

806. *Perfluoroalkyl Derivatives of Sulphur. Part VII.* Alkyl Trifluoromethanesulphonates as Alkylating Agents, Trifluoromethanesulphonic Anhydride as a Promoter for Esterification, and Some Reactions of Trifluoromethanesulphonic Acid.*

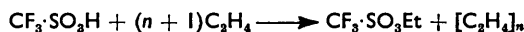
By T. GRAMSTAD and R. N. HASZELDINE.

The reactions of trifluoromethanesulphonic acid are shown to be dominated by its very strong acidity. It gives its ethyl ester with ethylene, ethanol, or diethyl ether. It forms a stable solid monohydrate, which, like the acid, gives the anhydride on dehydration (P_2O_5). Trifluoromethanesulphonic anhydride acts as a "promoter" for esterification, but its mixture with hydrogen peroxide does not have the oxidising power of peroxytrifluoroacetic acid. The amide and anilide and the disulphone $(CF_3 \cdot SO_2)_2CH_2$ are strongly acidic, and the esters are valuable as a source of carbonium ions and for *O*-, *C*-, and *N*-alkylation. Other aspects of the chemistry, and infrared spectra, are recorded and discussed.

THIS paper reports a general study of the reactions of the strong, stable, and non-oxidising trifluoromethanesulphonic acid, a convenient synthesis of which was described in Part IV.¹

The Acid.—That trifluoromethanesulphonic acid is a strong acid is shown by conductivity measurements in water² and acetic acid.³ In many ways it resembles sulphuric acid, as shown by the following reactions.

Trifluoromethanesulphonic acid with ethylene at room temperature rapidly gives ethyl trifluoromethanesulphonate (cf. ethyl hydrogen sulphate) and a low polymer of ethylene:



It is very soluble in many oxygen-containing liquids, *e.g.*, alcohols, ethers, and ketones. Oxonium compounds are the first products, but further reaction often occurs, particularly on heating. Reaction with ethanol yields the ester as expected, but in addition dehydration and ether formation occur. Ethyl ether with trifluoromethanesulphonic acid gives a colourless liquid ($Et_2OH^+CF_3 \cdot SO_3^-$), stable at room temperature and boiling considerably higher than ether: cleavage to ethyl trifluoromethanesulphonate and ethylene occurs when the liquid is heated. The reactions of trifluoromethanesulphonic acid with ethylene, ethanol, and ethyl ether can thus be reversed.

A white, stable, solid by-product from many of these reactions was identified as the monohydrate, $H_3O^+CF_3 \cdot SO_3^-$. This does not fume in air, and is also formed when the fuming anhydrous acid is exposed to moist air or by distillation of equimolar amounts of

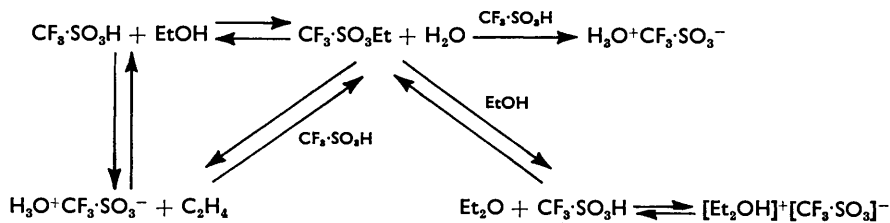
* Part VI, *J.*, 1957, 2640.

¹ Gramstad and Haszeldine, *J.*, 1956, 173.

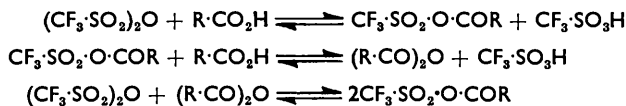
² Haszeldine and Kidd, *J.*, 1954, 4228.

³ Gramstad and Haszeldine, unpublished results.

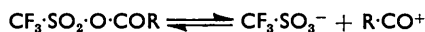
the acid and water. It has a low melting point (34°), and distils unchanged. Concentrated sulphuric acid dehydrates it only slowly, even when hot, and its ethereal solution is unaffected by anhydrous sodium sulphate. An excess of phosphoric anhydride or of



phosphorus pentachloride converts the monohydrate into the anhydride or the sulphonyl chloride respectively. Reaction of an excess of phosphoric anhydride with trifluoromethanesulphonic acid also gives trifluoromethanesulphonic anhydride. The marked difference in boiling point between the acid (162°) and the anhydride (84°) [cf. $\text{CF}_3\cdot\text{CO}_2\text{H}$ 72°, $(\text{CF}_3\cdot\text{CO})_2\text{O}$ 40°] is consistent with the hydrogen-bonding in the acid. Trifluoromethanesulphonic anhydride is a colourless, mobile liquid which is stable indefinitely in absence of organic matter. In presence of organic impurity the compound darkens rapidly, giving the appearance of being unstable. It is a powerful esterifying agent, and methanol, for example, gives a theoretical yield of methyl trifluoromethanesulphonate in a few minutes at room temperature. Furthermore, the anhydride is a "catalyst," or "promoter," for simple esterification reactions. Trifluoromethanesulphonic anhydride is better in some ways than trifluoroacetic anhydride, which has been studied⁴ extensively in this connection. In an organic medium trifluoromethanesulphonic acid is a much stronger acid than trifluoroacetic acid;³ the much greater inductive effect of the $\text{CF}_3\cdot\text{SO}_2$ group than of the $\text{CF}_3\cdot\text{CO}$ group suggests that the mixed anhydride $\text{CF}_3\cdot\text{SO}_2\cdot\text{O}\cdot\text{OZ}$ derived from the oxyacid ZOH is a better source of Z^+ , *e.g.*, an acyl carbonium ion when ZOH is a carboxylic acid ($\text{Z} = \text{R}\cdot\text{CO}$):



then



There is now a reasonable amount of evidence that acyl carbonium ions are involved in many organic processes.⁵ Furthermore, the acid strength of trifluoromethanesulphonic acid, greater even than that of perchloric acid,³ means that the acid, produced from the anhydride during esterification reactions, is itself a powerful catalyst. Trifluoromethanesulphonic anhydride thus probably functions in two ways: to form a mixed anhydride, and also to yield the catalyst trifluoromethanesulphonic acid. The last compound alone is often not as good an esterification promoter as its anhydride, since it can react with the alcohol in other ways, *e.g.*, by dehydration to give olefins or ethers, and by carbonisation. The similarity of trifluoromethanesulphonic acid to sulphuric acid also means that sensitive alcohols, *e.g.*, carbohydrates, are liable to be carbonised on treatment with trifluoromethanesulphonic acid, and for such alcohols trifluoroacetic anhydride is a better esterification promoter.

Trifluoromethanesulphonic anhydride has been used to prepare the esters shown in the annexed Table, where the yields are compared with those obtained⁴ by using trifluoroacetic anhydride as promoter. The reaction is exothermic and additional heating is necessary

⁴ Bourne, Stacey, Tatlow, and Tedder, *J.*, 1949, 2976; 1951, 718; Bourne, Randles, Stacey, Tatlow, and Tedder, *J. Amer. Chem. Soc.*, 1954, **76**, 3206.

⁵ For a review see Burton and Praill, *Quart. Rev.*, 1952, **6**, 302.

Yields of esters.

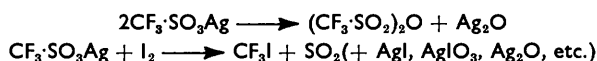
	Catalyst			Catalyst	
	(CF ₃ ·SO ₂) ₂ O	(CF ₃ ·CO) ₂ O		(CF ₃ ·SO ₂) ₂ O	(CF ₃ ·CO) ₂ O
<i>p</i> -NO ₂ ·C ₆ H ₄ ·CH ₂ ·OAc ...	87	83	(CH ₂ ·OBz) ₂	71	48
2-C ₁₀ H ₇ ·OAc	85	85	(CH ₂ ·CH ₂ ·CO ₂ Ph) ₂	77	57
<i>p</i> -NO ₂ ·C ₆ H ₄ ·CH ₂ ·OBz ...	82	69	2-C ₁₀ H ₇ ·O ₃ S·C ₆ H ₄ Me- <i>p</i> ...	38	13
PhOBz	87	82			

for only a short period, if at all. The marked increase in yield for formation of the toluene-*p*-sulphonate can again be attributed to the fact that trifluoromethanesulphonic acid is much stronger than the arylsulphonic acid, *i.e.*, formation of CH₃·C₆H₄·SO₂⁺ is facilitated; by contrast toluene-*p*-sulphonic acid and trifluoroacetic acid are of much the same strength in an organic medium. Trifluoromethanesulphonic anhydride should thus catalyse the formation of arylsulphones and ketones by Friedel-Crafts-type reactions, and should be a promoter for phosphorylation, nitration, etc., just like trifluoroacetic anhydride and with advantages or disadvantages predictable from the known properties. Some of these reactions will be described later.

Emmons *et al.* showed ⁶ that peroxytrifluoroacetic acid, prepared from trifluoroacetic anhydride and hydrogen peroxide, is a powerful yet specific oxidising agent. Our preliminary results show that trifluoromethanesulphonic anhydride-hydrogen peroxide or trifluoromethanesulphonic acid-hydrogen peroxide mixtures, *i.e.*, potential peroxytrifluoromethanesulphonic acid, CF₃·SO₄H, do not have the oxidising power of peroxytrifluoroacetic acid. This appears to be caused to some extent by the acid strength of trifluoromethanesulphonic acid and by its tendency to form its monohydrate. Thus dimethylnitrosamine, which peroxytrifluoroacetic acid oxidises smoothly to dimethylnitramine, is decomposed rather than oxidised by the sulphonic acid-peroxide solution. Similarly aniline gives mainly aniline trifluoromethanesulphonate and only 2–5% of nitrobenzene, whereas peroxytrifluoroacetic acid gave nitrobenzene in 82% yield. *cyclo*-Hexene also failed to yield *cyclohexane*-1:2-diol with a mixture of trifluoromethanesulphonic anhydride-hydrogen peroxide, whereas peroxytrifluoroacetic acid gives an 82% yield. Trifluoromethanesulphonic acid hydrate was a product from all these reactions, indicating that the 90% hydrogen peroxide was dehydrated, at least in part, by the acid. Although use of a large excess of the anhydride or of 100% hydrogen peroxide might give better results, with a greater concentration of the peroxy-compounds CF₃·SO₂·O·OH or (CF₃·SO₂)₂O₂, little or no advantage would be offered over peroxytrifluoroacetic acid. For this type of reaction therefore trifluoromethanesulphonic acid is too strong an acid.

Salts.—Inorganic salts of trifluoromethanesulphonic acid were described in Parts I and IV, and the marked thermal and chemical stability of salts of the homologous acids CF₃·[CF₂]₁₋₇·SO₃H was reported in Part VI.⁷

Sodium and potassium trifluoromethanesulphonates have low melting points (230°, 248°)¹ relative to the corresponding sulphates (884°, 588°) and resemble the hydrogen sulphates [240° (decomp.) 210°] more in this respect. The alkali-metal trifluoromethanesulphonates, which thus have a long and useful liquid range, are substantially unchanged at 400°. Trifluoromethanesulphonic acid itself is stable to at least 350° and its aqueous solution is stable to at least 275°. Pyrolysis of the acid in platinum at 650° affords sulphuryl fluoride, carbonyl fluoride, fluoroform, and carbon dioxide. This marked stability is also shown by the failure of silver trifluoromethanesulphonate to react appreciably with iodine at temperatures below 300°. At a much higher temperature trifluoromethanesulphonic anhydride is the main product and only a 0.5% yield of trifluoroiodomethane is obtained:



⁶ Emmons *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 4623; 1954, **76**, 3470, 3472; 1955, **77**, 89, 107, 189.

⁷ Gramstad and Haszeldine, *J.*, 1957, 2640.

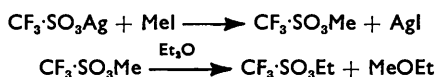
In contrast, silver trifluoroacetate reacts with iodine at 200° to give a 95% yield of trifluoroiodomethane ($\text{CF}_3\cdot\text{CO}_2\text{Ag} \longrightarrow \text{CF}_3\text{I}, \text{CO}_2, \text{AgI}$).⁸

Trifluoromethanesulphonic acid is best characterised by its organic salts, *e.g.*, aniline, *N*-ethylaniline, *NN*-diethylaniline, or triethylamine salts with characteristic infrared spectra. The aniline salt is useful for identifying small amounts of the acid, since it is formed quantitatively, is not hygroscopic, and is readily purified without recrystallisation. The *S*-benzylthiuronium salt is also useful in this connection.

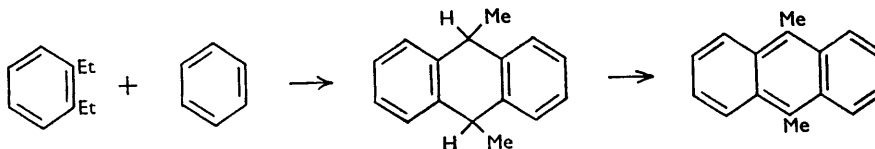
Trifluoromethanesulphonyl chloride with aniline gives the sulphonamide. This is also produced, though less readily, from trifluoromethanesulphonyl fluoride or the anhydride and aniline. Trifluoromethanesulphonanilide contains a strongly acidic amide-hydrogen atom which can be titrated with aqueous alkali; the anilide liberates carbon dioxide from sodium hydrogen carbonate. Trifluoromethanesulphonamide, prepared from the sulphonyl fluoride or chloride¹ or the anhydride and ammonia, is also a stronger acid than carbonic acid and can be titrated with aqueous alkali. Its *N*-halogeno-compounds, $\text{CF}_3\cdot\text{SO}_2\cdot\text{NHX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$), should thus be powerful electrophilic halogenating agents, better even than the halogen trifluoroacetates, $\text{CF}_3\cdot\text{CO}_2\text{X}$.⁹ The marked association in solid trifluoromethanesulphonamide, noted earlier¹ from its infrared spectrum, is in agreement with the above observations.

Alkyl Trifluoromethanesulphonates as Alkylating Agents.—Alkyl trifluoromethanesulphonates are readily prepared by reaction of silver trifluoromethanesulphonate with an alkyl iodide.¹ The strongly electron-attracting $\text{CF}_3\cdot\text{SO}_2$ group facilitates alkyl-oxygen fission, and the esters are therefore good alkylating agents. Ethyl trifluoromethanesulphonate decomposes at 150° to give trifluoromethanesulphonic acid, but is capable of effecting alkylation at appreciably lower temperatures. *O*-Alkylation of methanol gives ethyl methyl ether (65%): hydrolysis of the ethyl ester and formation of ethylene from the ethanol so produced accounts for the rest of the product.

O-Alkylation also occurs by ether cleavage. Thus methyl trifluoromethanesulphonate and diethyl ether yield ethyl trifluoromethanesulphonate and ethyl methyl ether as the main products, with small amounts of trifluoromethanesulphonic acid as by-product arising by decomposition of the ethyl ester. This *O*-alkylation explains why ethyl trifluoromethanesulphonate is formed, rather than the methyl ester, when methyl iodide and silver trifluoromethanesulphonate are mixed in diethyl ether; the methyl trifluoromethanesulphonate first formed alkylates the solvent:



Alkylation of benzene is effected by ethyl trifluoromethanesulphonate at room temperature, but is facilitated by heating under reflux: both mono- (mainly) and di-ethylbenzene are produced. 9 : 10-Dimethylantracene is believed to be a by-product:



9 : 10-Dimethylantracene was obtained by one of us from *o*-diethylbenzene and benzene in presence of aluminium chloride.¹⁰

N-Alkylations of NHEt_2 to NEt_3 and of NH_2Ph to $\text{NPhEt} + \text{NPhEt}_2$ were effected rapidly and essentially quantitatively at room temperature. Mono- or di-alkylation of

⁸ Haszeldine, *J.*, 1951, 584 *et seq.*

⁹ Haszeldine and Sharpe, *J.*, 1952, 993.

¹⁰ Berner, Gramstad, and Vister, *Acta Chem. Scand.*, 1953, **7**, 1255.

aniline depends only on reactant ratio. The products are obtained as their trifluoromethanesulphonates.

The above alkylations are probably catalysed by small amounts of trifluoromethanesulphonic acid present in the ester used, or produced by breakdown on warming. Use of trifluoromethanesulphonic acid in alkylation reactions offers several advantages over perchloric acid and its esters: it is a stronger acid, it is readily obtained anhydrous, and neither it nor its derivatives is explosive. It should find widespread use for alkylations involving alcohols, olefins, etc.

Trifluoromethanesulphonyl Fluoride.—This acid fluoride is readily obtained by electrochemical fluorination of methanesulphonyl fluoride,¹ and is potentially a good source of a CF₃·SO₂ group. The S-F bond is not highly reactive, as indicated earlier¹ by its slow hydrolysis by water and failure to react with ethanol at 100°. An attempt to convert it into the more reactive trifluoromethanesulphonyl chloride by reaction with aluminium trichloride was unsuccessful, as was an attempt to prepare the anhydride (CF₃·SO₂)₂O by reaction with silver trifluoromethanesulphonate.

Methylmagnesium iodide reacts readily with the fluoride to give methyl trifluoromethyl sulphone and bis(trifluoromethanesulphonyl)methane. The last compound arises by further reaction involving the acidic hydrogen of the sulphone. It is a strong acid as expected from the presence of two CF₃·SO₂ groups on one carbon atom; it is readily soluble in water, and gives a neutral sodium or silver salt by titration. Bis(trifluoromethanesulphonyl)methane in ether reacted with the sodium sulphate being used in one experiment as drying agent, to give the sodium salt. The disulphone is best isolated in this way after the Grignard reaction. Synthesis on a larger scale is best effected by interaction of methylmagnesium bromide and trifluoromethanesulphonyl fluoride in a stainless steel autoclave.

Infrared Spectra.—The annexed Table shows the characteristic asymmetric and symmetric -SO₂- bands and the C-F bands of certain of the compounds mentioned above. Assignments have been based on earlier studies on the -SO₂- and -SO₃- groups.^{11,1}

Compound *	Asymmetric stretching (μ)	Symmetric stretching (μ)	C-F stretching (μ)
<i>Sulphones</i>			
CF ₃ ·SO ₂ ·CH ₃ (l)	7·36	8·90	8·17, 8·35
(CF ₃ ·SO ₂) ₂ CH ₂ (s.f.)	7·15 or 7·36	9·00	8·20, 8·32
(CF ₃ ·SO ₂) ₂ CHAg (N)	7·45 or 7·58	8·88 or 9·08	8·26, 8·36
(CF ₃ ·SO ₂) ₂ CHNa (N)	7·56 or 7·66	8·81 or 9·13	8·15, 8·36
<i>Anhydride</i>			
(CF ₃ ·SO ₂) ₂ O (l)	6·80 } 6·85 } doublet	8·84	8·07
<i>Salts</i>			
CF ₃ ·SO ₃ ⁻ ·H ₃ O ⁺ (s.f.)	7·68 or 7·82 †	9·64	8·00
CF ₃ ·SO ₃ ⁻ ·PhNH ₃ ⁺ (N)	7·80 †	9·60	8·10, 8·21
CF ₃ ·SO ₃ ⁻ ·PhNH ₂ Et ⁺ (N)	7·90 †	9·67	8·20
CF ₃ ·SO ₃ ⁻ ·PhNHEt ₂ ⁺ (N)	7·80 †	9·74	8·10, 8·19
CF ₃ ·SO ₃ ⁻ ·Et ₃ NH ⁺ (N)	7·80 †	9·70	8·04, 8·16

* l = liquid, N = Nujol or hexachlorobutadiene mull, s.f. = solid film.

† Tentative assignment.

The asymmetric stretching vibration for methyl trifluoromethyl sulphone lies at shorter wavelength than that in dimethyl sulphone (7·54 μ), as expected from the greater electron-attracting power of CF₃ than of CH₃. Replacement of CH₃ in methyl trifluoromethyl sulphone by the more electronegative ·CH₂·SO₂·CF₃ group should cause a further shift to shorter wavelength, and the 7·15 μ band is thus preferred as the asymmetric stretching vibration in bis(trifluoromethylsulphonyl)methane to the slightly weaker band at 7·36 μ. Definite distinction cannot be made between the possible bands at 7·45 or 7·58

¹¹ Haszeldine and Kidd, *J.*, 1955, 2901.

and 7.56 or 7.66 μ for the silver and sodium salts respectively. The symmetric SO_2 stretching vibration is near 9 μ for the above compounds. Bis(diethylsulphonyl)methane¹¹ has bands at 7.55 and 8.90 μ .

The spectrum of trifluoromethanesulphonic anhydride reveals the SO_2 vibrations at positions close to those¹ in the esters methyl and ethyl trifluoromethanesulphonate. Both anhydride and ester contain a covalent $\text{CF}_3\cdot\text{SO}_2\cdot\text{O}^-$ group; the anhydride has an electron-attracting $\text{CF}_3\cdot\text{SO}_2$ group attached, and its SO_2 asymmetric stretching vibration thus lies at slightly shorter wavelength (6.8 μ ; cf. 7.0 μ for the esters).

The spectra of the organic salts of trifluoromethanesulphonic acid, and of its hydrate, are consistent with the presence of a $\text{CF}_3\cdot\text{SO}_3^-$ group as in the alkali-metal salts studied earlier.^{11,1} The H_3O^+ band appears at 2.89 μ , and the N-H absorptions are weak bands near 3 μ .

EXPERIMENTAL

Electrochemical fluorination of methanesulphonyl fluoride, conversion of the resulting trifluoromethanesulphonyl fluoride into barium trifluoromethanesulphonate, and reaction of this salt with concentrated sulphuric acid gave trifluoromethanesulphonic acid.¹ The acid was stored in sealed containers and contact with moisture or organic matter was avoided. Reactions were carried out in sealed Pyrex tubes, filled and opened *in vacuo*, unless otherwise stated. Stringent precautions were taken to exclude moisture or air.

Some Reactions of Trifluoromethanesulphonic Acid.—(a) *With ethylene.* The acid (3.97 g., 26 mmoles), shaken with ethylene (0.74 g., 26 mmoles) in a sealed tube at 20° for 15 min., gave (i) ethyl trifluoromethanesulphonate (1.90 g., 40% based on ethylene used), b. p. 115°,¹ (ii) an unidentified gas (0.092 g.), (iii) unchanged ethylene (0.028 g., 4%), (iv) trifluoromethanesulphonic acid (1.1 g.), b. p. 74°/26 mm., and (v) a semi-solid material (0.7 g.) containing trifluoromethanesulphonic acid and polymerised ethylene from which the acid was removed by shaking with water. Distillation *in vacuo*, infrared spectroscopy, and molecular-weight determination were used to identify the fractions.

(b) *With ethanol.* Anhydrous ethanol (1.04 g., 23 mmoles) dissolved exothermically in trifluoromethanesulphonic acid (3.39 g., 23 mmoles). Distillation under reduced pressure gave (i) ethyl trifluoromethanesulphonate (1.8 g., 45%), b. p. 42°/40 mm., 115°/760 mm.,¹ (ii) trifluoromethanesulphonic acid (1.5 g.), identified *via* its aniline salt, and (iii) a residue (0.31 g.). The volatile products were ethyl ether (0.16 g., 19% based on ethanol) and ethylene (0.082 g., 13%), identified by their molecular weight and spectra.

(c) *With ethyl ether.* The acid (0.84 g., 5.6 mmoles) formed a colourless solution with anhydrous ether (0.70 g., 8.9 mmoles) which was heated in a sealed tube at 85° for 2 hr. Distillation, etc., gave ethyl ether (0.31 g., 45%), ethyl trifluoromethanesulphonate (0.43 g., 43%), ethylene (0.03 g., 6%), and a mixture of trifluoromethanesulphonic acid and its monohydrate.

(d) *Thermal stability.* There was no reaction when anhydrous trifluoromethanesulphonic acid (1.1 g.) was heated *in vacuo* at 350° for 7 hr. A 5% aqueous solution of the acid was unchanged at 275° for 5 hr. (no F^- liberated; $\text{CF}_3\cdot\text{SO}_3\text{Na}$ obtained quantitatively on titration).

Passage of trifluoromethanesulphonic acid (3.1 g.) through a platinum tube at 650° gave sulphuryl fluoride (61%), carbonyl fluoride (43%), carbon dioxide, fluoroform (9%), and hydrogen fluoride.

(e) *S-Benzylthiuronium salt.* The acid (0.41 mmole) in water (2 ml.), mixed with *S*-benzylthiuronium chloride (0.41 mmole) in water (2 ml.) gave a white precipitate, recrystallised from water and dried *in vacuo* over phosphoric anhydride, of the *S*-benzylthiuronium salt (87%) (Found: C, 34.2; H, 3.7. $\text{C}_9\text{H}_{11}\text{O}_3\text{N}_2\text{S}_2\text{F}_3$ requires C, 34.4; H, 3.5), m. p. 139—140°.

Trifluoromethanesulphonic Acid Monohydrate.—The acid (0.94 g., 6 mmoles), distilled with water (0.11 g., 6 mmoles), gave *trifluoromethanesulphonic acid monohydrate* (0.88 g., 84%) (Found: C, 7.1; H, 1.9%; equiv., 168. $\text{CH}_3\text{O}_4\text{F}_3\text{S}$ requires C, 7.1; H, 1.8%; equiv., 168), b. p. 96°/1 mm., m. p. 34°, as a white hygroscopic solid which does not fume in air. Neutralisation of an aqueous solution of the hydrate with sodium carbonate, freeze-drying, and extraction of the residual solid with acetone followed by evaporation of the extract to dryness, gave sodium trifluoromethanesulphonate,¹ identified by means of its infrared spectrum and mixed m. p.

Trifluoromethanesulphonic Anhydride.—Trifluoromethanesulphonic acid (32.1 g.) was mixed

with phosphoric anhydride to give a thick paste, then heated *in vacuo* by means of a free flame, and the volatile material was transferred to a trap cooled to -183° . Rapid initial heating is to be avoided since the mixture darkens. Redistillation from phosphoric anhydride gave trifluoromethanesulphonic anhydride (25.0 g., 83%) (Found: C, 8.5; H, 0%; equiv., 141. Calc. for $C_2O_5F_6S_2$: C, 8.5; H, 0%; equiv., 141), b. p. 84° . The anhydride reacts relatively slowly with water or 0.05*N*-aqueous sodium hydroxide, but rapidly turns blue litmus red. Unlike trifluoromethanesulphonic acid, it does not fume in air.

In an attempt to prepare the anhydride by reaction of the acid with an excess of thionyl chloride at 125° for 4.5 hr. no reaction was detected.

The anhydride (1.0 mmole) reacted instantly with ammonia (10% excess), to give the chloroform-soluble trifluoromethanesulphonamide¹ (84%), m. p. 119° , and ammonium trifluoromethanesulphonate.

Trifluoromethanesulphonic anhydride (0.560 g., 2 mmoles) and anhydrous methanol (0.057 g., 1.8 mmoles) were kept at room temperature for 15 min. The more volatile products were transferred to an apparatus for manipulation of volatile compounds and distilled *in vacuo*, to give methyl trifluoromethanesulphonate (0.290 g., 99%) (identified spectroscopically¹). The residue of higher b. p. was trifluoromethanesulphonic acid.

Trifluoromethanesulphonic Anhydride as an Esterification Promoter.—(a) *4-Nitrobenzyl acetate.* 4-Nitrobenzyl alcohol (0.20 g.), glacial acetic acid (0.7 ml.), and trifluoromethanesulphonic anhydride (1.0 ml.), were shaken at 60° for 5 min., then poured slowly into aqueous sodium hydrogen carbonate. Extraction with chloroform, drying, and evaporation of the solvent gave 4-nitrobenzyl acetate (87%), m. p. 78° (from aqueous ethanol).

(b) *β -Naphthyl acetate.* The anhydride (1.0 ml.), β -naphthol (0.50 g.), and acetic acid (4.0 ml.), heated to 40° for 5 min., then treated as in (a) above, gave β -naphthyl acetate (85%), m. p. 70° (from aqueous ethanol).

(c) *4-Nitrobenzyl benzoate.* The anhydride (1.0 ml.), benzoic acid (1.0 g.), and 4-nitrobenzyl alcohol (0.20 g.), treated as in (a), gave *p*-nitrobenzyl benzoate (82%), m. p. 89° (from aqueous ethanol).

(d) *Phenyl benzoate.* Phenol (0.60 g.), the anhydride (2 ml.), and benzoic acid (1.4 g.) similarly gave phenyl benzoate (87%), m. p. 70° (from aqueous ethanol).

(e) *Ethylene dibenzoate.* Ethylene glycol (0.40 g.), benzoic acid (1.6 g.), and the anhydride (2 ml.), heated on a water-bath for 10 min., then worked up as in (a), gave ethylene dibenzoate (71%), m. p. 73° (from ethanol–light petroleum).

(f) *Phenyl adipate.* Adipic acid (0.50 g.), trifluoromethanesulphonic anhydride (1.0 ml.), and phenol (0.60 g.), treated as in (b), gave phenyl adipate (77%), m. p. 106° (from aqueous ethanol).

(g) *β -Naphthyl toluene-*p*-sulphonate.* Toluene-*p*-sulphonic acid (0.90 g.), β -naphthol (0.55 g.), and the anhydride (2 ml.), treated as in (a) but with ether for extraction, gave β -naphthyl toluene-*p*-sulphonate (38%), m. p. 124° (from ethanol).

Blank experiments showed that the yield of ester was not as high when trifluoromethanesulphonic acid was used instead of trifluoromethanesulphonic anhydride.

Attempted Oxidations with Hydrogen Peroxide and Trifluoromethanesulphonic Acid or Trifluoromethanesulphonic Anhydride.—(a) *Dimethylnitrosamine.* The nitrosamine (0.27 g., 3.6 mmoles) was added slowly to a solution of 90% hydrogen peroxide (0.25 ml., 8.9 mmoles) in trifluoromethanesulphonic acid (1.35 g., 8.9 mmoles). Vigorous reaction set in after 5 min. with copious evolution of oxides of nitrogen; the experiment was abandoned.

(b) *Aniline.* (i) To a suspension of 90% hydrogen peroxide (0.92 ml., 33 mmoles) in methylene chloride (20 ml.), cooled to 0° , was added trifluoromethanesulphonic acid (5.0 g., 33 mmoles). The solution was stirred for 15 min., and the cooling bath removed. Aniline (0.78 g., 8.3 mmoles) in methylene chloride (5 ml.), added dropwise during 10 min., caused an exothermic reaction with deposition of a solid. The mixture was heated under reflux for 2 hr. and the methylene chloride was decanted from the solid, then washed with water (2×50 ml.) and 10% aqueous sodium carbonate (10 ml.), and dried (Na_2SO_4). Distillation gave methylene chloride and nitrobenzene (0.040 g., 4%), identified spectroscopically. The solid deposited during the initial reaction was extracted with ether. The insoluble solid was aniline trifluoromethanesulphonate (1.56 g., 77%). After being dried (Na_2SO_4) the ethereal extracts were distilled, to give trifluoromethanesulphonic acid and its monohydrate (2.1 g., 38%), m. p. 34° , b. p. $96^{\circ}/1$ mm.

A second experiment, without methylene chloride, gave only a low yield of nitrobenzene.

(ii) Trifluoromethanesulphonic anhydride (5.64 g., 20 mmoles) in methylene chloride (5 ml.) was cooled to 0° and 90% hydrogen peroxide (0.49 g., 18 mmoles) was added. The mixture was stirred for 15 min. and the ice-bath was then removed whilst aniline (0.939 g., 10 mmoles) in methylene chloride (5 ml.) was added during 10 min. A solid was deposited. The mixture was heated under reflux for 1 hr., then the solution was decanted from the aniline trifluoromethanesulphonate, washed with water (50 ml.), 10% aqueous sodium carbonate (50 ml.), dried (Na_2SO_4), and distilled, to give methylene chloride and a residue of nitrobenzene (0.022 g., 2%) identified spectroscopically.

(d) *cycloHexene*. (i) *cycloHexene* (1.30 g., 16 mmoles) was added slowly to a mixture of trifluoromethanesulphonic anhydride (5.64 g., 20 mmoles) and 90% hydrogen peroxide (0.49 ml., 18 mmoles) at 0°. The cooling bath was removed and 30 min. later a vigorous reaction ensued which carbonised the reactants.

(ii) *cycloHexene* (1.30 g., 16 mmoles) in methylene chloride (10 ml.) was added slowly to a stirred mixture of trifluoromethanesulphonic anhydride (5.64 g., 20 mmoles), 90% hydrogen peroxide (0.49 ml., 18 mmoles), and methylene chloride (10 ml.). The mixture was heated under reflux for 1 hr. and the solvent was evaporated. The residue was treated with anhydrous methanol and heated under reflux for 4 hr. Distillation gave only methyl trifluoromethanesulphonate and trifluoromethanesulphonic acid monohydrate (2.10 g., 31%), b. p. 102°/2 mm., m. p. 34°, and no 1 : 2-*cyclohexanediol*; a black tar remained.

(e) *Comparison with peroxytrifluoroacetic acid*. To a solution of trifluoroacetic anhydride (0.17 ml., 120 mmoles) and 90% hydrogen peroxide (2.7 ml., 100 mmoles) in methylene chloride (20 ml.) at 0° was added aniline (2.35 ml., 25 mmoles) in methylene chloride (10 ml.) during 15 min. The exothermic reaction caused the solution to boil, and the mixture was finally heated under reflux for 1 hr. It was washed with water (50 ml.), 10% aqueous sodium carbonate (50 ml.), dried (Na_2SO_4), and distilled to give methylene chloride and nitrobenzene (2.56 g., 82%). There was no formation of aniline trifluoroacetate.

Organic Salts of Trifluoromethanesulphonic Acid.—Aniline (2.0 g., 21.5 mmoles) reacted vigorously with trifluoromethanesulphonic acid (3.2 g., 21.3 mmoles), to give aniline trifluoromethanesulphonate (5.2 g., 100%) (Found: C, 34.4; H, 3.3; N, 5.6. Calc. for $\text{C}_7\text{H}_8\text{O}_3\text{NF}_3\text{S}$: C, 34.6; H, 3.3; N, 5.8%), m. p. 263° (decomp.), soluble in water, ethanol, or acetone, and insoluble or only slightly soluble in ether, benzene, or carbon tetrachloride. The salt, readily purified by washing with ether, provides the best method for the spectroscopic identification of small amounts of trifluoromethanesulphonic acid.

N-Ethylaniline trifluoromethanesulphonate (0.92 g., 100%) (Found: C, 40.2; H, 4.1; N, 5.4. $\text{C}_9\text{H}_{12}\text{O}_3\text{NF}_3\text{S}$ requires C, 39.9; H, 4.4; N, 5.2), m. p. 67°, is not hygroscopic and is analytically pure after being washed once with ether.

NN-Diethylaniline trifluoromethanesulphonate (0.94 g., 100%) (Found: C, 44.4; H, 5.6; N, 5.0. $\text{C}_{11}\text{H}_{16}\text{O}_3\text{NF}_3\text{S}$ requires C, 44.2; H, 5.4; N, 4.7%) crystallised at 0° overnight. The solid, washed once with ether, had m. p. 65°; it is not hygroscopic.

A mixture of the *NN*-diethylaniline and *N*-ethylaniline salts gave a semi-solid material similar to that obtained on alkylation of aniline by means of ethyl trifluoromethanesulphonate.

Triethylamine trifluoromethanesulphonate (Found: C, 33.2; H, 6.1; N, 5.4. $\text{C}_7\text{H}_{16}\text{ONF}_3\text{S}$ requires C, 33.6; H, 6.4; N, 5.6%) is a hygroscopic solid, m. p. 41°.

Trifluoromethanesulphonanilide.—Trifluoromethanesulphonyl chloride (1.0 mmole; prepared by reaction of trifluoromethanesulphonic acid monohydrate with a 200% excess of phosphorus pentachloride), anhydrous ether (10 ml.), and aniline (1.95 mmoles), reacted at room temperature during 4 hr. to give aniline hydrochloride and the ether-soluble trifluoromethanesulphonanilide (87%) (Found: C, 37.1; H, 2.7; N, 6.1%; equiv., 225. Calc. for $\text{C}_7\text{H}_8\text{O}_2\text{NF}_3\text{S}$: C, 37.3; H, 2.7; N, 6.2%; equiv., 225), m. p. 67° (from light petroleum).

The acid fluoride (0.91 mmole), ether (10 ml.), and aniline (1.95 mmoles), heated at 80° for 12 hr., gave trifluoromethanesulphonanilide (66%), m. p. 66–67°.

The anhydride (2.01 mmoles), anhydrous ether (15 ml.), and aniline (0.99 mmole) at room temperature gave aniline trifluoromethanesulphonate (87%), insoluble in ether, and the ether-soluble trifluoromethanesulphonanilide (91%), m. p. 67.0–67.5°.

Miscellaneous Reactions of Trifluoromethanesulphonic Acid Derivatives.—(a) Trifluoromethanesulphonyl fluoride did not react with aluminium chloride (1.3 g.) or silver trifluoromethanesulphonate in a sealed tube at 50° (2 days).

(b) Silver trifluoromethanesulphonate (5.0 g., 19 mmoles), mixed with dry powdered iodine (12.3 g., 90 mmoles) and heated first in an oil bath, later strongly with a free flame, in a flask connected to traps cooled in liquid oxygen, gave trifluoromethanesulphonic anhydride (0.11 g., 4%) and trifluoroiodomethane (0.018 g., 0.5%) identified by infrared spectroscopy. A further quantity of trifluoromethanesulphonic anhydride remained in the reaction vessel.

(c) Sodium trifluoromethanesulphonate (0.21 g.) was unaffected at 350° for 2 hr., and only 2% of the theoretical amount of fluoride was liberated after 2 hr. at 400°. Traces of water lower the temperature required for decomposition. A similar result was obtained with potassium trifluoromethanesulphonate.

Sodium trifluoromethanesulphonate (0.90 g.) was unaffected by being heated with water at 290° and liberated 5% of the theoretical amount of fluoride after 2 hr. at 350°.

Thermal Stability of Ethyl Trifluoromethanesulphonate.—The ester (0.50 g.), heated in a 10 ml. sealed tube at 150° for 24 hr., became brown. Infrared spectroscopic examination of the volatile products showed that ethylene, ethyl trifluoromethanesulphonate, and ethyl ether were absent. The less-volatile products were distilled, to give trifluoromethanesulphonic acid (0.21 g., 50%), b. p. 69°/28 mm., identified by means of its aniline salt, and a dark brown residue (0.13 g.) which fumed in air and was shown to consist mainly of trifluoromethanesulphonic acid by conversion into its aniline salt. No unchanged ethyl trifluoromethanesulphonate was detected.

O-Alkylation.—(a) *Alkylation of methanol.* Ethyl trifluoromethanesulphonate (0.89 g., 5 mmoles) and anhydrous methanol (0.13 g., 4 mmoles) were heated in a 10 ml. sealed tube at 100° for 16 hr. Distillation of the volatile product gave ethylene (30%) identified by means of its infrared spectrum. The residual liquid was treated with water (2 ml.) and distillation *in vacuo* gave ethyl methyl ether (0.16 g., 65%) (Found: *M*, 59. Calc. for C₃H₈O: *M*, 60), identified spectroscopically. Yields are based on the ester taken. The reaction temperature used in this experiment was unnecessarily high, since in a qualitative experiment ethyl methyl ether was liberated at room temperature.

(b) *Reaction of methyl trifluoromethanesulphonate with ethyl ether.* Methyl trifluoromethanesulphonate (1.87 g., 11 mmoles, freshly distilled from phosphoric anhydride), heated under reflux with anhydrous ethyl ether (10 ml.) in a 50 ml. flask, gave methyl trifluoromethanesulphonate (0.18 g., 10%), b. p. 99°, ethyl trifluoromethanesulphonate (1.30 g., 64%), b. p. 115°, and trifluoromethanesulphonic acid (0.14 g., 8%). The identities of the first two compounds were confirmed by infrared spectroscopy and that of the acid by means of its aniline salt.

In a second experiment, freshly dried and distilled methyl trifluoromethanesulphonate (1.328 g., 8 mmoles) and anhydrous ethyl ether (1.072 g., 14.5 mmoles) were condensed *in vacuo* into a 20 ml. tube which was then sealed and heated to 80° for 2 hr. Distillation of the products *in vacuo*, molecular-weight determination, and infrared spectroscopy showed that the following were present: methyl trifluoromethanesulphonate (0.12 g., 9%), ethyl trifluoromethanesulphonate (0.65 g., 45%), diethyl ether (0.56 g., 52%), and ethyl methyl ether (0.38 g., 78% yield based on the ester taken). In addition there was an unidentified fraction (0.33 g.); trifluoromethanesulphonic acid (0.045 g., 4%) remained as least volatile fraction, identified by means of its aniline salt. The above alkylation occurs at room temperature, and the yield is increased by less than 5% by heating at 80°.

(c) *Reaction of silver trifluoromethanesulphonate with methyl iodide in ethyl ether.* Silver trifluoromethanesulphonate (9.1 g., 35 mmoles), dried *in vacuo* over phosphoric anhydride, was suspended in anhydrous ethyl ether (50 ml.), then methyl iodide (6.0 g., 42 mmoles) was added with stirring. Precipitation of silver iodide occurred immediately and the reaction was complete at room temperature. Expulsion of ethyl methyl ether was ensured by heating on a water bath for 0.5 hr. Decantation of the ethereal solution from the silver iodide (8.3 g., 100%), and distillation, gave ethyl trifluoromethanesulphonate (2.9 g., 46%) (Found: C, 20.0; H, 2.9. Calc. for C₂H₅O₃F₃S: C, 20.2; H, 2.8%), b. p. 115°, with an infrared spectrum identical with that of the compound prepared by interaction of ethyl iodide and silver trifluoromethanesulphonate.¹ There was no indication of the presence of methyl trifluoromethanesulphonate.

C-Alkylation.—*Alkylation of benzene.* Ethyl trifluoromethanesulphonate (7.14 g., 40 mmoles) formed a colourless solution with anhydrous benzene (3.00 g., 39 mmoles) which became brown when heated under reflux for 8 hr. Two layers separated on cooling. The lower layer consisted of trifluoromethanesulphonic acid, identified by means of its aniline salt, and the upper layer consisted of benzene and alkylated benzene. After addition of water (20 ml.) the whole was extracted with ether (200 ml.), and the ethereal extract was washed three times with water

(100 ml.) to remove trifluoromethanesulphonic acid. Distillation of the dried (Na_2SO_4) ethereal extract gave benzene (0.28 g., 9%), b. p. 80° , ethylbenzene (1.43 g., 35%) (Found: C, 90.4; H, 9.9. Calc. for C_8H_{10} : C, 90.6; H, 9.4%), b. p. 136° , diethylbenzene (1.0 g., 19%) (Found: C, 89.3; H, 10.6. Calc. for $\text{C}_{10}\text{H}_{14}$: C, 89.6; H, 10.5%), b. p. 182° , and a residue (0.38 g.) which solidified. The last fraction showed a strong violet-blue fluorescence when dissolved in benzene; its ultraviolet and infrared spectra closely resembled those of 9 : 10-dimethylanthracene.¹⁰

N-Alkylation.—(a) *Alkylation of diethylamine.* Ethyl trifluoromethanesulphonate (6.00 g., 33.7 mmoles) reacted vigorously with diethylamine (2.50 g., 33.8 mmoles), to give a viscous yellow liquid which crystallised at 0° overnight, to give *triethylamine trifluoromethanesulphonate* (8.4 g., 100%) (Found: C, 33.0; H, 6.0; N, 5.3. $\text{C}_7\text{H}_{16}\text{NO}_3\text{F}_3\text{S}$ requires C, 33.6; H, 6.4; N, 5.6%) as a white hygroscopic solid, m. p. 41° , identical with the salt prepared directly from trifluoromethanesulphonic acid.

(b) *Alkylation of aniline.* Ethyl trifluoromethanesulphonate (0.54 g., 3 mmoles) reacted exothermically with aniline (0.28 g., 3 mmoles), to give a mixture (0.81 g.) of *N*-ethylaniline trifluoromethanesulphonate (90%) and *NN*-diethylaniline trifluoromethanesulphonate (10%). The mixture was analysed by infrared spectroscopy using pure specimens of the salts as reference compounds.

Reaction of Trifluoromethanesulphonyl Fluoride with Methylmagnesium Iodide.—To methylmagnesium iodide [from methyl iodide (18.6 g., 131 mmoles) and magnesium (3.2 g., 132 mmoles)] in dry ether (25 ml.) was added trifluoromethanesulphonyl fluoride (10 g., 66 mmoles) and the sealed reaction tube was allowed to warm to room temperature. An immediate reaction occurred and white crystals were deposited. After 12 hr. at 20° distillation of the more volatile products gave only ether and unchanged trifluoromethanesulphonyl fluoride (1.6 g., 16%). The material in the tube was dissolved in 25% aqueous sulphuric acid (30 ml.) and extracted with ether (1 l.). Iodine was removed by shaking the extract with silver powder, and the dried (Na_2SO_4) extract was distilled, to give *methyl trifluoromethyl sulphone* (1.0 g., 12%) (Found: C, 16.4; H, 1.9. $\text{C}_2\text{H}_3\text{O}_2\text{F}_3\text{S}$ requires C, 16.2; H, 2.0%), b. p. 129° , and *bis(trifluoromethanesulphonyl)methane* (0.54 g., 7%) (Found: C, 12.9; H, 0.7. $\text{C}_3\text{H}_2\text{O}_4\text{F}_6\text{S}_2$ requires C, 12.9; H, 0.7%), b. p. $90^\circ/15\text{ mm.}$, m. p. 35° after sublimation *in vacuo*.

Methyl trifluoromethyl sulphone is only slightly soluble in water at room temperature and gives an acid solution. Bis(trifluoromethanesulphonyl)methane is very soluble in water, giving an acid solution which can be titrated with dilute aqueous sodium hydroxide to phenolphthalein (Found: equiv., 280. $\text{C}_3\text{H}_2\text{O}_4\text{F}_6\text{S}_2$ requires equiv., 280).

Bis(trifluoromethanesulphonyl)methane (0.11 g.) was dissolved in water (6 ml.) and neutralised with solid sodium carbonate. Evaporation to dryness and ether-extraction (200 ml.), followed by evaporation to dryness of the dried extract, gave the *sodium salt* (0.12 g., 99%) (Found: C, 12.2; H, 0.6; F, 37.3; S, 21.2%; *M*, 306. $\text{C}_3\text{HO}_4\text{F}_6\text{S}_2\text{Na}$ requires C, 11.9; H, 0.3; F, 37.8; S, 21.2%; *M*, 302), m. p. 257° . The molecular weight was determined cryoscopically in acetone. The sodium salt is very soluble in water, giving a neutral solution, is soluble in ethanol or acetone, less soluble in ether, slightly soluble in benzene and chloroform, and insoluble in light petroleum or carbon tetrachloride.

The *silver salt* (Found: Ag, 27.6. $\text{C}_3\text{HO}_4\text{F}_6\text{S}_2\text{Ag}$ requires Ag, 27.9%) was similarly prepared by neutralisation of bis(trifluoromethanesulphonyl)methane (0.20 g.) in water (10 ml.) with solid silver carbonate. The salt, obtained quantitatively, had m. p. $>360^\circ$ and was readily soluble in water, acetone, ethanol, ether, and benzene.

Reaction of Trifluoromethanesulphonyl Fluoride with Methylmagnesium Bromide.—Magnesium (3.2 g., 132 mmoles), methyl bromide (12.5 g., 132 mmoles), and ether (50 ml.) were allowed to react in a 250 ml. autoclave, then trifluoromethanesulphonyl fluoride (10.0 g., 66 mmoles) was introduced. After 12 hr. at 20° , distillation of the more volatile products gave unchanged trifluoromethanesulphonyl fluoride (1.1 g., 11%). Water (15 ml.) was added to the autoclave and the aqueous solution was extracted with ether (1 l.); the ethereal extract, dried (Na_2SO_4) and then evaporated to dryness, gave the sodium salt ($\text{CF}_3\text{SO}_2\text{CH}_2\text{Na}$) (4.8 g., 55%) (Found: Na, 7.6. Calc. for $\text{C}_2\text{HO}_2\text{F}_3\text{S}_2\text{Na}$: Na, 7.6%), m. p. 257° , identified spectroscopically.

A similar result was obtained by reaction of methylmagnesium bromide (from 12.5 g. of methyl bromide) and trifluoromethanesulphonyl fluoride (10.0 g.) in a 100 ml. sealed tube. The sodium salt was isolated in 64% yield (5.0 g.).

Infrared Spectra.—The following spectra were recorded on a Perkin-Elmer Model 21 Spectrophotometer with sodium chloride optics.

$\text{CF}_3\cdot\text{SO}_3^-\text{H}_3\text{O}^+$: Film on rock salt plate; some reaction with plate probable. 2·89 (m), 5·8(w), 6·12 (w), 7·68, 7·82, 8·00 (s. triplet), 8·43, 8·60 (s. doublet), 9·50, 9·64, 9·69 (m. triplet), 13·05 μ (w).

$\text{CF}_3\cdot\text{SO}_3^-\text{PhNH}_3^+$: Mulls in Nujol and hexachlorobutadiene. 3·30 (s. broad), 3·78 (m), 6·10, 6·29 (w. doublet), 6·50 (w), 6·67 (w), 6·80 (w), 7·80 (s), 8·10, 8·21 (s. doublet), 8·38 (w), 8·55 (s), 8·65 (s), 8·80 (w), 9·60 (s), 9·75 (w), 13·10 (m), 13·45 (s), 14·57 μ (s).

$\text{CF}_3\cdot\text{SO}_3^-\text{PhNH}_2\text{Et}^+$: Mulls in Nujol and hexachlorobutadiene. 3·15, 3·35, 3·60 (s. triplet), 6·24, 6·30 (w. doublet), 6·67 (w), 6·89 (w), 7·05 (w), 7·21 (w), 7·9, 8·2 (s. broad doublet), 8·57 (s), 9·10 (m), 9·67, 9·7 (s. doublet), 10·92 (w), 11·25 (w), 11·45 (w), 12·75 (m), 13·15 (m), 13·38 (s), 14·55 μ (s).

$\text{CF}_3\cdot\text{SO}_3^-\text{PhNHEt}_2^+$: Mulls in Nujol and hexachlorobutadiene. 3·32, 3·37 (w. doublet), 3·65, 3·73 (w. doublet), 6·24 (w), 6·70 (m), 6·79 (m), 6·89 (m), 7·0 (w), 7·21 (m), 7·80 (s), 8·10, 8·19 (s. doublet), 8·60 (s), 9·25 (w), 9·46 (w), 9·74 (s), 11·88 (m), 13·1 (m), 14·36 μ (s).

$\text{CF}_3\cdot\text{SO}_3^-\text{Et}_3\text{NH}^+$: Mulls in Nujol and hexachlorobutadiene. 3·27 (w), 3·35 (w), 6·76 (m), 7·14 (w), 7·80, 8·04, 8·16 (s. triplet), 8·63 (s), 9·70 (s), 11·90 (w), 13·17 μ (w).

$\text{CF}_3\cdot\text{SO}_2\cdot\text{CH}_3$: Liquid film. 3·32 (m), 3·42 (m), 7·10 (m), 7·36 (s), 7·55 (m), 7·74 (w), 8·17, 8·35 (s. doublet), 8·90 (s), 10·45 (s), 12·80 (s), 13·52 μ (s).

$(\text{CF}_3\cdot\text{SO}_2)_2\text{CH}_2$: Solid film. 3·35 (m), 3·43 (m), 7·15 (s), 7·36 (s), 7·64 (w), 8·20 (s), 8·32 (m. side band), 9·00 (s), 12·85, 12·92 (m. doublet), 13·45 (m), 13·70 μ (m).

$(\text{CF}_3\cdot\text{SO}_2)_2\text{CHNa}$: Nujol mull. 3·27 (w), 7·56, 7·66 (s. doublet), 8·15 (w), 8·36 (s), 8·81 (m), 9·13 (m), 10·20 (s), 11·83 (s), 15·17 μ (s).

$(\text{CF}_3\cdot\text{SO}_2)_2\text{CHAg}$: Nujol mull. 3·34, 3·43 (m. doublet), 7·45 (s), 7·58 (s), 8·26, 8·36 (s. doublet), 8·88 (m), 9·08 (m), 11·24 (m), 12·87 (w), 14·35 μ (s).

$(\text{CF}_3\cdot\text{SO}_2)_2\text{O}$: Liquid film. 6·80, 6·85 (s. doublet), 8·07 (s), 8·84 (s), 12·66 (s), 13·51 (s), 14·20 μ (w).

s = strong; m = medium; w = weak.

A recent patent ¹² reports the following compounds without analytical data: $(\text{CF}_3\cdot\text{SO}_2)_2\text{O}$, b. p. 80·5°; $\text{CF}_3\cdot\text{SO}_3\text{H}\cdot\text{Ph}\cdot\text{NH}_2$, m. p. 250—255°; $\text{CF}_3\cdot\text{SO}_2\cdot\text{NHPh}$, m. p. 65—66°.

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¹² Brice and Trott, U.S.P. 2,732,398.