227. *Reaction of Trifluoromethanesulphenyl Chloride with Ammonia, Amines, and Phosphine.*

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The reaction of trifluoromethanesulphenyl chloride with ammonia yields trifluoromethanesulphenamide, $CF_3{\cdot}S{\cdot}NH_2$ and bistrifluoromethanesulphenimide $(CF_3S)_2NH$. Analogous reactions occur with methylamine, dimethylamine, and aniline. Trifluoromethanesulphenyl chloride and ethanethiol give ethyl trifluoromethyl disulphide. With phosphine it gives bistrifluoromethylthiophosphine $(CF_3{\cdot}S)_2PH$ and tristrifluoromethylthiophosphine $(CF_3{\cdot}S)_3P$. Some reactions of these compounds have been studied. The general behaviour of the sulphenyl chloride resembles that of known alkyl and aryl sulphenyl derivatives.

TRIFLUOROMETHANESULPHENYL CHLORIDE was first prepared by photochemical reaction of bistrifluoromethyl disulphide with chlorine.[1] Its aqueous and alkaline hydrolysis and the reaction with hydrogen peroxide have been studied.[2] It reacts with mercury to form bistrifluoromethyl disulphide, and with trifluoromethanethiol and hydrogen sulphide to form the fluoroalkyl di- and tri-sulphides, respectively.[1] The main object of the present investigation was to study its behaviour as an acid chloride and compare its reactions with those of other sulphenyl chlorides.

The reaction with ammonia gave an almost quantitative yield of trifluoromethanesulphenamide, $CF_3{\cdot}S{\cdot}NH_2$, or, with a higher proportion of the sulphenyl chloride, of trifluoromethanesulphenimide $(CF_3{\cdot}S)_2NH$: no $(CF_3{\cdot}S)_3N$ was found. Methylamine, dimethylamine, and aniline behaved similarly and formed *N*-methyl- and *NN*-dimethyltrifluoromethanesulphenamide, $CF_3{\cdot}S{\cdot}NHMe$ and $CF_3{\cdot}S{\cdot}NMe_2$, and trifluoromethanesulphenanilide, $CF_3{\cdot}S{\cdot}NHPh$. These reactions are characteristic of an acid chloride. Methanesulphenyl chloride, which has been described recently,[3,4] is very unstable and its reaction with ammonia is unknown, but the reactions of numerous other alkane- and arene-sulphenyl chlorides resemble those of the fluoroalkyl compound.[5] This analogy is also evident in the reaction of trifluoromethanesulphenyl chloride with ethanethiol, which gives the disulphide $CF_3{\cdot}S{\cdot}S{\cdot}C_2H_5$. The comparatively high thermal stability of trifluoromethanesulphenyl chloride is matched by that of the trichloro-analogue.[6] The reaction of the latter with ammonia has not been reported but, with amines, simple elimination of hydrogen chloride occurs if the temperature is low, whereas at higher temperatures the trichloromethyl group is decomposed. The trichloro-compound also behaves normally with compounds containing an S–H bond.[6]

The Trouton constants of the new fluoroalkyl compounds are: $CF_3{\cdot}S{\cdot}NH_2$, 25·5; $(CF_3{\cdot}S)_2NH$, 25·1; $CF_3{\cdot}S{\cdot}NHMe$, 25·1; $CF_3{\cdot}S{\cdot}NHPh$, 24·1; $CF_3{\cdot}S{\cdot}NMe_2$, 22·2. These values indicate association in all but the last, which may be attributed to hydrogen

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[1] Haszeldine and Kidd, *J.*, 1953, 3219.
[2] Haszeldine and Kidd, *J.*, 1955, 2901.
[3] Schneider, *Ber.*, 1951, **84**, 911.
[4] Brintzinger, Koddebusch, and Kling, *Ber.*, 1950, **83**, 87.
[5] Reid, " Organic Chemistry of Bivalent Sulphur," Vol. I, Chap. 3, Chem. Publ. Co., N.Y., 1958.
[6] Sosnovsky, *Chem. Rev.*, 1958, **58**, 509.

bonding. Dry hydrogen chloride reacts quantitatively with the compounds to form the sulphenyl chloride and ammonium chloride or the amine hydrochloride. Billman and O'Mahony found that organic sulphenamides possess weak basic properties, but do not form salts such as hydrochlorides,[7] and both they and trichloromethanesulphenamides also yield the corresponding sulphenyl chloride with dry hydrogen chloride.[8]

Trifluoromethanesulphenamide is very slowly attacked by water at ordinary temperatures, liberating sulphur. Dilute hydrochloric acid gives bistrifluoromethyl disulphide, ammonium chloride, and trifluoromethanesulphinic acid. The initial attack appears to be on the S–N bond. This is followed by hydrolysis of the sulphenyl chloride as suggested by Haszeldine and Kidd.[2] Small amounts of carbonyl sulphide and fluoride ion are also formed:

$$CF_3{\cdot}S{\cdot}NH_2 + 2HCl = CF_3{\cdot}SCl + NH_4Cl$$

$$3CF_3{\cdot}SCl + 2H_2O = CF_3{\cdot}SO_2^- + CF_3{\cdot}S_2{\cdot}CF_3 + 3Cl^- + 4H^+$$

Trifluoromethanesulphenamide is incompletely hydrolysed by 15% aqueous sodium hydroxide at room temperature to fluoroform, ammonia, sulphur, fluoride, sulphide, and carbonate but, at 75°, breakdown to ammonia, sulphur, fluoride, sulphide, and carbonate is complete. These products suggest the intermediate formation of bistrifluoromethyl disulphide, the alkaline hydrolysis of which has been studied in detail.[2,9] Preliminary experiments have shown that trifluoromethanesulphenamide is slowly decomposed by ammonia at ordinary temperatures but is completely decomposed at 180°. At this temperature the sulphenamide itself is stable and may be recovered unchanged after being heated in an evacuated glass tube.

The reaction of trifluoromethanesulphenyl chloride with phosphine gave bistrifluoromethylthiophosphine $(CF_3{\cdot}S)_2PH$ and tristrifluoromethylthiophosphine, according to the proportions of the reactants. No comparable reaction has been reported with alkane- or arene-sulphenyl halides, though similar products might be expected. Preliminary experiments on the reaction of sulphur dichloride with phosphine show that hydrogen chloride is eliminated and chlorothiophosphine, $Cl{\cdot}S{\cdot}PH_2$, appears to be formed, though it has not yet been fully characterised. This reaction, and that of alkyl- and aryl-phosphines with sulphur dichloride is being further investigated. Trifluoromethanesulphenyl chloride and arsine gave a complex mixture of products, from which the thiol, $CF_3{\cdot}SH$, and hydrogen chloride were isolated. Here arsine behaves primarily as a reducing agent.

Bis- and tris-trifluoromethylthiophosphine decomposed at 40—50°. The tris-compound formed an unstable adduct with chlorine, which decomposed just below 0° and gave a mixture of products including phosphorus trichloride, bistrifluoromethyl disulphide, and trifluoromethanesulphenyl chloride. Dry hydrogen chloride did not react with tristrifluoromethylthiophosphine. It was, however, slowly attacked by air-free water, and both the bis- and the tris-compound were decomposed by aqueous alkali to sulphur, sulphide, fluoride, phosphite, and carbonate. These products indicate that the hydrolysis of the $CF_3{\cdot}S$ group follows the same course as that of the thiol, $CF_3{\cdot}SH$, which was investigated by Haszeldine and Kidd.[2,3]

The infrared spectra of some fluoroalkyl compounds containing the $CF_3{\cdot}S$ group have been discussed by Nabi and Sheppard.[10] The sulphenamides, data for which are tabulated on p. 1108, show absorption in the region 473—463 cm.$^{-1}$, which is within the region (490—445 cm.$^{-1}$) suggested by these authors for the C–S stretching frequency. Carbon–fluorine stretching frequencies occur at 1200—1100 cm.$^{-1}$, where there are two strong maxima in each case except for $(CF_3{\cdot}S)_2NH$, which has three, characteristic of the presence of two CF_3 groups. Each compound has one strong band at about 750 cm.$^{-1}$ and another

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[7] Billman and O'Mahony, *J. Amer. Chem. Soc.*, 1939, **61**, 2340.
[8] Connolly and Dyson, *J.*, 1934, 822.
[9] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2198.
[10] Nabi and Sheppard, *J.*, in the press.

at 590—545 cm.$^{-1}$, due respectively to CF_3 asymmetrical and symmetrical deformations. Nitrogen–hydrogen stretching frequencies lie in the region 3450—3360 cm.$^{-1}$, and $-NH_2$ deformation is represented by one band at 1590 cm.$^{-1}$. The absorption bands due to vibrations of the CH_3 and C_6H_5 groups present in some of the compounds occur at their usual frequencies. A medium strong band at about 2800 cm.$^{-1}$ in the spectra of $CF_3{\cdot}S{\cdot}NMe_2$ and $CF_3{\cdot}S{\cdot}NHMe$ is characteristic of *N*-methyl compounds in which the lone pair of electrons on the nitrogen atoms is not involved in conjugation. Divergent values for the S–N stretching frequency have been reported from Raman and infrared studies of such compounds as the alkane- and arene-sulphonamides and sulphur nitride, and this value cannot be identified in the $CF_3{\cdot}S{\cdot}N$ compounds studied. Its position is probably largely dependent on the nature of the attached groups.

EXPERIMENTAL

Trifluoromethanesulphenyl chloride was prepared by the action of chlorine on bistrifluoromethyl disulphide. It was separated from chlorine, which is otherwise difficult to remove, by adding excess of iodine, with which chlorine forms products of low volatility.

Preparation of Trifluoromethanesulphenamide.—Trifluoromethanesulphenyl chloride (1·059 g., 7·76 mmoles) and ammonia (0·264 g., 15·52 mmoles) reacted at $-45°$ in a Carius tube. The products were separated by fractional condensation. The fraction which condensed at $-78°$ was treated with calcium chloride to remove traces of ammonia and refractionated. It was *trifluoromethanesulphenamide* (0·895 g., 98%) (Found: C, 9·75; H, 2·0; N, 11·9; S, 27·0%; *M*, 117. CH_2NF_3S requires C, 10·3; H, 1·7; N, 12·0; S, 27·35%; *M*, 117). Sulphur was estimated as barium sulphate after decomposition with 15% sodium hydroxide at 75°, oxidation with hydrogen peroxide, and evaporation with hydrochloric acid to remove fluoride. The vapour pressure ($-55°$ to 18°) was given by $\log_{10} p$ (mm.) $= 8{\cdot}46 - 1783/T$. The b. p. was 46·5° (extrap.), the latent heat of vaporisation 8160 cal./mole, Trouton's constant 25·5, and the m. p. $-89°$.

Reactions of Trifluoromethanesulphenamide.—(a) *With hydrogen chloride.* The sulphenamide (0·198 g.) and dry hydrogen chloride (0·087 g.) reacted immediately in a sealed tube at room temperature to form trifluoromethanesulphenyl chloride (0·225 g., 97%) (Found: *M*, 137. Calc. for $CClF_3S$: *M*, 136·5). The identity was checked by the infrared spectrum.

(b) *With water and dilute acid.* The sulphenamide (0·225 g.) was shaken with water (5 ml.) at 20° (24 hr.) and 84% was unchanged. The water became turbid, owing to liberation of sulphur. Trifluoromethanesulphenamide (0·240 g.), when shaken with 2N-hydrochloric acid (5 days, 20°), gave 0·112 g. of bistrifluoromethyl disulphide (Found: *M*, 201. Calc. for $C_2F_6S_2$: *M*, 202), the infrared spectrum of which was checked. A small amount of more volatile reaction product was identified by its infrared spectrum as carbonyl sulphide (a strong doublet at 2080, 2060 cm.$^{-1}$) (Found: *M*, 57. Calc. for COS: *M*, 60). The white solid obtained by freeze-drying the hydrolysate contained ammonium chloride and also showed infrared absorption at 3400—3200, 1160, 1065, and 998 cm.$^{-1}$, characteristic of the $CF_3{\cdot}SO_2{\cdot}$ group.

(c) *With aqueous alkali.* The sulphenamide (0·194 g.) and 15% sodium hydroxide solution (5 ml.) in a sealed tube (3 days, 20°) gave unchanged sulphenamide (0·04 g.) (Found: *M*, 115. Calc. for CH_2NF_3S: *M*, 117), ammonia (0·065 g.), and fluoroform (0·091 g.) (Found: *M*, 71·6. Calc. for CHF_3: *M*, 70). The hydrolysate contained $CO_3^{=}$, F^-, and $S^{=}$. A similar experiment at 75° (48 hr.) with 0·258 g. of the sulphenamide gave ammonia (0·034 g.) as the only volatile product. The hydrolysate contained S, $S^{=}$, $CO_3^{=}$, and F^-. The total sulphur in it was estimated as barium sulphate (Found: S, 69·8 mg. Calc. for $CF_3{\cdot}S{\cdot}NH_2$ taken: S, 70·5 mg.).

(d) *With ammonia.* Trifluoromethanesulphenamide (0·259 g., 2·21 mmoles) and dry ammonia (0·0376 g., 2·21 mmoles) were sealed in a Carius tube (60 ml.). After 24 hr., 0·244 g. of the sulphenamide was recovered by vacuum fractionation (Found: *M*, 117). The identity was checked by the infrared spectrum. In a similar reaction with excess of ammonia at 180° no sulphenamide was recovered.

Preparation of Bistrifluoromethanesulphenimide.—Trifluoromethanesulphenyl chloride (1·96 g., 14·4 mmoles) and ammonia (0·366 g., 21·5 mmoles) reacted immediately in a sealed tube at room temperature. The volatile products gave a fraction which condensed in a bath at $-63°$. It was treated with calcium chloride to remove traces of ammonia and identified as *bistrifluoromethanesulphenimide* (1·24 g., 70%) (Found: S, 28·5; F, 51·9%; *M*, 217. $C_2HNF_6S_2$ requires

S, 29·5; F, 52·5%; *M*, 217). The residue in the reaction tube was ammonium chloride (Found: Cl, 66·1. Calc. for H_4NCl: Cl, 66·4%). A very small amount of a volatile yellow solid reaction product was not identified. Vapour pressures of the sulphenimide (—30° to 20°) were given by $\log_{10} p$ (mm.) = 8·38 — 1905/*T*. The extrapolated b. p. was 73°, the latent heat of vaporisation 8720 cal./mole, Trouton's constant 25·2, and the m. p. —47°. In a further experiment with 0·599 g. of the sulphenyl chloride and 0·099 mmole of ammonia under the same conditions, unchanged sulphenyl chloride (0·055 g.) was recovered. The sulphenimide (0·19 g.) was again formed. There was again a small amount of a volatile yellow solid in the product, but it appeared to be a mixture, and attempts to identify the compound $N(S{\cdot}CF_3)_3$ were unsuccessful.

Preparation of N-*Methyltrifluoromethanesulphenamide.*—Trifluoromethanesulphenyl chloride (1·00 g., 7·33 mmoles) and methylamine (0·45 g., 14·6 mmoles) reacted in a sealed tube at —22°, forming methylamine hydrochloride (Found: Cl, 52·1. Calc. for CH_6NCl: Cl, 52·5%). The volatile products on fractionation gave N-*methyltrifluoromethanesulphenamide*, which condensed at —74° (0·938 g., 97·7%) (Found: C, 18·1; H, 3·5; N, 10·7%; *M*, 135. $C_2H_4NF_3S$ requires C, 18·3; H, 3·05; N, 10·7%; *M*, 131). Vapour pressures (—50° to 21°) were given by $\log_{10} p$ (mm.) = 8·36 — 1754/*T*. The extrapolated b. p. was 47°, the latent heat of vaporisation 8028 cal./mole, and Trouton's constant 25·1.

Preparation of NN-*Dimethyltrifluoromethanesulphenamide.*—Trifluoromethanesulphenyl chloride (1·00 g., 7·33 mmoles) and dimethylamine (0·694 g., 14·65 mmoles) reacted similarly to form dimethylamine hydrochloride (Found: Cl, 42·8. Calc. for C_2H_8NCl: Cl, 44·0%) and NN-*dimethyltrifluoromethanesulphenamide*, which condensed at —63° (0·967 g., 91%) (Found: S, 21·9; F, 38·5%; *M*, 144. $C_3H_6NF_3S$ requires S, 22·1; F, 39·3%; *M*, 145). The compound exploded when heated in oxygen during the analysis for carbon and hydrogen by microcombustion. Vapour pressures (—50° to 23°) were given by $\log_{10} p$ (mm.) = 7·72 — 1578/*T*. The extrapolated b. p. was 53°, the latent heat of vaporisation 7220 cal./mole, Trouton's constant 22·1, and the m. p. —92°.

Reaction of NN-*Dimethyltrifluoromethanesulphenamide with Hydrogen Chloride.*—The sulphenamide (0·319 g., 2·2 mmoles) and dry hydrogen chloride (0·241 g., 6·60 mmoles) reacted at —21° to form dimethylamine hydrochloride (0·140 g.) (Found: C, 29·0; H, 9·3; N, 17·5. Calc. for C_2H_8NCl: C, 29·4; H, 9·8; N, 17·2%). Fractionation of the volatile products gave trifluoromethanesulphenyl chloride (0·218 g.) (Found: *M*, 136. Calc. for $CF_3{\cdot}SCl$: *M*, 136·5), unchanged hydrogen chloride (0·788 g.), and a fraction (*M*, 86) containing trifluoromethanesulphenyl chloride and hydrogen chloride.

Preparation of Trifluoromethanesulphenanilide.—Trifluoromethanesulphenyl chloride (1·04 g., 7·6 mmoles) and aniline (1·00 g., 11 mmoles) in ether (10 ml.) at 20° gave aniline hydrochloride (Found: C, 55·8; H, 6·4; N, 11·0. Calc. for C_6H_8NCl: C, 55·6; H, 6·2; N, 10·8%). Vacuum fractionation of the ether solution gave *trifluoromethanesulphenanilide* (1·79 g., 76%) (Found: C, 43·7; H, 2·7; N, 7·1. $C_7H_6NF_3S$ requires C, 43·5; H, 3·1; N, 7·25%). It was an oily liquid with an aromatic smell. Vapour pressures, determined with an isoteniscope (60—140°), were given by $\log_{10} p$ (mm.) = 8·17 — 2454/*T*. The extrapolated b. p. was 191°, the latent heat of vaporisation 11,230 cal./mole, and Trouton's constant 24·2.

Preparation of Ethyl Trifluoromethyl Disulphide.—Trifluoromethanesulphenyl chloride (1·00 g., 7·33 mmoles) and ethanethiol (0·454 g., 7·33 mmoles) reacted in a Carius tube at room temperature. Fractionation gave *ethyl trifluoromethyl disulphide* (0·542 g., 45·6%) (Found: F, 33·9; S, 38·4%; *M*, 162. $C_3H_5F_3S_2$ requires F, 35·2; S, 39·5%; *M*, 162). Hydrogen chloride (0·233 g.; *M*, 36·5) was also recovered. The disulphide was a colourless liquid with a smell like that of the thiol. Vapour pressures (—20° to 30°) were given by $\log_{10} p$ (mm.) = 7·85 — 1766/*T*. The extrapolated b. p. was 82°, the latent heat of vaporisation 8080 cal./mole, and Trouton's constant 22·7.

Reaction of Trifluoromethanesulphenyl Chloride with Phosphine.—Trifluoromethanesulphenyl chloride (1·20 g., 8·77 mmoles) and phosphine (0·0994 g., 2·92 mmoles) reacted in a sealed tube at —95°, forming a white solid and a yellow liquid. The solid disappeared and the colour was discharged as the tube attained room temperature. Fractionation of the products gave hydrogen chloride (0·312 g., 8·54 mmoles) (Found: *M*, 36·7. Calc. for HCl: *M*, 36·5). A fraction which condensed at —45° gave, on refractionation at —35°, *tristrifluoromethylthiophosphine* (0·937 g., 2·80 mmoles) (Found: C, 11·1; S, 28·1; F, 51·9%; *M*, 336. $C_3F_9S_3P$ requires C, 10·8; S, 28·7; F, 51·2%; *M*, 334). The compound was decomposed for analysis by heating in a sealed tube with 15% aqueous sodium hydroxide (70°, 10 hr.). It was a colourless liquid which was stable at 20° but decomposed above 50°. The vapour pressure was 30·5 mm. at 20° and 70·6 mm. at 50°, giving a extrapolated b. p. of about 180°. The m. p. was −75°.

The sulphenyl chloride (2·40 g., 17·6 mmoles) and phosphine (0·299 g., 8·78 mmoles) when allowed to react under similar conditions gave hydrogen chloride (0·574 g.). Repeated fractionation of the less volatile products gave *bistrifluoromethylthiophosphine* (0·40 g.) (Found: C, 9·45; S, 27·1; F, 49·0%; *M*, 238. $C_2HF_6S_2P$ requires C, 10·3; S, 27·3; F, 48·7%; *M*, 234), tristrifluoromethylthiophosphine (0·792 g.) (Found: C, 11·1; S, 27·8; F, 52·1%; *M*, 338), and a fraction (0·231 g.; *M*, 281) which was probably a mixture of these two compounds. Bistrifluoromethylthiophosphine was also formed in 72% yield from an equimolar mixture of the reactants. Its vapour pressure was 149 mm. at 40°, above which temperature it decomposed. In an attempt to prepare trifluoromethylthiophosphine, $CF_3{\cdot}S{\cdot}PH_2$, the sulphenyl chloride (1·00 g., 7·33 mmoles) and phosphine (0·50 g., 14·6 mmoles) were mixed, but the volatile products were not satisfactorily separated.

Reactions of Tristrifluoromethylthiophosphine.—(a) *With hydrogen chloride and chlorine.* (i) From a mixture of tristrifluoromethylthiophosphine (0·212 g.) and dry hydrogen chloride at −74° both reactants were recovered quantitatively.

(ii) The phosphine (0·268 g., 0·8 mmole) and chlorine (0·058 g., 1·6 mmoles) were mixed in a vessel connected to a glass spiral manometer used as a null instrument. A white solid formed at −74° and, after material volatile at −45° had been pumped off, dissociation pressures were measured at increasing temperatures to 17°. There was a sharp break in the linear log p–$1/T$ curve at about −8°, indicating decomposition of an addition compound which was probably $(CF_3{\cdot}S)_3PCl_2$. The only decomposition product identified was $CF_3{\cdot}SCl$ (0·034 g.) (Found: *M*, 138. Calc. for $CClF_3S$: *M*, 136·5). A fraction (0·187 g.) of *M* 183 was probably a mixture of phosphorus trichloride and bistrifluoromethyl disulphide. These two compounds were identified by the infrared spectrum.

(b) *With water and aqueous alkali.* Tristrifluoromethylthiophosphine (0·326 g.) when shaken with water (2 ml.) at 20° (48 hr.) gave unchanged phosphine (0·10 g.) and carbonyl sulphide (0·020 g.) (Found: *M*, 57. Calc. for COS: *M*, 60). The aqueous solution was acid (pH 2·3) and contained fluoride and phosphate. With aqueous alkali decomposition was complete, as it was for bistrifluoromethylthiophosphine. No gaseous products were formed. This reaction was used in decomposing the compounds for analysis.

Reaction of Trifluoromethanesulphenyl Chloride with Arsine.—The chloride (0·90 g.) and arsine (0·171 g.) reacted in a sealed tube at −74° to yield a yellowish-brown solid, which gradually became deep brown. The volatile products were hydrogen chloride (0·045 g.), trifluoromethanethiol (0·380 g.) (Found: *M*, 102. Calc. for CHF_3S: *M*, 102) (identity checked by infrared spectrum), and trifluoromethanesulphenyl chloride (0·248 g.) (Found: *M*, 133. Calc. for $CClF_3S$: *M*, 136·5). A fraction of low volatility, which contained arsenic, evolved $CF_3{\cdot}SH$ and HCl slowly. It contained chlorine equivalent to 0·193 g. of arsenic trichloride. The brown solid was probably arsenic.

Reaction of Sulphur Dichloride with Phosphine.—Sulphur dichloride (0·323 g.) and phosphine (0·107 g.), in a sealed tube at −74°, gave yellow solids and a red liquid which gradually turned yellow and became viscous. Hydrogen chloride (0·051 g.) was recovered (Found: *M*, 38. Calc. for HCl: *M*, 36·5). Other volatile products were not satisfactorily separated. They were shown by infrared measurements to contain hydrogen chloride and phosphine, but other unidentified compounds were also present. The viscous liquid (*chlorothiophosphine*) was soluble in carbon disulphide but insoluble in ether and was decomposed by water with liberation of sulphur (Found: Cl, 34·5. H_2ClSP requires Cl, 35·4%).

Ultraviolet Absorption Spectra.—These were measured in the range 400—200 mμ with a Carey recording spectrometer (model 14). The following maxima and minima were observed.

		$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$ (mμ)	$\varepsilon_{min.}$
$CF_3{\cdot}S{\cdot}NH_2$	Vapour	210—200	—	—	—
$CF_3{\cdot}S{\cdot}NHMe$	Vapour	211	346	204	328
$CF_3{\cdot}S{\cdot}NHPh$	Ether solution	299	9790	—	—
$(CF_3{\cdot}S)_2NH$	Vapour	244 211	324 592	237	315
$(CF_3{\cdot}S)NMe_2$	Vapour	240—200	—	—	—
$CF_3{\cdot}S_2{\cdot}C_2H_5$	Vapour	239	269	216	136
$(CF_3{\cdot}S)_3P$	Vapour	262	1010	241	472

Infrared Absorption Spectra.—The spectra were recorded in the region 4000—400 cm.$^{-1}$ on a Perkin-Elmer model 21 double beam spectrometer, with sodium chloride or potassium bromide prisms. All were measured in the vapour phase with a 10 cm. cell, except trifluoromethanesulphenanilide, for which a liquid film was used. The frequencies (cm.$^{-1}$) and intensities are tabulated below.

$CF_3{\cdot}S{\cdot}NH_2$: 3450 s, 3360 s, 2650 w, 2285 w, 2230 w, 1900 w, 1590 s, 1380w, 1320 m, 1298 m, 1167 s, 1148 s, 1088 m, 878 s, 775 s, 758 s, 750 s, 700 m, 588 w, 512 s, 470 s, 423 m.

$(CF_3{\cdot}S)_2NH$: 3424 s, 3150 w, 2970 w, 2300 m, 1918 w, 1892 w, 1463 w, 1315 m, 1300 m, 1262 m, 1188 s, 1163 s, 1125 s, 1030 m, 878 s, 795 m, 752 s, 547 m, 473 m, 414 m.

$CF_3{\cdot}S{\cdot}NHMe$: 3415 s, 2970 s, 2830 s, 2305 m, 2280 m, 1887 m, 1735 w, 1590 w, 1465 m, 1425 s, 1402 s, 1305 m, 1292 m, 1262 m, 1168 s, 1143 s, 1073 s, 847 m, 797 m, 752 s, 552 s, 522 s, 472 m.

$CF_3{\cdot}S{\cdot}NMe_2$: 3000 m, 2930 s, 2880 s, 2800 s, 2290 w, 2252 w, 1890 w, 1475 s, 1265 m, 1218 s, 1175 s, 1145 s, 1053 m, 990 s, 755 m, 672 m, 558 s, 462 s.

$CF_3{\cdot}S{\cdot}NHPh$: 3360 s, 3055 m, 2875 w, 2775 w, 2515 w, 2260 w, 1942 w, 1848 w, 1770 w, 1705 w, 1602 s, 1498 s, 1477 s, 1389 m, 1283 m, 1227 s, 1162 s, 1115 s, 1027 m, 995 w, 922 m, 885 m, 820 w, 750 s, 692 s, 617 w, 580 w, 545 w, 503 m, 462 m.

The infrared spectra of $(CF_3S)_3P$ and $(CF_3S)_2PH$ are recorded elsewhere.[10]

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