Anal. Calcd. for $ReO_3(SO_3F)$: Re, 55.9; S, 9.6; F, 5.7. Found: Re, 55.5; S, 10.3; F, 6.2.

The compound is a very viscous, highly hygroscopic, yellow liquid with a melting point of approximately −33°. (A freezing point was not obtained since the liquid tended to supercool and solidified to a glass.)

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CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY,
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The Preparation of Trisdimethylaminostibine

BY KURT MOEDRITZER

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Dialkylamino derivatives of triply-connected phosphorus[1] and arsenic[2] have been prepared in good yields by the aminolysis of the corresponding trihalides.

$$MX_3 + 6NHR_2 \longrightarrow M(NR_2)_3 + 3NHR_2 \cdot HX \quad (1)$$

(M = P, As; X = halogen; R = alkyl). Preliminary experiments showed that antimony trichloride, when allowed to react with dimethylamine according to eq. 1, formed ill-defined addition products with the amine. At room temperature, a complex of the composition $SbCl_3 \cdot 4NH(CH_3)_2$ appeared to be stable. At 100° *in vacuo*, the complex lost one mole of dimethylamine to give $SbCl_3 \cdot 3HN(CH_3)_2$, but it did not sublime.

Recently it has been reported that dialkylamino compounds of transition metals[3,4] are readily obtained by treating the metal halide with lithium dialkylamides. We have applied this method to the preparation of trisdimethylaminostibine from antimony trichloride and lithium dimethylamide

$$SbCl_3 + 3LiN(CH_3)_2 \longrightarrow Sb[N(CH_3)_2]_3 + 3LiCl \quad (2)$$

The trisdimethylaminostibine was obtained in 62% yield. The compound is a colorless liquid which is extremely sensitive to moisture. Exposure to air causes the immediate formation of a white precipitate of Sb_2O_3 due to hydrolysis.

The proton n.m.r. spectrum of $Sb[N(CH_3)_2]_3$ exhibits one sharp resonance which is consistent with its structure. As shown in Table I, this resonance is downfield of that of the analogous arsenic compound which, in turn, is at a lower field than that of the corresponding phosphorus compound. For increasing electronegativity of the central atom, the methyl resonance appears at increasing values of the applied field. No definite trend has been observed for some tetrakisdimethylamino derivatives of group IV elements (Table I). This variation in resonance frequency with the electronegativity for dimethylamino compounds of group V elements is in marked contrast to that observed for methyl esters of inorganic acids.[5] In the latter case, it was found that the resonance for the methyl protons appears at decreasing values of the applied field as the electronegativity of the central atom increases. This is in agreement with the comfortable idea of increased deshielding of the methyl protons with increasing electronegativity of a heteroatom farther away in the molecule. The theory of the neighbor-anisotropy effect[6] indicates that the opposite behavior, shown in Table I for the group V compounds, is due to a change in the average angle between the nuclear axis of magnetic anisotropy of the atom M and the M–N bond in the moiety $M–NR_2$, when atom M is changed from P to As to Sb.

TABLE I

PROTON N.M.R. DATA OF SOME DIMETHYLAMINO DERIVATIVES OF GROUP IV AND V ELEMENTS

	δ, p.p.m.[a]	$J_{C^{13}-H}$, c.p.s.	Electronegativity of central atom
$P[N(CH_3)_2]_3$	−2.425[b]	132.5[c]	2.1[d]
$As[N(CH_3)_2]_3$	−2.533	131.8	2.0
$Sb[N(CH_3)_2]_3$	−2.700	131.5	1.9
$Si[N(CH_3)_2]_4$	−2.417	131.0	1.8
$Ge[N(CH_3)_2]_4$	−2.563	131.2	1.8
$Ti[N(CH_3)_2]_4$[e]	−3.033	132.5	1.5

[a] Measured as neat liquids relative to tetramethylsilane as internal standard. All signals shifted downfield by 0.03 p.p.m. upon dilution with 10 parts of benzene. [b] J_{P-H} = 8.7 c.p.s. [c] $J_{P-C^{13}-H}$ = *ca.* 8 c.p.s. [d] Electronegativities: L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 93. [e] Prepared by M. D. Rausch.

Experimental

Aminolysis of Antimony Trichloride.—A quantity of 9.7372 g. of dimethylamine was condensed on 2.8286 g. of antimony trichloride and sealed *in vacuo*. On warming to room temperature, a fairly vigorous reaction occurred forming a clear solution. After several days of standing at room temperature, the excess dimethylamine was distilled off, yielding a white solid residue analyzing as $SbCl_3 \cdot 4.089NH(CH_3)_2$. Heating of this residue at 100° *in vacuo* caused the distillation of additional dimethylamine, resulting in a residue of the composition $SbCl_3 \cdot 3.019NH(CH_3)_2$. Attempts to sublime this product *in vacuo* failed; the initially off-white material liquefied and turned black and no volatile products were observed.

Preparation of Trisdimethylaminostibine.—Special precautions, *e.g.*, carefully dried glass apparatus, were adopted to avoid hydrolysis. All procedures were performed under an atmosphere of dry oxygen-free nitrogen. Dried reagents were used.

To a cooled (Dry Ice–acetone) solution of 71.6 g. (1.1 moles) of *n*-butyllithium in 725 ml. of hexane was added a solution of 50.3 g. (1.1 moles) of dimethylamine in 500 ml. of diethyl ether and 350 ml. of hexane. The resulting suspension of lithium dimethylamide was then stirred at room temperature for 20 min. After cooling the flask again with Dry Ice–acetone, a solution of 85 g. (0.37 mole) of antimony trichloride in 150 ml. of diethyl ether was added over a period of 1 hr. Subsequently, the reaction mixture was refluxed for 1 hr., and, after removal of the solvents, the product distilled as a colorless liquid at 32–34° (0.45 mm.), yield 58 g. (62%).

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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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CONTRIBUTION FROM PENINSULAR CHEMRESEARCH, INC.,
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Trifluoromethylthiodifluoramine[1]

BY EUGENE C. STUMP, JR., AND CALVIN D. PADGETT

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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–NF₂ 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.

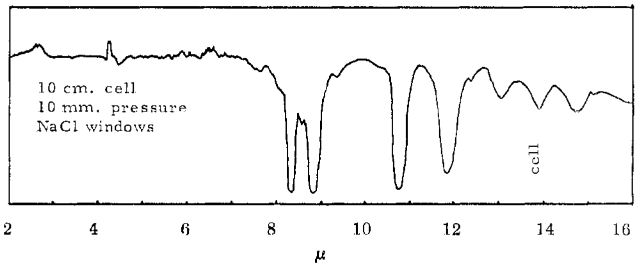

Fig. 1.—Infrared spectrum of CF_3SNF_2.

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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