OH(NH) band at 3.00 μ, a weak CH band at 3.25 μ; *no* aldehyde C=O band at 5.65 μ and *no* ethyleneimine bands at 10.95, 11.70, or 12.80 μ. There were present new bands at 8.30, 11.50, 12.00, 12.70, 13.10, 13.85, and 14.30 μ. An infrared spectrum of the solid product (m.p. 67–68°, recrystallized from benzene) which was isolated by evaporating ether from a portion of the solution was quite different. A melt smear showed no OH or NH band at 3.00 μ, but a strong band at 3.20 μ; CH deformation bands at 6.70–8.00 μ, CF bands at 8.25–10.00 μ, and new bands 10.65, 11.30, 11.65, and 14.50 μ. Bands at 10.80, 11.50, 13.10, 13.85, and 14.30 μ had disappeared. However, an ether solution freshly prepared from the isolated solid compound was identical to the original ether solution. *1-Hydroxy-1-aziridinyl-1,7-dihydroperfluorohexane* (VII) was analyzed.

Anal. Calcd. for $C_9H_{12}H_7NO$: C, 28.99; F, 61.1; N, 3.76. Found: C, 28.4; F, 61.9; N, 3.9.

At a 2:1 mole ratio. A solution of 7.94 g. (0.185 mole) of ethyleneimine in 100 cc. of dry ether was stirred at 0° while 30.0 g. (0.091 mole) of II (n = 3) was added during 45 min. The reaction temperature rose to 7–8° during the addition. Ether and unchanged ethyleneimine were evaporated under nitrogen, leaving 45.3 g. of liquid. A solid, m.p. 63–64°, 0.74 g., separated on cooling which gave an analysis corresponding to VII. Complete removal of ether from the product left 37.5 g. of liquid (100% yield for 2:1 addition product), but on standing, more crystals of VII began to form and distillation of 10.0 g. of the product mixture gave 3.9 g. of VII as a white solid which sublimed at 83–78° (0.7 mm.); m.p. 61–66°. Analysis and infrared spectra showed its identity with VII, m.p. 67–68°, isolated above. The 2:1 addition compound decomposed during distillation to a dark brown tar.

Reaction of II (n = 3) with 1-amino-2-(2-hydroxyethylamino)ethane. A solution of 33.0 g. (0.10 mole) of II (n = 3) in 50 cc. of dry benzene was stirred while 10.4 g. (0.10 mole) of 1-amino-2-(2-hydroxyethylamino)ethane was added over a 0.5-hr. period. The temperature rose from 23 to 60.5° in 10 min. and fell to 40° during the addition. The solution was distilled in Column A. Benzene, a water layer (2.0 cc.) and unchanged II (n = 3) (52.3 g.) distilled at 45–52° (300 mm.). The product taken in three fractions, b.p. 96° (1.0 mm.); n_D^{25} 1.3958–1.3998; 28 g., was obtained in 80% yield. (The residue was 1.7 g.) *N,N″-(7-H-dodecafluoroheptylidene)bis-[N′-(2-hydroxyethyl)ethylenediamine]* (VIII) was a viscous, colorless oil which was insoluble in water and 0.1*N* hydrochloric acid, but soluble in 1.2*N* hydrochloric acid. VIII reduced the surface tension of aqueous hydrochloric acid solution to 35.6 dynes/cm. at 2.0% concentration. An infrared spectrum showed a weak OH(NH) band at 3.00 μ, strong CH bands at 3.40 and 3.45 μ, and a large number of bands above 7.00 μ. The properties and analysis of VIII are consistent with the structure $H(CF_2)_6CH(NHCH_2CH_2NHCH_2CH_2OH)_2$.

Anal. Calcd. for $C_{15}F_{12}H_{24}N_4O_2$: C, 34.6; F, 43.8; H, 4.65; N, 10.75. Found: C, 36.6; F, 45.0; H, 3.7; N 10.2.

1,2-Dihydroperfluoroethane.[9,10] I (n = 1) (1030 g., 7.8 moles) was treated with chlorine (180 g., 2.54 moles) as above over a 6-hr. period. Hydrogen chloride was removed by sweeping with nitrogen and the crude mixture added dropwise to 50% aqueous potassium hydroxide solution. The gases evolved were collected in a trap, cooled in solid carbon dioxide, and redistilled, b.p. −19°; 164 g. (20% conversion, 63% yield based on chlorine); reported[8] b.p. −23°. NMR spectra showed only one peak ascribable to fluorine and one to hydrogen. Such a simple spectrum could only be given by the symmetrical molecule 1,2-dihydroperfluoroethane.

1,4-Dihydroperfluorobutane.[10] II (n = 2) (15 g., 0.065 mole) was dropped into 30 cc. of 50% aqueous potassium hydroxide solution. Heat developed and a gas was given off which was condensed and redistilled, b.p. 45°. NMR spectra indicated the presence of CHF_2 and CF_2 groups in the molecule.

1,6-Dihydroperfluorohexane.[10] II (n = 3) (25.0 g., 0.096 mole) was dropped into 100 cc. of 50% aqueous potassium hydroxide solution and refluxed for 1 hr. The organic layer after cooling was separated, washed alkali-free with water, dried, and distilled to give 22.9 g. (100%) of 1,6-dihydroperfluorohexane, b.p. 92.5°.

Anal. Calcd. for $C_6F_{12}H_2$: C, 23.8; F, 75.5. Found: C, 24.9; F, 75.9.

An NMR spectrum was consistent with the structure assigned.

WILMINGTON, DEL.

---

(10) I am indebted to J. F. Smith for this experiment.

[CONTRIBUTION NO. 674 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Iminosulfur Oxydifluorides

RICHARD CRAMER AND D. D. COFFMAN

Received April 11, 1961

A new class of sulfur compounds, the iminosulfur oxydifluorides, R—N=SOF_2, has been obtained by the reaction of primary amines with sulfur oxytetrafluoride.[1] Iminosulfur oxydifluorides are moderately resistant to hydrolysis, resembling, in this respect, sulfuryl fluoride, but react readily with the more basic amines. When attached to a benzene ring, the iminosulfur oxydifluoride group directs electrophilic substituents to the *para* position and is mildly activating.

Sulfuryl fluoride, SO_2F_2, reacts with ammonia[2] to give sulfamide (Equation 1), while thionyl fluoride, SOF_2, with ammonia and primary amines yields imines (Equations 2 and 3).[3]

$$NH_3 + SO_2F_2 \longrightarrow NH_2SO_2NH_2 \qquad (1)$$

$$RNH_2 + SOF_2 \longrightarrow RNHSOF \qquad (2)$$

$$RNHSOF \longrightarrow RN{=}SO \qquad (3)$$

When sulfur oxytetrafluoride, SOF_4, became easily accessible,[4,5] a study of its reaction with

---

(1) As this paper was in preparation for publication, F. Seel and G. Simon published a note [*Angew. Chem.*, **72**, 709 (1960)] which mentions the reaction of amines with sulfur oxytetrafluoride to give, apparently, iminosulfur oxydifluorides. No specific compounds are mentioned.

(2) W. Traube and E. Reubke, *Ber.*, **56**, 1661 (1923).

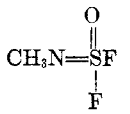
(3) M. Goehring and G. Voigt, *Ber.*, **89**, 1050 (1956).

(4) C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960).

primary amines was undertaken. Conceivable products are a diimide, an imide diamide, or possibly a tetraamide. Actually, it was found that a series of iminosulfur oxydifluorides could be obtained in high yields (Equation 4).

$$RNH_2 + SOF_4 \longrightarrow RN{=}SOF_2 + 2HF \qquad (4)$$

Properties which led to the structure assignment may be illustrated by the product from the reaction of methylamine and sulfur oxytetrafluoride. The liquid product, b.p. 39°, had elemental analyses corresponding to the formula CH_3NSOF_2. The infrared spectrum contained a band at 3.36 μ assignable to —C—H, bands at 6.7 μ and 7.75 μ resembling absorptions of sulfuryl fluoride and assignable to —N=S— and —S=O, a band at 7.05 μ assignable to CH_3—N—, and a broad band at 12.6 μ assignable to —S—F. The F^{19} NMR was a single peak in the same region as the F^{19} resonance in $—SO_2F$. There was a single proton resonance in the region expected for a methyl group attached to a nitrogen atom. The mass spectrogram had a principal peak at 114 corresponding to a singly charged parent molecule which has lost a hydrogen atom. Other iminosulfur oxydifluorides which have been synthesized are listed in Table I. It will be noted that they include bifunctional compounds containing carboxyl, aromatic hydroxyl, or aromatic amino groups.



$$CH_3N{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle F}{|}}{S}}F$$

(I)

TABLE I

IMINOSULFUR OXYDIFLUORIDES FROM AMINES AND SULFUR OXYTETRAFLUORIDE

Amine	Iminosulfur Oxydifluoride
CH_3NH_2	$CH_3N{=}SOF_2$
$C_6H_5NH_2$	$C_6H_5N{=}SOF_2$
p-$C_6H_4(NH_2)_2$	p-$C_6H_4(N{=}SOF_2)_2$
m-$C_6H_4(NH_2)_2$	m-$C_6H_4(N{=}SOF_2)_2$ m-$H_2NC_6H_4N{=}SOF_2$
p-$HOC_6H_4NH_2$	p-$HOC_6H_4N{=}SOF_2$
m-$O_2NC_6H_4NH_2$	m-$O_2NC_6H_4N{=}SOF_2$
$H_2N(CH_2)_5COOH$	$F_2OS{=}N(CH_2)_5COOH$

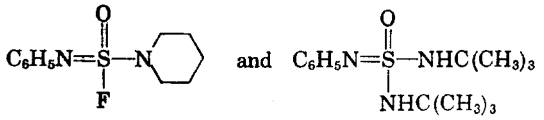
Iminosulfur oxydifluorides are relatively inert towards hydrolysis, resembling sulfuryl fluoride in this respect. Methyliminosulfur oxydifluoride required about 1.5 hours for hydrolysis by 10% sodium hydroxide at room temperature, one week with 10% hydrochloric acid, and three weeks in water alone. It dissolved in concentrated sulfuric acid and was recovered unchanged when this solution was added to water.

Although phenyliminosulfur oxydifluoride was completely hydrolyzed to the phenylsulfamate ion only after ten days by aqueous 10% sodium hydroxide, the reaction was so fast in 60:40 dioxane-water that the compound could be readily assayed by titration with 0.1M sodium hydroxide. Hydrolysis is presumed to go in two steps, as represented in Equations 5 and 6. The first step is practically instantaneous, while the second is definitely slower. Phenyliminosulfur oxydifluoride was not easily esterified and was recovered unchanged after being refluxed with ethanol for five hours. It reacted with alcoholic sodium ethylate to give, apparently, the ethyl ester of phenylsulfamic acid.

$$C_6H_5N{=}SOF_2 + 2OH^- \longrightarrow C_6H_5N{=}SO_2F^- + F^- + H_2O \qquad (5)$$

$$C_6H_5N{=}SO_2F^- + OH^- \longrightarrow C_6H_5NHSO_3^- + F^- \qquad (6)$$

The reactivity of phenyliminosulfur oxydifluoride towards amines was found to depend markedly upon the basicity of the amine. Thus, N-methylaniline, a weakly basic amine, did not react with phenyliminosulfur oxydifluoride after five hours at 130°. Furthermore, it was possible to isolate m-aminophenyliminosulfur oxydifluoride, and this indicates that the amino group in this compound is relatively inert. Piperidine and *tert*-butylamine both reacted readily with phenyliminosulfur oxydifluoride displacing one and two fluorines, respectively, to form the crystalline, water insoluble, organic solvent soluble amides:



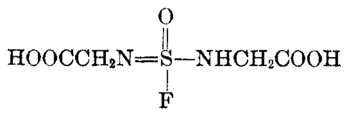
$$C_6H_5N{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle NHC(CH_3)_3}{|}}{S}}{-}NHC(CH_3)_3$$

Addition of chlorine to an equimolar mixture of phenyliminosulfur oxydifluoride and benzene at 0° resulted in chlorination of 35% of the oxydifluoride (in the *para* position), while only 18% of the benzene reacted. Thus, when attached to the benzene ring, the iminosulfur oxydifluoride group is moderately activating and *para*-directing, resembling the nitroso group.[6]

It was not possible to effect an addition to the —N=S— double bond. Reagents employed included hydrogen, hydrogen halides, halogens, dienes, and polymerization initiators such as radical generators and ionic catalysts.

The reaction of sulfur oxytetrafluoride with glycine (Equation 7) yielded a substituted iminosulfur oxydifluoride, (II).

$$2H_2NCH_2COOH + SOF_4 \longrightarrow$$



$$HOOCCH_2N{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle F}{|}}{S}}{-}NHCH_2COOH \qquad (7)$$

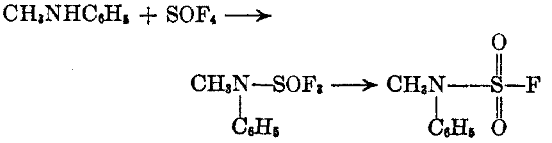
II

---

(5) W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, 82, 3838 (1960).

(6) C. K. Ingold, *J. Chem. Soc.*, 127, 515 (1925).

At 25–30°, *N*-methylaniline gave a hydrolytically sensitive amide (III) instead of an imino compound



$$CH_3NHC_6H_5 + SOF_4 \longrightarrow CH_3N(C_6H_5){-}SOF_3 \longrightarrow CH_3N(C_6H_5){-}SO_2{-}F \quad (8)$$

III

An interesting reaction was observed when phenylhydrazine was added to an ether solution of sulfur oxytetrafluoride at −30 to −20°. The hydrazine was oxidized to phenylazide in 24% conversion, while sulfur oxytetrafluoride was reduced to a compound of S(IV), presumably thionyl fluoride.

EXPERIMENTAL

Phenyliminosulfur oxydifluoride. A 500-ml. flask was fitted with a solid carbon dioxide–acetone-cooled condenser, a magnetic stirrer, and a side arm for attachment of a gas inlet tube or a dropping funnel. The flask was charged with 50 ml. of ether, chilled to about −40°, and sulfur oxytetrafluoride[4,5] (31 g., 0.25 mole) was introduced as a gas. The gas inlet tube was replaced with a dropping funnel, and aniline (24 g., 0.25 mole) in 50 ml. of ether was added during 15 min. After 0.5 hr. the reaction mixture was poured onto ice. The ether layer was separated, washed with water, cold aqueous sodium bicarbonate solution, cold dilute hydrochloric acid, finally with water, and then was distilled. Phenyliminosulfur oxydifluoride (35 g., 0.20 mole) was recovered boiling at 153–155° (atm. press.); 64° (20 mm.), n_D^{25} 1.475. The infrared spectrum contained, in addition to absorptions attributable to a benzene ring, bands at 6.9 μ and 7.6 μ corresponding to N=S=O and a broad band at 12.5 μ corresponding to S-F.

Since aniline is not a strong base and therefore does not react readily with phenyliminosulfur oxydifluoride, it is also possible to synthesize the latter by adding sulfur oxytetrafluoride to an ethereal solution of aniline. A 500-ml. flask fitted with solid carbon dioxide–acetone-cooled condenser, magnetic stirrer, and gas inlet tube was charged with ether (100 ml.) and aniline (24 g., 0.25 mole). Sulfur oxytetrafluoride (31 g., 0.25 mole) was introduced through a gas inlet tube above the surface of the aniline solution at room temperature. During the addition of the first half of the sulfur oxytetrafluoride, the reaction mixture became a thick slurry (as aniline hydrofluoride precipitated) and later became quite fluid (as the hydrofluoride reacted with sulfur oxytetrafluoride). The product was isolated as described in the foregoing paragraph. The yield was 33 g. (0.19 mole).

Hydrolysis of phenyliminosulfur oxydifluoride. Phenyliminosulfur oxydifluoride (1 g.) did not dissolve perceptibly in 10 ml. of aqueous 10% sodium hydroxide after 2 days at room temperature. After 5 days it had largely dissolved, and after 10 days the solution was homogeneous. When the solution was chilled in ice, sodium phenylsulfamate crystallized.

Hydrolysis in a homogeneous medium was much faster. By mixing an aqueous solution of sodium hydroxide with phenyliminosulfur oxydifluoride in dioxane, a homogeneous reaction mixture in 60:40 water-dioxane was obtained which was 0.0438*M* in sodium hydroxide and 0.0132*M* in phenyliminosulfur oxydifluoride. Titration of an aliquot of this solution with standard hydrochloric acid 3 min. after mixing showed that 0.0266 mole of alkali/l. had reacted with phenyliminosulfur oxydifluoride. Titration of another aliquot 3 hr. later showed that 0.0386 mole of alkali/l. had reacted. These results correspond to a fast reaction that consumed two equivalents of base and a slower reaction with one equivalent of base.

Esterification of phenyliminosulfur oxydifluoride. A solution of sodium ethoxide prepared by dissolving sodium (1.33 g., 0.058 mole) in 50 ml. of ethanol was added to phenyliminosulfur oxydifluoride (10 g., 0.058 mole) in 25 ml. of ethanol. The mixture became hot, and after several hours a voluminous precipitate appeared. The slightly alkaline mixture was filtered and concentrated to obtain a viscous liquid with the composition of ethyl phenylsulfamate.

Anal. Calcd. for $C_8H_{11}NSO_3$: C, 47.74; H, 5.51. Found: C, 48.00; H, 6.00.

The infrared spectrum contained peaks attributable to amino hydrogen (3.3 μ), to saturated C—H (3.35 and 3.45 μ), to $>NSO_2$—(7.35 and 8.5 μ) and to C—O—C (9.9 μ) in addition to absorptions attributable to a monosubstituted benzene ring. The proton magnetic resonance spectrum showed typical ethyl and monosubstituted phenyl absorption patterns.

Reaction of phenyliminosulfur oxydifluoride with amines. a. *N-Methylaniline.* A solution of phenyliminosulfur oxydifluoride (8.9 g., 0.05 mole), *N*-methylaniline (5.35 g., 0.05 mole), and 25 ml. of toluene was heated under reflux (about 135°) for 6 hr. The reactants were recovered unchanged by distillation at atmospheric pressure.

b. *Piperidine.* A solution of phenyliminosulfur oxydifluoride (17.7 g., 0.1 mole) in 50 ml. of ether was added during 10 min. to piperidine (17 g., 0.2 mole) in 50 ml. of ether. An exothermic reaction occurred with deposition of a slush of oil and solid which completely solidified after several hours. The mixture was poured into iced aqueous hydrochloric acid, and the ethereal layer was separated, washed with water, dried over anhydrous magnesium sulfate, and the ether was removed by distillation. The residue was recrystallized by chilling a methanolic solution with solid carbon dioxide. The product (19 g.) melted at 28°.

Anal. Calcd. for $C_{11}H_{15}N_2SOF$: S, 13.23; N, 11.56. Found: S, 13.27; N, 11.54.

c. *tert-Butylamine.* A solution of phenyliminosulfur oxydifluoride (17.7 g., 0.1 mole) in 50 ml. of ether was added to a solution of *tert*-butylamine (9.5 g., 0.13 mole) in 50 ml. of ether. An exothermic reaction occurred, and a solid separated. After about 20 hr. the mixture was filtered, and the filtrate distilled to give ether and 2 g. of unchanged phenyliminosulfur oxydifluoride, leaving 14 g. of solid. This was recrystallized from 25 ml. of *n*-hexane to give a white solid melting at 90°.

Anal. Calcd. for $C_{14}H_{25}N_3SO$: S, 11.31; N, 14.83. Found: S, 10.87; N, 14.40.

Competitive chlorination of phenyliminosulfur oxydifluoride and benzene. A solution of benzene (3.9 g., 0.05 mole), phenyliminosulfur oxydifluoride (8.9 g., 0.05 mole), and 0.2 g. of iodine was placed in a flask fitted with a magnetic stirrer and a solid carbon dioxide-cooled condenser. The mixture was cooled to 0° by an ice water bath, and gaseous chlorine (0.05 mole) was introduced. After 1 hr. the crude chlorination product was washed with aqueous sodium hydroxide and allowed to stand over mercury and calcium chloride. The crude filtrate weighed 12.3 g. It was distilled, yielding 0.036 mole of benzene (b.p. 83°), 0.009 mole of chlorobenzene (b.p. 52–58°) (32 mm.), 0.022 mole of phenyliminosulfur oxydifluoride (b.p. 67–78°) (32 mm.), and 0.018 mole of *p*-chlorophenyliminosulfur oxydifluoride (b.p. 95–98°) (35 mm.). These fractions were identified by comparison of their infrared absorption spectra with those of authentic specimens.

Methyliminosulfur oxydifluoride. A "Hastelloy-C" autoclave with a capacity of 400 ml. was charged with sulfur oxytetrafluoride (31 g., 0.25 mole) and methylamine (8 g., 0.25 mole). The reaction mixture was heated to 100° for 16 hr. The product was distilled from pelletted sodium fluoride to give 11 g. (0.1 mole) of colorless liquid, b.p. 39°, n_D^{25} 1.3259.

Anal. Calcd. for CH_3NSOF_2: C, 10.44; H, 2.63; S, 27.85; F, 33.01. Found: C, 10.22; H, 2.53; S, 27.55; F, 32.61.

It seems very likely that the first of the two methods described for the synthesis of phenyliminosulfur oxydifluoride could be conveniently adapted to the synthesis of methyliminosulfur oxydifluoride.

p-Phenylenebis(iminosulfur oxydifluoride). A flask fitted with a magnetic stirrer, a solid carbon dioxide-cooled condenser and a gas inlet tube was charged with *p*-phenylenediamine (54 g., 0.5 mole) and 300 ml. of acetonitrile. Sulfur oxytetrafluoride (124 g., 1.0 mole) was added to the stirred mixture over 1 hr. An exothermic reaction occurred, and a salt separated which dissolved almost completely as the reaction proceeded. The product (92 g., 0.33 mole) was isolated by the procedure described for the preparation of phenyliminosulfur oxydifluoride from aniline; b.p. 74° (8 mm.), $n_{\rm D}^{25}$ 1.4770.

Anal. Calcd. for $C_6H_4N_2S_2O_2F_4$: C, 26.09; H, 1.46; N, 10.14; S, 23.21; F, 27.51. Found: C, 26.49; H, 1.47; N, 10.45; S, 23.44; F, 27.87.

m-Phenylenebis(iminosulfur oxydifluoride). The procedure described for preparation of the *para* isomer was used. Sulfur oxytetrafluoride (31 g., 0.25 mole) was added to *m*-phenylenediamine (27 g., 0.25 mole) in 100 ml. of acetonitrile. The product, *m*-phenylenebis(iminosulfur oxydifluoride) (13 g., 0.047 mole), b.p. 53°, 2 mm, $n_{\rm D}^{25}$ 1.4742, was identified by its infrared absorption spectrum, which contained absorptions attributable to a benzene ring (3.25, 6.2, 6.25, and 6.7 μ) to N=S=O (6.95 and 7.7 μ) and to S—F (12.5 μ).

Anal. Calcd. for $C_6H_4N_2S_2O_2F_4$: C, 26.09; H, 1.46; N, 10.14. Found: C, 26.73; H, 1.62; N, 10.55.

m-Aminophenyliminosulfur oxydifluoride. The procedure for preparation of phenylenebis(iminosulfur oxydifluoride) was used. Sulfur oxytetrafluoride (31 g., 0.25 mole) was added to *m*-phenylenediamine (54 g., 0.5 mole) in 200 ml. of acetonitrile over a period of 1 hr. The reaction mixture was poured into ice water, and concentrated aqueous sodium sulfate solution was added to salt out an acetonitrile phase. The aqueous phase was separated, washed with water, and chilled in an ice bath. About 200 ml. of ether was added, and the solution, kept below 25°, was made alkaline with 10% aqueous sodium hydroxide. The ethereal solution was separated and dried over anhydrous magnesium sulfate. One-fourth of the dried solution was saturated with hydrogen chloride, and an orange solid precipitated which was soluble in water and ethanol, sparingly soluble in ethyl acetate and insoluble in ether. This solid appears to be the hydrochloride of *m*-aminophenyliminosulfur oxydifluoride containing the hydrochloride of *m*-phenylenediamine as a contaminant. Bands at 3.5 μ (broad) and 3.87 μ were ascribed to $—NH_3^+$ stretching; at 6.21 μ and 6.67 μ to aromatic C=C; at 6.37 μ and 6.53 μ to NH_3^+ deformation; at 6.94 μ and 7.59 μ to N=S=O; and at 12.82 μ (broad) to S—F.

Anal. Calcd. for $C_6H_6N_2SOF_2{\cdot}HCl/0.2\ C_6H_8N_2{\cdot}HCl$: C, 33.56; H, 3.44; N, 13.05: Found: C, 33.60; H, 3.74; N, 13.24.

The remainder of the ethereal solution was warmed under reduced pressure, and the residue (8 g.) was distilled in a molecular still at a pressure of about 0.01 mm. and a temperature of 40°. Pale yellow *m*-aminophenyliminosulfur oxydifluoride was identified by proton and F^{19} NMR and infrared absorption spectra. The infrared absorption contained bands attributable to an amino group (2.9, 2.95, 3.1, and 6.15 μ), to a benzene ring (3.25, 6.2, and 6.65 μ), to the group N=S=O (6.95 and 7.95 μ), and to an S-F bond (12.7 μ).

p-Hydroxyphenyliminosulfur oxydifluoride. As in the preparation of phenylenebis(iminosulfur oxydifluoride), *p*-aminophenol (25.5 g., 0.23 mole) in 100 ml. of acetonitrile was treated with sulfur oxytetrafluoride (29 g., 0.23 mole). The mixture was poured onto a mixture of ethyl ether and iced water and was neutralized with sodium bicarbonate. The ether layer was separated, dried over magnesium sulfate and concentrated, keeping the still pot below 25°. A dark oil was obtained which was insoluble in water but soluble in aqueous sodium hydroxide and which gave a purple color with ferric chloride. Distillation at about 45° (0.01 mm.) gave impure *p*-hydroxyphenyliminosulfur oxydifluoride (15 g., 0.078 mole, $n_{\rm D}^{25}$ 1.4891).

Anal. Calcd. for $C_6H_5NSO_2F_2$: C, 37.30; H, 2.61; F, 19.67. Found: C, 36.30; H, 2.82; F, 18.32.

The structure was confirmed by the infrared absorption spectrum which contained bands attributable to —OH (2.95 μ), to an N=S=O group (6.9 and 7.95 μ) and to an S-F bond (12 μ) in addition to the usual aromatic absorptions.

m-Nitrophenyliminosulfur oxidifluoride. *m*-Nitroaniline (69 g., 0.5 mole) in 200 ml. of ether was treated with sulfur oxytetrafluoride (62 g., 0.5 mole). The product was isolated by the procedure described for the phenylenebis(iminosulfur oxydifluoride)s. *m*-Nitrophenyliminosulfur oxydifluoride (70 g., 0.31 mole) was purified by distillation, b.p. 71° (1.5 mm.), $n_{\rm D}^{25}$ 1.5206.

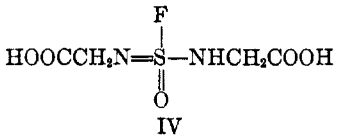
Anal. Calcd. for $C_6H_4N_2SO_3F_2$: C, 32.43; H, 1.82; F, 17.10. Found: C, 33.12; H, 2.01; F, 16.54.

ω-Carboxypentyliminosulfur oxydifluoride. Sulfur oxytetrafluoride (31 g., 0.25 mole) was added to ε-aminocaproic acid (33 g., 0.25 mole) in 100 ml. of acetonitrile during 1 hr. The reaction mixture was poured onto ice, ether was added, and the ether-acetonitrile solution was separated. This solution was washed with water, 100 ml. of water was added, and 20*M* sodium hydroxide added carefully with stirring until the solution was alkaline. The aqueous phase was separated and concentrated under reduced pressure. Acidification with dilute hydrochloric acid gave ω-carboxypentyliminosulfur oxydifluoride (6.5 g., 0.03 mole), melting about 0°. The crude product was sublimed at 50° (0.2 mm.) onto a solid carbon dioxide-cooled condenser.

Anal. Calcd. for $C_6H_{11}NSO_3F_2$: NE, 215. Found: NE, 215.

Identity was confirmed by the infrared absorption spectrum which contained bands attributable to a carboxyl group (broad band 3 μ to 4 μ together with 5.85 μ), to saturated C-H (3.4 μ), to N=S=O (6.95 and 7.9 μ), and to S-F (12.8 μ).

Reaction of glycine with sulfur oxytetrafluoride. Sulfur oxytetrafluoride (31 g., 0.25 mole) was added to a solution of glycine (19 g., 0.25 mole) in 100 ml. acetonitrile at 0°. The reaction product was stored with 20 g. of sodium fluoride at 0° for 2 weeks to remove hydrogen fluoride. The solution was filtered and concentrated at a temperature below 25°. The residue which is thought to be principally IV could not be distilled at 60° (0.02 mm.).



$$HOOCCH_2N{=}\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}NHCH_2COOH$$

IV

Anal. Calcd. for $C_4H_7O_5N_2SF$: C, 22.43; H, 3.29; S, 14.97; N, 13.09; F, 8.87; mol. wt., 214. Found: C, 23.74; H, 3.55; S, 15.42; N, 13.64; F, 10.87; mol. wt., (f.p. in acetone) 184.

Reaction of N-methylaniline with sulfur oxytetrafluoride. Sulfur oxytetrafluoride (31 g., 0.25 mole) was added to a solution of *N*-methylaniline (54 g., 0.5 mole) in 300 ml. of ether. No solid separated, although an exothermic reaction occurred. The reaction mixture was poured onto chopped ice, and a vigorous reaction ensued. The ethereal solution was separated, washed with dilute aqueous hydrochloric acid, dried over magnesium sulfate, and distilled. The product (30 g.) boiled at 68° (1.5 mm.), $n_{\rm D}^{25}$ 1.497.

Anal. Calcd. for $C_7H_8NSO_2F$: S, 16.94; N, 7.40; F, 10.04. Found: S, 17.05; N, 6.97; F, 9.92.

The reaction was rerun, and the crude product was poured onto pelletted sodium fluoride (instead of chopped ice) to remove hydrogen fluoride. The supernatant liquid was subjected to distillation in an attempt to recover $C_6H_5N(CH_3)SOF_3$, but after the ether had been removed, a vigorous reaction occurred during which the still pot was severely etched.

Phenylazide from phenylhydrazine and sulfur oxytetrafluoride. A flask fitted with a magnetic stirrer and a solid carbon dioxide-cooled condenser was chilled to −40° and charged with sulfur oxytetrafluoride (31 g., 0.25 mole) and 50 ml. of ether. A solution of phenylhydrazine (27 g., 0.25 mole) in 50 ml. of ether was added during 0.5 hr. The reaction mixture was poured onto ice and washed first with dilute alkali then with water. The odor of sulfur dioxide was quite evident, indicating reduction of sulfur oxytetrafluoride. Phenylazide (5 g.) was isolated by distillation. It was identified by its infrared and ultraviolet absorption spectra and by a color reaction[7] with aluminum chloride in benzene.

WILMINGTON, DEL.

---

[7] W. Borsche and H. Hahn, *Ber.*, **82**, 260 (1949).

[CONTRIBUTION FROM THE ENERGY DIVISION, OLIN MATHIESON CHEMICAL CORP.]

Aromatic Fluorine Compounds. I. Preparation of *p*-Fluoraniline by Catalytic Reduction of Nitrobenzene in Hydrogen Fluoride[1]

DELMER A. FIDLER, JAMES S. LOGAN, AND MAX M. BOUDAKIAN

Received February 1, 1961

A novel one-step method for the preparation of *p*-fluoroaniline by the catalytic reduction of nitrobenzene in anhydrous hydrogen fluoride is described. The suggested mechanism involves the reduction of nitrobenzene to *N*-phenylhydroxylamine followed by the *in situ* rearrangement of the latter in hydrogen fluoride to give *p*-fluoroaniline.

The primary objective of this study was to determine whether *p*-fluoroaniline (III) could be prepared by a more simplified fluorination route than the Schiemann reaction.[2,3] Thus, *p*-fluoroaniline can be prepared by the reduction of *p*-fluoronitrobenzene.[4] The latter is synthesized by the Schiemann reaction involving conversion of *p*-nitroaniline to *p*-nitrophenyldiazonium fluoborate, followed by decomposition to give *p*-fluoronitrobenzene. (Another route to *p*-fluoronitrobenzene involves nitration of fluorobenzene,[4] which in turn is obtained by the Schiemann reaction from aniline.[3]) Other known approaches to *p*-fluoroaniline such as the use of *p*-fluorobenzoic acid[5] in the Schmidt reaction or the treatment of *p*-bromofluorobenzene with potassium amide[6] also involve a prior Schiemann reaction.

Recently, two alternative routes toward the preparation of aromatic fluorine compounds have been reported. Finger and Kruse treated *p*-chloronitrobenzene with potassium fluoride to give *p*-fluoronitrobenzene.[7] Of more immediate interest to the present investigation is the observation by Titov and Baryshnikova that *p*-fluoroaniline could be obtained by the rearrangement of *N*-phenylhydroxylamine (II) in anhydrous hydrogen fluoride.[8,9] When this reaction was studied in this Laboratory, the previously reported[8] forty-eight-hour period was considerably shortened to reaction times as low as half an hour to give similar yields of *p*-fluoroaniline. In view of the reported catalytic reduction of nitrobenzene to *N*-phenylhydroxylamine,[10,11] and the rapid rearrangement of the latter in hydrogen fluoride to *p*-fluoroaniline,[8] this suggested a convenient one-step route to *p*-fluoroaniline by the catalytic reduction of nitrobenzene in anhydrous hydrogen fluoride. However, when Weinmayr catalytically hydrogenated (palladium catalyst on Nuchar) nitrobenzene in anhydrous hydrogen fluoride, only aniline and traces of *p*-aminophenol were reported.[12] Since the synthesis of *p*-chloraniline from nitrobenzene in concentrated hydrochloric acid was achieved by catalytic reduction (platinum oxide),[13] by electrolysis be-

---

[1] This work was sponsored by Chemical Corps Engineering Command, U. S. Army, Contract No. DA-18-064-CML-2696.

[2] G. Schiemann and R. Pillarsky, *Ber.*, **62**, 3035 (1925).

[3] A. Roe, *Org. Reactions*, **V**, 217 (1952). A modification of the Schiemann approach involves the formation and *in situ* decomposition of the aryldiazonium fluoride, ArN_2F.

[4] H. L. Bradlow and C. A. Vander Werf, *J. Am. Chem. Soc.*, **70**, 654 (1948).

[5] K. Takatori, Y. Yamada, T. Arai, and R. Nakazawa, *Yakugaku Zasshi*, **78**, 108 (1958); *Chem. Abstr.*, **52**, 11013 (1958).

[6] J. D. Roberts, C. W. Vaughan, Jr., L. A. Carlsmith, and D. Semenov, *J. Am. Chem. Soc.*, **78**, 611 (1956).

[7] G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6037 (1956).

[8] A. I. Titov and A. N. Baryshnikova, *Zhur. Obshcheĭ Khim.*, **23**, 346 (1953). These investigators did not find *o*-fluoroaniline or *p*-aminophenol in this rearrangement.

[9] The rearrangement of *N*-phenylhydroxylamine in hydrochloric acid to give *o*- and *p*-chloraniline has also been observed. T. W. J. Taylor and W. Baker in N. V. Sidgwick's *Organic Chemistry of Nitrogen*, Clarendon Press, Oxford, 1949, p. 163.

[10] T. W. J. Taylor and W. Baker, *Organic Chemistry of Nitrogen*, Clarendon Press, Oxford, 1949, p. 162.

[11] K. Brand and V. Steiner, *Ber.*, **55**, 875 (1922).

[12] V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 1762 (1955).

[13] C. O. Henke and J. V. Vaughen, U. S. Patent **2,198,249** (April 23, 1940).