

The ^{19}F and ^{31}P nmr data are recorded in Table III. The ^{19}F spectra consist of simple doublets centered in the ϕ^* 39–74 range with $J_{\text{P-F}}$ varying between 1020 and 1140 Hz for phosphorus(V) azides and $J_{\text{P-F}}$ 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 occurrence of two bands in their ultraviolet spectra similar to those of typical alkyl azides.^{11,12} However, because of inductive effects of the fluorophosphoryl or fluorothiophosphoryl groups, there is a marked shift to higher energies. Our values agree well with those reported by Ruff¹³ for FSO_2N_3 (199, 249 nm) and $\text{CF}_3\text{SO}_2\text{N}_3$ (195, 238 nm). These bands arise from $\pi_y \rightarrow \pi_x^*$ and $sp_x \rightarrow \pi_y^*$ transitions with the latter occurring

- (11) W. D. Clossen and H. B. Gray, *J. Amer. Chem. Soc.*, **85**, 290 (1963).
 (12) J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 889 (1964).
 (13) J. K. Ruff, *ibid.*, **4**, 567 (1965).

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 II) 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%; $\text{F}_2\text{P}(\text{O})\text{N}_3$, 79%; $\text{F}_2\text{P}(\text{S})\text{N}_3$, 89%; $\text{FP}(\text{O})(\text{N}_3)_2$, 100%; and $\text{FP}(\text{S})(\text{N}_3)_2$, 57%. In the case of F_2PN_3 , a fragment at m/e 166 is very likely attributable to $(\text{F}_2\text{PN})_2$ 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 $\text{F}_2\text{P}(\text{S})\text{N}_3$ found in this work with that reported at 100 eV² shows very good agreement.

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

Acknowledgments.—Fluorine research at the University of Idaho is supported by the National Science Foundation and the Office of Naval Research. We thank R. A. De Marco for mass spectra and D. T. Sauer for nuclear magnetic resonance spectra.

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

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Received November 30, 1971

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. $(\text{CF}_3)_2\text{C}=\text{NSCl}$ is readily converted to $(\text{CF}_3)_2\text{CF}=\text{NSF}_2$ by fluorinating agents.

The lithium salt of hexafluoroisopropylideneimine has been shown to react with compounds that contain labile halogens (Cl, F) to introduce the hexafluoroisopropylideneimine 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 $\text{LiN}=\text{C}(\text{CF}_3)_2$ 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 $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$ gives $(\text{CF}_3)_2\text{C}=\text{NSCl}$. 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), $(\text{CF}_3)_2\text{CCIN}=\text{S}=\text{NCCl}(\text{CF}_3)_2$. Although Seel has fluorinated Cl_3SCl stepwise to CF_3SF with KF at 150°C or with HgF_2 solely to CF_3SF and its dimer at 130°C,⁷ and CF_3SSCF_3 is readily fluorinated to CF_3SF_3 with

- (1) Alfred P. Sloan Foundation Fellow.
 (2) R. F. Swindell, T. J. Ouellette, D. P. Babb, and J. M. Shreeve, *Inorg. Nucl. Chem. Lett.*, **7**, 239 (1971).
 (3) R. F. Swindell, D. P. Babb, T. J. Ouellette, and J. M. Shreeve, *Inorg. Chem.*, **11**, 242 (1972).
 (4) B. Cetinkaya, M. F. Lappert, and J. McMeeking, *Chem. Commun.*, 215 (1971).
 (5) R. F. Swindell and J. M. Shreeve, *J. Amer. Chem. Soc.*, in press.

- (6) F. Seel, W. Gombler, and R. Budenz, *Angew. Chem., Int. Ed. Engl.*, **6**, 706 (1967).
 (7) F. Seel and W. Gombler, *ibid.*, **8**, 773 (1969).

TABLE I
INFRARED SPECTRA

| $(CF_3)_2C=NS_2$ | $(CF_3)_2C=NSCl$ | $(CF_3)_2C=NSN(CH_3)_2$ | $[(CF_3)_2C=N]_2S$ | $(CF_3)_2C=NSNH_2$ | $(CF_3)_2C=NSC\equiv N$ | $(CF_3)_2C=NSSCH_3$ |
|------------------|------------------|-------------------------|--------------------|--------------------|-------------------------|---------------------|
| 1630 w | 1630 m | 2980 w | 1335 m | 3460 w | 1640 w | 2950 w |
| 1335 s | 1330 s | 2960 m | 1305 m | 1615 w | 1335 m | 1610 w |
| 1260 s | 1270 vs | 1605 w | 1275 sh | 1340 m | 1265 s | 1440 w |
| 1240 sh | 1195 vs | 1450 w | 1250 vs | 1260 s | 1205 s | 1420 w |
| 1200 s | 980 s | 1380 w | 1205 s | 1195 s | 990 m | 1335 m |
| 980 s | 905 m | 1347 m | 1185 sh | 982 m | 745 m | 1250 s |
| 730 m | 750 m | 1255 s | 985 m | 715 m | 730 sh | 1190 s |
| 715 m | 715 s | 1190 s | 960 s | 490 w | | 990 m |
| | 540 w | 980 m | 940 sh | | | 955 sh |
| | 490 m | 725 m | 915 m | | | 735 |
| | 455 w | 680 w | 750 m | | | 710} d, m |
| | | | 720 m | | | |

TABLE II
 1H AND ^{19}F NMR SPECTRA

| Compound | ^{19}F nmr, ppm | 1H nmr, ppm (δ) |
|-------------------------|-------------------|-----------------------------|
| $[(CF_3)_2C=NS]_2$ | 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 | |

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 concomitant 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 monosubstituted product in each case, R_fNH_2 , $R_fN(CH_3)_2$, R_fSSCH_3 , and R_fCN (where $R_f = (CF_3)_2C=NS$).

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 apparatus¹⁰ was employed for compounds that react with mercury. Otherwise, an isoteniscope 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 analysis data are given in Tables I–III.

Bis(hexafluoroisopropylideneimino) Disulfide, $[(CF_3)_2C=N]_2S_2$.—In an inert atmosphere box, 6 ml of 2.34 M (14 mmol) *n*-butyllithium in hexane was transferred by syringe to a 100-ml Pyrex

TABLE III
ELEMENTAL ANALYSES AND THERMODYNAMIC DATA

| Compound | Mol wt | Elemental analyses, % ^a | | | | | Bp, °C | ΔH_v , kcal/mol | ΔS_v , eu | Log $P_{Torr} = A - B/T^\circ K$ | |
|-------------------------|------------------|------------------------------------|------------------|----------------|------------------|------------------|--------------------|-------------------------|-------------------|----------------------------------|------|
| | | S | C | H | F | N | | | | Cl | A |
| $[(CF_3)_2C=N]_2S_2$ | | 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) | 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) | 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) | | | | | |

^a Calculated values are in parentheses.

Experimental Section

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

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. S_2Cl_2 (0.61 g, 4.6 mmol) and 2-methylbutane (1.96 g, 24 mmol) 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 removed by shaking with

(8) E. W. Lawless and L. D. Harman, *Inorg. Chem.*, **7**, 391 (1968).

(9) O. Glemser and S. P. von Halasz, *Chem. Ber.*, **102**, 3333 (1969).

(10) K. B. Kellogg and G. H. Cady, *J. Amer. Chem. Soc.*, **70**, 3086 (1948).

mercury for 0.5 hr. Final purification of $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$ 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), $(\text{CF}_3)_2\text{-CCIN}=\text{S}=\text{NCCI}(\text{CF}_3)_2$.—A quartz vessel (220 ml) which contained 1.89 g (4.8 mmol) of $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$ 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. $[(\text{CF}_3)_2\text{-CCIN}=\text{S}=\text{N}]_2$ is also produced when $(\text{CF}_3)_2\text{C}=\text{NSCl}$ is photolyzed.

Chloro(hexafluoroisopropylideneimino)sulfur(II), $(\text{CF}_3)_2\text{C}=\text{NSCl}$.—By standard vacuum methods, 2.71 g (6.9 mmol) of $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$ 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 $(\text{CF}_3)_2\text{C}=\text{NSCl}$ was isolated. $(\text{CF}_3)_2\text{C}=\text{NSCl}$ is also produced when the two reactants are photolyzed at 2537 Å in a Rayonet "Srinivasan-Griffin" photochemical reactor. The yield is much lower and there are numerous other products.

Dimethylamino(hexafluoroisopropylideneimino)sulfur(II), $(\text{CF}_3)_2\text{C}=\text{NSN}(\text{CH}_3)_2$.—A 100-ml Pyrex bulb containing 0.67 g (2.90 mmol) of $(\text{CF}_3)_2\text{C}=\text{NSCl}$ and 0.32 g (7.3 mmol) of $(\text{CH}_3)_2\text{NH}$ 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(hexafluoroisopropylideneimino)sulfur(II), $(\text{CF}_3)_2\text{C}=\text{NSNH}_2$.—Starting materials, 0.288 g (1.24 mmol) of $(\text{CF}_3)_2\text{C}=\text{NSCl}$ 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 $(\text{CF}_3)_2\text{C}=\text{NSNH}_2$ stopped in a U-trap cooled at -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(hexafluoroisopropylideneimino)sulfur(II), $(\text{CF}_3)_2\text{C}=\text{NSC}\equiv\text{N}$.—Using standard vacuum techniques, 0.37 g (1.60 mmol) of $(\text{CF}_3)_2\text{C}=\text{NSCl}$ was condensed onto excess AgCN , which had been dried at 75° under dynamic vacuum, and 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 $(\text{CF}_3)_2\text{C}=\text{NSC}\equiv\text{N}$ was isolated (50.5%). Decomposition occurs at 82° .

Bis(hexafluoroisopropylideneimino)sulfur(II), $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}$.—Photolysis of 0.390 g (1.0 mmol) of $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$ contained in a 220-ml quartz vessel for 8 hr gave 0.320 g (0.9 mmol) of $(\text{CF}_3)_2\text{C}=\text{NSN}=\text{C}(\text{CF}_3)_2$ (90%) and a yellow solid (sulfur). The Hanovia lamp (Model 30620) was used. The compound was identified from its infrared spectrum.⁸

Methyl Hexafluoroisopropylideneimino Disulfide, $(\text{CF}_3)_2\text{C}=\text{NSSCH}_3$.— $(\text{CF}_3)_2\text{C}=\text{NSCl}$ (0.46 g, 2 mmol) and CH_3SH (0.096 g, 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 $(\text{CF}_3)_2\text{C}=\text{NSSCH}_3$ was obtained (45%). Small amounts of the monosulfide, $(\text{CF}_3)_2\text{C}=\text{NSCH}_3$, also were isolated (~10% yield).

Results and Discussion

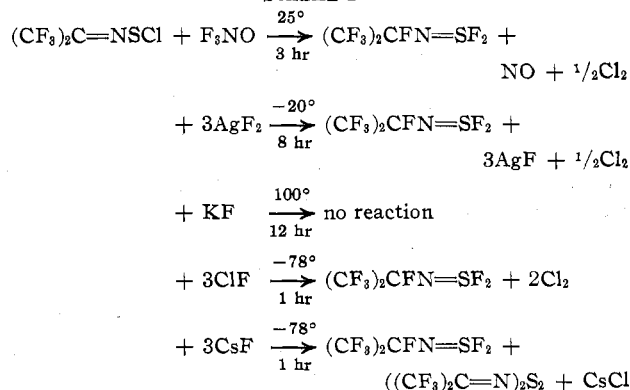
Disulfur dichloride reacts readily with hexafluoroisopropylideneiminolithium to form $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$ in high yield. The use of a solvent (2-methylbutane) greatly increases the yield from 48% in a neat reaction to 89%. The disulfur dichloride was distilled under an atmosphere of dry nitrogen to remove any sulfur dichloride which would react with $\text{LiN}=\text{C}(\text{CF}_3)_2$ to form $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}^2$ 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, $((\text{CF}_3)_2\text{CCIN}=\text{S})_2$. However, if the mixture of disulfide and chlorine is irradiated at 2537 Å through quartz using a Srinivasan-Griffin photochemical reactor, the sulfur-sulfur bond is severed and the reactive new sulfenyl compound $(\text{CF}_3)_2\text{C}=\text{NSCl}$ is formed. However, because of fewer side reactions and higher yield, $(\text{CF}_3)_2\text{C}=\text{NSCl}$ is better produced by heating the two reactants at 100° for 12 hr.

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, $(\text{CF}_3)_2\text{C}=\text{NSN}(\text{CH}_3)_2$ and $(\text{CF}_3)_2\text{C}=\text{NSNH}_2$, or sulfenyl cyanide, $(\text{CF}_3)_2\text{C}=\text{NSNC}\equiv\text{N}$. In the reaction of $(\text{CF}_3)_2\text{C}=\text{NSCl}$ 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 $(\text{CF}_3)_2\text{C}=\text{NSN}(\text{CH}_3)_2$, are all yellow.

The chemistry of $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$ and $(\text{CF}_3)_2\text{C}=\text{NSCl}$ 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 $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$ and Hg when they were photolyzed or thermolyzed, whereas the photolysis of CF_3SSCF_3 with Hg forms $(\text{CF}_3\text{S})_2\text{Hg}$.¹¹ Unlike with CF_3SCl , it is impossible to simply fluorinate the sulfenyl chloride to a sulfenyl fluoride. Instead, the perfluoroisopropylsulfur difluoride imine, $(\text{CF}_3)_2\text{CFN}=\text{SF}_2$,⁸ results in every case when fluorination occurs. Isolation of perfluoroisopropylideneiminosulfur 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 $\text{C}=\text{N}$ to $\text{N}=\text{S}$. The equations in Scheme I show the fluorina-

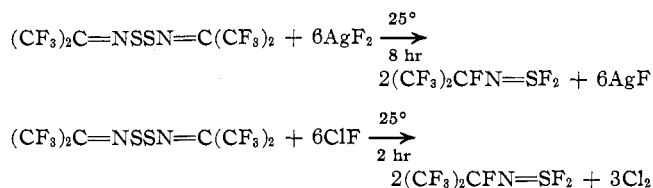
SCHEME I



tions that were tried in attempts to prepare the sulfur trifluoride. 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 $(\text{CF}_3)_2\text{C}=\text{NSF}$ forms but disproportionates to give $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$

and $(\text{CF}_3)_2\text{C}=\text{NSF}_3$ which subsequently rearranges to $(\text{CF}_3)_2\text{CFN}=\text{SF}_2$.

The disulfide also reacts with fluorinating agents as shown below.



Correlation of the ^{19}F nmr chemical shifts or of the infrared stretching frequencies of the $\text{C}=\text{N}$ moiety with the substituent group attached to the $(\text{CF}_3)_2\text{C}=\text{NS}$ group cannot 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 moiety, *e.g.*, CF_3SCl , CF_3SNH_2 , etc.

It is interesting to note that in the case of $(\text{CF}_3)_2\text{C}=\text{NSCl}$ and $(\text{CF}_3)_2\text{C}=\text{NSN}(\text{CH}_3)_2$, 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 in-

version energies. Ruff¹² reported that the CF_3 groups in $(\text{CF}_3)_2\text{C}=\text{NF}$ 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 and 65.4 ppm in $(\text{CF}_3)_2\text{C}=\text{NSCl}$ and $(\text{CF}_3)_2\text{C}=\text{NSN}(\text{CH}_3)_2$ are assigned to the CF_3 group trans to Cl and $\text{N}(\text{CH}_3)_2$, 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 $\text{C}=\text{N}$ stretching frequencies being lowered only by 35 cm^{-1} ($1640\text{--}1605 \text{ cm}^{-1}$) when the substituent is changed from dimethylamino to cyano. The $\text{C}=\text{N}$ stretching frequency in the $(\text{CF}_3)_2\text{C}=\text{NSCl}$ and $((\text{CF}_3)_2\text{C}=\text{N})_2\text{S}_2$ 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 $[(\text{CF}_3)_2\text{C}(\text{Cl})\text{N}]_2\text{S}$ where $(M - \text{Cl}^+)$ is the highest m/e , all spectra show rather intense molecule ion peaks.

Acknowledgment.—Fluorine research at the University of Idaho is supported by the Office of Naval Research and the National Science Foundation. We are indebted to Mr. R. A. De Marco for mass spectra and to Dr. D. T. Sauer and Mr. R. F. Swindell for nuclear magnetic resonance spectra.

(12) J. K. Ruff, *J. Org. Chem.*, **32**, 1675 (1967).

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New Cyclodisilazane Derivatives

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Received October 25, 1971

Cyclodisilazanes with mixed silicon-substituted groups $\{\text{Cl}(\text{CH}_3)\text{RSi}[\text{SiR}(\text{CH}_3)\text{N}]_2\text{SiR}(\text{CH}_3)\text{Cl}\}$ can be prepared either by heating mixtures of $[\text{R}(\text{CH}_3)\text{SiNH}]_3$ and $\text{R}(\text{CH}_3)\text{SiCl}_2$ or by treating $\text{HN}[\text{Si}(\text{CH}_3)\text{RCl}]_2$ with butyllithium and heating the product. One or both of the methods are shown to be applicable where R is ethyl, vinyl, phenyl, or 3,3,3-trifluoropropyl as well as methyl. The properties of the intermediate cyclotrisilazanes and disilazanes as well as the dialkylamino derivatives of the cyclodisilazanes are described.

Introduction

Recently, we reported the synthesis and properties of *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (1) and a number of its functional derivatives.^{1,2} In that work, 1 was obtained in good yields by heating dichlorodimethylsilane and hexamethylcyclotrisilazane or octamethylcyclotrisilazane at 175° . The work described in this paper encompasses an examination of procedures applicable to the synthesis of cyclodisilazane derivatives with mixed silicon-substituted groups, $\text{Cl}(\text{CH}_3)\text{RSi}[\text{SiR}(\text{CH}_3)\text{N}]_2\text{SiR}(\text{CH}_3)\text{Cl}$, as well as certain intermediates and derivatives.

Results

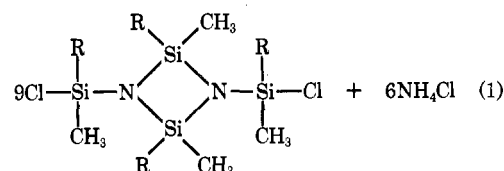
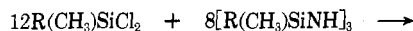
The structures and physical properties of substances examined in the course of this work are summarized in

(1) L. W. Breed, R. L. Elliott, and J. C. Wiley, Jr., *J. Organometal. Chem.*, **24**, 315 (1970).

(2) L. W. Breed, W. L. Budde, and R. L. Elliott, *ibid.*, **6**, 676 (1966).

Table I. The phenyl-, 3,3,3-trifluoropropyl-, vinyl-, and ethylcyclodisilazane derivatives could all be prepared by the method previously used to prepare 1, provided higher temperatures were used when larger groups were present.

Although 4 and 5 could be satisfactorily obtained by



2, R = 3,3,3-trifluoropropyl

3, R = phenyl

4, R = vinyl

5, R = ethyl