Anal. Calcd. for $C_8H_{18}N_3Sb$: C, 28.37; H, 7.14; N, 16.55; Sb, 47.94. Found: C, 28.09; H, 7.05; N, 16.70; Sb, 48.15.

N.m.r. Measurements.—The n.m.r. spectra were obtained with a Varian A-60 spectrometer. The dialkylamino compounds with P,[1] As,[2] Si,[7] Ge,[8] and Ti[4] as central atoms were prepared according to methods in the literature. Their proton n.m.r. data are reported here for the first time or have appeared in communications from this laboratory in connection with some other studies.[9]

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Trifluoromethylthiodifluoramine[1]

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Recently, three compounds containing a difluoramino group bonded to a hexavalent sulfur atom have been reported. These novel compounds are SF_5NF_2,[2] FSO_2NF_2,[3] and $CF_3SF_4NF_2$.[2a]

We wish to report the synthesis of a compound of divalent sulfur containing the S–NF_2 group. This compound, trifluoromethylthiodifluoramine, has been prepared in our laboratory by the ultraviolet irradiation of bis(trifluoromethyl) disulfide and tetrafluorohydrazine in the gas phase in a quartz or Vycor 7910 flask.

$$CF_3SSCF_3 + N_2F_4 \xrightarrow{h\nu} CF_3SNF_2$$

Since both CF_3SSCF_3[4] and N_2F_4[5] are known to cleave homolytically to give $CF_3S\cdot$ and $\cdot NF_2$ free radicals, respectively, it is likely that this reaction proceeds by the combination of the two radicals.

The structural assignment of this compound is based on nuclear magnetic resonance and infrared analysis, both of which are consistent with the structure CF_3SNF_2. The infrared spectrum is shown in Fig. 1 and shows peaks typical of CF_3S– compounds at 8.32 (s), 8.56 (m), 8.79 (s), and 13.01 (m) μ. The latter peak is assigned to C–S stretching and compares with CF_3SCF_3 (13.13 m), CF_3SSCF_3 (13.20 m), CF_3SSSCF_3 (13.15 m), and CF_3SCl (13.10 m). A strong peak at 10.73 μ is assigned to N–F stretching.

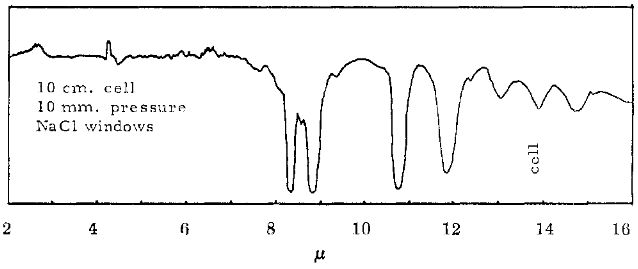

Fig. 1.—Infrared spectrum of CF_3SNF_2.

The reaction was carried out by condensing the reactants into an evacuated 1-l. Vycor 7910 or quartz flask followed by irradiation using a Hanovia Model 3066 lamp. The formation of CF_3SNF_2 could be monitored by the appearance of infrared absorption at 10.80 μ.

Trifluoromethylthiodifluoramine is a white solid and colorless liquid and is a gas at 25°. It is apparently somewhat unstable at room temperature. A 30–35% solution in CCl_4 sealed in a Pyrex n.m.r. tube almost completely decomposed in 2 hr. to give a complex mixture. Products of this decomposition which have been identified are SF_5NF_2, CF_4, SOF_2, SO_2, and SiF_4. Several others remain unidentified.

In spite of its instability, CF_3SNF_2 could be obtained in a pure state by passing the product mixture through a 24-ft. g.l.c. column (0.5 in. o.d.) packed with 25% dinonyl phthalate on Chromosorb. At 25° and a helium flow rate of 175 cc./min. the retention time was 59 min.

Small quantities of trifluoromethylthiodifluoramine have also been obtained in the ultraviolet-catalyzed reaction of N_2F_4 with both 2,2,4,4-tetrafluoro-1,3-dithietane and bis(trifluoromethyl) trithiocarbonate. It is also formed when a mixture of bis(trifluoromethyl) disulfide and N_2F_4 is passed through an electric discharge and in the stirred bed fluorination of thiourea. An early attempt to prepare CF_3SNF_2 by heating the two reactants in a stainless steel autoclave was unsuccessful. No reaction was observed after 24 hr. at 150°, but after 16 hr. at 225° trifluoromethyliminosulfur difluoride ($CF_3N{=}SF_2$) was found to be a major product.

The n.m.r. spectrum[6] of CF_3SNF_2 showed two peaks. One peak, at 35.2 p.p.m. relative to CF_3COOH, was a triplet by 7.2 c.p.s. and was due to the CF_3S group. The second peak, at −179.6 p.p.m., was broad and attributed to the NF_2 group. Because of decomposition of the sample, relative areas could not be accurately determined but they appear to be in the correct ratio for CF_3SNF_2.

The molecular weight of a small sample determined by the vapor density method was 144. This low value (mol. wt. calcd. for CF_5NS: 153) might be attributed to the known presence of SOF_2 and SiF_4 as minor impurities.

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