$$NH_2F + F\cdot \longrightarrow NHF\cdot + HF \qquad (11)$$
$$NHF\cdot + F_2 \longrightarrow NHF_2 + F\cdot \qquad (12)$$
$$NHF_2 + F \longrightarrow NF_2\cdot + HF \qquad (13)$$
$$NF_2\cdot + F_2 \longrightarrow NF_3 + F\cdot \qquad (14)$$

The formation of dinitrogen tetrafluoride can be explained by the combination of two difluoramino radicals

$$2NF_2\cdot \longrightarrow N_2F_4 \qquad (15)$$

while difluoramine could be formed as shown in Equation (12). The formation of dinitrogen difluoride can then occur by reaction of the $NF_2\cdot$ and $NHF\cdot$ radicals followed by elimination of hydrogen fluoride from the trifluorohydrazine formed

$$NHF\cdot + NF_2\cdot \longrightarrow [NHF\text{-}NF_2] \longrightarrow N_2F_2 + HF \quad (16)$$

The fact that dinitrogen difluoride yields were of the order of 5% or less is in accord with the relatively low order of probability of collision of these two radicals. Although these mechanisms are not rigorously proven by the experimental data, they fit the existing theory for such reactions and also give a logical explanation of the results.

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[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

The Direct Synthesis of Difluoramine[1]

BY JEREMIAH P. FREEMAN, AL KENNEDY AND CHARLES B. COLBURN

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Difluoramine, HNF_2, was prepared in yields up to 75% by the reduction of tetrafluorohydrazine with mercaptans, preferably thiophenol. Arsine also was useful in this reaction.

Recently three groups have reported the isolation of difluoramine, HNF_2, as a by-product of various fluorination reactions: (1) from the passage of nitrogen trifluoride saturated with water vapor over a heated bed of arsenic (trace quantities)[2]; (2) from the fluorination of urea and subsequent decomposition of intermediate products[3]; (3) and from the fluorination of ammonia (trace quantities).[4]

A new, direct and simple method has now been found that produces difluoramine in good yield. Heating tetrafluorohydrazine,[5] N_2F_4, with thiophenol in an evacuated bulb produces difluoramine in 74% yield. The product was readily purified by fractional condensation in a high vacuum line. A second distillation removed the last traces of N_2F_4 and difluoramine of 99% purity (mass spectrometer) was obtained. The material remaining in the reaction bulb was unreacted thiophenol and diphenyl sulfide. The over-all reaction then is

$$N_2F_4 + C_6H_5SH \longrightarrow 2HNF_2 + C_6H_5SSC_6H_5$$

Higher reaction temperatures led to further reaction and the production of nitrogen. Similar results were obtained when metal bombs rather than glass reactors were used. Aliphatic mercaptans were not as useful as thiophenol because they also caused the reduction of tetrafluorohydrazine to nitrogen. Interestingly, glass vessels could not be used for the aliphatic mercaptan reactions.

The earlier synthesis based on nitrogen trifluoride, water and arsenic suggested the intermediacy of tetrafluorohydrazine and arsine. Further experiments showed that this mixture did indeed yield difluoramine. Arsine reacted slowly with tetrafluorohydrazine in a steel reactor at room temperature but more conveniently at 50° to produce arsenic and difluoramine (52% yield). After several successful reactions, the reaction began to occur explosively. A new reactor was then used and all subsequent reactions occurred at a normal rate. The explosive reaction may have been caused by air which leaked into this system.

Nitrogen trifluoride did not react with arsine under similar conditions up to temperatures of 175°. Above 175°, the arsine decomposed while the nitrogen trifluoride remained unreacted.

The difluoramine was identified by its infrared spectrum and mass spectral cracking pattern.[2] Amounts up to two liters (S.T.P.) have been stored in Pyrex vessels for long periods without decomposition. However, old vacuum systems which have become etched or which contained unknown residual materials could not be used for storage, nor could metal bombs. In these systems difluoramine reverted to tetrafluorohydrazine.

Experimental[6]

Thiophenol and Tetrafluorohydrazine.—Twelve milliliters (0.107 mole) of thiophenol was placed in a 1-l. round-bottomed flask equipped with a magnetic stirrer and attached to a vacuum line. The thiophenol was degassed and 483 cc. (0.0215 mole) of tetrafluorohydrazine[5] was condensed in using a liquid nitrogen cold bath. The resulting mixture was allowed to warm to room temperature and then was immersed in an oil-bath. The mixture was stirred for 4 hours at a bath temperature of 50°. The bath was then removed and the flask allowed to cool to room temperature. The contents were then distilled *in vacuo* through a series of U-tubes cooled at −80°, −128° (methylcyclohexane slush) and −196°, respectively. The product retained in the

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(1) This research was carried out under Army Ordnance Contract DA-01-021-ORD-5135.

(2) A. Kennedy and C. B. Colburn, THIS JOURNAL, **81**, 2906 (1959).

(3) E. A. Lawton and J. Q. Weber, *ibid.*, **81**, 4755 (1959).

(4) S. I. Morrow, D. D. Perry, M. S. Cohen and C. W. Schoenfelder, Abstracts, 137th Meeting, American Chemical Society, Cleveland, Ohio, April 1960, p. 11-M.

(5) C. B. Colburn and A. Kennedy, THIS JOURNAL, **80**, 5004 (1958).

(6) All gas volumes mentioned were measured at standard conditions of pressure and temperature.

$-128°$ bath was distilled through another $-128°$ bath to a $-196°$ bath. Mass spectrum analysis[3] of the $-128°$ fraction showed it to be 99% **difluoramine**; yield 587 cc. (74%).

The contents of the $-196°$ traps were combined and the recovered N_2F_4 measured; yield 100 cc. (21%).

The material remaining in the reaction flask proved to be a mixture of unreacted thiophenol and diphenyl disulfide. The disulfide was isolated by dissolving the residue in ether, washing it with alkali to remove the thiophenol and removing the ether. The solid residue, m.p. 58–60° (lit.[7] m.p. 60–62°), had an infrared spectrum identical to that of an authentic sample of diphenyl disulfide.

n-Butylmercaptan and Tetrafluorohydrazine.—A mixture of 2.25 g. (0.025 mole) of *n*-butylmercaptan and 125 cc. (0.0056 mole) of tetrafluorohydrazine was heated in a stainless steel bomb for 2 hours at 50–60°. The bomb was cooled, the nitrogen which was produced was vented, and the difluoramine was collected in the same manner described; yield 98 cc. Several distillations were required to obtain 22 cc. (9%) of 98% pure difluoramine.

Arsine and Tetrafluorohydrazine.—The arsine was prepared by treatment of sodium arsenite with zinc and sulfuric acid.[8] A 300-cc. high pressure Hoke stainless steel cylinder was charged with 150 cc. (0.0007 mole) each of tetrafluorohydrazine and arsine and then immersed in a water-bath at 50° for 1 hour. The gaseous contents had the following composition: HNF_2, 53 mole %; N_2O, 34 mole %; AsH_3, 8.5 mole %; and N_2F_4, 4.3 mole %. Distillation of the product through a $-130°$ bath (*n*-pentane slush) concentrated the difluoramine (88% pure), but last traces of arsine could not be removed; yield 156 cc. (52%). The nitrous oxide may have arisen from metal oxides present in the bomb, or from reaction of the products with the glass vacuum line.

CAUTION! During these experiments several traps, kept in liquid nitrogen protecting vacuum pumps, exploded when opened to the air and permitted to warm toward room temperature. It should always be remembered that several explosions have occurred[2,3] with difluoramine when condensed at $-196°$.

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[7] H. Lecher *Ber.*, **48**, 525 (1915).

[8] E. C. Markham and S. E. Smith, "General Chemistry," Houghton Mifflin Co., Boston, Mass., 1955, p. 362.

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION, ST. LOUIS, MISSOURI]

Principles of Phosphorus Chemistry. VII. Reorganization of Polyphosphoryl Halides[1]

BY LEO C. D. GROENWEGHE, JOHN H. PAYNE AND JOHN R. VAN WAZER

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There are families of phosphoryl and thiophosphoryl halides, which were prepared as mixtures by reorganizing various proportions of POX_3, PSX_3, P_2O_5 and/or P_2S_5. The phosphoryl halides consist of un-ionized compounds in which there is one non-bridging oxygen atom for each phosphorus atom and the phosphorus atoms are connected to each other through oxygen bridges, with halogen atoms filling the rest of the four coördination sites per phosphorus. Thiophosphoryl halides result when some or all of the oxygen atoms are replaced by sulfur. In the reorganizing chloride system, sulfur preferentially replaces the non-bridging oxygens, as exemplified by the new compound, $Cl_2(S)POP(S)Cl_2$. In the phosphoryl chloride system, the equilibrium proportions of orthophosphoryl chloride and end, middle and branching groups were found to change with the empirical composition approximately in the manner previously predicted for the ideally random reorganization of uncharged molecules. Partial separation of randomly reorganized phosphoryl chloride mixtures was effected by thermal diffusion and vacuum distillation.

The first two members of the series of phosphoryl chlorides are known. These are the orthophosphoryl chloride, $OPCl_3$ and the pyrophosphoryl chloride, $Cl_2(O)POP(O)Cl_2$. Pyrophosphoryl chloride has been made by reacting phosphorus trichloride with nitrogen dioxide[2,3] and also by reacting orthophosphoryl chloride with phosphorus pentoxide in sealed tubes.[4,5] From this latter reaction, Gustavson[4] assumed that metaphosphoryl chloride was formed as the main product whereas Huntly[5] envisaged a complicated mixture of homologs from which he was able to separate and identify the ortho- and pyrophosphoryl chlorides. The "dissociation" and "reversible reaction" discussed by Huntly correspond to the more sophisticated concept of reorganization employed here.

It has been suggested[6] that polyphosphoryl chlorides form by reacting orthophosphoryl chloride with limited amounts of water so that hydrogen chloride is liberated. This may well be the case (see Paper VI of this series[7]) but, as will be shown later in this article, the methods employed[8] did not demonstrate the existence of polyphosphoryl halides. Very shortly after the manuscript of this paper was completed in late 1958, an article[9] covering similar subject matter appeared in the literature with an oversimplified interpretation. Some of the errors appearing in Grunze's work[9] are mentioned in the body of this paper.

Experimental Techniques

This study consisted of mixing various proportions of an orthophosphoryl halide and/or an orthothiophosphoryl halide with various proportions of phosphorus pentoxide and/or phosphorus pentasulfide. The orthophosphoryl halides and orthothiophosphoryl halides were the same preparations described in Paper V of this series.[10] The phosphorus pentoxide was a Baker C. P. product and the phosphorus pentasulfide was a Monsanto commercial-grade material. Both of them were well crystallized and of high purity. The reactants were heated in rocking thick-walled, sealed Pyrex tubes at 230° for about 65 hr. Since the compositions of the products thus obtained varied very little from the

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[1] The subject matter of this paper has been presented at several scientific meetings—the 133rd A. C. S. meeting in San Francisco, and the 134th A. C. S. meeting in Chicago, and at a number of the A. C. S. Local Sections in the Midwest during the month of March, 1957.

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[3] R. Klement and K. Wolf, *Z. anorg. u. allgem. Chem.*, **282**, 149 (1955).

[4] G. Gustavson, *Ber.*, **4**, 853 (1871).

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