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Organic *N*-Fluoroimines

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The available information about the methods of synthesis of *N*-fluoroimines and their reactions with nucleophiles and electrophiles and with oxidants and reductants as well as pyrolytic and photolytic reactions are surveyed. The reaction mechanisms are discussed and certain aspects of the practical applications of the reactions are examined. The bibliography includes 184 references.

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I. INTRODUCTION

Organic *N*-fluoroimines are characterised by the presence of the C=NF group in the molecule. The first information about the synthesis of fluorine–nitrogen compounds of this class was obtained at the beginning of the 1950s. In subsequent years, the number of publications steadily increased, the most vigorous research in this field having been carried out in the last decade when easy methods for the synthesis of *N*-fluoroimines were developed.

N-Fluoroimines exhibit a wide variety of reactivities owing to the presence of the C=N and N–F bonds. Depending on their structures, it is possible to find in the chemical properties of organic *N*-fluoroimines a definite analogy with the chemical properties of familiar classes of organic compounds such as perfluoroketones, carboxylic acid halides, and certain others. On the other hand, the chemistry of these compounds has its distinctive features, so that the study of their chemical properties is of interest both from the standpoint of the deepening of the theoretical ideas about the chemistry of carbon linked by a double bond to a heteroatom and as regards synthetic research. At the same time, compounds of this class can find extensive practical applications.

There have so far been no reviews on organic *N*-fluoroimines. Individual data on the methods of synthesis and chemical properties of these compounds can be found in a number of papers [1-5] and also in monographs [6-10]. The synthesis and reactions of perfluorinated *N*-fluoroimines with nucleophiles have been examined by Dyatkin et al. [11] The present review covers the entire fundamental literature on *N*-fluoroimine published up to May, 1976.

II. METHODS OF SYNTHESIS

The main methods for the preparation of *N*-fluoroimines are fluorination of nitrogen compounds by elemental fluorine, dehydrofluorination of aminodifluoroalkanes, the interaction of tetrafluorohydrazine with acetylenes, and reductive dehalogenation or difluoroperhalogenoalkylamines. *N*-Fluoroimines are also obtained in reactions of bromine or iodine compounds with tetrafluorohydrazine and in the homolysis of geminal bis(difluoroamino)-derivatives. In addition, there exist examples of the synthesis of individual *N*-fluoroimines which are not general.

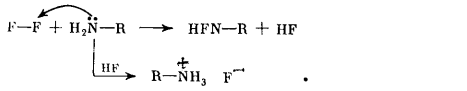
1. Fluorination of Nitrogen Compounds by Elemental Fluorine

As early as 1951, Haszeldine [12] fluorinated acetonitrile and trifluoroacetonitrile over gold gauze and obtained, among other products, compounds for which he proposed the structure of perfluoroiminoethane $CF_3CF{=}NF$ and perfluoroformimine $F_2C{=}NF$. The formation of $F_2C{=}NF$ was later noted in the fluorination of acetonitrile [13], methylformamide, and methyl thioisocyanate [14] in the gas phase. The formation of *N*-fluoroimino-derivatives was demonstrated also in the fluorination of perhalogenonitriles [15] and tris(trifluoromethyl)-*s*-triazines [16].

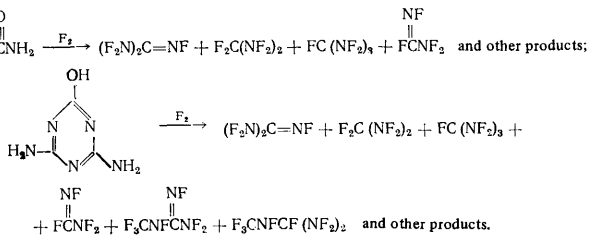
The fluorination of nitrogen compounds by elemental fluorine has become in the last decade one of the fundamental methods for the synthesis of *N*-fluoroimines. This was assisted to a considerable degree by the improvement of the fluorination technique and apparatus and, what is most important, the methods for the isolation and identification of the reaction products. The fact that many unique compounds, highly fluorinated at the nitrogen atom, such as pentafluoroguanidine, tetrafluoroformamidine, *NNN'*-trifluoroamidines, etc., can be obtained by this method has also been enormously important. Various nitrogen compounds may be fluorinated in powder form, as suspensions in an inert organic solvent, and as solutions in aqueous or organic solvents.

The solid-phase fluorination of nitrogen derivatives has been most widely investigated. In order to make the reaction conditions milder, a diluent is used as a rule. Sodium fluoride, which not only plays the role of a diluent but also combines with the hydrogen fluoride evolved in the reaction (the latter is a fluorination inhibitor), is usually employed for this purpose [17-27]. The fluorination mechanism, which is based on the attack on the nitrogen atom by the fluorine molecule [4,5,8], permits the conclusion that the successful occurrence of the process requires that the electron pair at the nitrogen atom should remain free. On the other hand, the presence of hydrogen fluoride in the reaction leads to its inhibiting the process with

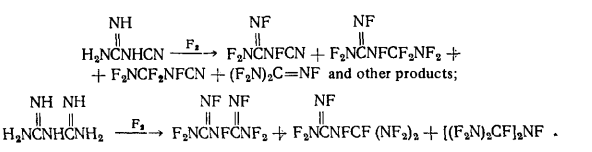
the formation of the corresponding hydrofluoride, which is incapable of further reaction with fluorine:



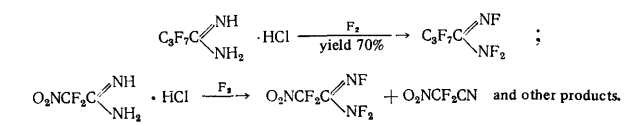
Numerous studies have been devoted to the preparation of pentafluoroguanidine by this method. Guanidine and its derivatives as well as various nitrogen compounds whose molecules contain guanidine structural fragments have been fluorinated, namely guanidinium salts (sulphate, carbonate, hydrochloride, etc.),[21,25,28,29] guanylurea and its sulphate[30-32], biguanide[32-36], ammeline and its salts[17,28,29,32,33,37,38], melamine[33], and cyanoguanidine[26,32]. Fluorination results in the formation of complex mixtures of products, for example:



The maximum yield of pentafluoroguanidine does not exceed 25% under these conditions[25]. Apart from pentafluoroguanidine, the reaction products include various difluoroamino-, fluoroimino-, and difluoroaminofluoroimino-derivatives. The formation of cyanoperfluoroguanidine[19,26,39] and perfluorobiguanide in the fluorination of their hydrogen analogues has been demonstrated[18,20,33,40]:

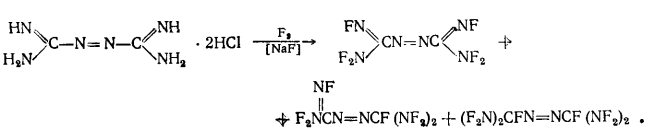


The fluorination of the hydrochlorides of tetrafluorobutyramidine and difluoronitroacetamidine is completed by the formation of the corresponding *NNN'*-trifluoroamidines[27]

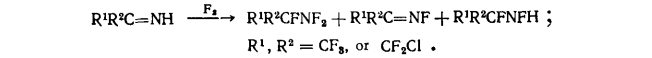


The fluorination of the *N*-fluoroamidines of perfluorocarboxylic acids[32], which can be obtained, for example, by the reaction of *N*-fluoroimidoyl fluorides with ammonia, also leads to the formation of perfluoroalkylamidines.

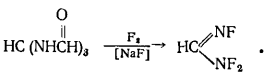
Hexafluoroazodiformamidine (in the form of three isomers), mixed with other products, is formed in the fluorination of azodiformamidinium salts in the presence of sodium fluoride[24,41]:



The fluorination of polyfluoroalkylketimines[42] is completed by the formation of the following reaction products:

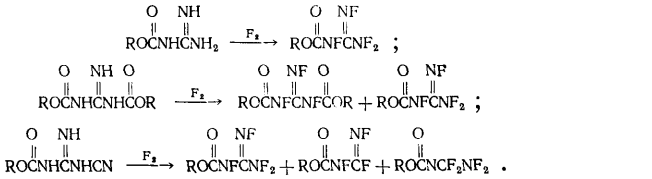


The attempts to obtain unsubstituted *NNN'*-trifluoroamidines $R_HC(=NF)NF_2$ by the solid-phase fluorination of the hydrochlorides of the corresponding amidines were unsuccessful[27]; the alkyl residue of the initial molecule is fluorinated and appreciably degraded. Only the synthesis of *NNN'*-trifluoroformamidine by the fluorination of a mixture of tri-(*N*-formylamino)methane with sodium fluoride is known[23]:



A characteristic feature of the solid-phase fluorination reaction involves the use of various metal fluorides, whose role is apparently not restricted to that of diluents and binders of hydrogen fluoride (see above). It is natural to suppose that metal fluorides behave as catalysts[43]. This property is manifested most distinctly by caesium fluoride in the fluorination of, for example, perfluoroacetone imine[43], which leads to an almost quantitative yield of the saturated perfluoroamino-derivative.

The fluorination of nitrogen compounds in solution, which is a convenient method for the preparation of difluoroaminoalkanes[44], has not found extensive applications in the synthesis of *N*-fluoroimines. However, pentafluoroguanidine has been obtained by the fluorination of aqueous solutions of guanidinium salts[45,46] at pH 8–9 in a thin layer, the formation of which was ensured by a special design of the reactor, The fluorination of alkoxycarbonylguanidines in acetonitrile at 0°C has been shown by Grakauskas and Baum[47,48] to lead to the formation of guanidines fluorinated at the nitrogen atom:



In all cases the yield of fluorination products did not exceed 15%.

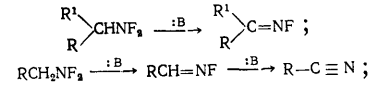
The attempt to use the fluorination of acetonitrile solutions of heptafluorobutyramidine or its hydrochloride in order to synthesis the *NNN'*-trifluoroamidine of heptafluorobutyric acid was unsuccessful[27]. Only the solvent was fluorinated in this reaction.

The possibility of employing other fluorinating agents in order to synthesise *N*-fluoroimines has not been studied systematically. There have been only individual reports of the synthesis of *N*-fluoroimines on treatment of nitrogen compounds with mercury(II) fluoride[6,49] and trifluoromethyl hypofluorite[50].

2. Dehydrofluorination of Difluoroaminoalkanes

Difluoroamino-compounds with hydrogen atoms in the α-position relative to the difluoroamino-group are capable of dehydrofluorination[3,5,51,52]. By virtue of the unusual amphoteric nature of difluoroaminoalkanes, the reaction can be carried out under the influence of both bases and Lewis acids[2,51]. Basic reagents are used in preparative syntheses. If the initial compound contains the $-CH_2NF_2$ group, the dehydrofluorination takes place in two stages: the first stage leads to the formation of the fluoroimino-group $-CH{=}NF$ and the second is completed by the formation of a cyano-group. If the initial

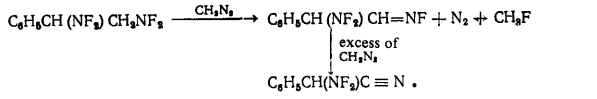
compound contains the $\rangle CHNF_2$ group, the elimination of an HF molecule from it leads to the formation of the fluoroimino-group $\rangle C{=}NF$, which is incapable of further dehydrofluorination:



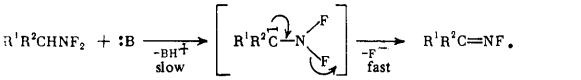
R and $R^1 \neq H$; :B = dehydrofluorinating agent.

When there are no hydrogen atoms in the α-position relative to the difluoroamino-group, the latter is as a rule resistant to the action of bases [52,53]. When the molecule of the initial compound contains several difluoroamino-groups, products of incomplete dehydrofluorination can be obtained under certain conditions [51-54].

From the practical point of view, the dehydrofluorination of compounds containing the $\rangle CHNF_2$ group is most important for the synthesis of N-fluoroimine. A characteristic feature of the $\rangle CH_2NF_2$ group is its conversion into a cyano-group [51,52,55-59], although the formation of an intermediate N-fluoroimine cannot be ruled out, for example [51,52]:



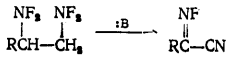
Depending on the conditions, the dehydrofluorination of difluoroamino-derivatives can proceed via different mechanisms. Bearing in mind that in the majority of studies fairly strong bases (triethylamine, pyridine, etc.) have been used for dehydrofluorination, preference should probably be given to the $E1cB$ (or similar) mechanism [51, 52,60,61]:



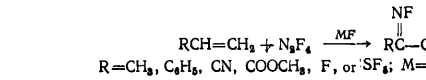
At the same time a bimolecular $E2$ mechanism has been proposed for the dehydrofluorination of difluoroamino-alkanes in aqueous organic solutions [53,54,60], this being supported, according to the authors, by the large negative activation entropies and also by the absence of the isomerisation of the diastereoisomers of 2,3-bis-(difluoroamino)-butane in their dehydrofluorination reaction [54]; the latter is of pseudo-first order and has an activation energy of 13–20 kcal mole^{-1}. [53,54,60]

Various dehydrogenating agents are used to remove hydrogen fluoride; they can be arranged in the following sequence in terms of their activities: $C_2H_5OH < H_2O < CH_2N_2 < C_5H_5N < (C_2H_5)_3N < C_2H_5ONa$. [60] Bases such as pyridine [27,51,52,58,62-64], sodium alkoxides [65-69], triethylamine [51,52,70,71], alkali metal fluorides [55,57,59,72-77], and aqueous alkaline solutions [52,56,61,66] are used for the preparative syntheses of N-fluoroimines. The employment of the alkaline solutions may be complicated by a series of further reactions (the haloform decomposition, the hydrolysis of cyano-, amide, and ester groups, and decarboxylation) [52,61]. In certain cases, for example in the synthesis of bis(fluoroimino)cyclohexenes [78], specially selected dehydrofluorinating agents are used. Organic solvents, namely chlorohydrocarbons, Freons, acetonitrile, alcohols, etc. are widely used in the synthesis of N-fluoroimines.

When bases are allowed to act on vicinal primary-secondary bisdifluoroamino-derivatives, N-fluoroimino-nitriles are formed [51,52,58,72]:



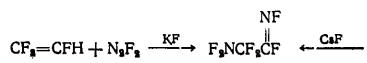
The interaction of terminal olefins with tetrafluorohydrazine in the presence of an alkali metal fluoride is a variant of this method [55,57,72]:



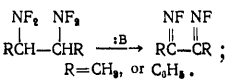
$R = CH_3$, C_6H_5, CN, $COOCH_3$, F, or SF_5; $M = Na$, K, or Cs.

Olefins with electronegative substituents are particularly readily involved in this reaction. Addition products are probably formed initially and are then dehydrofluorinated under the reaction conditions [55].

Later this reaction was extended to the synthesis of perfluoroimines [73,74]. For example, when tetrafluorohydrazine reacts with trifluoroethylene in the presence of potassium fluoride, the N-fluoroimidoyl fluoride derived from difluoroaminodifluoroacetic acid is formed in a yield exceeding 60%. This product is also formed when 1,2-bis(difluoroamino)trifluoroethane is acted upon by caesium fluoride [76]:

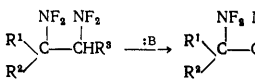


Vicinal bis(fluoroimino)alkanes have been obtained by the dehydrofluorination of vicinal and bis(difluoroamino)-alkanes [53,54,56,62,70,71,77-79], for example:



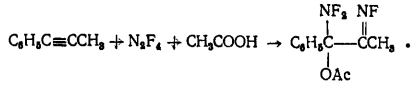
$R = CH_3$, or C_6H_5.

α-Difluoroaminofluoroimines are formed from vicinal bis(fluoroamino)alkanes containing one secondary difluoroamino-group [56,65,66,68,69,71,76,80]:

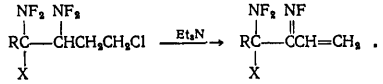


R^1, $R^2 = Alk$, Ar, Hal, NF_2, or $OPO(OR)_2$; $R^3 = Alk$, or Ar.

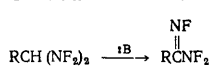
The dehydrofluorination of α-acetoxy-$\alpha\beta$-bis(difluoroamino)-derivatives does not lead to the formation of α-acetoxy-α-(difluoroamino)fluoroimines [61]. Such a fluoroimine has been obtained from methylphenylacetylene, tetrafluorohydrazine, and acetic acid [81]:



N-Fluorovinylimines are formed as a result of the simultaneous dehydrofluorination and dehydrochlorination of vicinal bis(difluoroamino)alkanes containing the β-chloroethyl group [71]:



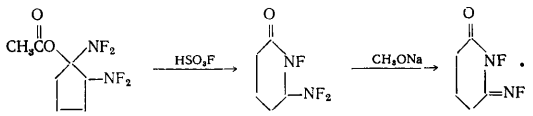
The synthesis of NNN'-trifluoroamidines as a result of the dehydrofluorination of geminal bis(difluoroamino)-alkanes has been described [27,53,63,64]:



A preparative method has been developed for the synthesis of compounds of this kind [27,63,64] using dehydrofluorinating

agents such as pyridine, piperidine, quinoline, and aqueous sodium hydroxide. Best yields are achieved when pyridine is used [27].

3-Fluoroimino-2-fluoro-2-azacyclohexanone has been obtained by the dehydrofluorination of 3-difluoroamino-2-fluoro-2-azacyclohexanone [67]:

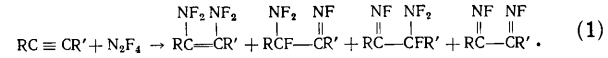


The dehydrofluorination of the *cis*- and *trans*-isomers of 9,10-bis(difluoroamino)-9,10-dihydroanthracene leads to the formation of 9,10-bis(fluoroimino)anthracene [82], the *trans*-isomer splitting off hydrogen fluoride more readily than the *cis*-isomer.

When 1,1,2-tris(difluoroamino)alkanes are dehydrofluorinated, the corresponding fluoroimines are formed readily [66,68,71,80]. However, the dehydrofluorination of 1,1,3-tris(difluoroamino)cyclohexane on treatment of the latter with sodium methoxide, undertaken to obtain the corresponding fluorimine, proved unsuccessful [83], probably owing to the instability of the resulting *N*-fluoroimine, caused by the presence of the methylene group with mobile hydrogen atoms [$-C(NF_2)_2CH_2C(=NF)-$].

3. The Interaction of Tetrafluorohydrazine with Acetylenes

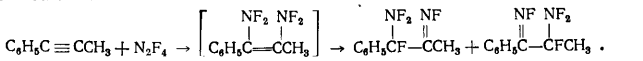
The reaction of tetrafluorohydrazine with acetylenes is a convenient method for the synthesis of α-difluoroaminofluoroimines:



(1)

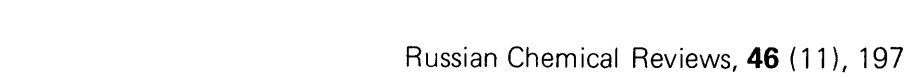
The first stage involves the formation of a bis(difluoroamino)alkene, which subsequently isomerises to the corresponding *N*-fluoroimine. The rearrangement of difluoroaminoalkenes to *N*-fluoroimines, which was first reported by Bumgardner [84], is based on the higher thermodynamic stability of the C–F and C=N bonds compared with that of the N–F and C=C bonds [85], but there is as yet no unanimous view concerning its mechanism. Many workers support a radical mechanism of this rearrangement, initiated, for example, by heat or ultraviolet light [8]. On the other hand, the stereospecificity of the rearrangement of the products of the addition of tetrafluorohydrazine to allene in the presence of fluoride ions shows that the isomerisation may be based on a heterolytic mechanism [86].

The process is as a rule carried out with heating in a solvent under pressure, best results having been obtained with higher acetylenes (no products were isolated when unsubstituted acetylene was used [85]). In most cases, the main reaction products are α-difluoroaminofluoroimines. Bis(difluoroamino)alkenes could be isolated only in the reaction of tetrafluorohydrazine with hex-2-yne [87] and perfluoroacetylenes [86], their formation sometimes constituting the main process in the latter case. Perfluoroderivatives of 1,2-bis(difluoroamino)alkenes can isomerise to the corresponding *N*-fluoroimines on heating or irradiation [86]. When tetrafluorohydrazine interacts with asymmetric acetylenes, the intermediate bis(difluoroamino)-alkenes can arrange with formation of two products. For example, methylphenylacetylene gives rise to both isomers [85]:

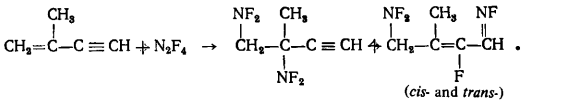


However, phenylpropiolyl fluoride yields only one rearrangement product, namely $C_6H_5CF(NF_2)C(=NF)COF$.

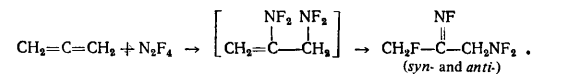
It is of interest that only one mole of tetrafluorohydrazine reacts with hexa-2,4-diyne [85]. This involves 1,2- and not 1,4-addition:



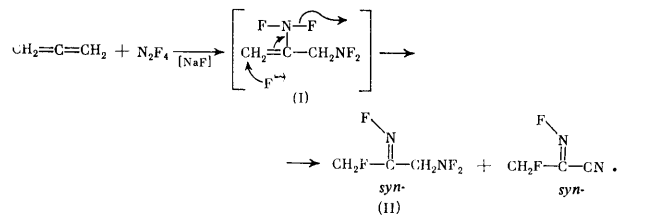
On the other hand isopropenylacetylene gives rise to 1,2- and 1,4-addition products [85]:



The formation of α-difluoroaminofluoroimines is also observed in the reaction of tetrafluorohydrazine with allene [85,86]:



When the reaction is catalysed by fluoride ions, the rearrangement of the intermediate product (I) becomes stereospecific, since only the *syn*-isomer (II) is formed together with its dehydrofluorination product [86]:

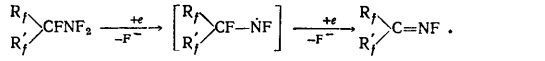


The reactions of tetrafluorohydrazine with acetylenes can also give rise to 1,2-bis(fluoroimino)alkenes [see Eqn.(1)], whose formation is favoured by prolonged heating and a higher temperature [79]. It has been shown for the synthesis of 2,3-bis(fluoroimino)hexafluorobutane and bis(fluoroimino)succinonitrile that the reaction can be regarded as a convenient method of synthesising vicinal bis(fluoroimino)-derivatives [79].

4. Reductive Dehalogenation of Perhalogenoalkyldifluoroamines

Perhalogenoalkyldifluoroamines containing the NF_2 group at a primary or secondary carbon atom are converted into *N*-fluoroimines on reductive dehalogenation. The reducing agents most often used are dicyclopentadienyliron (ferrocene) [88–91], iron pentacarbonyl [92–94], and mercury [95–98]; silver or silver nitrite [99] and potassium or tetrabutylammonium iodides [100] are more rarely used.

The process is based on the successive transfer of electrons from the reducing agent to the difluoroamino-derivative accompanied by twofold elimination of the fluoride ion [92]:



The reaction involving perhalogenoalkyldifluoroamines containing the NF_2 group at a secondary carbon atom stops at the stage involving the formation of the *N*-fluoroimine [89–91]. As a result of the elimination of a further two

fluoride ions, the corresponding nitriles may be formed from primary perhalogenoalkyldifluoroamines [90,92]. However, by selecting a suitable reducing agent (ferrocene is best) [88-90,101], it is possible to obtain *N*-fluoroimine in this case too:

$$R_fCF_2NF_2 \xrightarrow{(C_5H_5)_2Fe} R_fCF{=}NF\ ;$$
$$R_f{=}C_3F_7 \text{ or } CFCl_2\ .$$

The reduction of difluoroaminotrihalogenomethanes with iron pentacarbonyl [93,94] or mercury [95-97] leads to *N*-fluorodihalogenoformimines:

$$F_nCl_{3-n}CNF_2 \xrightarrow{A} F_nCl_{2-n}C{=}NF\ ;$$
$$A{=}Hg \text{ or } (CO)_5Fe;\quad n = 0, 1, \text{or } 2.$$

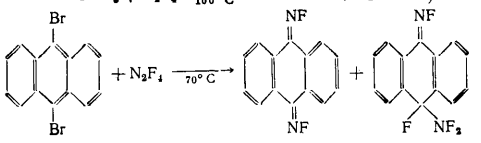
Difluoroaminodichlorofluoromethane reacts best, the reactions involving difluoroaminochlorodifluoro- and difluoroaminotrichloro-methanes proceeding with more difficulty. Ferrocene does not reduce these compounds. When difluoroaminodichloroacetonitrile is reduced with mercury, 1-cyano-*N*-fluoroformimidoyl chloride is formed in a high yield [98].

There have been reports that the reduction of dichlorobis(difluoroamino)methane with silver or silver nitrite leads to dichloro-*N*-fluoroformimine [99], although as a rule the reduction of *gem*-bis(difluoroamino)perfluoroalkanes is completed by the formation of diazirines [88,102,103].

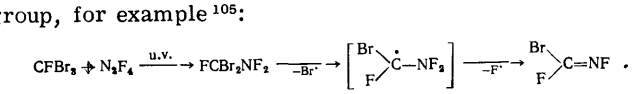
5. Reactions of Bromine- or Iodine-containing Compounds with Tetrafluorohydrazine

The formation of *N*-fluoroimines is observed in the reactions of tetrafluorohydrazine with certain bromine- or iodine-containing compounds. These reactions have not so far found wide-scale applications, although they frequently lead to a high yield of *N*-fluoroimines, for example, in the reaction of tetrafluorohydrazine with bromo- and iodo-perhalogenoethylenes [77,104], tribromofluoromethane [105], and 9,10-dibromoanthracene [82]:

$$CBr_2{=}CBr_2 + N_2F_4 \xrightarrow{155^\circ C} CBr_2F{-}CBr(=NF) + F_2NCBrF{-}CBr(=NF)\ ;$$
$$CF_2{=}CFI + N_2F_4 \xrightarrow{100^\circ C} F_2NCF_2{-}CF(=NF) + F_2NCF_2{-}CFINF_2\ ;$$
$$CFBr_2 + N_2F_4 \xrightarrow[100^\circ C]{u.v.} BrFC{=}NF + F_2C{=}NF\ ;$$



α-Bromo- or α-iodo-difluoroamino-derivatives are formed in the first stages of these reactions. The homolytic elimination of a halogen atom leads to the formation of the radical species $RR^1\dot{C}{-}NF_2$, which is converted into an *N*-fluoroimine as a result of the elimination of a fluorine atom from the difluoroamino-group, for example [105]:



6. Homolysis of Geminal Bis(difluoroamino)-derivatives

The homolytic decomposition of difluoroamino-derivatives containing the $-C(NF_2)_2-$ group leads to the formation of *N*-fluoroimines. The reaction begins with the dissociation of the weakest C–N bond [32,106]; the resulting radical $RR^1\dot{C}{-}NF_2$ is stabilised with formation of the corresponding *N*-fluoroimine, the decomposition being usually initiated by ultraviolet irradiation [107] or heat [106,108-110]. Thus photolysis of bis(difluoroamino)-dihalogenomethanes in the presence of N_2O leads to the formation of *N*-fluorodihalogenoformimines [107]:

$$XFC(NF_2)_2 \xrightarrow[N_2O]{u.v.} XFC{=}NF\ ;$$
$$X{=}F \text{ or } Cl\ .$$

The thermal decomposition of poly(difluoroamino)-halogenomethanes [32,106,109], tris(difluoroamino)methoxy-methane [109], 2,2-bis(difluoroamino)propane [110], as well as azobis(difluoroamino)fluoromethane and [bis(difluoro-amino)fluoromethylazo]trifluoroformamidine in the presence of carbon monoxide [108] has been described:

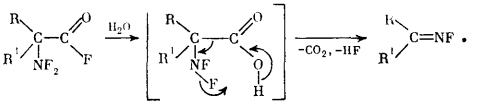
$$RC(NF_2)_3 \xrightarrow{\Delta} RC(=NF)NF_2 \text{ and other products;}$$
$$R{=}NF_2,\ F,\ Cl, \text{ or } OCH_3\ ;$$
$$(CH_3)_2C(NF_2)_2 \xrightarrow[780^\circ C]{} CH_2CF{=}NF + (CH_3)_2C{=}NF + CH_2NF_2 + HCN + HF\ ;$$
$$(F_2N)_2CFN{=}NCF(NF_2)_2 \xrightarrow[160^\circ C]{CO} FN{=}CFN{=}NCF{=}NF\ ;$$
$$(F_2N)_2CFN{=}NC(=NF)NF_2 \xrightarrow[120^\circ C]{CO} FN{=}CFN{=}NC(=NF)NF_2\ .$$

The composition of the pyrolysis products depends both on the structure of the initial poly(difluoroamino)-compound and on temperature. Under optimum conditions, the yield of *N*-fluoroimines may reach 60–70% [106,110].

It is noteworthy that formation of *N*-fluoroimines is also observed in the pyrolysis of difluoroaminofluorodiazirine [111] and trifluoronitrosomethane [112] and in the photolysis of azofluoroiminofluoromethane [108].

7. Other Methods

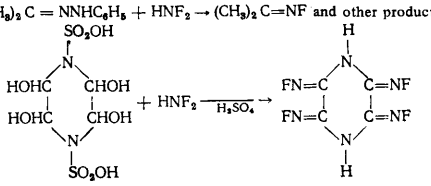
Apart from the methods discussed above, a number of reactions leading to the formation of *N*-fluoroimines merit attention. These include primarily the hydrolysis of the fluorides of α-difluoroaminoperhalogenocarboxylic acids [113-115]. The formation of α-difluoroaminoperhalogeno-carboxylic acid in the first stage is postulated, the acid being subsequently decarboxylated with simultaneous elimination of hydrogen fluoride. A cyclic concerted mechanism has been proposed for the decarboxylation [114,115]:



When aqueous dioxan was allowed to react with difluoro-aminodifluoroacetyl fluoride, the free acid was isolated [114]. The hydrolysis of methyl α-cyano-α-difluoroamino-propionate apparently proceeds via a similar mechanism with formation of *N*-fluoroiminopropionitrile [61]. When α-difluoroaminohexafluoroisobutyryl fluoride is acted upon by caesium fluoride, perfluoroacetone *N*-fluoroimine is formed [116].

Certain *N*-fluoroimines have been obtained with the aid of difluoroamine [117,118]:

$$(CH_3)_2C{=}NNHC_6H_5 + HNF_2 \rightarrow (CH_3)_2C{=}NF \text{ and other products}$$



When sodiomalonic ester reacts with F_2NOSO_2F, diethyl *N*-fluoroiminomalonate is formed[119]:

$$NaCH(COOC_2H_5)_2 + F_2NOSO_2F \xrightarrow[CH_3CN]{} FN{=}C(COOC_2H_5)_2 .$$

The formation of *N*-fluoroimines is observed in the reaction of certain α-bromodifluoroamino-derivatives with liquid ammonia[120] or pyridine[48]:

$$C_6H_5CBr_2NF_2 \xrightarrow{\text{liq. } NH_3} C_6H_5CBr(=NF) ;$$

$$C_6H_5CBr(NF_2)CH_2NF_2 \xrightarrow{C_5H_5N} C_6H_5\overset{NF}{\overset{\|}{C}}CN \xleftarrow{C_5H_5N} C_6H_5CBr(NF_2)CN .$$

Treatment of a dialkylfluoroamine (III) with silica gel led to *N*-fluorobenzimidoyl fluoride[121]:

$$\underset{\text{(III)}}{C_6H_5CF_2NFCH(CH_3)CH_2CH_3} \xrightarrow[10^\circ C]{\text{silica gel}} C_6H_5CF(=NF) .$$

N-Fluoroimines have been isolated when $F_2NCCl_2SF_5$ was treated in succession with silver(II) fluoride and water[122] and also after the joint pyrolysis of perfluoro-2-azapropene[123] or perfluoropropene[124] with nitrogen trifluoride over caesium fluoride.

III. PHYSICOCHEMICAL PROPERTIES

The *N*-fluoroimino-compounds known at the present time are in most cases liquids and more rarely gases or solids. They are stable on storage in dry glass vessels, but in a moist atmosphere they may gradually hydrolyse and interact with the glass.

The most complete physicochemical characteristics have been determined for pentafluoroguanidine[30]:

Boiling point, °C	−2, 3 ± 1
Melting point, °C	−148 to −146
Density (Ref.25), g ml^{-1}	1.51 (0°C)
Vapour pressure equation	$\lg p = 7,322 - 1203/T$
Heat of evaporation, kcal mole^{-1}	5.50
Trouton's constant	20.3
Enthalpy of formation (Ref.125), kcal mole^{-1}	+ 23

Liquid column chromatography has been used to isolate pure specimens of this compound[126].

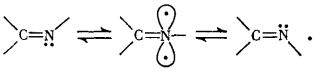
The thermodynamic characteristics of *N*-fluoroimines have been little investigated. It has been found that the enthalpy of formation of *NNN'*-trifluorohexanamidine is -51.653 ± 0.14 kcal mole^{-1}.[127] The corresponding quantity calculated for *N*-fluoromethyleneimine by various methods is 12.4 [128] and 16.1 kcal mole^{-1}.[128,129] The energy of the $n-\pi^*$ transition has been calculated for *N*-fluoromethyleneimine[130] and has been found to be 6.35 eV.

The geometrical parameters of the C=NF group, calculated for the $H_2C{=}NF$, $HFC{=}NF$, $F_2C{=}NF$,[131] and $FN{=}C{=}NF$ structures[132], can serve as approximate values for the entire class of *N*-fluoroimino-compounds. It follows from the calculations that the C=N bond length is 1.26–1.29 Å, the F–N–C bond angle is in the range 108° to 118°, and the N–F bond length is approximately 1.38 Å (approximately 1.25 Å according to other data, but the authors[132] acknowledge that this value is low). The above geometrical parameters for the C=N–F group are close to the corresponding values of the same parameters for related classes of compounds[2,9,133].

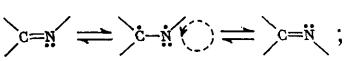
Calculation of the effective charges on the carbon and nitrogen atoms of the C=NF group[131] showed that they vary in the series of compounds $H_2C{=}NF$, $NFC{=}NF$, and $F_2C{=}NF$ from −0.034–+0.389 for the carbon atom and from −0.081 to −0.140 for the nitrogen atom. These results can probably be used, for example, in comparing the reactivities of various *N*-fluoroimines in relation to nucleophiles.

N-Fluoroimines containing non-identical substituents at the carbon atom of the C=NF group can exist in two isomeric forms (*syn*- and *anti*-). These isomers have been isolated in many instances. All three possible isomers of 2,3-bis(fluoroimino)butane[62] and αα-bis-(fluoroimino)bibenzyl[70] have been obtained. The *N*-fluoroimine isomers differ in their physicochemical characteristics, but the differences are small. Thus the *syn*- and *anti*-isomers of 1-cyano-*N*-fluoroformimidoyl fluoride have the following properties respectively: boiling point 2° ± 0.5°C and −3° ± 0.5°C; heat of evaporation 6.58 and 6.34 kcal mole^{-1}; vapour pressure equation $\lg p = -1440/T + 9.13$ and $\lg p = -1390/T + 8.01$.[55,72] The differences between the retention times of the stereoisomers in gas–liquid chromatography permit their isolation in a pure form. The structures of the *N*-fluoroimine isomers can be reliably determined by ^{19}F NMR and mass spectroscopy[27,47,55,62]. In certain cases, *N*-fluoroimines are formed in one (or mainly in one) of the possible isomeric forms. Sometimes this can be explained by the influence of steric factors when one of the substituents at the carbon atom of the fluoroimino-group is large (for example, t-alkyl,[53] SF_5, and $COOCH_3$ [55]) and in other cases by the stereospecificity of the formation of the *N*-fluoroimino-compound[47,86].

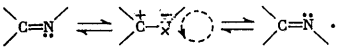
The stereoisomers of *N*-fluoroimines are fairly stable under the usual conditions and also on moderate heating[27]. Theoretical calculations showed that the energy of the isomerisation of the stereoisomers of *N*-fluoroimines is fairly high. Thus it amounts to 32.5 kcal mole^{-1} for *N*-fluoromethyleneimine[134] and 22.4 kcal mole^{-1} for difluorocarbodiimide[132]. These values were obtained on the hypothesis that the isomerisation mechanism involves the transfer of two non-bonding electrons from the nitrogen atom with an sp^2-hybrid orbital to a pure *p* orbital[134]:



Under certain conditions, for example on ultraviolet irradiation, the conversion of one isomeric form of the *N*-fluoroimine into the other may be observed. Thus irradiation of *syn*-bromofluoromethylenefluoroimine[105] and also of *syn,syn*- and *syn,anti*-2,3-bis(fluoroimino)-butanes[62] leads to their isomerisation. The conversion of the *syn*-isomers of *NNN'*-trifluoromonochloroaceto- and *NNN'*-trifluorobutyro-amidines into their *anti*-isomers is observed when the substances are kept in an ethereal solution of HCl.[135] It is suggested that in these instances isomerisation involves the formation of a single C–N bond (which permits rotation of the NF group) via mechanism (2) (on ultraviolet irradiation) or (3) (on treatment with HCl)[134]:



(2)



(3)

NMR Spectra

The presence of the fluorine atom makes it possible to investigate *N*-fluoroimines by ^{19}F NMR. The ^{19}F NMR

spectra have been recorded for the majority of the *N*-fluoroimines describes in the literature and occupy an important place in the determination of their structures.

The chemical shift of the signal due to the ^{19}F nucleus in the C=NF group varies within wide limits, from +60 to −90 p.p.m. (relative to CCl_3F).[5,136] The upper values of this range are characteristic of *N*-fluoroimines containing the C−F bond at the fluoroimino-group. The signals for other *N*-fluoroimines are as a rule observed in weaker fields. The most intense shielding is observed in perfluoromethyleneimine $F_2C{=}NF$,[105] for which $\delta(NF)$ = +67.0 p.p.m. (relative to CCl_3F). The nitrogen and oxygen atoms exhibit a similar shielding effect when they are linked to the C=NF group. The CN group can probably manifest both shielding and deshielding effects[136]. The chemical shifts of the signal due to the ^{19}F nucleus in the *syn*- and *anti*-isomers of *N*-fluoroimines are different, which has been used to determine the stereochemistry of these compounds, particularly in combination with ^1H NMR spectra[27,55]. The ^{19}F NMR spectra of various *N*-fluoroimines have been examined in a review[136].

Infrared Spectra

Two absorption regions in the infrared spectra are characteristic of *N*-fluoroimines, being associated with the presence in these compounds of both the C=N double bond and the N−F bond. The vibrations of the carbon–nitrogen double bond in the majority of *N*-fluorimines are manifested in the range 1600–1680 cm^{-1}. The same absorption region is characteristic also of other compounds with the C=N bond[133]. Hypsochromic and bathochromic shifts of the absorption band due to the multiple bond have been observed for certain *N*-fluoroimines, which is associated with the nature of the substituents at the carbon atom of the fluoroimino-group. For example ν(C−N) is 1745 cm^{-1} for perfluoromethyleneimine[93] and 1553 cm^{-1} for *N*-fluoroiminomalonodinitrile[72].

The vibration of the N−F bond is manifested by one or two bands[55] in the range 840–1000 cm^{-1}. When other nitrogen–fluorine bonds are present in the *N*-fluoroimine, the absorption in this region is more complex[5].

The absorption bands corresponding to identical bonds in the geometrical isomers of *N*-fluoroimines have similar positions[53,55,62,72,79,137] and in certain cases the infrared spectra of the isomers may be identical[27].

Mass Spectra

Mass spectrometry is being used on an increasingly wide scale as a physicochemical method for the investigation of *N*-fluoroimines[23,25,26,28,30,35,39,41,55,62,91,137–139]. However, the number of studies in which mass spectra were used as the main method for the determination of the structures of *N*-fluoroimines is extremely limited. Mention may be made of only one study[62], where mass spectrometry was used to elucidate the structure of the isomers of 2,3-bis(fluoroimino)butane.

Explosive Properties

Organic *N*-fluoroimines exhibit explosive properties to a greater or lesser extent. Compounds containing difluoroamino-groups together with the fluoroimino-group are particularly sensitive to external influences and properties of this kind are enhanced with increase of the number of difluoroamino-groups[5]. Pentafluoroguanidine is extremely explosive[25]. Explosions of this compound have been observed on friction, impact, and following other external influences, as well as in phase transitions (this happens particularly frequently on fusion). Studies involving such compounds require special precautions.

IV. CHEMICAL PROPERTIES

Among organic derivatives of nitrogen containing the N−F bond, *N*-fluoroimines have been found to be the most reactive. The wide variety of reactions in which these compounds may be involved is in many respects determined by the presence of the C=N double bond. These include in the first place numerous reactions with nucleophiles and electrophiles and also oxidation, reduction, etc. reactions.

1. Hydrolysis

The hydrolysis of pentafluoroguanidine and tetrafluoroformamidine has been investigated in greatest detail[25,30,31,126,140]. In contrast to the hydrolytically stable saturated difluoroaminoalkanes, these compounds are hydrolysed comparatively readily. Pentafluoroguanidine and tetrafluoroformamidine react particularly rapidly and exothermically with aqueous solutions of alkalis[30,140]; the reaction is accompanied by the evolution of an equivalent amount of nitrogen, which is used for the gas-volumetric analysis of these compounds[126]. The hydrolysis of pentafluoroguanidine and tetrafluoroformamidine on treatment with water proceeds over a period of several hours and the compounds react even more slowly with concentrated sulphuric acid. The hydrolysis products in the latter two cases are carbon dioxide, difluoroamine, hydrogen fluoride, and hydroxylamine. When pentafluoroguanidine reacts with concentrated hydrochloric acid, chlorodifluoroamine is also formed[140].

The hydrolysis of *N*-fluoroimidoyl fluorides of perfluorocarboxylic acids leads to the formation of the corresponding acids[16,141]:

$$R_fCF{=}NF \xrightarrow{H_2O} R_fCOOH\ ;$$

$$R_f{=}CF_3,\ \text{or}\ CF_2NF_2\ .$$

It has been shown for *N*-fluoroimidoyl fluoride derived from difluoroaminodifluoroacetic acid[11,141,142] that the first stage of the reaction involves the formation of the *N*-fluoroimidic acid (IV), whose structure has been demonstrated by ^{19}F NMR, infrared spectroscopy, and reaction with diazomethane. The attempts to isolate the *N*-fluoroimidic acid in a free form were unsuccessful:

$$F_2NCF_2\overset{\overset{NF}{\|}}{C}F \xrightarrow[\text{ether}]{H_2O} \left[F_2NCF_2\overset{\overset{NF}{\|}}{C}OH\right] \xrightarrow[\text{ether}]{CH_2N_2} F_2NCF_2\overset{\overset{NF}{\|}}{C}OCH_3\ .$$

(IV)

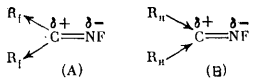
It has also been noted that *C*-chlorodifluoroformimine may be stored over water for 50 h without appreciable decomposition[93], while perfluoroketone *N*-fluoroimines do not change on contact with concentrated sulphuric or fluorosulphonic acid[11].

The hydrolysis of hydrogen-containing *N*-fluoroimines has been described in only two instances. Cyclohexanone was obtained on boiling *N*-fluoroiminocyclohexane with 2 M aqueous sulphuric acid[59]. Similarly, butyl methyl

carbonate is formed in the hydrolysis of butyl methyl *N*-fluoroiminocarbonate[57] with an aqueous-alcoholic solution of HCl.

2. Reactions with Nucleophiles

The reactivity of *N*-fluoroimines in relation to nucleophiles is determined by the polarisation of the C=N bond, which is responsible for the electron deficiency at the carbon atom and depends to a large extent on the nature of the substituents linked to this atom. Substituents manifesting a $-I$-effect (A) increase the reactivity of *N*-fluoroimines in relation to nucleophiles, while those with a $+I$-effect (B) reduce it:



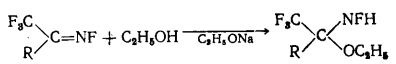
(A) (B)

Substituents such as perfluoroalkyl, NF_2, halogeno-, etc. ensure the highest reactivity in relation to nucleophiles.

A diminution of the nucleophilic properties of the given reactant hinders its reaction with the *N*-fluoroimine. This is shown most clearly in the interaction of *N*-fluoroimines with alcohols and amines[143,144]. In the reactions with substances showing reduced nucleophilic properties, basic catalysts are usually employed (triethylamine, pyridine, urea, etc.).

The addition of nucleophiles begins with anionic attack on the positively polarised carbon atom of the C=NF group with a simultaneous shift of the π electrons of the C=N bond to the nitrogen atom. On treatment with nucleophiles having a mobile hydrogen atom, which are most frequently used in these reactions (for example alcohols, amines, hydrogen cyanide, nitrous acid, etc.), the corresponding *N*-fluoroamino-derivatives are formed. They are sometimes fairly stable and their presence has been demonstrated by various methods of physicochemical analysis; in other instances, these compounds undergo further reactions, which depend on their structure, reaction conditions, and other factors.

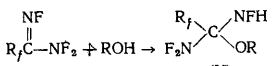
Alcohols. Perfluoroketone *N*-fluoroimines and nitriles of α-fluoroiminoperfluorocarboxylic acids are capable of combining with aliphatic alcohols at the C=N bond in the presence of sodium alkoxide[11,142,145,146]. The resulting *gem*-fluoroaminoalkoxy-derivatives are fully stable on storage and distillation:



R=CF_3 or CN.

The reaction of perfluoroketone *N*-fluorimines is reversible and, on binding the alcohol (for example, with acetic anhydride) as the acetate[143], the equilibrium may be displaced towards the formation of the initial *N*-fluoroimine.

Pentafluoroguanidine[32,45,143,147-159] and perfluoroamidines[27] also give rise to the addition products (V) in reactions with alcohols:

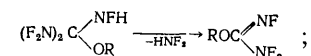


(V)

$R_f = NF_2$, C_3F_7, or CF_2NO_2.

In addition, pentafluoroguanidine is capable of forming adducts also with other compounds containing the hydroxy-group (organic acids, oximes, hydroxamic acid, amidoximes, as well as phenols with electronegative substituents, etc.)[143,154]. Methyl and ethyl alcohols, which are highly nucleophilic, react extremely vigorously with pentafluoroguanidine under the usual conditions. On the other hand, alcohols with electronegative substituents and carboxylic acids require the use of a basic catalyst (urea, triethylamine, and pyridine) for the reaction to reach completion. Trifluoroacetic acid does not react with pentafluoroguanidine under analogous conditions.

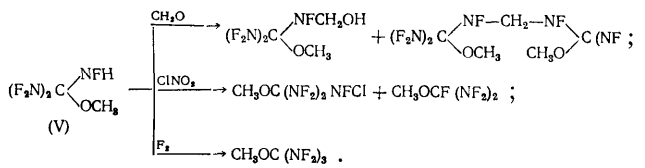
The products of the addition of alcohols to pentafluoroguanidine are converted into the corresponding alkoxytrifluoroformamidines on heating or on treatment with metal fluorides (NaF, AgF_2) as a result of the elimination of difluoroamine[32,143,154]. In certain other cases, this reaction proceeds spontaneously:



R=CH_3, $CH(CH_3)_2$, or CH_2CO.

The products of the addition of alcohols to perfluoroamidines are stable only in solutions, from which they cannot be isolated[27].

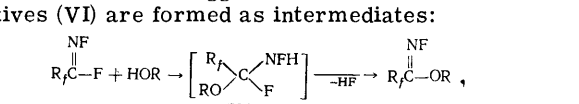
The hydrogen atom of the fluoroamino-group in compounds of type (V) is fairly mobile and capable of being substituted by other atoms or groups of atoms, for example[143]:



(V)

The last reaction has found extensive applications in the synthesis of tris(difluoroamino)methyl ethers from the corresponding bis(difluoroamino)fluoroaminoalkoxy-derivatives obtained by the interaction of pentafluoroguanidine with alcohols such as ethylene glycol, glycerol[154], methanol and ethanol[143,147,159], ethanol ammonium perchlorate[149,150,155], 2,2-dinitropropane-1,3-diol[157], tris(hydroxymethyl)nitromethane[152], 2,3-bis(hydroxymethyl)oxiran[148,151,153], tetrakis(hydroxymethyl)phosphonium chloride[45], trinitroethanol[158], alcohols containing the difluoroamino-group[154,156], and acetone oxime[143]. Ethers containing the difluoroamino-group have also been obtained by fluorinating the products of the addition of methanol to perfluoroamidines[27].

The products of the interaction of alcohols with *N*-fluoroimidoyl fluorides derived from perfluorocarboxylic acids and 1-cyano-*N*-fluoroformimidoyl fluoride are the corresponding *N*-fluoroimino-ethers[72,74,141,143,145]. It has been suggested[143] that fluoroamino-derivatives (VI) are formed as intermediates:

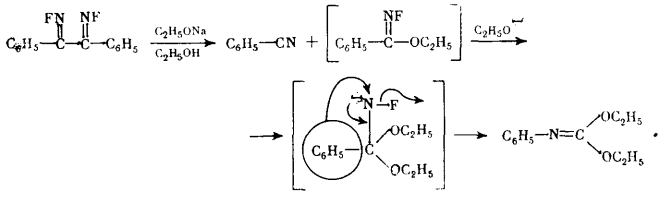


(VI)

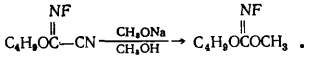
$R_f = CF_3$, CF_2NF_2, or CN.

N-Fluoroimines containing alkyl or aryl substituents at the carbon atom are less reactive in reactions with alcohols. Thus, whereas *NNN'*-trifluoroamidines derived from perfluorocarboxylic acids combine smoothly with alcohols (see above), *NNN'*-trifluoroamidines derived from non-fluorinated acids do not react with alcohols even in the presence of a catalyst[27].

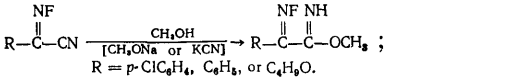
The reactions of *N*-fluoroimines containing alkyl or aryl substituents proceed as a rule in the presence of an excess of the alkoxide and may be accompanied by the rearrangement of the carbon skeleton of the molecule. Thus, on treatment of α-fluoroiminoarylacetonitriles with an excess of sodium alkoxide in alcohol, mixtures of the corresponding aryl cyanide and *N*-aryliminocarbonates are formed[57,58]. Analogous products have been obtained from αα-bis(fluoroimino)bibenzyl[70]. The reaction mechanism apparently involves a rearrangement similar to that of the Beckmann rearrangement, for example:



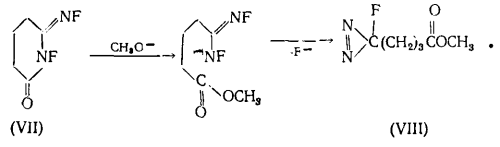
Under analogous conditions, the cyano-group of α-fluoroiminobutoxyacetonitrile exhibits pseudohalogen properties and is replaced by the methoxy-group[57]:



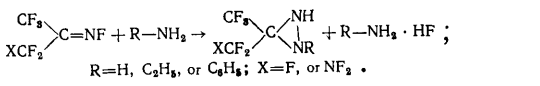
On the other hand, the reaction of α-fluoroiminoaryl- and α-fluoroiminobutoxy-acetonitriles with methyl or ethyl alcohol in the presence of catalytic amounts of potassium alkoxide or cyanide is completed by the formation of the imino-esters of α-fluoroiminocarboxylic acids as a result of the addition of the alcohol to the C≡N group and does not involve the fluoroimino-group[57]:



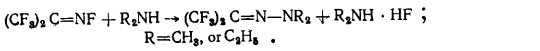
When the fluoroimine (VII) reacts with sodium methoxide, the diazirine (VIII) is formed[67]:



Amines. Perfluoroketone and *N*-fluoroimines react readily with ammonia and primary amines at a temperature as low as −78°C, forming the corresponding diaziridines[11,142,144-146]:



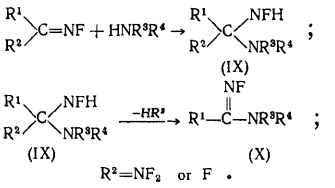
In the reactions with secondary amines, the main products are *NN*-dialkylhydrazones of perfluoroketones[11,142,144,146]:



It is suggested that these products are obtained as a result of complex reactions of the unstable geminal amino-fluoroamino-derivatives formed in the first stage[11,144]. The mechanism of these reactions has been examined in detail in a review[11].

The reactions of the nitriles of α-fluoroiminoperfluoro-carboxylic acids with amines usually lead to similar results. However, the reactions with primary amines yield, together with diaziridines, *N*-alkyl-*N'*-fluoro-amidines owing to the manifestation of pseudohalogen properties by the cyano-group[11,142].

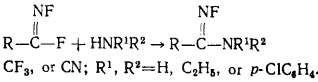
The interaction of ammonia and amines with penta-fluoroguanidine[32,144,154,159-162], perfluorobiguanide[161,162], *N*-fluoroiminomalonodinitrile[137], 1-cyano-*N*-fluoroform-imidoyl fluoride[137], cyanoperfluoroformamidine[37,137,159,160,162,163], bis(difluoroamino)fluoromethylazotrifluoroform-amidine[107], α-fluoroiminoperfluorovaleronitrile[37], tetrafluoroformamidine[144], and *N*-fluorotrifluoroacet-imidoyl fluoride[144] has also been investigated. The *N*-fluoroimines enumerated above give rise to products of type (IX) in their reactions with amines. In certain cases, these products can be converted into new *N*-fluoroimines (X) as a result of the elimination of difluoroamine or hydrogen fluoride:



The interaction of *N*-fluoroimines with amines is promoted by the use of polar solvents such as acetonitrile, dimethyl ether, and tetrahydrofuran[144].

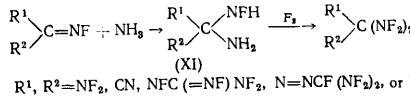
This reaction has been investigated in greatest detail in relation to pentafluoroguanidine, which proved to be reactive with respect to not only amines but also other compounds containing the N−H bond (carboxylic acid amides, imides, and amidines, nitroamines, hydrazine derivatives, etc.)[32,144,159]. The stability of the product of the addition of the amine to pentafluoroguanidine is determined by the nature of the amine involved in the reaction[144]. For example, the interaction of pentafluoroguanidine with ammonia and *p*-cyano- and *p*-trifluoromethyl-anilines gives rise to adducts which are stable at low temperatures. On being heated to room temperature, they lose difluoro-amine with formation of the corresponding trifluoro-guanidines. The products of the addition of more basic amines are unstable even at low temperatures. Thus reactions with n-butylamine and dimethylamine result in the formation of alkyltrifluoroguanidines even at −78°C.

When amines react with *N*-fluoroimidoyl fluorides, *N*-fluoroamidines are formed as a result of the elimination of HF from the intermediate addition product[55,72,144]:



On the other hand, the products of the addition of ammonia to 1-cyano-*N*-fluoroformimidoyl fluoride can apparently exist at low temperatures[128].

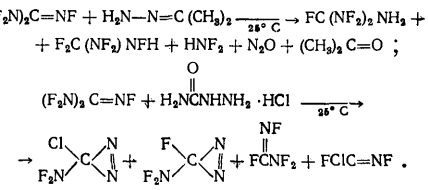
Among the entire wide variety of the products of the addition of amines to *N*-fluoroimines, the ammonia addition products (XI) have now found practical application. It has been shown in numerous instances that the hydrogen atoms in the amino- and fluoroamino-groups of these compounds can be substituted by fluorine atoms[37,107,137,144,159-163]:



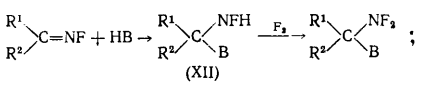
This reaction led to the synthesis of many new difluoro-amino-derivatives. The reaction with pentafluoroguanidine

yielded a compound containing the maximum possible number of difluoroamino-groups at a single carbon atom—tetrakis(difluoroimino)methane [144,159-162].

Pentafluoroguanidine reacts with acetone hydrazone and semicarbazide hydrochloride, forming a complex mixture of products as a result of the decomposition and rearrangement of the intermediates [144]:



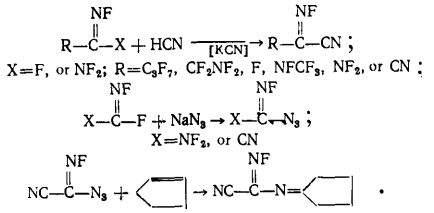
Other nucleophiles. Reactants with less pronounced nucleophilic properties such as HN_3,[164] HNCO,[36,165-170] HCN,[11,32,37,137,142] HBr,[138] and HF [143] have also been used in the reactions with *N*-fluoroimines. Their products are mainly the corresponding *N*-fluoroamino-derivatives (XII), which are converted into difluoroamino-compounds on fluorination with elemental fluorine [36,37,138,143,164,167-170]:



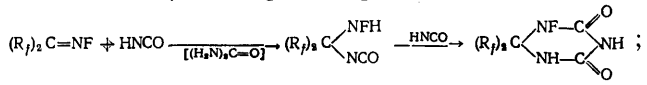
(XII)

(a) B=N_3; R^1=F, or NF_2; R^2=F, NF_2, N_3;
(*b*) B=Br, or NCO*, F; $R^1=R^2=NF_2$;
(c) B=CN; $R^1=R^2=CF_3$ (not fluorinated).

The reaction with a nucleophile sometimes results in the formation of a substitution and not an addition product. This happens when hydrogen cyanide reacts with pentafluoroguanidine [32,37,137], cyanotrifluoroformamidine [137], and *N*-fluoroimidoyl fluorides from perfluorocarboxylic acids [11,37] in the presence of catalytic amounts of potassium cyanide and also on treatment of tetrafluoroformamidine [171] and 1-cyano-*N*-fluoroformimidoyl fluoride [55,72] with NaN_3. The 1-cyano-*N*-fluoroformimidoyl azide formed in the latter case is stable only in solution; on treatment with cyclopentene, it yields 1-cyano-*N*-cyclopentylidene-*N'*-fluoroformamidine [55,72]:



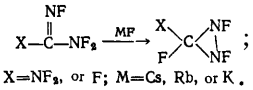
The addition of isocyanic acid to *N*-fluoroimines leads to *N*-fluoroamino-derivatives which react with a second HNCO molecule, forming cyclic products (XIII): [144,165]



(XIII)

R_f=CF_3, or NF_2.

On treatment with alkali metal fluorides, pentafluoroguanidine and tetrafluoroformamidine isomerise to diaziridines [35,88,172,173]:

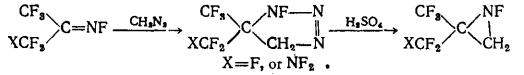


X=NF_2, or F; M=Cs, Rb, or K.

† The second fluorination product is $C(NF_2)_4$.

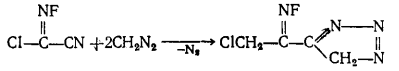
Caesium fluoride is most reactive in this process. The reaction involving tetrafluoroformamidine results in the formation, together with the diaziridine, of a dimer whose structure has not been finally established [172,173].

Perfluoroketone *N*-fluoroimines react with diazomethane even in the cold, forming triazolines, which can be converted into the corresponding aziridines [11,142]:

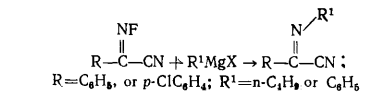


X=F, or NF_2.

1-Cyano-*N*-fluoroformimidoyl chloride reacts with two moles of diazomethane [11,142]:



The interaction of α-fluoroiminoarylacetonitriles with organomagnesium compounds leads to *N*-substituted α-iminonitriles in low yields [57]. α-Fluoroiminobutoxyacetonitrile does not undergo this reaction:

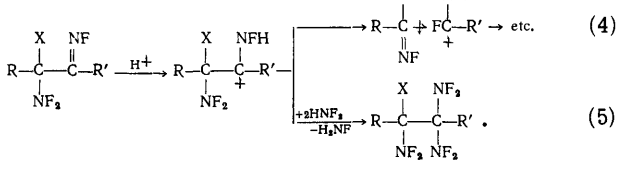


R=C_6H_5, or *p*-ClC_6H_4; R^1=n-C_4H_9 or C_6H_5

3. Reactions with Electrophiles

The reactions of *N*-fluoroimines with electrophiles have been less thoroughly investigated. Reactions with electrophiles are characteristic of *N*-fluoroimines in which the carbon atom of the C=NF group is linked to hydrogen-containing alkyl or aryl groups. Among these reactions, those of strong inorganic acids and Lewis acids with α-difluoroaminofluoroimines have been studied in greatest detail [65,66,69,80,174,175].

In principle, the site of attack by the electrophile may be the nitrogen atom or the fluorine atom of the fluoroimino-group. In the former case, treatment with inorganic acids should lead to the formation of the cation $\overset{+}{C}-NFH$. This cation, which has been obtained, for example, from α-(difluoroamino)fluoroimine, could decompose by mechanism (4) (similarly to the decomposition of, for example, 1-diethylphosphato-2-difluoroamino-derivatives in an acid medium [68]); in the presence of a difluoroamine, reaction via mechanism (5) is also possible [66]:



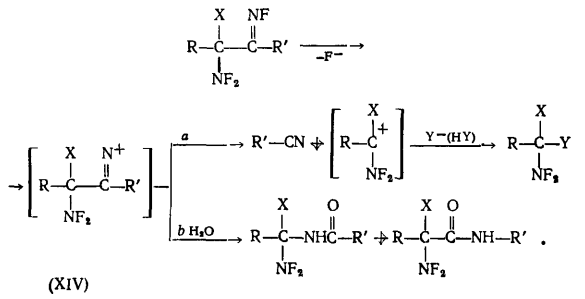
(4)

(5)

However, this mechanism has not been demonstrated experimentally, although the possibility of its occurrence under certain conditions cannot be ruled out.

It is generally accepted that the primary step in the reactions under consideration is attack by the electrophile on the fluorine atom of the fluoroimino-group, leading to the formation of a complex as a result of donor–acceptor interaction between a molecule of the *N*-fluoroimine and the electrophile [2]. The decomposition of this complex leads to the formation of a cation (XIV) with a sextet of electrons at the nitrogen atom. The carbon skeleton of

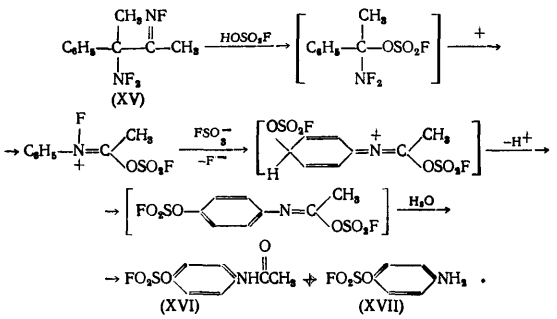
the initial molecule is then cleaved with formation of a carbonium ion (pathway *a*), whose further reaction depends on the reaction conditions. The second pathway (pathway *b*) involves a rearrangement analogous to the Beckmann rearrangement, and is completed by the formation of the corresponding amides. Cases are known where both pathways operate simultaneously:



(XIV)

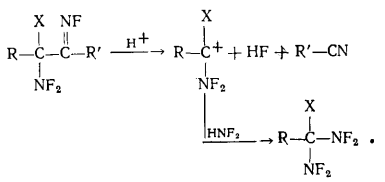
The reaction of α-difluoroaminofluorimines with boron trifluoride[66,69] leads to compounds containing a $\rangle C(NF_2)F$ group (pathways *a*).

The mechanism of the reaction between 2-difluoroamino-3-fluoroimino-2-phenylbutane (XV) and fluorosulphonic acid is more complex[65,69,175], the product of this reaction being *p*-fluorosulphonyloxyacetanilide (XVI) and *p*-fluorosulphonyloxyaniline (XVII):



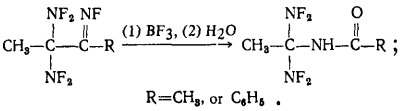
(XV) (XVI) (XVII)

The intermediate α-difluoroaminocarbonium ion formed in the reactions is stabilised by combining with fluoride or fluorosulphonate ions. However, it can also be stabilised by reaction with other substances present in the reaction medium[176,177]. Thus difluoroamine is alkylated by the carbonium cation with formation of *gem*-bis(difluoroamino)-derivatives:

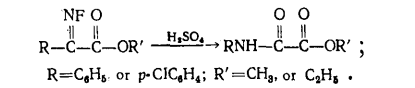


This method made it possible to synthesise many hitherto unobtainable geminal derivatives, such as 1-halogeno-1,1-bis(difluoroamino)- and 1,1,1-tris(difluoroamino)alkanes[66,174], which could not be obtained from the corresponding carbonyl compounds. Fluorosulphonic acid proved to be the most effective reagent in these reactions, but in certain cases the best yields of the final products were obtained using concentrated sulphuric acid.

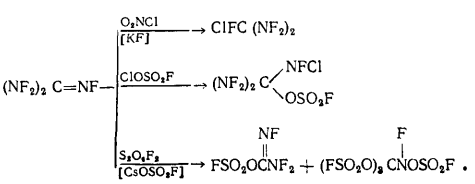
The interaction of $\alpha\alpha$-bis(difluoroamino)fluoroimines with BF_3 proceeds via pathway *b* with formation of the corresponding amides[66]:



The interaction of α-fluoroiminoarylacetate esters with concentrated sulphuric acid leads to analogous results[57]:



N-Fluoroimines containing electronegative substituents at the carbon atom of the C=NF group (perfluoroalkyl, fluoro-, difluoroamino-, and other groups) are less reactive in reactions with electrophiles. This is indicated, for example, by the inertness of perfluoroacetone *N*-fluoroimine in relation to concentrated sulphuric acid and fluorosulphonic acid[11]. At the same time, *N*-fluoroimines of this kind can be involved in reactions with stronger electrophiles. For example, the reactions of pentafluoroguanidine with nitryl chloride[178], chlorine fluorosulphate[179], and peroxydisulphuryl difluoride[180] are known, but their mechanisms have not been elucidated:



4. Oxidation and Reduction Reactions

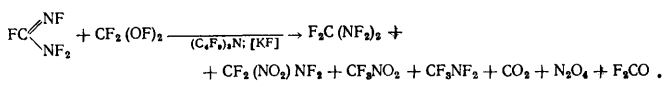
In view of the degree of oxidation of the nitrogen atom in the C=NF group, *N*-fluoroimines are capable of undergoing both oxidation and reduction reactions; reactions of the latter type are more characteristic of these compounds, owing to the presence of the relatively weak nitrogen–fluorine bond (bond energy 65–75 kcal mole^{-1}).

In the presence of the NF_2 group in the α-position relative to the fluoroimino-group, the behaviour of each of these groups with respect to oxidants and reductants will be different, since the nitrogen atom in the difluoroamino-group is in a higher state of oxidation than in the fluoroimino-group. The first stage of the reactions of geminal difluoroaminofluoroimino-compounds with reductants therefore probably proceeds via the NF_2 group and that with oxidants via the =NF group.

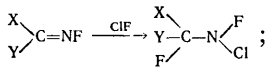
The available literature information about the oxidation of *N*-fluoroimines is mainly restricted to the reactions of pentafluoroguanidine. Under the usual conditions, pentafluoroguanidine is resistant to the action of gaseous fluorine[166] and also of solid potassium permanganate and silver vanadate[103]. Concentrated nitric acid[103] and aqua regia[99,103,140] decompose pentafluoroguanidine to carbon dioxide, hydrogen fluoride, and nitrogen oxides. In the latter case, dichlorobis(difluoroamino)methane is also formed. When pentafluoroguanidine reacts with manganese dioxide, mainly the *cis*- and *trans*-isomers of difluorodiazine are formed[95].

Talbot and Koshar investigated the oxidation of pentafluoroguanidine, trifluoro-*C*-halogenoformamidines, and perfluoroamidines by perfluoroalkyl hypofluorites in the

presence of catalytic amounts of potassium fluoride or cyanide [28,29,139]. These reactions proceed in an extremely complex manner via different pathways and involve the formation of fluorination, oxidation, and degradation products, for example:



When chlorine fluoride reacts with *N*-fluorohalogenoformimines, the corresponding (chlorofluoroamino)-halogenomethanes are formed readily as a result of the addition of a ClF molecule to the C=N bond of the initial imine [97]:

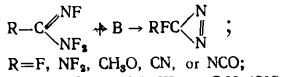


X, Y=F or Cl.

The reaction involving perfluoroacetone *N*-fluoroimine proceeds only in the presence of caesium fluoride [97].

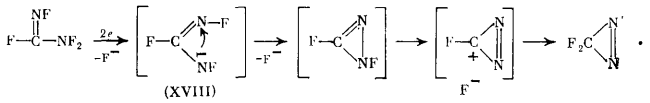
N-Fluoroimines readily react with various reductants. For example, they vigorously evolve iodine from aqueous solutions of potassium iodide [32,103,126], which may be used as a qualitative test for these compounds. The products of the reduction of *N*-fluoroimines in these reactions have not been determined in most cases. On the other hand, it has been shown that, when perfluoroacetone *N*-fluoroimine is treated with an aqueous acetonitrile solution of potassium iodide in the presence of acetic acid, perfluoroacetone and ammonia are formed [100].

The reduction of *N*-fluoroimines containing the trifluoroguanyl group by ferrocene [88,102,181], diphenylamine, hydroquinone [88,103,181] and potassium iodide [88,103] in various solvents leads to the formation of diazirines:



R=F, NF_2, CH_3O, CN, or NCO;
B= $(C_6H_5)_2Fe$, $(C_6H_5)_2NH$, KI, or $C_6H_4(OH)_2$.

Despite the fact that the yields of products are low, this reaction proved to be convenient for the synthesis of various diazirines [88]. The proposed reaction mechanism includes the reduction of the NF_2 group with elimination of the fluoride ion and the formation of the anion (XVIII) capable of cyclising to *N*-fluorodiazirine. The subsequent rearrangement, apparently via the intermediate diazirinium cation, is completed by the formation of the final product [102]:

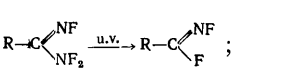


(XVIII)

5. Pyrolysis and Photolysis

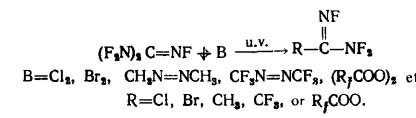
The pyrolysis of *N*-fluoroimines has been studied only in relation to pentafluoroguanidine and tetrafluoroformamidine [25,30,31]. It has been established by differential thermal analysis that these compounds are thermally less stable than the corresponding poly(difluoroamino)perfluoromethanes [30]. Rapid decomposition of pentafluoroguanidine is observed at 243°C and that of tetrafluoroformamidine at 208°C. Slow decomposition of pentafluoroguanidine begins only at 205°C. The main products of the decomposition of these compounds are CF_4, NF_3, and N_2.

The photolysis of *N*-fluoroimines has been studied in greater detail. Thus, it has been found that irradiation of compounds with the trifluoroguanyl group by ultraviolet light leads to the substitution of the difluoroamino-group by fluorine [38]:



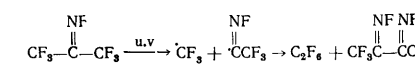
R=F, NF_2, or C_2F_7.

In the presence of compounds capable of generating a radical species such as chlorine and bromine atoms, trifluoromethyl radicals, etc., the difluoroamino-group can be substituted by them [32,38,88], which constitutes the basis of the method for the synthesis of various *NNN'*-trifluoroamidines from pentafluoroguanidine [32]:

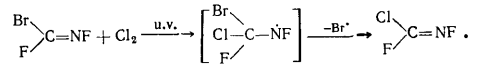


B=Cl_2, Br_2, $CH_3N{=}NCH_3$, $CF_3N{=}NCF_3$, $(R_fCOO)_2$ etc ;
R=Cl, Br, CH_3, CF_3, or R_fCOO.

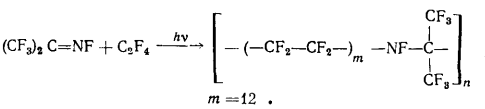
When perfluoroacetone *N*-fluoroimine was irradiated with ultraviolet light *in vacuo*, hexafluoroethane was identified in the reaction product; it may be formed via the following mechanism [91]:



The primary step in the above photolytic reactions is the decomposition of the initial *N*-fluoroimine into two radicals, one of which contains the fluoroimino-group. The recombination of this radical with other radicals leads to various *N*-fluoroimino-compounds. At the same time, the photolytic reactions of *N*-fluoroimines can proceed via a mechanism involving the initial addition of the radical species to the C=N bond. This mechanism has been proposed, for example, for the formation of *C*-chlorodifluoromethyleneimine on irradiation of *C*-bromodifluoromethyleneimine in the presence of chlorine [97]:



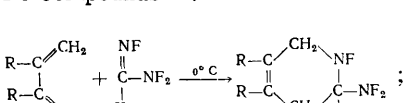
The interaction of perfluoroacetone *N*-fluoroimine with tetrafluoroethylene on γ-irradiation is completed via the formation of the corresponding copolymer [91]:



m =12 .

6. Other Reactions

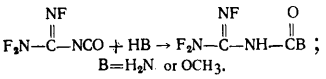
Pentafluoroguanidine and tetrafluoroformamidine readily undergo the Diels–Alder reaction with formation of heterocyclic compounds [182]:



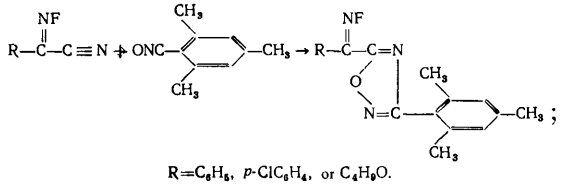
X=F or NF_2; R=H, CH_3 etc.

In the presence of catalytic amounts of caesium fluoride, perfluoroguanidine reacts with formaldehyde [183], forming the copolymer $[(F_2N)_2CNF(CH_2O)n]y$, where $n = 1-6$ and $y > 1$.

If the functional group in the *N*-fluoroimine molecule is more reactive than the C=NF group, then frequently only the former reacts, while the C=NF group remains unchanged. Thus, the reaction of trifluoroguanyl isocyanate with methanol and ammonia involves the isocyanate group [184]:

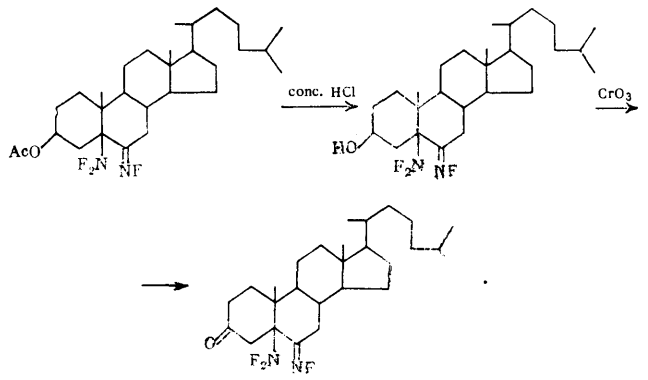


The cyano-group in α-fluoroiminoaryl- and α-fluoroiminobutoxy-acetonitriles can be involved in the 1,3-cycloaddition reactions with a nitrile oxide [57]:

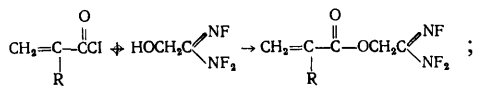


R=C_6H_5, *p*-ClC_6H_4, or C_4H_9O.

The acetoxy-group in 3β-acetoxy-5-difluoroamino-6-(fluoroimino)cholesterol can be hydrolysed to the hydroxy-group, which may be oxidised to the oxo-group [76]:

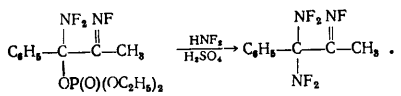


2-Difluoroamino-2-fluoroiminoethanol is acylated by acryloyl and methacryloyl chlorides [64]:



R=H or CH_3.

When α-(diethoxyphosphoryloxy)-α-difluoroamino-fluoroimines are treated with difluoroamine in the presence of concentrated sulphuric acid, the phosphoryloxy-group is replaced by the difluoroamino-group [66,68]:



α-Acetoxy-α-difluoroaminofluoroimines are decomposed under analogous conditions [66,68,81].

V. CERTAIN ASPECTS OF PRACTICAL APPLICATIONS

Judging from the literature data, the interest in the synthesis of *N*-fluoroimines is mainly associated with the search for new components of rocket fuels and explosives. *N*-Fluoroimines usually serve as the starting materials for further syntheses. Pentafluoroguanidine is most frequently used for this purpose; it has led to the synthesis of compounds regarded as oxidants of rocket fuels [tetrakis(difluoroamino)methane [144,159-162], tris(difluoroamino)methyl ethers derived from nitroalcohols [152,157,158], bis(difluoroamino)fluoronitromethane [28,139], etc. as well as energetically suitable binders or plasticisers for solid rocket fuels [37,148-151,156,158,182,183]. In certain cases, *N*-fluoroimines are themselves regarded as components of rocket fuels, for example *NNN'*-trifluoroformamimidine [23], 2,3,5,6-tetrakis(fluoroimino)piperazine [118], trifluoroguanyl isocyanate and its derivatives [184], perfluorobiguanide, and 1-[bis(difluoroamino)fluoromethyl]-1,2,3,3,-tetrafluoroguanidine [18-20,40]. A mixture of pentafluoroguanidine with nitrogen oxides has been proposed as an oxidant for rocket fuels [21]. Certain *N*-fluoroimino-compounds containing a large number of oxidising groups have been suggested as explosives [23,24] or as starting materials for the synthesis of the latter [137,160-163].

Physiologically active substances have been found among *N*-fluoroimines. For example, difluoroamino-fluoroiminosteroids inhibit the growth of the prostate gland [76]. Fluoroiminocycloalkanes and fluoroiminocycloalkenes are regarded as intermediates for the synthesis of bactericidal preparations [78].

The use of *N*-fluoroimines as monomers for copolymerisation and as polymerisation initiators is of definite interest. Thus perfluoroacetone *N*-fluoroimines readily copolymerises with tetrafluoroethylene, forming a thermoplastic polymer, whose properties are close to those of Teflon [91]. 1,2-Bis(fluoroimino)-compounds are capable of initiating the polymerisation of, for example, ethylene and tetrafluoroethylene [79]. A number of patents are devoted to the employment of *N*-fluoroimines (mainly perfluoro-derivatives) for the synthesis of diazirines [35,88,99,181], which are potential monomers and sources of biradicals.

Certain *N*-fluoroimines have been suggested as corrosion inhibitors [72], bleaching agents [24], and oxidants in chemical reactions [23].

REFERENCES

1. J. Hoffman and R. G. Neville, Chem. Rev., 62, 1 (1962).
2. A. V. Fokin and Yu. M. Kosyrev, Chem. Rev., 35, 1897 (1966).
3. J. K. Ruff, Chem. Rev., 67, 665 (1967).
4. A. V. Fokin and Yu. M. Kosyrev, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 15, 81 (1970).
5. J. P. Freeman, "Advance in Fluorine Chemistry" London, 1970, Vol. 6, p. 287.
6. A. M. Lovelace, D. Roach, and W. Postelneck, "Aliphatic Fluorine Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1961.
7. M. Hudlicky, "Chemie Organickych Sloucenin Fluoru" (Chemistry of Organic Fluorine Compounds) (Translated into Russian), Goskhimizdat, Moscow, 1961.
8. W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1972.
9. A. V. Pankratov, "Khimiya Ftoridov Azota" (The Chemistry of Nitrogen Fluoride), Izd. Khimiya, Moscow, 1973.
10. A. V. Fokin, Yu. N. Studnev, and L. D. Kuznetsova, "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods of Investigation of Organic Compounds), Izd. Khimiya, Moscow, Book 24, pp. 7–466.

11. B.L.Dyatkin, K.N.Makarov, and J.L.Knunyants, Tetrahedron, 27, 51 (1971).
12. R.N.Haszeldine, Research (London), 4, 338 (1951).
13. J.A.Cuculo and L.A.Bigelow, J.Amer.Chem.Soc., 74, 710 (1952).
14. J.A.Attaway, R.H.Grot., and L.A.Bigelow, J.Amer.Chem.Soc., 81, 3599 (1959).
15. B.C.Bishop, J.B.Hynes, and L.A.Bigelow, J.Amer.Chem.Soc., 86, 1827 (1964).
16. J.B.Hynes, B.C.Bishop, B.Y.Pranaw, and L.A.Bigelow, J.Amer.Chem.Soc., 85, 83 (1963).
17. US.P.3 450 762 (1969).
18. US.P.3 350 448 (1967).
19. US.P.3 367 968 (1968).
20. US.P.3 555 094 (1971).
21. US.P.3 354 011 (1967).
22. US.P.3 410 853 (1968).
23. US.P.3 393 238 (1968).
24. US.P.3 326 889 (1967).
25. R.A.Davis, J.L.Kroon, and D.A.Rausch, J.Org. Chem., 32, 1667 (1967).
26. D.A.Rausch and J.J.Hoekstra, J.Org.Chem., 33, 2522 (1968).
27. D.L.Ross, C.L.Coon, and M.E.Hill, J.Org. Chem., 35, 3093 (1970).
28. US.P.3 387 033 (1968).
29. US.P.3 541 128 (1970).
30. R.J.Koshar, D.R.Husted, and C.D.Wright, J.Org.Chem., 32, 3859 (1967).
31. R.J.Koshar, D.R.Husted, and C.D.Wright, "Abstracts of the 4th International Symposium on Fluorine Chemistry, Esters Park, Colorado, 1967", p.30.
32. US.P.3 726 903 (1973).
33. US.P.3 461 162 (1969).
34. US.P.3 564 562 (1971).
35. US.P.3 345 359 (1967).
36. US.P.3 699 094 (1972).
37. US.P.3 394 142 (1968).
38. US.P.3 403 087 (1968).
39. US.P.3 548 000 (1970).
40. US.P.3 361 815 (1968).
41. J.B.Hynes, T.E.Austin, and L.A.Bigelow, Inorg. Chem., 7, 1647 (1968).
42. US.P.3 399 234 (1968).
43. J.K.Ruff, J.Org.Chem., 32, 1675 (1967).
44. V.Grakauskas, Intra-Science Chem.Report, 5, 85 (1971).
45. US.P.3 548 003 (1970).
46. US.P.3 372 192 (1968).
47. V.Grakauskas and K.Baum, J.Org.Chem., 34, 2840 (1969).
48. V.Grakauskas and K.Baum, "V Mezhdunarodnyi Simpozium po Khimii Ftora, Tezisy Dokladov" (The Vth International Symposium on Fluorine Chemistry. Abstracts of Reports), Izd.Nauka, Moscow, 1969, p.8.
49. W.Hückel, Nachr.Akad.Wiss, Gottingen, Math.-Physik Klasse, 55, No.1 (1946).
50. D.H.R.Barton, R.H.Hesse, M.M.Pechet, and T.Toh Hee, J.Chem.Soc., Perkin Trans.I, 732 (1974).
51. A.V.Fokin, Yu.M.Kosyrev, N.P.Novoselov, and N.A.Brusentsova, Zhur.Obshch.Khim., 39, 1135 (1969).
52. A.V.Fokin, Yu.M.Kosyrev, N.P.Novoselov, and N.A.Brusentsova, Dokl.Akad.Nauk SSSR, 183, 1361 (1968).
53. S.K.Brauman and M.E.Hill, J.Org.Chem., 34, 3381 (1969).
54. S.K.Brauman and M.E.Hill, J.Amer.Chem.Soc., 89, 2131 (1967).
55. A.L.Logothetis and G.N.Sausen, J.Org.Chem., 31, 3689 (1966).
56. R.C.Petru and J.P.Freeman, J.Org.Chem., 32, 4034 (1967).
57. T.E.Stevens, J.Org.Chem., 33, 2660 (1968).
58. T.E.Stevens, J.Org.Chem., 32, 670 (1967).
59. C.M.Sharts, J.Org.Chem., 33, 1008 (1968).
60. A.V.Fokin, Yu.M.Kosyrev, and N.P.Novoselov, Zhur.Obshch.Khim., 39, 1337 (1969).
61. A.V.Fokin, Yu.M.Kosyrev, N.P.Novoselov, and N.A.Brusentsova, Zhur.Obshch.Khim., 39, 1141 (1969).
62. S.K.Brauman and M.E.Hill, J.Amer.Chem.Soc., 89, 2127 (1967).
63. US.P.3 714 254 (1973).
64. US.P.3 732 288 (1973).
65. T.E.Stevens, J.Org.Chem., 33, 2664 (1969).
66. T.E.Stevens, J.Org.Chem., 34, 2451 (1969).
67. T.E.Stevens and W.H.Graham, J.Amer.Chem. Soc., 89, 182 (1967).
68. J.P.Freeman, R.C.Petru, and T.E.Stevens, J.Amer.Chem.Soc., 91, 4778 (1969).
69. T.E.Stevens, Tetrahedron Letters, 3017 (1967).
70. F.A.Johnson, C.Hancy, and T.E.Stevens, J.Org. Chem., 32, 466 (1967).
71. C.O.Parker and T.E.Stevens, J.Org.Chem., 37, 922 (1972).
72. US.P.3 215 709 (1965).
73. B.L.Dyatkin, K.N.Makarov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1134 (1968).
74. B.L.Dyatkin, K.N.Makarov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 657 (1968).
75. A.S.Filatov and M.A.Englin, Zhur.Obshch.Khim., 38, 1408 (1968).
76. US.P.3 196 167 (1965).
77. G.N.Sausen and A.L.Logothetis, J.Org.Chem., 33, 2330 (1968).
78. US.P.3 479 404 (1969).
79. US.P.3 337 605 (1967).
80. J.P.Freeman, "V Mezhdunarodnyi Simpozium po Khimii Ftora, Tezisy Dokladov" (The Vth International Symposium on Fluorine Chemistry, Abstracts of Reports), Izd.Nauka, Moscow, 1969, p.6.
81. W.H.Graham, "154th Meeting of the American Chemical Society, Abstracts of Papers, Chicago, 111", 1967, S-159.
82. A.L.Logothetis, J.Org.Chem., 31, 3686 (1966).
83. T.E.Stevens, Org.Prep.and Procedures, 2, 53 (1970).
84. C.L.Bumgardner, Tetrahedron Letters, 3683 (1964).
85. R.C.Petry, C.O.Parker, F.A.Johnson, T.E.Stevens, and J.P.Freeman, J.Org.Chem., 32, 1534 (1967).
86. G.N.Sausen and A.L.Logothetis, J.Org.Chem., 32, 2261 (1967).
87. A.V.Fokin, V.I.Zimin, Yu.N.Studnev, and L.D.Kuznetsova, Zhur.Org.Khim., 7, 247 (1971).
88. US.P.3 637 663 (1972); Chem.Abs., 76, 113 195 (1972).
89. US.P.3 674 785 (1972); Chem.Abs., 77, 151 998 (1972).
90. R.A.Mitsch, J.Amer.Chem.Soc., 87, 328 (1965).

91. US. P. 3 577 460 (1971).
92. A. S. Filatov, M. A. Englin, and V. I. Yakutin, Zhur. Obshch. Khim., 39, 1325 (1969).
93. V. A. Ginsburg and K. N. Smirnov, Zhur. Obshch. Khim., 39, 1331 (1969).
94. V. A. Ginsburg and K. N. Smirnov, Zhur. Obshch. Khim., 37, 1413 (1967).
95. R. DeMarco, L. Zaborowski, and J. M. Shreeve, "3rd European Symposium on Fluorine Chemistry, Resumes, 1970", p. 42.
96. L. M. Zaborowski and J. M. Shreeve, J. Amer. Chem. Soc., 92, 3665 (1970).
97. R. F. Swindell, L. M. Zaborowski, and J. M. Shreeve, Inorg. Chem., 10, 1635 (1971).
98. L. M. Zaborowski and J. M. Shreeve, Inorg. Chem., 10, 407 (1971).
99. US. P. 3 355 492 (1967).
100. R. L. Rebertus, J. J. McBrady, and J. G. Gagnon, J. Org. Chem., 32, 1944 (1967).
101. US. P. 3 509 197 (1970).
102. R. A. Mitsch, J. Org. Chem., 33, 1847 (1968).
103. R. L. Rebertus and P. E. Toren, J. Org. Chem., 32, 4045 (1967).
104. US. P. 3 700 708 (1972).
105. D. H. Dybvig, Inorg. Chem., 5, 1795 (1966).
106. J. M. Sullivan, A. E. Axworthy, and T. J. Houser, J. Phys. Chem., 74, 2611 (1970).
107. US. P. 3 403 086 (1968).
108. J. B. Hynes, T. E. Austin, and L. A. Bigelow, Inorg. Chem., 11, 418 (1972).
109. F. C. Rauch and A. J. Fauelli, J. Phys. Chem., 78, 2189 (1974).
110. D. S. Ross, T. Mill, and M. E. Hill, J. Amer. Chem. Soc., 94, 8776 (1972).
111. R. A. Mitch, E. W. Neuvar, and P. H. Ogden, J. Heterocycl. Chem., 4, 389 (1967).
112. A. Ya. Yakubovich, S. P. Makarov, V. A. Ginsburg, N. F. Privezentseva, and L. L. Martynova, Dokl. Akad. Nauk SSSR, 141, 125 (1961).
113. B. L. Dyatkin, K. N. Makarov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2582 (1967).
114. R. A. Bekker, B. L. Dyatkin, and M. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1060 (1967).
115. B. L. Dyatkin, R. A. Bekker, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2245 (1966).
116. D. T. Meshri and J. M. Shreeve, J. Amer. Chem. Soc., 90, 1711 (1968).
117. C. L. Bumgardner and J. P. Freeman, Tetrahedron Letters, 5547 (1966).
118. B. P. 1 081 866 (1967).
119. A. V. Fokin, Yu. N. Studnev, and L. D. Kuznetsova, USSR P. 311 902 (1971); Byul. Izobret., No. 25 (1971).
120. K. Baum, J. Org. Chem., 34, 3377 (1969).
121. R. F. Merritt and F. A. Johnson, J. Org. Chem., 32, 416 (1967).
122. L. M. Zaborowski and J. M. Shreeve, Inorg. Chim. Acta, 5, 311 (1971).
123. M. A. Englin, I. V. Ermakova, and V. I. Yakutin, Zhur. Obshch. Khim., 39, 1134 (1969).
124. R. D. Dresdner, F. N. Tlumac, and J. A. Young, J. Amer. Chem. Soc., 82, 5831 (1960).
125. G. C. Sinke, C. J. Thompson, R. E. Jostad, L. C. Walker, and A. C. Swanson, J. Chem. Phys., 47, 1852 (1967).
126. R. L. Rebertus, K. L. Fiedler, and G. W. Kottong, Analyt. Chem., 39, 1867 (1967).
127. G. A. Carpenter, M. F. Zimmer, E. E. Baroody, and R. A. Robb, J. Chem. Eng. Data, 16, 46 (1971).
128. L. Radom, W. J. Hehre, and J. A. Pople, J. Chem. Soc. A, 2299 (1971).
129. L. Radom, W. J. Hehre, and J. A. Pople, J. Amer. Chem. Soc., 93, 289 (1971).
130. R. Ditchfield, J. E. Bene, and J. A. Pople, J. Amer. Chem. Soc., 94, 703 (1972).
131. J. M. Howell, J. Amer. Chem. Soc., 98, 886 (1976).
132. M. S. Gordon and F. Herbert, J. Amer. Chem. Soc., 90, 2471 (1968).
133. K. Reid, "A Course of Physical Organic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1972.
134. F. Kerek, G. Ostrogovich, and Z. Simon, J. Chem. Soc. B, 541 (1971).
135. A. V. Fokin, V. P. Stolyarov, V. S. Galakhov, and A. T. Uzun, Izv. Akad. Nauk SSSR, Ser. Khim., 2159 (1973).
136. W. S. Brey and J. B. Hynes, Fluorine Chem. Rev., 2, 111 (1968).
137. US. P. 3 654 341 (1972).
138. US. P. 3 354 217 (1967).
139. US. P. 3 585 218 (1971).
140. R. L. Rebertus and B. M. Nippoldt, J. Org. Chem., 32, 4044 (1967).
141. K. N. Makarov, B. L. Dyatkin, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 958 (1969).
142. K. N. Makarov, Candidate's Thesis, Institute of Organic Derivatives of the Elements, USSR Academy of Sciences, Moscow, 1970.
143. J. L. Zollinger, C. D. Wright, J. J. McBrady, D. H. Dybvig, F. A. Fleming, G. A. Kurhojce, R. A. Mitsch, and E. W. Neuvar, J. Org. Chem., 38, 1065 (1973).
144. C. D. Wright and J. L. Zollinger, J. Org. Chem., 38, 1075 (1973).
145. B. L. Dyatkin, K. N. Makarov, and I. L. Knunyants, "V Mezhdunarodnyi Simpozium po Khimii Ftora, Tezisy Dokladov" (The Vth International Symposium on Fluorine Chemistry. Abstracts of Reports), Izd. Nauka, Moscow, 1969, p. 3.
146. K. N. Makarov, B. L. Dyatkin, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 192 (1968).
147. A. V. Fokin, V. S. Galakhov, V. P. Radchenko, and V. P. Stolyarov, Izv. Akad. Nauk SSSR, Ser. Khim., 199 (1970).
148. US. P. 3 441 520 (1969).
149. US. P. 3 449 433 (1969).
150. US. P. 3 624 156 (1971).
151. US. P. 3 721 698 (1973); Chem. Abs., 78, 135 642 (1973).
152. US. P. 3 564 055 (1971).
153. US. P. 3 564 023 (1971).
154. US. P. 3 707 555 (1972).
155. US. P. 3 692 838 (1973).
156. US. P. 3 564 056 (1971).
157. US. P. 3 548 004 (1970).
158. US. P. 3 692 837 (1972).
159. US. P. 3 758 555 (1973).
160. US. P. 3 663 621 (1972); Chem. Abs., 77, 74 818 (1972).
161. US. P. 3 683 560 (1972); Chem. Abs., 78, 29 216 (1973).
162. US. P. 3 654 369 (1972).
163. US. P. 3 654 361 (1972).
164. US. P. 3 405 143 (1968).
165. W. C. Firth, H. R. Frank, and E. G. Schriffert, J. Org. Chem., 38, 1080 (1973).
166. W. C. Firth, H. S. Frank, and M. D. Meyrs, J. Org. Chem., 38, 1088 (1973).
167. US. P. 3 574 710 (1971).

168. US. P. 3 693 034 (1972); Chem. Abs., 78, 32 239 (1973).
169. US. P. 3 755 404 (1973).
170. US. P. 3 733 360 (1973).
171. US. P. 3 405 144 (1968).
172. US. P. 3 345 360 (1967); Chem. Abs., 68, 95 828 (1968).
173. W. C. Firth, J. Org. Chem., 33, 3489 (1968).
174. US. P. 3 439 017 (1968).
175. T. E. Stevens, Chem. Comm., 1181 (1967).
176. S. P. Freeman, W. H. Graham, and C. O. Parker, J. Amer. Chem. Soc., 90, 121 (1968).
177. A. V. Fokin, Yu. M. Kosyrev, V. A. Makarov, and N. P. Novoselov, Dokl. Akad. Nauk SSSR, 186, 112 (1969).
178. US. P. 3 358 028 (1967).
179. A. V. Fokin, V. A. Komarov, A. T. Uzun, A. M. Gukov, and Yu. N. Studnev, Izv. Akad. Nauk SSSR, Ser. Khim., 727 (1975).
180. US. P. 3 721 694 (1973); Chem. Abs., 78, 13 641 (1973).
181. US. P. 3 407 232 (1968).
182. US. P. 3 594 385 (1971).
183. US. P. 3 354 211 (1967).
184. US. P. 3 488 735 (1970).