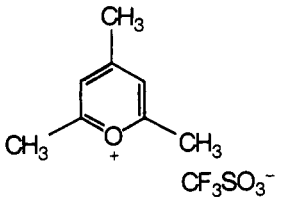
Gramstad and Haszeldine[11] have prepared a number of organic trifluoromethanesulfonates. Aniline, *N*-ethylaniline, and *N,N*-diethylaniline all reacted quantitatively with the acid. These nonhygroscopic salts were obtained analytically pure after washing with ether, and they were suggested to be good derivatives for identifying small amounts of trifluoromethanesulfonic acid. The anilinium salt which was especially recommended for this purpose[11] melts at 267–268 °C after purification by recrystallization.[43]

Tetraalkylammonium trifluoromethanesulfonates have been prepared from the tetraalkylammonium halides or hydroxides.[44]

$$(CH_3CH_2CH_2)_4N^+Br^- + CF_3SO_3H \xrightarrow{H_2O} (CH_3CH_2CH_2)_4N^+CF_3SO_3^- + HBr \quad (80\%)$$

(Quaternary salt formation via alkylation of tertiary amines is presented in section III.D.) These quaternary salts are extremely valuable as supporting electrolytes in nonaqueous organic electrochemistry. They possess excellent solubility in organic solvents and dissociate to give a solution of very low specific resistance. There is also indication of an interest in the polarographic use of certain lanthanide trifluoromethanesulfonates.[38] Half-wave potentials were found to be quite similar to those of the analogous perchlorate salts. The oxidative and reductive stability of the trifluoromethanesulfonate anion combined with its low degree of nucleophilicity make it ideal for electrochemical applications. Scott and Taube[45] have shown that the nucleophilicity of the trifluoromethanesulfonate ion toward chromium(III) is only slightly greater than that of the perchlorate ion. In another study, the specific adsorption of the trifluoromethanesulfonate ion on mercury was found to be similar to that of perchlorate and nitrate ions.[46] Certainly a big disadvantage to the usage of perchlorates in electrochemical or other applications is the potential for explosive decomposition during purification or drying operations. In contrast, trifluoromethanesulfonates can be simply prepared and purified or dehydrated.

When a mixture of *tert*-butyl alcohol and acetic anhydride is treated with trifluoromethanesulfonic acid, a salt is formed.[47] Presumably, *tert*-butyl alcohol serves as a convenient source of isobutylene which is acylated twice enroute to the stable pyrylium species.



Analogous pyrylium perchlorates are highly valued synthetic intermediates because of their versatility, even though they are highly explosive if handled improperly. This hazard may be eliminated by the use of either trifluoromethanesulfonate or tetrafluoroborate anions. In some cases, the greater solubility of the trifluoromethanesulfonate in organic solvents could also be advantageous. A few of the well-known applications for pyrylium salts include the synthesis of pyridines, 4*H*- and 2*H*-pyrans, 2-acylfurans, azulenes, and benzene derivatives.[48,49]

2. Ester Formation

The exothermic reaction of alcohols with trifluoromethanesulfonic acid leads to esters, but ethers and olefins can also be formed which greatly limits the usefulness of this reaction.[11]

$$CF_3SO_3H + CH_3CH_2OH \rightarrow \underset{(45\%)}{CF_3SO_3CH_2CH_3} + \underset{(19\%)}{(CH_3CH_2)_2O} + \underset{(13\%)}{CH_2{=}CH_2}$$

The acid reacts reversibly with ethylene or ethyl ether to give the ethyl ester.[11,50] Addition of the acid to olefins or cyclopropanes under mild conditions should provide a rather general synthesis of the alkyl trifluoromethanesulfonates. Olah[51] has reported the facile preparation of esters from the addition of fluorosulfuric acid to ethylene, propylene, vinyl chloride and vinylidene fluoride. However, styrene, butadiene, and isobutylene gave mainly polymeric or oligomeric materials. Similar results would be expected with trifluoromethanesulfonic acid if suitably mild conditions are employed.

Methyl or ethyl esters are most conveniently prepared by the reaction of trifluoromethanesulfonic acid, or its barium salt, with methyl or ethyl sulfates.[50,52-55]

$$2CF_3SO_3H + (CH_3)_2SO_4 \rightarrow 2CF_3SO_3CH_3 + H_2SO_4$$

Even though the methyl and ethyl esters have relatively low boiling points, they are generally isolated by distillation under reduced pressure. The ethyl ester decomposes slowly at its atmospheric boiling point, and it rapidly decomposes at 150 °C to give ethylene and trifluoromethanesulfonic acid.[11]

In one reported instance, an alkyl ester was prepared by the treatment of a diazo compound with an excess of the acid.[56]

$$p\text{-}CH_3C_6H_4SO_2CHN_2 + CF_3SO_3H \xrightarrow[0\ ^\circ C]{CH_3CO_2C_2H_5} p\text{-}CH_3C_6H_4SO_2CH_2OSO_2CF_3 + N_2$$

The first perfluoroalkyl trifluoromethanesulfonate to be reported was obtained in an unusual manner.[57,58] Electrolysis of trifluoromethanesulfonic acid at low temperature provided the thermally unstable bis(trifluoromethanesulfuryl) peroxide. The products of the explosive decomposition of this peroxide at about 10 °C were sulfur trioxide, perfluoroethane, and trifluoromethyl trifluoromethanesulfonate. In contrast to the hydrocarbon alkyl esters, the perfluorocarbon ester is quite resistant to hydrolysis.

Other methods of alkyl ester formation are based on the anhydride or silver salt of trifluoromethanesulfonic acid and are mentioned in sections III.A and III.B.

Vinyl trifluoromethanesulfonates have been extensively utilized in solvolysis studies (see section III.D.). They have been prepared by addition of the acid to acetylenes, allenes, or an acyltriazine.[59-64]

$$(C_6H_5)_2C{=}C(C_6H_5)N{=}NN(C_6H_5)COCH_3 + CF_3SO_3H \xrightarrow[-50\ ^\circ C]{CH_2Cl_2} (C_6H_5)_2C{=}C(C_6H_5)OSO_2CF_3$$

$$H_2C{=}C{=}CH_2 + CF_3SO_3H \rightarrow H_2C{=}C(CH_3)OSO_2CF_3$$

$$CH_3C{\equiv}CCH_3 + CF_3SO_3H \rightarrow \underset{65/35\ (trans/cis)}{CH_3CH{=}C(CH_3)OSO_2CF_3}$$

Summerville and Schleyer[61] established that cis addition was the predominant occurrence when either the deuterated acid was added to 1-hexyne or the protonic acid was added to 1-hexyne-*1-d*. It was necessary to use an excess of the acetylene and to neutralize the reaction mixture before distillation in order to prevent acid-catalyzed double-bond migration.

Vinyl trifluoromethanesulfonates are generally more thermally stable than their saturated counterparts; this enhanced stability allows them to be purified by preparative gas chromatography. Under very carefully controlled conditions, some of the more stable bicyclic and tricyclic alkyl trifluoromethanesulfonates have also been isolated or purified by this method.[65]

The anhydride of trifluoromethanesulfonic acid has been extensively employed in the synthesis of vinyl esters from ketones (section III.B).

3. Acid Anhydride and Acid Halide Formation

Brice and Trott[8] first reported the isolation of trifluoromethanesulfonic acid anhydride. It was obtained as a by-product from the synthesis of trifluoromethanesulfonyl chloride.

$$CF_3SO_3H \xrightarrow[\Delta]{PCl_5} \underset{(53\%)}{CF_3SO_2Cl} + \underset{(20\%)}{(CF_3SO_2)_2O}$$

Considerably better yields of the anhydride (65–83%) are realized by treatment of the acid with phosphorus pentoxide.[11,43,52] Redistillation of crude anhydride from a small amount of phosphorus pentoxide provides a pure product which does not fume upon brief exposure to the atmosphere.

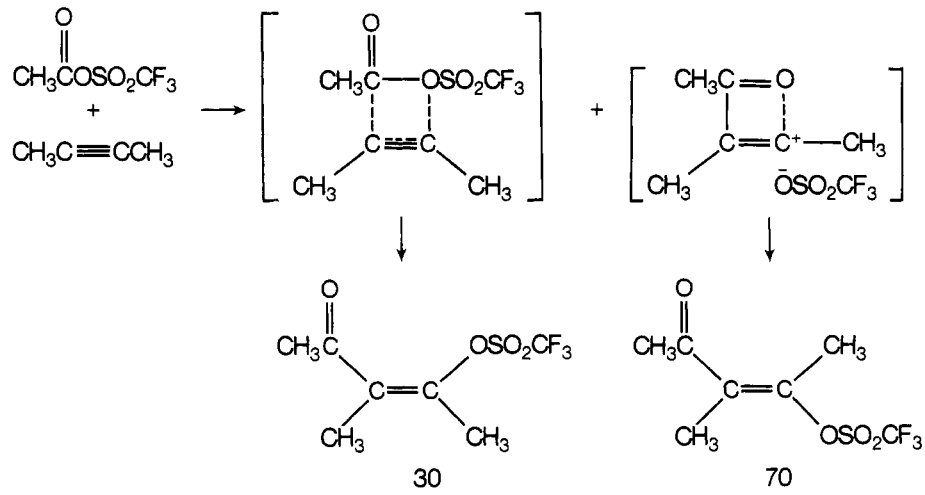
Trifluoromethanesulfonyl fluoride has almost exclusively been made by electrochemical fluorination of methanesulfonyl fluoride (or chloride) in liquid hydrogen fluoride.[8-11] Small amounts of hydrogen fluoride which may codistill with the sulfonyl fluoride may be removed by the use of sodium fluoride, or by another method[66] which involves the passage of crude material through a heated tube filled with activated aluminum oxide. However, removal of all of the hydrogen fluoride may not be desirable, since fluoride ion can serve as a useful catalyst in certain reactions (section III.C). The sulfonyl chloride has been obtained from the reaction of trifluoromethanesulfonic acid with phosphorus pentachloride or phosphorus pentachloride–zinc chloride complex;[5,8] however, it can be prepared in higher yield by other methods (sections III.A and III.C). Surprisingly, thionyl chloride was found to be completely unreactive toward trifluoromethanesulfonic acid,[11] but no attempted reactions using thionyl chloride with a basic catalyst or an equivalent of dimethylformamide have been reported.

Trifluoromethanesulfonyl bromide has been prepared only by a multistep synthesis which involved trifluoromethylsulfenyl fluoride and anhydrous hydrogen bromide.[67] Interestingly, even the sulfonyl bromide did not hydrolyze readily. Trifluoromethanesufonyl iodide has not been described.

4. Friedel–Crafts Reactions

Mixed trifluoromethanesulfonic–carboxylic acid anhydrides (acyl trifluoromethanesulfonates) are formed upon addition of

SCHEME I



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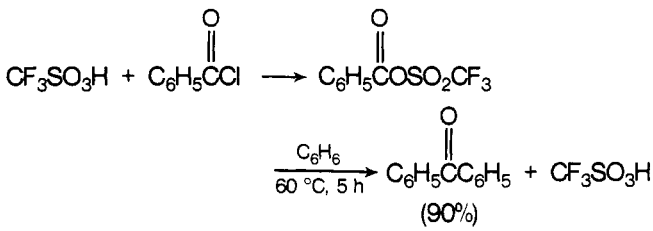
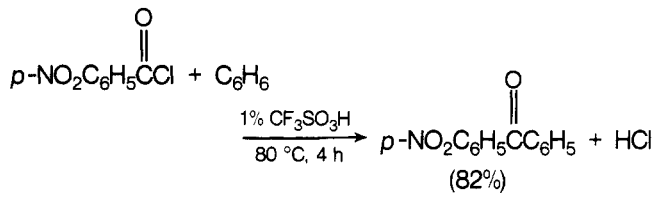
an acyl chloride[68,69] or acetic anhydride[69-72] to trifluoromethanesulfonic acid. These mixed anhydrides are extremely powerful Friedel–Crafts acylating agents. Effenberger and Epple[68] allowed a number of the mixed anhydrides to react with aromatic compounds. Even nonactivated aromatic species like benzene and chlorobenzene were acylated in high yield.



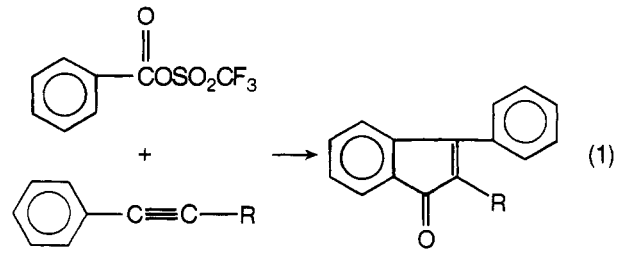
Anisole could be conveniently acylated by using mixtures of either acetyl chloride or benzoyl chloride combined with a small amount of trifluoromethanesulfonic acid; and with a higher concentration of the acid, benzene or toluene could be acylated.[69] By comparison, perchloric acid was a very poor substitute for trifluoromethanesulfonic acid.

In an independent study, Effenberger and Epple[73,74] developed an excellent acylation procedure that required only a catalytic amount of trifluoromethanesulfonic acid.



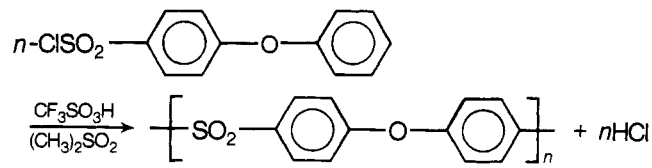
A comparison of the catalytic activity of various Brønsted and Lewis acids showed that trifluoromethanesulfonic acid was far superior to all of the other acids tested. The economic advantages to the use of a catalytic amount of trifluoromethanesulfonic acid in place of the large excess of anhydrous aluminum chloride commonly used in acylations may spark future developments in this area. Of course, with active aromatic compounds such as aryl ethers, polynuclear arenes, alkyl-substituted acyl compounds and thiophene, acylation by anhydrides or acid fluorides occurs readily in the presence of only catalytic amounts of ferric chloride, iodine, zinc chloride, or iron.[75] Thus, a variety of ways to avoid excessive quantities of aluminum chloride are available.

Acylation of alkynes by acyl trifluoromethanesulfonates led to mixtures of *trans*- and *cis*-β-ketovinyl trifluoromethanesulfonates (Scheme I).[76] Presumably, an equilibrium is involved between the ion pair and donor–acceptor complex and, as would be expected, electron-donating substituents favor the ion pairs; this in turn leads to an increase in the trans/cis ratio. When aroyl trifluoromethanesulfonates are employed, indenones may be formed by electrophilic attack of an intermediate vinyl cation on the aroyl nucleus. In fact, exclusive indenone formation occurred when the vinyl cation was stabilized by an α-phenyl substituent (eq 1). These reactions are quite similar to the addition of acid chloride–aluminum chloride complexes to acetylenes in which β-chlorovinyl ketones are formed. Here, there is less tendency toward indenone formation. Presumably, this is due to the greater nucleophilicity of the relatively soft tetrachloroaluminate anion. Few actual yields were given for the acyl trifluoromethanesulfonate reactions, so it is difficult to assess their preparative significance; however, both vinyl trifluoromethanesulfonates and indenones are useful chemical intermediates.



(1)

Trifluoromethanesulfonic acid has been utilized as a catalyst in the Friedel–Crafts condensation of aromatic sulfonyl chlorides with aromatic compounds (eq 2).[77] Typical active concentrations of the acid catalyst were 0.1 to 1.0 mole per cent.



(2)

Isomerization and cracking of alkanes or alkyl-substituted aromatic hydrocarbons as well as alkylation of alkenes or arenes under strong acid catalysis fall within the broad scope of Friedel–Crafts-type reactions. In view of (1) the high acid strength of trifluoromethanesulfonic acid and (2) the long known effectiveness of combinations of strong Lewis acids with strong Brønsted acids, it is somewhat surprising that patents dealing with such usage of this acid, alone or in combination with Lewis acids, have been of very recent origin. The present surge of interest probably reflects the marked increase in the demand for motor fuels of greater octane number. The antimony pentafluoride–trifluoromethanesulfonic acid combination was used to prepare high octane alkylates from reactions of alkanes or alkyl

TABLE II. Isomerization of *n*-Heptane at 25 °C under 1500 psi of Hydrogen for 3 h

Acid system	% conversion	C_3	C_4	C_5	C_6	C_7	Total cracking
SbF_5/HF	96.0	15.0	34.0	Trace	Trace	50.0	49.0
AsF_5/HF	95.0	23.9	45.0	0.6	0.8	29.4	70.3
SbF_5/CF_3SO_3H	96.8	14.9	26.0	0.5	0.8	56.6	42.2

aromatic hydrocarbons with olefins.[78] This catalyst mixture is also highly effective for the isomerization of straight-chain or slightly branched hydrocarbons to the more highly branched isomers.[22,23,79-81] Since the octane rating increases with the greater amount of branching, this reaction is of substantial commercial importance to the petroleum industry. When a superacid catalyst system was used for the isomerization of an alkane such as *n*-heptane, it was essential to supply a rather high partial pressure of hydrogen to minimize undesirable cracking.[79] Although the Lewis acid–hydrogen fluoride system was generally very effective, one rather close comparison indicates a possible advantage of the trifluoromethanesulfonic acid system—namely, less cracking at high per cent conversions (Table II). However, a comparison of the percentage distribution of the components of the heptane fraction was not disclosed for the trifluoromethanesulfonic acid–antimony fluoride system, so that the significance of the decreased cracking is partially obscured. Some isomerization of hexane in the neat acid occurs, but the amount is greatly increased when antimony pentafluoride is added to the system.[80] It appears that this combination is particularly effective on a solid support such as fluoridized alumina, sodium fluoride, aluminum phosphate, or charcoal.[81] The use of trifluoromethanesulfonic acid may allow the detection of intermediates in carbocyclic rearrangements of more complex alkanes. Certain of these intermediates might not otherwise survive under stronger catalysis by aluminum chloride or fluorosulfonic acid–antimony pentafluoride. Such has reportedly been the case in the adamantane rearrangement of tricycloundecanes.[82,83]

Trifluoromethanesulfonic acid was also one of several acids employed in combination with niobium or tantalum pentafluoride to form a catalyst system capable of converting benzene or toluene to ethylbenzene.[84] Furthermore, trifluoromethanesulfonic acid can be advantageously utilized in place of a boron trifluoride–hydrogen fluoride mixture for the extraction of *m*-xylene from *p*-xylene.[85,86] Pure *m*-xylene could also be isomerized to *p*-xylene at elevated temperatures. For example, a 50:50 mixture of *m*- and *p*-xylenes was obtained when pure *m*-xylene was heated in the presence of the acid at 100 °C for 50 h.

Nyberg[87] prepared a series of diphenylmethane derivatives by the trifluoromethanesulfonic acid catalyzed reaction of aromatic compounds with benzyl acetates.

$$C_6H_6 + C_6H_5CH_2OCCH_3 \xrightarrow[CHCl_3,\ \Delta,\ 12\ h]{CF_3SO_3H} (C_6H_5)_2CH_2 \quad (48\%)$$

In contrast to the slow reaction shown above, decamethyldiphenylmethane was isolated in 72% yield after allowing pentamethylbenzyl acetate to react with pentamethylbenzene for only 15 min at room temperature. Hydride ion abstraction by the proposed benzyl cation intermediate was competitive with Friedel–Crafts benzylation when a stabilized benzyl system such as pentamethylbenzyl acetate was allowed to react with a weakly nucleophilic aromatic compound such as benzene. Similar benzylations have been reported in which boron trifluoride etherate[88] and sulfuric acid[89] were the acid catalysts.

During the last several decades, a large number of stable nitronium salts have been utilized as potent Friedel–Crafts nitrating agents.[90] Recently, Coon and co-workers[91,92] found that a mixture of nitronium trifluoromethanesulfonate and trifluoromethanesulfonic acid monohydrate was extremely effective for the nitration of aromatic compounds.

$$2CF_3SO_3H + HNO_3 \rightarrow NO_2^+CF_3SO_3^- + H_3O^+\ CF_3SO_3^-$$

The mixture is a white crystalline, hygroscopic solid that is amenable to reaction in a wide variety of solvents under essentially heterogeneous conditions. By the proper choice of reaction conditions, nearly quantitative yields coupled with high positional selectivity can be achieved in the nitration of many aromatic compounds. The high selectivity and reactivity of nitronium trifluoromethanesulfonate under the conditions represented in Table III is noteworthy. Indeed, nitration was still rapid at −110 °C where only 0.23% of the meta isomer was obtained. Presently, there is little evidence to suggest that the selectivity of nitronium trifluoromethanesulfonate would be significantly greater than that of other nitrating species in a variety of other reaction media. Comparisons from heterogeneous to homogeneous reaction conditions should be cautious at best, especially when extremely rapid reactions are involved.

In another study,[93] nitronium trifluoromethanesulfonate was isolated from the low-temperature reaction of dinitrogen pentoxide with the anhydride of trifluoromethanesulfonic acid in the presence of ozone. Subsequently, a similar reaction performed under somewhat different conditions has been reported to provide a quantitative yield of the nitronium salt as a white crystalline, hygroscopic solid which decomposes at 213–215 °C.[94] In tetramethylene sulfone solution, nitronium trifluoromethanesulfonate gave somewhat poorer yields of nitro derivatives than nitronium tetrafluoroborate with benzene or *p*-dichlorobenzene, but it produced a considerably better yield with benzotrifluoride.[94] Nitronium trifluoromethanesulfonate which is uncomplexed with the hydronium species may also be prepared directly from trifluoromethanesulfonic acid.[95,96]

$$N_2O_5 + CF_3SO_3H \xrightarrow[20-35\ °C]{ClCH_2CH_2Cl} NO_2^+CF_3SO_3^- + HNO_3$$

$$NO_2Cl(\text{excess}) + CF_3SO_3H \rightleftharpoons NO_2^+CF_3SO_3^- + HCl$$

In order to drive the nitryl chloride reaction to completion it is necessary to periodically remove hydrogen chloride. Effenberger and Geke[95] have compared the nitration potentials of nitronium–hydronium trifluoromethanesulfonate mixture, nitronium trifluoromethanesulfonate, and nitronium tetrafluoroborate. Under selected heterogeneous conditions, the trifluoromethanesulfo-

TABLE III. Nitration of Toluene with Nitronium Salts in Methylene Chloride

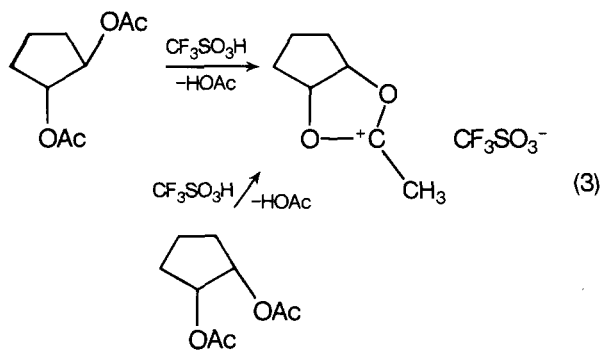
Nitronium salt	Temp, °C	Time, min	Yield, %	Mononitrotoluene isomer ratios		
				Ortho	Meta	Para
$NO_2^+BF_4^-$	−65	150	70.2	56.55	0.65	42.80
$NO_2^+PF_6^-$	−65	150	88.5	46.44	0.81	52.75
$NO_2^+CF_3SO_3^-\cdot H_3O^+CF_3SO_3^-$	−60	1	>99	62.18	0.54	37.28
$NO_2^+CF_3SO_3^-\cdot H_3O^+CF_3SO_3^-$	−90	180	>99	61.32	0.36	38.32
$NO_2^+FSO_3^-\cdot H_3O^+FSO_3^-$	−60	120	89	62.76	0.72	36.52

nates were much more effective than the tetrafluoroborate. However, the latter was more effective under selected homogeneous conditions, and the ineffectiveness of the nitronium–hydronium trifluoromethanesulfonate mixture was particularly evident in the homogeneous system.

5. *Miscellaneous Reactions and Uses*

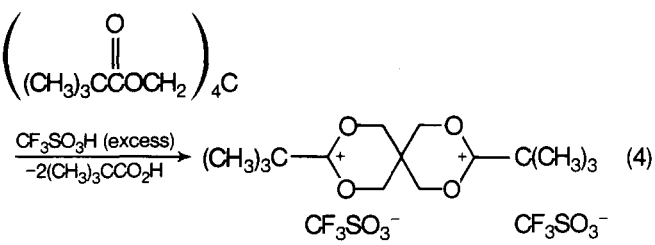
Cyclic acetals, such as trioxane, 1,3-dioxolane, and 2,2-dimethyl-1,3-dioxolane, have been homopolymerized and copolymerized with trifluoromethanesulfonic acid as the catalyst.[97] The acid has also been added to the list of known catalysts for the cationic polymerization of tetrahydrofuran.[98] However, the use of the acid anhydride resulted in not only a faster rate of polymerization, but also in a polymer that was essentially difunctional instead of monofunctional (see section III.B).

Paulsen and co-workers[99,100] have observed acetoxonium cation formation when *cis*- or *trans*-1,2-cyclopentanediol diacetate was treated with trifluoromethanesulfonic acid (eq 3).



(3)

Similar reactions of other diol diacetates were examined. Backside participation was suggested to account for the accelerated reactions of the trans compounds. Several triol triacetates also gave acetoxonium cations, and pentaerythritol tetrapivalate gave a dication upon treatment with the acid (eq 4).[99] By comparison, only the monocation was obtained from



(4)

a similar reaction in hydrogen fluoride.[101] Paulsen and coworkers[102,103] have also studied the fate of acetoxonium ions generated from the addition of trifluoromethanesulfonic acid to 2,3,5-tri-*O*-acetyl-1,6-anhydro-α-D-glactofuranose and 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-talopyranose.

Dalziel and Aubke[28] reported the isolation of iodine tris(trifluoromethanesulfonate) from a trifluoromethanesulfonic acid solution of iodine and peroxydisulfuryl difluoride. Although it is

$$I_2 + 3S_2O_6F_2 + 6CF_3SO_3H \longrightarrow 2I(OSO_2CF_3)_3\downarrow + 6FSO_3H$$
(mp 119 °C)

stable to about 170 °C under vacuum, the iodo compound decomposed above that temperature to form sulfur trioxide and trifluoromethyl trifluoromethanesulfonate. The perfluoroalkyl ester was identical with the compound which was obtained earlier from the thermal decomposition of bis(trifluoromethanesulfuryl) peroxide.[57,58] Other examples of similar iodo compounds include iodine tris(fluorosulfonate),[104] iodine tris(perchlorate),[105] and iodine tris(trifluoroacetate).[106] The bonding in iodine tris(trifluoromethanesulfonate), like iodine tris(fluorosulfonate), was thought to involve both monodentate and bidentate sulfonate ligands based on infrared and Raman spectral evidence. However, some structural dissimilarity between these two compounds is evident in the experimental observation that the former is extremely soluble in fluorosulfonic acid, while the latter is only very slightly soluble in trifluoromethanesulfonic acid. It has been suggested that different degrees of polymerization in these compounds account for this dissimilarity. Iodine tris(trifluoromethanesulfonate) precipitates when a slight excess of trifluoromethanesulfonic acid is added to a solution of iodine tris(fluorosulfonate) in fluorosulfonic acid.

The reaction of trifluoromethanesulfonic acid anhydride with iodine tris(trifluoroacetate)[93] gave a product identified as iodine tris(trifluoromethanesulfonate). It had a considerably higher melting point (190–192 °C) than that reported by Dalziel and Aubke.[28] This may indicate that dimorphs were obtained under the different reaction conditions, but it would seem that a structural comparison is warranted.

The reduction of iodine tris(trifluoromethanesulfonate) with a stoichiometric amount of iodine gave iodine trifluoromethanesulfonate.[28] A polymeric structure with bidentate bridging trifluoromethanesulfonate groups was postulated for this compound, and further characterization was reported to be in progress.

Trifluoromethanesulfonic acid liberates hydrogen chloride from titanium tetrachloride.[58]

$$CF_3SO_3H + TiCl_4 \xrightarrow[-HCl]{25\ ^\circ C} Cl_3TiOSO_2CF_3 \xrightarrow{60\ ^\circ C} TiCl_4 + Cl_2Ti(OSO_2CF_3)_2$$

Upon heating, trichloro(trifluoromethanesulfonato)titanium(IV) disproportionated to give the more thermally stable dichlorobis(trifluoromethanesulfonato)titanium(IV). Schmeisser and co-workers[4] were able to displace a third chlorine under more stringent conditions, but the fourth chlorine could not be displaced by the acid. Excess trifluoromethanesulfonic acid caused the displacement of two chlorine atoms from silicon tetrachloride; however, the resultant bis(trifluoromethanesulfonate) readily disproportionated. As with titanium tetrachloride, no tetrakis(trifluoromethanesulfonate) could be obtained.

$$SiCl_4 \xrightarrow[(excess)]{CF_3SO_3H} Cl_2Si(OSO_2CF_3)_2 \rightarrow SiCl_4 + Cl_3SiOSO_2CF_3 + ClSi(OSO_2CF_3)_3$$

In contrast, both thorium and zirconium tetrachlorides gave the tetrakis(trifluoromethanesulfonates) in quantitative yield.[4]

Tetraorganosilicon, -tin, and -lead compounds were also allowed to react with trifluoromethanesulfonic acid.[4,107] No reaction was observed with tetramethylsilane, but benzene was liberated from tetraphenylsilane. Other examples were reported in which cleavage of tin–carbon and lead–carbon bonds occurred.

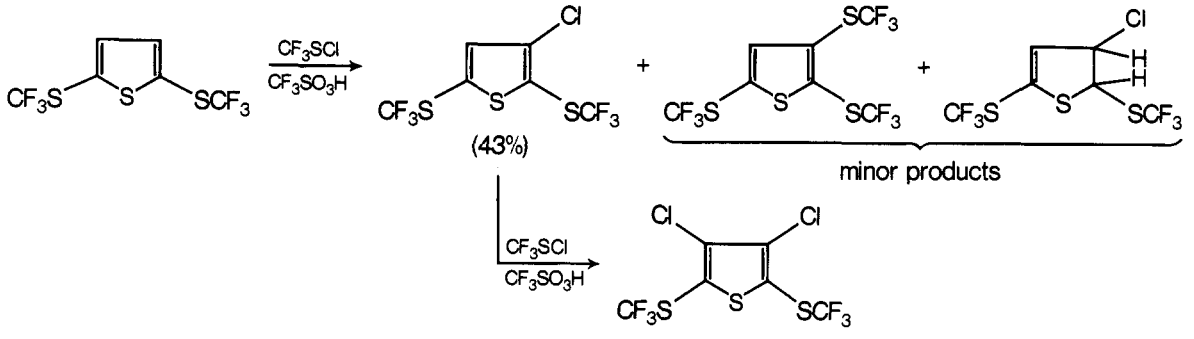
$$(C_6H_5)_4Si \xrightarrow{CF_3SO_3H} C_6H_5Si(OSO_2CF_3)_3 + C_6H_6 \quad (22\%)$$

$$(CH_3)_4Sn \xrightarrow[(excess)]{CF_3SO_3H} (CH_3)_2Sn(OSO_2CF_3)_2 + CH_4 \quad (82\text{–}100\%)$$

$$(CH_3)_4Sn \xrightarrow[0\ ^\circ C]{CF_3SO_3H} (CH_3)_3Sn(OSO_2CF_3) + CH_4 \quad (\sim 100\%)$$

$$(C_2H_5)_4Pb \xrightarrow{CF_3SO_3H} (C_2H_5)_2Pb(OSO_2CF_3)_2 + C_2H_6 \quad (\sim 100\%)$$

SCHEME II



Even at −50 °C, tetramethyltin reacted quickly with the acid to give trimethyltin trifluoromethanesulfonate. The infrared spectral frequencies of both tin(IV) trifluoromethanesulfonates[107] did not agree with the typical spectra of alkali metal sulfonates.[5,9,16,29,40,108,109] It is noteworthy that some ambiguity exists in certain vibrational assignments due to the fact that sulfur–oxygen and carbon–fluorine vibrations of identical symmetry (A′ and E) are found in the same spectral range. Interestingly, many features of the infrared spectrum of trimethyltin trifluoromethanesulfonate were in excellent agreement with those of dimethyltin bis(fluorosulfonate), and it has been proven by x-ray diffraction studies that the latter has bridging, bidentate fluorosulfonate ligands.[110] Mössbauer spectra have also supported the bidentate nature of the two tin(IV) compounds.[111,112]

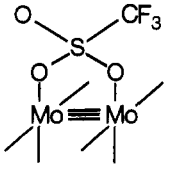
Several other organotin compounds have been allowed to react with trifluoromethanesulfonic acid.[111,112] The tin–chlorine bond is cleaved in preference to the tin–carbon bond at room temperature or lower.

$$(CH_3)_3SnCl + 2CF_3SO_3H \rightarrow (CH_3)_2Sn(OSO_2CF_3)_2$$

$$CH_3SnCl_3 + 2CF_3SO_3H \rightarrow CH_3SnCl(OSO_2CF_3)_2$$

Only one example of an organogermanium trifluoromethanesulfonate has been cited.[28] The bonding in trimethylgermanium trifluoromethanesulfonate was reported to involve covalently bonded monodentate trifluoromethanesulfonate groups, and thus it is similar to the corresponding trimethylsilicon compound.

Treatment of tetraacetatodimolybdenum(II) with trifluoromethanesulfonic acid in dry ethyl acetate solvent produced an unusual complex trifluoromethanesulfonate salt in which four ethyl acetates were coordinated in a bridging bidentate fashion.[113] Upon heating at 100 °C under vacuum, the ethyl acetate was replaced by trifluoromethanesulfonate as the bridging bidentate ligand.



A comparison of the infrared sulfur–oxygen stretching frequencies of the molybdenum complex with those of trimethyltin trifluoromethanesulfonate showed that the former is even more strongly complexed in a bridging bidentate manner than the latter. Pure tetrakis(trifluoromethanesulfonato)dimolybdenum(II) was not obtained by this method since an acetate impurity, which was also present in the ethyl acetate complex salt, could not be removed. Merely eliminating the ethyl acetate solvent provided a route to the pure tetrakis complex.

A highly unusual derivative of trifluoromethanesulfonic acid was formed when xenon difluoride was condensed onto a slight excess of the acid.[114]

$$XeF_2 + CF_3SO_3H \xrightarrow[-HF]{<0\ °C} FXeOSO_2CF_3$$

The solid which remained after removal of the solvent was identified as the mono(trifluoromethanesulfonate) by its Raman spectrum. Like xenon bis(perchlorate) and xenon fluoride (methanesulfonate), the trifluoromethanesulfonate detonated on warming to room temperature. Although many perchlorates are known detonators, this is the only example of that behavior among trifluoromethanesulfonates.

Trifluoromethanesulfonic acid has been used to remove acid labile amino-protecting groups, such as benzyloxycarbonyl, *p*-methoxybenzyloxycarbonyl, *tert*-butoxycarbonyl, and *p*-toluenesulfonyl.[115,116] The protected amino acids were dissolved in methylene chloride or trifluoroacetic acid and treated with an excess of trifluoromethanesulfonic acid in the presence of anisole. Generally, a nearly quantitative cleavage was effected within 15 min at 20 °C. Presumably, the anisole served as a scavenger for the reactive alkylating agents formed as by-products in the cleavage reactions. The *p*-toluenesulfonyl group required 45–60 min at 40 °C for complete deprotection. This lesser reactivity would suggest that the other protecting groups previously mentioned could be very selectively cleaved under mild conditions with trifluoromethanesulfonic acid. Other reagents that appear to function equally well in the removal of amino-protecting groups are liquid hydrogen fluoride and boron tris(trifluoroacetate) in trifluoroacetic acid.[117]

Recently, trifluoromethanesulfonic acid was found to possess some advantages over other strong acids as a solvent for electrochemical studies.[118,119] By the use of a gold electrode, very high potentials can be obtained. Thus, trifluoromethanesulfonic acid could be particularly useful for the examination of certain electrochemical oxidation reactions. In this regard, we point out that α,β unsaturated carbonyl compounds and lactones have been obtained from anodic oxidation of alkanes and carboxylic acids in fluorosulfonic acid.[120]

Trifluoromethanesulfonic acid promotes the chlorination of electron-deficient arenes by trifluoromethylsulfenyl chloride (Scheme II).[121] A similar treatment of benzene gave trifluoromethylmercaptobenzene in 70% yield, but further reaction of this electron-deficient species led predominantly to the chlorinated arenes.

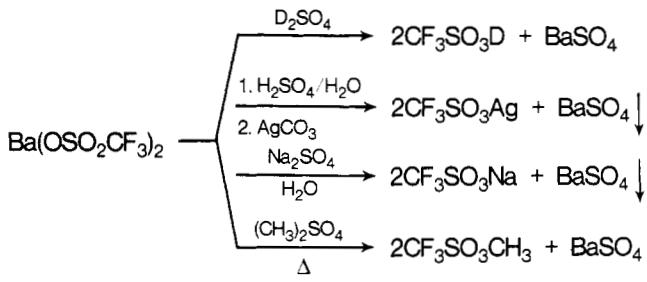
Under a variety of conditions, trifluoromethanesulfonic acid will catalyze the polymerization of styrene. While other strong Brønsted acids and Lewis acids produce a similar result, trifluoromethanesulfonic acid or acetyl perchlorate allow the very selective formation of the linear dimer, *trans*-1,3-diphenyl-1-butene, in a nonpolar solvent such as benzene at 50 °C.[122]

III. Reactions of Some Derivatives of Trifluoromethanesulfonic Acid

A. Reactions of Salts

Salts of trifluoromethanesulfonic acid are generally soluble in polar organic solvents, and they possess high thermal stability

SCHEME III



in comparison to many analogous salts with other organic anions. The barium salt, for instance, can be conveniently recrystallized from acetone, and it is thermally stable to above 370 °C.[9] Since barium can easily be removed as its insoluble sulfate, this salt has been widely used to prepare not only the pure parent acid (section II.A) but also deuteriotrifluoromethanesulfonic acid, silver[2,9] or alkali metal[108,123] trifluoromethanesulfonates, and the methyl ester (Scheme III).[55]

Calcium trifluoromethanesulfonate has been substituted for the barium salt in a metathetical reaction with zinc sulfate.[124] Pure zinc trifluoromethanesulfonate was obtained upon evaporation of the filtered aqueous solution. This salt has given the highest reported yield of the sulfonyl chloride upon reaction with a molten phosphorus pentachloride–zinc chloride complex.

$$(CF_3SO_3)_2Zn + PCl_5 \cdot 2ZnCl_2 \xrightarrow[\Delta]{} CF_3SO_2Cl + POCl_3 \quad (94\%)$$

Silver trifluoromethanesulfonate, though it is stable in the presence of iodine at temperatures below about 300 °C,[11] reacts readily with simple alkyl iodides under mild conditions to give esters.

$$CF_3SO_3Ag + CH_3I \xrightarrow{25\ °C} CF_3SO_3CH_3 + AgI \quad (69\%)$$

The alkyl iodides that have been successfully allowed to react in this manner include the methyl,[8,9,11,125,126] ethyl,[9,11,126–128] propyl,[126,128] isopropyl,[126] hexyl,[126] and decyl[126] iodides. Substitution reactions of alkyl halides with silver trifluoromethanesulfonate are much more prone to rearrangement than is the case with silver toluenesulfonate. The weaker nucleophile requires more participation by silver and a greater degree of carbon–halogen bond breaking in the transition state. Therefore, it is not unexpected that solvent would influence the degree of isomerization when substrates capable of rearrangement are allowed to react with silver trifluoromethanesulfonate. A rather dramatic solvent effect is exemplified in Table IV.[126] The lack of any rearrangement in excess propyl iodide or benzene solvents is due to complexation of the silver ions by the solvent. In view of the fact that the isopropyl ester is an especially potent alkylating agent, it is surprising that alkylation of the benzene was not observed. Others have found that benzyl iodide gives a solid polymer upon treatment with the silver salt in acetonitrile, and that diphenylmethane is obtained when the reaction is carried out in benzene.[129] Here, the aromatic solvent was alkylated, presumably by the initially formed benzyl trifluoromethanesulfonate.

$$CF_3SO_3Ag + C_6H_5CH_2I \xrightarrow[\Delta]{C_6H_6} C_6H_5CH_2C_6H_5 \quad (58\%)$$

The silver salt reacts with acyl chlorides to give mixed carboxylic–sulfonic acid anhydrides[68,76] and with aryl sulfonyl bromides to produce trifluoromethanesulfonic–arenesulfonic acid anhydrides.[130]

$$CF_3SO_3Ag + C_6H_5COCl \longrightarrow CF_3SO_3COC_6H_5 \quad (\sim 90\%)$$

TABLE IV. Reactions of Propyl Iodide with Silver Trifluoromethanesulfonate at Ambient Temperature

Solvent	Propyl ester/isopropyl ester	Time, h	Yield, %
CCl_4	34/66	2	97
$CFCl_2CF_2Cl$	34/66	2	97
C_5H_{12}	34/66	2	97
CH_2Cl_2	59/41	2	95
$C_6H_6/CFCl_2CF_2Cl$ (50/50)	51/49		98
$C_6H_6/CFCl_2CF_2Cl$ (67/33)	77/23		94
C_6H_6	100/0	18	92
n-C_3H_7I	100/0		

$$CF_3SO_3Ag + C_6H_5SO_2Br \longrightarrow CF_3SO_3SO_2C_6H_5 \quad (\sim 90\%)$$

Although the latter acid anhydrides were too thermally unstable for isolation in the pure state, they were characterized by ^1H NMR spectroscopy and by their nearly quantitative conversion to aryl sulfones upon reaction with aromatic compounds.

A substantial number of alkyl- and arylsilicon trifluoromethanesulfonates have been prepared from the silver salt and alkyl- or arylsilicon chlorides.[4]

$$3CF_3SO_3Ag + CH_3SiCl_3 \xrightarrow[12\ h]{80\ °C} CH_3Si(OSO_2CF_3)_3 + 3AgCl \quad (46\%)$$

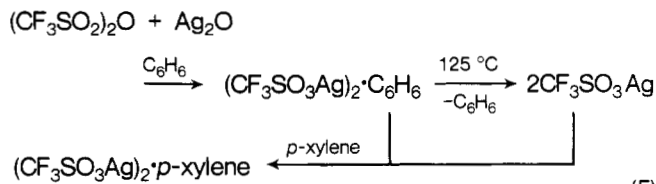
$$3CF_3SO_3Ag + C_6H_5SiCl_3 \xrightarrow[75\ h]{25\ °C} C_6H_5Si(OSO_2CF_3)_3 + 3AgCl$$

$$2CF_3SO_3Ag + (C_6H_5)_2SnCl_2 \xrightarrow[22\ °C,\ 2\ h]{THF} (C_6H_5)_2Sn(OSO_2CF_3)_2 + 2AgCl \quad (96\%)$$

Alkyl- or aryltin chlorides underwent sulfonation under milder conditions as would be expected.

Silver trifluoromethanesulfonate, like many other trifluoromethanesulfonate salts, possesses good solubility in organic solvents and monomers. These salts can be used as latent catalysts in the curing or polymerization of cationic sensitive monomers.[131,132] For example, when a catalytic amount of the silver salt and a "halide promoter" such as silver chloride or an aryl chloride are mixed with an epoxy resin and then exposed to actinic light, a cure takes place.[131] Interestingly, many trifluoromethanesulfonate salts will catalyze the cure of epoxy resins at elevated temperatures in the absence of additional cocatalysts.[132] Their nonvolatility, noncorrosiveness, low moisture sensitivity, and good organic solubility combine to make these salts an attractive class of latent catalysts.

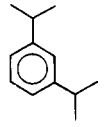
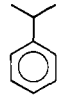
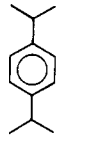
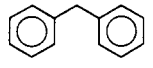
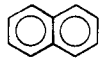
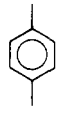
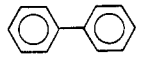
Silver trifluoromethanesulfonate forms a benzene complex which consists of two salt units per benzene molecule (eq 5).[133] As with cuprous trifluoromethanesulfonates,[30,31] the silver(I) salt selectively complexed with arenes.[133,134]



(5)

Dines[32,134,135] prepared cuprous trifluoromethanesulfonate complexes from the reaction of the acid anhydride with cuprous oxide and a suitable complexing agent. The extensive list of

TABLE V. Selectivity Factors of Various Aromatic Compounds

Aromatic	α^a	Aromatic	α^a
	0.01		0.04
	0.04		5.1
	0.46		3.0
	1.24		25.0
	16.0		43.0

^{a} Benzene = 1.

complexing agents included many phosphorus and nitrogen species, as well as olefinic and aromatic compounds.[134] The relative extent of ligand exchange for the benzene complex in equilibrium with various other aromatic compounds was determined, and some selected examples are shown in Table V.

Both the silver(I) and copper(I) trifluoromethanesulfonates were preferable to other silver(I) and copper(I) salts for the separation of closely boiling hydrocarbon mixtures comprised of one or more aromatic or olefinic compounds. Interestingly, with the trifluoromethanesulfonates, the geometrical shape of the arene was more important than π basicity in determining the stability of the arene–metal complexes.

Kochi and Jenkins[33] have made a comparison between cupric acetate and cupric trifluoromethanesulfonate in the electron-transfer oxidation of alkyl radicals. For a given radical, the former promotes oxidative elimination, while the latter promotes oxidative solvolysis (Scheme IV). A greater degree of carbonium

SCHEME IV

$$R\cdot + Cu(OX)_2 \rightleftharpoons RCu(OX)_2 \quad (OX = OAc,\ OSO_2CF_3)$$

$$RCu(OX)_2 \xrightarrow{\text{elimination}} R(-H) + CuOX + HOX$$

$$RCu(OX)_2 \xrightarrow{\text{solvolysis}} R^+[Cu(OX)_2]^- \xrightarrow{HOAc} ROAc + CuOX + HOX$$

ion character for the proposed metastable alkyl copper trifluoromethanesulfonate intermediate was evident not only in the greater amount of solvolysis but also in a larger amount of rearranged products from elimination and solvolysis. In the course of this study, it was discovered that cupric acetate can be titrated to a visual endpoint with anhydrous trifluoromethanesulfonic acid.[33]

$$Cu(OAc)_2 + 2CF_3SO_3H \xrightarrow{HOAc} Cu(OSO_2CF_3)_2$$

(dark green) (colorless)

Salomon and Kochi[136-139] have found that the benzene–cuprous trifluoromethanesulfonate complex is an excellent reagent for the preparation of cationic copper(I)–olefin complexes. The relatively weakly coordinated benzene was easily displaced by olefins, and the resulting stable olefinic complexes were very soluble in many organic solvents. The stoichiometry of these copper(I)–olefin complexes generally differed from that of analogous complexes formed from cuprous halides. This difference was attributed to the weakly coordinating nature of the trifluoromethanesulfonate anion. The high solubility in many organic solvents and the high thermal stability of the cuprous trifluoromethanesulfonate complexes presents a striking contrast to the insolubility and instability of many similar complexes derived from cuprous halides. Salomon and Kochi[137,138] noted that upon complexation of an olefin with cuprous trifluoromethanesulfonate, the vinyl proton resonance shifted upfield with monodentate olefins and downfield with polydentate olefins. Furthermore, analysis of ^{13}C NMR spectra showed that the upfield shift of vinyl carbons upon complexation was large for monodentate olefins and small for polydentate olefins.[138] Therefore, the cuprous trifluoromethanesulfonate–benzene complex could be a useful ^{13}C NMR shift reagent for olefins.

The previously mentioned properties of the benzene complex recommended its use as a homogeneous catalyst for a variety of reactions. In one application, it served extremely well as the copper catalyst for the cyclopropanation of olefins with diazo compounds.[140]

$$RCH{=}CH_2 + N_2CHCO_2Et \xrightarrow{(CuOSO_2CF_3)_2\cdot C_6H_5} R\text{-}\langle\text{cyclopropane}\rangle\text{-}CO_2Et + N_2$$

The active cuprous species could also be conveniently formed in situ from cupric trifluoromethanesulfonate due to a facile reduction by the diazo compound. In contrast to most other copper catalysts, cuprous trifluoromethanesulfonate promotes cyclopropanation of the least alkylated olefin (eq 6). This rep-

$$CH_2N_2 + \langle\text{alkene}\rangle + \langle\text{alkene}\rangle \xrightarrow[\sim 5\ ^\circ C]{(CuOSO_2CF_3)_2\cdot C_6H_6} \langle\text{cyclopropane}\rangle + \langle\text{alkene}\rangle \quad (6)$$

21 : 79

resents a striking example of how ligands of low nucleophilicity can alter the course of a reaction. The very weak coordination between copper(I) and the trifluoromethanesulfonate (or tetrafluoroborate) anion allows greater copper(I)–olefin coordination prior to methylene transfer than is the case when more nucleophilic anions are present. The selectivity observed in the cyclopropanation reactions could result from more stable copper(I) complexes being formed with the least alkylated olefins so that their equilibrium concentrations would be higher. Another suggested consideration was the degree of diazo compound coordination with the copper(I)–olefin complexes prior to or simultaneous with cyclopropanation.[140]

Vinylcyclopropanes have been prepared by the copper trifluoromethanesulfonate or hexafluoroacetylacetonate catalyzed reaction of olefins with vinyldiazomethane.[141] Cupric trifluoromethanesulfonate, after in situ reduction to the cuprous salt, was far more efficacious than cuprous chloride, tri-*n*-butylphosphinecopper(I) iodide, or several other typical catalysts (eq 7).

$$\langle\text{cyclohexadiene}\rangle + N_2CHCH{=}CH_2 \xrightarrow{Cu(OSO_2CF_3)_2} \langle\text{vinylcyclopropane}\rangle \quad (7)$$

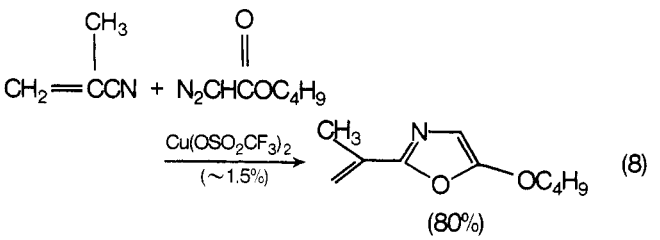
(1.2/1.0 : endo/exo)

(20%)

However, cupric trifluoromethanesulfonate cannot be used for the vinylcyclopropanation (or cyclopropanation) of highly nucleophilic vinyl ethers. Dihydropyran, for instance, underwent

a violently exothermic polymerization in the presence of a trace amount of the salt.

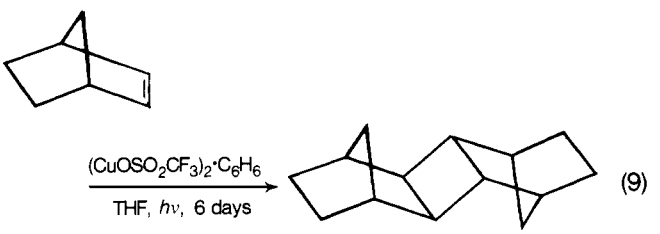
Oxazoles were synthesized by the 1,3-dipolar addition of ketocarbenes to nitriles with varying degrees of success.[142] Cupric trifluoromethanesulfonate was generally more efficient than palladium acetate. The nitrile group, which is well known to complex with copper(I) and copper(II), was selectively attacked when unsaturated nitriles were employed (eq 8). Mea-



(8)

surement of the volume of evolved nitrogen clearly shows the initial rapid reduction of the cupric salt by the diazo compound. Verification of this reduction was obtained from polarographic and EPR studies.

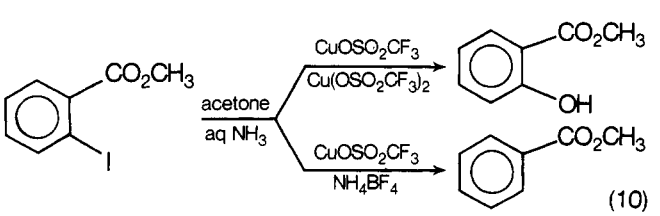
Some cuprous trifluoromethanesulfonate complexes have recently been found to be superior catalysts for olefin photodimerization (eq 9).[143-145] Olefins which have been successfully



(9)

dimerized in this manner include norbornene, *endo*-dicyclopentadiene, cyclopentene, cyclohexene, and cycloheptene.

Ullman-type couplings of activated halides, which are usually performed with copper powder at elevated temperatures, can be carried out under mild, homogeneous conditions with a cuprous trifluoromethanesulfonate–ammonia complex.[146,147] For example, either *p*-iodonitrobenzene or *o*-bromonitrobenzene provides 2,2′-dinitrobiphenyl upon addition to an acetone solution which contains cuprous trifluoromethanesulfonate and 5% aqueous ammonia. The yield of biaryl from the latter halide was increased by the use of a smaller volume of 20% aqueous ammonia along with a small quantity of cupric trifluoromethanesulfonate.[147] In some cases, the reaction course was greatly altered by use of the more concentrated aqueous or anhydrous ammonia or with supplementary additives such as the cupric salt and ammonium tetrafluoroborate (eq 10).



(10)

Several other specialized uses of certain salts of trifluoromethanesulfonic acid have been reported. Pyrolysis of rare earth trifluoromethanesulfonates provided rare earth fluorides in high purity.[35-37]

$$Ln(OSO_2CF_3)_3 \xrightarrow[\Delta]{\text{argon}} LnF_3 + 3SO_2 + 3COF_2$$

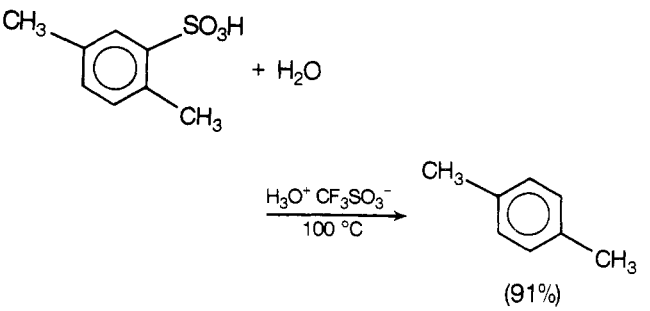
Possibly owing to the rapid removal of water from the system, the use of hydrated salts did not interfere with isolation of the rare earth fluorides. Pyrolysis of the analogous fluorosulfonate or trifluoroacetate salts failed to give the rare earth fluorides.

Mercuric trifluoromethanesulfonate reacts with bromotrichloromethane to give the trichloromethyl ester in good yield.[148]

$$Hg(OSO_2CF_3)_2 + 2BrCCl_3 \rightarrow 2CF_3SO_2OCCl_3 + HgBr_2$$
(79%)

A similar reaction occurred with either carbon tetrachloride or iodotrichloromethane; however, the yield of trichloromethyl ester was significantly lower. Perhaps mercuric trifluoromethanesulfonate will also prove useful for the generation of acyl trifluoromethanesulfonates from acid chlorides or acid bromides.

As we mentioned earlier, trifluoromethanesulfonic acid is so strong that it forms a stable hydrate which may truly be classed as a salt. This stable hydronium species was shown to be a somewhat more active catalyst than phosphoric acid for the hydrolytic desulfonation of aromatic sulfonic acids.[149] Hydronium



trifluoromethanesulfonate is also a more effective electrolyte than 85% phosphoric acid in hydrocarbon–air fuel cells.[150,151] Although the solubility of propane in these media is similar, oxidation occurs at a significantly greater rate in the former electrolyte. At 135 °C the limiting current density for the electrochemical oxidation of propane on a platinum electrode was enhanced by a factor of 15 in hydronium trifluoromethanesulfonate. Likewise, the oxidation of hydrogen proceeded more rapidly. It was suggested that the trifluoromethanesulfonate anion may have a lower adsorptivity on platinum; thus there would be more sites available for the oxidation reactions.[151] This factor coupled with other advantages should make hydronium trifluoromethanesulfonate an excellent medium for additional mechanistic studies of electrochemical reactions.

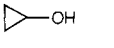
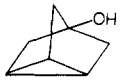
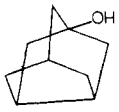
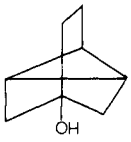
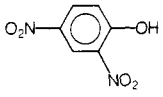
B. Reactions of the Acid Anhydride

1. Hydroxy Compounds

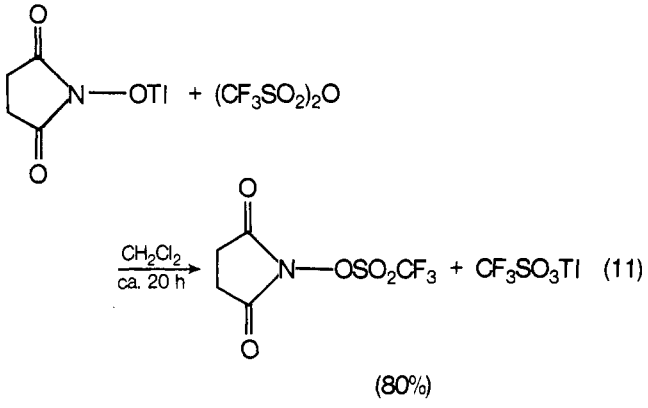
Gramstad and Haszeldine[11] isolated the methyl ester in quantitative yield from the reaction of anhydrous methanol with a slight excess of trifluoromethanesulfonic acid anhydride. The ethyl ester may be prepared in the same manner. In many cases, it is desirable to carry out the reaction in pyridine as a solvent or, preferably, in methylene chloride as the solvent with a stoichiometric amount of pyridine as a coreactant. This not only allows the esterification to take place under mild conditions (ca. 0 °C), but it also allows the removal of the acid by-product as the pyridinium salt. The use of lithium, sodium, or thallium alcoholates serves the same purpose as the use of a stoichiometric amount of pyridine. Here the metal trifluoromethanesulfonate by-products can also be conveniently separated from the esters. Some examples of hydroxy compounds that have been esterified with trifluoromethanesulfonic anhydride are given in Table VI.

Chapman and Freedman[157,158] recommended the thallium(I) salt procedure for the preparation of trifluoromethanesulfonates of phenols, *N*-hydroxysuccinimides, and *N*-hydroxyphthalimides (eq 11). Alternatively, aryl trifluoromethanesulfonates are formed

TABLE VI. Esterification with Trifluoromethanesulfonic Anhydride

Hydroxy compounds	Base	Solvent	Yield, %	Ref
n-C_4H_9OH	C_5H_5N	CH_2Cl_2		44
n-$C_5H_{11}OH$	C_5H_5N	CH_2Cl_2	85	52
$(CH_3)_2CHOH$	C_5H_5N	CCl_4	90 ± 5	52
$CH_2=CHCH_2OH$	C_5H_5N	CCl_4	75 ± 5	52
$HC\equiv CCH_2OH$	C_5H_5N	CCl_4	80 ± 5	52
$FC(NO_2)_2CH_2OH$	C_5H_5N	CH_2Cl_2	42	52
$HOCH_2CH(OH)$-CH_2OH	C_5H_5N	CH_2Cl_2	98[a]	52
$HC\equiv CCH_2CH_2OH$	Na_2CO_3	CH_2Cl_2	60	152
	C_5H_5N	C_5H_5N		153, 154
	C_5H_5N	C_5H_5N		155
	RLi	$(C_2H_5)_2O$	95 ± 5	155
	C_5H_5N	C_5H_5N	60	65
	n-C_4H_9Li	n-C_5H_{12}		156
C_6H_5OH	$TlOC_2H_5$[b]			153
	$TlOC_2H_5$[b]	CH_2Cl_2	80	157

[a] This represents an isolated yield of $CF_3SO_2OCH_2(OSO_2CF_3)$-$CH_2OSO_2CF_3$. [b] The thallium(I) phenoxide was isolated prior to the reaction with trifluoromethanesulfonic anhydride.



(80%)

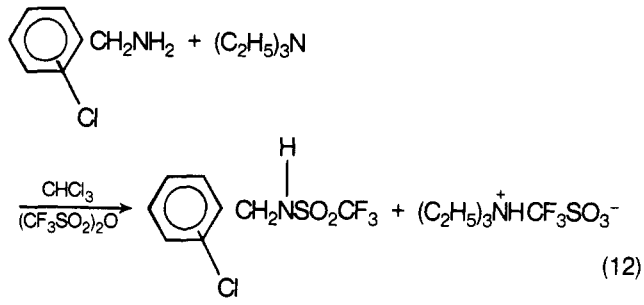
in very high yields by the reaction of phenols with *N,N*-bis(trifluoromethanesulfonyl)aniline (section III.E).

2. Ammonia and Amines

Trifluoromethanesulfonic acid anhydride reacts instantaneously with either anhydrous ammonia or aqueous ammonium hydroxide to give trifluoromethanesulfonamide.[11,43,50]

$$(CF_3SO_2)_2O + 2NH_3 \rightarrow CF_3SO_2NH_2 + NH_4^+CF_3SO_3^-$$
(mp 119 °C)

Solvents such as anhydrous ether and methylene chloride are generally used in the case of amine–acid anhydride reactions. Harrington and Trepka[159] successfully prepared over 20 new trifluoromethanesulfonamides according to a procedure which involved the addition of a stoichiometric amount of triethylamine as the acid acceptor (eq 12). Particularly high isolated yields of

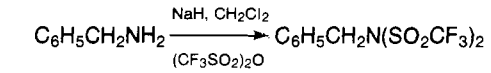


(12)

sulfonamides are common when very mild reaction conditions (−78 to −20 °C)[160-162] are employed. Likewise, the sulfonimide of aniline resulted from the use of 2 equiv of the anhydride and triethylamine.[163]

(92%)

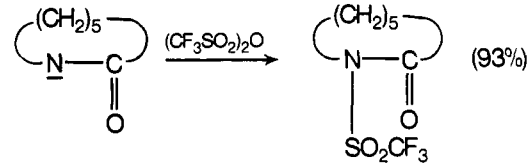
Sodium hydride is also an effective base for the direct conversion of primary amines to trifluoromethanesulfonimides.[164]



Benzoylhydrazine and *tert*-butoxycarbonylhydrazine have been converted to *N*-acyl-*N'*-trifluoromethanesulfonylhydrazines with the anhydride.[165] These derivatives are useful for the selective transformation of primary and activated secondary halides to acyl hydrazones.

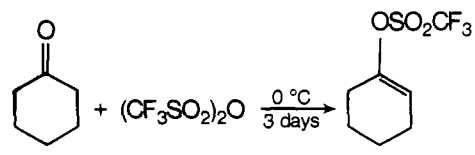
3. Miscellaneous Reactions and Uses

Amide anions readily react with the anhydride. For example, a cyclic acyltrifluoromethanesulfonamide was synthesized from the lithium salt of caprolactam.[162,163]

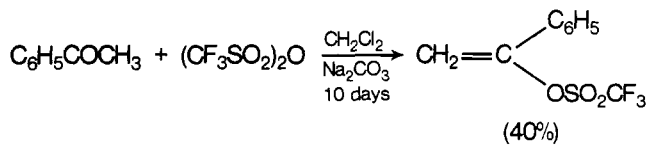


Trifluoromethanesulfonyl azide has been generated in situ from the anhydride and sodium azide in a water–methylene chloride solvent mixture.[166] This active azide converted *n*-hexylamine, 2,4,4-trimethylpent-2-ylamine, and *tert*-butylamine directly to the corresponding alkyl azides.

Enolizable cyclic and acyclic ketones are known to slowly react with trifluoromethanesulfonic anhydride to give vinyl trifluoromethanesulfonates.[61-63,167-173]



(45%)

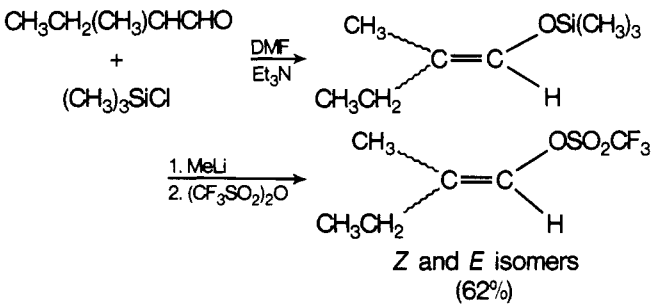


(40%)

Bases such as sodium carbonate, pyridine, and 2,6-lutidine have been used as buffers and catalysis for enolization of the ketones. In some cases it has been advantageous to react the preformed sodium or lithium enolates with either trifluoromethanesulfonyl fluoride[174] or the anhydride.[175] Only readily enolizable aldehydes

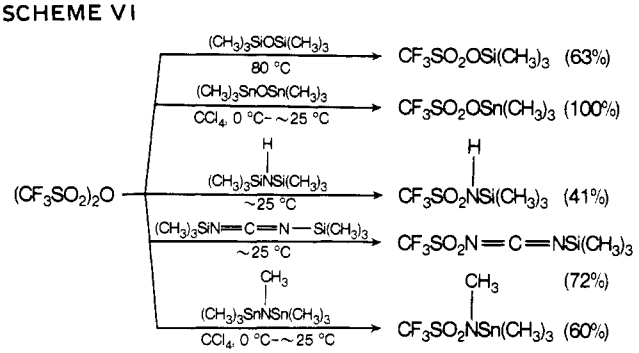
such as diphenylacetaldehyde provide vinyl esters directly upon reaction with trifluoromethanesulfonic anhydride (Scheme V).[167,175] The preparation of vinyl esters from the addition of trifluoromethanesulfonic acid to acetylenes, allenes, and an acyltriazine has already been mentioned (section II.2).

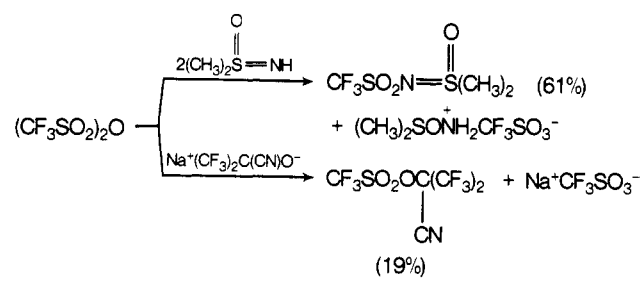
SCHEME V



Trifluoromethanesulfonic acid anhydride underwent cleavage when treated with a variety of silicon and tin compounds at moderate temperatures (Scheme VI).[176,177] Roesky and Giere[176] also allowed dimethylsulfoximide and the hexafluoroacetone–sodium cyanide addition product to react with trifluoromethanesulfonic anhydride. The ^{19}F NMR spectrum of the ester produced from the latter reaction indicated long-range fluorine–fluorine coupling (J(F–F) = 1.2 Hz) (Scheme VII).

SCHEME VI





The acid anhydride has been cleaved by certain metal salts. Tiers[124] found that sodium fluoride, aluminum chloride, and zinc chloride were especially effective.

$$(CF_3SO_2)_2O + NaF \rightarrow CF_3SO_2F + CF_3SO_3^-Na^+$$

Copper(I) and silver(I) trifluoromethanesulfonate complexes, which have been previously mentioned in conjunction with their preparation from trifluoromethanesulfonic acid, also have been obtained from the corresponding reaction of the anhydride.[32,133,134,136] Use of the anhydride eliminates the potential necessity of azeotropic removal of the water formed in the previously mentioned procedure.

Smith and Hubin[98] discovered that trifluoromethanesulfonic acid anhydride and fluorosulfonic acid anhydride (pyrosulfuryl fluoride) are active catalysts for the polymerization of tetrahydrofuran. The polytetramethylene oxide thus obtained was a living, dicationically active polymer (Scheme VIII). As such, it could react with other cationically polymerizable monomers, or it could be terminated by a wide variety of monomeric nucleophilic species, polymeric living anions, or active hydrogen compounds.[55,98,178–181] The ratio of trifluoromethanesulfonic anhydride to tetrahydrofuran monomer largely determined the degree of polymerization. Recent kinetic studies have shown that an equilibrium exists between intermediary ester and oxonium ion, and the latter species is predominantly responsible for propagation of the polymer chain.[53–55,182–184] Dicationically active polytetramethylene oxide has also been obtained from the use of bis(trifluoromethanesulfonate) esters as catalysts, while monocationically active polymer emanates from catalysis by mono(trifluoromethanesulfonate) esters or trifluoromethanesulfonic acid itself.

Other cyclic ethers have been allowed to react with the anhydride. Oxepane underwent ring-opening polymerization in nitrobenzene solvent, and oxirane was cyclodimerized in methylene chloride.[185,186] In the latter case, dioxane was produced in 91% yield at complete conversion of the oxirane. Use of trifluoromethanesulfonic acid produced less dioxane and more poly(ethylene oxide). On the other hand, a higher yield of dioxane was obtained when the methyl ester was employed in place of the anhydride.[186]

Penczek and co-workers[183] have compared other catalysts with trifluoromethanesulfonic anhydride for their overall efficiency in the copolymerization of 1,3,5-trioxane with 1,3-dioxolane. The anhydride gave a superior combination of short induction time, high polymerization rate, and high degree of polymerization.

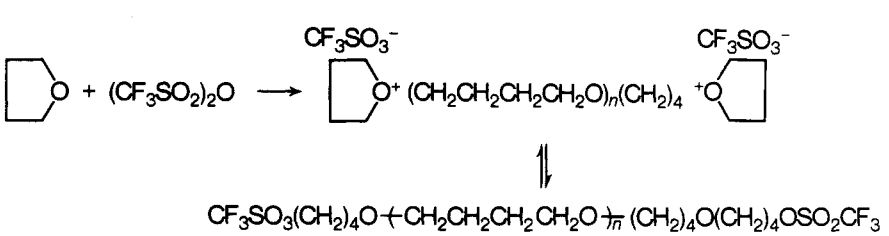
The addition of trifluoromethanesulfonic acid anhydride to dimethyl sulfoxide at −78 °C gave a sulfonium species which decomposed at room temperature or upon exposure to moisture.[187] Synthetic utility was demonstrated when it was found that some α,β and β,γ unsaturated alcohols could be oxidized to unsaturated ketones under extremely mild conditions by the salt. Yields were quite dependent upon solvent polarity. Hendrickson and Schwartzman[188] have also converted triphenylphosphine oxide to triphenylphosphine–bis(trifluoromethanesulfonate) with the anhydride. This moisture-sensitive species was found to activate the dehydration of secondary alcohols and amides. It also accelerated the esterification and amidation of carboxylic acids.

C. Reactions of the Acid Halides

1. Hydroxy Compounds

Trifluoromethanesulfonyl fluoride exhibits a low degree of reactivity toward alcohols, reminiscent of its reactivity toward

SCHEME VIII



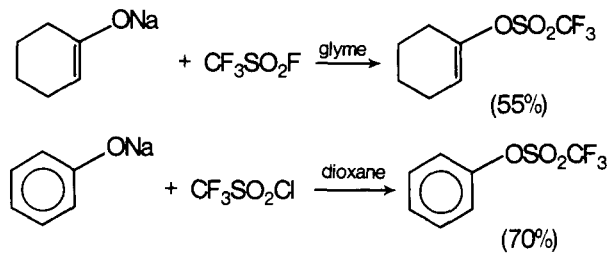
water. Gramstad and Haszeldine[9] observed that no reaction occurred when ethanol was heated at 100 °C with the sulfonyl fluoride. Sodium ethoxide reacted, but the products were sodium *trifluoromethanesulfonate and diethyl ether rather than the desired ester.*

$$CF_3SO_2F + C_2H_5ONa \rightarrow [CF_3SO_3C_2H_5]$$
(excess)

$$\xrightarrow{C_2H_5ONa} CF_3SO_3Na \quad (84\%) + (C_2H_5)_2O$$

Burdon and McLoughlin[189] noted that even with a considerable excess of the sulfonyl fluoride over sodium ethoxide, diethyl ether and sodium trifluoromethanesulfonate were the only products. However, alkoxides which contain strong electron-withdrawing groups,[189-192] sodium enolates,[174] and aryloxides[189,193,194] provide esters upon reaction with trifluoromethanesulfonyl halides.

$$CF_3CH_2OH + CF_3SO_2F \xrightarrow{C_5H_5N} CF_3CH_2OSO_2CF_3 \quad (25\%)$$
$$\xrightarrow[CH_2Cl_2]{(C_2H_5)_3N} CF_3CH_2OSO_2CF_3 \quad (74\%)$$



In some cases, the reaction of a sodium enolate with the sulfonyl fluoride was found to be preferable to the reaction of the corresponding ketone with trifluoromethanesulfonic anhydride for the preparation of vinyl esters.[174]

2. Ammonia, Hydrazine, and Amines

Ammonia,[8,9] primary alkyl amines,[195,196] and secondary alkyl amines[9,197] all react readily with the sulfonyl halides to give trifluoromethanesulfonamides.

$$CF_3SO_2F + (C_2H_5)_2NH \rightarrow CF_3SO_2N(C_2H_5)_2 + (C_2H_5)\overset{+}{N}H_2F^-$$
(83%)

Hydrazine has been utilized in the conversion of the sulfonyl fluoride to the sulfonyl chloride via chlorination of the intermediary sulfonylhydrazine.[198]

$$CF_3SO_2F + NH_2NH_2 \xrightarrow{-5 \text{ to } 30\ ^\circ C} CF_3SO_2NHNH_2 \cdot HF$$

$$\xrightarrow[CCl_4]{Cl_2} CF_3SO_2Cl$$

At temperatures above 30 °C, trifluoromethanesulfonyl fluoride is reduced by hydrazine.[199,200] Trifluoromethanesulfinic acid, long known to be a relatively unstable compound,[5] was isolated upon distillation of the hydrazinium salt from concentrated sulfuric acid.[199]

$$2CF_3SO_2F + 5NH_2NH_2 \rightarrow 2CF_3SO_2^-[N_2H_5]^+ + N_2 + 2[N_2H_5]^+F^-$$

The sulfonyl chloride has been reduced by zinc dust,[5] aqueous potassium sulfite,[201] and by potassium iodide in acetone.[202] The latter two methods conveniently provide potassium trifluoromethanesulfinate in good yields.

Arylamines are less reactive toward trifluoromethanesulfonyl fluoride than primary or secondary alkyl amines, but under the appropriate conditions sulfonanilides were obtained.[11,203,204]

$$C_6H_5NH_2 + CF_3SO_2F \xrightarrow[\text{autoclave}]{120\ ^\circ C,\ 20\ h} C_6H_5NHSO_2CF_3 \quad (45\%)$$

Sulfonylation of deactivated anilines, such as the di- and trihalogenated derivatives, generally requires use of the more reactive anhydride.

3. Miscellaneous Reactions

Trifluoromethanesulfonyl fluoride, a tertiary aliphatic amine, and an alkoxysilane when mixed together gave a quaternary ammonium trifluoromethanesulfonate.[205,206]

$$CF_3SO_2F + (CH_3)_3N + CH_3OSi(CH_3)_3 \rightarrow \overset{+}{(CH_3)_4N}CF_3SO_3^- + (CH_3)_3SiF \quad (73\%)$$

The mechanism of this reaction presumably involves base-assisted formation of methyl trifluoromethanesulfonate and a subsequent alkylation of triethylamine. If an aryloxysilane is used instead of an alkoxysilane, the resultant product is an aryl trifluoromethanesulfonate.[207,208] Like alkoxysilanes, aryloxysilanes require a catalyst, such as a tertiary amine or fluoride ion, in order to react with trifluoromethanesulfonyl fluoride.

$$CF_3SO_2F + C_6H_5OSi(CH_3)_3 \xrightarrow[\text{autoclave, 100 °C}]{(C_2H_5)_3\overset{+}{N}HF^-} C_6H_5OSO_2CF_3 \quad (99\%) + (CH_3)_3SiF$$

The aryloxysilane method appears to offer a versatile alternative to the direct reaction of phenoxides with trifluoromethanesulfonyl fluoride for the preparation of aryl esters. It was claimed that a variety of substituents on the aromatic nucleus, including the amino group, cause little or no interference with ester formation.[208]

Sulfones may be prepared by the reaction of alkyl Grignard reagents with trifluoromethanesulfonyl fluoride. The use of methylmagnesium iodide led to low yields of methyl trifluoromethyl sulfone and bis(trifluoromethanesulfonyl)methane.[8,11]

$$CF_3SO_2F + CH_3MgI \xrightarrow{(C_2H_5)_2O} CF_3SO_2CH_3 \quad (21\%) + (CF_3SO_2)_2CH_2 \quad (5\%)$$

Koshar and Mitsch[209,210] obtained much improved yields with alkylmagnesium chlorides, and they found that solvents which are more basic than diethyl ether promote disulfone formation.

$$CF_3SO_2F + 3CH_3MgCl \xrightarrow{(C_2H_5)_2O} CF_3SO_2CH_3 \quad (70\%) + (CF_3SO_2)_2CH_2 \quad (7\%)$$

$$CF_3SO_2F + 2CH_3MgCl \xrightarrow{THF} (CF_3SO_2)_2CH_2 \quad (80\%)$$

Yagupol'skii and co-workers[211] have reported the preparation of diethyl (trifluoromethanesulfonyl)malonate via treatment of the sulfonyl fluoride with an organosodium compound.

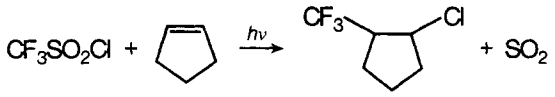
$$CF_3SO_2F + 2NaCH(CO_2C_2H_5)_2 \xrightarrow[50\ ^\circ C]{THF} CF_3SO_2CH(CO_2C_2H_5)_2 \quad (40\%) + CH_2(CO_2C_2H_5)_2$$

The trifluoromethylsulfonylmalonic ester was quantitatively converted to ethyl trifluoromethanesulfonylacetate upon heating with 40% sulfuric acid. Further treatment with 80% sulfuric acid liberated some trifluoromethanesulfonylacetic acid.

Although these Grignard or organosodium reactions with the sulfonyl fluoride may be quite useful, certain trifluoromethyl

sulfones have been formed in somewhat higher yields from the reaction of alkyl bromides with potassium trifluoromethanesulfinate.[202] Additional methods for the synthesis of trifluoromethyl sulfones have been mentioned in previous reviews.[1,212]

Tiers[213,214] and Brown[198] have reported the free-radical addition of trifluoromethanesulfonyl chloride to carbon–carbon double bonds. The addition occurs with loss of sulfur dioxide.



$$CF_3SO_2Cl + CH_2{=}CHSiCH_3(OC_2H_5)_2 \xrightarrow[\text{peroxide}]{\text{benzoyl}} CF_3CH_2CHClSiCH_3(OC_2H_5)_2 + SO_2 \quad (45\%)$$

Lindner and co-workers[215-218] have carried out the reaction of trifluoromethanesulfonyl chloride with a large number of transition metal carbonyl compounds.

$$CF_3SO_2Cl + Na[Mn(CO)_5] \xrightarrow[-60\ ^\circ C]{THF} CF_3SO_2Mn(CO)_5 \quad (30\text{–}40\%)$$

$$CF_3SO_2Cl + Na[Re(CO)_5] \xrightarrow{THF} CF_3SO_2Re(CO)_5 \quad (10\%)$$

$$CF_3SO_2Cl + Fe(CO)_5 \xrightarrow[-80 \text{ to } 25\ ^\circ C]{THF} CF_3SO_2FeCl \cdot (THF)_2 \quad (98\%)$$

$$CF_3SO_2Cl + Fe(CO)_5 \xrightarrow[-80 \text{ to } -30\ ^\circ C]{\text{heptane}} CF_3SO_2Fe(CO)_4Cl \xrightarrow[-4CO]{25\ ^\circ C} CF_3SO_2FeCl \quad (80\%)$$

Solvent-free trifluoromethanesulfonyl transition metal chlorides were also obtained by heating vanadium, chromium, molybdenum, or tungsten hexacarbonyl with trifluoroethanesulfonyl chloride.[218]

$$CF_3SO_2Cl + V(CO)_6 \xrightarrow{120\ ^\circ C} CF_3SO_2VCl + 6CO \quad (80\%)$$

Some bis(trifluoromethanesulfonato) complexes of molybdenum, iron, and nickel were also prepared, albeit in low yields.

$$[\pi\text{-}C_5H_5Ni(CO)]_2 + 2CF_3SO_2Cl \xrightarrow[THF]{25\ ^\circ C} (CF_3SO_2)_2Ni(THF)_2 \quad (8\%)$$

D. Reactions of Esters

1. Alkylation

Nucleophilic displacement of the trifluoromethanesulfonate anion from hydrocarbon alkyl esters of trifluoromethanesulfonic acid is generally a very facile reaction. Hence, these esters are powerful alkylating agents. Examples have been reported of the alkylation of poor nucleophiles such as diethyl ether,[11] benzene,[11,125,219] toluene,[219] and methyl iodide[220] under moderate conditions.

$$CF_3SO_2OCH_3 + (C_2H_5)_2O \xrightarrow{80\ ^\circ C,\ 2} CF_3SO_2OC_2H_5 + C_2H_5OCH_3 \quad (45\%)$$

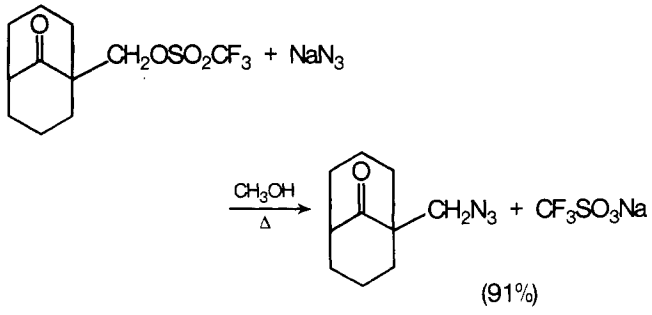
$$CF_3SO_2OC_2H_5 + C_6H_6 \xrightarrow{\text{reflux}} C_6H_5C_2H_5 + C_6H_4(C_2H_5)_2, \text{ etc.}$$

Olah and Nishimura[219] observed that alkylation of benzene or toluene by isopropyl trifluoromethanesulfonate was especially facile. In the absence of a solvent or catalysts, the isopropylation occurred at 25 °C, while in sulfur dioxide solvent and aluminum trichloride catalyst the reaction took place at −78 °C. Alkylation by the methyl or ethyl esters at room temperature required a Friedel–Crafts type catalyst and a solvent such as nitromethane or 1,1,2-trichlorotrifluoroethane. In uncatalyzed reactions, a decreasing order of effective leaving groups was as follows: trifluoromethanesulfonate > fluorosulfonate > chlorosulfonate > trifluoroacetate. However, little reactivity difference existed when aluminum trichloride or antimony pentafluoride catalysts were employed.

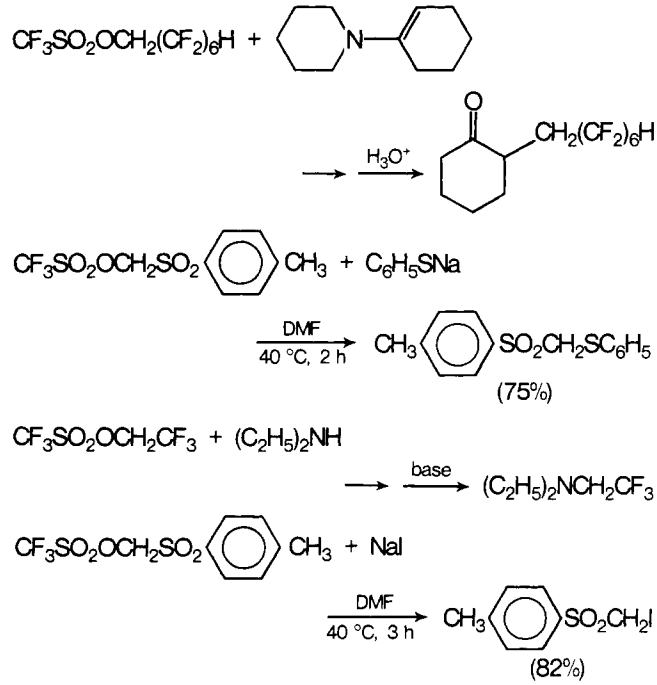
When methyl iodide was allowed to react with perdeuterated methyl trifluoromethanesulfonate, an equilibrium was established after 40 h at 40 °C in which the methyl group was evenly distributed between methyl iodide and the methyl ester.[220]

$$CH_3I + CF_3SO_2OCD_3 \rightleftharpoons CD_3I + CF_3SO_2OCH_3$$

Similar results were obtained when ethyl iodide was allowed to react with methyl trifluoromethanesulfonate. More nucleophilic species such as cyanide, azide, acetate, or dimedone anions have been alkylated by a bicyclic trifluoromethanesulfonate, whereas the corresponding *p*-toluenesulfonate generally failed to yield the directly substituted product.[221] Here, a synthetic advantage results from the use of the more reactive trifluoromethanesulfonate ester; however, in many instances the *p*-toluenesulfonate group is adequate for substitution reactions involving nucleophilic species such as those mentioned above.



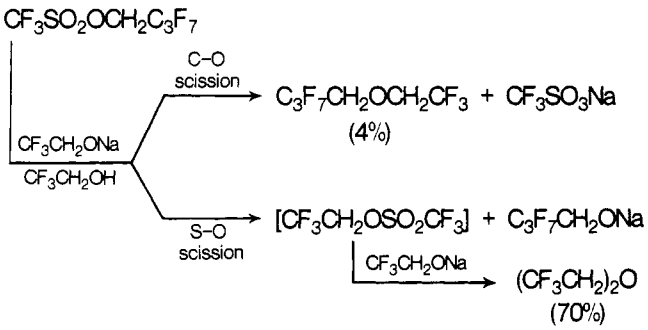
Alkyl trifluoromethanesulfonates, including many of those which are deactivated by strong electron-withdrawing substituents in the alkyl moiety, can alkylate amines, alkoxides, phenoxides, mercaptides, and enamines.[56,189-192,222-224] Inorganic ions such as halide, azide, and thiocyanate are also suitable



nucleophiles.[56] These reactions proceed much more readily than do those of the corresponding arenesulfonates and alkyl esters of polyphosphoric acid.

It has been suggested that the reaction of a polyfluorinated alkoxide with a polyfluoroalkyl trifluoromethanesulfonate may be an excellent general synthesis of polyfluoroalkyl ethers.[189] When dissimilar polyfluorinated groups are present in the ester and alkoxide, both the symmetrical and unsymmetrical ethers are formed (Scheme IX).[192] Since isolation of the pure components of the ether mixture has proven to be very difficult, the synthetic usefulness of this reaction is somewhat limited. The preferential sulfur–oxygen bond cleavage, which was evident in the polyfluorinated alkoxide reactions, was still prevalent when a nonfluorinated alkoxide was employed.[192] The only other report of sulfur–oxygen bond cleavage in alkyl trifluoromethanesulfonates was observed in the reaction of 2,2,2-trifluoroethyl trifluoromethanesulfonate with a Grignard reagent.[225]

SCHEME IX



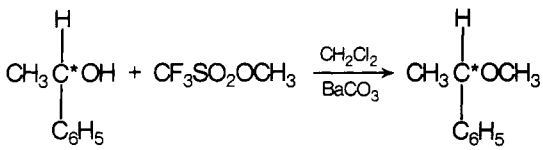
Highly reactive esters, such as allyl, propargyl, isopropyl, and pentyl trifluoromethanesulfonates alkylate alcohols of low nucleophilicity under essentially neutral or basic conditions.[52]

$$CF_3SO_2OCH_2CH{=}CH_2 + CH_3C(NO_2)_2CH_2OH \xrightarrow[Na_2SO_4]{CH_2Cl_2} CH_2{=}CHCH_2OCH_2C(NO_2)_2CH_3 \quad (53\%)$$

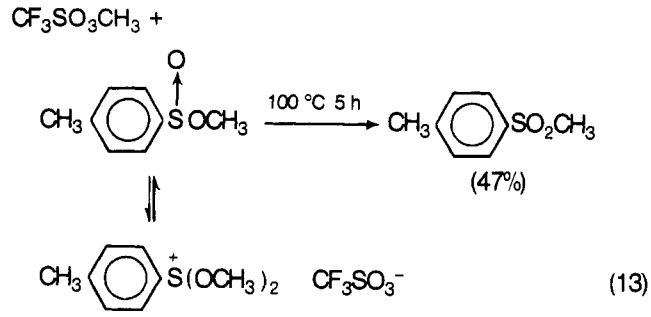
$$CF_3SO_2OC_5H_{11}\text{-}n + CF_3CH_2OH \xrightarrow[K_2CO_3]{CH_2Cl_2} n\text{-}C_5H_{11}OCH_2CF_3 \quad (86\%)$$

The synthetic utility of these active trifluoromethanesulfonates is emphasized by the failure of the corresponding *p*-toluenesulfonate to react with trinitroethanol or other similarly deactivated alcohols. Another very reactive ester, benzyl trifluoromethanesulfonate, has been used to prepare a benzyl ether carbohydrate derivative under extremely mild conditions.[223]

Optically active ethers have been prepared by the reaction of alkyl trifluoromethanesulfonates with an optically active alcohol.[50] A greater retention of optical activity than found in other ether synthesis was claimed.



Recently, it was established that dialkoxysulfonium ions are formed when methyl halosulfonates or methyl trifluoromethanesulfonate are allowed to react with sulfinates (eq. 13).[226] At an elevated temperature, methyl trifluoromethanesulfonate catalyzed the conversion of methyl *p*-toluenesulfinate to methyl *p*-tolyl sulfone, but under ambient conditions this sulfonium species was quite stable. By contrast, the corresponding dimethoxysulfonium fluorosulfonate was quantitatively converted to *p*-toluenesulfinyl fluoride and methyl sulfate during the course of 2 days.



(13)

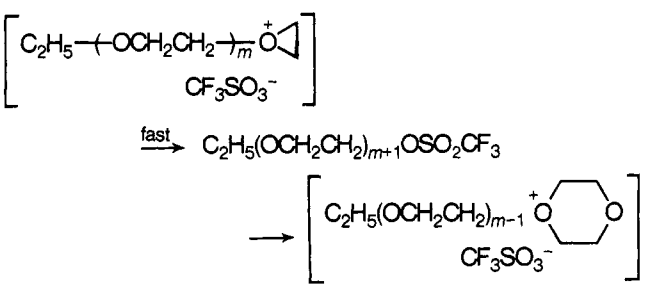
Alkylation of tetrahydrofuran by alkyl trifluoromethanesulfonates results in the formation of polytetramethylene oxide.[53-55,179-181] The mechanism involves a macroion–macroester equilibrium (section III.B) of the propagating species. Some discussion has centered on whether the macroester or macroion is the more readily propagated species. Saegusa and co-workers[53,54,185,186] favor the macroester in nonpolar solvents and the macroion in polar solvents, while Penczek and coworkers[189,227] believe that the cyclic oxonium macroion is always much more active than the macroester. Polar solvents would be expected to shift the equilibrium in favor of the macroion and also stabilize the transition state for a macroester–monomer reaction. Indeed, polar solvents significantly increase the overall rate of polymerization. A similar rate enhancement was observed upon the addition of certain Lewis acid type salts.[227] The macroion–macroester equilibrium in the alkyl trifluoromethanesulfonate (or alkyl fluorosulfonate) initiated polymerizations has been extensively studied by proton,[53,54,184,227-229] fluorine,[54,229,230] and carbon-13[231] NMR spectroscopy. The latter may well prove to be the most useful tool in the further elucidation of the mechanism of this type and other cationic ring-opening polymerizations.

Kinetic analysis of data obtained from ^1H NMR spectroscopy on the ethyl trifluoromethanesulfonate initiated polymerization of 3,3-bis(chloromethyl)oxacyclobutane has provided evidence for an ester rather than oxonium ion type propagating species.[232] The chloromethyl substituents would tend to destabilize intermediate oxonium ions and also decrease the nucleophilic reactivity of the monomer. Additional ^1H NMR evidence suggests that propagation via macroester–monomer combination predominates when either oxepane[185] or oxirane[186] is treated with alkyl trifluoromethanesulfonates. In the latter case, the small ring size would make the initially formed macroion quite unstable, but a backbiting reaction of the ester can form the stable six-membered cyclic oxonium which liberates dioxane (Scheme X).

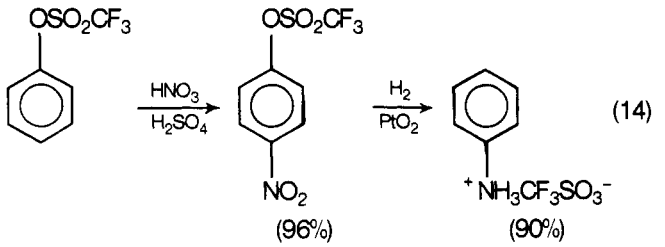
2. Aryl Esters

In sharp contrast to the alkyl esters, aryl trifluoromethanesulfonates possess high thermal stability and are unaffected by water, alcohols, ethers, and tertiary amines. Yagupol'skii and Nazaretyan[194] found that nitration of the phenyl ester gave almost exclusively the *p*-nitro isomer despite the powerful inductive electron withdrawal of the trifluoromethanesulfonyl

SCHEME X

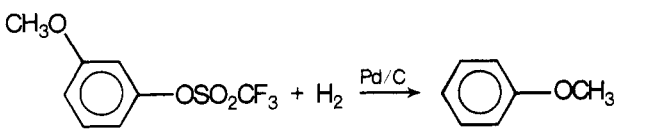


moiety. Reduction of the *p*-nitrophenyl trifluoromethanesulfonate with hydrogen on platinum dioxide resulted in cleavage of the trifluoromethanesulfonate anion from the aromatic ring (eq 14).



(14)

This reductive removal of the trifluoromethanesulfonate group potentially provides the basis for an attractive scheme for the dehydroxylation of aromatic compounds. Limited success has been achieved in extending the reduction to other compounds (eq 15).[194,220]



(15)

Aryl trifluoromethanesulfonates react readily with sodium methoxide in methanol to give methyl ethers.[220] In another reaction with a strong base, phenyl trifluoromethanesulfonate has been converted to phenol by the action of sodium hydroxide in 50% aqueous dioxane.[62] The mechanism of these reactions has not been conclusively elucidated.

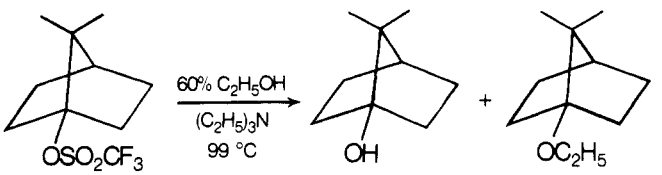
3. Solvolysis and Miscellaneous Reactions

Solvolysis of *p*-toluenesulfonates (tosylates) or other arenesulfonates has been a useful probe for the elucidation of organic reaction mechanisms. The introduction of esters of trifluoromethanesulfonic acid (triflates) has greatly extended the range of organic substrates amenable to kinetic study under solvolytic conditions. Many systems that were formerly "inert" have been examined with the aid of the labile trifluoromethanesulfonate leaving group. The trivial term "triflate" which was introduced by Streitwieser and co-workers[127] as a substitute for trifluoromethanesulfonate has pervaded much of the literature on this subject.

Hansen[190] made a quantitative comparison of the acetolysis rates for methyl trifluoromethanesulfonate and methyl *p*-toluenesulfonate. Amazingly, the former was more than 10^4 times as reactive as the latter. Subsequent studies have indicated that there is no dramatic mechanistic difference between the solvolysis of alkyl trifluoromethanesulfonates and arenesulfonates. For example, a similar low dependence on solvent ionizing power and high dependence on solvent nucleophilicity was observed for the solvolysis of either class of primary ester.[127,128] This points to little carbonium ion character coupled with an important contribution from a covalent type solvent–carbon interaction in the transition state. It is generally concluded that these solvolyses are mechanistically intermediary between the idealized S_N1- and S_N2-type reactions. In a close comparison, Lee and Unger[233] examined the solvolyses of 2-phenylethyl-*1-*^{14}C trifluoromethanesulfonate and *p*-toluenesulfonate in unbuffered acetic acid. Product analysis indicated nearly the same degree of rearrangement (32%) of the ^{14}C label from the primary to secondary carbon atoms. The importance of internal return was demonstrated by monitoring the partial solvolysis of 2-phenylethyl-*2,2-*d_2 trifluoromethanesulfonate in perdeuterioacetic acid by proton NMR spectroscopy. After 5 h, a 35% rearrangement of the deuterium label in the acetate product and a 33% deuterium scrambling in the unreacted ester were observed. Similarly, an extensive internal return process was operative when the corresponding *p*-toluenesulfonate was solvolyzed. Interestingly, an incongruency was noted when the solvolysis of the ^{14}C-labeled esters was carried out in the presence of sodium azide. This strong nucleophile surpressed the rearrangement to a significantly greater extent with the *p*-toluenesulfonate. In view of the $10^{4.9}$ rate factor disparity for solvolysis of these substrates,[234] the likelihood of different contributions from the various mechanistic components involved is overwhelming.

Traynham and Elakovich[156] compared the product distributions that resulted from acetolysis of some highly reactive secondary alkyl trifluoromethanesulfonates and *p*-toluenesulfonates. Elimination was the major mode of reaction, but substitution with a predominant inversion of configurations also occurred. Thus, a closely associated ion pair, rather than a free carbocation, was indicated.

The enhanced reactivity of trifluoromethanesulfonates has permitted the determination of solvolysis rates for certain secondary or tertiary polycyclic compounds that could not be conveniently solvolyzed with an arenesulfonate leaving group.[65,153-155] Even the highly active 2,2,2-trifluoroethanesulfonates are about 400 times less reactive than trifluoromethanesulfonates.[235] The rate of solvolysis of 1-apocamphyl and 4-tricyclyl trifluoromethanesulfonates have been compared in an effort to examine possible carbonium ion stabilization by the face of a cyclopropane ring (eq 16 and 17).[65] Extrapolation



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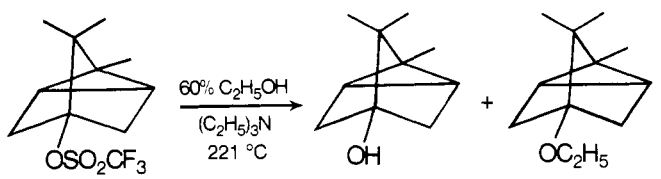


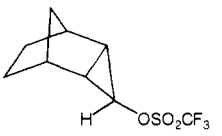
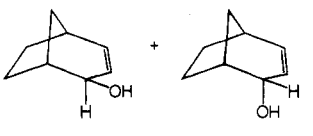
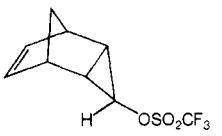
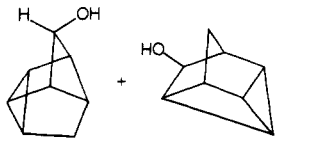
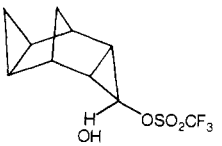
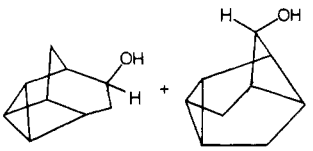
(17)

of the data to 25 °C showed that the 1-apocamphyl ester was solvolyzed 3×10^4 times faster than the 4-tricyclyl ester. This rate difference agreed fairly well with that predicted on the basis of semiempirical strain energy calculations. Certainly, no evidence was found for carbonium ion stabilization by the face of a cyclopropane ring. A similar conclusion was reached by Schleyer and co-workers[155] upon comparison of the rates of solvolysis of 4-nortricyclyl trifluoromethanesulfonate and other bridgehead esters.

Creary[236] found evidence for an unsubstituted cyclopropyl cation in the solvolysis of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-*exo*-3-yl trifluoromethanesulfonate. Since the leaving group was exo to the small ring fused to the cyclopropyl group, electrocyclic cyclopropyl opening is disfavored. The exclusive ring-opened products (Table VII) presumably arose from rearrangement of a discrete cyclopropyl cationic intermediate. Rate enhancements and the nature of the products obtained from solvolysis of the analogous esters shown in Table VII suggest a marked anchimeric assistance to the developing cationic center. Actually, the olefinic and cyclopropyl groups have a rate-retarding inductive effect so that the anchimeric assistance is not adequately reflected in the relative solvolysis rates.

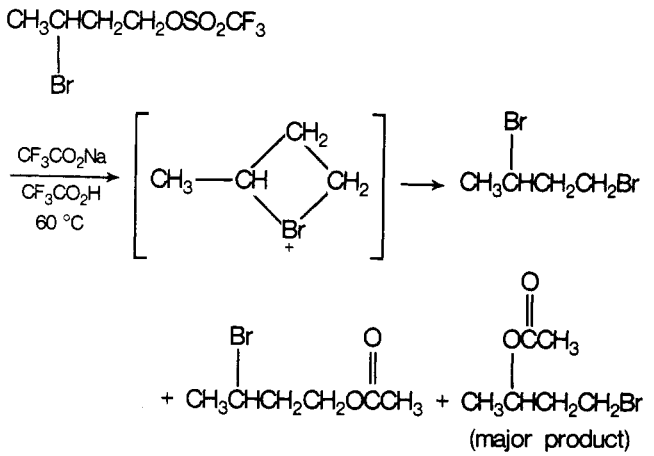
Several systems have been discovered in which direct nucleophilic displacement of the trifluoromethanesulfonate ion competes with intramolecular participation or cyclization. Pe-

TABLE VII. Some Solvolytic Evidence for Anchimeric Assistance

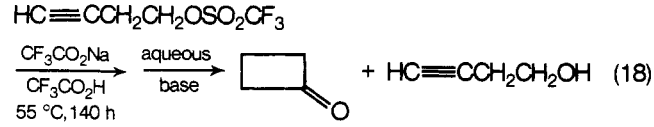
Substrate	Major products	k_1, s^{-1}	k_{rel} (100 °C)
		5.31×10^{-7}	1
		4.32×10^{-5}	81
		3.75×10^{-6}	7.1

terson and Boron[237] found evidence of four-membered ring halonium ion intermediates in the trifluoroacetolysis of 3-halo-1-butyl trifluoromethanesulfonates (Scheme XI). The relative

SCHEME XI

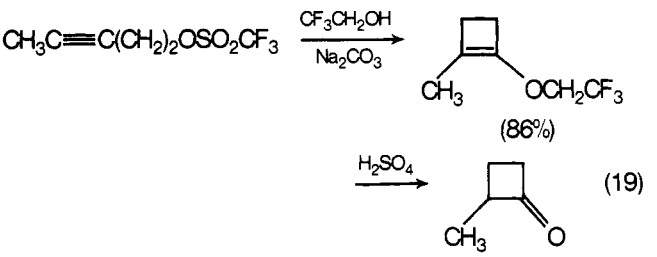


halogen reactivity in this 1,3-halogen participation was I > Br ≫ Cl. Only a few per cent of primary chlorides resulted from the trifluoroacetolysis of the 3-chloro-1-butyl ester. Trifluoroacetolysis of other primary sulfonate–secondary halide compounds has implicated three-, five-, and six-membered ring halonium ions due to favored 1,2, 1,4, and 1,5 halogen shifts.[238] Hummel and Hanack[152,239] observed a homopropargyl rearrangement in the trifluoroacetolysis of 3-butyn-1-yl trifluoromethanesulfonate. Cyclobutanone and 3-butyn-1-ol were isolated in a 76:24 ratio, respectively (eq 18). In comparison, only 4% of cyclo-



(18)

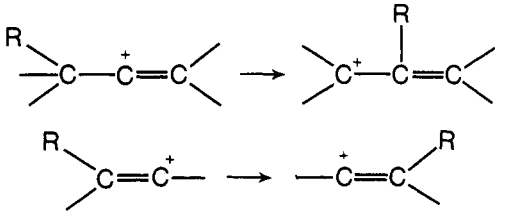
butanone was obtained from a similar reaction which involved 3-butyn-1-yl *m*-nitrobenzenesulfonate. Acetylenic bond participation in solvolysis of trifluoromethanesulfonates has also provided 2-methyl-, 2-ethyl-, 2-isopropyl-, and 2-trifluoromethylcyclobutanone from the corresponding acetylenic compounds.[240,241] The isolation of a cyclobutene intermediate in the trifluoroethanolysis of 3-pentyn-1-yl trifluoromethanesulfonate provides strong evidence for the generation of a cyclobutenyl cation (eq 19).[241]



(19)

Relatively little information has appeared on nucleophilic substitution at a saturated carbon atom in emulsions. The use of a trifluoromethanesulfonate ester has given preliminary indication of an effective micellar control on the rate and stereochemical outcome of such reactions.[242] Extrapolation of hydrolysis rate data from aqueous acetone to a pure water medium established some basis for comparative studies in an emulsion. Accordingly, it was found that hydrolysis of 1-methylheptyl trifluoromethanesulfonate in either the cationic or anionic emulsion state was greatly retarded relative to the extrapolated rate of hydrolysis in solution.

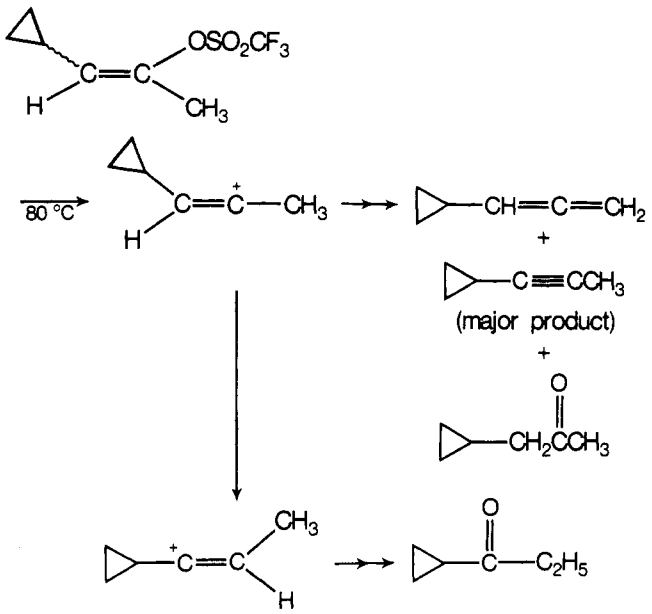
The solvolysis of vinyl trifluoromethanesulfonates has been the subject of numerous investigations.[59-64,167-173,243-252] This topic has also been included in several review articles on vinyl cations.[253,254] Essentially all of the evidence reported to date strongly indicates that the solvolysis of vinyl trifluoromethanesulfonates involves ion-pair formation. In fact, these solvolysis reactions appear to be the method of choice for the generation of alkyl-substituted vinyl cations. Rearrangements of the initially formed cationic species are common. Migration of an alkyl or aryl group to the double bond or across the double bond is well known.[253,254] The driving force for the rearrangement is the formation of the more stable vinyl carbonium ion.



Recently, the first example of a 1,2-hydride shift across a double bond in the solvolysis of a vinyl compound was reported.[247] The hydride shift occurred during the solvolysis of *cis*- and *trans*-3-cyclopropyl-2-propen-2-yl trifluoromethanesulfonate in aqueous trifluoroethanol (Scheme XII). The greater stability of a cyclopropylvinyl carbonium ion, which was created by a 1,2-hydride shift, resulted in the subsequent formation of some cyclopropyl ethyl ketone. Solvolysis of the cis isomer provided evidence for a greater degree of vinyl cation character since less alkyne and more cyclopropyl acetone were formed. A possible competitive synchronous β-elimination to an alkyne would be less likely with the cis isomer. Jäckel and Hanack[248] have also reported a 1,2-hydride shift toward a double bond. Buffered trifluoroethanolysis of 3-methyl-1-buten-2-yl trifluoromethanesulfonate yielded 3-trifluoroethoxy-3-methylbutene-1 along with products of an unrearranged vinyl cation. The driving force for hydride shift rather than methyl migration is the formation of the stable tertiary carbonium ion.

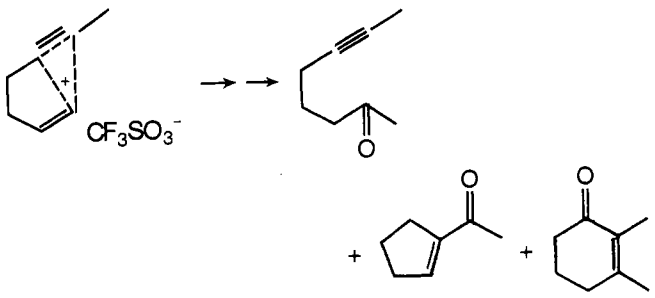
Interestingly, an inversion component was quite evident in the buffered trifluoroethanolysis of *cis*- and *trans*-3-methyl-2-hepten-2-yl trifluoromethanesulfonates.[250] The cis and trans esters gave a 4.6 and 2.4 trans/cis trifluoroethyl vinyl ether product

SCHEME XII

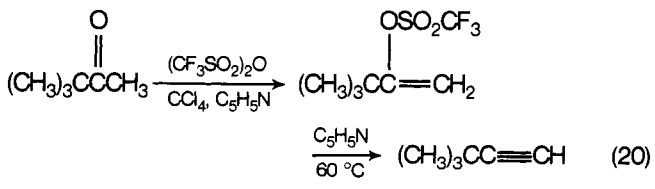


ratio, respectively. This partial inversion of stereochemistry obviates the exclusive involvement of either free vinyl cations or direct S_N2 displacement. Based on the present knowledge, the most plausible rationale involves ion pairs, and it allows a certain degree of shielding by the departing trifluoromethanesulfonate anion.

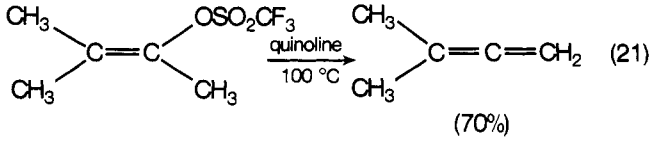
The low nucleophilicity and high ionizing power of trifluoroethanol solvent and the relative high reactivity of vinyl trifluoromethanesulfonates have been utilized in establishing evidence for the participation of remote double[250] and triple[251] bonds with vinyl cations in solvolysis reactions. For instance, cyclic and acyclic ketones were obtained from 6-octyn-2-en-2-yl trifluoromethanesulfonate.



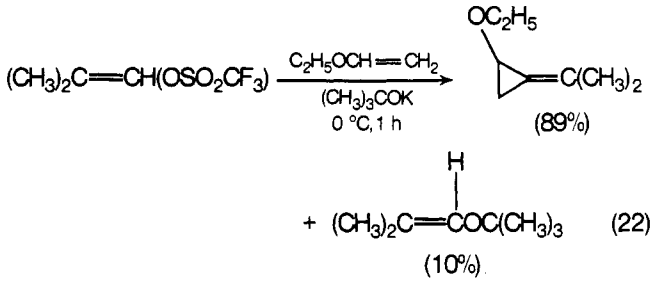
Certain vinyl trifluoromethanesulfonates have been quite successfully employed as synthetic intermediates. In one instance, highly pure *tert*-butylacetylene was obtained from pinacolone (eq 20).[173] Other vinyl esters may be converted to



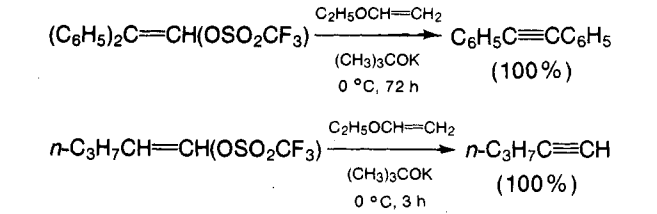
1,1-di-, tri-, or tetrasubstituted allenes by a similar procedure (eq 21).[255] Under the conditions employed there was no rearrangement of the allene to the isomeric alkyne.



Treatment of 2,2-dialkyl-substituted vinyl trifluoromethanesulfonates with potassium *tert*-butoxide in the presence of an olefin generated methylenecyclopropanes in high yield (eq 22).[175] This reaction was reported to be one of the best, if not

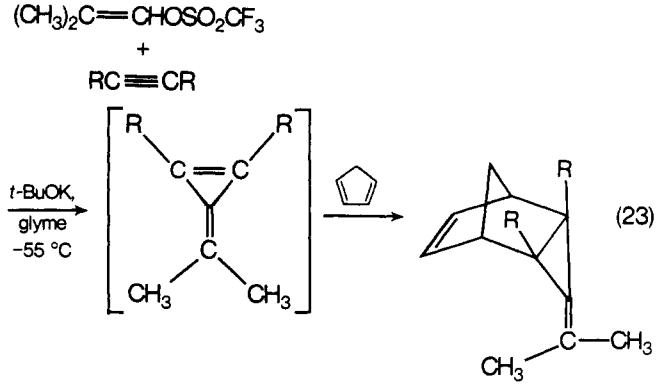


the best, known sources of unsaturated carbenes or carbenoids. The results were entirely different if the vinyl trifluoromethanesulfonate possessed either a β-hydrogen or β-aryl group. Alkyne formation resulted from an initial α elimination which was followed by a rapid rearrangement of the unsaturated carbene.[175,256]



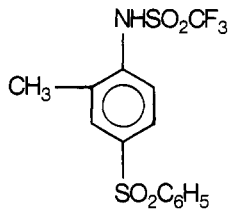
The possibility of preferential E2 elimination in β hydrogen containing trifluoromethanesulfonates was quashed by a deuterium-labeling study. No kinetic deuterium isotope effect and a complete lack of stereochemical consequence resulted from the incorporation of a β deuterium in place of the β hydrogen. Stang and Mangum[257,258] have provided additional insight into the nature of the carbene generated from primary vinyl triflates which contain neither a β hydrogen nor a β-aryl group. They observed a 98% stereoselective addition of isopropylidenecarbene to *cis*- and *trans*-2-methoxy-2-butene and stereospecific addition to *cis*- and *trans*-2-butene. These results were essentially unchanged when the reactions were carried out in an inert fluorocarbon diluent. Hence, the presence of a singlet rather than triplet carbene was inferred. Furthermore, crown ethers had no noticeable influence on the relative reactivity of isopropylidenecarbene with *p*-methylstyrene–styrene, styrene–cyclohexene, or other styrene mixtures. This suggests that the carbene is free from any association with potassium ion since the latter was effectively complexed by the crown ethers.

Remarkably, the addition of a vinyl trifluoromethanesulfonate derived unsaturated carbene to dialkylacetylenes has provided the heretofore inaccessible simple alkyl-substituted methylenecyclopropenes (eq 23).[259] Although polymerization prevents isolation at room temperature, the new compounds are stable at −20 °C in solution.

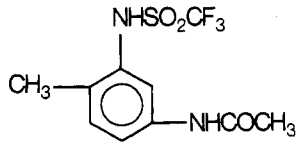


E. Reactions of Sulfonamides and Sulfonimides

Much of the preparative interest in derivatives of trifluoromethanesulfonamides stems from the biological activity inherent in so many of these compounds.[159,195,196,260-263] The increased acidity and lipophilicity that are imparted by the inclusion of the trifluoromethanesulfonyl moiety often transforms compounds of moderate biological activity into highly active species. Two of the most active trifluoromethanesulfonamido derivatives that have been reported are the specific herbicide, Destun®, and the turf-growth retardant, Sustar®. Other related compounds possess antiinflammatory[262,263] or anticonvulsant[195] activity.



Destun

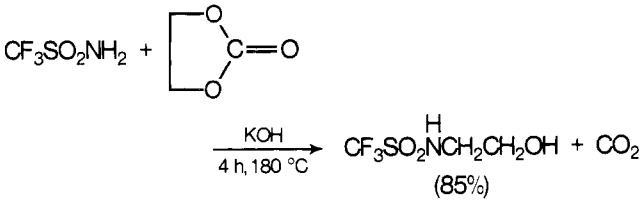


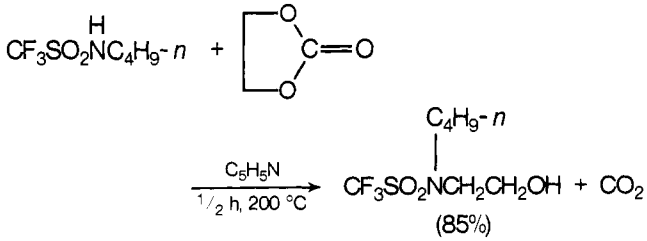
Sustar

Alkyl derivatives of trifluoromethanesulfonamide are commonly prepared by treatment of an amide anion with an alkyl halide.[159,161-163]

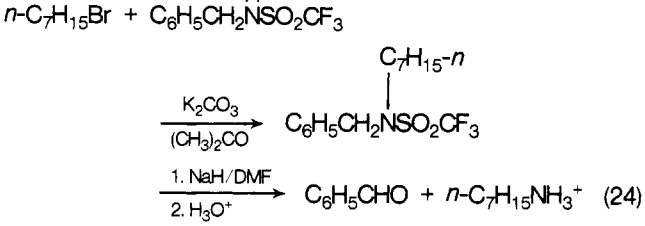
$$CF_3SO_2NH_2 + CH_3I \xrightarrow[(CH_3)_2CO]{Na_2CO_3} CF_3SO_2NHCH_3 + CF_3SO_2N(CH_3)_2 \quad (97\%)$$
$$80 : 20$$

Of course, many of the same compounds can be prepared directly from the reaction of trifluoromethanesulfonyl fluoride with primary or secondary amines (section III.C). A variety of bases may be used to generate the amide anion, but the alkali metal carbonates are often preferred when a high degree of monoalkylation is desired. Addition of 1,2-alkylene carbonates, such as ethylene carbonate, to an amide anion is a useful method for the preparation of *N*-(β-hydroxyalkyl)trifluoromethanesulfonamides.[264] Alternately, a β-hydroxyalkyl chloride may be used in place of the 1,2-alkylene carbonate.



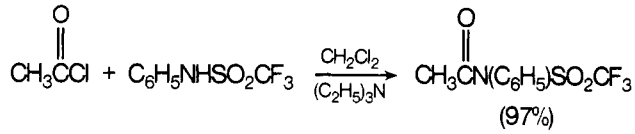


Hendrickson and co-workers[161,162] have developed a new Gabriel synthesis of primary amines based on the initial facile alkylation of *N*-benzyltrifluoromethanesulfonamide (eq 24).



(24)

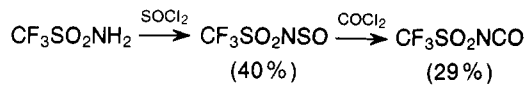
Acylation of *N*-alkyltrifluoromethanesulfonamides[163,195] or trifluoromethanesulfonanilide[163] proceeds readily to give the *N*-acyl compounds in very high yield.

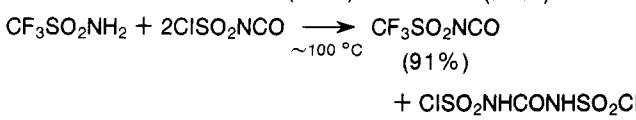


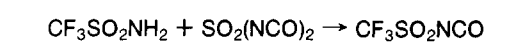
(97%)

Similar yields are often obtained when primary carboxamides are allowed to react with trifluoromethanesulfonic acid anhydride. The *N*-acyl,*N*-phenyl- or *N*-acyl,*N*-benzyltrifluoromethanesulfonamides smoothly acylate amines, and they have proven to be superior to other reagents for the acylation of pyrroles.[163]

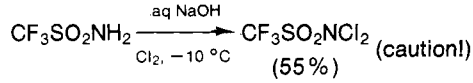
Trifluoromethanesulfonamide reacts with thionyl chloride or chlorosulfonyl isocyanate to give the imino sulfoxide[197] or isocyanate[265,266] derivatives. As would be expected, these compounds hydrolyze readily upon contact with atmospheric moisture.





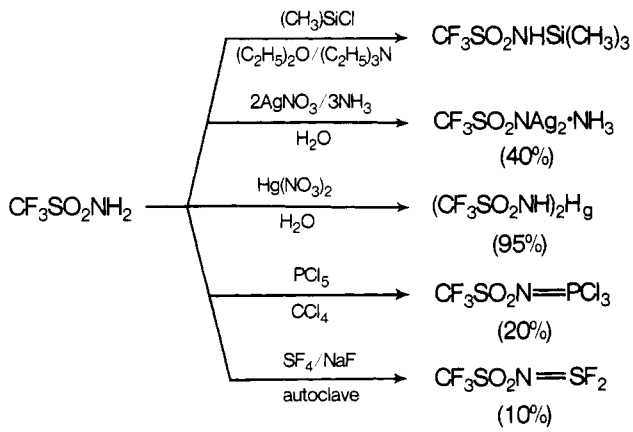


The disilver salt of trifluoromethanesulfonamide provided an additional route to both the isocyanate and isothiocyanate, albeit in low yield.[267] Here, phosgene and thiophosgene were coreactants. It is prudent to exercise caution when working with certain dimetal salts of the amide because of their potentially explosive character. Rubbing of the anhydrous disodium salt, prepared from treatment of the amide with sodium in methanol, has led to an explosive decomposition.[268] This impact sensitivity extends to the *N,N*-difluoro- and *N,N*-dichlorotrifluoromethanesulfonamide derivatives.[268]



Other derivatives of trifluoromethanesulfonamide were obtained from reactions with trimethylchlorosilane,[176] ammoniacal silver nitrate,[267] mercuric nitrate,[267] phosphorus pentachloride, and sulfur tetrafluoride (Scheme XIII).[197]

SCHEME XIII



Trifluoromethanesulfonimides, which are prepared either by the addition of 2 equiv of trifluoromethanesulfonic anhydride to a primary amine or by treatment of the sulfonamide anion with

1 equiv of the anhydride, exhibit a wide range of thermal stability. The *N-aryl sulfonimides*[163,203,269] are stable solids that are generally nonhygroscopic and soluble in many organic solvents. *N,N*-Bis(trifluoromethanesulfonyl)aniline can conveniently be used to transfer a trifluoromethanesulfonyl group to phenols, primary amines, or secondary aliphatic amines under mild conditions (eq 25 and 26).[163] The trifluoromethanesulfonanilide

$$C_6H_5N(SO_2CF_3)_2 + C_6H_5OH \xrightarrow{(C_2H_5)_3N} C_6H_5OSO_2CF_3 + C_6H_5\overset{H}{\underset{|}{N}}SO_2CF_3 \quad (25)$$

(95%)

$$C_6H_5N(SO_2CF_3)_2 + \text{C}_6\text{H}_{11}\text{NH} \xrightarrow{(C_2H_5)_3N} \text{C}_6\text{H}_{11}\text{NSO}_2\text{CF}_3 + C_6H_5\overset{H}{\underset{|}{N}}SO_2CF_3 \quad (26)$$

(88%)

coproduct of these reactions can easily be separated from secondary sulfonamides by extraction with aqueous sodium carbonate, but its removal from other primary sulfonamides was more difficult. *N,N*-Bis(trifluoromethanesulfonyl)aniline has also been employed in the separation of secondary aromatic amines from primary amines or secondary aliphatic amines since only the latter species react. The recovery of primary or secondary aliphatic amines from the resultant sulfonamides was easily accomplished by hydride reductions.[161,162] The high efficiency found for both the amine sulfonylation and sulfonamide reduction recommend this procedure as an alternate method for the protection of amines.

n-Hexylbis(trifluoromethanesulfonimide) is also quite thermally stable, but the benzyl imide decomposed above −15 °C.[164] The carbon–nitrogen bond in the latter compound was cleaved by nucleophiles such as bromide, methoxide, or cyanide in a dipolar aprotic solvent.[162,164]

$$C_6H_5CH_2N(SO_2CF_3)_2 \xrightarrow[HMPA]{NaCN} C_6H_5CH_2CN \quad (80\%)$$

The *tert*-butyl imide, which was presumably formed from the reaction of *tert*-butylamine with 2 equiv of trifluoromethanesulfonic acid anhydride, decomposed at −78 °C to give a quantitative amount of isobutylene.[162]

IV. Summary

The attractive physical and chemical properties of trifluoromethanesulfonic acid have led workers in many fields of chemistry to the discovery of numerous significant applications of this acid. Often, other strong acids promote a different reaction path, or they are less effective and selective toward the promotion of the same mode of reaction. Trifluoromethanesulfonic acid has been successfully employed as a catalyst in various Friedel–Crafts type alkylation, acylation, and polymerization reactions. At the other end of the spectrum, the acid has been used as a solvent for ESR studies and as a nonaqueous, strong acid titrant.

The same factors that contribute to the chemical and physical stability of trifluoromethanesulfonic acid or its conjugate base help create utility for the simple acid derivatives such as salts and esters. Tetraalkylammonium trifluoromethanesulfonates are a boon to nonaqueous electrochemistry. The cuprous salt provides a high degree of selective complexation with aromatic, olefinic, and certain other types of compounds. Procedures have been described for the separation of complex mixtures of hydrocarbons based on this selective complexation. Hydronium trifluoromethanesulfonate is perhaps the best known electrolytic medium for hydrocarbon–air fuel cells. Salts of trifluoromethanesulfonic acid are generally more soluble in organic solvents than salts of other strong organic or inorganic acids. This can be very beneficial in homogeneous catalysis systems as in the cyclopropanation of olefins with diazo compounds. Alkyl esters have synthetic value as alkylating agents. The solvolysis of trifluoromethanesulfonates occurs 10^4 to 10^5 times faster than solvolysis of the corresponding *p*-toluenesulfonates. Thus, kinetic data may be obtained under considerably more moderate conditions by the use of the better leaving group. The solvolysis of vinyl esters have been shown to involve vinyl cations. Some vinyl trifluoromethanesulfonates have been employed in the generation of vinyl carbenes (or carbenoid species) while acetylenes have been prepared from others.

Finally, it should be pointed out that much of the subject matter for this review was of recent origin. Hopefully, this comprehensive compilation will further accelerate the already rapid growth of chemical knowledge on trifluoromethanesulfonic acid and its derivatives.

V. Addendum

Many pertinent articles and patents have appeared since this review was originally completed. The references mentioned below are indexed according to the section designations of the main text.

II.A. McCallum and Pethybridge have measured the conductance of trifluoromethanesulfonic and four other acids in anhydrous $(CH_3)_2SO$.[270]

II.A. A higher σ_I and a similar σ_p value to those reported by Yagupol'skii and Nazaretyan[194] for the trifluoromethanesulfonate group has been reported.[271] The resultant new σ_R value (−0.36) points to a substantially greater electron donation through $p\pi$–$p\pi$ interactions than was previously attributed to this group.

II.B.1. The x-ray crystal structure has been reported for both the hemi- and dihydrates of trifluoromethanesulfonic acid.[272] A phase diagram depicted solid phases for the hemi-, di-, tetra-, and pentahydrate as well as the most stable monohydrate.

II.B.1. Iodosyl and iodyl trifluoromethanesulfonate have been isolated and characterized.[273]

II.B.2. Olah and Ohyama have reported a simplified procedure for the preparation of trifluoromethyl trifluoromethanesulfonate.[274] Some quaternary ammonium salts that decompose at atmospheric pressure were obtained from this poor trifluoromethylating agent in sealed tube reactions.

II.B.4. An improved method for the production of para-alkylated phenols has been claimed.[275] Certain aryl sulfonic acids or trifluoromethanesulfonic acid effectively catalyze the rearrangement of ortho and meta isomers to the desired phenols without concomitant corrosion of glass-lined or stainless steel equipment.

II.B.5. The addition of aliphatic nitriles to trifluoromethanesulfonic acid afforded trialkyl *s*-triazines under mild conditions.[276] Triaryl *s*-triazines were also conveniently prepared.

II.B.5. Trifluoromethanesulfonic acid has been recommended as a nonoxidizing alternative to perchloric acid for high-temperature aqueous chemistry.[277] No oxidation of various divalent metal ions was detected after 24 h in 1.0 m acid at 570 K.

II.B.5. In a report overlooked by the reviewers, trifluoromethanesulfonic acid was used in a study that demonstrated the reversibility of the Fries rearrangement.[278]

II.B.5. Roberts has reported a detailed kinetic investigation of the trifluoromethanesulfonic acid catalyzed addition of acetic acid to some cyclic and strained bicyclic olefins.[279] The addition was nonstereospecific in contrast to some analogous hydrogen bromide catalyzed reactions. New pK_a and H_0 values for dilute solutions of trifluoromethanesulfonic acid in acetic acid were obtained.

III.A. Mercuric trifluoromethanesulfonate has been cited as a catalyst for the transformation of cyclic oligomeric dihalophosphazines into soluble linear dihalophosphazine polymers.[280]

III.A. Zinc or cobalt trifluoromethanesulfonate in combination with triethylamine catalyzes the formation of dimers and trimers of acrylonitrile or methacrylonitrile.[281]

III.A. Alkylsulfonic and arylsulfonic trifluoromethanesulfonic mixed anhydrides have been prepared from silver trifluoromethanesulfonate.[282,283] Sulfonylation of acetonitrile and various aromatic compounds was achieved under generally milder conditions than employed in the traditional Lewis acid catalyzed sulfone syntheses.

III.A. Cohen and Cristea carried out a kinetic investigation of the homogeneous copper(I) trifluoromethanesulfonate induced Ullmann coupling of *o*-bromonitrobenzene.[284] Free radicals were excluded as intermediates.

III.A. Polytetrahydrofuran has been grafted onto polyvinyl chloride by the addition of silver trifluoromethanesulfonate to a THF solution of polyvinyl chloride.[285] Similar grafts to other chlorinated polymeric backbones were also mentioned.

III.A. Anderson and Stang have reported an improved synthesis of 2,6-di-*tert*-butyl-4-methylpyridine via the pyrylium trifluoromethanesulfonate.[286]

III.A. The reaction of silver trifluoromethanesulfonate with α,ω-diGrignard reagents provided a useful route to four-, five-, and six-membered ring compounds.[287]

III.A. A patent describing the use of the acid monohydrate as a fuel cell electrolyte has appeared.[288]

III.B.1. The procedure for the preparation of mono-, bis-, tris-, and tetrakis(triphenylphosphine)copper(I) trifluoromethanesulfonate has been published.[289] The anion is a bidentate bridging ligand in the dimeric 1:1 complex.

III.B.3. Phosphazenes have been isolated from the reaction of trifluoromethanesulfonyl azide with certain trivalent phosphorus compounds.[290] Trihalophosphazenes could be prepared from the combination of phosphorus trihalides with sodium *N*-chlorotrifluoromethanesulfonamide.

III.C.3. Bis(trifluoromethanesulfonyl)methane and other highly electron-deficient methylene compounds readily condense with various aldehydes and *N*-formyl compounds.[291]

III.D.1. Additional examples of advantageous methylation or benzylation of carbohydrates under mild conditions with trifluoromethanesulfonate esters and a sterically hindered acid acceptor have appeared.[292,293] The efficacy of these esters in the derivatization of certain sugars was exemplified in comparisons with 2,2,2-trifluoroethanesulfonic, pentafluorobenzenesulfonic, and toluenesulfonic esters.[294]

III.D.1. Evidence has been reported for the first successful alkylation of a 1-azirine.[295]

III.D.1. Another full paper has appeared on the mechanism of alkyl trifluoromethanesulfonate-initiated polymerization of THF.[296]

III.D.1. An improved synthesis of *p*-toluenesulfonylmethyl trifluoromethanesulfonate and the utilization of this ester in the formation of nitrogen ylides has been described.[297]

III.D.3. More solvolysis studies including a largely unsuccessful attempt to solvolyze aryl trifluoromethanesulfonates have appeared.[298-300]

III.D.3. Advantages have been cited for the use of trimethylsilyl trifluoromethanesulfonate in the preparation of silyl enol ethers from enolizable carbonyl compounds.[301] Silylation at the oxygen atom of esters and amides can be difficult to achieve by other means.

III.D.3. Haszeldine and co-workers have reported the preparation of *N,N*-bis(trifluoromethylamino)trifluoromethanesulfonate.[302] This compound is susceptible to nucleophilic attack at nitrogen, sulfur, and even the carbon of the bistrifluoromethylamino fragment.

V. References

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