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New Hypofluorites Containing Nitrogen

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13. ABSTRACT

Dimethylchlorotin carboxylates, $(CH_3)_2ClSnOOCR$; R = CH_3, CF_3, C_2F_5, C_3F_7, CF_2Cl, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, CH_2I, are prepared by heating trimethyltin chloride with an excess of the appropriate acid at 100°. These compounds have been studied by ^1H and ^{19}F nmr, infrared, and Mossbauer spectroscopy. Based on this spectral data, in the solid state or in methylene chloride or chloroform, penta-coordinate tin is present. The solids are polymeric with bridging carboxylate units. In solution, the non-fluorinated carboxylate-containing compounds are very likely chelate monomers, while the remaining compounds retain polymeric character.

Mixed phosphorus chloride fluorides undergo ready reaction with sodium azide to provide an excellent route to new azide-containing compounds, including F_2PN_3, $F_2P(O)N_3$, $FP(O)(N_3)_2$, and $FP(S)(N_3)_2$. In addition, the previously reported $F_2P(S)N_3$ is easily prepared by this method. F_2PN_3 has particularly limited stability.

Hexafluoroisopropylideniminolithium reacts with disulfur dichloride to give bis(hexafluoroisopropylidenimino)disulfide which undergoes two different types of reactions with chlorine to yield bis(2-chlorohexafluoroisopropylimino)sulfur(IV) and chloro(hexafluoroisopropylidenimino)sulfur(II). The latter gives new sulfur(II) compounds with reactants that contain active hydrogen or with silver salts. $(CF_3)_2C{=}NSCl$ is readily converted to $(CF_3)_2CF{=}NSF_2$ by fluorinating agents.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
chlorodifluoramine						
difluorodiazine						
bis(trifluoromethyl) sulfoxide						
bis(trifluoromethyl) sulfide						
dimethylchlorotin carboxylates						
trimethyltin chloride						
fluorophosphorus azides						
hexafluoroisopropylideniminolithium						
bis(hexafluoroisopropylidenimino) disulfide						
bis(2-chlorohexafluoroisopropylimino)sulfur(IV)						
chloro(hexafluoroisopropylidenimino)sulfur(II)						
through-space coupling in ^{19}F nmr						
sulfur diimide						
rearranged derivatives of sulfur tetrafluoride, trifluoromethylsulfur trifluoride and bis(trifluoromethyl)sulfur difluoride						
insertion of sulfur dioxide and carbon dioxide						
difluoroaminocarbonyl pseudohalides						
tetrafluorourea						
chlorocarbonyl fluorosulfate						

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13. Abstract Continued

Long range spin-spin coupling of fluorine on terminal CF_3 groups separated by ten bonds is observed in the ^{19}F nmr of the new sulfur diimide $(CF_3)_2CFN=S=NC(CF_3)_2N=C(CF_3)_2$.

Isolation of six extensively rearranged products (I-VI) from reactions of sulfur tetrafluoride with hexafluoroisopropylideniminolithium demonstrates that simple, metathetical reactions do not occur. A possible mechanism is proposed. Similar rearranged products (VII-IX) form from the lithium salt with CF_3SF_3 and $(CF_3)_2SF_2$. Long range coupling of nuclei separated by 10 σ bonds is observed in the ^{19}F nmr spectrum of (III).

$(CF_3)_2C=NS(O)OLi$ and $(CF_3)_2C=NC(O)OLi$ which result from insertion reactions of SO_2 and CO_2 with $(CF_3)_2C=NLi$, react with $SOCl_2$ and $COCl_2$, respectively, to prepare the heretofore unisolable intermediates, $(CF_3)_2C(Cl)NSO$ and $(CF_3)_2C(Cl)NCO$.

Improved yields of $NF_2C(O)Cl$ are obtained by short term (4-6 hr) photolysis of N_2F_4 with oxalyl chloride. Reactions of $NF_2C(O)Cl$ with AgCN, AgNCS, AgNCO, $Hg(SCF_3)_2$ and $Hg(ON(CF_3)_2)_2$ give the new difluoroaminocarbonyl pseudohalides: $NF_2C(O)CN$, $NF_2C(O)NCS$, $NF_2C(O)NCO$, $NF_2C(O)SCF_3$, and $NF_2C(O)ON(CF_3)_2$. With excess of either Ag_2O at 0° or HgO at -78°, $NF_2C(O)Cl$ is converted to $(NF_2)_2CO$ and CO_2 in nearly quantitative yield. Chlorocarbonyl fluorosulfate results when $NF_2C(O)Cl$ is mixed with $S_2O_6F_2$ or $BrOSO_2F$.

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CHLORODIFLUORAMINE AND DIFLUORODIAZINE

by

Leon M. Zaborowski*, Ronald A. De Marco* and Jean'ne M. Shreeve*

Checked by Max Lustig#

Chlorodifluoramine has been prepared by reaction of difluoramine with boron trichloride[1], phosgene[2] or hydrogen chloride[2]; treating a mixture of sodium azide and sodium chloride with fluorine[3]; reaction of chlorine trifluoride with ammonium fluoride[4]; reaction of chlorine and difluoramine in the presence of potassium fluoride[5]; and photolysis of tetrafluorohydrazine and sulfinyl chloride.[6]

Difluorodiazine has been prepared by the thermal decomposition of fluorine azide[7], electrolysis of ammonium hydrogen fluoride[8], reaction of nitrogen trifluoride with mercury vapor in an electric discharge[9], dehydrofluorination of difluoramine[10], treatment of a solution of N,N-difluorourea with a concentrated potassium hydroxide solution[11], reaction of sodium azide and fluorine[12], decomposition of $N_2F^+Sb_2F_{11}^-$[13], and reaction of tetrafluorohydrazine and excess aluminum chloride at -78°[14]. However, each of these methods suffers from one or more disadvantages including low[4,8,9,11,12,14] or erratic[2,3] yields, tendency to explode[3,4,7], use of a very hazardous reagent[1,2,5,10] (difluoramine is extremely shock sensitive as a solid), and indirect method of preparation[13].

The following are convenient methods for the preparation of chlorodifluoramine and difluorodiazine in reproducibly good yields by the reaction of difluoramidofluorosulfate with sodium chloride and the photolysis of tetrafluorohydrazine and bromine.

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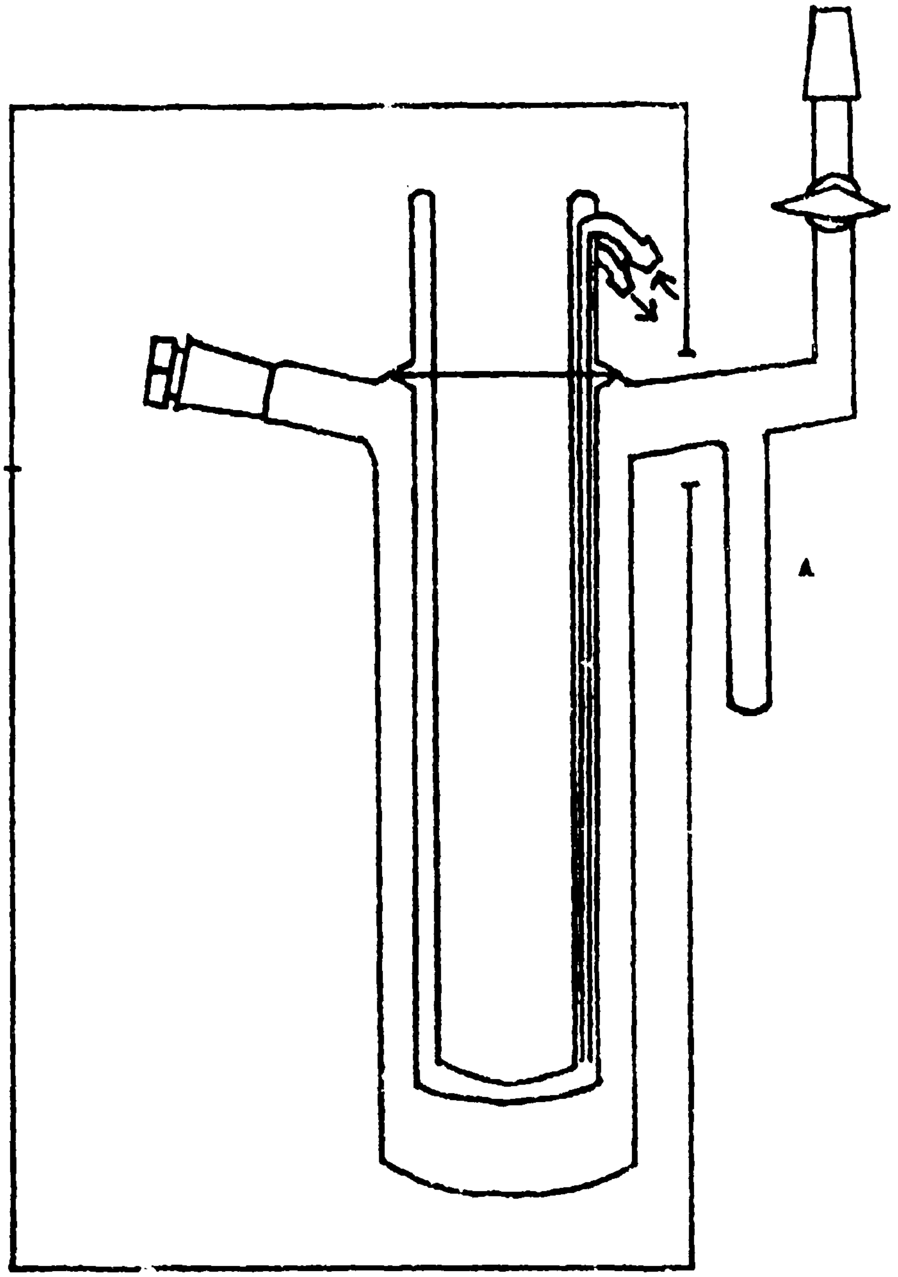

Pyrex photolysis vessel with water-cooled quartz probe.

CAUTION. Care should be exercised in handling tetrafluorohydrazine, chlorodifluoramine and difluorodiazine since N-halogen compounds are known to exhibit explosive properties. Any apparatus used should be clean and free of organic materials. Liquid nitrogen should be used for condensing reagents.

PROCEDURE

In the following procedures a standard glass vacuum line with high-vacuum stopcocks (lubricated with Kel-F 90 grease*) is used. Due to the reactivity of many of the compounds with mercury, it is convenient to use a null point pressure device, such as a Booth-Cromer[16] pressure gauge or spiral gauge. A mercury manometer covered with Kel-F 3 oil* can be used.

A. CHLORODIFLUORAMINE

$$2N_2F_4 + 2SO_3 \xrightarrow{h} 2NF_2OSO_2F + N_2F_2$$

$$NF_2OSO_2F + NaCl \xrightarrow{CH_3CN} NF_2Cl + NaOSO_2F$$

Difluoramidofluorosulfate is prepared by the photolysis of tetrafluorohydrazine and sulfur trioxide (55% yield)[17] or essentially quantitatively by the reaction of N_2F_4 and peroxodisulfuryl difluoride ($S_2O_6F_2$).[18]

A 300 ml Pyrex glass vessel fitted with a Teflon stopcock** and containing a Teflon-coated stirring bar is charged with excess reagent grade sodium chloride (0.052 mole). After evacuation on the vacuum line, 3 ml of dry acetonitrile followed by difluoramidofluorosulfate (0.010 mole), are distilled into the vessel which is at -195°. The mixture is warmed to room temperature and is stirred with a magnetic stirring device for two hr (behind a safety shield). The volatile compounds are removed under static

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(*) Minnesota Mining and Manufacturing Company

(**) Fischer and Porter Co., Warminster, Pa.

vacuum from the reaction vessel held at -78° (to retain acetonitrile) to a trap at -195°. Then as the latter warms from -195°, the material is separated by passing through traps at -135 and 195°. The first trap contains acetonitrile and small amounts of unreacted starting material while the trap at -195° will have pure chlorodifluoramine (0.0094 mole, > 90%).[19] NF_2Cl passes the trap at -135° slowly under good vacuum. Although chlorodifluoramine can be stored for long periods in Pyrex at -195°, for reasons of safety, it is suggested that only small amounts (< 0.01 mole) be retained.

B. DIFLUORODIAZINE

$$N_2F_4 + Br_2 \xrightarrow{h\nu} N_2F_2$$

Reagent grade bromine is used without further purification. It can be stored under static vacuum for long periods at room temperature in an ordinary Pyrex tube equipped with a Teflon* stopcock. Tetrafluorohydrazine** is used without further purification.

Photolysis is carried out in an 850 ml Pyrex vessel equipped with a water-cooled quartz probe. The ultraviolet light source is a 450-w lamp*** with a Vycor filter***. To reduce the dangers from a possible explosion or eye damage from ultraviolet radiation, the reaction vessel shown in Figure ___ is contained in a wooden box.

The photolysis bulb is connected to the vacuum line via a 10/30 standard taper joint and is evacuated. Bromine (0.004 mole) and tetrafluorohydrazine (0.002 mole) are condensed into the cold finger (A) at -195°. The mixture expands into the bulb as it warms to room temperature. The lamp is turned on only after the Vycor filter is in place, the cold tap water is passing through the water jacket, and the reagents are at room temperature. Photolysis time for an 850-ml bulb is about 90 min.

(*) Fischer and Porter Co., Warminster, Pa.

(**) Air Products and Chemicals, Allentown, Pa.

(***) Hanovia L-679A36 and filter 7910, Hanovia Lamp Division, Engelhard Hanovia, Inc., Engelhard, N. J.

After the photolysis is completed, the reaction mixture is transferred under dynamic vacuum to a trap at -195°. The small amount of nitrogen formed in the reaction is expelled by the pumping system. The mixture is allowed to warm slowly to room temperature (an empty Dewar cooled to -195° with liquid nitrogen is convenient) and a trap-to-trap separation is performed using traps at -140 and -195°. The first trap contains N_2O_4 and Br_2. The photolysis vessel contains a white solid, probably $(NO)_2SiF_6$.

Difluorodiazine contaminated with SiF_4 and NF_3 is held at -195°. This mixture is passed through a sodium fluoride trap to remove SiF_4 by the formation of Na_2SiF_6. Difluorodiazine may be separated from nitrogen trifluoride by gas chromatogrphy using a 25 ft x 0.25 in. aluminum or copper column packed with 20% FC-43[*] on acid-washed Chromosorb P. A helium flow rate of 0.5 cc/sec is used and the column is held at -63°. Nitrogen trifluoride, *trans*-difluorodiazine and *cis*-difluorodiazine elute in that order. The yield is 70% difluorodiazine (53% *trans*).

With a 5-l. bulb, using 0.015 mole bromine and 0.009 mole tetrafluorohydrazine, the same yield results after 90 min of photolysis.

Although difluorodiazine can be stored for long periods in Pyrex glass at -195° or in metal at room temperature, for reasons of safety, it is suggested that only small amounts (0.01 mole) be retained.

PROPERTIES

Chlorodifluoramine is a white solid at -195°, a colorless liquid at -184°, and boils at -67°. The vapor pressure curve is given by the equation $\log P_{mm} = \frac{-950}{T} + 7.478$. The infrared spectrum consists of the

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(*) Minnesota Mining and Manufacturing Company. The checker reports substantially identical results using perfluorotri-tertiarybutylamine on Chromosorb P.

the following peaks: 1853 w, 1755 w, 1695 w, 1372 w, 926 s, 855 s, 746 m, 694 s cm^{-1}.[1] The ^{19}F nmr shows a broad triplet centered at -141.5 ppm relative to an internal reference of CCl_3F.

Cis-difluorodiazine is a colorless liquid at -195° with a boiling point of -105.7°. The vapor pressure curve follows the equation $\log P_{mm} = \frac{-803.0}{T} + 7.675$. The infrared spectrum consists of the following peaks: 1538 w, 1513 w, 954 s, 904 s, 883 s, 738 vs cm^{-1}.[20] The ^{19}F nmr shows a broad triplet centered at -136.1 ppm relative to an internal reference of CCl_3F.

Trans-difluorodiazine is a white solid melting at -172° and boiling at -111.4°. The vapor pressure curve is given by the equation $\log P_{mm} = \frac{-742}{T} + 7.470$. The infrared spectrum is a strong band at 995 cm^{-1}.[20] The ^{19}F nmr gives a broad triplet centered at -94.4 ppm relative to an internal reference of CCl_3F.

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BIS(TRIFLUOROMETHYL) SULFOXIDE

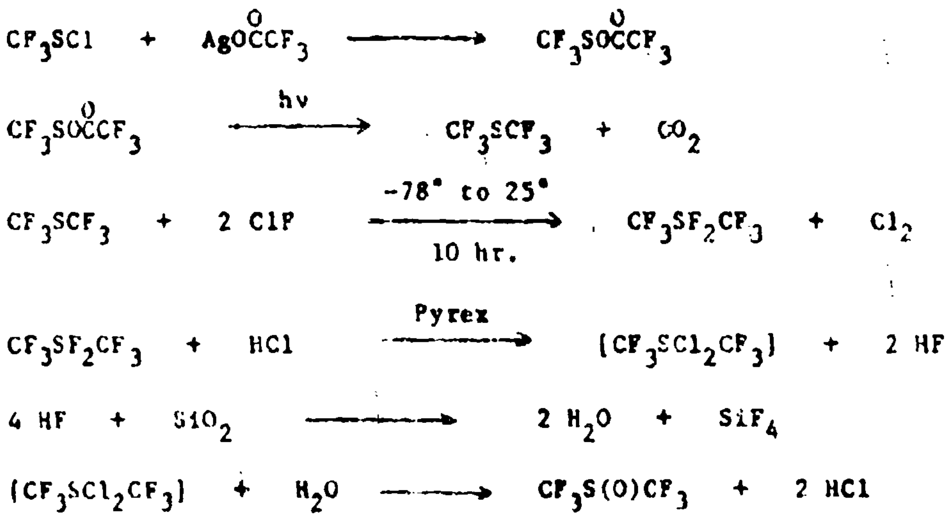
By

Dennis T. Sauer* and Jean'ne M. Shreeve*

Bis(trifluoromethyl) sulfoxide has been previously prepared[1] by the elemental fluorination of bis(trifluoromethyl) sulfide at -78° in hexafluoroethane followed by subsequent hydrolysis of the bis(trifluoromethyl)sulfur difluoride. This method suffers from the fact that elemental fluorine must be used, a solvent is needed and yields are low.

Oxidation of bis(trifluoromethyl) sulfide with commercially obtainable chlorine monofluoride in the absence of solvent yields bis(trifluoromethyl)sulfur difluoride in > 90% yield.[2,3] Pure bis(trifluoromethyl)sulfur difluoride is resistant to hydrolysis and is stable storage in Pyrex at 25° for extended periods of time. Reaction of bis(trifluoromethyl)sulfur difluoride with anhydrous HCl in a clean Pyrex bulb results in the formation of bis(trifluoromethyl) sulfoxide in good yield. This preparative method has been extended resulting in the preparation of $CF_3S(O)C_2F_5$, $CF_3S(O)\underline{n}\text{-}C_3F_7$ and $C_2F_5S(O)C_2F_5$.[2,3]

GENERAL PROCEDURES



$$CF_3SCl + Ag\overset{O}{O}CCF_3 \longrightarrow CF_3SO\overset{O}{C}CF_3$$

$$CF_3SO\overset{O}{C}CF_3 \xrightarrow{h\nu} CF_3SCF_3 + CO_2$$

$$CF_3SCF_3 + 2\ ClF \xrightarrow[10\ hr.]{-78^\circ\ to\ 25^\circ} CF_3SF_2CF_3 + Cl_2$$

$$CF_3SF_2CF_3 + HCl \xrightarrow{Pyrex} [CF_3SCl_2CF_3] + 2\ HF$$

$$4\ HF + SiO_2 \longrightarrow 2\ H_2O + SiF_4$$

$$[CF_3SCl_2CF_3] + H_2O \longrightarrow CF_3S(O)CF_3 + 2\ HCl$$

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Bis(trifluoromethyl) sulfide was prepared by the photolysis of trifluoromethylsulfenyl trifluoroacetate.[4] Other preparative methods,[5,6] have been difficult to reproduce or produce the monosulfide in small yield. Oxidation of bis(trifluoromethyl) sulfide with chlorine monofluoride proceeds smoothly as the metal reactor containing the mixture is slowly warmed from -78 to 25° over 10 hours. No cleavage products are formed and the desired bis(trifluoromethyl)sulfur difluoride is isolated in > 90% yield. The reaction of the sulfur difluoride with anhydrous HCl to produce bis(trifluoromethyl) sulfoxide is presumed to proceed through the bis(trifluoromethyl)sulfur dichloride intermediate. Since HF is produced when HCl reacts with bis(trifluoromethyl)-sulfur difluoride in Pyrex, water is formed which results in hydrolysis of the bis(trifluoromethyl)sulfur dichloride intermediate. Attempts to isolate the sulfur dichloride intermediate by reaction of HCl and bis(trifluoromethyl)sulfur difluoride in the presence of NaF in a nickel bomb resulted in the formation of bis(trifluoromethyl) sulfide and chlorine quantitatively.

$\underline{CF_3SO\overset{O}{C}CF_3}$

Procedure: Ten mmoles of trifluoromethylsulfenyl chloride* (CF_3SCl) is reacted with excess silver trifluoroacetate* at 25°C for 10 minutes in a one-liter Pyrex vessel to produce trifluoromethylsulfenyl trifluoroacetate ($CF_3SO\overset{O}{C}CF_3$) quantitatively. $CF_3SO\overset{O}{C}CF_3$ may be freed from trace amounts of CF_3SCl by passage through a -78°C (acetone) slush bath which retains the pure $CF_3SO\overset{O}{C}CF_3$.

Properties: Trifluoromethylsulfenyl trifluoroacetate is a colorless liquid at 25°C. The ^{19}F NMR resonances occur at 47.3 ppm (CF_3S) and 76.5 ppm ($CF_3C(O)O$) with no coupling observed between the trifluoromethyl groups.[4] The infrared spectrum consists of bands at 1835 (m), 1805 (w,sh), 1317 (w), 1246 (m-s), 1202 (vs), 1190 (s,sh), 1120 (m-s), 1069 (s), 835 (w), 765 (w-m) and 720 (w) cm^{-1}

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*Peninsular ChemResearch

CF_3SCF_3

Procedure: Ten mmoles of trifluoromethylsulfenyl trifluoroacetate are photolyzed for 3/4 hour through Pyrex with a Hanovia "Utility" Ultraviolet Quartz Lamp (140 watt) producing bis(trifluoromethyl) sulfide and CO_2 quantitatively. Pure bis(trifluoromethyl) sulfide is retained in a -120°C slush bath (diethyl ether) while CO_2 slowly sublimes into a -183° bath during trap-to-trap distillation.

Properties: Bis(trifluoromethyl) sulfide exists as a colorless gas at room temperature and condenses to a colorless liquid. The vapor pressure of bis(trifluoromethyl) sulfide is given by the equation $\log P_{mm} = 7.82 - 1239.1/T$ from which the b.p. is calculated as -22.2°.[5] The ^{19}F NMR consists of a single resonance at 38.6 ppm. The infrared spectrum contains bands at 1220 (s), 1198 (vs), 1160 (s), 1078 (vs), 758 (m), and 475 (w) cm^{-1}.

$CF_3SF_2CF_3$

Procedure: Reaction of bis(trifluoromethyl) sulfide with chlorine monofluoride* is carried out in a 75 ml stainless steel Hoke bomb. The bomb is evacuated and in a typical preparation, 10 mmoles of bis(trifluoromethyl) sulfide and 22 mmoles of chlorine monofluoride are added at -183°C. The vessel is then warmed to -78°C and slowly allowed to warm to 25°C over a 10 hour period. The product mixture is first separated by fractional condensation. The bis(trifluoromethyl)sulfur difluoride ($CF_3SF_2CF_3$) is retained in a -98° slush bath while any unreacted CF_3SCF_3, ClF and Cl_2 pass into a -183° bath. The $CF_3SF_2CF_3$ may be further purified by gas chromatography utilizing a 17 ft. 20% Kel-F Oil (3M Co.) on Chromasorb-P column. Final purification gives $CF_3SF_2CF_3$ in > 90% yield based on the amount of monosulfide used.

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*Ozark Mahoning Company

Properties: Bis(trifluoromethyl)sulfur difluoride is a colorless gas at 25°C which condenses to a colorless liquid. A boiling point of 21°C is calculated from a Clausius-Clapeyron plot according to the equation $\log P_{mm} = 8.00 - 1507/T$. ^{19}F NMR resonances at 58.0 (CF_3) and 14.2 ppm (SF_2) integrate to the proper 6:2 ratio with $J_{SF_2-CF_3} = 19.5$ cps. The infrared spectrum contains bands at 1281 (vs), 1260 (s), 1215 (m-s), 1144 (m), 1081 (vs), 766 (m), 677 (s) and 507 (m) cm^{-1}.

$\underline{CF_3S(O)CF_3}$

Procedure: Four mmoles of bis(trifluoromethyl)sulfur difluoride react with 16 mmoles anhydrous HCl* in a clean one-liter Pyrex vessel for 24 hrs to give bis(trifluoromethyl) sulfoxide in 70% yield. The bis(trifluoromethyl) sulfoxide is purified by fractional condensation. The desired sulfoxide is retained in a -78°C slush bath while any unreacted HCl and $CF_3SF_2CF_3$ pass into a -183° bath. Further purification by gas chromatography, utilizing a 17 ft 20% Kel-F on Chromasorb-P column, enables isolation of pure $CF_3S(O)CF_3$. When this reaction is carried out in a metal bomb, no sulfoxide is formed. The products isolated were identified as CF_3SCF_3, Cl_2 and unreacted HCl.

Properties: Bis(trifluoromethyl) sulfoxide is a colorless liquid at 25°. A normal boiling point of 37.3°C is calculated from a Clausius-Clapeyron plot according to the equation $\log P_{mm} = 7.66 - 1483/T$. Conformational spectral properties include a molecular ion in the mass spectrum (2.1%) and a single ^{19}F resonance at 64.5 ppm. The infrared spectrum contains bands at 1244 (vs) 1191, 1187 (doublet, s), 1121 (m-s), 1105 (vs), 752 (w) and 468 (w) cm^{-1}.

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*Matheson

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Preparation and Spectral Studies of Dimethylchlorotin Carboxylates

by

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Summary

Dimethylchlorotin carboxylates, $(CH_3)_2ClSnOOCR$; R = CH_3, CF_3, C_2F_5, C_3F_7, CF_2Cl, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, CH_2I, are prepared by heating trimethyltin chloride with an excess of the appropriate acid at 100°. These compounds have been studied by ^1H and ^{19}F nmr, infrared, and Mössbauer spectroscopy. Based on this spectral data, in the solid state or in methylene chloride or chloroform, penta-coordinate tin is present. The solids are polymeric with bridging carboxylate units. In solution, the nonfluorinated carboxylate-containing compounds are very likely chelate monomers, while the remaining compounds retain polymeric character.

Introduction

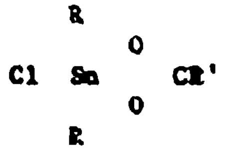
Dialkylchlorotin carboxylates ($R_2ClSnOOCR'$) have been prepared by a variety of methods including the reactions of dialkyltin dichlorides with carboxylic acids or salts of these acids.[1] Recently we reported[2] the syntheses of diorganochlorotin carboxylates in high yield *via* the reactions of triorganotin chlorides with carboxylic acids which involve the rather unexpected displacement of methane[3]

$$(CH_3)_3SnCl + RCO_2H \qquad (CH_3)_2SnClO_2CR + CH_4$$

R = CH_3, CF_3, C_2F_5, C_3F_7, CF_2Cl, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, CH_2I

This is particularly interesting when the dialkylchlorotin product is compared with the trimethylsilyl perfluoroacetate obtained in 80% yield from the analogous reaction with trimethylchlorosilane and CF_3COOH[4] with hydrogen chloride as the only other product.

Some of the structural aspects of organotin compounds have been reviewed by Okawara and Wada.[5] Extensive work on the infrared as well as nuclear magnetic resonance and Raman spectra and X-ray data confirm that most compounds of the type R_3SnCO_2R' occur as polymeric solids (pentacoordinated tin) with planar trimethyl and bridging carboxylate groups.[6-14] In solution, or in the liquid phase, the compounds are monomeric. Formation of the polymeric structure is impeded by steric hindrance of bulky alkyl groups and also does not occur with thio- or dithio-acetates. Thus, i-Pr_3SnOAc was found to exist as a monomeric liquid at 25° rather than as a five-coordinate polymer. Infrared spectral studies of halogen-substituted tributyl tin acetates also indicate four coordinate structures in solution.[15] In contrast, the structure of compounds of the type $R_2ClSnCO_2R'$ is thought to be five coordinate and monomeric in solution, presumably with chelate carboxylate groups.[16]



$$\mathrm{Cl}\ \overset{R}{\underset{R}{\mathrm{Sn}}}\ \overset{O}{\underset{O}{\ }}\ \mathrm{CR'}$$

$R = C_2H_5$, n-C_3H_7, H

$R' = CH_3$

We have now prepared ten compounds of this type where R is methyl and R' is a variety of haloalkyl groups and have attempted through available spectral techniques (vibrational, mass, nmr and Mössbauer) to establish the structure of these materials. We report our conclusions below.

Experimental

Preparation of Dimethylchlorotin Carboxylates

A standard Pyrex glass high vacuum system was used for manipulating volatile materials and for separating the volatile products. All of the dimethylchlorotin carboxylates are prepared by sealing the reactants in a thick walled Pyrex tube. E.G., trimethyltin chloride (3.94 mmol) and an excess of trifluoroacetic acid (19.1 mmol) when heated at 100° for several hours form methane (3.94 mmol) quantitatively as measured by PVT techniques. The excess acid is removed under vacuum with concomittant heating when required. Essentially 100% conversion to the dimethylchlorotin trifluoroacetate (3.94 mmol) occurs. With the exception of the dimethylchlorotin monohaloacetates (~ 60% yield based on the amount of trimethyltin chloride converted), all preparations are essentially quantitative. Lower yields are due in part to the necessity for subliming the product from the reaction vessel.

Preparation of Trimethyltin Acetate

An excess of glacial acetic acid is added to a pyridine solution of trimethyltin chloride (2.5 mmol/cc). After stirring for several minutes, a white solid precipitated from solution. Pure trimethyltin acetate (1.9 mmol) was obtained by crystallization from water.

Methods

Elemental analyses of dimethylchlorotin perfluorocarboxylates and chlorodifluoroacetate were performed by aller Mikroanalytisches Laboratorium, Göttingen, Germany. Other compounds were analyzed by Bernard Schecter of this department. Some chlorine analyses were determined by using Volhard's method. The elemental analyses and melting point data are given in Table I. Melting points of the solid compounds were determined by using a Thomas Hoover capillary melting point apparatus.

TABLE 1. **Elemental Analysis of Dimethylchlorotin Carboxylates** $(CH_3)_2SnCl(O\overset{O}{\overset{\|}{C}}R)$

R	m.p., °C	C	H	Cl	Sn	F
CF_3	118	16.21	2.13	12.12	40.11	19.4
		(16.15)⁺	(2.02)	(11.93)	(39.94)	(19.18)
C_2F_5	103-104.5	17.26	1.90	10.41*	33.81	27.1
		(17.28)	(1.73)	(10.21)	(34.19)	(27.37)
C_3F_7	115	18.24	1.54	8.96*	29.51	33.0
		(18.13)	(1.51)	(8.93)	(29.59)	(33.49)
CF_2Cl	128-129	15.22	1.94	22.49	37.49	12.3
		(15.31)	(1.93)	(22.63)	(37.83)	(12.11)
CH_3	187-188**	---	---	---	---	---
CH_2Cl	129-130	17.52	2.93			
		(17.29)	(2.90)			
$CHCl_2$	130-131.5	15.60	2.52			
		(15.38)	(2.26)			
CCl_3	196	14.05	1.76			
		(13.85)	(1.74)			
CH_2Br	114-117	15.04	2.55			
		(14.90)	(2.50)			
CH_2I	127-128	13.55	2.60			
		(13.00)	(2.18)			

⁺ ( ) calculated percentage

* determined by Volhard method

** literature 184-186[17]

Infrared spectra were recorded by using a Perkin Elmer Model 621 grating spectrophotometer with a range of 4000-250 cm^{-1}. Spectra were calibrated from known peaks of a polystyrene film. Spectra of solids were obtained with pressed KBr discs or with nujol mulls. Spectra of liquids or solutions in $CHCl_3$ or CH_2Cl_2 at several concentrations up to about 0.2 M were recorded from compensated KBr cells. High resolution ^{19}F nmr spectra were obtained with a Varian HA-100 spectrometer operating at 94.1 mHz and ^1H nmr spectra were recorded with an A-60 nmr spectrometer. D_6-acetone or $CHCl_3$ was used as a solvent and tetramethylsilane and/or trichlorofluoromethane as internal references. The Mössbauer spectra were determined at the University of British Columbia by using apparatus described previously.[10] Tin(IV) oxide was used as the reference and the spectra were recorded at -196°.

Reagents

CF_3CO_2H, $C_2F_5CO_2H$, $C_3F_7CO_2H$ and CH_2BrCO_2H were obtained from Aldrich Chemical Co.; CF_2ClCO_2H from Pierce Chemical Co.; CH_2ICO_2H from Eastman; CH_3CO_2H and CH_2ClCO_2H from J. T. Baker Chemical Co.; and $CHCl_2CO_2H$ and CCl_3CO_2H from Matheson, Coleman and Bell. Trimethyltin chloride was purchased from Alfa Inorganics.

Results and Discussion

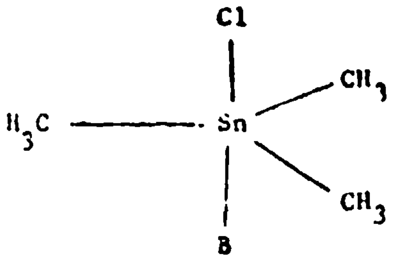
The reactions of trialkyltin chlorides with metal carboxylates have been used to prepare trialkyltin carboxylates.[1] However, we find that triorganotin chlorides react with carboxylic acids to give diorganochlorotin carboxylates[2] and alkane. Cleavage of the tin-carbon bond in tetraorganotin compounds has been used to prepare substituted organotin compounds,[18, 19] but dealkylation or dephenylation of triorganotin chlorides occurs only in a few cases.[20] However, in the reaction of tetraorganostannanes with hydrogen halides at higher temperature or for long periods at low temperature, diorganotin dihalides are formed.[21-24]

$$R_4Sn + HX \longrightarrow R_3SnX + RH$$

$$R_3SnX + HX \longrightarrow R_2SnX_2 + RH$$

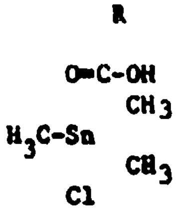
Recently Aubke <u>et al.</u>[25] reported that the reactions of HSO_3R (R = F, CF_3, Cl, Me, Et) with trimethyltin chloride yield $Me_2Sn(SO_3R)_2$ and methane and hydrogen chloride. They suggest the stepwise replacement of chloride by the acid anion followed by production of methane. However, under the conditions used in the present study, no HCl is obtained and a maximum of one mole of methane per mole of triorganotin chloride is produced regardless of the acid:tin compound ratio.

Triorganotin halides, in which the halogen atom sufficiently increases the acceptor strength of the molecule, have the tendency to interact with donor molecules to form trigonal bipyramidal adducts. The existence and structure (I) of five-coordinated tin addition compounds, $(CH_3)_3SnCl\cdot B$[26-28] where B is $(CH_3)_2SO$, Ph_3PO or $CH_3C(O)N(CH_3)_2$, have been based on nmr spin-spin coupling values (J_{Sn-CH_3}) and infrared studies.



(I)

The 1:2 molecular complexes of $SnCl_4$ and aromatic acids[29] have been isolated. For these compounds, Mössbauer studies have been used to lend support to the structure in which the carbonyl oxygen coordinates directly to the tin atom. Therefore, the reaction of trimethyltin chloride with carboxylic acids may occur via an adduct intermediate, such as II. Such an intermediate would favor formation of CH_4 rather than HCl. The Sn-Cl



(II)

bond energy in $(CH_3)_3SnCl$ is about 85 kcal/mole, while that of the Sn-C bond in $(CH_3)_4Sn$ is about 55 kcal.[30] Therefore, the Sn-C bond in $(CH_3)_3SnCl$ is expected to be weaker than the Sn-Cl bond and formation of CH_4 is not unexpected. Pemmon and Lustig[3] in a reaction of another strong acid, difluorodithiophosphoric acid, with trimethyltin chloride also observe quantitative formation of methane. This is also run without a base.

However, we have found in the presence of pyridine, trimethyltin chloride reacts with acetic acid to form trimethyltin acetate. Analogously, alkyltin chlorides form organostannoyl arsenates[31] with arsenic acids in the presence of triethylamine according to

$$R_{4-n}SnCl_n \quad + \quad nHOAs(O)R'_2 \quad + \quad n(C_2H_5)_3N \quad \rightarrow$$

$$n(C_2H_5)_3NHCl \quad + \quad R_{4-n}Sn(OAs(O)R'_2)_n$$

In these cases, the reactions could arise from nucleophilic attack by the acid anion at the positive tin center which would tend to weaken the Sn-Cl bond particularly when accompanied by the strong driving force provided by the formation of the quaternary ammonium chloride salt.

There is a marked difference in the behavior of $(CH_3)_3SnCl$ towards acids compared with that of $(CH_3)_3SiCl$[3,4] where HCl and not CH_4 is invariably formed. Again this is to be expected when it is noted that the bond energy for Si-C > Si-Cl while Sn-C < Sn-Cl.

Nuclear Magnetic Resonance Spectra

The ^{19}F nmr of some dimethylchlorotin carboxylates are listed in Table 2. The chemical shifts and coupling constants are in agreement with those reported for similar compounds.[32] The chemical shifts are essentially independent of the solvent used. No coupling between H-F or Sn-F is observed.

Methyltin derivatives are particularly suitable for ^1H nmr studies because the proton-tin coupling constants are determined easily. In recent years, many nmr studies have been carried out on trimethyltin carboxylates[6, 7] and dimethyltin diacetates,[33] but none of the dimethylchlorotin carboxylates has been examined. Table 3 includes the proton chemical shifts and proton-tin coupling constants for dimethylchlorotin carboxylates determined during this work.

The observed chemical shifts can be explained as a function of the screening constants of the substituents while the coupling constant values reflect the differences in the state of hybridization[3, 4] and the coordination number of the tin.[35] There is a systematic decrease in the screening constant of the CH_3 protons when methyl groups are successively displaced by the more electronegative chlorine atoms or acetyl groups on tin.[28, 34, 36-38] The $Sn-CH_3$ coupling constants, $J_{^{117}Sn-CH_3}$ and $J_{^{119}Sn-CH_3}$, increase with increasing electronegativity of the substituents and with the coordination number of tin. For the trimethyltin carboxylates,[34]

TABLE 3. Proton NMR Spectra of Dimethylchlorotin Carboxylates, $(CH_3)_2SnClO\overset{O}{\overset{\|}{C}}R$

R	δ_{CH_3-Sn}	$\delta_{O\overset{O}{\overset{\|}{C}}CH_nX_{3-n}}$	$J_{^{119}Sn-CH_3}$	$J_{^{117}Sn-CH_3}$
CH_3	1.075[a]	1.975	86	83
	1.160[b]	2.185	75	72.3
CH_2Cl	1.175[a]	4.333	90	86.5
	1.205[b]	4.210	77.5	74
$CHCl_2$	1.192[a]	6.550	91	87
	1.265[b]	6.060	77	73.5
CCl_3	1.209[a]		92	88
	1.283[b]		77	73.5
CH_2Br	1.100[a]	3.891	88	83
	1.230[b]	3.990	75.8	73.2
CH_2I	1.083[a]	3.687	88	84
	1.185[b]	3.820	77.5	73.8
CF_3	1.150[a]		88	84
	1.250[b]		72.3	69.5
C_2F_5	1.117[a]		88	84
	1.250[b]		74	71
C_3F_7	1.113[a]		90	86
	1.250[b]		74.5	71
$CClF_2$	1.200[a]		92	88
	1.260[b]		75	72

a D_6-acetone for solvent. TMS used as internal reference

b $CHCl_3$ for solvent. Recalibrated with $\delta_{CHCl_3} = 7.35$

TABLE 3. Proton NMR Spectra of Dimethylchlorotin Carboxylates, $(CH_3)_2SnClO\overset{O}{C}R$

R	δ_{CH_3-Sn}	$\delta_{O\overset{O}{\|}CCH_nX_{3-n}}$	$J_{^{119}Sn-CH_3}$	$J_{^{117}Sn-CH_3}$
CH_3	1.075[a]	1.975	86	83
	1.160[b]	2.185	75	72.3
CH_2Cl	1.175[a]	4.333	90	86.5
	1.205[b]	4.210	77.5	74
$CHCl_2$	1.192[a]	6.550	91	87
	1.265[b]	6.060	77	73.5
CCl_3	1.209[a]		92	88
	1.283[b]		77	73.5
CH_2Br	1.100[a]	3.891	88	83
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CH_2I	1.083[a]	3.687	88	84
	1.185[b]	3.820	77.5	73.8
CF_3	1.150[a]		88	84
	1.250[b]		72.3	69.5
C_2F_5	1.117[a]		88	84
	1.250[b]		74	71
C_3F_7	1.113[a]		90	86
	1.250[b]		74.5	71
$CClF_2$	1.200[a]		92	88
	1.260[b]		75	72

[a] D_6-acetone for solvent. TMS used as internal reference

[b] $CDCl_3$ for solvent. Recalibrated with $\delta_{CHCl_3} = 7.35$

$J_{^{119}Sn-CH_3}$ occurs around 59 Hz, thus in the vicinity observed for four-coordinated systems, e.g., tetramethyltin, J = 54.0 Hz and trimethyltin chloride, J = 58.5 Hz. Therefore, these carboxylates exist as monomers in nonpolar solvents.[6,7] In established five-coordinated tin compounds, such as the pyridine adduct of trimethyltin chloride,[35,39] or trimethyltin chloride in D_2O, the $Sn-CH_3$ coupling increases to 67.0 and 70.7 Hz, respectively. For dimethyltin diacetate, which contains six-coordinated tin based on COO- vibration frequencies in the infrared spectrum,[33] the $^{119}Sn-CH_3$ coupling constant is 82.5 Hz. Thus, the magnitude of the coupling constant can be used as a diagnostic tool in predicting the coordination number of tin in the dimethylchlorotin derivatives.

Since the $^{119}Sn-CH_3$ coupling constants for these new dimethylchlorotin carboxylates fall in the range 73-77 in $CHCl_3$ solution, the structure is one in which the tin atom is five-coordinated[40] as was suggested for $R_2Sn(Cl)O_2CCH_3$[16] (R = Et, n-Pr, n-Bu); while in D_6-acetone ($J_{^{119}Sn-CH_3}$ = 80 Hz), the tin must be six-coordinated resulting from the coordination of the carbonyl oxygen of acetone.

The linear relationship between the degree of s-character in the tin orbitals directed toward carbon and the coupling constants have been studied in detail by Holmes and Kaesz[34] and van der Kelen[29]. Interpolation from the function[34] relating $J_{^{119}Sn-CH_3}$ to the apparent s-character of the tin-atom orbital in the Sn-C bond indicates 39% s-character for the J value of 77 Hz in $CHCl_3$ solution and 43% s-character for 88 Hz in D_6-acetone solution which supports the above penta- and hexa-coordinated models for the dimethylchlorotin carboxylates.

Proton nuclear magnetic resonance measurements on the dimethylchlorotin carboxylates also show several other important features: the chemical shifts of $(CH_3)_2Sn$ protons show very little change in the deshielding of the methyl protons with increasing electron withdrawing ability of the R groups. The inductive effect predominates in the series R = CH_3, CH_2Cl, $CHCl_2$, CCl_3 since there is a regular decrease of the screening constant for RCOO- protons with increasing number of halosubstituants. Also, the inductive effect shows in the chemical shifts of RCOO- protons in the series CH_2Cl, CH_2Br, CH_2I. In this series, the tin-proton coupling constants show an irregular change, while they are essentially unaffected by increasing the number of chlorine substituents. The anisotropy effect must be the main contributing factor in the series R = CF_3, CF_2Cl, CCl_3.

Infrared Spectra

The completely rigorous assignment of the bands to their respective normal modes is impossible for these complex compounds. However, some assignments can be made by referring to the spectra of the corresponding sodium salts,[41,42] the trimethyltin carboxylates,[6, 8, 43] the dimethyltin diacetates,[33] and methyltin chlorides.[43-47] Particularly pertinent to this work is the Raman spectrum of $((CH_3)_2SnCl)^+$ (C_{2v}) as given for $(CH_3)_2SnCl_2$ in HCl solution.[46] Corresponding peaks can be found in the infrared and Raman spectra of dimethylchlorotin acetate (taken as representative). Many of the remaining bands may be identified by comparing with the spectrum of $NaOC(O)CH_3$ as shown in Table 4.

TABLE 4. Infrared and Raman Spectra of

$(CH_3)_2SnClO_2CCH_3$, $(CH_3)_2SnCl_2$ and NaO_2CCH_3

	$(CH_3)_2\overset{Cl}{Sn}O\overset{O}{C}CH_3$		$(CH_3)_2SnCl_2$		$NaO\overset{O}{C}CH_3$[41]
	IR[a,b]	Raman[c]	Raman[46] (in 9M HCl) ($(CH_3)_2SnCl^+$)	IR[43][b]	IR
$\nu_{a,CH}$	3014vw	3022 w	3025		2989
$\nu_{s,CH}$	2923 w	2930 m	2930		2936
	2852vw				
ν_{a,CO_2}	1550s	1572vw			1578
δ_{a,CH_3}	1450s	1453vw			1443
	1430s	1432vvw			1430
$\delta_{s}CH_3$	1403s	1413vvw		1410	1414
ν_{s,CO_2}		1352vvw			
δ_{CH_3-Sn}	1210w	1214 m			
	1196vw	1202 w	1204	1204	
CH_3 rock	1047vw				1042
	1015m				1009
ν_{C-C}	950vw	954w			924
Sn-CH_3 rock	815 sh			786	
	794 s			745	
COO scissor	685 s				646
COO out plane bend	613 w				615
$\nu_{a,Sn-C}$	576 m	577w	577	567	
$\nu_{s,Sn-C}$	527 w	532 vvs	518	575	
COO rock	493 w	500 w			460
ν_{Sn-Cl}	324 s	319 s	325		
	285 w	282 w			

TABLE 4. (con.)

Raman
217 w
200 w
149 m

a. For original spectrum in NaCl region, see Okawara[43]

b. KBr disc

c. Neat solid

The characteristic absorptions due to carbonyl asymmetric and Sn-C asymmetric and symmetric stretching frequencies and Sn-Cl vibrations are listed in Table 5. The fact that both asymmetric and symmetric stretches are observed for Sn-C indicates the presence of a nonlinear C-Sn-C moiety. Since it is difficult to assign $_{sCO_2}$ frequencies in the 1400-1300 cm^{-1} region in which C-H deformations also appear, these are omitted even though separation of $_{aCO_2}$ and $_{sCO_2}$ is used to detect the types of carboxyl groups by some authors.[48,49] The $_{aCO_2}$ frequencies increase generally with increasing electron withdrawing ability in the substituted carboxylate groups. The nujol mull spectra are essentially the same as spectra obtained from samples in KBr discs. In comparison of solution and solid state spectra, the $_{aSn-C}$, $_{sSn-C}$, $_{Sn-Cl}$ vibrations do not show significant changes.

However, the carbonyl vibrations do shift to higher energies for the nonfluorinated carboxylates (R = CH_3, CH_2Cl, $CFCl_2$, CCl_3, CH_2Br, CH_2I), e.g., for $(CH_3)_2ClSnO_2CCH_3$ the band for the asymmetric carbonyl shifts to 1598 from 1550 cm^{-1}. For $(CH_3)_3SnO_2CCH_3$,[7,10] with $_{aCO_2}$ at 1658 cm^{-1} in $CHCl_3$ solution shifted from 1570 cm^{-1} in the solid, the shift is that expected when changing from a monomeric ester form in solution to a bridged polymeric species (5-coordinate) in the solid. Also, from the spin-spin coupling constant, $J_{^{119}Sn-CH_3}$ = 58.2[50], for $(CH_3)_3SnO_2C(CH_3)$ in $CDCl_3$ solution, the tin is four-coordinated which indicates a normal ester. Because of the analogous infrared shift and the Sn-CH_3 coupling constants in the 75 Hz region for the nonfluorinated carboxylates in $CHCl_3$, it is likely that a monomeric non-ester acetoxy form is present, and tin has a coordination number of five. Cryoscopic measurements of molecular weight of $(C_2H_5)_2ClSnO_2CCH_3$ shows that it is monomeric in non-

TABLE 5. Characteristic Absorptions of Dimethylchlorotin Carboxylates $(CH_3)_2SnClO_2CR$

R	ν_{aCO_2}	ν_{aSn-C}	ν_{sSn-C}	ν_{Sn-Cl}
CH_3	1550[a]	576	527	324
	1548[b]	575	525	324
	1598[e]	560	523	*
	1572[d]	577	532	319
CH_2Cl	1598[a]	580	508	340
	1600[b]	580	510	338
	1635 [c]	580	530	340
$CHCl_2$	1624[a]	580	524	348
	1643 [c]	548	528	345
	1632[d]	586	528	350
CCl_3	1635[a]	583	530	340
	1635[b]	586	535	335
	1650 [c]	568	525	347
CH_2Br	1590[a]	585	528	340
	1590[b]	585	526	340
	1620 [c]	580	527	*
CH_2I	1550[a]	573	503	316
	1553[b]	573	510	316
	1610[c,e]	573	527	*
CF_3	1691[a]	580	521	345
	1690[b]	581	524	347
	1692 [c]	567	526	350
	1670[d]	578	526	347
C_2F_5	1686[a]	586	524	360
	1690[b]	588	525	360
	1690 [c]	570	526	348

TABLE 5. (con.)

	ν_{aCO_2}	ν_{aSn-C}	ν_{sSn-C}	ν_{Sn-Cl}
C_3F_7	1655[a]	588	525	355
	1668[b]	590	524	355
	1685[c]	568	570	348
	1671[d]	581	527	334
CF_2Cl	1688[a]	545	517	349
	1687[b]	555	527	340
	1680[c]	564	526	350

a. KBr discs. b. Nujol mull. c. CH_2Cl_2 solution. d. Raman

* Not observed e. $CHCl_3$ solution

polar solvents (benzene).[16] An infrared shift for ${}_{aCO_2}$ to higher energy is also observed (1550 to 1600 cm^{-1}) suggesting a nonester type of acetoxy group. This would support a monomeric chelate structure for the new compounds. Preliminary molecular weight determinations in $CHCl_3$ are inconclusive, although they do point to monomeric structures in solution, e.g., the experimental values exceed theoretical for monomeric species by about 25% for $(CH_3)_2ClSnO_2CCH_2I$ and $(CH_3)_2ClSnO_2CHCl_2$, but they are concentration independent.

All bands in the solution infrared spectra change proportionately with concentration which suggests that no monomer-polymer equilibrium exists.

For the compounds which have fluorine-containing carboxylate groups it should be noted that essentially no shift occurs in ${}_{aCO_2}$ in going from solid to CH_2Cl_2 solution with the exception of the C_3F_7 compound. This suggests that the structure for compounds with R = CF_3, C_2F_5, and CF_2Cl is not greatly different in solution. Nmr data point to five-coordinated systems in solution and Mössbauer to five-coordinated tin in the solids (see next section). Molecular weight determinations on $CF_3CO_2SnCl(CH_3)_2$ in $CHCl_3$ were: 10mg/cc, 919; 30 mg/cc, 927; and 60 mg/cc, 914. The formula weight for $CF_3CO_2SnCl(CH_3)_2$ is 297.5. Based on the experimental molecular weight, the compound must be at least trimeric or perhaps polymeric in chloroform solution. Similar results are obtained for the C_3F_7 case where experimental molecular weight values ranging between 761 and 1,433 were obtained (monomeric = 396). This then confirms the existence of these compounds in the solid state as polymeric structures with bridging COO- groups.

Mössbauer Spectra

The ^{119} Mössbauer isomer shifts and quadrupole splittings provide a good tool for the study of the coordination in tin compounds. The isomer shift of the ${}^{119}Sn$ resonance is related to the density of 5s electrons at the tin nucleus and the quadrupole splitting gives a measure of the deviation from cubic symmetry of the electron distribution about the tin atom. In Table 6 are found the ${}^{119}Sn$ Mössbauer data recorded at 80°K for some of the dimethylchlorotin carboxylates. The spectrum of each compound was a well-resolved doublet. The isomer shift ( ) values, relative to SnO_2, fall in the region 1.34 - 1.45 mm/sec and the quadrupole splittings ( ) values in the range 3.58 - 3.96 mm/sec. As is the case for dialkyltin dicarboxylates, no noticeable Mössbauer effect is present at ambient temperature.[51] Although room temperature Mössbauer effects reportedly reflect the presence of polymeric structures[52,53], the dicarboxylates still doubtlessly are polymeric even though the association is probably weak. The values for $(CH_3)_2ClSnO_2CR$ are slightly higher than those for tetraorganotin compounds and are similar to those of $(CH_3)_3SnO_2CCH_3$[10,14], $(CH_3)_3SnCN$[54] and $(CH_3)_3SnSCN$[54], which have been shown to have a polymeric structure with bridging CO_2, or CN or SCN groups and trigonal bipyramidal configuration around the tin atom.[12, 55, 56] The observed values are quite large and similar to those for compounds having trigonal bipyramidal structures, e.g., trimethyltin acetates,[6,7,10] $(CH_3)_3SnF$,[54] and $(CH_3)_3SnCN$.[54] Based on our Mössbauer data, all of the dimethylchlorotin carboxylates are pentacoordinate, and very likely polymeric in the solid state (i.e., 3.6 mm/sec, whereas for tetracoordinated R_3SnO_2CR' compounds, 2.3 mm/sec).[11]

TABLE 6. Mössbauer data for $(CH_3)_2SnClO_2CR$

Compound R	δ(mm/sec)*	Δ(mm/sec)*	$\rho\left(\frac{\Delta}{\delta}\right)$
CH_3	1.34	3.58	2.67
CH_2Cl	1.38	3.75	2.72
$CHCl_2$	1.45	3.91	2.70
CCl_3	1.45	3.96	2.73
CH_2Br	1.39	3.79	2.73
CF_3	1.44	3.85	2.67
C_2F_5	1.45	3.90	2.69
C_3F_7	1.40	3.83	2.74
CF_2Cl	1.42	3.84	2.70

*Values reproducible to 0.03 mm/sec.

Conclusion

Dimethylchlorotin carboxylates can be easily made by the reaction of trimethyltin chloride with appropriate acids. These compounds have been studied by a variety of spectroscopic methods in the solid state and in solution which cause us to argue as follows:

1) Based on $J_{^{119}Sn-CH_3}$ values obtained on solutions in $CHCl_3$ and on quadrupole splitting values for the solids, the compounds contain pentacoordinated tin. The position of $_{aCO_2}$ in the infrared spectra (solid or solution) is far removed from the usual organic ester frequency (1740 cm^{-1}) which suggests bridge or chelate COO- groups in pentacoordinated compounds.

2) For the nonfluorinated carboxylates, solution in $CHCl_3$ or CH_2Cl_2 is accompanied by a shift to higher frequencies of $_{aCO_2}$ which indicates a change of structure. Molecular weights done on our compounds are not convincing but the closely related molecule $(C_2H_5)_2ClSnO_2CCH_3$, for which a similar frequency shift occurs, is monomeric in solution. This is strong evidence for chelate monomers in solution and for COO-bridged polymeric structures in the solid.

3) For the fluorinated carboxylates, $_{aCO_2}$ is essentially zero when solution in $CHCl_3$ or CH_2Cl_2 occurs which indicates no change in structure. Molecular weight determinations on $(CH_3)_2ClSnO_2CCF_3$ point convincingly to polymers in solution (C_3F_7 is somewhat less certain) and thus to COO- bridged polymeric solids, hence eliminating pentacoordinate chelate monomers in the solid.

4) Comparison of our Mössbauer data with that of compounds of known structure also strongly points to a polymeric solid state for all of the dimethylchlorotin carboxylates.

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FLUOROPHOSPHORUS AZIDES*

by

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Abstract. Mixed phosphorus chloride fluorides undergo ready reaction with sodium azide to provide an excellent route to new azide-containing compounds, including F_2PN_3, $F_2P(O)N_3$, $FP(O)(N_3)_2$, and $FP(S)(N_3)_2$. In addition, the previously reported $F_2P(S)N_3$ is easily prepared by this method. F_2PN_3 has particularly limited stability.

Azidobis(trifluoromethyl)phosphine, which is modestly stable at 0° and decomposes slowly at 20°, was prepared some years ago by reaction chlorobis(trifluoromethyl)phosphine with lithium azide.[1] At 50°, slow decomposition occurs to give phosphonitriles, $((CF_3)_2PN)_x$. Difluorothiophosphoryl azide results from μ-oxo-bis(thiophosphoryl difluoride) with sodium azide.[2] Apparently this compound is stable and can be handled without difficulty. Although a number of organophosphorus azides are known and found to be fairly stable, there appear to be no others which also contain fluorine or a fluorine-containing species as a ligand.

In our synthesis, new azides result from P(III) and P(V) chloride fluorides and sodium azide

$$F_{3-x}P(E)Cl_x + xNaN_3 \xrightarrow{\text{solvent}} F_{3-x}P(E)(N_3)_x + xNaCl$$

$x = 1,2$; $E = O, S$

$X = 1$: E = absent

or hydrazoic acid displaces hydrofluoric acid from a monoazide

$$F_2P(O)N_3 + HN_3 \xrightarrow{60^\circ} FP(O)(N_3)_2 + HF$$

The role played by the solvent in the former reactions is an important one in some cases, but one which is not clearly understood. In other instances, e.g., with $F_2P(O)Cl$, reaction occurs to give a 76% yield of the monoazide without solvent. Mass spectra are particularly useful in confirming these mono- and di-azides since a molecule ion is observed in every case.

Experimental

General Methods.--A standard Pyrex vacuum system equipped with a Heise Bourdon tube gauge was used in all reactions. Purification of the azides was obtained either through trap-to-trap fractionation or by fractional codistillation.[3] Molecular weights were determined by the method of Regnault. Infrared spectra were recorded with either a Perkin-Elmer Model 621 or a Perkin-Elmer Model 457 spectrophotometer at 15 Torr in a cell of 5 cm path length with KBr windows. A Hitachi Perkin-Elmer Model RMU-6E spectrometer operating at an ionization potential of 70 eV at 25° was used to record mass spectra. Low resonance ^{19}F nuclear magnetic resonance spectra were obtained at 94.1 mHz with a Varian HA-100 spectrometer. The ^{31}P nuclear magnetic resonance spectra were recorded at 40.5 mHz on the latter instrument. For fluorine, trichlorofluoromethane was the internal reference in 25% solutions. For phosphorus, the external reference was 85% phosphoric acid. In addition, the di-azides were diluted to give 50% solutions in acetonitrile, while the mono-azides were run neat.

Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrometer on samples at pressures less than one Torr in a 10 cm quartz cell. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Reagents.--Chlorodifluorophosphine[4], and $F_2P(O)Cl$[5] were prepared by methods described in the literature. Sodium azide, obtained from K and K Laboratories, was purified by dissolving the salt in water, acidifying to litmus with HCl and precipitating the azide with acetone. After the salt was filtered, washed, and dried at 100°, it appeared to be free of hydrolysis products and reacted cleanly with the phosphorus halides. Hydrazoic acid is obtained in 80% yield from the reaction of gaseous HCl with sodium azide at 25° for 24 hr.

Both $FP(S)Cl_2$ and $F_2P(S)Cl$ are prepared in relatively high yields by modifying the method for PSF_3.[6] Fluorination of $SPCl_3$ with NaF at 140° for 0.5 hr. with sulfolane as solvent gives average yields of 30, 50 and 20% for the mono-, di-, and trifluoride, respectively. These products are easily separated with traps at -91, -120, and -183°. Purity was checked by comparison with published infrared spectra.[7]

Caution. Although we experienced minimal difficulties in handling these azides, they should be treated as potentially hazardous materials and prepared in less than 10 mmol amounts (much less than this for PF_2N_3).

General Preparative Procedure for P(III) and P(V) Azides.

Essentially the same method can be employed in the preparation of all of the new azides, although the success of the reaction seems to depend largely upon the presence of and type of solvent. In general, the appropriate P(III) or P(V) compound is condensed onto sodium azide which has been carefully dried after recrystallization.

a) Azidodifluorophosphine, F_2PN_3.--Difluorochlorophosphine (5 mmol), condensed onto sodium azide (1g) in one ml of toluene and allowed to react for two hrs at 25°, gives azidodifluorophosphine (4 mmol). The product is purified by trap-to-trap fractionation and is retained in a trap at -120° after passing -78°. (If no solvent is used, a very minor amount of F_2PN_3 forms with the major products, phosphorus trifluoride and nitrogen. When CH_3CN is used as a solvent, reaction takes place immediately on warming to 25° and produces nitrogen and PF_3 quantitatively Despite the low thermal stability of F_2PN_3, in the synthesis involving toluene, the reaction mixture can remain at 25° for more than 24 hrs without a trace of decomposition.) Care must be taken to maintain anhydrous conditions, since the hydrolysis product, HN_3, can be separated from the F_2PN_3 only with great difficulty. The experimentally determined molecular weight is 109.8 (111.0 theor.).

b) Difluorothiophosphoryl azide and fluorothiophosphoryl diazide, $F_2P(S)N_3$ and $FP(S)(N_3)_2$. Difluorothiophosphoryl chloride or fluorothiophosphoryl dichloride (10 mmol) is condensed onto a sodium azide (1g)-acetonitrile (1 ml) slurry at -183°. The reaction was complete on warming to 25° and after trap-to-trap purification either of the azides was obtained in greater than 80% yield. No reaction occurs without acetonitrile. $F_2P(S)N_3$ passes a trap at -63° and stops at -91°. $FP(S)(N_3)_2$ is stopped at -41° after passing a trap at -23°. $F_2P(S)N_3$ has been well characterized after having been prepared from $(F_2P(S))_2O$ + NaN_3.[7]

c) Difluorophosphoryl azide, $F_2P(O)N_3$.--Difluorophosphoryl chloride

(10 mmol) is condensed onto dry, recrystallized sodium azide (1g), warmed to and allowed to remain at 25° for 24 hr . Yields of greater than 76% were isolated from the trap at -78° having passed a trap at -20°. Acetonitrile is not useful as a solvent in this case since it cannot be separated easily from the product. The molecular weight is 127.3 (127.0 theor.) Anal. Calcd. for $F_2P(O)N_3$: F, 29.90; P, 24.40; N, 33.10. Found: F, 29.10; P, 23.80; N, 33.20.

Because of the possible hazardous nature of these compounds, vapor pressure data was obtained for only one compound, $F_2P(O)N_3$. Based on the following data (P_{Torr}, °K): 14.0, 256.7; 24.0, 265.2; 39.5, 273.2; 105.0, 290.7; 126.6, 293.5; 156.5, 298.2; 179.0, 301.5; 208.6, 304.0; 235.3, 307.0; 301.5, 312.5; 310.0, 313.2; 355.0, 316.0; 399.5, 319.0; 411.0, 319.5; 460.0, 321.8; 600.0, 329.0; 659.5, 331.3; 761.5, 335.2; 801.0, 336.2, the boiling point is 62°. From Clausius-Clapeyron equation, ΔH_{vap} = 6.9 kcal/mole and the Trouton' constant is 20.6 eu. The vapor pressure-temperature relationship is given by the equation $\log P_{Torr} = 8.56 - (1902/T°K)$.

d) Fluorophosphoryl diazide, $FP(O)(N_3)_2$.--This compound may be prepared by either of two methods. 1) Difluorophosphoryl chloride (10 mmol) is condensed onto 1g of sodium azide which has been exposed to the atmosphere and thus contains hydrolysis products and allowed to remain at 25° for 24 hrs. Fluorophosphoryl diazide results in greater than 60% yield. 2) An excess of hydrazoic acid (4 mmol) is condensed with difluorophosphoryl azide (1 mmol) and held at 60° for one hr. 93% of the latter compound was consumed and a 46% yield of the diazide was obtained. In addition, an unidentified white solid coated the walls of the vessel. Infrared spectra indicate the presence of bands attributable to N-H, N_3, P=O, and P-F stretching frequencies. The fluorophosphoryl diazide is isolated in a trap at -30° after having passed a trap at -12°. Anal. Calcd. for $FP(O)(N_3)_2$: F, 12.66; P, 20.66; N, 56.00. Found: F, 12.70; P, 20.80; N, 56.01.

Infrared, mass and nmr spectra of these azides are recorded in Tables 1, 2, and 3, respectively.

Results and Discussion

All of the new azides are colorless liquids at 25° and freeze to a glass when cooled. They are extremely sensitive to small amounts of water (e.g., moist air) and hydrolyze to yield hydrazoic, hydrofluoric and various phosphoric acids with the exception of F_2PN_3 which gives μ-oxo-bis(difluorophosphine) as the only phosphorus -containing product. The hydrolysis products were identified by comparing their infrared spectra with published data. The phosphorus(V) azides are thermally stable to at least 100° but, upon decomposition, the major products are phosphorus trifluoride, phosphoryl fluoride (or thiophosphoryl fluoride) and nitrogen.

Azidodifluorophosphine is unstable thermally and photolytically, and has on occasion exploded spontaneously at 25°. In all cases, the decomposition products are nitrogen, phosphorus trifluoride and various cyclic phosphonitrilic polymers of the type $(F_2PN)_x$ ($x \leq 6$). These polymers were separated by fractional codistillation and identified by comparison of their mass and infrared spectra with those reported in the literature.[8-10] Azidodifluorophosphine is explosively sensitive to sudden changes in pressure, e.g., expansion into a vacuum or a sudden surge when boiling.

TABLE 1

INFRARED SPECTRA, cm^{-1}

F_2PN_3	$F_2P(O)N_3$	$FP(O)(N_3)_2$	$F_2P(S)N_3$	$FP(S)(N_3)_2$	
2140 s	2175 s	2105 vs	2195 vs	2175 vs	ν_{N_3}
	1365 s	1330 vs			$\nu_{P=O}$
1260 s 1280	1265 s	1270 vs, br	1280 s	1262 s	ν_{N_3}
955 s	950 sh	910 s	955 vs	925 m	ν_{P-F}
835 s, br	907 s, br		930 sh		ν_{P-F}^{sym}
740 s	777 m	805 s	825 s	825 m	ν_{P-N}^{asym}
		760 w		775 m	
613 s	600 m	610 m	660 vw		
		570 w	575 mw	605 vw	
	430 m	430 s	415 mw	480 vvw	
		418 sh			

TABLE 2. MASS SPECTRA

m/e	Species	Relative Abundance				
		F_2PN_3	$F_2P(O)N_3$	$F_2P(S)N_3$	$FP(O)(N_3)_2$	$FP(S)(N_3)_2$
31	P	55.9	20	3.6	7.5	
42	N_3	16.2	44	4.5	37.6	40.5
50	PF	55			36.9	
63	PS			6.3		
64	FPN	51.7				
66	FPO		100			
69	F_2P	100	22	100		
77	SPN					100
80	$FP(O)N$				34.2	
82	FPS			3.6		
83	F_2PN	75.7				
85	F_2PO		60			
92	FPN_3	66.7			17.1	77.4
99	$F_2P(O)N$		68			
101	F_2PS			17.1		
108	$FP(O)N_3$		32			
111	F_2PN_3	27.9				
115	$F_2P(S)N$			2.7		
122	$FP(O)N_4$				43.8	
124	$FP(S)N_3$			1.8		9.5
127	$F_2P(O)N_3$		79			
131	$P(O)N_3)_2$				2.1	
133	$P(S)N_5$					7.1
134	$FP(N_3)_2$					4.8
138	$FP(S)N_4$					3.2
143	$F_2P(S)N_3$			89.1		
150	$FP(O)(N_3)_2$				100	
166	$(F_2PN)_2$	1.8				
	$FP(S)(N_3)_2$					57.1

TABLE 3.

^{19}F and ^{31}P NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	^{19}F (ɸ*)	^{31}P (ppm)	J_{P-F} (Hz)
F_2PN_3	57.5	----	1280
$F_2P(O)N_3$	73.5	15.3 tr	1042
$FP(O)(N_3)_2$	60.3	12.6 d	1020
$F_2P(S)N_3$	42.9^{2}	-56.3 tr	1140
$FP(S)(N_3)_2$	38.8	-65.6 d	1102

Fluorothiophosphoryl diazide has exploded at -183° which may be due to transformation from a glass-like material to a crystalline substance at that temperature. However, traces of hydrazoic acid may have been responsible for the observed explosions.

The ^{19}F and ^{31}P nmr data are recorded in Table 3. The ^{19}F spectra consist of simple doublets centered in the 39 to 74 ϕ^* range with J_{P-F} varying between 1020 to 1140 Hz for P(V) azides and J_{P-F} is 1280 Hz for F_2PN_3. The ^{31}P spectra are well resolved triplets or doublets depending on the presence of two or one fluorine atom(s). It should be noted that for both ^{19}F and ^{31}P chemical shifts the diazides and thiophosphoryl compounds resonate at lower field than monoazides and phosphoryl compounds, respectively. Spin-spin coupling interactions also decrease with number of azide groups. This would suggest greater electron delocalization from the phosphorus and fluorine atoms into the d orbitals of sulfur or π-system of the azide moiety. No ^{31}P nmr data are available for F_2PN_3 because, despite prerun checking for thermal stability, the compound detonated destroying the phosphorus probe.

The covalent nature of these azides is demonstrated by the occurence of two bands in their ultraviolet spectra similar to those of typical alkyl azides.[11, 12] However, due to inductive effects of the fluorophosphoryl or fluorothiophosphoryl groups, there is a marked shift to higher energies. Our values agree well with those reported by Ruff[13] for FSO_2N_3 ([illegible] nm) and $CF_3SO_2N_3$ (195, 238 nm). These bands arise from $\pi_y \longrightarrow \pi_x^*$ and $n_x \longrightarrow \pi_y^*$ transitions with the latter occurring at higher energy. Both transitions involve charge transfer from electron pairs largely localized on the nitrogen atom bonded to the phosphorus into antibonding π-orbitals on the other two nitrogen atoms.[11]

Mass spectral data (Table 2) are particularly helpful in confirming the existence of these five new azides since all fragment at 70 eV to give a molecular ion with an intensity of at least 28% base, e.g., F_2PN_3, 28%; $F_2P(O)N_3$, 79%; $F_2P(S)N_3$, 80%; $FP(O)(N_3)_2$, 100%, and $FP(S)(N_3)_2$, 57%. In the case of F_2PN_3, a fragment at m/e 166 is very likely attributable to $(F_2PN)_2$ although this species is not observed when the parent compound is decomposed either thermally or photolytically. As would be expected, the heavier fragments are due primarily to loss of nitrogen or fluorine. Comparison of the fragmentation pattern for $F_2P(S)N_3$ found in this work with that reported at 100 eV[2] shows very good agreement.

Some band assignments in the infrared spectra (Table 1) can be made. However, because of the disagreement in the literature regarding assignment of $\nu_{P=S}$, we have not attempted at this time to unequivocally make these assignments and work is continuing in this area. $\nu_{P=N}$ should be regarded as entirely tentative.

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Bis(hexafluoroisopropylidenimino)disulfide, Chloro(hexafluoroisopropylidenimino)sulfur(II) and Some Derivatives

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Hexafluoroisopropylideniminolithium reacts with disulfur dichloride to give bis(hexafluoroisopropylidenimino)disulfide which undergoes two different types of reactions with chlorine to yield bis(2-chlorohexafluoroisopropylimino)sulfur(IV) and chloro(hexafluoroisopropylidenimino)sulfur(II). The latter gives new sulfur(II) compounds with reactants that contain active hydrogen or with silver salts. $(CF_3)_2C=NSCl$ is readily converted to $(CF_3)_2CFN=SF_2$ by fluorinating agents.

The lithium salt of hexafluoroisopropylidenimine has been shown to react with compounds that contain labile halogens (Cl, F) to introduce the hexafluoroisopropylidenimino moiety intact.[2-5] The compounds formed are most often slightly volatile, yellow liquids or sublimable solids. In this work, advantage has been taken of the high reactivity of $LiN=C(CF_3)_2$ with disulfur dichloride to prepare bis(hexafluoroisopropylidenimino)disulfide in good yield. The reactions of this disulfide are somewhat more complicated than those of the simpler, saturated fluorinated alkyl disulfides in that the former has three reactive sites. Just as thermally induced chlorination of CF_3SSCF_3 leads to CF_3SCl, so heating chlorine with $((CF_3)_2C=N)_2S_2$ gives $(CF_3)_2C=NSCl$.[6] However, when the latter mixture is photolyzed through quartz, elemental sulfur is formed accompanied by double bond shifts and chlorination to give bis-(2-chlorohexafluoroisopropylimino)sulfur(IV), $(CF_3)_2CClN=S=NCCl(CF_3)_2$. Although Seel has fluorinated Cl_3SCl stepwise to CF_3SF with KF at 150° [6] or with HgF_2 solely to CF_3SF and its dimer at 130°, [7] and CF_3SSCF_3 is readily fluorinated to CF_3SF_3 with AgF_2, [8] analogous reactions do not occur with $(CF_3)_2C=NSCl$ or $((CF_3)_2C=N)_2S_2$ with fluorinating agents. Either no reaction occurs or fluorination with concomittant double bond shift takes place to give high yields of $(CF_3)_2CFN=SF_2$. [9] $(CF_3)_2C=NSCl$ reacts typically with compounds containing active hydrogen, e.g., NH_3, $(CH_3)_2NH$ and CH_3SH, or with silver salts, e.g., AgCN, to give the mono-substituted product in each case, R_fNH_2, $R_fN(CH_3)_2$, R_fSSCH_3, and R_fCN (where R_f = $(CF_3)_2C=NS$).

Experimental Section

Reagents.--Hexafluoroacetone, phosphorus oxychloride, and n-butyl lithium in hexane were obtained from Allied Chemical, Wilshire Chemical and Alfa Inorganic Chemicals. Practical disulfur dichloride (Eastman Organic) was purified by distillation under an atmosphere of dry nitrogen. The fraction boiling between 123-125° (690 Torr) was retained. Chlorine, silver cyanide and dimethylamine were received from J.T. Baker Co., Eastman Organic and Matheson Co.

General Methods.--Gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus under high vacuum. Infrared spectra were run on a Perkin-Elmer 457 spectrometer with a Pyrex glass cell of 5 cm length equipped with potassium bromide windows. Fluorine 19 nmr spectra were obtained on a Varian HA-100 spectrometer operating at 94.1 mHz and proton nmr spectra on a Varian A-60 spectrometer. Trichlorofluoromethane and tetramethylsilane were used as internal references. A Hitachi Perkin-Elmer RMU-6E mass spectrometer operating at an ionization potential of 70 eV was used to obtain mass spectra. Molecular weights were determined by Regnault's method in a vessel fitted with a Fischer-Porter Teflon stopcock after measuring pressures on a Heise-Bourdon tube gauge. For vapor pressure measurements, a Kellogg-Cady apparatus [10] was employed for compounds that react with mercury. Otherwise, an isoteniscopic method was employed.

Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Samples which were analyzed in house were fused with sodium. Chlorine and sulfur were determined gravimetrically as silver chloride and barium sulfate, and fluorine as fluoride ion with a specific ion electrode. Infrared and nmr spectral data as well as thermodynamic and elemental analyses data are given in Tables I-III.

Bis(hexafluoroisopropylidenimino)disulfide, $((CF_3)_2C=N)_2S_2$. In an inert atmosphere box, 6 ml of 2.34 molar (14 mmol) n-butyl lithium in hexane was transferred by syringe to a 100 ml Pyrex bulb fitted with a Teflon stopcock. Then, 1.31 g (14 mmol) of $(CF_3)_2C=NH$ was condensed into the bulb at -196° and the vessel was allowed to warm slowly in a dewar from -196° to 25° over a period of 8 hr. The hexane was removed under dynamic vacuum. 0.61 g (4.6 mmol) of S_2Cl_2 and 1.96 g (24 mmol) of 2-methylbutane were condensed onto the $(CF_3)_2C=NLi$ in the vessel at -196°. The vessel was again allowed to warm slowly to 25° (8 hr.). The $((CF_3)_2C=N)_2S_2$ was removed from the vessel at 25° under dynamic vacuum and collected in a U-trap at -20°. Traces of unreacted S_2Cl_2 were

TABLE I

INFRARED SPECTRA

$[(CF_3)_2C=NS]_2$	$(CF_3)_2C=NSCl$	$(CF_3)_2C=NSN(CH_3)_2$	$[(CF_3)_2C(Cl)N=]_2S$
1630 w	1630 m	2980 w	1335 m
1335 s	1330 s	2960 m	1305 m
1260 s	1270 vs	1605 w	1275 sh
1240 sh	1195 vs	1450 w	1250 vs
1200 s	980 s	1380 w	1205 s
980 s	905 m	1347 m	1185 sh
730 m	750 m	1255 s	985 m
715 m	715 s	1190 s	960 s
	540 w	980 m	940 sh
	490 m	725 m	915 m
	455 w	680 w	750 m
			720 m

$(CF_3)_2C=NSNH_2$	$(CF_3)_2C=NSC\equiv N$	$(CF_3)_2C=NSSCH_3$
3460 w	1640 w	2950 w
1615 w	1335 m	1610 w
1340 m	1265 s	1440 w
1260 s	1205 s	1420 w
1195 s	990 m	1335 m
982 m	745 m	1250 s
715 m	730 sh	1190 s
490 w		990 m
		955 sh
		735
		$710^{d,m}$

TABLE II

^{1}H and ^{19}F NMR SPECTRA

Compound	^{19}F NMR (ppm)	^{1}H NMR (ppm)(ν)
$[(CF_3)_2C=NS]_2$	67.7	---
$[(CF_3)_2C(Cl)N=]_2S$	74.1	---
$(CF_3)_2C=NSCl$	60.8 68.4	---
$(CF_3)_2C=NSN(CH_3)_2$	65.4 67.1	7.3
$(CF_3)_2C=NSNH_2$	68.6	6.7
$(CF_3)_2C=NSC\equiv N$	63.1	---
$(CF_3)_2C=NSSCH_3$	74.3	7.4
$(CF_3)_2C=NSCH_3$	69.3	---

TABLE III. ELEMENTAL ANALYSES AND THERMODYNAMIC DATA

Compound	MW	Elemental Analyses S	C	H	F	N	Cl	BP °C	ΔH_v kcal/mole	ΔS_v eu	$\log P_{Torr} = A - B/T\,°K$ A	B
$((CF_3)_2C{=}N)_2S_2$		16.32 (16.32)*	18.65 (18.35)		58.6 (58.3)	7.14 (7.15)		144.4	11.0	26.4	8.66	2415
$((CF_3)_2CClN)_2S$		7.39 (7.43)	18.1 (16.7)		52.4 (52.8)	6.30 (6.50)	16.44 (16.47)	131.5	10.4	25.7	8.50	2274
$(CF_3)_2C{=}NSCl$	230.9 (231.5)	13.69 (13.85)	15.48 (15.60)		50.9 (49.3)	6.12 (6.06)	15.08 (15.31)	95.4	9.0	24.3	8.17	1960
$(CF_3)_2C{=}NSN(CH_3)_2$	238.8 (240.2)	13.48 (13.34)	24.68 (25.00)	2.70 (2.52)	47.50 (47.46)	11.80 (11.66)		109.7	9.5	24.7	8.32	2081
$(CF_3)_2C{=}NSNH_2$	210.0 (212.1)	15.23 (15.12)	17.05 (16.98)	1.20 (0.94)	53.90 (53.75)	13.20 (13.20)		114.5	9.0	23.1	8.17	2052
$(CF_3)_2C{=}NSCN$	222.8 (222.1)	14.32 (14.43)			50.20 (51.30)			81.0 (321 Torr)				
$(CF_3)_2C{=}NSSCH_3$	242.0 (243.2)	26.35 (26.37)	19.51 (19.76)	1.12 (1.23)	46.62 (46.88)	5.72 (5.76)						
$(CF_3)_2C{=}NSCH_3$			22.80 (22.75)	1.50 (1.42)	54.4 (54.0)	6.57 (6.63)						

( )* Calculated

removed by shaking with mercury for 0.5 hr. Final purification of $((CF_3)_2C=N)_2S_2$ was effected by gas chromatography using a 22 ft column containing 5% SF-1265 on Chromosorb P. A yield of 4.1 mmol (89%) was obtained.

Bis(2-chlorohexafluoroisopropylimino)sulfur(IV), $(CF_3)_2CClN=S=NCCl(CF_3)_2$. A quartz vessel (220 ml) which contained 1.89 g (4.8 mmol) of $((CF_3)_2C=N)_2S_2$ and 0.507 g (7.2 mmol) of chlorine was irradiated for 48 hr with a Model 30620 Hanovia ultraviolet lamp. The product was isolated in a U-trap at -20° during trap-to-trap distillation and purified by gas chromatography using a 22 ft 5% SF-1265 on Chromosorb P column. A yield of 72% (3.5 mmol) was obtained. $[(CF_3)_2CClN=]_2S$ is also produced when $(CF_3)_2C=NSCl$ is photolyzed.

Chloro(hexafluoroisopropylidenimino)sulfur(II), $(CF_3)_2C=NSCl$. By standard vacuum methods, 2.71 g (6.9 mmol) of $((CF_3)_2C=N)_2S_2$ and 0.735 g (10.5 mmol) of chlorine were condensed into a 100 ml Pyrex bulb fitted with a Teflon stopcock and heated to 110° for 12 hr in an oil bath. During trap-to-trap distillation the compound stopped in a U-trap at -78°. After gas chromatography using a 1.5 ft 20% Kel-F on Chromosorb P column, 13.0 mmol (94%) of $(CF_3)_2C=NSCl$ was isolated. $(CF_3)_2C=NSCl$ is also produced when the two reactants are photolyzed at 2537 A in a Rayonet "Srinivasan-Griffin" photochemical reactor. The yield is much lower and there are numerous other products.

Dimethylamino(hexafluoroisopropylidenimino)sulfur(II), $(CF_3)_2C=NSN(CH_3)_2$. A 100 ml Pyrex bulb containing 0.67 g (2.90 mmol) of $(CF_3)_2C=NSCl$ and 0.32 g (7.3 mmol) of $(CH_3)_2NH$ was allowed to stand at 25° for 12 hr. A

U-trap at -78° retained the compound on trap-to-trap distillation. A yield of 96% (2.8 mmol) was obtained after gas chromatography employing a 1.5 ft 20% Kel-F on a Chromosorb P column.

Amino(hexafluoroisopropylidenimino)sulfur(II), $(CF_3)_2C=NSNH_2$. Starting materials, 0.288 g (1.24 mmol) of $(CF_3)_2C=NSCl$ and 0.052 g (3.10 mmol) of NH_3, were condensed into a 50 ml Pyrex vessel fitted with a Teflon stopcock at -196° and allowed to react at -20° for 1.5 hr. The $(CF_3)_2C=NSNH_2$ stopped in a U-trap cooled to -78° during trap-to-trap distillation and was purified by gas chromatography using a 1.5 ft 20% Kel-F on Chromosorb P column. A yield of 0.162 g (0.77 mmol) of product was isolated (62%).

Cyano(hexafluoroisopropylidenimino)sulfur(II), $(CF_3)_2C=NSC\equiv N$. Using standard vacuum techniques, 0.37 g (1.60 mmol) of $(CF_3)_2C=NSCl$ was condensed onto excess AgCN, which had been dried at 75° under dynamic vacuum, and was allowed to react for 6 hr. The compound was gas chromatographed using a 1.5 ft 20% Kel-F on Chromosorb P column, after being isolated in a U-trap at -78° during trap-to-trap distillation. 0.18 g (0.81 mmol) of $(CF_3)_2C=NSC\equiv N$ was isolated (50.5%). Decomposition occurs at 82°.

Bis(hexafluoroisopropylidenimino)sulfur(II), $((CF_3)_2C=N)_2S$. Photolysis of 0.390 g (1.0 mmol) of $((CF_3)_2C=N)_2S_2$ contained in a 220 ml quartz vessel for eight hr gave 0.320 g (0.9 mmol) of $(CF_3)_2C=NSN=C(CF_3)_2$ (90%) and a yellow solid (sulfur). The Hanovia lamp (Model 30620) was used. The compound was identified from its infrared spectrum.[3]

Methyl(hexafluoroisopropylidenimino)disulfide, $(CF_3)_2C=NSSCH_3$. 0.46 g of $(CF_3)_2C=NSCl$ (2 mmol) and 0.096 g of CH_3SH (2 mmol) were condensed into a 100 ml Pyrex vessel at -196° and the mixture was allowed to stand at -78° for 6 hr. After gas chromatographic purification with a 5.5 ft column of 8% SE-30 on Chromosorb P, 0.22 g (0.9 mmol) of $(CF_3)_2C{=}NSSCH_3$ was obtained (45%). Small amounts of the monosulfide, $(CF_3)_2C{=}NSCH_3$, were isolated, also (~10% yield).

Results and Discussion

Disulfur dichloride reacts readily with hexafluoroisopropylideniminolithium to form $((CF_3)_2C{=}N)_2S_2$ in high yield. The use of a solvent (2-methylbutane) greatly increases the yield from 48% in a neat reaction to 89%. The disulfur dichloride was distilled under an atmosphere of dry nitrogen to remove any sulfur dichloride which would react with $LiN{=}C(CF_3)_2$ to form $((CF_3)_2C{=}N)_2S^2$ which is difficult to separate from the disulfide. The latter undergoes reaction with chlorine in at least two different ways depending upon the conditions used. Photolysis of a mixture of the two materials in a quartz vessel with a Hanovia lamp (Model 30620) leads to the addition of a mole of chlorine per mole of disulfide and a double bond shift giving rise to a sulfur diimide, $((CF_3)_2CClN{=})_2S$. However, if the mixture of disulfide and chlorine is irradiated at 2537 A through quartz using a Srinivasan-Griffin photochemical reactor, the sulfur-sulfur bond is severed and the reactive new sulfenyl compound, $(CF_3)_2C{=}NSCl$ is formed. However, because of fewer side reactions and higher yield, $(CF_3)_2C{=}NSCl$ is better produced by heating the two reactants at 100° for 12 hours.

Compounds which contain active hydrogen, such as dimethylamine and ammonia, or silver pseudohalides, AgCN, easily react to break the S-Cl bond to form other substituted sulfenyl compounds, e.g., sulfenyl amines, $(CF_3)_2C{=}NSN(CH_3)_2$ and $(CF_3)_2C{=}NSNH_2$, or sulfenyl cyanide, $(CF_3)_2C{=}NSNC{\equiv}N$. In the reaction of $(CF_3)_2C{=}NSCl$ with dimethylamine or ammonia, hydrogen chloride is a product which must be consumed by excess base to preclude addition to the carbon-nitrogen double bond. The eight new compounds are all easily hydrolyzable liquids with vapor pressures less than 25 Torr at 25° and, with the exception of $(CF_3)_2C{=}NSN(CH_3)_2$, are all yellow.

The chemistry of $((CF_3)_2C{=}N)_2S_2$ and $(CF_3)_2C{=}NSCl$ is analogous to that of some simpler perfluorinated disulfides and sulfenyl chlorides, e.g., CF_3SSCF_3 and CF_3SCl. However, there are three points of difference. No reaction was found to occur between $((CF_3)_2C{=}N)_2S_2$ and Hg when they were photolyzed or thermolyzed whereas the photolysis of CF_3SSCF_3 with Hg forms $(CF_3S)_2Hg$.[11] Unlike with CF_3SCl, it is impossible to simply fluorinate the sulfenyl chloride to a sulfenyl fluoride. Instead, the perfluoroisopropylsulfur difluoride imine, $(CF_3)_2CFN{=}SF_2$,[8] results in every case when fluorination occurs. Isolation of perfluoroisopropylideniminosulfur trifluoride has proved impossible. It is likely that the latter does form but spontaneously undergoes fluoride ion migration from sulfur to carbon with a double bond shift from C=N to N=S. The following equations show the fluorinations that were tried in attempts to prepare the sulfur trifluoride

$$
(CF_3)_2C{=}NSCl \quad
\begin{array}{lll}
+ \ F_3NO & \xrightarrow[3\ \text{hr}]{25^\circ} & (CF_3)_2CFN{=}SF_2 + NO + 1/2\ Cl_2 \\
+ \ 3AgF_2 & \xrightarrow[8\ \text{hr}]{-20^\circ} & (CF_3)_2CFN{=}SF_2 + 3AgF + 1/2\ Cl_2 \\
+ \ KF & \xrightarrow[12\ \text{hr}]{100^\circ} & \text{no reaction} \\
+ \ 3ClF & \xrightarrow[1\ \text{hr}]{-78^\circ} & (CF_3)_2CFN{=}SF_2 + 2Cl_2 \\
+ \ 3CsF & \xrightarrow[1\ \text{hr}]{-78^\circ} & (CF_3)_2CFN{=}SF_2 + ((CF_3)_2C{=}N)_2S_2 + CsCl
\end{array}
$$

In the latter reaction, the CsF was activated by forming an adduct with hexafluoroacetone in acetonitrile and decomposing the adduct at 200° under dynamic vacuum. It is likely that $(CF_3)_2C{=}NSF$ forms but disproportionates to give $((CF_3)_2C{=}N)_2S_2$ and $(CF_3)_2C{=}NSF_3$ which subsequently rearranges to $(CF_3)_2CFN{=}SF_2$.

The disulfide also reacts with fluorinating agents as shown in the following

$$(CF_3)_2C{=}NSSN{=}C(CF_3)_2 + 6AgF_2 \xrightarrow[8\ hr]{25^\circ} 2(CF_3)_2CFN{=}SF_2 + 6AgF$$

$$(CF_3)_2C{=}NSSN{=}C(CF_3)_2 + 6ClF \xrightarrow[2\ hr]{25^\circ} 2(CF_3)_2CFN{=}SF_2 + 3Cl_2$$

Correlation of the ^{19}F nmr chemical shifts or of the infrared stretching frequencies of the C=N moeity with the substituent group attached to the $(CF_3)_2C{=}NS$ group can not be made based on first order effects, such as electronegativity. However, a similar lack of apparent order is observed for compounds containing the CF_3S moeity, e.g., CF_3SCl, CF_3SNH_2, etc.

It is interesting to note that in the case of $(CF_3)_2C{=}NSCl$ and $(CF_3)_2C{=}NSN(CH_3)_2$, the trifluoromethyl groups are magnetically nonequivalent giving rise to two ^{19}F nmr resonances in the CF_3 region for each compound. Apparently the other new compounds do not behave similarly because the temperature (about 30°) at which the nmr spectra are determined is above that of coalescence, where the CF_3 groups become magnetically equivalent. An ongoing study involves the determination of coalescence temperatures and inversion energies. Ruff[12] reported that the CF_3 groups in $(CF_3)_2C{=}NF$ are magnetically nonequivalent and that the CF_3 group trans to the imine fluorine is shifted to lower field. Based on this, the resonance bands at 60.8 ppm and 65.4 ppm in $(CF_3)_2C{=}NSCl$ and $(CF_3)_2C{=}NSN(CH_3)_2$ are assigned to the CF_3 group trans to Cl and $N(CH_3)_2$, respectively. No fluorine-hydrogen coupling is found and the proton nmr spectra are typical of the functional groups involved.

The infrared spectra of these compounds are reasonably simple, with C=N stretching frequencies being lowered only by 35 cm^{-1} (1640 to 1605 cm^{-1}) when the substituent is changed from dimethylamino to cyano. The C=N stretching frequency in the $(CF_3)_2C=NSCl$ and $((CF_3)_2C=N)_2S_2$ are the same (1630 cm^{-1}) which illustrates the insensitivity of the bond to substituents on the sulfur. The mass spectra are helpful in confirming the syntheses of these new compounds since, with the exception of $[(CF_3)_2C(Cl)N]_2S$ where $(M-Cl^+)$ is the highest m/e, all spectra show rather intense molecule ion peaks.

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THROUGH-SPACE COUPLING IN A NEW SULFUR DIIMIDE

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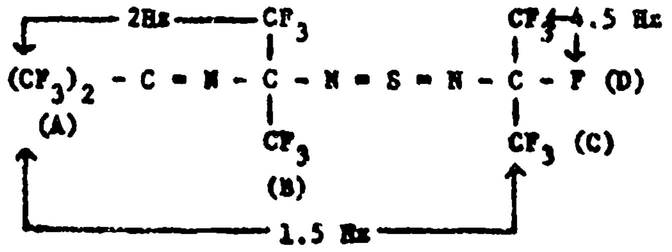
Recently (1) we reported the isolation of a new sulfur diimide, $(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}NC(CF_2)_2F$ obtained in 2% yield from the interaction of SF_4 with $LiN{=}C(CF_3)_2$ at 25°. In the ^{19}F nmr spectrum, coupling between terminal CF_3 groups is observed while the internal CF_3 groups couple to only the imine CF_3 groups. At 35°, four resonances are observed at 67.6, 73.6, 80.0 and 142ϕ. Based on the structural analogues listed in the Table, these resonances are assigned as follows:



$$(CF_3)_2-C=N-\underset{\underset{(B)}{CF_3}}{\overset{CF_3}{C}}-N=S=N-\underset{CF_3\ (C)}{\overset{CF_3}{C}}-F\ (D)$$

67.6ϕ	73.6ϕ	80ϕ	142ϕ
Broad	Heptet	Complex	Heptet
A	B	C	D

TABLE

^{19}F NMR (δ) OF STRUCTURAL ANALOGUES SHOWING CHARACTERISTIC RESONANCE REGIONS FOR CF_3 GROUPS[a]

	A	B	C	
$((\underline{CF_3})_2C{=}N)_2C(\underline{\underline{CF_3}})_2$ [3,b]	68.1 broad	75.4		
$(\underline{CF_3})_2C{=}NC(\underline{\underline{CF_3}})_2N{=}S{=}NC(\underline{\underline{CF_3}})_2N{=}C(\underline{CF_3})_2$ [3]	66.5 broad	73.5		
$(\underline{CF_3})_2C{=}NC(\underline{\underline{CF_3}})_2N{=}S{=}O$ [4]	65.5 broad	74.0		
$(CF_3)_2S{=}NC(\underline{\underline{CF_3}})_2N{=}C(\underline{CF_3})_2$ [3]	63.8 broad	73.1		Hz
$(\underline{\underline{\underline{CF_3}}})_2CFNH_2$ [5]			82.8 $^3J_{CF_3-F}$	4.4
$(\underline{\underline{\underline{CF_3}}})_2CFN{=}SF_2$ [5]			82.[illegible] $^3J_{CF_3-F}$	4.6
$(\underline{\underline{\underline{CF_3}}})_2CFN{=}C{=}O$ [4]			81.5	
$(\underline{\underline{\underline{CF_3}}})_2CFN{=}S{=}O$ [5]			81.2 $^3J_{CF_3-F}$	4.6
$(\underline{\underline{\underline{CF_3}}})_2CFN{=}SCl_2$ [5]			80.1 $^3J_{CF_3-F}$	5.3
$(\underline{\underline{\underline{CF_3}}})_2CFN{=}S{=}NCF(CF_3)_2$ [3]			79.6 $^3J_{CF_3-F}$	4.5
$(\underline{\underline{\underline{CF_3}}})_2CFN{=}SFCF_3$ [3]			81.5 $^3J_{CF_3-F}$	4.3

a Only resonances (and their assignments) similar to those occurring in the diimide are included

b Number of underscores correlates with type of CF_3 group

$\underline{\quad}$, A; $\underline{\underline{\quad}}$, B; $\underline{\underline{\underline{\quad}}}$, C;

Spin-spin decoupling of resonance A resolves the complex resonance C into a simple doublet arising from coupling with the adjacent F ($J_{CF_{3(C)}-F}$ = 4.5 Hz). Similarly the heptet B collapses to a single narrow resonance on decoupling resonance A. At 35° resonance A is structureless, broadened by coupling to the CF_3 groups B and C and also by geometric inversion about C=N. Cooling to 10° results in increased broadening of the resonance, whereas further cooling to -40° or heating to 80° sharpens the resonance, but again no fine structure is observed. Magnetic nonequivalence through inversion about nitrogen of the CF_3 groups in the hexafluoroisopropylidenimino moiety has been previously encountered (2,4). The heptet D is assigned to C-F which is split by the geminal CF_3 groups ($J_{F-CF_{3(C)}}$ = 4.5 Hz).

Examination of molecular models reveals a highly sterically hindered system in which no configuration appears to be free from unfavorable interaction with neighboring CF_3 groups or lone electron pairs. In order for the observed interaction to occur between CF_3(A) and CF_3(C), it is necessary to postulate a pseudo-cyclic configuration bringing the groups to within at least 2.5A of each other (6-8). Although several configurations are possible, skeletal flexibility and the existence of several geometric isomers makes assignment of a most likely configuration difficult. Since the terminal CF_3 groups are separated by ten sigma bonds and no splitting of F(D) by CF_3(A) is observed, it seems likely that through-space coupling is the dominant mechanism with little or no through-bond contribution. Furthermore, if through-bond coupling was significant it seems reasonable to postulate that CF_3(B) which is closer to CF_3(C) by two sigma bonds would add to the complexity of the resonances observed for C and D. The theoretical spectrum for CF_3(C), using the observed coupling constants of 4.5 Hz and 1.5 Hz to produce an overlapping doublet of heptets, is in excellent agreement with the experimentally obtained spectrum. Whether the coupling of CF_3(A) and CF_3(B) is through-bond or through-space can not be inferred.

Experimental

Fluorine 19 nmr spectra were obtained with a Varian HA-100 spectrometer by using trichlorofluoromethane as an internal standard.

SF_4 (3 mmol) was condensed onto $LiN=C(CF_3)_2$ (9) (12 mmol) at -196° and warmed slowly to 25°. After 12 hr, the reaction products were separated by low temperature distillation. $(CF_3)_2CFN=S=NC(CF_3)_2N=C(CF_3)_2$ was obtained in 2% yield after gas chromatographic purification of the fraction trapped at -10° by using a 5' SE-30 column heated to 50°.

The infrared spectrum is as follows: 1732 w, 1318 s, 1260 vs, 1218 vs, 1190 sh, 1095 m, 1075 w, 1012 m, 992 s, 970 sh, 942 w, 740 m, 720 sh, 685 w cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M-F^+$ (1); $M-CF_3^+$ (5); $M - C_3F_6N^+$ (25); $C_5F_{11}N_2S^+$ (5); $C_6F_{12}N^+$ (27); $C_5F_9N_3S^+$ (6); $C_4F_9N_2S^+$ (5); $C_5F_{10}N^+$ (12); $C_3F_7NS^+$ (7); $C_3F_6NS^+$ (24); $C_3F_6N^+$ (5); $C_2F_4NS^+$ (13); CF_4NS^+ (6); CF_3S^+ (5); CF_3^+ (100), SN^+ (57).

Anal. Calcd. for $C_9F_{19}N_3S$: C, 19.95; F, 66.50; N, 7.74; S, 5.82; Found, C, 20.05; F, 66.4; N, 7.81; S, 5.96.

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Some Extensively Rearranged Derivatives of Sulfur Tetrafluoride, Trifluoromethylsulfur Trifluoride and Bis(trifluoromethyl)sulfur Difluoride from Hexafluoroisopropylideniminolithium Reactions

by

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Abstract.--Isolation of six extensively rearranged products (I-VI) from reactions of sulfur tetrafluoride with hexafluoroisopropylideniminolithium demonstrates that simple, metathetical reactions do not occur. A possible mechanism is proposed. Similar rearranged products (VII-IX) form from the lithium salt with CF_3SF_3 and $(CF_3)_2SF_2$. Long range coupling of nuclei separated by 10 σ bonds is observed in the ^{19}F nmr spectrum of (III).

Reaction of sulfur tetrafluoride and hexafluoroisopropylideniminolithium does not follow the previously predictable metathesis reactions observed with inorganic chlorides and fluorides.[2,3,4] Instead, the generation of $(CF_3)_2CFN{=}SF_2$ (I) *in situ* by the action of $LiN{=}C(CF_3)_2$ on SF_4 results in the formation of five new compounds each of which arises directly or indirectly from attack of the lithium salt on the sulfur difluoride imide. Thus

$$
\begin{array}{lll}
 & (CF_3)_2CFN{=}SF_2 & \text{(I)} \\
 & (CF_3)_2CFN{=}S{=}NCF(CF_3)_2 & \text{(II)} \\
SF_4 + LiN{=}C(CF_3)_2 \longrightarrow & (CF_3)_2CFN{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2 & \text{(III)} \\
 & (CF_3)_2C{=}NC(CF_3)_2N{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2 & \text{(IV)} \\
 & (CF_3)_2C{=}NC(CF_3)_2N{=}C(CF_3)_2 & \text{(V)} \\
 & [(CF_3)_2C{=}N]_2S{=}NH & \text{(VI)}
\end{array}
$$

Isolation of each of the new products and subsequent reaction with the lithium salt indicates that each of the products results from a series of irreversible steps from reaction with a less highly substituted member. Similarly, reactions of CF_3SF_3 and $(CF_3)_2SF_2$ with $LiN{=}C(CF_3)_2$ indicate that stepwise substitution and product rearrangement occurs, producing analogues to compounds formed from reaction with SF_4.

$$CF_3SF_3 + LiN{=}C(CF_3)_2 \longrightarrow CF_3S(F){=}NCF(CF_3)_2 \qquad (VII)$$

$$(CF_3)_2SF_2 + LiN{=}C(CF_3)_2 \longrightarrow (CF_3)_2S{=}NCF(CF_3)_2 \qquad (VIII)$$

$$(CF_3)_2S{=}NC(CF_3)_2N{=}C(CF_3)_2 \qquad (IX)$$

EXPERIMENTAL

Materials.--SF_4 (K and K Laboratories, Inc.) and AgF_2 (Ozark-Mahoning Co.) were used without further purification. $(CF_3)_2C{=}NH$ was prepared according to the literature method[5] and dried over P_4O_{10}. n-Butyl lithium in hexane (Alfa Inorganics) was transferred into small glass bottles in an inert atmosphere box for ease in handling but otherwise was used as purchased. CF_3SF_3[6] and $(CF_3)_2SF_2$[7] were prepared by literature methods.

General Procedures.--Gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon-tube gauge. Volatile starting materials and purified products were measured quantitatively by PVT techniques. Reactants and products of lower volatility were weighed. For gas chromatographic separations, the columns were constructed of 0.25 in copper tubing packed with 8% SE-30 (Loenco) on Chromosorb W or 20% Kel-F oil (3M Co.) on Chromosorb P. In most cases, fractional condensation was used to effect crude separation prior to gas chromatography. Vapor pressure studies were carried out by using the method of Kellogg and Cady[8] or by an isoteniscopic method.

Infrared spectra of volatile products were recorded with a Perkin-Elmer 457 spectrometer by using a 5 cm gas cell equipped with KBr windows.

Nonvolatile liquids were run neat between NaCl discs. Fluorine 19 nmr spectra were obtained with a Varian HA-100 spectrometer by using trichlorofluoromethane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

1. Reactions of SF_4 and Derivatives

Preparation of $(CF_3)_2CFN{=}SF_2$ (I).--Sulfur tetrafluoride (4 mmol) was condensed onto $LiN{=}C(CF_3)_2$ (12 mmol) at -196° and warmed slowly to 25°. After 41 hr, the volatile products were separated by gas chromatography by using a 5' SE-30 column heated to 30° and (I) was obtained in 22% yield. Other products isolated were (II) (6%) and small amounts of (III), (IV), and (V). Physical and spectral data for (I) have been reported previously.[9]

Reaction of (I) and $LiN{=}C(CF_3)_2$.--$(CF_3)_2CFN{=}SF_2$ (2.64 mmol) was condensed onto $LiN{=}C(CF_3)_2$ (12 mmol) at -196° and warmed rapidly to 25°. After 20 hr, the volatile compounds were separated by trap-to-trap distillation and further purified by gas chromatography by using a 5' SE-30 column heated to 60°. Major products identified were (V) (52%), (VI) (24%), (IV) (9.5%), $(CF_3)_2C{=}NSN{=}C(CF_3)_2$[2,3] (1.1%) and $(CF_3)_2C{=}NH$ (0.1 mmol).

Preparation of $(CF_3)_2CFN{=}S{=}NCF(CF_3)_2$ (II).--$[(CF_3)_2C{=}N]_2S$ (22 mmol) was distilled into a 75 ml stainless steel Hoke bomb which contained AgF_2 (3 g) at -196° and allowed to warm to 25°. After standing at 25° for 2.75 hr, $(CF_3)_2CFN{=}S{=}NCF(CF_3)_2$ (II) was obtained in almost quantitative yield. Bis(heptafluoroisopropyl)sulfur diimide is a colorless liquid with a boiling point of 106.8° obtained from the equation log P_{Torr} = 8.17 − 2013/T. Vapor pressure data are as follows (T, °K; P, Torr): 326, 100; 342.7, 200; 348.2, 250; 353, 300; 361.2, 400; 367.5, 500; 371.5, 550; 373.0, 600; 375.5, 650; 377.7, 702. The molar heat of vaporization is 9.2 kcal and the Trouton constant is 24.3 e.u.

The ^{19}F nmr spectrum shows a broadened complex resonance at 145.3ϕ assigned to the equivalent isopropyl fluorines and a doublet (J_{CF_3-F} = 4.5 Hz) at 79.6 ϕ for the CF_3 groups. The infrared spectrum measured at 4 Torr is as follows: 1287 vs, 1263 vs, 1227 s, 1195 m, 1130 m, 1092 m, 1030 s, 995 s, 958 w, 740 sh, 732 s, 540 w, cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): M^+ (1); $M-F^+$ (5); $M-F_2{}^+$ (5); $M-F_3{}^+$ (1); $M-CF_3{}^+$ (22); $C_5F_9N_2S^+$ (2); $C_3F_6NS^+$ (25); $C_3F_5NS^+$ (4); $C_2F_4NS^+$ (25); $C_2F_5N^+$ (4); $C_2F_4{}^+$ (11); $CF_3{}^+$ (100); SN^+ (27).

Anal. Calcd. for $C_6F_{14}N_2S$: C, 18.19; F, 66.80; N, 7.04; S, 8.05; Found: C, 18.30; F, 66.6; N, 7.02; S, 8.09.

$(CF_3)_2CFN=S=NCF(CF_3)_2$ is obtained in 6% yield when SF_4 (4 mmol) is reacted with $(CF_3)_2C=NLi$ (11.5 mmol).

Reaction of (II) and $LiN=C(CF_3)_2$.--$(CF_3)_2CFN=S=NCF(CF_3)_2$ (1 mmol) was condensed onto $LiN=C(CF_3)_2$ (6.9 mmol) at −196° and warmed slowly to 25°. After 20 hr, the volatile materials were removed and identified by gas chromatographic retention times, infrared and ^{19}F nmr spectra to be primarily (IV) and (V), $(CF_3)_2C=NH$ and some (III). No (I) or (VI) was observed.

Preparation of $(CF_3)_2CFN=S=NC(CF_3)_2N=C(CF_3)_2$ (III).--SF_4 (3 mmol) was condensed onto $LiN=C(CF_3)_2$ (12 mmol) at −196° and warmed slowly to 25°.

After 12.25 hr, the reaction products were separated by low temperature distillation. $(CF_3)_2CFN{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$ was obtained in 2% yield after gas chromatographic purification of the fraction trapped at -10° by using a 5' SE-30 column heated to 50°. Other compounds isolated were (I), (II), (V) and (VI).

The infrared spectrum is as follows: 1732 w, 1318 s, 1260 vs, 1218 vs, 1190 sh, 1095 m, 1075 w, 1012 m, 992 s, 970 sh, 942 w, 740 m, 720 sh, 685 w cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M{-}F^+$ (1); $M{-}CF_3^+$ (5); $M - C_3F_6N^+$ (25); $C_5F_{11}N_2S^+$ (5); $C_6F_{12}N^+$ (27); $C_5F_9N_3S^+$ (6); $C_4F_9N_2S^+$ (5); $C_5F_{10}N^+$ (12); $C_3F_7NS^+$ (7); $C_3F_6NS^+$ (24); $C_3F_6N^+$ (5); $C_2F_4NS^+$ (13); CF_4NS^+ (6); CF_3S^+ (5); CF_3^+ (100), SN^+ (57).

Anal. Calcd. for $C_9F_{19}N_3S$: C, 19.95; F, 66.50; N, 7.74; S, 5.82; Found, C, 20.05; F, 66.4; N, 7.81; S, 5.96.

Reaction of (III) and $LiN{=}C(CF_3)_2$.--$(CF_3)_2CFN{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$ (0.3 mmol) was condensed onto $LiN{=}C(CF_3)_2$ (2.4 mmol) at -196° and warmed slowly to 25°. After 10 hr, the volatile compounds were removed and identified by their infrared spectra as (V) (0.27 mmol), $(CF_3)_2C{=}NH$ (trace) and (IV) (trace). No (I), (II) or (VI) was observed.

Preparation of $(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$ (IV).--After removal of the volatile compounds observed in the preparation of (III), the "dry" solid residue in the reaction vessel was heated at 100° under dynamic vacuum and a nonvolatile, bright yellow liquid was collected in a vessel fitted with a rubber septum to facilitate gas chromatographic separation. The liquid was injected onto a 5' SE-30 column heated to 60° and pure

$(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$ was obtained in yields as high as 51%. Bis[2-(hexafluoroisopropylimino)hexafluoroisopropyl]sulfur diimide is hydrolytically stable with a boiling point of 197° at 200 Torr.

The ^{19}F nmr shows a broad singlet at 66.5ϕ which is further broadened as the temperature is lowered to 10°. At 70° this becomes a sharp singlet. A second resonance at 73.5ϕ is a sharp singlet of area equal to the first and is essentially unaffected by temperature changes. The infrared spectrum (liquid, NaCl discs) is as follows: 1735 m, 1320 vs, 1160-1235 vs, 1075 s, 1010 s, 985 s, 960 s, 938 m, 791 w, 768 w, 756 s, 740 s, 690 s cm^{-1}. Principal peaks in the mass spectrum correspond to the ions. (relative intensity): $M - CF_3^+$ (1); $M - C_3F_6N^+$ (9); $M - C_6F_{12}N_2^+$ (4); $C_3F_6NC_3F_6^+$ (100); $C_5F_{10}N^+$ (15); $C_5F_8N^+$ (4); $C_4F_8N^+$ (6); $C_3F_6NS^+$ (17); $C_3F_5NS^+$ (2); $C_3F_6N^+$ (2); CF_3S^+ (7); $C_3F_3N^+$ (9); CF_3^+ (90); SN^+ (9).

Anal. Calcd. for $C_{12}F_{24}N_4S$: C, 20.90; F, 66.40; N, 8.14; S, 4.65; Found, C, 20.98; F, 65.2; N, 8.18; S, 4.55.

Reaction of (IV) and $LiN{=}C(CF_3)_2$.--$(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$ (0.59 mmol) was injected into a vessel containing $LiN{=}C(CF_3)_2$ (3 mmol) which had been heated to 70° under dynamic vacuum to remove excess $(CF_3)_2C{=}NH$. The vessel was warmed slowly from -196° to 25°. After standing for 1.25 hr at 25°, the only volatile product obtained was (V) (0.58 mmol) identified by its infrared spectrum. Chlorine (0.9 mmol) was added to the reaction vessel and after three hours the only volatile product observed was $(CF_3)_2C{=}NCl$ (0.9 mmol). No volatile sulfur-containing product was obtained.

Preparation of $(CF_3)_2C=NC(CF_3)_2N=C(CF_3)_2$ (V).-- Sulfur tetrafluoride (0.96 mmol) was condensed onto $LiN=C(CF_3)_2$ (2.4 mmol) at -196° and allowed to warm rapidly to 25°. After 0.3 hr the volatile products were removed and separated by gas chromatography by using a 5' SE-30 column at 50°. Pure $(CF_3)_2C=NC(CF_3)_2N=C(CF_3)_2$ was obtained in 39% yield from the mixture containing (I), (II), (IV) and (VI). 2,2-[Bis(hexafluoroisopropylideneimino)] hexafluoropropane is a colorless liquid having a boiling point of 109° from the equation log P_{Torr} = 7.76 - 1857/T. Vapor pressure data are as follows (T, °K; P, Torr): 314.5, 71; 321.5, 93; 327.5, 118; 335.5, 162; 344.7, 231; 351.5, 292; 358.3, 368; 363.0, 425; 368.3, 510; 375.0, 620. The molar heat of vaporization is 8.4 kcal. and the Trouton constant is 22.0 e.u.

The ^{19}F nmr spectrum shows a broad resonance at 68.1ϕ assigned to the four terminal CF_3 groups. Thirteen peaks centered at 75.4ϕ are assigned to the CF_3 groups on the center carbon atom ($J_{CF_3-CF_3}$ = 6.2 Hz). The peak area ratio is 2:1. The infrared spectrum (5 Torr) is as follows: 1755 m, 1320 vs, 1265 vs, 1245 vs, 1232 vs (sh), 1212 vs, 1190 m, 1090 w, 1050 m, 1000 s, 960 m, 760 w, 740 m, 722 m, 690 m cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M - F^+$ (1); $M - CF_3^+$ (2); $M - C_2F_5^+$ (1); $C_3F_6NC_3F_6^+$ (18); $C_2F_4NC_3F_6^+$ (7); $C_2F_3NC_3F_6^+$ (1); $C_2F_2NC_3F_6^+$ (2); $CF_2NC_3F_6^+$ (5); $C_3F_7^+$ (3); CF_2CN^+ (2); CF_3^+ (100); $C_3N_2^+$ (1); CF_2^+ (2).

Anal Calcd. for $C_9F_{18}N_2$: C, 22.60; F, 71.51; N, 5.89; Found, C, 22.48; F, 71.4; N, 6.27.

Reaction of (V) and $LiN=C(CF_3)_2$ --$[(CF_3)_2C=N]_2C(CF_3)_2$ (1.3 mmol) and $LiN=C(CF_3)_2$ (8 mmol) did not react after 8 hr at 25°.

Preparation of $(CF_3)_2C{=}NS({=}NH)N{=}C(CF_3)_2$ (VI).—$(CF_3)_2CFN{=}SF_2$ (2.64 mmol) was condensed onto $LiN{=}C(CF_3)_2$ (12 mmol) at -196° and warmed rapidly to 25°. After 20 hr, the products were separated by low temperature distillation and the contents of the warmest trap (-40°) further purified by gas chromatography using a 5' SE-30 column at 60°. Bis(hexafluoroisopropylidenimino)sulfurimine was obtained in 24% yield and is a colorless, readily sublimable, crystalline solid which melts at 38.5°.

The ^{19}F nmr spectrum is a singlet at 80.30. The ^1H nmr spectrum is a broad singlet at 6.6τ. The infrared spectrum is as follows: 3460 m, 1490 m, 1290 s, 1255 vs, 1240 vs, 1218 sh, 1185 s, 1020 w, 960 s, 815 w, 728 s, 710 s, 540 w cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M - NH^+$ (1); $M - F^+$ (2); $C_6F_{12}N^+$ (2); $M - CF_3^+$ (25); $M - CF_4^+$ (1); $M - C_3F_6^+$ (19); $C_5F_9N^+$ (2); $C_3F_6NSNH^+$ (5); $C_3F_6NS^+$ (7); $C_3F_5N_2S^+$ (2); $C_3F_6N^+$ (3); $C_2F_4NS^+$ (2); CF_3SNH^+ (9); $C_2F_3NH^+$ (30); CF_3^+ (100); C_2FN^+ (11); SNH^+ (25); SN^+ (35).

Anal. Calcd. for $C_6HF_{12}N_3S$: C, 19.20; H, 0.27; F, 60.79; N, 11.20; S, 8.54. Found, C, 18.96; H, 0.48; F, 60.9; N, 11.21; S, 8.37.

$[(CF_3)_2C{=}N]_2SNH$ is also obtained in much lower yields when SF_4 and $LiN{=}C(CF_3)_2$ react.

II. Reactions of CF_3SF_3

Preparation of $CF_3SF{=}NCF(CF_3)_2$ (VII).--CF_3SF_3 (7 mmol) was condensed onto $LiN{=}C(CF_3)_2$ (4.8 mmol) at -196° and warmed slowly to 25°. After 24 hr the products were separated by trap-to-trap distillation using baths at -43°, -78° and -194°. Unreacted CF_3SF_3 and a small amount of $CF_3\overset{O}{S}F$ (from hydrolysis of CF_3SF_3) were recovered from the bath at -194°. Pure

$CF_3SFN=CF(CF_3)_2$ was obtained in 60% yield, after purification by gas chromatography of the product which stopped in the bath at -78°, by using a 2.5' Kel-F column at 30°. A nonvolatile yellow liquid, which stopped at -48° and subsequently slowly solidified at 25°, could not be purified by gas chromatography.

N-heptafluoroisopropyl-S-trifluoromethyl-monofluorosulfurimide is a colorless liquid with a boiling point of 62.9° obtained from the equation log $P_{Torr} = 7.84 - 1666/T$. vapor pressure data are as follows (T, °K; P, Torr): 301, 200; 306.5, 250; 310.7, 300; 314.7, 350; 318.2, 400; 321, 450; 324, 500; 327, 550; 328.7, 600; 332.7, 693. The molar heat of vaporization is 7.95 kcal and the Trouton constant is 23.6 e.u.

The ^{19}F nmr spectrum is discussed in a later section of the paper. The infrared spectrum is as follows: 1315 m, 1295 s, 1270 vs, 1255 vs, 1198 s, 1132 vs, 1094 s, 1018 m, 988 vs, 760 w, 722 m, 678 s, 542 w, 468 w, 450 m cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M - 2F^+$ (1); $M - 3F^+$ (1); $M - CF_3^+$ (12); $C_3F_7NS^+$ (2); $C_3F_6NS^+$ (11); $C_3F_5NS^+$ (1); $C_2F_4NS^+$ (12), C_2F_3NS (2); CF_4S^+ (2); CF_3S^+ (5); $C_2F_4^+$ (3); $C_2F_2N^+$ (2); CF_3^+ (100); SF^+ (8); CF_2^+ (3); NS^+(13).

Anal. calcd. for $C_4F_{11}NS$: C, 15.84; F, 69.0; N, 4.62; S, 10.54; Found C, 15.94; F, 69.3; N, 4.66; S, 10.66.

III. Reactions of $(CF_3)_2SF_2$

Preparation of $(CF_3)_2S=NCF(CF_3)_2$ (VIII).--$(CF_3)_2SF_2$ (5 mmol) was condensed onto $LiN=C(CF_3)_2$ (7.2 mmol) at -196° and warmed slowly to 25°. After 18.5 hr the products were separated by trap-to-trap distillation using baths at -40°, -78° and -184° $(CF_3)_2S=NCF(CF_3)_2$ which stopped in a bath at -40° was obtained pure in 71% yield after purification by gas chromatography using a 7' Kel-F column at 25°. Other products observed in the separation included small amounts of $[(CF_3)_2C{=}N]_2$ and $(CF_3)_2S{=}NC(CF_3)_2N{=}C(CF_3)_2$ (IX).

N-heptafluoroisopropyl-S,S-bis(trifluoromethyl)-sulfurimide is a colorless liquid with a boiling point of 89.1° obtained from the equation, $\log P_{Torr} = 7.40 - 1640/T$. Vapor pressure data are as follows (T, °K; P, Torr): 314.2, 150; 321.7, 200; 328.0, 250; 333.2, 300; 337.7, 350; 342.2, 400; 345.5, 450; 349.7, 500; 352.0, 550; 355.0, 600; 357.7, 650; 359.7, 695. The molar heat of vaporization is 7.5 kcal. and the Trouton constant is 20.7 e.u.

The ^{19}F nmr spectrum contains resonances at 138, 81.2 and 64φ in the ratio of 1:6:6, respectively. The resonance at 138φ, assigned to the isopropyl fluorine, is an overlapping heptet of heptets from splitting by two CF_3 groups on carbon (J_{F-CF_3C} = 4.7 Hz) and two CF_3 groups on sulfur (J_{F-CF_3S} = 1.6 Hz). The resonance at 81.2φ is assigned to the CF_3 groups on carbon and is an overlapping doublet of heptets split by the isopropyl fluorine (J_{CF_3C-F} = 4.7 Hz) and the remaining CF_3 groups ($J_{CF_3C-CF_3S}$ = 1.4 Hz). At 64φ, the CF_3 groups on sulfur are split by the isopropyl fluorine (J_{CF_3S-F} = 1.6 Hz) and the remaining two CF_3 groups ($J_{CF_3S-CF_3C}$ = 1.4Hz). The infrared spectrum is as follows: 1322 m, 1300 m, 1262 vs, 1212 s, 1138 vs, 1089 vs, 990 m, 760 w, 732 m, 700 w, and 455 m, cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): M^+ (17); $M - F^+$ (10); $M - CF_3{}^+$ (10); $M - CF_4{}^+$ (18); $M - CF_5{}^+$ (10); $M - C_2F_6{}^+$ (10); $C_3F_6NS^+$ (32); $C_3F_5NS^+$ (7); $C_2F_5{}^+$ (15); CF_3S^+ (45); CF_2NS^+ (5); CF_2S^+ (8); $CF_3{}^+$ (100); NS^+ (11).

Anal. Calcd. for $C_5F_{13}NS$: C, 17.00; F, 69.9; N, 3.98; S, 9.08; Found: C, 16.41; F, 70.0; N, 4.12; S, 8.69.

Preparation of $(CF_3)_2S{=}NC(CF_3)_2N{=}C(CF_3)_2$ (IX).—$(CF_3)_2S{=}NCF(CF_3)_2$ (1.35 mmol) was condensed onto $LiN{=}C(CF_3)_2$ (4.8 mmoles) at -196° and warmed slowly to 25°. After 18 hr, the product which stopped in a bath at -30° was purified by gas chromatography using a 5' SE-30 column heated to 50°. Pure $(CF_3)_2S{=}NC(CF_3)_2N{=}C(CF_3)_2$ was obtained in 82% yield.

2,4,4,6-tetrakis(trifluoromethyl)-2-thia-3,5-diaza-2,5-perfluoroheptadiene is a colorless liquid with an extrapolated boiling point of 136.6°. The equation $\log P_{Torr} = 8.21 - 2183/T$ holds for temperatures below 100°. Above this temperature, the compound decomposes to $CF_3SN{=}C(CF_3)_2$ and an unidentified solid. Vapor pressure data to 100° are as follows (T, °K; P, Torr): 330.0, 40; 341.2, 65; 348.0, 90; 354.0, 111; 360.0, 140; 365.0, 170; 369.0, 198; 373.0, 232. The molar heat of vaporization is 9.8 kcal. and the Trouton constant is 23.9 e.u.

The ^{19}F nmr shows single sharp resonances at 73.10, and 62.70 and a broad resonance of 63.80. Peaks are in the ratio 1:1:1. The resonance at 73.10 is assigned to the internal CF_3 groups, the resonance at 62.70 assigned to the CF_3 groups on sulfur, and the broadened resonance at 63.80 assigned to the CF_3 groups adjacent to the imine moiety. The infrared spectrum is as follows: 1730 w, 1322 m, 1285 m, 1255 vs, 1232 s, 1218 s, 1168 m, 1128 s, 1085 s, 998 m, 970 w, 935 m, 754 w, 735 m, and 690 m cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M - C_2F_6NS^+$ (15); $C_4F_9NS^+$ (45); $C_4F_8NS^+$ (22); $C_4F_8N^+$ (15); $C_3F_6NS^+$ (45); $C_3F_5NS^+$ (15); $C_3F_6N^+$ (22); $C_2F_4NS^+$ (2);

$C_2F_3NS^+$ (6); $C_2F_5^+$ (15); $C_2F_2NS^+$ (9); CF_3S^+ (47); CF_2NS^+ (20); CF_2S^+ (9); $C_2F_2N^+$ (23); CF_3^+ (100); CFS^+ (7); SF^+ (12); CF_2^+ (18). [$M-C_2F_6^+$ (<1)]

Anal. Calcd. for $C_8F_{18}N_2S$: C, 19.30; F, 68.6; N, 5.63; S, 6.43; Found: C, 19.65; F, 68.5; N, 6.08; S, 6.69.

RESULTS AND DISCUSSION

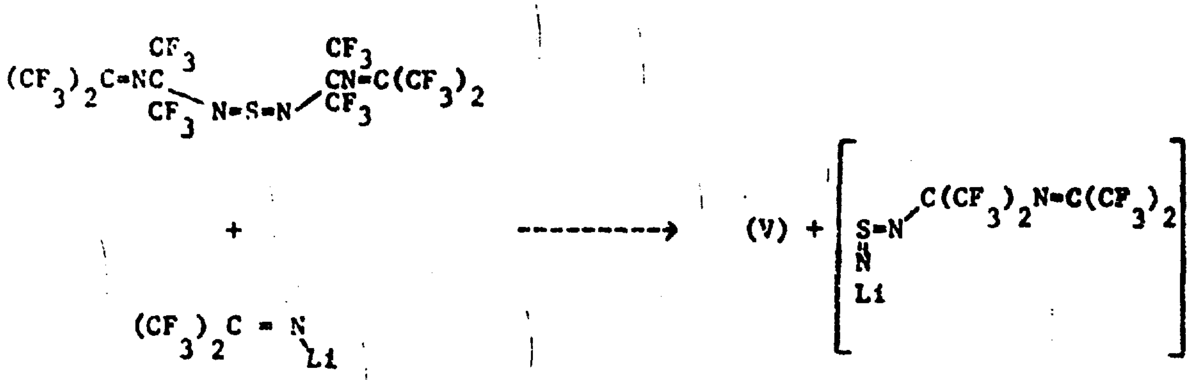
Many examples of the preparation and reactions of the general class of compounds sulfur difluoride imides ($R-N=SF_2$) and sulfur diimides ($R-N=S=N-R$) have been reported recently,[10-23] (and references therein) and the chemistry of the former is covered in a review on sulfur-nitrogen-fluorine compounds.[24] The principal method for preparing $RN=SF_2$ compounds utilizes reactions of nitrogen-containing species with SF_4 and the sulfur difluoride imide so formed may undergo further reaction to form sulfur diimides.

By reacting SF_4 with the lithium salt of hexafluoroisopropylidenimine in varying stoichiometries six compounds in isolable yields are formed, including three new sulfur diimides which arise from the *in situ* generation of a sulfur difluoride imide "intermediate"--$(CF_3)_2CFN=SF_2$. (I)

(I) has been prepared in high yield by the reaction of

$$SF_4 + (CF_3)_2C=NH \xrightarrow{CsF} (CF_3)_2CFN=SF_2\ ^{9}$$

but the more highly substituted members (II) - (VI) have not been previously reported. Compounds (I) and (II) are readily isolated when the ratio of $LiN=C(CF_3)_2$ to SF_4 is less than 4:1, but neither is observed if SF_4 is the limiting reagent. With the exception of (VI), each higher member of the series can be made from reaction of its antecedent and the lithium salt, with none of the lower members being produced. Thus, adding pure (II) to $(CF_3)_2C{=}NLi$ results in the formation of (III), (IV) and (V) with no (I) or (VI) being observed. Sulfurdiimides have been shown to react with polar organic molecules to cleave the N=S bonds,[21] which explains the formation of 0.58 mmol of (V) as the only volatile product observed when 0.59 mmol of (IV) reacts with $LiN{=}C(CF_3)_2$



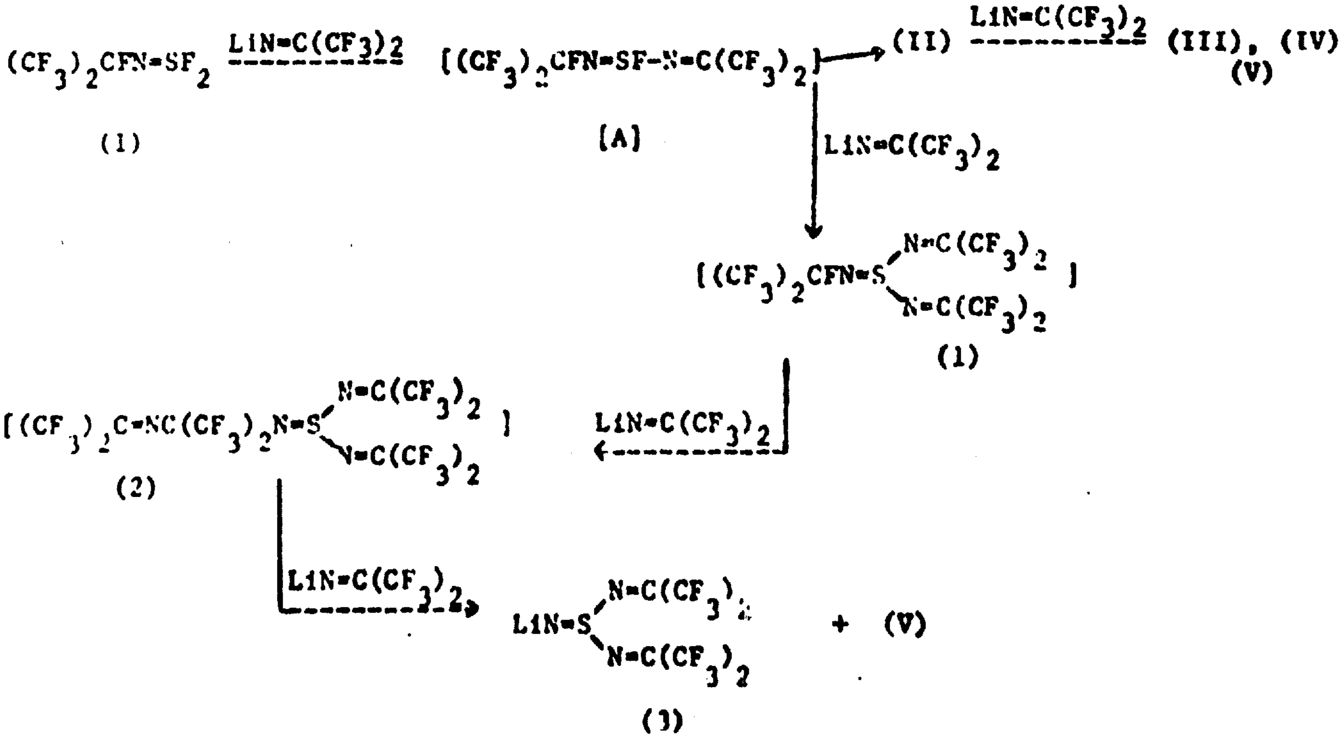
The N atom on the lithium salt is the nucleophilic site and the S=N bond is presumed to have broken and new S=N bonds formed to produce (V) and a proposed lithium salt which was not isolated.

The mechanism of formation of products (I), (II) and (VI) is difficult to deduce. Whether a simple metathetical reaction occurs between F and the $(CF_3)_2C{=}N$ moiety to form a transient intermediate which rearranges by fluoride ion migration to a more electropositive center cannot be demonstrated without isolating the postulated intermediate, i.e.,

$$(CF_3)_2CFN{=}SF_2 + LiN{=}C(CF_3)_2 \dashrightarrow \underset{[A]}{[(CF_3)_2CFN{=}SF{-}N{=}C(CF_3)_2]} \dashrightarrow$$

$$(CF_3)_2CFN{=}S{=}NCF(CF_3)_2$$

The formation of $CF_3(F)S{=}NCF(CF_3)_2$ (VII) (discussed later in this section) and the recently reported synthesis of a previously unknown aminosulfurmonofluoride imide ($-N{=}SF{-}NR_2$)[25] could argue for the existence of [A] even though the possibility of structural rearrangement of these imides is not likely. Further implicit evidence for this, or some similar intermediate, arises from the formation of $[(CF_3)_2C{=}N]_2S{=}NH$ (VI). None of this new sulfurimine is observed in reaction of (II), (III), (IV) or (V) with the lithium salt, therefore, the precursor to the product probably arises from reaction of SF_4 or (I). Since reaction of (I) results in greater yields of (VI) than does reaction of SF_4 it seems reasonable to postulate an intermediate (A) which can either rearrange to form (II) and subsequently (III), (IV) and (V) or which can itself undergo reaction with the lithium salt to form a precursor to (VI). Thus



Addition of $(CF_3)_2C=NH$ to the solid residue remaining after pulling off the volatiles results in the formation of (VI) in yields as high as 24%.

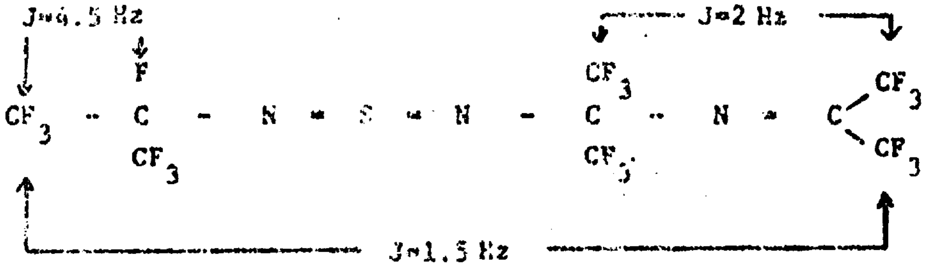
$$(3) + (CF_3)_2C=NH \longrightarrow [(CF_3)_2C=N]S=NH + LiN=C(CF_3)_2$$

Some of (VI) is usually observed in the volatile products before addition of $(CF_3)_2C=NH$. In the preparation of $LiN=C(CF_3)_2$, formed by adding excess $(CF_3)_2C=NH$ to n-BuLi, slightly more than a 1:1 uptake of parent imine is observed which is not recovered even after pumping on the solid for several hours. When the lithium salt is heated to 70° under dynamic vacuum excess $(CF_3)_2C=NH$ is pulled off the solid and subsequent reaction with SF_4 produces very little (VI) until $(CF_3)_2C=NH$ is added to the solid.

In an entirely analogous series of reactions, $(CF_3)_2SF_2$, and $LiN=C(CF_3)_2$ react to produce the monosubstituted rearranged compound $(CF_3)_2S=NCF(CF_3)_2$ (VIII) which in turn reacts readily with the lithium salt to form the disubstituted derivative $(CF_3)_2S=NC(CF_3)_2N=C(CF_3)_2$ (IX). Unlike (IV), (VIII) does not undergo further reaction with $LiN=C(CF_3)_2$ and is thermally less stable, decomposing above 100° to $CF_3SN=C(CF_3)_2$ and an unidentified yellow solid.

Metathesis reactions of CF_3SF_3 and $LiN=C(CF_3)_2$ were not as predictable as were the above sulfur (IV) reactions. The monosubstituted product $CF_3SF=NCF(CF_3)_2$ was readily obtained in reasonable yields when excess CF_3SF_3 was used, but yields dropped to almost zero when CF_3SF_3 was the limiting reagent. Instead, a nonvolatile, yellow liquid was formed which could not be purified by gas chromatography and which slowly solidified at 25°. Numerous resonances were observed in the ^{19}F nmr of the neat liquid but none which could be reasonably assigned to higher homologues of the parent. When $CF_3SF=N-CF(CF_3)_2$ and $LiN=C(CF_3)_2$ were reacted in varying proportions, for varying times, with or without solvent the same intractable yellow mixture recurred. In one attempted gas chromatographic purification, a very small amount of compound was obtained with a C=N band at 1732 cm^{-1} in the infrared, and four ^{19}F nmr resonances in the expected regions for the disubstituted derivative. Insufficient compound was isolated for characterisation.

An interesting example of through-space coupling of remote fluorine nuclei is observed in the ^{19}F nmr spectrum of $(CF_3)_2CFN{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$. Resonances occur at 142, 80, 73.7 and 67.6φ in the ratio of 1:6:6:6. On the basis of structural analogues the assignments are given in Fig. 1.[34]



$$CF_3-\overset{F}{\underset{CF_3}{C}}-N=S=N-\overset{CF_3}{\underset{CF_3}{C}}-N=C(CF_3)_2$$

CF_3 Multiplicity

A	B	C
80φ	73.6φ	67.6φ
(i) Complex	(i) Heptet	(i) very broad at 10°
(ii) Doublet when C decoupled	(ii) Singlet when C decoupled	(ii) sharper at +30° and -40°

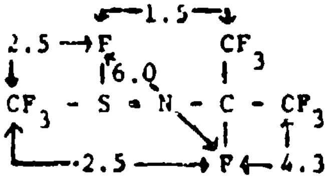
Fig 1 ^{19}F nmr of $(CF_3)_2CFN{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$

The resonance at 142φ is assigned to the isopropyl fluorine and is a heptet due to splitting from the 6 vicinal fluorine atoms (J_{F-CF_3} = 4.5 Hz). A complex resonance at 80φ assigned to the (A) CF_3 groups (see Fig. 1) is resolved into a simple doublet when (C) is decoupled (J_{CF_3-F} = 4.5 Hz).

(C) also couples with (B) splitting the latter into a heptet ($J_{(B)-(C)}$ = 2 Hz) which becomes a singlet at 73.60 when (C) is decoupled. The broadening of (C) arises not only from coupling to (A) and (B) but also from inversion about the C-N single bond adjacent to the imine moiety.[2,3,26,27,28,29,30] Cooling the sample results in a very broad nmr signal for (C) at 10°, which is considerably sharpened by lowering the temperature to -40°. Heating to 80° also produces a sharper resonance for (C).

Coupling of the remote ^{19}F nuclei by bonding electrons through ten sigma bonds is probably negligible, the dominant coupling contributions more likely arising from non-bonded electron interaction. Through space coupling is dependent on molecular geometry, thus the geometry of the molecule must allow for a configuration in which the terminal CF_3 groups are within at least 2.5 A of each other.[31,32,33]

The ^{19}F nmr of $CF_3S(F)=NC(F)(CF_3)_2$ shows resonances at 145.2, 81.5, 72.9 and 11.10 in the ratio of 1:6:3:1 respectively. The following interactions are observed. (Coupling constants in Hz)



The resonance at 145.20 assigned to the isopropyl fluorine and the S-F resonance at 11.10 are complex multiplets each being split by all the other fluorine atoms in the molecule. The resonance at 81.50 is assigned to the CF_3 groups attached to carbon and at -45° is a doublet of doublets from splitting by the single fluorine atoms on carbon and sulfur. At 72.9φ, the resonance assigned to CF_3 attached to S is split into a triplet from equal coupling to the two single fluorines. The unexpectedly large coupling of the isopropyl fluorine to CF_3-S could indicate non-bonded electron interaction but, if this is the case, the molecular geometry is such that the remote CF_3 groups do not couple significantly through space. Examination of molecular models renders this latter contingency unlikely. On the premise that through-bond spin spin coupling is the predominant mechanism and from comparison of coupling constants in structural analogues, the isopropyl fluorine is assumed to couple to the two CF_3 groups on carbon more strongly than does the S-F, however, this assignment is not unequivocal. Decoupling experiments were inconclusive.

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Insertion of SO_2 and CO_2 into $(CF_3)_2C=NLi$

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Recently[1] we reported the facile introduction of the hexafluoroisopropylidenimino group into a series of compounds from reaction of $LiN=C(CF_3)_2$ with inorganic halides. On the basis of these results and results from reaction of SF_4 with $LiN=C(CF_3)_2$[2] we proposed that the reactions proceed in an irreversible series of steps although it was not possible to isolate intermediates for other than the SF_4 reactions.

When $LiN=C(CF_3)_2$ reacts with $SOCl_2$ or $COCl_2$, even with the coreactants in large excess, the major products observed are $(CF_3)_2C=NC(CF_3)_2NSO$ or $(CF_3)_2C=NC(CF_3)_2NCO$ with no trace of the symmetrical sulfoxide $[(CF_3)_2C=N]_2SO$, or substituted urea $[(CF_3)_2C=N]_2CO$. In an attempt to prepare the latter compounds and further substantiate the stepwise mechanism a different synthetic technique was devised which might eliminate the formation of the postulated but unisolated intermediate $(CF_3)_2CClN=E=O$ (where E = S or C).

We have observed that SO_2 and CO_2 insert quantitatively into $LiN=C(CF_3)_2$ giving new lithium salts which are stable in glass at 25° for extended periods. Reaction of these with $SOCl_2$ or $COCl_2$ were expected to form intermediates which, if stable to loss of SO_2 or CO_2 respectively, would react further to form the symmetrical compounds.

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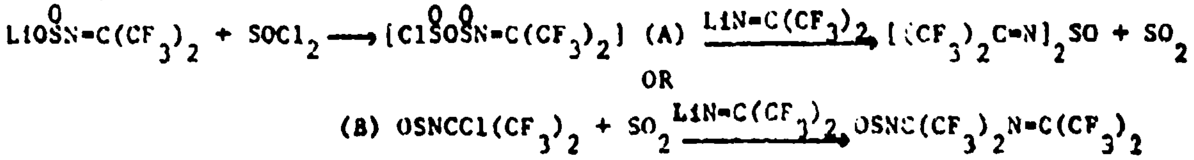
On the other hand, if the intermediates were unstable, they should react further giving rise to rearranged compounds. Thus for $SOCl_2$:



$$\mathrm{LiO\overset{O}{S}N{=}C(CF_3)_2 + SOCl_2 \longrightarrow [Cl\overset{O}{S}O\overset{O}{S}N{=}C(CF_3)_2]\ (A) \xrightarrow{LiN=C(CF_3)_2} [(CF_3)_2C{=}N]_2SO + SO_2}$$

OR

$$\mathrm{(B)\ OSNCCl(CF_3)_2 + SO_2 \xrightarrow{LiN=C(CF_3)_2} OSNC(CF_3)_2N{=}C(CF_3)_2}$$

Experimental Section

Insertion of SO_2 into $(CF_3)_2C=NLi$

SO_2 (10mmol) was condensed onto $(CF_3)_2C=NLi$ (7.2 mmol) at -196° and allowed to warm slowly to 25°. After 2 hr excess SO_2 (2.7 mmol) was removed under vacuum leaving a finely divided cream colored solid(I).

Reaction of (I) and $SOCl_2$

$SOCl_2$ (6.45 mmol) was condensed onto I(2.7 mmol) at -196° and warmed slowly to 25°. After 12 hr the products were separated by gas chromatography using a 2 ft 20% Kel-F on Chromosorb P column to give $(CF_3)_2C(Cl)N=S=O$ (73% yield) and $(CF)_2C=NC(CF_3)_2N=S=O$[1] (16% yield).

$(CF_3)_2CClNSO$ is a colorless liquid with a boiling point of 90.2° obtained from the equation $\log P_{torr} = 8.26 - 1954/T$. The molar heat of vaporization is 8.94 kcal and the Trouton constant is 24.6 eu. The ^{19}F nmr spectrum shows a singlet at 76.3φ. The infrared spectrum is as follows: 1328 m, 1282 vs, 1248 vs, 1198 m, 965 m, 932 m, 752 w, 725 m cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M-F^+$(4), $M-Cl^+$(25), $C_3F_6ClN^+$(2), $C_3F_5NCl^+$(37), $M-CF_3^+$(100), C_2F_4NSO(13), $SOCl^+$(26), CF_3^+(93), SCl^+(25), SO_2^+(33), CF_2^+(13), SO^+(73).

Anal. Calcd for C_3ClF_6NS: C, 14.54; Cl, 14.33; F, 46.1; N, 5.67; S, 12.92; Found C, 14.56; Cl, 14.03; F, 45.8; N, 5.71; S, 12.96.

$(CF_3)_2CClNSO$ is also formed when II and $SOCl_2$ react.

Insertion of CO_2 in $(CF_3)_2C{=}NLi$

CO_2 (10 mmol) and 5 ml of 2-methylbutane were condensed onto $(CF_3)_2C{=}NLi$ (7 mmol) at -196° and allowed to warm slowly to 25°. A vigorous exothermic reaction occurred while still cold which results in a detonation when no 2-methylbutane is used. The latter acts as a heat sink. After 1 hr excess CO_2 (2.8 mmol) and heat sink were removed under vacuum leaving a finely divided cream colored solid (II).

Reaction of (II) + $COCl_2$

$COCl_2$ (8 mmol) was condensed onto II (3.8 mmol) at -196° and warmed slowly to 25°. After 8 hr the products were separated by gas chromatography using a 2 ft 20% Kel-F on Chromasorb P column to give $(CF_3)_2CClN{=}C{=}O$ (50% yield) and $(CF_3)_2C{=}NC(CF_3)_2N{=}C{=}O$[1] (9% yield).

$(CF_3)_2CClNCO$ is a colorless liquid with a boiling point of 50.3° obtained from the equation $\log P_{torr} = 7.81 - 1594/T$. The molar heat of vaporization is 7.35 kcal and the Trouton constant is 22.7 eu. The ^{19}F nmr spectrum shows a singlet at 77.4ϕ. The infrared spectrum is as follows: 2275 vs, 1520 m, 1292 vs, 1248 vs, 1190 m, 1028 s, 962 s, 932 s, 755 m, 722 m cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M{-}F^+$(7), $M{-}Cl^+$(34), $M{-}CF_3^+$ (100), $M{-}CF_2Cl^+$(26), $CFClNCO^+$(31), CF_2NCO^+(70), CF_2CN^+(9), CF_3^+(61), CF_2N^+(57), CF_2^+(9).

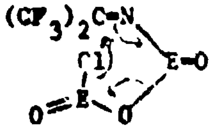
Anal. Calcd for C_4ClF_6N: C, 21.12; Cl, 15.60; F, 50.03; N, 6.17; Found C, 21.00; Cl, 15.42; F, 50.3; N, 6.23.

$(CF_3)_2CClNCO$ is also formed when II and $[ClC(O)]_2$ or $SOCl_2$ react.

Results and Discussion

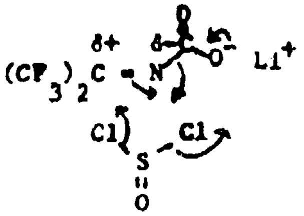
The synthesis of $(CF_3)_2CClNSO$ and $(CF_3)_2CClNCO$ indicates that these products were indeed the postulated intermediates in the formation of $(CF_3)_2C{=}NC(CF_3)_2NSO$ and $(CF_3)_2C{=}NC(CF_3)_2NCO$ since reaction of the intermediates with $LiN{=}C(CF_3)_2$ gives the latter compounds.

No trace of $[(CF_3)_2C{=}N]_2SO$ or $[(CF_3)_2C{=}N]_2CO$ was observed in the above reactions. The products obtained indicate that the proposed intermediates $(CF_3)_2C{=}N\overset{O}{S}O\overset{O}{S}Cl$ and $(CF_3)_2C{=}N\overset{O}{C}O\overset{O}{C}Cl$ are short lived since SO_2 and CO_2 are eliminated at temperatures as low as -30°. The migration of chloride and formation of SO_2 or CO_2 can be rationalized from the pseudo six membered ring.



E = S or C

However, if this intermediate does form, a competing mechanism is probably operative also since reaction of $SOCl_2$ and II gives primarily $(CF_3)_2CClNSO$ with $(CF_3)_2CClNCO$ as a minor product. Reaction of $COCl_2$ with I gives traces of these compounds also but little reaction occurs after 12 hrs at 25°. The formation of these products indicates that nucleophilic attack at the electron deficient double bond may occur.



but the lack of reactivity between $COCl_2$ and I is puzzling. Isotopic labelling experiments would be of help in resolving this problem.

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SOME CHEMISTRY OF DIFLUOROAMINOCARBONYL CHLORIDE. A NEW ROUTE TO PERFLUOROUREA.

by

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Abstract. Improved yields of $NF_2C(O)Cl$ are obtained by short term (4-6 hr) photolysis of N_2F_4 with oxalyl chloride. Reactions of $NF_2C(O)Cl$ with AgCN, AgNCS, AgNCO, $Hg(SCF_3)_2$ and $Hg(ON(CF_3)_2)_2$ give the new difluoroaminocarbonyl pseudohalides: $NF_2C(O)CN$, $NF_2C(O)NCS$, $NF_2C(O)NCO$, $NF_2C(O)SCF_3$, and $NF_2C(O)ON(CF_3)_2$. With excess of either Ag_2O at 0° or HgO at -78°, $NF_2C(O)Cl$ is converted to $(NF_2)_2CO$ and CO_2 in nearly quantitative yield. Chlorocarbonyl fluorosulfate results when $NF_2C(O)Cl$ is mixed with $S_2O_6F_2$ or $BrOSO_2F$.

This work concerns a modified preparation[2,3] of difluoroaminocarbonyl chloride, $NF_2C(O)Cl$, and some of its chemistry on which a preliminary report has recently appeared.[4] It is now possible to prepare the compound in amounts which make studying its chemistry feasible. Only with AgNCS and $Hg(ON(CF_3)_2)_2$ does $NF_2C(O)Cl$ undergo metathetical reactions at or below 25°. With AgCN, AgNCO and $Hg(SCF_3)_2$, higher temperatures, longer reaction times and, in some cases, recycling of unreacted $NF_2C(O)Cl$ is necessary to ensure yields greater than 50%. It is likely that perfluorourea arises via decarboxylation of an unstable symmetrical anhydride intermediate formed when $NF_2C(O)Cl$ reacts with either HgO or Ag_2O. This provides a facile, much less hazardous route to

$(NF_2)_2CO$ than the original method of pyrolyzing $KOCN_2F_5$.[2,5] Reactions of $NF_2C(O)Cl$ with several other silver, mercury and alkali metal salts which do not result in new compounds are also described.

Surprisingly, both peroxydisulfuryl difluoride, $S_2O_6F_2$ and bromine fluorosulfate, $BrOSO_2F$ form chlorocarbonyl fluorosulfate, $ClC(O)OSO_2F$,[6] at 25° with $NF_2C(O)Cl$. Other methods for preparing $ClC(O)OSO_2F$, as well as some of its reaction chemistry, are detailed below.

Experimental

Caution!--Nitrogen-fluorine-containing compounds are strong oxidizing agents and should be handled with proper shielding and other safety precautions. Although we experienced no difficulty in handling these materials, it should be reported that the German analyst was injured when a sample of $NF_2C(O)NCO$ exploded in his hand. These difluoroaminocarbonyl compounds are very sensitive to hydrolysis and can be handled successfully only under highly anhydrous conditions.

Starting materials.--Most reagents used are available from standard chemical supply houses. $AgNCO$,[7] $Hg(ON(CF_3)_2)_2$,[7,8] $Hg(SCF_3)_2$,[8,9] $(CF_3)_2NOH$,[10] $Hg(OSO_2F)_2$,[11] $S_2O_6F_2$,[12] $BrOSO_2F$,[13] and $(CF_3)_2C{=}NLi$[14] were synthesized via literature methods.

Preparation of Difluoroaminocarbonyl Chloride, $NF_2C(O)Cl$.

There are two methods available for the synthesis of $NF_2C(O)Cl$: 1) chlorination of $NF_2C(O)F$ with Al_2Cl_6:[2] and 2) photolysis of a mixture of $Cl(CO)_2Cl$ and N_2F_4.[3] The former method requires first the preparation of $NF_2C(O)F$ (15% yield); then its subsequent conversion to $NF_2C(O)Cl$ which occurs in rather high yield (76%) when mmol amounts are used. However, when the conversion reaction is scaled up by 16-fold, none of the carbonyl chloride is obtained. Therefore, we have modified the latter method to increase the conversion of $Cl(CO)_2Cl$ from 20 to 40% thus making it a method by which preparative amounts of $NF_2C(O)Cl$ can be realized.

In a typical preparation, 112 torr (30 mmol) of $Cl(CO)_2Cl$ is placed in a 5 l. Pyrex bulb equipped with a water-cooled quartz finger. An additional 168 torr (45 mmol) of N_2F_4 is added to the bulb. The mixture is irradiated for 6 hr with a Pyrex-filtered, medium pressure, 450 watt ultraviolet lamp (Hanovia L-679A36, Engelhard Hanovia, Inc.) and a crude separation is effected by fractional condensation. Approximately 18% of the complex product mixture is not condensable at -183° (N_2). The fraction stopped at -183° consists of ~37 mmol of highly volatile material, mostly N_2F_4, N_2F_2, FCOCl, SiF_4, and NF_2Cl. The trap at -139° contains ~10 mmol of a nearly equal mixture of $NF_2C(O)Cl$ and $COCl_2$ plus other minor impurities. The trap at -108° contains ~31 mmol of a similar mixture. The fractions at -108° and -139° are recombined and separated by gas chromatography using a 19 ft x 0.25 in o.d. aluminum column packed with 20% Kel-F-3 oil on Chromasorb P. Two mmol samples can be successfully separated without flooding the column. $NF_2C(O)Cl$ elutes before phosgene. Great care must be taken to keep the column and collection system completely anhydrous.

Reactions of $NF_2C(O)Cl$ with Pseudohalide Salts.--A similar method is used for the preparation of all the new difluoroaminocarbonyl pseudohalides. A measured amount of $NF_2C(O)Cl$ is condensed into a reaction vessel containing an excess of the dry silver or mercury salt. The reaction is allowed to proceed at a suitable temperature for an appropriate length of time depending upon the reactivity of the salt. The volatile products are removed, separated by fractional condensation, and any unreacted $NF_2C(O)Cl$ is recycled to the vessel for additional reaction. Both Pyrex flasks with Teflon valves and stainless steel Hoke bombs can be used successfully (see Table 1). All react extremely rapidly with water by the following general reaction

$$NF_2C(O)X + H_2O \longrightarrow HNF_2 + CO_2 + HX$$

where X = CN, NCO, NCS, $(CF_3)_2NO$, CF_3S

At 25°, these compounds are colorless, with the exception of yellow $NF_2C(O)NCS$, volatile liquids which are stable in glass and in contact with mercury (except $NF_2C(O)SCF_3$). $NF_2C(O)NCS$ exhibits some thermal instability at 25° to form a yellow polymeric material. The rate of decomposition becomes very rapid above 60°.

Reactions with salts which did not produce new compounds.

In most cases, the C-N bond of the $NF_2C(O)Cl$ is cleaved with concomitant loss and/or destruction of the NF_2 group. In some cases, especially where considerable heating is required to produce reaction, the solid seems to catalyze the decomposition of $NF_2C(O)Cl$ to yield the self-fluorination product $NF_2C(O)F$. Compounds reacted with $NF_2C(O)Cl$, reaction temperature(s) and volatile products are as follows:

a) CF_3CO_2Ag; -78 to 25°; $(CF_3CO)_2O$.

b) AgBr or KBr; >100°; Br_2, $NF_2C(O)F$, $NF_2C(O)NCO$.

c) AgI; 25°; I_2, $NF_2C(O)F$, $NF_2C(O)NCO$.

d) $AgClO_4$; 25°; hydrolysis products of $NF_2C(O)Cl$.

e) AgO; 25°; CO_2, NF_3, SiF_4, noncondensable gas.

f) Ag_2S; 25°; $NF_2C(O)F$, $NF_2C(O)NCO$, COS.

g) $NaOCH_3$; -106°; $(CH_3O)_2CO$, trace N_2F_4.

TABLE 1

PROPERTIES OF $NF_2C(O)X$ COMPOUNDS

Salt (mmol $NF_2C(O)Cl$)	Temp. Time(hr)	Product % yield	Elemental Analyses (%) C	 F	 N	 S	$\log P_{Torr}$ = A-B/T A	 B	 ΔH_v kcal/m	 ΔS_v e.u.	MP	BP
AgSCN (2.0)	25°(0.7)	$NF_2C(O)NCS$ 94	17.28 (17.40)*	28.0 (27.5)	20.75 (20.28)	23.53 (23.22)	-	-	-	-	- 92	-
AgNCO (2.0)	40-70°(8)	$NF_2C(O)NCO^a$ 60	19.51 (19.68)	31.4 (31.1)	23.10 (22.96)	---	8.26	1762	8.1	24.6	- 99	54.4
AgCN (2.0)	110°(7+8)^b	$NF_2C(O)CN$ 66		35.3^c (35.8)			8.33	1544	7.1	24.9	-101	10.2
$Hg(SCF_3)_2$ (1.0)	65°(5)^b	$NF_2C(O)SCF_3$ 80	13.16 (13.27)	52.2 (52.5)	7.74 (7.73)	17.66 (17.71)	6.72	1213	5.5	17.6	-119	42.5
$Hg(ON(CF_3)_2)_2$ (1.0)	-95°(10)^b	$NF_2C(O)ON(CF_3)_2$ 69.5	14.01 (14.53)	60.4 (61.3)	11.33 (11.29)	---	8.19	1645	7.5	24.3	-103	36.8

( )* calculated

a yields significantly larger when AgNCO freshly prepared

b recycle

c determined from ^{19}F nmr data

h) NaN_3 or KN_3; 80°; CO_2, 4% $NF_2C(O)N_3$.[15]

i) $Hg(OSO_2F)_2$; 100°; CO_2, N_2O, $NF_2C(O)F$, SO_2, SiF_4, FCOCl, NF_2OSO_2F.

NMR Spectra of $NF_2C(O)X$ Compounds.--The ^{19}F nmr spectra consist of broadened resonances for the fluorine bonded to nitrogen but no coupling between fluorine and nitrogen is observed. High resolution ^{19}F nmr spectra were obtained with a Varian Model HA-100 spectrometer operating at 94.1 MHz with an internal reference of CCl_3F.

Compound	N-F, ϕ	C-F, ϕ	J_{NF-CF}, Hz
$NF_2C(O)CN$	-30.8 s	-	-
$NF_2C(O)NCO$	-35.4 s	-	-
$NF_2C(O)NCS$	-36.0 s	-	-
$NF_2C(O)SCF_3$	-37.4 s	40.7 t	3.6
$NF_2C(O)ON(CF_3)_2$	-34.8 s	68.4 s	-

Infrared data for $NF_2C(O)X$ Compounds.--The infrared spectra, recorded with a Perkin-Elmer Model 621 grating spectrometer using a 5 cm cell equipped with KBr windows, for these five new $NF_2C(O)X$ compounds are: $NF_2C(O)CN$, 2243m, 1805vs, 1796vs, 1151s, 988vs, 789w, 694m, 687m, 481w, 470w; $NF_2C(O)NCO$, 2281vvs, 2220m,sh, 1835vs, 1814s,sh, 180[illegible],sh, 1443, 1415m,sh, 1137m 1093mw, 988s, 820mw, 774m, 613mw; $NF_2C(O)NCS$ - 2035m,sh, 1970vs,br, 1958s sh, 1816s, 1240ms, 1206m, 949mw, 898m, 888m, 864ms, 733m; $NF_2C(O)SCF_3$ - 1956vs, 1816ms, 1787ms, 1197s, 1145m, 1120s, 1064m, 938m, 704s, 765m; $NF_2C(O)ON(CF_3)_2$ - 1885s, 1384w, 1322vs, 1270vs, 1238vs, 1221s, 1191m, 1158s, 1060s, 1013m, 911ms, 960mw,sh, 885m, 794w, 716m, 713s, 659w, cm^{-1}.

Preparation of Perfluorourea, $(NF_2)_2CO$.--In a typical preparation of perfluorourea, 1 mmol of $NF_2C(O)Cl$ is condensed into a 65 ml Pyrex flask containing 15.6 mmol of dry, unused yellow HgO and the reaction proceeds for 2.5 hr at

-78°. The volatile products (1.12 mmol) are $(NF_2)_2CO$, CO_2 and traces of $NF_2C(O)F$ and HNF_2. In a two stage purification, the products are separated first by fractional condensation in traps at -110 or -118° ($NF_2C(O)Cl$), at -138° ($(NF_2)_2CO$ contaminated with hydrolysis product HNF_2), and at -183° (CO_2 and $NF_2C(O)F$). Final purification of perfluorourea is attained by removal of HNF_2 using 5A molecular sieves (30/60 granular, Wilkins Instrument and Research, Inc.). The sieves are carefully predried by strong heating under dynamic vacuum. The best results are obtained by condensing the perfluorourea-difluoramine mixture onto the sieves at -183°, warming the flask to 25° over a 5 min period, and then immediately removing the volatile material. The yield of $(NF_2)_2CO$ is > 95%. Contact times longer than 10 min result in poor recovery of $(NF_2)_2CO$ as well as the formation of some noncondensable gas.

Silver(I) oxide may also be used to prepare $(NF_2)_2CO$ but longer reaction time and higher temperature are required. In a typical preparation, 0.5 mmol $NF_2C(O)Cl$ is allowed to react with 11 mmol of dry Ag_2O in a 65 ml Pyrex flask. After 21 hr at 0°, the volatile products were fractionated with traps at -183 (0,346 mmol CO_2 and $NF_2C(O)F$), -138 (0.21 mmol of nearly pure $(NF_2)_2CO$), -120 and -110°. The latter two traps are essentially empty. The yield of $(NF_2)_2CO$ is ~82%.

Spectral properties of $(NF_2)_2CO$.--*Infrared* bands appear at 1866s, 1859s, 1806w,sh, 1151m, 979ms, 931vs, 847m,tr, 721m,br, 472w, 331m and 255w, cm^{-1}. The *ultraviolet* spectrum was recorded on a Perkin-Elmer Model 202 spectrophotometer using a sample at 0.7 torr in a 10 cm quartz cell. In the range from 190-390 nm, one broad absorption was observed with a maximum at 202 nm. The *^{19}F nmr* spectrum was obtained on a 20 mole-% solution in $CFCl_3$ as a single broad resonance at -33.4ϕ (*vs* -30.8 ppm with external reference). The *mass* spectrum which was recorded at 70 ev shows no molecular ion but fragments of hydrolysis products are present. The base peak is NF_2^+ and the spectrum includes (m/e, species, relative %age): 18, H_2O^+, 25.3; 20, HF^+, 7.0; 28, CO^+, N_2^+, 61.3; 30, NO^+, 6.4; 32, O_2^+, 11.7; 33, NF^+, 49.6; 34, HNF^+, 20.6; 42, NCO^+, 14.6; 43, $HNCO^+$, 6.0; 44, CO_2^+, 78.2; 47, COF^+, 22.3; 52, NF_2^+, 100; 53, HNF_2^+, 29.8; 61, $FNCO^+$, 52.8; 63, FCO_2^+, 6.7; 66, COF_2^+, 4.5; 69, CF_3^+, 7.9; 80, F_2NCO^+, 54.6; 113, F_2NCONF^+, trace.

Preparation of Chlorocarbonyl Fluorosulfate.--There are four methods by which this compound can be prepared but the first two are impractical on the preparative scale. Method four is the most useful. 1) $NF_2C(O)Cl$ + $S_2O_6F_2$, in equimolar amounts (0.5 mmol), are held in a Pyrex tube for 10 hr at 25° and give equal quantities of NF_2OSO_2F[16] and $ClC(O)OSO_2F$. 2) $NF_2C(O)Cl$ + $BrOSO_2F$, in equimolar amounts (0.5 mmol), are held in a Pyrex tube for 1 hr at 25° and react according to $NF_2C(O)Cl + BrOSO_2F \longrightarrow ClC(O)OSO_2F + N_2F_4 + Br_2$. 3) $BrOSO_2F$ (1 mmol) + $COCl_2$ (7.3 mmol), after 16 hr at -65°, gave $ClC(O)OSO_2F$ (0.54 mmol, 54% yield) and BrCl. 4) The thermal reaction between $(COCl)_2$ and $S_2O_6F_2$ gives yields of $ClC(O)OSO_2F$ which are superior to those obtained via photolysis, but each method has an advantage. a) In a typical thermal reaction, 2.1 mmol each of $(COCl)_2$ and $S_2O_6F_2$ are heated slowly to 43° for 30 hr in a 150 ml Pyrex glass tube. The products are separated by use of traps at -183° (1.3 mmol $COCl_2$, CO_2 and Cl_2), -95° (0.1 mmol $S_2O_5F_2$), -78° (2.46 mmol impure $ClC(O)OSO_2F$, 58% yield), and at -47° (trace $Cl(CO)_2OSO_2F$). Carbon monoxide formed passed a trap at -183°.

When equimolar amounts of $(COCl)_2$ and $S_2O_6F_2$ are thermolyzed, the $ClC(O)OSO_2F$ which is trapped is contaminated with unreacted $S_2O_6F_2$ from which it cannot be easily separated by fractional condensation. The best procedure is to use an excess of $(COCl)_2$ (30-50%) and, since it cannot be separated efficiently from the product by fractional condensation, to destroy the unreacted $(COCl)_2$ in the product mixture by photolysis through Pyrex.

b) In a typical photochemical preparation, 1.0 mmol each of $(COCl)_2$ and $S_2O_6F_2$ are irradiated through Pyrex for 4.5 hr in a Srinivasan-Griffin reactor equipped with sixteen 21-watt 3000A uv lamps. Fractional condensation of the products gives in a trap at -183° (1.33 mmol $COCl_2$ and Cl_2), at -78° (0.74 mmol $ClC(O)OSO_2F$, ~37% yield), and at -47° (trace $ClC(O)OSO_2F$).

Chlorocarbonyl fluorosulfate of good purity was then obtained by allowing the product from a) or b) to slowly pass a trap at -47° and to stop in a trap at -64°. Final purification was achieved by gas chromatography using a 3 ft x 0.25 in 20% FS-1265 on Anakrom Tee-Six column at 25°.

Properties of Chlorocarbonyl Fluorosulfate.--$ClC(O)OSO_2F$ is a colorless, dense liquid with a vapor pressure of about 100 torr at 25°. It dissolves readily in halocarbon greases to give a characteristic brown viscous mess which makes handling it in gear with Teflon or metal valves necessary. A glass is formed when $ClC(O)OSO_2F$ is cooled. An experimental molecular weight of 161.8 (162.5) was obtained. Anal. Calcd. for $ClC(O)OSO_2F$: Cl, 21.81; F, 11.7; S, 19.73. Found: Cl, 21.55; F, 11.5; S, 19.97. Infrared spectral bands occur at 1830s, 1492s, 1257s, 1016vs, 871m, 841s, 782m, 657w, and 577s, cm^{-1}. The ^{19}F nuclear magnetic resonance spectrum consists of a single peak at -44.7ϕ. In the mass spectrum no molecular ion occurs, but a fragment $M-Cl^+$ is observed.

Reactions of Chlorocarbonyl Fluorosulfate.--The following reactants and conditions were used and products formed. Invariably, the C-O bond is broken.

a) NH_3 (N_2 diluent); 0°; CO_2, $COCl_2$, COFCl, COF_2, HNCO, SO_2F_2, NH_4^+ salt.

b) $(CH_3)_2NH$; 25°; CO_2, $COCl_2$, SO_2F_2, SiF_4, white solid.

c) AgNCO, -78°; CO_2, $COCl_2$, SiF_4.

d) $(CF_3)_2C{=}NLi$; -78°; $COCl_2$, unidentified isocyanate.

e) KF; 50°; No reaction.

f) CsF; 50°; $COCl_2$, CO_2, COF_2, SO_2F_2, COClF.

g) AgF_2; 25°; CO_2, COF_2, COClF, SiF_4, $S_2O_5F_2$.

Results and Discussion

Oxalyl chloride when photolyzed with an excess of N_2F_4 through Pyrex glass for several hours is more than 40% converted to $NF_2C(O)Cl$ and, while large quantities of other volatile products are formed, preliminary trap-to-trap separation followed by gas chromatography permits good separation of the $NF_2C(O)Cl$. Phosgene is the most difficultly separated contaminant.

$$N_2F_4 \quad + \quad (COCl)_2 \xrightarrow[\text{Pyrex}\atop h\nu]{25^\circ} NF_2C(O)Cl,\ N_2F_2,\ FCOCl,\ COCl_2$$

Higher energy radiation allows generation of a higher concentration of $\cdot C(O)Cl$ radicals but no $NF_2C(O)Cl$ can be isolated under these conditions probably due to photolytic decomposition of the product. In Pyrex glass, there is no evidence of decomposition of $NF_2C(O)Cl$ below 180° at which temperature, after 12 hr, traces of $NF_2C(O)F$ and CO begin to appear. At 240°, complete degradation occurs to produce CO_2, SiF_4, N_2F_4, $COCl_2$, COClF and Cl_2. At intermediate temperatures, the decomposition appears to proceed initially *via* a self-fluorination reaction

$$4NF_2C(O)Cl \longrightarrow 2NF_2C(O)F \quad + \quad NF_2C(O)NCO \quad + \quad CO \quad + \quad 2Cl_2$$

Hydrolysis occurs very readily with only traces of moisture making anhydrous

$$NF_2C(O)Cl + H_2O \longrightarrow HNF_2 + HCl + CO_2$$

conditions an absolute necessity.

Difluoroaminocarbonyl chloride is completely consumed after 40 min upon contact with carefully dried AgSCN at 25°, the major product being $NF_2C(O)NCS$ (94% yield). Some $NF_2C(O)F$ and COF_2 are also formed, the respective amounts increase with reaction time and at the expense of the $NF_2C(O)NCS$. This compound is a faintly yellow liquid which freezes to a white solid and which at 25° commences to decompose slowly to a yellow polymeric material. Decomposition becomes appreciable above 60° and precludes the determination of a normal boiling point although the vapor pressure is about 29 torr at 25°.

Recycling of difluoroaminocarbonyl chloride is necessary after initial contact with AgCN, $Hg(SCF_3)_2$, and $Hg(ON(CF_3)_2)_2$ at various temperatures for several hours in order to completely consume the $NF_2C(O)Cl$. Although prevention of the hydrolysis of these compounds is difficult, it is imperative with $NF_2C(O)CN$ because of one of the hydrolysis products, HCN, is impossible to remove by fractional condensation and attempts to remove it with 4A molecular sieves or gas chromatography were unsuccessful.

For the mercury salt reactions, temperature control as well as temperature range are important since altering the temperature by a few degrees can cause the reaction to proceed to an entirely different set of products. When $NF_2C(O)Cl$ was treated with mercury(II) bis(trifluoromethyl)nitroxide, $Hg(ON(CF_3)_2)_2$, at 0°, $((CF_3)_2NO)_2CO$[17] and N_2F_4 were the only volatile products. After lowering the reaction temperature to -78°, $NF_2C(O)ON(CF_3)_2$ was obtained in 19% yield but $((CF_3)_2NO)_2CO$ was by far the major component (71%). However, at -95°, the yield of $((CF_3)_2NO)_2CO$ falls to ~25%, and $NF_2C(O)ON(CF_3)_2$ increases to 69.5% after a single recycle to utilize the $NF_2C(O)Cl$ completely. While other examples of displacement of $\cdot NF_2$ by $(CF_3)_2NO\cdot$ or $Hg(ON(CF_3)_2)_2$ are not known, $Hg(ON(CF_3)_2)_2$ can, at low temperatures, cause H, or X (F, Cl, Br, I) to be displaced or replaced in a variety of organic and inorganic materials. Although $NF_2C(O)ON(CF_3)_2$ is stable at least to its boiling point (36.8°), whether or not it is stable to further attack by $Hg(ON(CF_3)_2)_2$ at 25 or 0° is unknown. This would be helpful in understanding the production of $((CF_3)_2NO)_2CO$.

An alternate synthesis of $NF_2C(O)ON(CF_3)_2$ is provided not unexpectedly by the reaction between $NF_2C(O)F$ and $(CF_3)_2NOH$ at -50 to -78° in the presence of excess dry CsF for several hours. Some $((CF_3)_2NO)_2CO$ is formed also which makes this reaction analogous to that of $(CF_3)_2NOH$ with COF_2 or $COCl_2$[17] using the same conditions where the majority of product is the mono or disubstituted carbonyl depending on the relative amounts of reactants.

Reaction temperatures in excess of 65° result in the production of large amounts of $NF_2C(O)F$, SiF_4, COF_2 and CO_2 at the expense of $NF_2C(O)SCF_3$ in the reaction of $(CF_3S)_2Hg$ with $NF_2C(O)Cl$. After 5 hr contact of $NF_2C(O)Cl$ with $Hg(SCF_3)_2$ at 65° and a single recycle of the unreacted $NF_2C(O)Cl$, an 80% yield of $NF_2C(O)SCF_3$ is realized. In order to free $NF_2C(O)SCF_3$ from the small quantity of CF_3SSCF_3 formed in the reaction, gas chromatographic separation is necessary.

Photolysis or thermolysis of $NF_2C(O)ON(CF_3)_2$ does not result in decarboxylation to form an unsymmetrical hydrazine but rather, e.g., after 9 hr at 150°, all has been converted to $FC(O)ON(CF_3)_2$, $CF_3N{=}CF_2$, CF_3NCO, SiF_4, NO, $(CF_3)_2NH$ and noncondensable gases, N_2 and CO. No attack was observed by photolysis through a Vycor filter while irradiation through quartz produced approximately the same products as thermal decomposition although at a faster rate.

Molecular ions are not observed in the mass spectra for any of the $NF_2C(O)X$ compounds and fragments arising from hydrolysis products are present in all spectra. For compounds in which the CF_3 moiety occurs, the CF_3^+ ion is the base peak whereas in $NF_2C(O)CN$, and $NF_2C(O)NCS$, $M-NF_2^+$ is the base peak.

Although perfluorourea, $(NF_2)_2CO$ does result from the pyrolysis at 95° of $KOCN_2F_5$, this method is involved, hazardous and the yield is low.[2] We find that while both Ag_2O and yellow HgO will convert $NF_2C(O)Cl$ to $(NF_2)_2CO$, probably through an anhydride intermediate which rapidly decarboxylates, the product is formed at lower temperature and nearly quantitatively with HgO.

$$NF_2C(O)Cl \xrightarrow[-78^\circ]{HgO} (NF_2C(O)O(O)CNF_2) \longrightarrow (NF_2)_2CO \quad + \quad CO_2$$

Difluoroaminocarbonyl chloride with an excess of Ag_2O gives $(NF_2)_2CO$ in yields exceeding 80% when the reaction is carried out at 0° for 20 hr whereas $(NF_2)_2CO$ is produced essentially quantitatively at -78° after 2-3 hr with yellow HgO. The amount of $NF_2C(O)F$ formed at the expense of the $(NF_2)_2CO$ may be reduced by limiting the contact time of $(NF_2)_2CO$ with the solid. Tetrafluorourea is extremely water sensitive, even more so than $NF_2C(O)Cl$ or $NF_2C(O)F$, and can be handled successfully only under "bone-dry" conditions. The reactivity of HgO is greatly reduced after one reaction and for greatest efficiency should be fresh for each reaction.

Perfluorourea appears to be thermally stable in Pyrex to 80° where self-fluorination begins to produce $NF_2C(O)F$ and noncondensable products (N_2 by mass spectrum). At 140°, the rate of thermal decomposition becomes appreciable, and the first trace of SiF_4 appears. The quantity of $NF_2C(O)F$ diminishes at 160°, until finally at 180° the condensable pyrolysis products consist of SiF_4, COF_2 and N_2F_4. When equimolar amounts of $(NF_2)_2CO$ and FNO are combined in a 95 ml Monel bomb at 25° and at -78°, the products are N_2F_4, COF_2, NO and some $NF_2C(O)F$ with no evidence for a nitrite as is observed for the analogous reaction between $(CF_3)_2CO$ and FNO.[18]

Chlorocarbonyl fluorosulfate can be prepared in fair yields by photolysis or thermolysis of a mixture of $S_2O_6F_2$ and $(COCl)_2$ which suggests combination of $FSO_2O\cdot$ and $\cdot C(O)Cl$ radicals. It undergoes slow hydrolysis

$$ClC(O)OSO_2F + H_2O \longrightarrow HCl + CO_2 + HOSO_2F$$

$ClC(O)OSO_2F$ is stable in Pyrex glass up to 100° where it slowly commences to give traces of $COCl_2$, CO_2 and noncondensable gas. At 160°, thermal decomposition is complete

$$ClC(O)OSO_2F \xrightarrow[SiO_2]{160^\circ} CO_2 + COCl_2 + SiF_4 + SO_2$$

Although not the best preparative methods, the more interesting chemically are the reactions of $NF_2C(O)Cl$ with $S_2O_6F_2$ and with $BrOSO_2F$ where, in each case, the production of $ClC(O)OSO_2F$ is not the one predicted based on the previous chemistry of $S_2O_6F_2$ or $BrOSO_2F$ where chlorine would invariably be attacked or, as above with $Hg(ON(CF_3)_2)_2$, at warmer temperatures, both the C-N and C-Cl bonds would be severed.

The unexpected reaction behavior of $ClC(O)OSO_2F$ in which the C-O bond is apparently the weakest may arise from the extreme stability of the fluorosulfate radical, but whatever the cause, this fact precludes its use as a synthetic reagent under the conditions tried here.

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