DERIVATIVES OF THE NITROGEN FLUORIDES

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CONTENTS

I. INTRODUCTION

The purpose of this article is to review some of the more recent preparative investigations in the field of nitrogen–fluorine chemistry. Previous reviews (20, 21, 108) have thoroughly dealt with the preparation of the basic nitrogen fluoride derivatives and their physical and spectral properties. The emphasis here will accordingly be on the preparative and derivative chemistry of the basic nitrogen fluorides: NF_3, N_2F_4, N_2F_2, and HNF_2.

Although the initial attempt to prepare a nitrogen fluoride was reported in 1903 (125), it was not until 1928 that Ruff first obtained nitrogen trifluoride (126). The preparation of several related materials such as HNF_2, H_2NF, and NF_2 was also claimed in subsequent studies; these were later shown to be in error. Fourteen years later, two other nitrogen fluorides were prepared and characterized. Haller isolated fluorine azide from the interaction of fluorine and hydrazoic acid (62) and obtained difluorodiazine from its decomposition.

Except for the studies by Bigelow of the action of fluorine on organic nitrogen compounds and a few other scattered reports, the field of nitrogen–fluorine chemistry received little attention after 1942. This changed in 1958 when the preparation of N_2F_4 was first achieved (24). Since that time there has been a rapid growth in the interest and effort in this area of chemistry.

II. NITROGEN–FLUORINE BOND FORMATION

The direct approach to the preparation of nitrogen fluorides involves the fluorination of a nitrogen-containing substrate. The major difficulty encountered is in controlling the reaction. Since large heats of reaction are involved in the formation of many metal or nonmetal fluorine bonds, extensive cleavage of the substrate often occurs. Therefore, the conditions under which the fluorination is performed appear to be critical in determining the course of reaction. Often the products obtained by fluorination of a single substrate can be widely varied depending on such factors as contact time, temperature, and the presence or absence of an inert heat exchanger, solvent, or catalyst. The most general methods of fluorination which produce nitrogen–fluorine bonds are electrochemical fluorination, high-temperature vapor-phase fluorination, and fluorination in a polar medium or in the presence of a catalyst.

A. ELECTROCHEMICAL FLUORINATION

The first successful preparation of a nitrogen fluoride was accomplished by electrolysis of molten ammonium

bifluoride using a copper cathode and carbon anode in a heated cell. In addition to nitrogen trifluoride smaller amounts of oxygen, ozone, nitrous oxide, hydrogen, and nitrogen are formed (125). A reinvestigation of this process resulted in the isolation of two additional nitrogen fluorides. Colburn (25) and his co-workers obtained both of the isomers of difluorodiazine in low yield (5–10%). Tetrafluorohydrazine can also be obtained in even smaller yields if a fluoride ion acceptor is added to the melt (19). Thus, electrolysis at 145° of a mixture of ammonium bifluoride and phosphorus pentachloride produces a mixture which consists of 92% NF_3, 7% N_2F_2 (both isomers), and 0.5% N_2F_4. Unfortunately this is hardly a practical method of preparation of tetrafluorohydrazine.

The electrochemical fluorination of organic nitrogen compounds, such as aniline, pyridine, or piperidine, in anhydrous hydrogen fluoride has also been reported to produce nitrogen trifluoride (131–133). Under the appropriate conditions it is possible to obtain several perfluorinated cyclic amines in addition to the NF_3. Unsaturated amines such as pyridine are converted to the corresponding saturated derivative (79).

$$C_5H_5N \xrightarrow[HF]{[F]} C_5F_{10}NF$$

Some perfluorobipiperdyl is also formed in the above fluorination. Morpholine can be converted to perfluoromorpholine in a similar manner (134).

B. VAPOR-PHASE FLUORINATION OF NITROGEN COMPOUNDS

The action of elemental fluorine on various organic and inorganic nitrogen-containing compounds has led to the preparation of numerous nitrogen fluoride derivatives. Fluorinations have been performed under a variety of conditions, but for the purpose of this review they will be divided into radical and polar fluorinations although the distinction between these two broad classes is not always clear. Reactions which are classified as radical fluorinations are usually carried out in the gas phase and in the absence of nucleophilic solvents or reagents. Since metal flow reactors have generally been used in this type of fluorination, it is difficult to assess the role of the always present metal fluorides in the reactor. Polar fluorinations are considered to be those which involve the action of fluorine on a substrate in a polar medium or, if the substrate itself is a nucleophile, in the presence of an excess of the substrate.

Most of the advances in the field of nitrogen in fluoride derivative chemistry before the preparation of tetrafluorohydrazine were accomplished by radical fluorination of organic nitrogen compounds. The general method that has been employed is to allow known amounts of the substrate to mix with fluorine in the vapor phase over a copper metal packing. Variation in the temperature, ratio of fluorine to substrate to diluent (usually helium or nitrogen), and the residence time in the reactor are parameters which can be controlled. Reactors of several different geometries have been used (*e. g.*, T-shaped, concentric ring, or straight-packed tube) since the design of the reactor is also found to be important.

The fluorination of simple amines such as CH_3NH_2, $(CH_3)_2NH$, and C_2H_4NH yield CF_3NF_2, $(CF_3)_2NF$, and $C_2F_5NF_2$ (51). Nitriles (4, 12) can also be converted to perfluoroalkyldifluoramines. For example, CF_3CN is converted to $C_2F_5NF_2$ and $C_2F_5N{=}NC_2F_5$. Similarly $C_3F_7NF_2$ and $C_3F_7N{=}NC_3F_7$ are obtained from the fluorination of C_2F_5CN. The azo compounds are formed in higher yield when the fluorination is carried out under mild conditions and the difluoramino compounds are formed under more vigorous fluorination conditions. The first preparation of a bisdifluoramino compound, $NF_2CF_2CF_2NF_2$, was achieved by vapor-phase fluorination of cyanogen (118). A more complete discussion of the preparation of perfluorocarbon nitrogen fluoride derivatives may be found in a recent review (67).

The reaction of fluorine with several of the nitrogen oxides produces nitrogen fluorides in high yield under the right conditions. Nitric oxide or nitrogen dioxide react rapidly with fluorine to form nitrosyl fluoride and nitryl fluoride in 90% yield (41). The kinetics of these two reactions have been studied (77, 116). The suggested mechanisms for the formation of nitrosyl fluoride and nitryl fluoride are quite similar except that fluorescence is observed in the first case.

$$F_2 + \cdot NO \xrightarrow{k_1} NOF + F\cdot \quad \text{(slow)}$$

$$F\cdot + \cdot NO \longrightarrow NOF^* \longrightarrow NOF + h\nu$$

$$NOF^* \xrightarrow{M} NOF$$

$$F_2 + N_2O \xrightarrow{k_1} NO_2F + F\cdot \quad \text{(slow)}$$

$$NO_2 + F\cdot \xrightarrow{M} NO_2F \quad \text{(fast)}$$

An interesting preparation of nitrosyl fluoride which utilizes cesium fluoride as the fluorinating agent has just been reported (117).

$$N_2O_4 + CsF \longrightarrow NOF + CsNO_3$$

This reaction is analogous to the reaction between an alkali metal fluoride and dinitrogen pentoxide (107). Both reactions are most likely ionic in nature.

$$N_2O_5 + MF \longrightarrow NO_2F + MNO_3$$

Recently the fluorination of nitrous oxide has been reported (98). The reaction is carried out in the gas phase at high temperature.

$$N_2O + 2F_2 \longrightarrow NF_3 + NOF$$

The best yield (~60%) is obtained at 700° and a N_2O/F_2 ratio of 1:1.5. Small amounts of difluorodiazine and nitryl fluoride are also formed.

Some of the physical properties of nitrosyl fluoride and nitryl fluoride are summarized in Table I.

TABLE I

Property	NOF	NO_2F
Bp, °C	−132.5	−166
Mp, °C	−59.9	−72.5
Critical temp, °C		76.3
Density (temp, °C)	1.326 (−59.9)	1.571 (−101)
Trouton constant	21.3	21.2
Dipole moment	1.81	
ΔH_f, kcal/mole	−15.8	26
ΔH_v, kcal/mole	4.6	4.3

C. FLUORINATION IN A POLAR SOLVENT

A recent important development in the preparation of nitrogen fluoride derivatives is the use of a polar solvent as the fluorination medium for organic nitrogen compounds. Several solvents have been employed, but most of the reported fluorinations have been carried out in water. Urea (56) or sulfamide (141) can be converted to the corresponding N,N-difluoro derivatives by the passage of dilute fluorine through a cold aqueous solution of the substrate.

$$CO(NH_2)_2 + 2F_2 \xrightarrow{H_2O} NH_2CONF_2 + 2HF$$

$$SO_2(NH_2)_2 + 2F_2 \xrightarrow{H_2O} NH_2SO_2NF_2 + 2HF$$

The N,N-difluorourea is isolated by extraction of the aqueous solution with methylene chloride and purified by sublimation. The sulfamide derivative cannot be isolated since it decomposes upon removal of the solvent. However, it can be extracted into ether, and the addition of triphenylphosphine oxide to the extract results in the isolation of the complex $H_2NSO_2NF_2{\cdot}(C_6H_5)_3P{=}O$.

The fluorination of N,N-dimethylsulfamide does not proceed in an analogous manner since N,N-difluoro-N′,N′-dimethylsulfamide is not formed. Instead cleavage of the S–N bond occurs and dimethylfluoramine is produced (142).

$$(CH_3)_2NSO_2NH_2 + F_2 \xrightarrow{H_2O} (CH_3)_2NF + FSO_2NH_2$$

Carbamates also undergo fluorination in aqueous media (7, 8, 57). The difluoramino derivative cannot be isolated in this reaction.

$$HNF_2COR + F_2 \longrightarrow HNFCOR + HF$$

However, in a nonaqueous polar solvent such as acetonitrile or dimethylformamide the N,N-difluorocarbamate derivatives are obtained (57). They hydrolyze rapidly in acidic aqueous solution to HNF_2 and carbon dioxide. The fluorination of N-alkyl-substituted ureas and carbamates produces the alkyldifluoramines in addition to the N-fluoro derivative of the substrate.

$$CH_3NHCNHCH_3 \xrightarrow[H_2O]{F_2} CH_3NF_2 + CH_3NFCNFCH_3$$

5% 27%

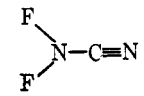
$$CH_3NHCOC_2H_5 \xrightarrow[H_2O]{F_2} CH_3NFCOC_2H_5 + CH_3NF_2$$

trace 60%

The fluorination of a phosphate-buffered aqueous solution of cyanamide produces N,N-difluorocyanamide in about 20% yield (102).

$$H_2NCN + 2F_2 \xrightarrow{H_2O} F_2NCN + 2HF$$

The structure of this material is believed to be



and not the isomeric carbodiimide structure, FN=C=NF, because of the presence of a strong infrared band in the C≡N stretching region. This material undergoes an interesting rearrangement in the presence of CsF to form difluorodiazirine (102).

$$F_2NC{\equiv}N \xrightarrow[25°]{F^-} F_2C\!\!<\!\!\begin{matrix}N\\ \|\\ N\end{matrix}$$

D. SALT AND CATALYTIC FLUORINATION REACTIONS

The heterogeneous fluorination of inorganic salts containing anions such as azide or nitrite has been successfully used by several workers to prepare nitrogen fluoride derivatives. This method can perhaps be considered as a polar fluorination although little is known about the mechanism of the reaction. Thus the fluorination of sodium nitrite can be used to prepare nitryl fluoride (6). The reaction of sodium azide with fluorine produces both isomers of difluorodiazine in good yield. This reaction is believed to proceed *via*

$$2NaN_3 + 2F_2 \longrightarrow N_2F_2 + N_2$$

the initial formation of fluorine azide which is subsequently decomposed to difluorodiazine by passage of the gases exiting from the reactor through a heated nickel tube (119). Several interesting variations of the fluorination of sodium azide have been reported. For example, if sodium chloride is mixed with the sodium azide, chlorodifluoramine is obtained upon fluorination (5). Some chlorine azide is also produced, but, by maintaining the temperature of the reactor below 0°, its formation may be suppressed. If chlorine monofluoride is used instead of fluorine, dichlorofluoramine is obtained (139). In both of these reactions chloronitrene derived from the decomposition of chlorine azide is believed to be the intermediate which reacts with the halogenating agent to give the final product.

$$ClN_3 \longrightarrow ClN + N_2$$
$$ClN + F_2 \longrightarrow F_2NCl$$
$$ClN + FCl \longrightarrow Cl_2NF$$

Although the fluorination of potassium cyanide gives only low yields of trifluoromethyldifluoramine, this material can be obtained in an almost quantitative yield by the fluorination of potassium thiocyanate at −78°.

$$KSCN + 6F_2 \longrightarrow SF_6 + CF_3NF_2 + KF$$

No other carbon- or sulfur-containing species were found even when a deficiency of fluorine was employed (124).

Several examples of the catalytic fluorination of nitrogen compounds have been reported (124). For example, the reaction between CF_3CN or C_2F_5CN and fluorine in the presence of activated cesium fluoride is almost quantitative at −78°. Some variations in the conversion occur which seem to depend on the history of the cesium fluoride used in the reaction.

$$R_fCN + 2F_2 \xrightarrow[-78°]{CsF} R_fCF_2NF_2$$

In the absence of cesium fluoride, the nitrile can be recovered unchanged. In a similar fashion the imine, $(CF_3)_2C{=}NH$, is converted to $(CF_3)_2CFNF_2$ by treatment with 2 equiv of fluorine in the presence of cesium fluoride (124). Two other examples of this type of fluorination are known. These are shown below.

$$SF_2{=}NR_f + 2F_2 \xrightarrow[-25°]{CsF} \overset{F}{SF_5}NR_f \quad (96)$$

$$R_f = CF_3 \text{ or } C_2F_5$$

$$O{=}SF_2{=}NCOF + F_2 \xrightarrow[-20°]{CsF} O{=}SF_2{=}NF + COF_2 \quad (122)$$

Another method of fluorination which may be closely related to the catalytic fluorination procedure has been developed. The basis of this method involves the use of an alkali metal fluoride as a diluent and perhaps as a catalyst. Thus, the direct fluorination of a mixture of aminoiminomethanesulfinic acid and sodium fluoride at 0° produces bis(difluoramino)difluoromethane (81).

$$H_2N\overset{\overset{NH}{\|}}{C}SO_2H + 6F_2 \longrightarrow F_2NCF_2NF_2 + SO_2F_2 + 4HF$$

In addition to the above products, small amounts of FSO_2NF_2 were also found. This method is capable of extension to other polar materials such as urea, thiourea, melamine, and guanidine (32). In the last example fluorination of guanidine monohydrofluoride mixed with sodium fluoride at 0° using excess fluorine results in the formation of perfluoroguanidine, $(NF_2)_2C{=}NF$. Perfluoroguanidine is reported to be very explosive and highly reactive. It decomposes according to the equation

$$(F_2N)_2C{=}NF \longrightarrow CF_4 + 1.5N_2 + 0.5F_2$$

III. The Difluoramino Group

Compounds containing the difluoramino group, $-NF_2$, constitute a majority of the known nitrogen fluoride derivatives. The method of synthesis of compounds in this class is also more varied than for other classes of functional groups. The preparation of several members of this class by the fluorination of nitriles, amines, and carbamates has already been discussed. Others may be obtained from thermal or photolytic reactions of tetrafluorohydrazine with the appropriate substrate or by reaction of difluoramine or chlorodifluoramine. These will be considered in this section.

A. Tetrafluorohydrazine, Difluoramine, and Chlorodifluoramine

There are two basic approaches available for the preparation of tetrafluorohydrazine. They are the oxidation of difluoramine and the abstraction of a fluorine radical from nitrogen trifluoride. The latter method was employed in the original preparation of tetrafluorohydrazine. Copper metal was used as a fluorine acceptor in this study, but several other materials have since been shown to be suitable. Thus, the passage of nitrogen trifluoride over a fluidized carbon bed at 440° results in a 75% conversion of the nitrogen trifluoride to tetrafluorohydrazine. The yield is approximately 75% also (135). The disadvantage of this method is that one of the principle impurities, hexafluoroethane, is difficult to separate from the tetrafluorohydrazine. Alternately mercury either in an electric discharge (45) or at 325° (36) may be used as a fluorine acceptor. The yields of tetrafluorohydrazine are 65 and 55%, respectively. The conversion is very low in the first case and about 60% in the second so that the thermal method is preferable. A homogeneous gas-phase reaction employing nitric oxide and nitrogen trifluoride may also be used to prepare tetrafluorohydrazine.

$$NO + NF_3 \longrightarrow NOF + 0.5N_2F_4$$

The best conversion, about 30%, is obtained at approximately 600° (99).

One of the factors that make this type of synthesis of tetrafluorohydrazine feasible is the difference in the consecutive NF bond energies in nitrogen trifluoride. This difference became apparent as a result of several studies. Tetrafluorohydrazine was shown to be in equilibrium with the difluoramino free radical. An average value of 20 ±1 kcal/mole for the enthalpy of the dissociation was obtained by four independent methods (34, 66, 72, 114). This value together with the heat of formation of tetrafluorohydrazine permits the calculation of the heat of formation of the NF_2 radical. The difference in the heats of formation of nitrogen tri-

$$N_2F_4 \rightleftharpoons 2NF_2$$

fluoride and the NF_2 radical gives the first NF bond energy in nitrogen trifluoride as 57 kcal/mole. Since the average bond energy of nitrogen trifluoride is 66 kcal/mole (2), the two remaining bonds must average 71 kcal/mole. This difference in bond energies means that the removal of fluorine from nitrogen trifluoride will be stepwise and that the first step is most easily accomplished. This situation is just the opposite than that found for ammonia in which the bond energy required to break the first N–H bond is larger than the average energy needed to remove the next hydrogen. The correlation between the observed NF and NH bond distances and the calculated bond energies is quite good (Table II).

TABLE II

Bond	Energy, kcal/mole	Bond distance, A
NF_2–F	57	1.371
NF–F	71	1.365 (13)
F_2N–NF_2	20	1.480 (13)
NH_2–H	104	1.008
NH–H	88	1.024
H_2N–NH_2	60	1.450

The alternate method of preparation of tetrafluorohydrazine involves the oxidation of difluoramine in solution (100, 101). Although several oxidizing agents may be used, the best results are obtained by employing an acidified solution (pH 1 to 2) of ferric chloride. The conversion of difluoramine to tetrafluorohydrazine is practically quantitative and the product is obtained in high purity. The difficulties in the purification of the crude tetrafluorohydrazine present in the other preparations are not encountered in this synthesis.

Various physical properties of the NF_2 radical have been determined. Studies on the infrared spectrum (63, 64, 73), the ultraviolet spectrum (52, 72), the mass spectrum (23, 91), and the epr spectrum (22, 40, 42, 64, 78), as well as the group electronegativity (39), of the NF_2 radical, have been determined. Some of the physical properties of tetrafluorohydrazine are presented in Table III.

TABLE III

Property	N_2F_4	HNF_2	$ClNF_2$
Bp, °C	−73	−23.6	−67
Mp, °C	...	−116	...
ΔH_{vap}, cal/mole	2769	5940	4350
Trouton constant	19.21	23.7	21.0
Critical temp, °C	−39.3	130	...
ΔH_f, kcal/mole	−29.7	...	...

Difluoramine is another basic nitrogen fluoride derivative which contains a NF_2 group. Although its preparation was first claimed by Ruff and Staub (127), a comparison of the reported physical properties with those found by Kennedy and Colburn (80) indicated that the earlier work was in error. Difluoramine was found by the latter workers as a minor product from the thermal reaction of elemental arsenic with nitrogen trifluoride. Arsine, apparently formed from arsenic and the moisture present in the system, was responsible for its formation. The yield of difluoramine is greatly increased by the substitution of thiophenol for arsine (50).

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

Several other methods of producing difluoramine are also known (84, 86). The aqueous fluorination procedure has led to the development of very simple preparations. Aqueous solutions of N,N-difluorourea (58) or N,N-difluorosulfamide undergo hydrolysis in acidic media to form difluoramine in good yield. It is not necessary to isolate the urea or sulfamide derivative since difluoramine is liberated from the crude reaction mixture by allowing it to stand at ambient temperature. A nonoxidizing acid such as sulfuric or phosphoric acid should be used to acidify the reaction mixture; otherwise, some tetrafluorohydrazine may be obtained. Some of the physical properties of difluoramine are presented in Table III.

Although chlorodifluoramine was first prepared by the reaction of difluoramine with boron trichloride (110), more convenient preparative methods are now available. The reaction between fluorine and a mixture of sodium azide and sodium chloride was mentioned in the preceding section. Although chlorine reacts with tetrafluorohydrazine to produce chlorodifluoramine in low conversion (see discussion later), its reaction with difluoramine in the presence of an alkali metal fluoride gives a good yield of chlorodifluoramine (43).

$$HNF_2 + Cl_2 + MF \longrightarrow ClNF_2 + MHClF$$

Difluoramine was also found to react with hydrogen chloride in the gas phase to produce chlorodifluoramine and ammonium bifluoride although the yields were reported to be erratic (85). Hypochlorous acid reacts with a solution of N,N-difluorosulfamide to form chlorodifluoramine in moderate yield. It is not clear whether difluoramine is involved in the reaction (141). Some of the physical properties of chlorodifluoramine are included in Table III.

Chlorodifluoramine has moderate thermal stability in Pyrex but is rapidly decomposed by ultraviolet irradiation. The decomposition is reversible and an equilibrium mixture is formed after prolonged irradiation.

$$2NF_2Cl \rightleftharpoons N_2F_4 + Cl_2$$

A determination of the equilibrium constant as a function of temperature gave a heat of the reaction of −12 kcal/mole (109). The photochemical decomposition of chlorodifluoramine was found to be autocatalytic. Chlorine is responsible for this behavior since the addition of small amounts of chlorine to chlorodifluoramine

greatly accelerates the rate of its photolytic decomposition, whereas the addition of tetrafluorohydrazine has no effect on the rate. This suggests the following mechanism.

$$NF_2Cl \overset{h\nu}{\rightleftharpoons} NF_2\cdot + Cl\cdot$$
$$NF_2Cl + Cl\cdot \longrightarrow Cl_2 + NF_2\cdot$$
$$Cl_2 \overset{h\nu}{\longrightarrow} 2Cl\cdot$$
$$2NF_2\cdot \rightleftharpoons N_2F_4$$

B. COUPLING REACTIONS OF THE NF_2 RADICAL

Because of the facile equilibrium between tetrafluorohydrazine and the difluoramino radical most of the reported reactions of tetrafluorohydrazine are probably those of the NF_2 radical. Therefore, reactions of tetrafluorohydrazine appear to be typical free-radical reactions such as coupling, abstraction, or addition. Only two reversible coupling reactions have been studied in detail: the dimerization of the NF_2 radical and the coupling of the NF_2 radical with nitric oxide to form the deeply colored nitrosodifluoramine (74). This equilibrium system was studied spectroscopically.

$$2NO + N_2F_4 \rightleftharpoons 2NONF_2 \rightleftharpoons 2NO + 2NF_2$$

The dependence of the absorption at 5500 A on temperature and pressure is first order with respect to the tetrafluorohydrazine concentration (75). A value of 20.4 ± 1.5 kcal/mole is obtained for the heat of formation of nitrosodifluoramine, and this in turn leads to a heat of dissociation of 10.1 ± 1.5 kcal/mole.

The difluoramino radical couples with other free radicals which have been generated in its presence. It adds to the relatively stable fluorosulfate radical (obtained from the dissociation of peroxydisulfuryl difluoride at ambient temperature) to form FSO_2ONF_2 (94). In most cases, however, activation of the system is necessary in order to produce the other radical. This has been accomplished either thermally, photolytically, or by a selective fluorination technique.

The thermal decomposition of azoisobutane or azoisobutyronitrile in the presence of tetrafluorohydrazine to form *t*-butyldifluoramine or $(CH_3)_2C(CN)NF_2$ are examples of thermal activation (112). Another reaction which is probably similar is the thermal reaction of disulfur decafluoride with tetrafluorohydrazine. It has been suggested that the primary step in the thermal decomposition of disulfur decafluoride involves the cleavage of the sulfur–sulfur bond to produce two SF_5 radicals. When the decomposition is carried out in the presence of tetrafluorohydrazine, SF_5NF_2 is obtained (17, 138).

Photolytic activation may also be used to produce radicals which can then react with the NF_2 radical. Irradiation of mixtures of trifluoromethyl disulfide and tetrafluorohydrazine produces CF_3SNF_2 (137). Since both trifluoromethyl disulfide and tetrafluorohydrazine cleave to give CF_3S (14) and NF_2 radicals, it is likely that the reaction proceeds by recombination of these radicals. Other examples include the photolysis of mixtures of methyl or ethyl iodide and tetrafluorohydrazine which produce the corresponding alkyldifluoramines (46) and the formation of N,N-difluoramides by irradiation of diketones in the presence of tetrafluorohydrazine at ambient temperature (112).

$$RC(=O)-C(=O)R \xrightarrow{h\nu} 2RC(=O)\cdot$$
$$RC(=O)\cdot + NF_2\cdot \longrightarrow RC(=O)NF_2$$
$$R = H,\ CH_3,\ \text{or}\ C_6H_5CH_2$$

The use of photolytically excited benzophenone to abstract hydrogen from a series of aliphatic ethers results in the preparation of several α-difluoramino ethers if tetrafluorohydrazine is present (31).

$$C_6H_5C(=O)C_6H_5 \xrightarrow{h\nu} C_6H_5C(\cdot O)C_6H_5 \xrightarrow{RH}$$
$$R\cdot + C_6H_5C(H)(O)C_6H_5 \xrightarrow{\cdot NF_2} RNF_2$$

In all of the above photolytic reactions only the substrate is activated by light absorption and the NF_2 radical is not excited.

An alternate method of producing radicals in the presence of tetrafluorohydrazine is by selective fluorination of the substrate. The generalized reaction scheme is

$$A + [F] \longrightarrow AF\cdot$$
$$AF\cdot + \cdot NF_2 \longrightarrow FANF_2$$

The major difficulty in this approach is in achieving controlled fluorination of the substrate so that large amounts of AF_2 are not formed. One of the fluorinating agents that has been successfully used is difluorodiazine (93). The fluorination is achieved by thermal activation.

$$0.5N_2F_2 + A \longrightarrow FA\cdot + 0.5N_2$$
$$AF\cdot + \cdot NF_2 \longrightarrow FANF_2$$
$$A = SO_2 \text{ or } SF_4$$

The yields of FSO_2NF_2 and SF_5NF_2 are practically quantitative. Nitrogen trifluoride has also been used as a fluorinating agent and simultaneously as a source of the NF_2 radical. Thus, if a mixture of perfluoropropene and nitrogen trifluoride is passed over a bed of cesium fluoride at 320°, substantial amounts of $(CF_3)_2CFNF_2$ are formed along with $(CF_3)_2C{=}NF$. The mechanism of this reaction is not known, but the scheme below was proposed (35).

$$CF_3CF{=}CF_2 + NF_3 \longrightarrow (CF_3)_2CF\cdot + NF_2\cdot$$
$$(CF_3)_2CF\cdot + \cdot NF_2 \longrightarrow (CF_3)_2CFNF_2$$
$$2(CF_3)_2CF\cdot \longrightarrow (CF_3)_2CFCF(CF_3)_2$$
$$(CF_3)_2CFNF_2 \xrightarrow[-2F]{\text{metal}} (CF_3)_2C{=}NF$$

The relatively large amount of perfluoroalkane formed is probably a result of the lack of an efficient source of NF_2 radicals.

The NF_2 radical may also be used as a fluorinating agent if it is photolytically activated with light of a wavelength of 2600 A. This activation results in decomposition of the radical to nitrogen trifluoride and difluorodiazine (16).

$$NF_2 \xrightarrow{h\nu} NF_2^* \longrightarrow F\cdot + NF$$
$$2NF \longrightarrow N_2F_2$$
$$F\cdot + \cdot NF_2 \longrightarrow NF_3$$

The exact mode of the formation of the difluorodiazine is not known and it may not involve direct coupling of the N-fluoronitrene as shown above. When the photolytic decomposition of the NF_2 radical is carried out in the presence of a substrate capable of reacting with the fluorine radicals produced, then nitrogen trifluoride is not formed. The general reaction which occurs under these circumstances can be written as

$$NF_2 \xrightarrow{h\nu} NF_2^* \longrightarrow NF + F\cdot$$
$$A + F\cdot \longrightarrow AF\cdot$$
$$AF\cdot + NF_2\cdot \longrightarrow FANF_2\cdot$$

A variety of different substrates can be employed. Thus, sulfur dioxide and sulfur trioxide are converted to FSO_2NF_2 and FSO_3NF_2, respectively (94). Sulfur tetrafluoride and tetrafluorohydrazine react under these conditions to form SF_5NF_2. If trifluoroiodomethane is present in this system, then $CF_3SF_4NF_2$ is also obtained (90). Similarly carbon monoxide is converted to $FCONF_2$ under similar conditions (48). This latter compound is of some interest since it is absorbed by alkali metal fluorides to give an unknown species which may be the anion, $NF_2CF_2O^-$. Decomposition of the adduct formed between $FCONF_2$ and potassium fluoride at 95° results in the formation of perfluorourea (49). Photolysis of mixtures of methane and tetrafluorohydrazine appears to be more complicated. Apparently hydrogen abstraction by the fluorine radical occurs and the resulting CH_3 radical couples with the NF_2 radical to give methyldifluoramine (15).

$$CH_4 + F\cdot \longrightarrow CH_3\cdot + HF$$
$$CH_3\cdot + \cdot NF_2 \longrightarrow CH_3NF_2$$

Even when *trans*-2-butene is employed, hydrogen abstraction is also observed and $CH_3CH{=}CHCH_2NF_2$ is formed. Concurrently the addition of the elements of nitrogen trifluoride to the double bond occurs to approximately the same extent (15).

$$CH_3CH{=}CHCH_3 + F\cdot \longrightarrow CH_3CHFCHCH_3$$
$$CH_3CHFCHCH_3 + NF_2\cdot \longrightarrow CH_3CHFCH(NF_2)CH_3$$

These reactions are believed to be initiated by fluorine radicals rather than the activated NF_2 radical (NF_2^* in the decomposition scheme) since no bisdifluoramino products are formed. Support for the proposed photolytic decomposition scheme has been obtained from matrix infrared studies which showed the formation of N-fluoronitrene during photolysis of tetrafluorohydrazine (26).

C. ABSTRACTION REACTIONS OF THE NF_2 RADICAL

The NF_2 radical is capable of abstracting hydrogen atoms from several types of compounds. The previously discussed reaction of tetrafluorohydrazine with arsine or thiophenol is undoubtedly an example of this type of reaction. Several other examples have also been reported. Aldehydes may be converted to N,N-difluoramides by treatment with tetrafluorohydrazine (112).

$$RC(=O)-H + NF_2\cdot \longrightarrow RC(=O)\cdot + HNF_2$$
$$RC(=O)\cdot + NF_2\cdot \longrightarrow RC(=O)-NF_2$$

More recently Trotman-Dickenson and his co-workers have found that when a mixture of tetrafluorohydrazine and alkane is heated, the alkane is consumed at a rate which is consistent with the following scheme (59).

$$RH + \cdot NF_2 \longrightarrow R\cdot + HNF_2$$
$$R\cdot + NF_2\cdot \longrightarrow RNF_2$$

Acetone appears to behave in a similar manner at elevated temperatures although the products were not isolated (60). An almost certain example of the abstraction of a fluorine atom by a NF_2 radical is the reaction of fluorine with tetrafluorohydrazine since the kinetics of this reaction are best rationalized by the scheme (86)

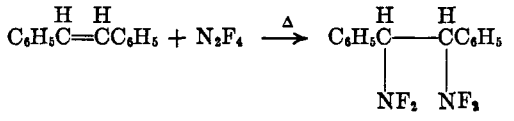
$$N_2F_4 \rightleftharpoons 2NF_2\cdot$$
$$F_2 + NF_2\cdot \longrightarrow NF_3 + F\cdot$$
$$F\cdot + NF_2\cdot + M \longrightarrow NF_3 + M$$

D. ADDITION REACTIONS OF THE NF_2 RADICAL

The addition of the NF_2 radical to olefins and acetylenes appears to be a general process (111). A large variety of olefins has been employed including several

$$>C{=}C< \; + \; N_2F_4 \longrightarrow >C(NF_2)-C(NF_2)<$$

olefinic steroids (88). Some of the steroid adducts that have been prepared are 3β-acetoxy(5,6-bisdifluoramino)cholestane, 5,6-bisdifluoraminocholestan-3β-ol, and 5,6-bisdifluoraminocholestan-3-one. Another example includes the addition of tetrafluorohydrazine to *trans*-stilbene which produces a mixture of the *meso* and *dl* isomers. The former can be isolated in 37% yield while the latter is obtained in 50% yield (76).



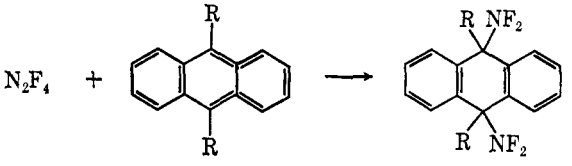
The observed lack of stereospecificity is expected for radical additions to *trans*-stilbene.

The kinetics of the addition of tetrafluorohydrazine to simpler olefins has been studied in detail (33). No simple relationship was found between the rate and the concentration of either the NF_2 radical or tetrafluorohydrazine. However, the data are consistent with the following mechanism (O = olefin).

$$N_2F_4 \rightleftharpoons 2NF_2$$
$$O + NF_2\cdot \longrightarrow \cdot ONF_2{}^*$$
$$\cdot ONF_2{}^* + M \longrightarrow \cdot O + \cdot NF_2$$
$$\cdot ONF_2{}^* + M \longrightarrow \cdot ONF_2 + M$$
$$\cdot ONF_2 \longrightarrow O + NF_2$$
$$\cdot ONF_2 + NF_2 \longrightarrow O(NF_2)_2$$

The energy of activation for the first step (*i. e.*, the formation of $\cdot ONF_2{}^*$) varies as the ionization potential of the olefin changes and is in the range of 10 to 15 kcal/mole for the olefins studied. This demonstrates the electrophilic nature of the NF_2 radical.

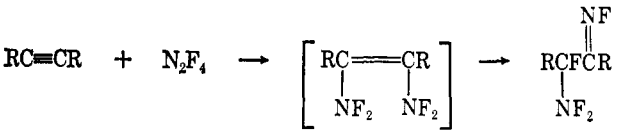
Tetrafluorohydrazine also adds readily to polycyclic aromatic hydrocarbons such as anthracene or substituted anthracenes at moderate temperatures (50–100°) (87).



R = H, Cl, F, Br

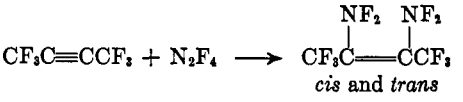
Addition occurs at the 9 and 10 positions, and both the *cis* and *trans* isomers can be isolated. Reversible dissociation of these adducts is possible if hydrogen is not present in the 9 and 10 positions. The observed addition rate is first order in the concentration of both the aromatic hydrocarbon and tetrafluorohydrazine (18). Although several mechanisms are possible, a choice cannot be made between a radical addition mechanism or an electrophilic addition mechanism on the basis of the available data.

The reaction of tetrafluorohydrazine with acetylenes is more complicated than that with olefins, although the over-all reaction appears to be similar (113, 128). However, the vinylbisdifluoramine intermediate is apparently not stable in most cases and undergoes rearrangement. The general reaction observed for normal acetylenes is

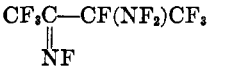


R = C_6H_5, $COOCH_3$, CN, and CH_3

The reaction of hexafluoro-2-butyne with tetrafluorohydrazine gives strong support for this reaction scheme. If the reaction is conducted at 170° the intermediate vinyldifluoramine derivative is isolated in 90% yield as a 40:80 mixture of the *cis* and *trans* isomers (128).

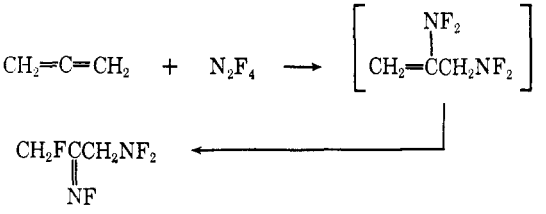


If, however, the reaction is performed at 195° the major product isolated is the rearranged compound

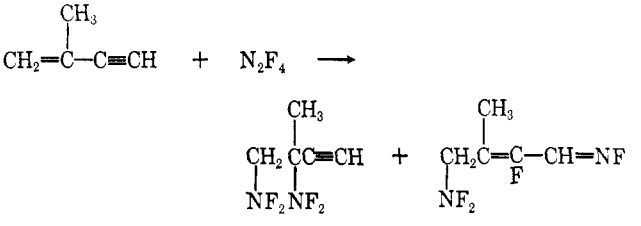


The bisdifluoramino vinyl derivative undergoes rearrangement on heating to 195° to give the N-fluorimino derivative in high yield.

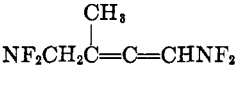
A few special cases are worth mentioning. For example, allene appears to undergo a rearrangement similar to that described above for the acetylenic derivatives when treated with tetrafluorohydrazine. The reaction is best described by the following equations



Isopropenylacetylene and N_2F_4 give a more complex mixture (113).



The latter product is believed to arise from the rearrangement of the 1,4 addition product



E. REACTIONS OF DIFLUORAMINE AND CHLORODIFLUORAMINE

The use of either difluoramine or chlorodifluoramine to introduce NF_2 groups into molecules has not been well documented. Several examples have already been

discussed (*e.g.*, the $HNF_2 \rightarrow N_2F_4$ and the $HNF_2 \rightarrow ClNF_2$ conversions). Recently the reaction of difluoramine with several organic carbonium ion precursors was investigated (55). For example, the reaction of difluoramine with trityl bromide in liquid sulfur dioxide produces trityldifluoramine in good yield. This system appears to be reversible since trityldifluoramine can be converted to difluoramine by treatment with concentrated sulfuric acid (54). Several other examples are shown below

$$(CH_3)_2C{=}CH_2 + HNF_2 \xrightarrow{H_2SO_4} (CH_3)_3CNF_2$$

$$C_6H_5CH_2OH + HNF_2 \xrightarrow[SO_2]{CF_3COOH} (C_6H_5)_2CH_2NF_2 + H_2O$$

$$C_6H_5CCl_3 + HNF_2 \xrightarrow{CF_3COOH} C_6H_5CCl_2NF_2 + HCl$$

$$CH_3C(OCH_3)_3 + HNF_2 \xrightarrow{neat} CH_3C(OCH_3)_2NF_2 + CH_3OH$$

All of these reactions are believed to involve the formation of an intermediate carbonium ion species which subsequently reacts with the difluoramine.

Chlorodifluoramine was found to react rapidly and quantitatively with mercury to form mercurous chloride and tetrafluorohydrazine (109). Organomercury compounds also react with cholordifluoramine according to the equation

$$3ClNF_2 + 2R_2Hg \longrightarrow N_2F_4 + RCl + RNF_2 + 2RHgCl$$
$$R = CH_3,\ C_2H_5,\ \text{and}\ n\text{-}C_4H_9$$

When either divinylmercury or diphenylmercury is employed only the alkyl (aryl) chloride is formed (109). The reaction of chlorodifluoramine with olefins, when carried out at 120°, produces all three of the possible products. However, at lower temperatures only the dichloro and the chlorodifluoramino products are observed. This is believed to be attributable to the high (by comparison with chlorine radicals) activation energy for the reaction (109)

$$NF_2Cl + CH_2{=}CH_2 \xrightarrow{120°} ClCH_2CH_2Cl + ClCH_2CH_2NF_2 + NF_2CH_2CH_2NF_2$$

$$NF_2{\cdot} + CH_2{=}CH_2 \longrightarrow NF_2CH_2CH_2$$

IV. Other Nitrogen Fluoride Functional Groups

In addition to the large class of compounds which contain the NF_2 group, numerous examples of compounds are known which contain other types of functional nitrogen fluoride groups. These have been classified according to the type of group that is present. The groups to be considered in this section are: the fluorimino group, =NF; the secondary fluoramine group, >NF; the N′-fluorodiimide N-oxide group

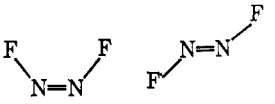
$$\begin{matrix} O \\ \uparrow \\ -N{=}NF \end{matrix}$$

and the oxydifluoramino group, $-ONF_2$.

A. THE FLUORIMINO GROUP

Difluorodiazine may perhaps be considered the parent compound in this class. It was first prepared in 1942 by the thermal decomposition of fluorine azide (6), but because of the dangerous nature of fluorine azide little further work on the chemistry of difluorodiazine has been reported until recent years. In 1959, Colburn and co-workers found that both isomers of difluorodiazine can be produced by electrolysis of molten ammonium fluoride. This observation was also confirmed by Schmeisser (129). The two isomers of difluorodiazine can be separated by low-temperature distillation.

The structure of these two isomers has been the subject of several investigations. The bulk of the available evidence (*e.g.*, mass spectrometric, electron diffraction (13), double nuclear magnetic resonance (106), and microwave spectral studies (82)), indicate that the two isolated forms are the *cis* and *trans* isomers as shown below.



The N–F and N–N bond lengths in the *cis* isomer are 1.409 and 1.209 A. The N–F bond length in the *trans* isomer is slightly shorter (1.398 A) than that in the *cis* isomer while the N–N bond length (1.224 A) is longer (13). It is interesting that the two fluorines in the *cis* isomer are not in a plane; presumably, this is due to steric or electronic repulsion. Some of the physical properties of the isomers are presented in Table IV.

TABLE IV

Property	*cis*-N_2F_2	*trans*-N_2F_2
Bp, °C	−105.7	−111.4
ΔH_{vap}, cal/mole	3670	3400
Critical temp, °C	−1	−13
Mp, °C	< −195	−172

Isomerization of either of the two isomers of difluorodiazine to an equilibrium mixture has been reported to occur in the temperature range of 70–90° in the presence of activated stainless steel (69, 92). The role of the activated stainless steel is not exactly known but no isomerization occurs in quartz reactors. It is possible that the isomerization is catalyzed by metal fluorides. The equilibrium concentration of the *cis* isomer is approximately 90% in the mixture. From the measured values of the heats of formation of the *cis* and *trans* isomers (*e.g.*, 16.4 and 19.4 kcal/mole, respectively) a heat of isomerization of 3 kcal/mole is obtained (1). Although the *cis* isomer is more stable thermodynamically, it is also more reactive than the *trans* isomer toward glass, mercury, and arsenic(V) fluoride. Its thermodynamic stability is unusual in view of its strained configuration.

Investigation of the chemical reactivity of difluorodiazine has been hindered by the lack of a convenient synthesis for this material. Recently several new syntheses have been developed which utilize other nitrogen fluoride derivatives. Although the reaction of nitrogen trifluoride with mercury vapor in a discharge produces difluorodiazine in about 15% yield as well as tetrafluorohydrazine (45), the low conversion and low pressures involved make the production of significant amounts of difluorodiazine by this method a time-consuming process. A more practical synthesis is based on the dehydrofluorination of difluoramine. This may be accomplished by using potassium fluoride, either in the dry state or in a concentrated aqueous solution at pH 8.6. Both isomers of difluorodiazine are obtained in an over-all yield of 75% (83).

$$2KF + 2HNF_2 \longrightarrow N_2F_2 + 2KHF_2$$

Yet another synthesis involves the treatment of a solution of N,N-difluorourea with a concentrated potassium hydroxide solution. Difluorodiazine is produced in about 35% yield along with lesser amounts (10–15%) of tetrafluorohydrazine (71). The concentrations of the solutions, the temperature, and the mode of addition are factors in determining the yield. In general, higher yields are obtained at low temperatures and high concentrations.

Little data are available concerning the mechanism of these reactions although the latter reaction was shown to be intermolecular by N^{15}-exchange studies. Formation of difluorodiazine is postulated to have occurred *via* coupling of two N-fluoronitrenes. Support for this type of coupling has been obtained from low-temperature studies on fluorine azide. The photolytic decomposition of fluorine azide in an argon matrix at 4°K produces N-fluoronitrene which can be identified by infrared spectroscopy (103). Warming the matrix allows the N-fluoronitrene to diffuse and infrared bands attributed to this species disappear. New bands due to *cis*-difluorodiazine and possibly the *trans* isomer appear. However, the possibility of a reaction between the N-fluoronitrene and fluorine azide to form difluorodiazine and nitrogen cannot be ruled out.

Two preparations of the pure *trans* isomer of difluorodiazine have been reported. The decomposition of the salt $N_2F_3Sb_2F_{11}$ (see discussion later) with either iodine, ferrocene, or nitrosyl chloride produces *trans*-difluorodiazine in 90% yield. The reaction can be carried out either in arsenic trifluoride or in liquid sulfur dioxide (120, 123).

$$N_2F_3Sb_2F_{11} + 2(C_5H_5)_2Fe \longrightarrow N_2F_2 + 2(C_5H_5)_2FeSbF_6$$

Alternately tetrafluorohydrazine may be allowed to react with excess aluminum chloride at −78° (68), and *trans*-difluorodiazine is obtained in 48% yield. Only one preparation of the pure *cis* isomer has been reported. The reaction of potassium fluoride with the salt N_2FAsF_6 in anhydrous hydrogen fluoride produces this isomer in high yield (105) (see the later discussion).

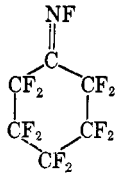
Compounds which contain a N-fluorimino group bonded to carbon (>C=NF) are best known in the perfluorocarbon series. These may be prepared by two essentially different methods. The fluorination of organic nitrogen compound leads to a large number of such products. Some of the techniques used have already been discussed and several examples have been given. Some specific compounds will now be considered. The simplest member of this class of compounds is trifluoromethylenimine, CF_2=NF. Although it was first prepared by the action of fluorine on acetonitrile (30), better yields are obtained from the fluorination of N-methylformamide (4). Trifluoromethylenimine is a colorless gas, bp —101°, which attacks mercury and liberates iodine from potassium iodide solution. The configuration of the reactor is important in these vapor-phase fluorinations. For example, fluorination of CF_3CN in a T-shaped reactor failed to produce any CF_3CF=NF, whereas if the reaction is carried out in a jet reactor the fluorimine is formed. Two other chlorinated nitriles, $CClF_2C{\equiv}N$ and $CCl_3C{\equiv}N$, can also be converted to the corresponding fluorimines (12). The reaction of nitrogen trifluoride with perfluoropropene to produce $(CF_3)_2C$=NF has already been discussed (35). It is not known whether this material arose from the primary interaction of the propene with a nitrogen fluoride species or whether it is a decomposition product of $(CF_3)_2CFNF_2$. An alternate preparation of $(CF_3)_2C$=NF involves the fluorination of the corresponding imine in the presence of potassium fluoride. Although the N-fluoro compound can be obtained in 75% yield, some of the difluoramino derivative is also formed (124).

$$(CF_3)_2C{=}NH + F_2 \xrightarrow{KF} (CF_3)_2C{=}NF + HF$$

The other general preparative method for compounds containing the >C=NF group involves either the reductive defluorination of the corresponding $>CFNF_2$ compound or the dehydrofluorination of the corresponding $>CHNF_2$ compound. The reductive defluorination may be achieved by using ferrocene as the reducing agent (104). The general reaction for aliphatic derivatives is

$$R_fCF_2NF_2 + 2(C_5H_5)_2Fe \longrightarrow R_fCF{=}NF + 2(C_5H_5)_2FeF$$

Similarly 1-difluoraminoperfluorocyclohexane can be converted to



by treatment with ferrocene. Reductive defluorination of the bisdifluoramino derivative, $NF_2CF_2CF_2CF_2NF_2$, gave the bisfluorimino compound, $FN{=}CFCF_2CF{=}NF$, in 57% yield. The scope of this method will undoubtedly be extended as more starting materials become available.

A number of compounds of the type RC(=NF)CN have been reported recently (89). The method of preparation involves the reaction of N_2F_4 with a terminal olefin in the presence of 3 equiv of sodium or cesium fluoride. The reaction is believed to be a two-step process, although the intermediate bisdifluoramino adduct was not isolated.

$$RCH{=}CH_2 + N_2F_4 \longrightarrow [RCHNF_2CHNF_2]$$

$$RCCN \;(\overset{\|}{NF}) + 3MHF_2 \xleftarrow{3MF}$$

R = F, CN, SF_5, $COOCH_3$, and CH_2OOCCH_3

Other groups such as alkyl, aryl, or alkyl chains bearing functional groups can also be used. The compounds

$$SF_5C(\overset{\|}{NF})CN \text{ and } NF{=}C(CN)_2$$

are formed in yields of 15 and 66%, respectively. Both the *syn* and *anti* isomers of fluoriminofluoroacetonitrile, FC(=NF)CN are produced and can be separated in yields of 53 and 17%, respectively. The fluorine bound to carbon in FC(=NF)CN undergoes nucleophilic displacement (89).

$$FC(\overset{\|}{NF})CN + X^- \longrightarrow XC(\overset{\|}{NF})CN + F^-$$

X = N_3, NH_2, $N(C_2H_5)_2$, and $SO_2C_6H_5$

A photolytic method for the preparation of CFBr=NF has been reported (38). Prolonged photolysis of mixtures of N_2F_4 and $FCBr_3$ gives both the *syn* and *anti* isomers of CFBr=NF which can be separated by vapor-phase chromatography. In addition, a small amount of $FCBr_2NF_2$ is formed. Irradiation of the pure *syn* isomer converts some of it to the *anti* isomer, but the reverse transformation does not occur under the same conditions. The *anti* isomer of CBrF=NF undergoes reaction with fluorine radicals to produce trifluoromethylenimine in 70% yield.

$$FCBr{=}NF + F\cdot \longrightarrow CF_2{=}NF + Br\cdot$$

A similar reaction occurs between chlorine and CFBr=NF if the system is irradiated. Both the *syn* and *anti* isomers of FCCl=NF are formed.

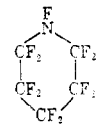
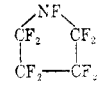
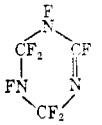
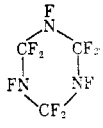
A single example of an =NF group bonded to sulfur is known. The fluorination of $O{=}SF_2{=}NCOF$ in the presence of cesium fluoride produces $O{=}SF_2{=}NF$ in low yield (122). This material possesses some unusual features. It is unstable and decomposes to fluorine, nitrogen, and thionyl fluoride. Furthermore, it is absorbed by cesium fluoride to form an anionic complex, OSF_3NF^-. An attempt to extend this method of fluorination to $SF_2{=}NCOF$ resulted in the formation of SF_5NF_2 only and no evidence for $SF_2{=}NF$ was found.

B. THE SECONDARY N-FLUORAMINE GROUP

Only a few examples are known of compounds of the general form R_2NF and no systematic preparative route has been developed for their synthesis. Although the preparation of what might be considered as the parent compound in this class, fluoramine, has been reported (127), it has never been satisfactorily characterized and some doubt remains as to its existence. On the other hand, several bisperfluoroalkylfluoramines can be obtained by the fluorination of amines, nitriles, or amides. Since the technique involved has already been discussed only a few examples will be considered here. Fluorination of dimethylamine with elemental fluorine produces $(CF_3)_2NF$ in low yield (51). Better yields are obtained using dimethylformamide as the substrate (4). Several cyclic perfluoramines can also be prepared by the electrochemical fluorination of pyridine and other amines (134) or by the use of cobalt trifluoride as the fluorinating agent (65). The direct fluorination of some dinitriles or cyanuric fluoride also produces cyclic derivatives (11, 70). A summary of some of the known compounds is given in Table V. The preparation of dimethylfluoramine by the fluorination of N,N-dimethylsulfonamide in aqueous media has already been discussed.

The N-fluorocarbamates, HNFCOOR, which are prepared by fluorination of aqueous solutions of the

TABLE V

Compound	Method of preparation	Ref
$(CH_3)_2NF$	$F_2 + (CH_3)_2NC(\overset{\|}{O})H$	4
	Electrochemical fluorination of pyridine or CoF_3 and pyridine	65, 134
	$F_2 + NCCF_2CF_2CN$	11
	$(FCN)_3 + F_2$	70
	$(FCN)_3 + F_2$	70
$CF_3NFCF_2NFCF_3$	$(FCN)_3 + F_2$	70
$CF_3NFC_2F_5$	$F_2 + CF_2(CN)_2$	11
$(CH_3)_2NF$	$F_2 + (CH_3)_2NSO_2NH_2$	142

corresponding carbamate (57), dissolve in cold aqueous base to form the unstable salts

$$NaN(F)COOR$$

Solutions of these salts may in turn be converted to

$$FN(Cl)COOR,\ FN(Br)(COOR),\ FN(COOR)_2,\ \text{or}\ CH_3N(F)COOR$$

by the action of chlorine, bromine, ethyl chloroformate, or dimethyl sulfate, respectively (57).

Several samples which contain sulfur bonded to a >NF group have been reported. One such class of compounds, $SF_5N(F)R_f$, can be obtained in low yield by the cesium fluoride catalyzed fluorination of the corresponding perfluoroalkylimino sulfur difluorides as already discussed. The other known example is $FN(SO_2F)_2$ (93). It is formed by the action of dilute gaseous fluorine on $HN(SO_2F)_2$. The yield is almost quantitative and the product, a clear liquid, was isolated by distillation. No chemical reactions have been reported for these materials.

C. THE N′-FLUORODIIMIDE N-OXIDE GROUP

There are several examples of compounds which contain the —N(→O)═NF group. All known derivatives are prepared by essentially the same reaction, the interaction of tetrafluorohydrazine (or difluoramine in pyridine) with a nitroso compound (47, 136).

$$2CF_3NO + N_2F_4 \longrightarrow 2CF_3N(\rightarrow O){=}NF + 2[F]$$

$$RNO + HNF_2 \xrightarrow{\text{pyridine}} RN(\rightarrow O){=}NF + C_5H_5NHF$$

$R = C_6H_5$ and substituted phenyls (136)

The ultraviolet and F^{19} nmr spectral properties of $CF_3N(\rightarrow O){=}NF$ are more consistent with the assignment of the N′-fluorodiimide N-oxide structure to the product than one of the other possibilities, such as $CF_3ON{=}NF$, $CF_3NFN{=}O$, or $CF_3N{=}NOF$ (47). The reaction of the aryl-N′-fluorodiimide N-oxides with Grignard reagents gives confirmation of the structural assignment of the N′-fluorodiimide N-oxide group since known azoxy derivatives are produced (136).

$$ArN(\rightarrow O){=}NF + RMgX \longrightarrow ArN(\rightarrow O){=}NR + MgFX$$

D. THE OXYDIFLUORAMINO GROUP

Trifluoramine oxide, $NF_3{\rightarrow}O$, has recently been prepared by two groups independently using rather different methods (9, 44). These are outlined below.

$$2NF_3 + O_2 \xrightarrow{\text{electric discharge}} 2NF_3O$$

$$3NOF + 2IrF_6 \longrightarrow 2NOIrF_6 + NF_3O$$

Trifluoramine oxide is a stable gas, resistant to hydrolysis, and it does not attack glass or mercury at ambient temperature. Photolysis of trifluoramine oxide at −196° in a matrix produces the relatively stable $NF_2O\cdot$ radical which can be identified by its nine-line esr spectrum. A further discussion of some of the reactions of trifluoramine oxide will be found in a later section.

Although it is not strictly correct to state that trifluoramine oxide is the parent compound in the class of compounds containing a ONF_2 group, compounds of this type will be considered here. Only three such compounds have been completely characterized. These are FSO_2ONF_2 (95), SF_5ONF_2 (61, 121), and CF_3ONF_2 (61, 130). The preparation of FSO_2ONF_2 has already been described under the coupling reactions of the NF_2 radical. The preparation of the other two compounds probably involves a similar mechanism since they are produced in the photolytic reaction of tetrafluorohydrazine with the corresponding hypofluorite derivative. Both of these equations are idealized since numerous side products are also formed. The latter reaction can

$$SF_5OF + N_2F_4 \xrightarrow{h\nu} SF_5ONF_2 + NF_3$$

$$CF_3OF + N_2F_4 \xrightarrow{h\nu} CF_3ONF_2 + NF_3$$

be carried out with thermal activation (130). A brief report mentioned an alternate preparation of such materials based on the reaction between trifluoramine oxide and a perfluoroolefin (44). Complete details were not given.

$$CF_2{=}CF_2 + NF_3O \xrightarrow{\text{catalyst}} CF_3CF_2ONF_2$$

The chemical reactivity of compounds containing the ONF_2 group has not been extensively investigated although several reactions of FSO_2ONF_2 have been noted (121). The action of fluoride and chloride anions on FSO_2ONF_2 differ markedly. Fluoride ion catalyzes its decomposition while chloride ion reacts according to the equation

$$FSO_2ONF_2 + Cl^- \longrightarrow ClNF_2 + SO_3F^-$$

$$FSO_2ONF_2 \xrightarrow{F^-} SO_2F_2 + NOF$$

Addition of FSO_2ONF_2 to perfluoroolefins has also been observed (97).

$$FSO_2ONF_2 + CF_2{=}CF_2 \longrightarrow FSO_2OCF_2CF_2NF_2$$

The product can be converted to an acid fluoride by the action of fluoride ion.

$$FSO_2OCF_2CF_2NF_2 \xrightarrow{F^-} SO_2F_2 + NF_2CF_2C(=O)F$$

V. COMPLEXES AND IONIC NITROGEN FLUORIDE DERIVATIVES

A. COMPLEXES OF DIFLUORAMINE

The interaction of difluoramine with various Lewis acids has been investigated by observing the vapor pressure–temperature relationship for these systems (27). Boron trifluoride and difluoramine form a complex which is stable at low temperatures but undergoes reversible dissociation upon warming. The enthalpy of the reaction

$$HNF_2(g) + BF_3(g) \rightleftharpoons HNF_2 \cdot BF_3(s)$$

is −21.0 kcal/mole. Since little change is noted in the NH region of the infrared spectrum of the complex over that in solid difluoramine, the bonding probably involves the unshared electron pair on nitrogen. With boron trichloride and difluoramine a complex is also obtained, but it undergoes irreversible dissociation on warming and chlorodifluoramine is produced (110). The complex formed between phosphorus pentafluoride and difluoramine is stable only below −50°. Above this temperature it decomposes to yield hydrogen fluoride, phosphorus pentafluoride, and the *cis* and *trans* isomers of difluorodiazine. Evidence for complex formation between ethyl or methyldifluoramine and phosphorus pentafluoride or boron trifluoride has been found. The complexes, however, are stable only at low temperatures. On warming the alkyldifluoramines undergo dehydrofluorination to form acetonitrile or HCN, respectively.

Difluoramine exhibits amphoteric behavior since weak complexes are formed with sulfur dioxide (27) as well as other basic solvents. The enthalpy of the reaction

$$HNF_2(g) + SO_2(g) \longrightarrow HNF_2 \cdot SO_2(s)$$

is −12.5 kcal/mole. An infrared study of the solvolysis of difluoramine in various solvents indicated the following order for the degree of interaction: $H_2O < CH_3OH < CH_3CN < HCONH_2 < HCON(CH_3)_2 < (CH_3)_2SO$ (28). In fact, the complexes formed with dimethylformamide and dimethyl sulfoxide show low vapor pressure at ambient temperature.

Attempts to protonate difluoramine with the halo acids was not successful and only slight interaction was noted even at low temperature. However, solutions of difluoramine in a 1:5 mixture of SbF_5–HSO_3F exhibit low vapor pressure (115). The large downfield shift of the fluorine band in the F^{19} nmr spectrum suggests that protonation is occurring in this strong acid medium. However, the lack of resolution of this band is probably indicative of a rapid exchange process.

Complexes are formed between difluoramine and the heavier alkali metal fluorides (83).

$$MF + HNF_2 \longrightarrow MF \cdot HNF_2$$
$$M = K, Rb, \text{ or } Cs$$

The difluoramine may be removed at low temperature from the potassium and rubidium fluoride complexes. However, if these systems are allowed to stand at ambient temperature, dehydrofluorination of the difluoramine occurs and both isomers of difluorodiazine are liberated. The cesium fluoride complex explodes on warming to 0°. An infrared study of these complexes indicates that hydrogen bonding is probably responsible for complexation ($KF \rightarrow HNF_2$) (37). The infrared spectrum of the cesium fluoride complex gave indications for the presence of another species which was postulated to be $CsNF_2 \cdot HF$ (37), but further data are needed to confirm this.

Difluoramine has been reported to react with trimethylamine alane to form an aluminum difluoramino derivative (53). The compound is a white solid which

$$3HNF_2 + AlH_3 \cdot N(CH_3)_3 \longrightarrow F_2AlNF_2 \cdot N(CH_3)_3 + N_2 + 2H_2 + 2HF$$

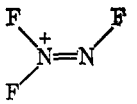
oxidizes aqueous hydriodic acid. This is the only reported derivative of a metal–difluoramino compound.

B. COMPLEXES OF TETRAFLUOROHYDRAZINE

Tetrafluorohydrazine was found to interact with several Lewis acids, especially those which are capable of accepting fluoride ions. A study of the vapor pressure–temperature relationship of the systems BF_3–N_2F_4 and BCl_3–N_2F_4 indicates only weak interaction below −120 and −78°, respectively. By employing the stronger Lewis acid, antimony pentafluoride, two stable complexes can be isolated (120, 123). If $AsF_3 \cdot SbF_5$ is allowed to react with tetrafluorohydrazine at atmospheric pressure, a complex having the composition $N_2F_4 \cdot 2SbF_5$ is obtained. At lower N_2F_4 pressures (<100 mm) another complex, $N_2F_4 \cdot 3SbF_5$, is formed. The latter complex can be converted to the former by reaction with sulfur dioxide at low temperatures.

$$N_2F_4 \cdot 3SbF_5 + SO_2 \xrightarrow{-64°} N_2F_4 \cdot 2SbF_5 + SO_2SbF_5$$

The complex $N_2F_4 \cdot 2SbF_5$ was shown to be the salt $N_2F_3^+Sb_2F_{11}^-$ and not a molecular adduct by F^{19} nmr spectroscopy. The spectrum in the NF region demonstrates the presence of three different types of fluorines in equal abundance. This is consistent with the formulation of the cation as



where the rotation about the N–N bond is restricted. Even at 120° no rotation appears to occur. The characteristic spectrum of the $Sb_2F_{11}^-$ anion is also present. The N_2F_4 can be recovered from the salt by treatment with potassium fluoride or by thermal decomposition

at 200° under vacuum. The salt is very reactive toward most organic materials. The most important reaction of the salt (that which produces *trans*-N_2F_2) has already been discussed.

C. COMPLEXES OF DIFLUORODIAZINE

A study of the interaction of difluorodiazine with Lewis acids has led to the characterization of another nitrogen fluoride cation. The *cis* isomer of difluorodiazine reacts with arsenic pentafluoride at ambient temperature to form the complex $N_2F_2 \cdot AsF_5$ (105). No reaction occurs when the *trans* isomer is used. On the other hand, when antimony pentafluoride is employed as the Lewis acid both isomers of difluorodiazine react to produce the same product, $N_2FSb_2F_{11}$ (123). Solutions of $N_2F_2 \cdot AsF_5$ in anhydrous hydrogen fluoride are stable and *cis*-difluorodiazine may be recovered from the complex by addition of sodium fluoride to such solutions. No *trans*-difluorodiazine is formed in this reaction.

$$NaF + N_2F_2 \cdot AsF_5 \xrightarrow{HF} cis\text{-}N_2F_2 + NaAsF_6$$

The F^{19} nmr spectrum of the complex in anhydrous hydrogen fluoride shows only one type of fluorine bound to nitrogen. The observed NF coupling constant is much larger than found in difluorodiazine or in other nitrogen fluorides. This suggests that the NF bond has an increased amount of s character over that in difluorodiazine. This is consistent with formulation of the complex as N-fluorodiazonium hexafluorarsenate, $N_2F^+AsF_6^-$, since the s character in the NF bond for the resonance form of the cation, $F—N^+{\equiv}N$, is greater than in difluorodiazine.

Two reactions of this complex have been reported. They are summarized by the equations (105)

$$N_2FAsF_6 + AgClO_4 \longrightarrow AgAsF_6 + N_2O + ClO_3F$$
$$N_2FAsF_6 + NH_4SO_3F \longrightarrow NH_4AsF_6 + N_2O + SO_2F_2$$

D. COMPLEXES OF TRIFLUORAMINE OXIDE

The recently reported trifluoramine oxide forms solid 1:1 complexes with arsenic pentafluoride or antimony pentafluoride (9, 44). However, no solid complex with boron trifluoride exists at ambient temperature and atmospheric pressure. These complexes appear to be salts containing the NF_2O^+ cation since their F^{19} nmr spectra in anhydrous hydrogen fluoride consists of a low-field triplet (J_{NF} = 250 cps) and a high-field singlet whose relative area ratios are 1:3. Little other information on these salts is available at this time.

E. FLUOROAMMONIUM CATIONS

Two recent preliminary notes have reported the preparation of tetrafluoroammonium salts (29, 140). The basis for the preparation is the reaction of nitrogen trifluoride with fluorine in the presence of a strong fluoride ion acceptor. Suitable activation can be achieved either by high pressures and temperatures

$$NF_3 + F_2 + SbF_5 \xrightarrow[85\ atm]{200°} NF_4SbF_6$$

or by glow discharge at −78°

$$NF_3 + F_2 + AsF_5 \xrightarrow[-78°]{\text{glow discharge}} NF_4AsF_6$$

The F^{19} nmr spectrum of the NF_4^+ cation consists of a triplet (J_{NF} = 231 cps) centered at −215 ϕ. Both salts are surprisingly stable. Thermal decomposition of the hexafluoroantimonate occurs only above 300°.

$$NF_4SbF_6 \xrightarrow{\Delta} NF_3 + F_2 + SbF_5$$

This is undoubtedly due in large part to kinetic factors rather than thermodynamic factors.

Some evidence has been presented for the existence of other N-fluoroammonium derivatives and related compounds. The complex which results from treatment of dimethylfluoramine with anhydrous hydrogen chloride may contain the $(CH_3)_2NHF^+$ cation (142). The evidence for the presence of this ion is based on the solubility characteristics of the complex and on its F^{19} nmr spectrum. The salt, N-fluoro-N-methylisopropylidenimonium tetrafluoroborate, can be obtained from the reaction of *t*-butyldifluoramine with boron trifluoride (10).

$$(CH_3)_3CNF_2 + BF_3 \xrightarrow{-78°} (CH_3)_2C{=}\overset{F}{\underset{+}{N}}CH_3BF_4^-$$

Evidence was found for a similar rearrangement of other alkyldifluoramines in strong sulfuric acid but no products could be isolated.

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