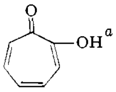
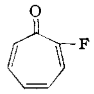
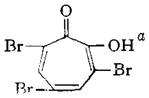
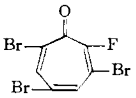
TABLE IX

REACTIONS OF HYDROXYLIC COMPOUNDS WITH SF_4

Starting material					Products[b]			Analyses, %			
								Calculated		Found	
Structure	Moles	Moles SF_4	Temp., °C.	Time, hr.	Structure	Yield, %	Properties	C	H	C	H
	0.02	0.065	60	10		28	M.p. 74–75°	67.7	4.0	67.7	4.3
	0.0033	0.02	60	8		57	M.p. 134–142°	23.2	0.6	23.4	0.9

[a] Experiment included 5 ml. of benzene as solvent; reaction run in a sealed platinum tube (capacity 15 ml.) which was heated while under nitrogen pressure in a shaker tube. [b] Infrared spectra of products in agreement with structures shown.

therefore require more vigorous conditions than those without electron-attracting groups, and such is found to be the case. Compounds having fluoroalkyl groups or fluorine atoms attached to the carbonyl group prove to be very sluggish in reactions with SF_4. A temperature of 250° and use of BF_3 catalyst was required to convert 2,2,3,3-tetrafluoropropionyl fluoride to 1H-perfluoropropane. Carbonyl fluoride similarly requires vigorous conditions for transformation to carbon tetrafluoride. The conditions required for reaction are far more vigorous than those necessary for acyl fluorides and ketones having electron-releasing groups attached to the carbonyl group.

Experimental

Details on the preparation and properties of SF_4 may be found elsewhere.[1]

The reactions with SF_4 were carried out in stainless steel- or "Hastelloy"-lined shaker tubes of 80-ml. to 1000-ml. capacity. Liquid or solid reactants were placed in the shaker tube under a nitrogen atmosphere, the head was screwed into place, the tube was cooled to solid carbon dioxide temperature, the nitrogen was removed with a vacuum pump and gaseous reactants (HF, BF_3, SF_4, etc.) were condensed into the shaker tube. After being heated for the prescribed period, the shaker tube was allowed to cool. In cases where the gaseous products were of interest, these were condensed into an evacuated stainless steel cylinder at liquid nitrogen temperature; otherwise, excess SF_4 and volatile by-products were vented from the tube. Liquid or solid products were recovered when the tube was opened, and pure products were obtained by the usual processes of distillation, recrystallization and sublimation. When it was necessary to remove HF from the crude mixture, this usually was accomplished by either (1) pouring the crude mixture into water and recovering the product by filtration, extraction or steam distillation, or (2) pouring the crude mixture into a suspension of sodium fluoride ($NaF + HF \rightarrow NaHF_2$) in an inert solvent having a boiling point considerably removed from that of the product desired, followed by filtration and fractional distillation. In some cases removal of HF from a solid or high boiling liquid was accomplished by vaporization of the HF and absorption into solid NaF or NaOH. Reaction times and temperatures, amounts of reactants, nature and amount of catalyst and identity and yield of products are given in the tables. Although the yields of products obtained vary widely, in very few specific cases has an effort been made to find optimum reaction conditions. Where infrared and mass spectrometric analyses were carried out, they are indicated in the tables and were in agreement with the structural assignments. In all cases the hydrogen and fluorine nuclear magnetic resonance spectra were in agreement with the structures of the products.

Acknowledgments.—We are indebted to Drs. F. S. Fawcett, R. J. Harder, J. F. Harris, C. M. Langkammerer, R. V. Lindsey, E. L. Muetterties, A. L. Oppegard, B. C. Pratt, R. E. Putnam, M. S. Raasch, J. C. Sauer, R. M. Scribner, W. A. Sheppard, O. W. Webster and B. D. Wilson for helpful discussions and for providing some of the experimental results listed in the tables.

WILMINGTON, DELAWARE

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Chemistry of Sulfur Tetrafluoride.[1] III. Organoiminosulfur Difluorides

BY WILLIAM C. SMITH, CHARLES W. TULLOCK, RONALD D. SMITH AND VAUGHN A. ENGELHARDT

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An investigation of the chemistry of sulfur tetrafluoride has uncovered a new class of substances, the organoiminosulfur difluorides. These compounds, which have the general formula $RN{=}SF_2$, have been obtained by the reaction of sulfur tetrafluoride with organic and inorganic compounds having carbon–nitrogen multiple bonds. The chemical and physical data support the postulated iminosulfur difluoride structure for these substances The organoiminosulfur difluorides, unlike the unstable $C_6H_5N{=}SCl_2$, have high thermal stability, but the nitrogen–sulfur bond is unstable toward water and ethanol, and gross decomposition of the $—N{=}SF_2$ grouping takes place. Reaction of phenyliminosulfur difluoride, $C_6H_5N{=}SF_2$, with sodium methoxide and with phenyllithium was limited to the sulfur–fluorine bonds, however, and the new iminosulfur derivatives, $C_6H_5N{=}S(OCH_3)_2$ and $C_6H_5N{=}S(C_6H_5)_2$, were prepared. A direct synthesis of the trifluoromethyl derivative, $CF_3N{=}SF_2$, from an inorganic thiocyanate, chlorine and a metal fluoride also is described.

The synthesis of a compound having the empirical formula F_3NS has been reported by Glemser and Schröder.[2] This compound was assigned the structural formula $FN{=}SF_2$ on the basis of chemical evidence and was the first example of an iminosulfur difluoride. An organoiminosulfur dichloride

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[1] Paper II, W. R. Hasek, W. C. Smith and V. A. Engelhardt, THIS JOURNAL, **81**, 543 (1960).

[2] O. Glemser and H. Schröder, *Z. anorg. allgem. Chem.*, **284**, 97 (1956).

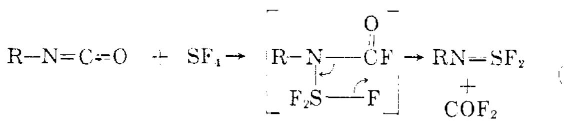
having the formula $C_6H_5N{=}SCl_2$ has been described by Michaelis,[3] but the material was reported to be stable only in solution and could not be isolated.

A new class of compounds, the organoiminosulfur difluorides, was uncovered in an investigation of the chemistry of sulfur tetrafluoride (SF_4). These sulfur fluoride derivatives have the general formula $RN{=}SF_2$ and are prepared by the reaction of SF_4 with compounds that have carbon–nitrogen multiple bonds.

Synthesis of Organoiminosulfur Difluorides.—Routes to three types of organoiminosulfur difluorides are available based on SF_4.[4] Compounds of the type $RN{=}SF_2$ are obtained by the reaction of organic isocyanates with SF_4. Products of the type $RCF_2N{=}SF_2$ are prepared from nitriles and SF_4. The compound $CF_3N{=}SF_2$ is the product of the reaction between SF_4 and inorganic compounds containing one carbon–nitrogen multiple bond.[5] The reactions of SF_4 with compounds having the requisite carbon–nitrogen unsaturation are not, however, limited to those falling in the three broad classes above. Organoiminosulfur difluorides have also been obtained by the reaction of SF_4 with such compounds as benzalaniline and cyanuric acid. Cyanogen reacted with SF_4 at 350° to give both the mono- and bis-iminosulfur difluorides. The trifluoromethyl derivative also has been prepared in good yield by the reaction of an inorganic thiocyanate with chlorine and metal fluorides such as sodium and zinc fluorides.

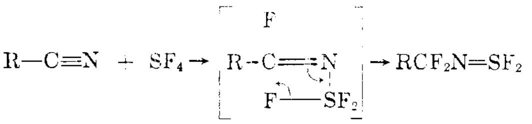
In the synthesis of iminosulfur fluorides based on the reaction of SF_4 with nitriles, there was often only a very narrow temperature range in which the desired reaction could be carried out satisfactorily. Below the operable temperature region no reaction occurred whereas at temperatures above the operable range significant secondary reactions took place. Acetonitrile was particularly resistant to attack by SF_4 and underwent little or no reaction at temperatures up to 260°. At this latter temperature there was extensive decomposition and the product isolated was $CH_2FCF_2N{=}SF_2$ rather than $CH_3CF_2N{=}SF_2$. This fluorination of a C–H bond, which was the only example of a hydrogen replacement reaction observed in this work, may be partly the result of the very high synthesis temperatures. However, this type of fluorination may be limited to nitriles having α-hydrogen atoms.

The reaction of isocyanates with SF_4 gives an iminosulfur difluoride derivative and carbonyl fluoride is formed as a by-product. A speculative mechanism by which this reaction may proceed is illustrated in equation 1. It is suggested that the first step involves the addition of the elements



$$R{-}N{=}C{=}O + SF_4 \rightarrow \left[\begin{array}{c} R{-}N{-}\overset{\overset{O}{\|}}{C}F \\ F_2S{-}F \end{array}\right] \rightarrow \begin{array}{c} RN{=}SF_2 \\ + \\ COF_2 \end{array} \qquad (1)$$

of SF_4 across the carbon–nitrogen bond and then the indicated rearrangement and the elimination of carbonyl fluoride. The reaction of nitriles with SF_4 may proceed by a similar type of mechanism, as illustrated in equation 2. If it is assumed that the first step is an addition reaction then the



$$R{-}C{\equiv}N + SF_4 \rightarrow \left[\begin{array}{c} R{-}\overset{F}{C}{=}N \\ F{-}SF_2 \end{array}\right] \rightarrow RCF_2N{=}SF_2 \qquad (2)$$

iminosulfur difluoride derivative might form by an intramolecular rearrangement. It should be noted that the mechanisms proposed above are also similar to that proposed for the reaction of SF_4 with carbonyl compounds.[1] A mechanism formally similar to that proposed for the nitriles may also operate in the case of the reactions of cyanogen bromide and of inorganic cyanates, cyanides and thiocyanates with SF_4; however, other reactions involving replacement of the atom or group bonded to the –CN portion of the molecule would necessarily be involved.

$$M^+OCN^- + 2SF_4 \rightarrow CF_3N{=}SF_2 + SOF_2 + MF \quad (3)$$

$$2K^+SCN^- + 3SF_4 \rightarrow 2CF_3N{=}SF_2 + 3S + 2KF \quad (4)$$

Structure and Chemical Properties of the Organoiminosulfur Difluorides.—The iminosulfur difluoride structure $-N{=}SF_2$ of these new sulfur fluoride derivatives was found to be consistent with the infrared, F^{19} magnetic resonance and mass spectrometric data of these compounds. A feature of the infrared spectra of these compounds is a band in the 7.15–7.35 μ region which is associated with the N=S grouping. The formation of the derivatives described below by metathetical reactions involving the fluorine atoms bonded to sulfur provided further support for the postulated structure. The data furnish no information as to whether the nitrogen–sulfur link is predominantly $N{=}S$ or $\overset{+}{N}{-}\overset{-}{S}$.

The iminosulfur difluorides have a surprisingly high thermal stability as indicated by the temperature required for the synthesis of some of them. The chemical reactivity of these compounds is quite pronounced, however. Phenyliminosulfur difluoride is attacked by water and by ethanol at room temperature with cleavage of both the sulfur–fluorine and iminosulfur linkages. In several of its reactions phenyliminosulfur difluoride behaves similarly to thionyl chloride. Thus, reaction with *o*-phenylenediamine gave 2,1,3-benzothiadiazole,[6] and reaction with anisole in the presence of zinc chloride afforded 4,4′-dimethoxydiphenyl sulfide.[7] These reactions are analogous to those that take place between thionyl chloride and the above compounds.[6,7] The nitrogen–sulfur bond was cleaved when the phenyl derivative was reduced with

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[3] A. Michaelis, *Ann.*, **274**, 173 (1893).

[4] William C. Smith, U. S. Patent 2,862,029 (1958).

[5] L. A. Bigelow, J. A. Attaway, R. H. Groth and A. F. Maxwell (American Chemical Society Meeting, Atlantic City, N. J., September 16–21, 1956; p. 16M) presented a paper on the "Direct Fluorination of Amides and the Indirect Fluorination of Cyanuric Chloride." The authors reported orally that the direct fluorination of methyl thiocyanate at 97° gave a 27% yield of SF_5CN, b.p. –6°. The similar boiling points of their product and that found for $CF_3N{=}SF_2$ suggests that the product prepared by these workers was the iminosulfur difluoride derivative.

[6] A. Michaelis, *Ann.*, **274**, 262 (1893).

[7] F. Loth and A. Michaelis, *Ber.*, **27**, 2540 (1894).

lithium aluminum hydride, and the nitrogen-containing product was shown to be aniline. The trifluoromethyl derivative also was degraded completely by a 10% aqueous sodium hydroxide solution at 25°. Metathetical reactions involving only the S–F bond were achieved successfully, however, by the reaction of phenyliminosulfur difluoride with sodium methoxide and with phenyllithium. In this manner, examples of two new types of derivatives, $C_6H_5N{=}S(OCH_3)_2$ and $C_6H_5N{=}S(C_6H_5)_2$, having iminosulfur linkages were prepared.

Experimental

The reactions of SF_4 with compounds having carbon–nitrogen unsaturation were carried out in 145-ml. "Hastelloy"-lined pressure vessels at autogenous pressure with agitation. In each case the nitrogen-containing compound was charged into a nitrogen-flushed pressure vessel, the reactor cooled to −78° in a solid carbon dioxide bath and evacuated to about 1 mm. pressure, and the desired amount of SF_4 added. Volatile products were collected in evacuated stainless steel cylinders cooled in liquid nitrogen; liquid products were kept in bottles fabricated of "Teflon" tetrafluoroethylene resin. Mass spectrometric analyses of volatile products were carried out by sampling with the cylinder in the inverted position.

Trifluoromethyliminosulfur Difluoride. a. From Cyanogen Bromide and SF_4.—Cyanogen bromide (42 g., 0.40 mole) and SF_4 (88 g., 0.80 mole) were heated together at 150° for 2 hr. and then at 200° for 14 hr. The liquid product appeared to be bromine and oxidized iodide ion to iodine. The crude volatile product (63 g.) was distilled in a low-temperature still to give 22 g. of $CF_3N{=}SF_2$, b.p. −6°. The product, characterized by mass spectrometric analysis, was obtained in 37% yield.

Calcd. for CF_5NS: F, 62.06; S, 20.94. Found: F, 63.33, 63.65; S, 19.77, 19.71.

The proposed structure for this material is based on nuclear magnetic resonance and mass spectrometric studies. The F^{19} magnetic resonance spectrum of this compound consists of two chemically shifted components, one located in the region characteristic of fluorine bonded to sulfur and the other in the region for fluorine bonded to carbon. The relative intensities of the S–F and C–F peaks were approximately in the ratio 2:3. Nuclear spin coupling between the fluorine atoms bonded to carbon and sulfur was not resolved.

Mass spectrometric studies furnish strong support for this proposed structure. A material with a mass/charge ratio of 153, corresponding to the parent compound, was one of the more abundant species. Other principal fragment ions had mass/charge ratios of 46, 65, 69, 70 and 134, corresponding to the fragment ions NS^+, NSF^+, CF_3^+, SF_2^+ and CF_3NSF^+. Less abundant ions had mass/charge ratios of 31, 32, 50, 51 and 115, ascribed to the CF^+, S^+, CF_2^+, SF^+ and CF_3NS^+ ions. The +1 and +2 isotope ions for C^{13}, N^{15}, S^{33} and S^{34} were also in agreement.

b. From Sodium Cyanide and SF_4.—Sodium cyanide (9.8 g., 0.20 mole) and SF_4 (66 g., 0.60 mole) were heated together at 200° for 2 hr., at 250° for 8 hr. and finally at 300° for 2 hr. The volatile product (63 g.) was shown by mass spectrometric analysis (inverted sampling) to contain 13–15 mole % $CF_3N{=}SF_2$, together with unreacted SF_4(63–68%), thionyl fluoride (14–17%), a small amount of nitrogen and a small amount (1–2 mole %) of a material that may be S_2F_2. The yield of $CF_3N{=}SF_2$, based on the mass spectrometric data, was 29%.

c. From Sodium Thiocyanate and SF_4.—Sodium thiocyanate (16.2 g., 0.20 mole) and SF_4 (66 g., 0.60 mole) were heated together at 200° for 2 hr., at 250° for 4 hr., at 300° for 4 hr. and finally at 350° for 2 hr. The crude volatile product (68 g.) was shown by mass spectrometric analysis to contain 20–24 mole % $CF_3N{=}SF_2$, possibly 1.5–3 mole % S_2F_2 and unreacted SF_4. The yield of $CF_3N{=}SF_2$ was about 69% based on NaSCN as calculated from the mass spectrometric data.

d. From Cyanuric Acid or Inorganic Cyanates and SF_4.—Cyanuric acid (19.4 g., 0.15 mole) and SF_4 (97 g., 0.90 mole) were heated together at 100° for 2 hr. at 150° for 2 hr., at 200° for 2 hr., at 250° for 4 hr. and finally at 300° for 4 hr. The volatile product (38.5 g.) contained 25–30 mole % $CF_3N{=}SF_2$, as shown by mass spectrometric analysis; the other major volatile product was thionyl fluoride. In another experiment it was shown that little or no reaction took place at 200°. Potassium cyanate gave only a small amount of $CF_3N{=}SF_2$ when heated with an excess of SF_4 at 350°. The SF_4 was recovered essentially unchanged.

e. From Ammonium or a Metal Thiocyanate, a Metal Fluoride and Chlorine.—The reaction of a metal thiocyanate or of ammonium thiocyanate with a metal fluoride and chlorine in a pressure vessel provides a convenient route to $CF_3N{=}SF_2$. Metal thiocyanates which may be employed include alkali metal, calcium and lead thiocyanates. The fluorinating agents that have been used successfully include sodium, potassium and zinc fluorides. The syntheses were all accomplished in good yield at an upper temperature of 235°. In a typical experiment a bomb lined with "Hastelloy-C" was charged with 62 g. (0.76 mole) of NaSCN and 175 g. (4.17 moles) of NaF. The bomb then was flushed with nitrogen, closed and evacuated to about 1 mm. pressure and then charged with 142 g. (2.00 moles) of chlorine. The pressure vessel was heated with agitation at 75° for 3 hr., at 150° for 1 hr. and finally at 235° for 6 hr. There was obtained 92 g. of volatile material which was transferred to a stainless-steel cylinder cooled in liquid nitrogen. Distillation of this product in a low-temperature fractionation unit gave 57 g. of $CF_3N{=}SF_2$, boiling at −7 to −5°. The yield was 49% based on sodium thiocyanate.

Phenyliminosulfur Difluoride.—Phenyl isocyanate (59.5 g., 0.50 mole) and SF_4 (61 g., 0.55 mole; 10% excess) were heated together at 100° for 4 hr., at 150° for 6 hr. and then at 100° for 4 hr. The volatile product (41 g.) was shown by mass spectrometric analysis to contain 80 mole % carbonyl fluoride (COF_2), 6 mole % SOF_2, 1 mole % CO_2 and unreacted SF_4. The crude liquid product was light orange and weighed 77.5 g.; this was distilled at reduced pressure to give 71.2 g. (88% yield) of phenyliminosulfur difluoride boiling at 36–36.5° (2 mm.). The absence of unreacted phenyl isocyanate in the product was established by infrared analysis.

Calcd. for $C_6F_2H_5NS$: C, 44.71; F, 23.58; H, 3.13; N, 8.69; S, 19.90; mol. wt., 161. Found: C, 44.12; F, 24.00; H, 3.40; N, 8.27; S, 19.76; mol. wt., 162, 168.

Infrared examination of the product showed a CH band at 3.25 μ, aromatic C=C bands at 6.25, 6.3 and 6.7 μ, and monosubstituted aromatic bands at 13.2 and 14.6 μ. A band at 7.15 μ, which appeared in all of the products having the postulated iminosulfur difluoride structure, has been ascribed to the $-N{=}SF_2$ grouping. Infrared examination was employed during studies leading to the synthesis conditions described above as a method for determining the purity of the product. Unreacted phenyl isocyanate present in the crude product obtained in other runs tended to codistil with the desired product and this was identified qualitatively by infrared examination.

The F^{19} magnetic resonance spectrum of the product consisted of a single component in the region characteristic of fluorine bonded to sulfur.

The temperature at which the desired reaction takes place is critical. When the reaction was run at a maximum temperature of 170°, only carbonaceous product was obtained, and at 100° the reaction was incomplete. The reaction also apparently must be carried out in the presence of a slight excess of SF_4; a considerable amount of black tar was formed when an excess of the isocyanate was employed and reaction was incomplete when stoichiometric amounts of the reagents were used.

α,α-Difluorobenzyliminosulfur Difluoride.—Benzonitrile (20.6 g., 0.20 mole) and SF_4 (44 g., 0.40 mole; 100% excess) were heated together at 180° for 2 hr. and then at 250° for 16 hr. The bomb was bled to atmospheric pressure and clear, light-green liquid product was recovered from the bomb; this product, weighing 41 g., was distilled at reduced pressure to give 28.0 g. of pale yellow product boiling at 33° (3 mm.). This product was slightly impure, as indicated by a slightly low value for fluorine on elemental analysis. Infrared studies indicated that the impurity was unreacted benzonitrile, and the product was purified by redistillation to give 20.5 g. (48% yield) of colorless product, b.p. 55.0° (11 mm.).

Calcd. for $C_7F_4H_5NS$: F, 35.99; S, 15.18. Found: F, 35.88, 35.73; S, 15.11, 15.10.

Infrared studies showed that this product had adsorption bands at 3.25, 6.2 and 6.7 μ similar to those observed for the phenyl derivative, together with a band at 7.15 μ ascribed to the $-N{=}SF_2$ grouping. There was also a broad band in the 9.5 μ region characteristic of the C–F grouping.

The F^{19} magnetic resonance spectrum of this compound consists of two chemically shifted components of equal intensity with each component split into a triplet. The resonance centered around 4028 c.p.s. is characteristic of fluorine bonded to sulfur, and that centered around 525 c.p.s is in the range of resonances for fluorine bonded to carbon. The multiplet spacing in each instance was 17 c.p.s.

The desired product was obtained pure in reasonable yield only if the quantities of reagents and reaction temperatures were controlled within narrow limits. The presence of unchanged benzonitrile in the crude product was undesirable because of the tendency for this material to codistil with the desired product. Incomplete reaction took place at 220°, and at 280° appreciable decomposition occurred. The reaction could be carried out satisfactorily at 250° if SF_4 was in excess to the extent of 100–150%, but when an excess of 200% was employed, the yield of crude liquid product was lower.

Cyanodifluoromethyliminosulfur Difluoride and 1,1,2,2-Tetrafluoroethane-1,2-bis-(iminosulfur difluoride).[8]—Cyanogen (16 g., 0.31 mole) and SF_4 (76 g., 0.70 mole) were heated together at 350° for 8 hr. The bomb was bled to atmospheric pressure through a trap cooled in acetone–solid carbon dioxide, and the latter allowed to warm to room temperature. The small amount of liquid remaining in the trap was combined with that recovered from the reactor and distilled through an 18″ spinning-band still. There was obtained 3.9 g. (8%) of cyanodifluoromethyliminosulfur difluoride, b.p. 56–60° (760 mm.), and 20.7 g. (26%) of 1,1,2,2-tetrafluoroethane-1,2-bis-(iminosulfur difluoride), b.p. 57–59° (106 mm.). The products were very reactive and difficult to purify. The F^{19} magnetic resonance and infrared spectra were consistent with the indicated structures.

Calcd. for $C_2F_4N_2S$: F, 47.48; S, 20.02. Found: F, 47.63; S, 19.09.

Calcd. for $C_2F_8N_2S_2$: C, 8.96; F, 56.68; N, 10.45; S, 23.91. Found: C, 9.64; F, 57.92; N, 11.06; S, 24.54.

Pentafluoroethyliminosulfur Difluoride.[9]—Trifluoroacetonitrile (38 g., 0.40 mole) and SF_4 (54 g., 0.50 mole) were heated together at 350° for 14 hr. The volatile products were transferred to a stainless-steel cylinder cooled in liquid nitrogen and then distilled in a low-temperature still. There was obtained 55 g. (70%) of a colorless liquid, b.p. 22–24°, identified as pentafluoroethyliminosulfur difluoride by its nuclear magnetic resonance spectra and its mass spectrometer pattern.

1,1,2-Trifluoroethyliminosulfur Difluoride.—Acetonitrile (12.3 g., 0.30 mole) and SF_4 (65 g., 0.60 mole) were heated together at 160° for 2 hr., at 200° for 2 hr., at 230° for 9 hr. and finally at 260° for 0.5 hr. The crude product isolated was a yellow-brown, clear liquid which reacted vigorously with glass. It was possible, however, to isolate on distillation 2.7 g. of colorless liquid which boiled at 46° at 760 mm. This material, believed to have the structure $FH_2CCF_2N{=}SF_2$, was obtained in 7% yield.

Calcd. for $C_2F_5H_2NS$: C, 14.37; F, 56.85; H, 1.21; S, 19.19. Found: C, 15.64; F, 57.24; H, 1.29; S, 19.14.

Several attempts to obtain this product in higher yield were unsuccessful. No reaction took place at 230°; when the reaction was scaled up in the same pressure vessel, the rupture disc of the reactor blew at temperatures as low as 200°.

It would appear that the replacement of hydrogen with fluorine encountered in this reaction is characteristic of hydrogen α to the nitrile group. The reaction of pivalonitrile (20.8 g., 0.25 mole) with SF_4 (81 g., 0.75 mole) at 280° did not involve a hydrogen replacement. Nuclear magnetic resonance studies indicated that the only fluorine-containing product was one having a spectrum similar to that ascribed to $C_6H_5CF_2N{=}SF_2$, and the product is therefore believed to be $(CH_3)_3CCF_2N{=}SF_2$.

Reactions of Phenyliminosulfur Difluoride. a. Hydrolysis.—Ten grams of phenyliminosulfur difluoride was poured into a beaker containing 300 ml. of distilled water. The water warmed up slowly and a mild evolution of gas occurred. The iminosulfur fluoride, which was water-insoluble, slowly reacted and dissolved. After removing a small amount of precipitate by filtration, the aqueous solution was concentrated under vacuum on a steam-bath to give a solid residue which, after being washed with absolute ethanol and dried under nitrogen, weighed 5.0 g. The solid was acidic to litmus and reacted with aqueous alkali to give a water-insoluble oil which reacted readily with benzoyl chloride to give N-phenylbenzamide, m.p. 163°. It is apparent that the hydrolysis of phenyliminosulfur difluoride results in cleavage of the nitrogen–sulfur bond.

b. **Reaction with Sodium Methoxide.**—A solution of 10.8 g. (0.20 mole) of sodium methoxide in 70 ml. of absolute methanol was treated dropwise with 16.1 g. (0.10 mole) of phenyliminosulfur difluoride. The addition required 20 minutes during which time the reaction temperature was maintained at 20–27° using ice-water as an external coolant. Some decomposition occurred because the iminosulfur difluoride ran down the side of the flask rather than dropping directly into the alcoholic solution. A solid precipitated during the addition period; this was filtered off and the filtrate was concentrated on a steam-bath under nitrogen. Additional solid precipitated on the addition of benzene and this also was removed. The benzene solution was distilled at 8 mm. pressure and 9.2 g. (49%) of orange distillate boiling sharply at 122° was collected. Elemental analysis confirmed that this product was phenyliminosulfur bis-(methoxide).

Calcd. for $C_8H_{11}O_2NS$: C, 51.87; H, 5.99; S, 17.31. Found: C, 50.86, 50.76; H, 6.08, 6.27; S, 16.78, 17.09.

c. **Reaction with Phenyllithium.**—A filtered solution of phenyllithium prepared from 157 g. (1.0 mole) of bromobenzene and 14.7 g. (2.1 g. atoms) of lithium in 750 ml. of ethyl ether was added dropwise during 1 hr. to a stirred solution of phenyliminosulfur difluoride (69 g., 0.428 mole) in 200 ml. of dry ether kept at −30° by an acetone–Dry Ice bath. After the addition was complete, the mixture was allowed to warm to room temperature, and 200 ml. of saturated ammonium chloride solution was added. The mixture then was filtered, and the organic layer of the filtrate was washed with water and dried over anhydrous magnesium sulfate. The ether was evaporated, and the residue was distilled from a Claisen flask to give 64 g. of a mixture of solid and liquid, b.p. 25–110° (0.5 mm.). This distillate was fractionated to give 4.33 g. of aniline, b.p. 38–40° (1.2 mm.), m.p. of benzoyl derivative, 163.5–164°. A second fraction, 4.60 g., b.p. 40–107° (1.2 mm.), contained mostly biphenyl, m.p. 68–69° after crystallization from ethanol. A mixed m.p. with an authentic sample of biphenyl was 68–69°. The third fraction (38.4 g., b.p. 106–109° (1.2 mm.)) contained triphenyl sulfilimine. An intermediate fraction of 0.55 g., b.p. 109–129° (1.2 mm.), then was obtained. The final fraction, 10.6 g., b.p. 129–134° (1.2 mm.), consisted of diphenyl disulfide, m.p. and mixed m.p. with diphenyl disulfide 59–60° after crystallization from ethanol. Fraction three contained an appreciable amount of product having the $-N{=}S\langle$ linkage and an over-all spectrum consistent with triphenylsulfilimine, $C_6H_5N{=}S(C_6H_5)_2$. However, an impurity identified as diphenyl sulfide by infrared was also present, and elemental analyses indicated the triphenylsulfilimine (18% yield) and diphenyl sulfide were present in approximately a 1:1 ratio.

Calcd. for $C_{18}H_{15}NS{\cdot}C_{12}H_{10}S$: C, 77.71; H, 5.44; N, 3.02; S, 13.83. Found: C, 78.46; H, 5.95; N, 3.16; S, 14.12.

d. **Reaction with *o*-Phenylenediamine.**—A slurry of 11 g. (0.11 mole) of *o*-phenylenediamine in 100 ml. of dry ethyl ether was added to a stirred solution of phenyliminosulfur difluoride (8.0 g., 0.05 mole) in 100 ml. of dry ether. The mixture was stirred under reflux for 1 hr., and the solid that formed was removed by filtration. The filtrate was washed with water, 5% hydrochloric acid and water and then was dried over anhydrous magnesium sulfate. Removal of the ether under reduced pressure left a dark semi-solid from which a volatile, yellow solid could be sublimed at 35° (0.25 mm.). The sublimate was crystallized from petroleum ether at −78° and resublimed to give 3.0 g.

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[8] The collaboration of Dr. W. R. Hasek in carrying out this experiment is gratefully acknowledged.

[9] The authors are indebted to Dr. W J. Middleton for this experiment.

(44%) of 2,1,3-benzothiadiazole, m.p. 41.5–42.5°. A mixed melting point with an authentic sample of 2,1,3-benzothiadiazole was 41.5–43°.

e. **Reaction with Anisole.**—Phenyliminosulfur difluoride (16 g., 0.1 mole) was added to a mixture of 30 ml. of anisole and 2.5 g. of fused zinc chloride at 0°. The dark mixture was allowed to warm to room temperature and was stirred for 15 hr. The mixture then was heated on a steam-bath for 1 hr., cooled and poured onto a mixture of ice and concentrated hydrochloric acid. Separation of the product from tarry material was effected by extraction with benzene. The benzene solution was washed with 10% sodium hydroxide solution and water, and next was dried over anhydrous magnesium sulfate. Removal of solvent and excess anisole, with subsequent distillation of the residue, yielded 9.16 g. (37%) of 4,4′-dimethoxydiphenyl sulfide as a viscous liquid, b.p. 158–161° (0.5 mm.), which soon solidified. Crystallization from petroleum ether at −78° gave colorless plates, m.p. 44–45° (lit.[7] m.p. 45–46°).

In order to confirm the structure of the product as 4,4′-dimethoxydiphenyl sulfide, 1.0 g. was dissolved in 20 ml. of glacial acetic acid, and a solution of 1.0 g. of potassium permanganate in 15 ml. of water was added. After 1 hr. at room temperature, the mixture was poured onto ice, and the solid was collected by filtration. Crystallization from ethanol gave 0.73 g. of 4,4′-dimethoxydiphenyl sulfone, m.p. 129.5–130.5° (lit.[10] m.p. 129–130°).

f. **Reduction by Lithium Aluminum Hydride.**—A solution of 4 g. (0.025 mole) of phenyliminosulfur difluoride in 25 ml. of dry ethyl ether was added dropwise during 2.5 hr. to a stirred mixture of 6 g. of lithium aluminum hydride in 75 ml. of ether. An extremely vigorous reaction occurred. The excess lithium aluminum hydride was decomposed by adding ethyl acetate; then 200 ml. of 20% sodium hydroxide solution was added, and the mixture was extracted with ether. After the ether solution had been washed with water and dried over anhydrous magnesium sulfate, the ether was distilled. To the residual brown oil was added 50 ml. of 10% sodium hydroxide solution and 7 ml. of benzoyl chloride. The mixture was shaken for 30 minutes, and the solid was collected by filtration. Crystallization of the solid from ethanol gave 0.31 g. of benzanilide, m.p. 160–161°. A mixed melting point with an authentic sample of benzanilide was 162–163°.

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WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE INSTITUTE FOR ORGANIC CHEMISTRY T.N.O., UTRECHT, HOLLAND]

Infrared Absorption Spectra of Some IVth Group Organometallic Compounds

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The infrared absorption spectra of compounds of the type $(C_6H_5)_4M$, $(C_6H_5)_3MCH{=}CH_2$, $(C_6H_5)_2M(CH{=}CH_2)_2$, $(C_6H_5)_3MCH_2CH{=}CH_2$ and $(C_6H_5)_2M(CH_2CH{=}CH_2)_2$ in which M = Si, Ge, Sn and Pb have been recorded in the region of 3500–680 cm.$^{-1}$. Empirical assignments have been made for specific vibrations. Comparison of the spectra revealed a shift of some characteristic band frequencies to longer wave lengths in the series M = Si, Ge, Sn and Pb. The preparation of triphenylallylsilane, triphenylvinyl-, diphenyldivinyl- and diphenyldiallylgermane, triphenylvinyl- and diphenyldivinyllead, compounds not previously described, is given.[2]

Although considerable work has been done in the field of infrared spectroscopy of organosilicon compounds, there have been relatively few reports in the literature of the spectra of organometallic compounds of the other IVth main group elements. In connection with a program involving the reactions of organotin hydrides with vinyl- and allyl-substituted IVth group phenylmetal compounds,[3] infrared spectra of organometallic derivatives of the type $(C_6H_5)_4M$, $(C_6H_5)_3MCH{=}CH_2$, $(C_6H_5)_2M(CH{=}CH_2)_2$, $(C_6H_5)_3MCH_2CH{=}CH_2$ and $(C_6H_5)_2M(CH_2CH{=}CH_2)$ in which M = Si, Ge, Sn and Pb in the region of 3500–680 cm.$^{-1}$ were recorded. This paper deals with tentative band assignments and with characteristic differences in the spectra when passing from Si to Pb as the central metal atom.

Experimental

Preparation of Compounds.—Tetraphenylsilane[4] was prepared by a Wurtz reaction, tetraphenylgermane,[5a] tetraphenyltin[5b] and tetraphenyllead[6] were prepared by a Grignard reaction, phenylmagnesium chloride in tetrahydrofuran (THF) being used as the phenylating agent.[7]

These compounds were converted into the corresponding triphenylmetal monohalides $(C_6H_5)_3MX$ and diphenylmetal dihalides $(C_6H_5)_2MX_2$ by published procedures. Triphenylbromosilane $(C_6H_5)_3SiBr$, prepared by Ladenburg[8] by heating equimolecular amounts of tetraphenylsilane and bromine in a sealed tube, was obtained in an appreciably higher yield (76%) by carrying out the reaction in a high-boiling solvent (ethylene bromide).

The phenylmetal halides were converted into the corresponding vinyl and allyl derivatives by reaction with vinylmagnesium bromide in THF[9] and with allylmagnesium bromide in diethyl ether.[10] Stock solutions of these reagents were stored in calibrated flasks under nitrogen. Molarities were determined by titrating a hydrolyzed aliquot with standard acid.[11] Storage for considerable time did not result in appreciable decrease in reactivity. All reactions were carried out in an atmosphere of dry nitrogen.

Triphenylvinylsilane,[12,13] triphenylvinyltin,[14] diphenyldivinylsilane,[13] diphenyldivinyltin,[15] triphenylallylgermane,[16] triphenylallyltin,[17] triphenylallyllead,[18] diphenyldi-

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[1] U. S. Army Research and Engineering Command, Natick Mass.; work done in Utrecht under the auspices of a Secretary of the Army Research Fellowship.

[2] Juenge and Cook have reported the preparation of triphenylvinyllead and diphenyldivinyllead at the 135th Meeting of the American Chemical Society, April, 1959, Boston, Mass.

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