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The reactions of the trifluoromethyl disulfide group, $\text{CF}_3\text{SS}-$, with ammonia and amines. A new preparation of sulfenamides

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Bistrifluoromethyl disulfide reacts with ammonia and primary and secondary amines, forming the compounds CF_3SNH_2 , RNHSCF_3 , and R_2NSCF_3 , respectively; also produced are ammonium fluoride and thiocyanate, or a substituted thiourea and hydrogen fluoride, which forms a salt with the amine or thiourea.

Simple sulfenamides, RSNH_2 , can be prepared from ammonia and a trifluoromethyl disulfide, RSSCF_3 ; ammonium fluoride and thiocyanate are also produced. Since the trifluoromethyl disulfides are formed from thiols and trifluoromethanesulfonyl chloride, the reaction offers a simple method for the conversion of thiols into sulfenamides.

The new compounds *N*-propyltrifluoromethanesulfenamide, *N,N*-diethyltrifluoromethanesulfenamide, bis(pentafluorobenzene)sulfenamide, pentafluorophenyltrifluoromethyl disulfide, and *n*-propyltrifluoromethyl disulfide have been prepared and characterized.

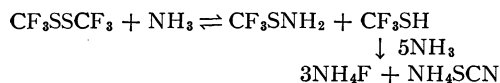
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INTRODUCTION

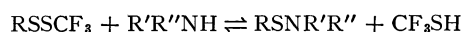
Bistrifluoromethyl disulfide has briefly been reported to react with excess ammonia, forming trifluoromethanesulfenamide, ammonium fluoride, and thiocyanate (1).



This reaction must be similar to the hydrolysis of bistrifluoromethyl disulfide (2), involving the initial fracture of the S—S bond, and can be represented as an equilibrium forced to the right by the ammonolysis of the trifluoromethanethiol.

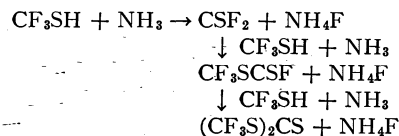


If this mechanism is correct, trifluoromethyl disulfide derivatives, RSSCF_3 , would be expected to react with amines, provided that the trifluoromethanethiol can be removed from the equilibrium.



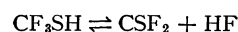
Trifluoromethanethiol has been reported

to react with ammonia (molecular ratio 1.0:1.0) according to the following scheme (3).



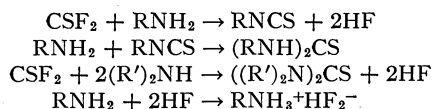
Neither of the products trifluoromethyl fluorodithioformate or bistrifluoromethyl trithiocarbonate was ever found in the products of the reaction of ammonia with bistrifluoromethyl disulfide, but the ratio of NH_3 to $(\text{CF}_3\text{S})_2$ was always greater than 2.5:1.0. Ammonolysis of trifluoromethyl fluorodithioformate or bistrifluoromethyl trithiocarbonate may produce ammonium fluoride and thiocyanate, but thiocarbonyl fluoride reacts with excess ammonia, giving ammonium fluoride and thiocyanate (4).

If thiocarbonyl fluoride is formed immediately in the decomposition of trifluoromethanethiol, any compound capable of

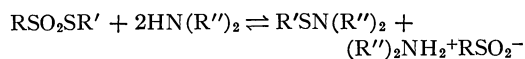


reacting with thiocarbonyl fluoride and

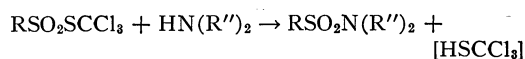
absorbing the hydrogen fluoride, such as primary or secondary amines, ought to be capable of decomposing bistrifluoromethyl disulfide, provided that the S—S bond can be fractured initially.



The reaction of thiosulfonates with amines has recently been reported to be an equilibrium of the type shown below (5).



This is a good synthetic method for preparing sulfenamides which are otherwise difficult to prepare, e.g. allyl sulfenamides. When $\text{R}' = \text{CCl}_3$, a different decomposition occurred.



The trichloromethanethiol could not be isolated and lost hydrogen chloride, forming thiophosgene, which reacted with the amine to form a substituted thiourea; the hydrogen chloride was removed from the reaction as the amine hydrochloride.

The reactions of bistrifluoromethyl disulfide with ammonia, *n*-propylamine, diethylamine, hexamethyldisilazane, trifluoromethanesulfenamide, and trimethylamine, and those of ammonia with pentafluorophenyltrifluoromethyl disulfide and *n*-propyltrifluoromethyl disulfide were studied.

RESULTS AND DISCUSSION

n-Propylamine and diethylamine react with bistrifluoromethyl disulfide to form substituted trifluoromethyl sulfenamides, substituted thioureas or isothiureas, and

$$3\text{Et}_2\text{NH} + \text{CF}_3\text{SSCF}_3 \rightarrow \text{Et}_2\text{NSCF}_3 + (\text{Et}_2\text{N})_2\text{CS} + 3\text{HF}$$

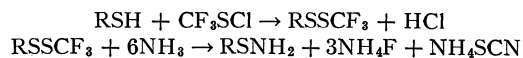
hydrogen fluoride. The hydrogen fluoride is removed by combination with the basic thiourea in the diethylamine reaction, but in the propylamine reaction some must combine with the propylamine, since more than 3 moles of propylamine is used per mole of disulfide. The sulfenamides formed

probably have no basic properties, since amines containing a —SCF₃ group are very weakly basic and the —SCF₃ group is broken off with hydrogen chloride (6); amides or amines containing the —SCF₃ group would therefore not be expected to form salts with hydrogen fluoride.

No reaction was observed with trimethylamine and bistrifluoromethyl disulfide, since there are no hydrogen atoms on the nitrogen to cause fracture of the S—S bond. There is no evidence of any adduct formation. The non-reaction of trifluoromethanesulfenamide and hexamethyldisilazane with bistrifluoromethyl disulfide must be due to the virtual absence of basic properties in these amines (6, 7) or in any thioureas formed, and hence the hydrogen fluoride which would be formed cannot be removed.

Ammonia reacts with *n*-propyltrifluoromethyl disulfide to give *n*-propyltrifluoromethanesulfenamide, which partially decomposes to polymeric thiopropionaldehyde and ammonia. Ammonia reacts with pentafluorophenyltrifluoromethyl disulfide, forming ammonium fluoride, ammonium thiocyanate, and bispentafluorobenzenesulfenamide; it is more probable that the latter is formed by the decomposition of pentafluorobenzenesulfenamide, than that pentafluorobenzenesulfenamide reacts again with the disulfide, since no trace of pentafluorobenzenesulfenamide was detected, and trifluoromethanesulfenamide will not react with the S—S bond in bistrifluoromethyl disulfide.

The conversion of a thiol into a sulfenamide, via the trifluoromethyl disulfide, as shown by the scheme below, is undoubtedly



better and more convenient than the usual method of chlorination of the thiol and reaction of the sulfonyl chloride with ammonia (8). *N*-Substituted trifluoromethanesulfenamides can be prepared by the reaction of an organic amine with trifluoromethanesulfonyl chloride (6) more easily than, or as easily as, by the reaction of an organic amine with bistrifluoromethyl disulfide.

EXPERIMENTAL

All volatile materials were handled in a high-vacuum apparatus, the taps of which were greased with Kel-F 90 grease. Solids were handled in a dry box. Infrared spectra were recorded on a Perkin-Elmer 237B or 521 instrument. Chemicals available commercially were purified by standard techniques: the RSCF_3 compounds were prepared from CF_3SCl and RSH (6). Microanalyses, difficult because of the presence of the CF_3 - and (or) C_6F_5 -groups, were performed by Mikroanalytisches Laboratorium Beller, Goettingen, Germany. Molecular weights of gases were determined by Regnault's method.

Reaction of Bistrifluoromethyl Disulfide with Ammonia

A white precipitate was formed immediately when 5.5 mmoles of bistrifluoromethyl disulfide was mixed with 31.9 mmoles of ammonia. No ammonia was found in the volatile products; a -45° volatile fraction was a mixture of $(\text{CF}_3\text{S})_2$ and CF_3SNH_2 .

Anal. Found: mol. wt. 128.8.

The fraction involatile at -45° was CF_3SNH_2 , which was confirmed by its infrared spectrum (6).

Anal. Calcd. for $\text{CH}_2\text{F}_3\text{N}$: mol. wt. 117.1. Found: mol. wt. 114.6.

The solid residue consisted of the NH_4^+ , F^- , and SCN^- ions. The amount of volatile materials recovered was 610 mg, and the amount of solid materials 980 mg, which is in accordance with the equation $(\text{CF}_3\text{S})_2 + 6\text{NH}_3 \rightarrow \text{CF}_3\text{SNH}_2 + 3\text{NH}_4\text{F} + \text{NH}_4\text{SCN}$ (theoretically, 0.2 mmole of $(\text{CF}_3\text{S})_2 + 5.3$ mmoles of $\text{CF}_3\text{SNH}_2 = 660$ mg of volatile material + 991 mg of solid material = 5.3 mmoles of $\text{NH}_4\text{SCN} + 15.9$ mmoles of NH_4F).

When the molecular ratio of $(\text{CF}_3\text{S})_2$ to NH_3 was 1.0:2.5, the reaction proceeded as above. The volatile fraction consisted of $(\text{CF}_3\text{S})_2$ and CF_3SNH_2 ; the solid residue was a mixture of NH_4F and NH_4SCN .

Reaction of Bistrifluoromethyl Disulfide with n-Propylamine

Bistrifluoromethyl disulfide (5.44 mmoles) and *n*-propylamine (16.3 mmoles) were allowed to warm very slowly from -50° to room temperature; a colorless gel formed. Traces of this gel remained after fractionation; a -50° volatile portion consisted of only bistrifluoromethyl disulfide (1.56 mmoles), the identity of which was confirmed by its molecular weight and infrared spectrum (9). A -50° involatile portion (206 mg), given off slowly from the oily residue, had a vapor pressure of ca. 30 mm at room temperature; analysis showed it to be fairly pure *n*-propyltrifluoromethanesulfenamide, which was confirmed by the similarity of the CF_3SNH -vibrations of its infrared spectrum to those in the spectrum of *N*-methyltrifluoromethanesulfenamide (6).

Anal. Calcd. for $\text{C}_4\text{H}_8\text{F}_3\text{SN}$: C, 30.2; H, 5.1; S, 20.1. Found: C, 33.2; H, 5.4; S, 21.7.

This was difficult to separate from trifluoromethyl disulfide, and 486 mg of a mixed fraction was recovered. An involatile oil (600 mg), consisting of

deep-brown droplets in a light-brown liquid, which turned solid after some time, remained.

Reaction of Bistrifluoromethyl Disulfide with Diethylamine

A mixture of 20.5 mmoles of diethylamine and 6.87 mmoles of bistrifluoromethyl disulfide was allowed to warm to room temperature from -40° over a period of 20 h (more rapid warming resulted in a violent reaction); two immiscible layers were formed, which were separated into an involatile oil (1 490 mg) and a colorless volatile liquid (1 100 mg) by fractionation. The volatile liquid had a vapor pressure of ca. 33 mm at room temperature, and was identified as *N,N*-diethyltrifluoromethanesulfenamide (6.4 mmoles).

Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{F}_3\text{NS}$: C, 34.6; H, 5.8; N, 8.1; S, 18.5. Found: C, 35.4; H, 6.2; N, 8.2; S, 18.9.

Its infrared spectrum had vibrations of the CF_3SN group similar to those of *N,N*-dimethyltrifluoromethanesulfenamide (6). The infrared spectrum of the oil indicated the presence of an isothiourea (10).

Reaction of Bistrifluoromethyl Disulfide with Trifluoromethanesulfenamide

No reaction was observed when CF_3SNH_2 and $(\text{CF}_3\text{S})_2$ (molecular ratio 1.0:1.0) were allowed to stand at room temperature for 2 days, or heated to 60° for 5 days.

Reaction of Bistrifluoromethyl Disulfide with Hexamethyldisilazane

There was no reaction when a mixture of 6.14 mmoles of $(\text{Me}_2\text{Si})_2\text{NH}$ and 6.0 mmoles of $(\text{CF}_3\text{S})_2$ was held at 20° for 5 days, or heated to 60° for 63 h.

Reaction of Bistrifluoromethyl Disulfide with Trimethylamine

There was an immediate formation of a small quantity of white precipitate when 8.61 mmoles of $(\text{CF}_3\text{S})_2$ and 17.14 mmoles of Me_3N were mixed; no further solid was formed when the mixture was allowed to stand at room temperature. The volatile products consisted entirely of $(\text{CF}_3\text{S})_2$ and Me_3N , which could be separated almost completely by vacuum distillation at -80° . The infrared spectrum of the very small amount of brown solid recovered showed it to contain the Me_3NH^+ and SiF_6^{2-} ions (11, 12); this may have been due to a trace of water forming a base with the trimethylamine and hydrolyzing the disulfide.

Preparation of Pentafluorophenyltrifluoromethyl Disulfide

Pentafluorophenyltrifluoromethyl disulfide, an involatile colorless oil at room temperature, was formed in a 90% yield when equimolecular quantities of pentafluorothiophenol and trifluoromethanesulfenyl chloride were mixed; the resulting hydrogen chloride was removed by distillation at -95° .

Anal. Calcd. for $\text{C}_7\text{F}_8\text{S}_2$: C, 28.0; F, 50.7; S, 21.4. Found: C, 28.2; H, 0.00; F, 50.7; S, 21.1.

Reaction of Pentafluorophenyltrifluoromethyl Disulfide with Ammonia

A white precipitate was formed immediately when 2.57 mmoles of $C_6F_5SSCF_3$ and 21.45 mmoles of ammonia were mixed. After the mixture was allowed to stand for 2 days at room temperature, ammonia (8.0 mmoles) was the only volatile product. Extraction of the white solid residue with ether left a material containing the NH_4^+ , F^- , and SCN^- ions (481 mg \equiv 2.58 mmoles of $C_6F_5SSCF_3$ having reacted); the ether-soluble material was bis(pentafluorobenzene)sulfenimide (1.28 mmoles), m.p. 79–80°, which could be purified further by vacuum sublimation.

Anal. Calcd. for $C_{12}HF_{10}NS_2$: C, 34.9; H, 0.2; N, 3.4; S, 15.5. Found: C, 34.4; H, 0.2; N, 3.6; S, 14.9.

Preparation of n-Propyltrifluoromethyl Disulfide

The reaction of equimolecular amounts of *n*-propanethiol and trifluoromethanesulfonyl chloride yielded hydrogen chloride, volatile at -80° , and *n*-propyltrifluoromethyl disulfide (90%), a colorless liquid with a vapor pressure of 30 mm at room temperature.

Anal. Calcd. for $C_4H_7F_3S_2$: C, 27.3; H, 4.0; F, 32.3. Found: C, 29.3; H, 4.3; F, 32.1.

Reaction of n-Propyltrifluoromethyl Disulfide with Ammonia

Mixing 2.97 mmoles of *n*-propyltrifluoromethyl disulfide and 17.88 mmoles of ammonia resulted in the immediate formation of a white precipitate. After the mixture was allowed to stand at room temperature for 16 h, ammonia (5.3 moles) was the only readily volatile product; an oil remained which was distilled with difficulty under vacuum. Extraction of the white solid residue with ether left a white solid containing the NH_4^+ , F^- , and SCN^- ions (370 mg \equiv 1.98 mmoles of *n*-PrSSCF₃ having reacted).

An oil (180 mg) was extracted with ether; chemical analysis showed this to be mainly polymeric thiopropionaldehyde, formed from the decomposition of the sulfenamide. No N—H bands were observed in the infrared spectrum of the oil.

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