Complexation of Pd(II) at C5B in the dimer shortens the C5B-C4B and C5B-C6B bonds by about 0.03 Å and lengthens the C4B-O4B and C6B-O6B bonds by about 0.03 Å compared with free barbituric acid. 11 The C4B-C6B angle is about 2° greater than in uncomplexed ligand. Other ring bond lengths including those to complexed N1B are less affected. The greatest bond angle change is at C2B-N1B-C6B, which is about 4° less and more nearly trigonal in the complex than in the free ligand.

The geometry of the barbiturate complex happens to be convenient for dimer formation. However, the existence of coordination sites at the two ends of the barbiturate ligand makes polymeric linkages seem even more likely in general, and this appears a possible mechanism for forming the polymeric linkages in the platinum blues. Distances between Pd and the two nitrogens of diaminoethane are unequal with the bond between Pd-N(1) being 0.035 Å shorter than that between Pd-N(2). This difference may reflect a greater trans effect of a tetrahedral carbon compared to a trigonal nitro-

Acknowledgment. Support received for instrumentation

under National Science Foundation Grant GP-41679 is gratefully acknowledged.

Supplementary Material Available: Tables of the observed structure factors (7 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) C. M. Flynn, Jr., T. S. Viswanathan, and R. B. Martin, J. Inorg. Nucl. Chem.,
- 39, 437 (1977). (2) M. C. Lim and R. B. Martin, *J. Inorg. Nucl. Chem.*, 38, 1911, 1915 (1976).
- (3) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, Inorg. Chem., 6, 197
- (4) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
 (5) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175
- (1975).
- (6) D. T. Cromer and J. A. Ibers, ref 4.
- (7) G. M. Mockler, D. P. Freyberg, and E. Sinn, J. Chem. Soc., Dalton Trans., 447 (1976).
- (8) See paragraph at end of paper regarding supplementary material.
 (9) A. G. Swallow and M. R. Truter, *Proc. R. Soc. London, Ser. A*, 254, 205 (1960); A. C. Hazell and M. R. Truter, *ibid.*, 254, 218 (1960).
- (10) B. M. Craven, *Acta Crystallogr.*, 17, 282 (1964).
 (11) G. A. Jeffrey, S. Ghose, and J. O. Warwicker, *Acta Crystallogr.*, 14, 881 (1969); W. Bolton, ibid., 16, 166 (1963).

Some Chemistry of Fluorinated Octahedral Sulfur Compounds

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Abstract: Reactive nucleophiles such as C₆F₅SLi and CF₃SLi readily attack cis-SF₄(OCF₃)₂, SF₅Cl, CF₃SF₄Cl, and cis- $CF_3SF_4CF_3$ to form $(R_F)_2S_3$ and $(R_F)_2S_2$ $(R_F = C_6F_5, CF_3)$ plus CF_2O , R_FSCI , CF_3CI , and CF_4 , respectively. With C_6F_5Li , cis-SF₄(OCF₃)₂ yields (C₆F₅)₂SF₂, (C₆F₅)₂SO, C₆F₆, and CF₂O; SF₅Cl gives (C₆F₅)₂SO and C₆F₆; CF₃SF₄Cl forms $(C_6F_5)_2S$, C_6F_6 , and CF_3CI ; and cis- $CF_3SF_4CF_3$ produces $CF_3SF_2CF_3$ and C_6F_6 . With $LiN=C(CF_3)_2$, cis- SF_4X_2 (X = OCF_3 , OSO_2F) gives $SF_3X=NCF(CF_3)_2$; cis- $CF_3SF_4CF_3$ forms $(CF_3)_2SF_2=NCF(CF_3)_2$ and $(CF_3)_2SF_2=NC(CF_3)_2$ - $NCF(CF_3)_2$ N= $C(CF_3)_2$; and $\dot{S}F_4CF_2SF_4\dot{C}F_2$ yields $(CF_3)_2CFN=SF_2(CF_2)_2SF_2=NCF(CF_3)_2$. In reactions with alcohols, ROH (R = $(CF_3)_2(CH_3)C$, $CH_3(CH_2)_8CH_2$, $(CH_3)_3C$, $C_6H_5CH_2CH_2$), $cis-SF_4(OCF_3)_2$ produces the respective olefins $(CF_3)_2$ - $C=CH_2$, $CH_3(CH_2)_7CH=CH_2$, $(CH_3)_2C=CH_2$, and $C_6H_5CH=CH_2$.

There is active research interest in the utilization of trigonal bipyramidal or octahedral sulfur compounds for investigating the stereochemistry about the sulfur atom. Earlier we reported the successful syntheses of a variety of stable new penta- and tetracoordinated sulfur(VI) compounds by stepwise defluorination reactions of SF_5X (X = Cl, Br) and CF_3SF_4Cl with the reactive nucleophile LiN= $C(CF_3)_2$.

However, with the exception of sulfonium salts,²⁻⁵ few compounds are available as suitable model compounds of trigonal bipyramidal⁶⁻⁸ or octahedral sulfur. The behavior of trigonal bipyramidal sulfur with halogen ligands is evident from the literature, 9-13 although utilization of these compounds for such stereochemical studies has been rare. In fact, $(C_6H_5)_2S(OC(CF_3)_2C_6H_5)_2$, which was prepared by Martin and co-workers, ¹⁴⁻¹⁹ is the only example of a useful model trigonal bipyramidal sulfur compound leading to sulfilimines, epoxides, and olefins.

It is interesting to compare the behavior of octahedral sulfur compounds with that of compounds with trigonal bipyramidal sulfur. This work describes the stereochemical results which suggest that the octahedral sulfur compounds such as cis- $SF_4(OCF_3)_2$, $cis-SF_4(OSO_2F)_2$, $cis-CF_3SF_4CF_3$, SF_5Cl ,

SF₅Br, and CF₃SF₄Cl are useful reagents with unusual properties for synthetic utility.

Results and Discussion

The sulfurane, $(C_6F_5)_4S$, which is the first example of a compound with four carbon atoms bonded to sulfur, was synthesized by Sheppard et al. 20,21 by the replacement of the sulfur-fluorine atoms of $C_6F_5SF_3$ in reaction with C_6F_5Li at -78 °C. This interesting compound is stable only to 0 °C.

We find that pentafluorothiophenyllithium readily attacks cis-SF₄(OCF₃)₂ or SF₅Br at -78 °C to form bis(pentafluorophenyl)trisulfane and bis(pentafluorophenyl)disulfane. However, in its reaction with SF₅Cl, in addition to the di- and trisulfanes, C₆F₅SCl is also produced.

$$cis\text{-SF}_{4}(\text{OCF}_{3})_{2} \xrightarrow[\text{Et}_{2}\text{O}/-78\text{ °C}]{\text{C}_{6}\text{F}_{5}\text{SLi}}} (\text{C}_{6}\text{F}_{5})_{2}\text{S}_{3}$$

$$+ (\text{C}_{6}\text{F}_{5})_{2}\text{S}_{2} + \text{COF}_{2}$$

$$\text{SF}_{5}\text{Br} \xrightarrow[\text{Et}_{2}\text{O}/-78\text{ °C}]{\text{C}_{6}\text{F}_{5}\text{SLi}}} (\text{C}_{6}\text{F}_{5})_{2}\text{S}_{3} + (\text{C}_{6}\text{F}_{5})_{2}\text{S}_{2} + [\text{Br}_{2}]$$

$$SF_5Cl \xrightarrow{C_6F_5SLi} (C_6F_5)_2S_3 + (C_6F_5)_2S_2 + C_6F_5SCl$$

Regardless of the molar ratio of the reactants, these are the only products obtained.

A similar type of behavior is also observed in the nucleophilic reactions of trifluorothiomethyllithium.

$$cis$$
-SF₄(OCF₃)₂ $\xrightarrow{\text{CF}_3\text{SLi}}$ (CF₃)₂S₃ + (CF₃)₂S₂ + COF₂
SF₅Cl $\xrightarrow{\text{CF}_3\text{SLi}}$ (CF₃)₂S₃ + (CF₃)₂S₂ + CF₃SCl

In contrast, the reaction of equimolar amounts of pentafluorophenyllithium with cis-SF₄(OCF₃)₂ produces bis(pentafluorophenyl)sulfur difluoride, bis(pentafluorophenyl) sulfoxide, hexafluorobenzene, and carbonyl fluoride. It is likely that bis(pentafluorophenyl) sulfoxide is formed by hydrolysis of bis(pentafluorophenyl)sulfur difluoride in the presence of traces of moisture.

$$cis$$
-SF₄(OCF₃)₂ $\xrightarrow{C_6F_5Li}$ (C₆F₅)₂SF₂
+ (C₆F₅)₂SO + C₆F₆ + COF₂

In an attempt to establish the reaction path, the reaction was carried out with an excess of pentafluorophenyllithium. Under these conditions the products isolated were $(C_6F_5)_2S$, $(C_6F_5)_2$, C_6F_6 , and COF_2 . The fluorine atoms of $(C_6F_5)_2SF_2$ were replaced rapidly as the latter undergoes further attack by the nucleophile. Subsequent reduction of sulfur(IV) to sulfur(II) gives rise to bis(pentafluorophenyl) sulfide and decafluorobiphenyl. 20,21

$$cis\text{-SF}_{4}(OCF_{3})_{2} \xrightarrow{\text{excess } C_{6}F_{5}Li} (C_{6}F_{5})_{2}SF_{2} + C_{6}F_{6} + COF_{2}$$

$$C_{6}F_{5}Li \downarrow (C_{6}F_{5})_{2} + (C_{6}F_{5})_{2}S \longleftarrow [(C_{6}F_{5})_{6}S]$$

A likely intermediate in the reaction of SF_5X (X = Cl, Br) with C_6F_5Li is the highly unstable (C_6F_5)₂SXF. Although it was not possible to isolate the latter compound, its hydrolysis product, bis(pentafluorophenyl) sulfoxide, was found.

$$SF_{s}X \xrightarrow{C_{\theta}F_{s}Li} [(C_{\theta}F_{s})_{2}SXF] + C_{\theta}F_{\theta}$$

$$\xrightarrow{H_{2}O} (C_{\theta}F_{s})_{2}SO$$

Based on our earlier studies which indicate that the sulfur-fluorine bonds in SF_5X are severed readily when the molecule is attacked by nucleophiles, we postulate the tetracoordinate intermediate, $(C_6F_5)_2SXF$. This is also supported by the isolation of hexafluorobenzene only and none of either chloropentafluorobenzene or bromopentafluorobenzene.

Reactions of CF₃SF₄Cl with pentafluorothiophenyllithium and pentafluorophenyllithium as nucleophiles were carried out and again reduction of sulfur(VI) to sulfur(II) occurred. In addition, chlorotrifluoromethane was an unexpected product.

$$CF_{3}SF_{4}CI \longrightarrow (C_{6}F_{5})_{2}S_{3} + (C_{6}F_{5})_{2}S_{2} + CF_{3}CI$$

$$CF_{3}SF_{4}CI \longrightarrow (C_{6}F_{5})_{2}S + C_{6}F_{6} + CF_{3}CI$$

With cis-CF₃SF₄CF₃, the following reactions occur.

$$cis-CF_3SF_4CF_3 \longrightarrow CF_3SF_3CF_3 + CF_4$$

$$C_6F_5Li \longrightarrow CF_3SF_3CF_3 + C_6F_6$$

In the case with each of these sulfur hexafluoride derivatives which undergoes nucleophilic attack by these reactive lithium salts, the initial attack is most likely at the equatorial position on sulfur where the fluorine atoms exhibit a large negative ¹⁹F NMR chemical shift or at the S-O bond. A rapid ligand exchange proceeds stepwise to the tri- (I) or tetra- (II) equato-

rially substituted derivatives. The next step is the collapse of the hexacoordinated species via equatorial-equatorial or axial-equatorial coupling.

Reactions of pentafluorothiophenyllithium with cis- $SF_4(OCF_3)_2$ and SF_5Br lead to bis(pentafluorophenyl)trisulfane and bis(pentafluorophenyl)disulfane exclusively, whereas reaction with SF_5Cl also gives pentafluorophenyl-sulfenyl chloride. The pentafluorophenylsulfenyl bromide decomposes to bis(pentafluorophenyl)disulfane. There is no evidence for the formation of $(C_6F_5S)_2SF_2$ which might result from reaction intermediate type II, but also which would be expected to be unstable toward further decomposition. Scheme I accounts for the above results.

Scheme

$$F = \begin{cases} C_{6}F_{5}SLi \\ C_{6}F_{5}SLi \\ C_{6}F_{5}SLi \\ C_{6}F_{5}SLi \\ C_{6}F_{5}SLi \\ F = \begin{cases} C_{6}F_{5}SLi \\ C_{6}F_{5}SLi \\ F = \begin{cases} C_{6}F_{5}SLi \\ C_{6}F_{5}$$

Thus for the type II intermediate, axial-equatorial coupling occurs to leave bis(pentafluorophenyl)trisulfane and produce C_6F_5SX (C_6F_5SX (X = Br) \rightarrow (C_6F_5S)₂ + Br₂) and C_6F_5SF which reacts with ether to form (C_6F_5S)₂ and unisolable fluoro ether degradation products. The absence of (C_6F_5S)₂SFX (X = F, Cl, Br) or (C_6F_5S)₂SO precludes equatorial-equatorial coupling as a viable decomposition route to (C_6F_5S)₂.

However, with pentafluorophenyllithium, the formation of bis(pentafluorophenyl)sulfur difluoride, in which the sulfur atoms are axial, requires reaction intermediate type I rather than type II as in reaction A. In the case of type I, equatorial-equatorial coupling would occur exclusively to produce the observed products and not either chloro- or bromopenta-fluorobenzene where possible as in reaction B. This is so.

$$F = \begin{cases} F \\ OCF_3 \end{cases} \xrightarrow{C_4F_5Li} F = \begin{cases} F \\ OCF_3 \end{cases} \xrightarrow{C_6F_5} C_6F_5 \\ C_6F_5 = \begin{cases} F \\ C_6F_5 \end{cases} \xrightarrow{C_6F_5} C_6F_5 \end{cases}$$

$$C_4F_5 + (C_4F_5)_2SF_2 \xrightarrow{F} C_6F_5$$

$$C_6F_5 = \begin{cases} F \\ C_6F_5 \end{cases} \xrightarrow{C_6F_5} C_6F_5$$

$$C_6F_5 = \begin{cases} F \\ C_6F_5 \end{cases} \xrightarrow{C_6F_5} C_6F_5$$

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$$C_6F_5 = \begin{cases} F \\ F \\ F \end{cases} \xrightarrow{C_6F_5} C_6F_5$$

$$C_6F_5 = \begin{cases} F \\ F \\ F \end{cases} \xrightarrow{C_6F_5} C_6F_5$$

$$C_6F_5 = \begin{cases} F \\ F \\ F \end{cases} \xrightarrow{C_6F_5} C_6F_5$$

$$C_6F_5 = \begin{cases} F \\ F \\ F \end{cases} \xrightarrow{C_6F_5} C_6F_5$$

$$C_6F_5 = \begin{cases} F \\ F \\ F \end{cases} \xrightarrow{C_6F_5} C_6F_5$$

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$$C_6F_5 = \begin{cases} F \\ F \\ F \end{cases} \xrightarrow{C_6F_5} C_6F_5$$

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$$C_6F_5 = F \\ F \end{cases} \xrightarrow{C_6F_5} F \xrightarrow{C_6F_5} C_6F_5$$

$$C_6F_5 = F \\ F \end{cases} \xrightarrow{C_6F_5} F \xrightarrow{C_6F_5} F$$

Nucleophilic attack on the sulfur at the equatorial position can be used to advantage to produce sulfur(VI) imides when several sulfur hexafluoride derivatives are allowed to react with lithium hexafluoroisopropylidenimine. In each case, fluoride ion migration from sulfur to a more electropositive center at carbon is observed. $^{22-24}$ The reaction of LiN=C(CF₃)₂ with cis-SF₄X₂ (X = OCF₃, OSO₂F) involves preferential breaking of the sulfur-oxygen bond with subsequent fluoride ion migration.

$$cis$$
-SF₄X₂ + LiN=C(CF₃)₂ \rightarrow SF₃X=NCF(CF₃)₂
X = OCF₃, OSO₂F (+ COF₂, SO₃)

With an excess of nucleophile, $SF_2(=NCF(CF_3)_2)_2^{25}$ was obtained in low yield.

In contrast, the compounds cis-CF₃SF₄CF₃ and $(CF_2SF_4)_2$, in which the equatorial sulfur fluorine atoms exhibit large negative ¹⁹F NMR chemical shifts, can be reacted with LiN= $(CF_3)_2$ without breaking the equatorial sulfurcarbon bonds.

$$cis$$
-CF₃SF₄CF₃ + LiN=C(CF₃)₂ \rightarrow (CF₃)₂SF₂=NCF(CF₃)₂
1II

$$\xrightarrow{\text{LiN=C(CF}_3)_2} (\text{CF}_3)_2 \text{SF}_2 = \text{NC(CF}_3)_2 \text{N=C(CF}_3)_2$$

$$\text{IV}$$

Interestingly, when this reaction is carried out with an excess of nucleophile the remaining two sulfur-fluorine atoms in III are unscathed with attack occurring only at the electropositive isopropyl carbon center to produce IV. The geometry at the sulfur atom(s) in compounds III, IV, and V approaches tri-

$$CF_{2} \longrightarrow CF_{2} \longrightarrow CF_{3} \longrightarrow CF_{2} \longrightarrow F \longrightarrow F \longrightarrow F$$

Table I

| ROH | Olefin | Yield, % |
|---|-----------------------|-------------|
| (CF ₃) ₂ (CH ₃)COH | $(CF_3)_2C=CH_2$ | 75 |
| $CH_3(CH_2)_8CH_2OH$ | $CH_3(CH_2)_7CH=CH_2$ | 68 |
| (CH ₃) ₃ COH | $(CH_3)_2C = CH_2$ | 64 |
| PhCH ₂ CH ₂ OH | PhCH=CH ₂ | 72 |

gonal bipyramidal with the fluorine atoms bonded to sulfur occupying axial positions. The $\nu_{S-Fasym}$ and ν_{S-Fsym} vibrational modes are at 828 m, 576 w; 828 m, 582 w; and 848 m, 583 cm⁻¹ w, respectively. These assignments agree well with the analogous axial vibrational modes in OSF₄ at 819 vs and 588 mw.²⁶

An interesting synthetic application of cis-SF₄(OCF₃)₂ is in the smooth conversion of alcohols to olefins. In addition to the olefin, carbonyl fluoride and sulfuryl fluoride are formed, also. Yields are given in Table I.

$$cis$$
-SF₄(OCF₃)₂ + 2ROH

$$\rightarrow$$
 >C=C< + COF₂ + SO₂F₂

Experimental Section

Materials. Literature methods were used to prepare $SF_5Cl_*^{27}$ $SF_5Br_*^{28}$ $CF_3SF_4Cl_*^{29}$ $CF_3SF_4CF_3,^{30}$ $cis-SF_4(OSO_2F)_2,^{31}$ $(CF_2SF_4)_2,^{32}$ $CF_3SH_*^{33}$ $LiN=C(CF_3)_2,^{34}$ and $CF_3OCl_*^{35}$ Pentafluorobenzene and pentafluorothiophenol, which are available from PCR, Inc., were used without further purification.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex vacuum line equipped with a Heise-Bourdon tube gauge. Volatile starting materials and purified products were measured quantitatively by PVT techniques. Vapor-pressure studies were carried out by using an isoteniscopic method.

Infrared spectra were obtained by using a Perkin-Elmer 457 spectrometer with a 10-cm gas cell fitted with KBr windows. The ¹⁹F spectrum was recorded using a Varian HA-100 spectrometer with CCl₃F as an internal standard. Mass spectra were obtained by using a Hitachi Perkin-Elmer RMIL-6E spectrometer at 17 eV

a Hitachi Perkin-Elmer RMU-6E spectrometer at 17 eV. **Preparation of cis-SF4(OCF₃)₂.** ³⁶ Sulfur tetrafluoride (5 mmol) was condensed into a 150-mL quartz vessel followed by 10 mmol of trifluoromethyl hypochlorite. The mixture was allowed to warm to 25 °C and was photolyzed for 24 h with a Hanovia utility ultraviolet quartz lamp. After this period, the remaining material was vacuum distilled and cis-SF4(OCF₃)₂ was retained in a trap at -78 °C. The yield ranged from 90 to 95%.

Reaction of C₆F₅SLi, With *cis*-SF₄(OCF₃). A hexane solution of *n*-butyllithium (8 mmol) was added via syringe through the side arm to a solution of pentafluorothiophenol (8 mmol) in dry ethyl ether (3 mL) under argon atmosphere in a 50-mL vessel with the temperature held at -78 °C. The reaction mixture was stirred for 1 h at -78 °C. *cis*-SF₄(OCF₃)₂ (2 mmol) was condensed into the vessel at -196 °C and the reaction mixture was held at -78 °C. After stirring for 5 h, CF₂O (2.68 mmol) was collected at -116 °C by trap-to-trap distillation. The involatile product was separated by filtration to give bis(pentafluorophenyl)trisulfane in a yield of 62%, mp 57–58 °C (lit. ³⁷ mp 57.5 °C). The filtrate solidified slowly in a refrigerator to give the bis(pentafluorophenyl)disulfane, mp 50–51 °C (lit. ³⁸ mp 50–51 °C), in a yield of 57%.

With SF₅Cl. Pentafluorosulfur chloride (2 mmol) and pentafluorothiophenyllithium (8 mmol) in Et₂O (3 mL) were condensed as above and after stirring for 5 h at -78 °C distillation gave $C_6F_5SCl^{39}$ (1.18 mmol) and $(C_6F_5S)_2$ (0.53 mmol). The involatile compound was recrystallized from petroleum ether to give bis(pentafluorophenyl)trisulfane in a yield of 73%.

With SF₅Br. Pentafluorosulfur bromide (2 mmol) and C_6F_5SLi (8 mmol) in dry Et_2O (3 mmol) were used as in the above reaction and worked up similarly. The products were $(C_6F_5S)_2$ (1.12 mmol) and $(C_6F_5)_2S_3$ (1.16 mmol, 58%). Bromine in ethyl ether was isolated as N-bromosuccinimide.

Reaction of CF₃SLi. With *cis*-SF₄(OCF₃)₂. Into a hexane solution of *n*-butyllithium (8 mmol) and dry ethyl ether (3 mL), CF₃SH (8 mmol) was condensed at -196 °C and after stirring for 2 h at -78 °C, *cis*-SF₄(OCF₃)₂ (2 mmol) was condensed into the vessel at -196 °C. The reaction mixture was allowed to warm to -78 °C, and was stirred for 5 h. The resulting mixture was fractionally distilled through a trap at -116 °C which retained CF₂O (2.27 mmol). A trap at -50 °C contained a mixture of (CF₃)₂S₃, (CF₃)₂S₂, and Et₂O. Final purification (via gas chromatography using a column of 20% Kel-F on Chromosorb P) gave (CF₃)₂S₃⁴⁰ (1.02 mmol) and (CF₃)₂S₂ (1.31 mmol).

With SF₅Cl. SF₅Cl (2 mmol) and CF₃SLi (8 mmol) in dry ethyl ether (3 mL) were condensed at -196 °C as above and worked up similarly. The products were separated by gas chromatography using a column of 20% Kel-F on Chromosorb P to give CF₃SCl (0.89 mmol), CF₃SSCF₃ (0.41 mmol), and (CF₃)₂S₃ (1.09 mmol).

Reaction of C_6F_5Li . With cis-SF₄(OCF₃)₂. A. Into a solution of pentafluorobenzene (6 mmol) and dry ethyl ether (3 mL) cooled to -78 °C under an argon atmosphere, a hexane solution of *n*-butyllithium (6 mmol) was added dropwise over 15 min. via a syringe through a side arm. After 1.5 h of stirring at -78 °C, cis-SF₄(OCF₃)₂ (2 mmol) was condensed into the vessel at -196 °C. The reaction mixture was allowed to warm to -78 °C and stirred for 5 h. After the trap-to-trap distillation, CF₂O (2.41 mmol) was collected at -116 °C and C_6F_6 (0.98 mmol) was also collected at -78 °C. Chromatography of the residual solid on silica separated the bis(pentafluorophenyl)sulfur difluoride (0.24 mmol), mp 74–76 °C (lit.^{41,42} mp 73–77 °C), and the bis(pentafluorophenyl) sulfoxide (0.97 mmol), mp 77–78 °C (lit.²¹ mp 77–78 °C).

B. C_6F_5Li (10 mmol) and cis-SF₄(OCF₃)₂ (2 mmol) in dry Et₂O (5 mL) were used as above and worked up similarly. CF₂O (2.56 mmol) and C_6F_6 (0.96 mmol) were collected by trap-to-trap distillation at -116 and -78 °C. The residual precipitate was dissolved in n-hexane, and the precipitate was filtered and recrystallized from tetrahydrofuran to give the decafluorobiphenyl (1.77 mmol), mp 206 °C (lit.⁴³ mp 206 °C). The filtrate was bis(pentafluorophenyl) sulfide (1.02 mmol), mp 84–85 °C (lit.⁴⁰ mp 84–85 °C).

With SF₅Cl. Pentafluorosulfur chloride (2 mmol) and pentafluorophenyllithium (6 mmol) in dry ethyl ether (3 mL) were used as in the above reaction and worked up in a similar manner. The distillation gave a mixture of C_6F_6 (0.88 mmol) and ethyl ether, and final purification by gas chromatography through use of a column which contained 20% Kel-F no. 3 oil on Chromosorb P. The involatile product was very unstable and hydrolyzed easily when exposed to air to give bis(pentafluorophenyl) sulfoxide in a yield of 60%.

With SF₅Br. Pentafluorosulfur bromide (2 mmol) and C_6F_5Li (6 mmol) in dry ethyl ether (3 mL) were condensed as above and worked up similarly. The mixture of C_6F_6 (0.78 mmol) and ethyl ether was separated from the majority of the involatile product by distillation and purified finally by gas chromatography using a column of 20% Kel-F no. 3 oil on Chromosorb P. The involatile material hydrolyzed to give bis(pentafluorophenyl) sulfoxide in a yield of 56%.

Reaction of CF₃SF₄Cl. With C₆F₅SLi. Into the solution of C₆F₅SLi (6 mmol) and ethyl ether (3 mL), CF₃SF₄Cl (2 mmol) was condensed at -196 °C and was allowed to warm slowly to -78 °C. After stirring for 5 h at -78 °C chlorotrifluoromethane (1.16 mmol) was collected at -196 °C by trap-to-trap distillation. The residual precipitate was filtered and recrystallized to give the bis(pentafluorophenyl)trisulfane (1.26 mmol). The oily material was solidified slowly in a refrigerator to give the bis(pentafluorophenyl)disulfane (0.69 mmol).

With C_6F_5Li , CF_3SF_4Cl (2 mmol) and C_6F_5Li (6 mmol) in ethyl ether (3 mL) were condensed as in the above reaction and worked up similarly. The resulting mixture was fractionally distilled to collect the chlorotrifluoromethane (1.06 mmol) and hexafluorobenzene (1.31 mmol). The residual solid was recrystallized from hexane to give the bis(pentafluorophenyl) sulfide.

Reaction of cis- and trans-CF₃SF₄CF₃. Into a solution of C_6F_5SLi (4 mmol) and ethyl ether (5 mL), cis- and trans-CF₃SF₄CF₃ (6.2 mmol, isomer ratio 1:2.1) was condensed and warmed slowly to -78 °C. After 5 h of stirring at -78 °C, the products were separated by low-temperature distillation. The tetrafluoromethane (3.21 mmol) was retained in a trap at -196 °C while a trap at -98 °C was used to remove unreacted cis- and trans-CF₃SF₄CF₃ (4.3 mmol, isomer ratio 1:14). The residual precipitate was recrystallized to give the bis(pentafluorophenyl)trisulfane (1.56 mmol).

With C₆F₅Li. Pentafluorophenyllithium (2 mmol) and cis- and

trans-CF₃SF₄CF₃ (6.2 mmol, isomer ratio 1:2.1) in ethyl ether (3 mL) were used as in the above reaction and worked up in a similar manner. The trap-to-trap distillation gave the bis(trifluoromethyl)sulfur difluoride (1.21 mmol)¹¹ in a trap at -98 °C. The product which was retained in a trap at -78 °C was purified finally by distillation. Hexafluorobenzene (1.16 mmol) was collected.

Preparation of SF₃(OSO₂F)=NCF(CF₃)₂. The literature method was used to prepare LiN=C(CF₃)₂ (2 mmol) in a rigorously flamedried 50-mL reaction vessel. The solvent was removed under dynamic vacuum leaving a brown, amorphous solid. Onto the solid was condensed SF₄(OSO₂F)₂³¹ (2.1 mmol) at -196 °C and the vessel was warmed slowly to ambient temperature. After 5 h the volatile product was separated by trap-to-trap distillation and SF₃(OSO₂F)=NCF(CF₃)₂ (1.27 mmol) was obtained. This compound is a colorless liquid with boiling point of 124 °C from the equation $\log P_{Torr} = 7.15 - 1695/T$. The molar heat of vaporization is 7.8 kcal and the Trouton constant is 19.5 eu.

The ¹⁹F NMR spectrum contains resonances at ϕ 144.1, 67.6, -36.9, -67.5, and -69.1 in the ratio 1:6:1:1:2, respectively. The resonance at ϕ 144.1 assigned to the isopropyl fluorine is split by two CF₃ groups on carbon ($J_{F-CF_3C} = 4.0 \text{ Hz}$), the two axial fluorines on sulfur $(J_{F-SFax} = 13.6 \text{ Hz})$, and the equatorial fluorine on sulfur $(J_{\text{F-SFeq}} = 7.6 \text{ Hz})$. The resonance at ϕ 67.6 is assigned to the CF₃ groups on carbon. At ϕ -36.9 the resonance of the fluorine on the OSO_2F group is split by the axial fluorines on sulfur $(J_{OSO_2F-SFax} =$ 9.6 Hz) and the equatorial fluorine on sulfur $(J_{OSO_2F-SFeq} = 2.1 \text{ Hz})$. The resonance at ϕ -67.5 is assigned to the equatorial fluorine on sulfur which is split by the axial fluorines on sulfur $(J_{SFeq-SFax} = 146)$ Hz), the fluorine on OSO₂F group, and the isopropyl fluorine. The axial fluorine atoms on sulfur resonate at ϕ -69.1. The infrared spectrum is as follows: 1478 s, 1370 s, 1296 s, 1245 s, 1211 m, 1119 m, 1058 w, 1034 w, 985 ms, 933 w, 913 ms, 837 m, 758 w, 726 w, 706 w, 578 w, 434 cm⁻¹ w.

Anal. Calcd for C₃NS₂O₃F₁₁: C, 9.70; N, 3.77. Found: C, 9.52; N, 3.76.

Preparation of SF₃(OCF₃)=NCF(CF₃)₂. *cis*-SF₄(OCF₃)₂ (2.3 mmol) was condensed onto LiN=C(CF₃)₂ (2 mmol) at -196 °C and then warmed slowly to ambient temperature. After 24 h, the product was separated by trap-to-trap distillation through a trap at -50 °C which retained the SF₃(OCF₃)=NCF(CF₃)₂ (1.68 mmol) and a trap at -116 °C which retained the CF₂O (1.41 mmol). A trap at -98 °C contained the *cis*-SF₄(OCF₃)₂ (0.16 mmol). SF₃(OCF₃)=NCF(CF₃)₂ is a colorless liquid with a boiling point of 116 °C from the equation log $P_{\text{Torr}} = 7.43 - 1770/T$. The molar heat of vaporization is 8.1 kcal and the Trouton constant is 20.8 eu.

The ¹⁹F NMR spectrum show resonances at ϕ 144.6, 83.3, 69.2, -51.2, and -58.1 in the ratio 1:3:6:1:2, respectively. The resonance at ϕ 144.6 assigned to the isopropyl fluorine atom is split by both axial and equatorial fluorine atoms on sulfur $(J_{F-SFax}=12.9, J_{F-SFeq}=7.1 \text{ Hz})$ and two CF₃ groups on carbon $(J_{F-CF_3C}=4.2 \text{ Hz})$. That at ϕ 83.3 is assigned to the OCF₃ group on sulfur and is an overlapping triplet of doublets split by the axial fluorine atoms on sulfur $(J_{OCF_3-SFax}=10.1 \text{ Hz})$ and the equatorial fluorine atom on sulfur $(J_{OCF_3-SFeq}=7.2 \text{ Hz})$. The resonance at ϕ 69.2 is assigned to the CF₃ groups on carbon. The resonance at ϕ –51.2 is assigned to the S-F equatorial fluorine atom, and that at ϕ –58.1 to the S-F axial fluorine atoms $(J_{SFax-SFeq}=148 \text{ Hz})$. The infrared spectrum is as follows: 1426 m, 1375 m, 1291 ms, 1261 s, 1239 s, 1146 ms, 989 ms, 926 m, 841 m, 708 w, 698 ms, 586 cm⁻¹ w.

Anal. Calcd for C₄NSOF₁₃: C, 13.45; N, 3.92. Found: C, 13.41; N, 3.88.

Preparation of (CF₃)₂SF₂=NCF(CF₃)₂. cis- and trans-CF₃SF₄CF₃ (5 mmol, isomer ratio 1:2.1) was condensed onto LiN= $C(CF_3)_2$ (1.5 mmol) and warmed slowly to ambient temperature. After 24 h, the products were separated by low-temperature distillation. Unreacted CF₃SF₄CF₃ (3.51 mmol) was recovered from the bath at -98 °C and $(CF_3)_2SF_2$ =NCF(CF₃)₂ (1.06 mmol) was also obtained at -78 °C. This compound is a colorless liquid with a boiling point of 102 °C obtained from the equation log $P_{Torr} = 7.45 - 1718/T$. The molar heat of vaporization is 7.7 kcal and the Trouton constant is 20.9

The ¹⁹F NMR spectrum contains resonances at ϕ 144.1, 78.3, 65.1, and -57.6 in the ratio 1:6:6:2, respectively. The resonances at ϕ 144.1, assigned to the isopropyl fluorine atom, is split by all other fluorines in the molecule ($J_{F-CF_3C} = 4.5$, $J_{F-SFax} = 13.9$, $J_{F-CF_3S} = 0.4$ Hz). The CF₃ groups on carbon at ϕ 78.3 are a doublet. At ϕ 65.1 the two

CF₃ groups on sulfur give an overlapping triplet of doublets from splitting by two axial fluorine atoms on sulfur $(J_{CF_3S-SFax} = 12.8 \text{ Hz})$ and the isopropyl fluorine atom. The S-F axial resonance at ϕ -57.6 is a doublet of heptets split by the isopropyl fluorine atom and the two CF₃ groups on sulfur. The infrared spectrum is as follows: 1333 m, 1298 w, 1260 s, 1205 s, 1158 s, 1121 w, 994 m, 921 w, 828 m, 740 m, 735 m, 706 w, 685 s, 576 w, 541 cm⁻¹ w.

Anal. Calcd for C₅NSF₁₅: C, 15.36; N, 3.58. Found: C, 15.28; N,

Preparation of (CF₃)₂SF₂=NC(CF₃)₂N=C(CF₃)₂. cis- and trans-CF₃SF₄CF₃ (2 mmol, isomer ratio 1:2.1) was condensed onto Li- $N=C(CF_3)_2$ (3 mmol) and warmed to ambient temperature. After 24 h the volatile products were fractionally distilled through a trap at -50 °C which retained the (CF₃)₂SF₂=NC(CF₃)N=C(CF₃)₂ (0.47 mmol) and a trap at -98 °C which retained unreacted $CF_3SF_4CF_3$ (1.42 mmol). $(CF_3)_2SF_2=NC(CF_3)_2N=C(CF_3)_2$ is a colorless liquid with a boiling point of 117 °C obtained from the equation $\log P_{\text{Torr}} = 8.16 - 2059/T$. The molar heat of vaporization is 9.4 kcal and the Trouton constant is 24.2 eu.

The ¹⁹F NMR spectrum shows resonances at ϕ 68.6, 66.9, 64.6, and -46.6 in the ratio 6:6:6:2, respectively. The resonance at ϕ 68.6 is assigned to the internal CF₃ groups (S=NC<), and the broadened resonance at ϕ 66.9 is assigned to the CF₃ groups adjacent to the imine moiety. At ϕ 64.6 the resonance of the CF₃ groups on sulfur is a triplet from splitting by two axial fluorine atoms on sulfur. The S-F axial fluorine atoms resonance at ϕ -46.6 is split by the CF₃ groups on sulfur $(J_{SFax-CF_3S} = 13.6 \text{ Hz})$ and the internal CF₃ groups on carbon $(J_{SFax-CF-C} = 1.3 \text{ Hz}).$

The infrared spectrum is as follows: 1730 w, 1331 m, 1271 s, 1259 s, 1209 s, 1156 ms, 1125 m, 996 ms, 828 m, 746 w, 736 m, 687 m, 582 cm^{-1} w.

Anal. Calcd for C₈N₂SF₂₀: C, 17.92; N, 5.23. Found: C, 17.86; N, 5.16.

Preparation of $\{-CF_2SF_2=(NCF(CF_3)_2)\}_2$. $\{-CF_2SF_4\}_2$ (2 mmol) was condensed onto LiN=C(CF₃)₂ (4.5 mmol) at -196 °C and warmed to ambient temperature. After 24 h the precipitate was recrystallized from *n*-hexane to give $\{CF_2SF_2=(NCF(CF_3)_2)\}_2$ in a yield of 61%, mp 76-77.5 °C.

The ¹⁹F NMR spectrum shows resonances at ϕ 144.5, 96.1, 69.1, and -41.0 in the ratio 2:4:12:4, respectively. The isopropyl fluorine resonance at ϕ 144.5 is a triplet of heptets split by the axial fluorine atoms on sulfur $(J_{F-SFax} = 14.8 \text{ Hz})$ and the CF₃ groups on carbon $(J_{\text{F-CF}_3\text{C}} = 3.1 \text{ Hz})$. The resonance at ϕ 96.1 is assigned to the CF₂ group, and the resonance at ϕ 69.1 is assigned to the CF₃ groups on carbon. At ϕ -41.0, the resonance of the axial fluorine atoms on sulfur is a multiplet from splitting by the isopropyl fluorine atom and the CF₂ groups $(J_{SFax-CF_3S} = 11.8 \text{ Hz})$. The infrared spectrum is as follows: 1369 m, 1276 ms, 1254 s, 1226 s, 1198 m, 1121 s, 1056 s, 988 ms, 842 m, 728 w, 691 ms, 583 cm⁻¹ w.

Anal. Calcd for C₈N₂S₂F₂₂: C, 15.85; N, 4.62. Found: C, 15.77; N, 4.53.

Preparation of Olefin, In a typical reaction, cis-SF₄(OCF₃)₂ (2 mmol) was condensed into a glass vessel which contained 2-methylhexafluoro-2-propanol (4 mmol) followed by 8 mmol of trimethylamine. The mixture was allowed to warm slowly to 25 °C and to remain for 3 h. After separation by trap-to-trap distillation, 2,2-di(trifluoromethyl)ethene (2.98 mmol) was retained in a trap at -116 °C while traps at -196 and -137 °C were used to remove the SO₂F₂

(1.08 mmol) and CF₂O (2.74 mmol). Other alcohols were run in a similar manner and the results are given in the Table I.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research.

References and Notes

- (1) For part 1 of this series see T. Kitazume and J. M. Shreeve, J. Am. Chem. Soc., 99, 3690 (1977).
- B. M. Trost, R. LaRochelle, and R. Atkins, J. Am. Chem. Soc., 91, 2175
- Y. Khim and S. Oae, *Bull. Chem. Soc. Jpn.*, **42**, 1968 (1969)
- R. LaRochelle and B. M. Trost, J. Am. Chem. Soc., 93, 6077 (1971).
- (5) N. E. Hester, Int. J. Sulfur Chem., 8, 119 (1973).
 (6) M. Allan, A. F. Janzen, and C. J. Willis, Can. J. Chem., 46, 3671 (1968).
- J. I. Darragh and D. W. Sharp, Angew. Chem., Int. Ed. Engl., 9, 73 1970).
- (8) D. B. Denny, D. Z. Denny, B. S. Campbell, and L. Shih, J. Am. Chem. Soc., 97. 3850 (1975
- W. A. Sheppard, J. Am. Chem. Soc., 84, 3058 (1962).
- (10) R. M. Rosenberg and E. L. Muetterties, Inorg. Chem., 1, 756 (1962).
- (11) D. T. Sauer and J. M. Shreeve, J. Fluorine Chem., 7, 1 (1971) (12) G. H. Sprenger and A. H. Cowley, J. Fluorine Chem., 7, 333 (1976).
- (13) S. D. Morse and J. M. Shreeve, *Inorg. Chem.*, **16**, 33 (1977).
 (14) J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93**, 2339 (1971).
- (15) R. J. Arhart and J. C. Martin, J. Am. Chem. Soc., 94, 5003 (1972).
- (16) L. J. Kaplan and J. C. Martin, J. Am. Chem. Soc., 95, 2017 (1973).
 (17) J. C. Martin, J. A. Franz, and R. J. Arhart, J. Am. Chem. Soc., 96, 4606
- (1974).
- J. A. Franz and J. C. Martin, J. Am. Chem. Soc., 97, 583, 6137 (1975).
- (19) P. Livant and J. C. Martin, J. Am. Chem. Soc., 98, 7851 (1976).
- W. A. Sheppard, J. Am. Chem. Soc., 93, 5597 (1971).
- (21) W. A. Sheppard and S. S. Foster, J. Fluorine Chem., 2, 53 (1972).
 (22) R. F. Swindell and J. M. Shreeve, J. Am. Chem. Soc., 94, 5713 (1972)
- (23) J. A. Gibson and R. Schmutzler, Z. Anorg. Allg. Chem., 416, 222 (1975).
- T. Kitazume and J. M. Shreeve, J. Fluorine Chem., 8, 437 (1976).
- (25) R. Mews, J. Varwig, and H. Steinheisser, Abstracts, 8th International Symposium on Fluorine Chemistry, Kyoto, Japan, Aug 1976, p 117.
- (26) K. O. Christe, private communication
- C. J. Schack, R. D. Wilson, and M. G. Warner, Chem. Commun., 1110 (1969).
- (28) T. A. Kovacina, A. D. Berry, and W. B. Fox, J. Fluorine Chem., 7, 430 (1976).
- S. L. Yu and J. M. Shreeve, Inorg. Chem., 15, 14 (1976)
- T. Abe and J. M. Shreeve, Inorg. Nucl. Chem. Lett., 9, 465 (1973)
- (31) J. M. Shreeve and G. H. Cady, J. Am. Chem. Soc., 83, 4521 (1961).
 (32) T. Abe and J. M. Shreeve, J. Fluorine Chem., 3, 17 (1973).
 (33) N. R. Zack and J. M. Shreeve, Synth. Commun., 4, 233 (1974).
- (34) R. F. Swindell, D. P. Babb, T. J. Ouellette, and J. M. Shreeve, Inorg. Chem., 11, 242 (1972).
- (35) C. J. Schack and W. Maya, J. Am. Chem. Soc., 91, 2902 (1969).
- (36) L. C. Duncan and G. H. Cady, *Inorg. Chem.*, 3, 850 (1964), *cis*-SF₄(OCF₃)₂ was prepared by the reaction of SF₄ with CF₃OOCF₃ or CF₃OF in a yield
- (37) M. E. Peach. Int. J. Sulfur Chem., 8, 27 (1973)
- (38) P. Robson, N. Stacey, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 4754
- (39) P. Sartori and A. Gulloch, Chem. Ber., 103, 3936 (1970).
- (40) G. A. R. Brandt, H. J. Emeléus, and R. N. Haszeldinoe, J. Chem. Soc., 2198 (1952)
- (41) D. B. Denney, D. Z. Denney, and Y. F. Idsu, J. Am. Chem. Soc., 95, 4064
- (42) W. A. Sheppard, L. J. Guggenberger, D. W. Ovenall, and P. Meakin, Abstracts, 8th International Symposium on Fluorine Chemistry, Kyoto, Japan,
- Aug 1976, p 038. (43) J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 4966 (1962).