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Fluorine-containing Imines

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Data on the methods of synthesis, certain physicochemical properties, and reactivities of fluorine-containing imines of known types are surveyed and the characteristic features of the variation of their properties due to the effects of the fluorine atoms and polyfluoro-substituents at the C = N bond are examined. The theoretical and applied aspects of the development of the chemistry of fluorine-containing compounds with a nitrogen-carbon double bond are discussed.
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I. INTRODUCTION

Imines of different structure, including azomethines (Schiff bases), hydrazones and azines, oximes, carbonylimines (iminoesters, amidines, and chloro- and dichlorocarbonylimines), nitrogen-containing heterocumulenes (isocyanates, isothiocyanates, keten imines, and carbodiimides) as well as substances of other types with a C=N double bond are close to alkenes as regards their importance. Their study is indissolubly linked with the foundation and development of organic chemistry as a science, the development of its methods and theory, particularly the stereochemistry of organic compounds and their reactions, tautomeric phenomena, isomerism, molecular rearrangements, the mechanisms of the stepwise and concerted reactions involving nucleophilic and electrophilic addition to a multiple bond, and cycloaddition reactions.

The applied importance of the chemistry of imines is inestimable. They are precursors or intermediates in the synthesis of many physiologically important substances of biogenic and abiogenic types. Imines are formed as intermediate species in the synthesis of many natural products, monomers for polymerisation, and precursors for other technically important materials. The chemistry of imines can be legitimately regarded as the foundation of the chemistry of heterocyclic compounds, which is vigorously developing and is of great practical importance. The study of the chemistry of imines and iminium salts throws light on processes involved in vital activity associated with the synthesis, metabolism, catabolism, and biocatalytic role of biogenic nitrogen-containing substances.

The first fluorine-containing imines were obtained more than 30 years ago and these compounds have been investigated vigorously during the last two decades. At the same time the extensive data accumulated over a short period on the fluorine-containing imines have made an important contribution to the general chemistry of compounds with a C=N bond.

The interest in fluorine-containing imines is due primarily to practical requirements. The development of components of high-energy fuel compositions, explosives, combustion accelerators, precursors for valuable lubricants and other materials, and intermediates in the synthesis of physiologically important substances constitutes a by no means complete list of problems in the solution of which the chemistry of fluorine-containing imines is involved. During recent years, the interest in the chemistry of fluorine-containing imines increased in connection with the appearance of unique fluorine-containing pesticides and medicinal drugs distinguished by the "suicidal" mechanism of action in relation to pyridoxal enzymes. The intensification of studies of the influence of the imine and iminium groups on the reactions of adjacent fluorine-containing substituents is due to this particular factor.

The available extensive data on fluorine-containing imines cannot be considered in a single article and this is not the aim of the present review. Here an attempt is made to summarise the most important information about fluorine-containing imines and to discover the characteristic features introduced by fluorine atoms of fluorine-containing substituents into various methods for the formation of compounds with an imine group and their properties.

The attainment of the aim formulated proved possible by virtue of the availability of monographs on the chemistry of imines[1-3] and the chemistry of organofluorine compounds[4,5], to which the reader is referred in order to become acquainted with the fundamental problems. It has also been promoted by the existence of data on specific problems in the chemistry of fluorine-containing imines. Thus data on *N*-polyfluoroalkylfluoro- and *N*-polyfluoroalkyldifluoro-carbonylimines (perfluoroaza-alkenes) have been examined by Knunyants and Gontar[6]. The chemistry of *N*-fluoroimino-compounds has been discussed in detail in a book[7], in reviews[8,9], and in an article of a review type[10]. An excellent review[11] deals with the chemistry of fluorine-containing keten imines. The existence of the above publications made it possible to reduce greatly the amount of factual data discussed here, the latter being limited to information in the field of fluorine-containing azomethines which had not been reviewed previously and the most important data on other fluorine-containing imines.

II. METHODS OF SYNTHESIS

Non-fluorinated imines are mainly synthesised by condensing amino-compounds with carbonyl compounds, by eliminating the vicinal substituents at the C–N bond in nitrogen-containing compounds, by the imine exchange reaction, by the condensation of nitroso-compounds with an activated methylene group in various substances, and also by the oxidation of secondary amines and their derivatives. The first method is the most general. Many specific methods for the synthesis of imines are also known. These include procedures based on the cleavage of unsaturated compounds by primary amines, on cycloaddition–decomposition reactions, on the isomeric transformations of unsaturated nitrogen-containing compounds, on the functional transformation of

compounds with an imine group, etc. Almost all these methods have been tested in the synthesis of fluorine-containing imines but by no means all proved suitable for this purpose.

It is believed[1] that the condensation of amines with non-fluorinated carbonyl compounds proceeds as a reversible process:

$$\rangle C{=}O + H_2NR \rightleftarrows \left[\rangle C\langle^{OH}_{NHR}\right] \rightleftarrows \rangle C{=}NR \quad .$$

In neutral media the rate-limiting stage is the formation of the addition product—the corresponding hemiaminal. However, fluorine-containing carbonyl compounds, especially perfluoroketones, are such powerful electrophiles that they interact vigorously not only with amines, hydrazines, and hydroxylamines but also with weak nucleophiles such as acid amides and sulphonamides[12-23], forming stable geminal aminohydroxy-compounds:

$$R_FR_F'C{=}O + H_2NR \rightarrow R_FR_F'C\langle^{OH}_{NHR} \quad ;$$

$$R = H, Alk, Ar, OH, NR_2, C(O)R, SO_2R \quad .$$

The synthesis of fluorine-containing imines is therefore not limited by the first stage except for amino-compounds whose basicity is extremely low and which are sterically hindered[24,25]. In most cases the second stage of the reaction—the dehydration of the geminal aminohydroxy-compound formed—is rate-limiting.

As a result of the above feature, by no means all fluorine-containing imines can be obtained by the condensation of fluorocarbonyl compounds with amino-compounds, by analogy with the corresponding hydrocarbon compounds. Under the usual conditions in the absence of a catalyst or in the presence of weak dehydrating agents (inorganic and carboxylic acids), only the imines of partly fluorinated carbonyl compounds are formed, for example, the anils of trifluoroacetone[17,26,27], the anil of trifluoroacetophenone[28], the imines of aromatic polyfluoro-substituted ketones and aldehydes[29-33], and the hydrazones of partly fluorinated ketones[34-36]. Fluorine-containing aldimines are readily formed under the usual conditions; instead of polyfluoroaldehydes, it is possible to employ in this instance their hydrates and other derivatives[37-41].

Among the imines of highly electrophilic perfluoroketones, only the hydrazones have been obtained by the condensation of the polyfluoroketones with hydrazines in trifluoroacetic acid[42,43]. Other types of perfluoroketone imines are not formed under the usual conditions in view of the stabilisation of the C—O bond in geminal aminohydroxy-compounds by perfluoroalkyl and especially trifluoromethyl groups[12-18]. The stabilisation effects are so marked that the thermolysis of the adducts obtained by the addition of perfluoroketones to amino-compounds does not lead to their dehydration but results in various destructive transformations, which lead to the formation of either the starting materials[17,18,20,24-26], or the products of their oxidation-reduction reactions[15,44,45], or the products of the "haloform" decomposition[8,36,46-49].

The adducts of amino-compounds with asymmetric polyfluoroketones frequently undergo the "haloform" decomposition even under mild conditions[36,47]:

$$R_FR_F'C{=}O + H_2NR \rightarrow R_FC(O)NHR + HR_F' \quad .$$

These reactions can be sometimes prevented by regulating the pH of the medium. Thus the phenylhydrazone and the oxime of difluoronitromethyl methyl ketone, which is highly sensitive to bases, are formed only in a neutral medium[48,49].

The stability of the adducts of perfluoroketones with amino-compounds is reduced and the tendency towards decomposition into the initial reactants increases with decrease of the basicity of the amino-compounds employed[17,18,24-26,50-52]. Thus the hemiaminals of hexafluoroacetone are stable substances which can be distilled without decomposition. On the other hand, the hemiamidals of hexafluoroacetone, obtained from carboxylic acid amines, are stable up to 100 °C [20,52] and those obtained from perfluorocarboxylic acid amides are stable only up to 50 °C:[24] the adducts of hexafluoroacetone with the amides of perfluorodicarboxylic acids are stable at atmospheric pressure only in solutions in the presence of an excess of hexafluoroacetone and at a temperature below 0 °C.[25] Thus the properties of the adducts of amino-compounds with polyfluoroketones vary within extremely wide limits, which must hinder the development of a general method for their conversion into fluorine-containing imines.

At the same time, under the conditions of concerted reactions, almost all the fluorine-containing geminal aminohydroxy-compounds could be involved in reactions involving dehydration by mild dehydrating agents. Thus various imines[19], hydrazones, and azines of polyfluoroketones[53], *N,N'*-bis(hexafluoroisopropylidene)diamides of perfluorodicarboxylic acids[25], and *N*-hexafluoroisopropylideneamidines[54] have been obtained by dehydration with $POCl_3$ in pyridine. Hexafluoroacetone azine[55] and the perfluoroacylimines of hexafluoroacetone[24] have been synthesised with the aid of $POCl_3$ in quinoline. Trifluoroacetic acid anhydride in pyridine or quinoline proved to be effective in the synthesis of the acylimines of perfluoroketones[56] and the phosphoryl- and sulphonyl-imines of hexafluoroacetone[57,58]:

$$R_FR_F'C{=}O + H_2NR \rightarrow R_FR_F'C\langle^{OH}_{NHR} \xrightarrow{-H_2O} R_FR_F'C{=}NR \quad ;$$

$$R = H, Alk, Ar, NH_2, NR_2, N{=}CR_2, C(O)R, C(O)R_F, P(OR)_2, S(O)Ar \quad .$$

Other dehydrating agents also proved to be effective. Thus thionyl chloride converts smoothly and almost quantitatively the adducts of polyfluoroketones and sulphonamides into the corresponding sulphonylimines[21,22]. Asymmetric fluorine-containing azines have been obtained by heating the adducts with P_2O_5.[59,60] Oleum has been used successfully to synthesise the perfluoroacylimines and the azine of hexafluoroacetone[50,61]. Pentafluoro-2-azopropene in the presence of KF proved to be an effective dehydrating agent in the synthesis of hexafluoroacetone acylimines[62]:

$$R_FR_F'C{=}O \xrightarrow{H_2NSO_2R} R_FR_F'C\langle^{OH}_{NHSO_2R} \xrightarrow{SOCl_2} R_FR_F'C{=}NSO_2R \quad ;$$

$$R_F, R_F' = CF_3, ClCF_2, O_2NCF_2; \; R = Me, Ph, 4\text{-}MeC_6H_4 \quad ;$$

$$(CF_3)_2C{=}NNH_2 + O{=}CRR' \xrightarrow{P_2O_5} (CF_3)_2C{=}N{-}N{=}CRR' \quad ;$$

$$R, R' = Alk, Ar$$

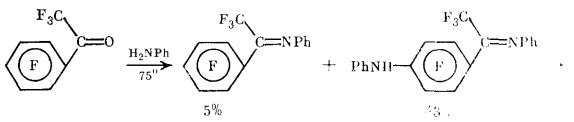
$$(CF_3)_2CNHC(O)R \xrightarrow{SO_3} (CF_3)_2C{=}NC(O)R \xleftarrow[-CF_3NCO,\,-HF]{CF_3N{=}CF_2} (CF_3)_2CNHC(O)R' \quad ;$$

$$R = CF_3, C_4F_9; \; R' = Me, Et, Ar \quad .$$

The use of mild dehydrating agents made it possible to extend greatly the assortment of imines obtained by the reactions of polyfluoroketones with amino-compounds. The considerable prospects for the further improvement and development of this method are now quite evident.

The preparative value of the condensation of polyfluoroketones with various amino-compounds in the presence of dehydrating agents is not limited to the synthesis of fluorine-containing imines and is acquiring increasing importance as a method of synthesis of a wide variety of fluorine- and

nitrogen-containing heterocycles[34,39,51,54,60,63-71]. They are formed on dehydration of the adducts of polyfluoroketones with amino-compounds containing functional groups such as OH, SH, NH_2, COOH, C≡N, etc. in the α-, β-, or γ-position relative to the NH_2 group. It is noteworthy that, when these reactions are carried out in highly electron-donating protophilic media, it is possible to eliminate the use of dehydrating agents, using instead an excess of the highly electrophilic polyfluoroketone[65-68]. In conclusion of the discussion of the reactions of polyfluoroketones with amino-compounds, we may mention one of the features of the condensation of perfluoroaryl ketones with amines associated with the ability of the fluorine atom in the perfluoroaryl group to undergo readily nucleophilic substitution which results in the formation of an amino-derivative[30,31]:



This process was facilitated by carrying out the condensation in the presence of $AlCl_3$ or H_2SO_4,[30,31] which led to simple and selective methods of synthesis of polyfluorinated Schiff bases (see the review of Gerasimova and Fokin[72]).

The imine exchange reactions, which are widely used in the syntheses of imines of the hydrocarbon series, proved suitable also for the preparation of certain fluorine-containing imines. The characteristic features of this method are the high stability of the fluorine-containing aminals and aminoketals, which like the geminal aminohydroxy-compounds, are frequently isolated in a pure state[17-20,25,56,58,59,71]. The transamination of fluorine-containing imines is therefore carried out as a severe thermal process[17-20] and the imine exchange takes place at room temperature only in the presence of amine acceptors[17,26,59]:

$$R_F^1R_F^2C{=}NR \xrightarrow{H_2NR'} R_F^1R_F^2C\begin{matrix}NHR\\NHR'\end{matrix} \xrightarrow{\Delta(H^+)} R_F^1R_F^2C{=}NR' .$$

The characteristic features of these reactions have not so far been studied in detail. It has only been shown that hexafluoroacetone imines can be used for the selective synthesis of the corresponding oximes and hydrazones. The acyl- and sulphonyl-imines of hexafluoroacetone can probably be regarded as precursors of the corresponding anils.

Certain side reactions accompanying the transamination of fluorine-containing imines are known. The imines of asymmetric polyfluoroketones undergo the haloform decomposition in these reactions[17]. In a number of cases reactions in which fluorine- and nitrogen-containing heterocyclic compounds are formed take place instead of the imine exchange.

The transformations of fluorine-containing geminal aminohydroxy-compounds and aminals into the corresponding imines can also be regarded as processes involving the elimination of vicinal substituents at the C–N bond in saturated fluorine- and nitrogen-containing compounds. Similar reactions (dehydrofluorination and reductive dehalogenation) are used widely in the syntheses of *N*-fluoroimines (see the review of Fokin et al.[8]). Thermal transformations of amino- and amido-ketals of polyfluoroketones in the presence of phosphorus pentoxide also lead to fluorine-containing imines[18,37,73]:

$$F_3C\begin{matrix}OR''\\NHR'\end{matrix}C(R) \xrightarrow{\Delta,\ P_2O_5} F_3C(R)C{=}NR' ;$$

$R = H, CF_3$; $R' = NHC(O)NH_2$, $C(O)R_F$, $SO_2C_6H_4CH_3$-*p* .

Cycloaddition–decomposition reactions have found extensive applications in the syntheses of fluorine-containing imines. This procedure proved to be one of the convenient methods for the preparation of difluorocarbonylimines[8], fluorine-containing keten imines, including compounds with perfluoroalkyl groups at the nitrogen atom[11], and also various fluorine-containing azomethines and acylimines of polyfluoroketones[15,17,20,26]. In many cases this method makes it possible to obtain imines which cannot be synthesised by other procedures. Thus the extension of the Staudinger reaction to fluorine-containing carbonyl compounds permitted the synthesis even of the imines of asymmetric ketones which undergo the "haloform" decomposition in other syntheses:

$$F_3C(R)C{=}O + Ph_3P{=}NR' \xrightarrow[-Ph_3PO]{\Delta} F_3C(R)C{=}NR' ;$$

R = Me, CF_3, O_2NCF_2; R' = H, Ph, C(O)Me, C(O)Ph, C(O)OEt .

Decomposition with formation of difluoronitromethane and trifluoroacetyliminotriphenylphosphorane has been noted only in the reaction of triphenylphosphine imine with nitroperfluoroacetone[26].

A modification of the Staudinger reaction, in which isocyanates and catalytic amounts of triphenylphosphines oxide[26,74] or dimethylformamide[75] are used instead of iminophosphoranes, is extremely interesting:

$$O{=}C{=}NR \xrightarrow[150-180^\circ]{X=O} \left[\begin{matrix}O-X\\ \diagdown\\ C\\ \diagup\\ O\end{matrix}\!\!-\!\!\begin{matrix}\\ \\ N-R\end{matrix}\right] \xrightarrow[-CO_2]{} X{=}NR \xrightarrow[-X=O]{(CF_3)_2C=O} (CF_3)_2C{=}NR ;$$

X = Ph_3P, R = Ar; X = $(CH_3)_2NCH$, R = C_6F_5 .

In the absence of catalysts, this reaction does not take place even under much more severe conditions.

The interaction of hexafluoroacetone with thionylimines in the presence of CsF [76] and the thermal reactions of octafluoroisobutene with nitrosobenzene[77] are apparently processes of the cycloaddition–decomposition type:

$$(CF_3)_2C{=}O \xrightarrow[-SO_2]{O=S=NAr} (CF_3)_2C{=}NAr \xleftarrow[-COF_2]{ON-Ph} (CF_3)_2C{-}CF_2 .$$

Many cyclodecomposition reactions, leading to fluorine-containing imines, have no analogues in the hydrocarbon series. Thus the nucleophilic cleavage of tetrakis(trifluoromethyl)-1,3-dithietan by amino-compounds leads to various hexafluoroacetone imines[78]. The yield of the reaction products is higher the lower the basicity of the amino-compound:

$$(CF_3)_2C\begin{matrix}S\\ \diagup\\ \diagdown\\ S\end{matrix}C(CF_3)_2 \xrightarrow{H_2N-R} (CF_3)_2C{=}NR .$$

2,2,6,6-Tetrakis(trifluoromethyl)-1,3,5-oxathiazines and the corresponding 1,3,5-oxadiazines are effective precursors of hexafluoroacetone thioacylamines[63,79-82] and hexafluoroisopropylideneamidines[54,83]. Thermolysis with elimination of hexafluoroacetone leads in these cases to the derivatives of 1,3-thiazete and 1,3-diazete, which are converted into imines under certain conditions:

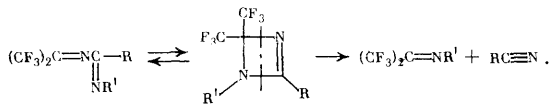
$$2(CF_3)_2C{=}O + H_2NC(X)R \xrightarrow{POCl_3,\ C_5H_5N} \begin{matrix}F_3C & CF_3\\ & O \quad X\\ F_3C & \diagdown \diagup\\ & N\\ F_3C & \quad R\end{matrix}$$

$$\xrightarrow{-CF_3COCF_3} \begin{matrix}CF_3\\ F_3C-X\\ \quad\diagdown\\ \quad N\\ \quad\diagup\\ \quad R\end{matrix} \rightleftarrows (CF_3)_2C{=}NC(X)R ;$$

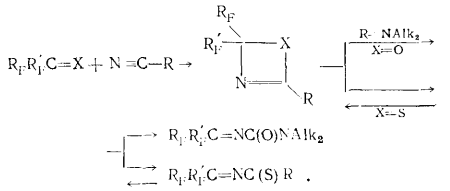
X = S, NR .

Derivatives of 1,3-thiazete proved to be extremely stable, undergoing electrocyclic reactions only on heating to 150 °C.[79] On the other hand, derivatives of 1,3-diazete

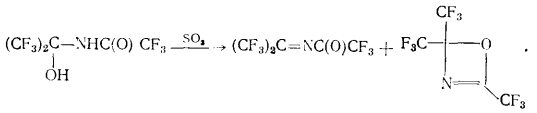
readily isomerise under the usual conditions to amidines and the presence of these compounds in the equilibrium mixture has been confirmed by the isolation of the products of their retro-[2 + 2]-cycloaddition[54]:



The formation of fluorine-containing 1,3-oxazetes and 1,3-thiazetes in [2 + 2]-cycloaddition reactions of polyfluoroacetones and hexafluorothioacetone with acid nitriles has been demonstrated recently[84]. In contrast to derivatives of 1,3-thiazete and 1,3-diazete, 1,3-oxazetes isomerise reversibly to acylimines:

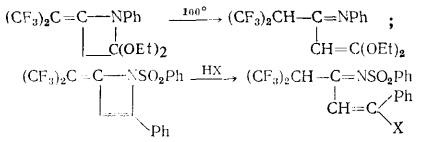


It is noteworthy that the dehydration of the adduct of hexafluoroacetone and trifluoroacetamide by sulphur trioxide also leads to a four-membered unsaturated heterocycle—2,2,4-tris(trifluoromethyl)-1,3-oxazete, which was isolated in the form of a complex with SO_3.[50] The oxazete stabilised by three trifluoromethyl groups does not change at 150 °C and undergoes irreversible ring opening only in the presence of bases:

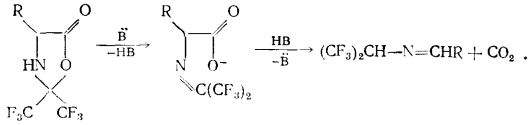


This indicates a concerted mechanism of the condensation of polyfluoroketones with acid amides in the presence of dehydrating agents and one may expect that, under certain conditions, the products of these reactions may be exclusively 1,3-oxazates.

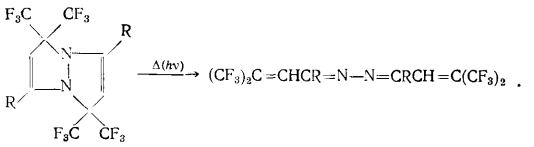
Among other electrocyclic reactions leading to fluorine-containing imines, mention should be made of the transformations of cyclic [2 + 2]-adducts of fluorine-containing keten imines with a ketenal or with acetylenes, ring opening being accompanied by a proton shift[85,86]:



The anionotropic cyclodecomposition with formation of fluorine-containing imines in the catalysed reactions of 2,2-bis(trifluoromethyl)-1,3-oxazolidin-5-ones is of interest[87]:

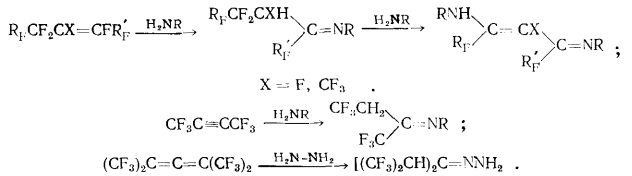


The formation of symmetrical fluorine-containing azines in high yields in the thermal or photolytic decomposition of the adducts of hexafluoroacetone azine with acetylenes is likewise striking[88]:

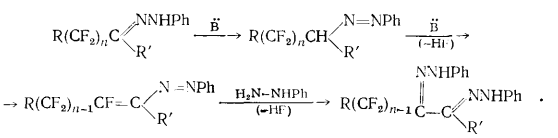


The electrocyclic reactions described are distinguished by high selectivity, so that the formation of fluorine-containing imines in various heterocyclic reactions of fluorine- and nitrogen-containing compounds constitutes a kinetically and thermodynamically most favourable process.

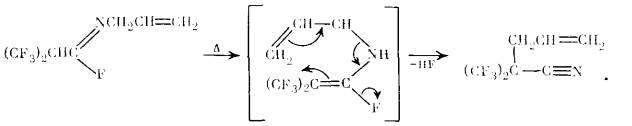
Many methods of synthesis characteristic of fluorine-containing imines alone are based on the reactions of amino-compounds with polyfluoroalkenes. Terminal polyperfluoroalkenes are converted in these reactions into imidoyl fluorides, which are intermediates in the synthesis of keten imines[11], and into hydroxamoyl fluorides, amidines, hydrazidines, etc.[5]. The analogous reactions of amino-compounds with inner perfluoroalkenes, perfluorocycloalkenes, alkynes, and allenes initially lead in all cases to α-hydropolyfluoroketone imines[89–91] and, under conditions suitable for dehydrofluorination, the imines formed undergo further reactions with formation of iminoenamines[92–99], iminonitriles[91], and iminoketen imines[100], for example:



The characteristics of these reactions specified above show that prototropic shifts from C to N in CCN triad systems are less characteristic of fluorine-containing imines than of the imines of non-fluorinated carboxylic ketoacids. Triad prototropism of the enamine–imine and enehydrazine–hydrazone type therefore takes place extremely rapidly and the equilibrium is fully displaced to compounds with a C=N bond. However, the azo–hydrazone prototropism is achieved relatively easily, which has been manifested by the mild conditions in the conversion of fluorine-containing hydrazones into polyhydrazones[34,38–40,43,101]:



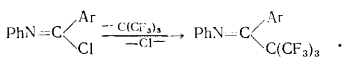
The conditions governing the thermal 1,3-sigmatropic transformations of *N*-allyl-2*H*-hexafluoroisobutyroimidoyl fluoride[102], which can be achieved only under the conditions of the C → N proton shift, may serve as a qualitative characteristic of the tendency of fluorine-containing imines to undergo triad prototropism of the imine–enamine type:



Since the "aza-Claisen" rearrangement of the compound takes place on heating above 120 °C, the energy barrier to the process must be estimated as more than 15 kcal mol^{-1}.

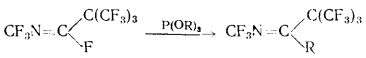
A large number of special methods for the synthesis of fluorine-containing imines, based on the anionotropic and free radical reactions of fluorine- and nitrogen-containing compounds, on cycloaddition reactions, etc., have been described.

Nonafluoro-t-butylpotassium readily reacts with chlorocarbonylimines to form products of the nucleophilic substitution of the chlorine atom[103]:



These reactions resemble the reactions of chlorocarbonylimines with organometallic compounds widely investigated in hydrocarbon chemistry.

The alkylation of certain fluorocarbonylimines has been achieved with the aid of trialkyl phosphites[104]:

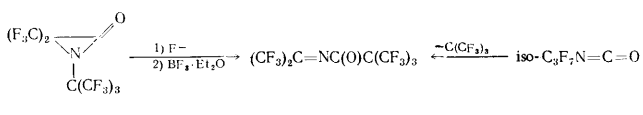


Fluorophosphoranes are apparently intermediates in this case.

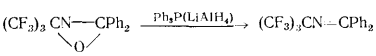
Hexafluoroacetone perfluoroisopropylimine is formed on reaction of hexafluoroacetone with bromocyanogen or perfluoroisopropyl isocyanate in the presence of potassium fluoride[105]:



The reaction of nonafluoro-t-butylcaesium with perfluoroisopropyl isocyanate led to hexafluoroacetone nonafluoropivaloylimine[106]. An elegant synthesis of this compound has also been achieved by the nucleophilic opening of the ring of the corresponding perfluoro-α-lactam by the fluoride ion:

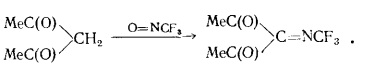


Benzophenone perfluoro-t-butylimine has been obtained by the nucleophilic deoxygenation of the corresponding oxaziridine[107]:

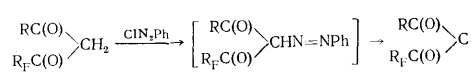


Analogous syntheses are also known for non-fluorinated imines.

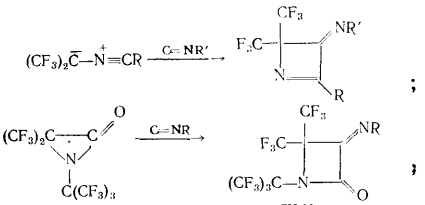
In the presence of bases, trifluoronitrosomethane reacts with acetylacetone, which made it possible to obtain diacetyl ketone trifluoromethylimine[108]:

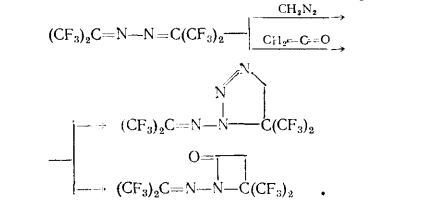


This reaction can be regarded as an analogue of the condensation of nitroso-compounds via the activated methylene group of strong CH acids (the Ehrlich–Sachs reacton), which has been widely investigated in hydrocarbon chemistry. Like non-fluorinated β-diketones, fluorine-containing β-diketones react with benzenediazonium chloride[34,70]:



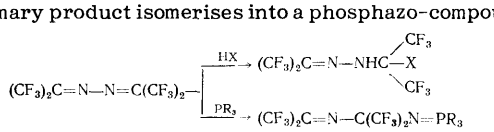
The [3 + 1]-,[81,109–113] [2 + 2]-,[86,114] and [2 + 3]-cycloaddition[115] reactions have been used successfully for the synthesis of cyclic fluorine-containing imines:



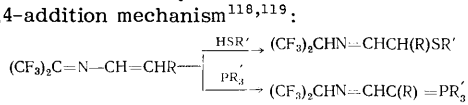


The trimerisation of fluorine-containing 1,3-diazadienes with a terminal methylene group also leads to similar compounds[54].

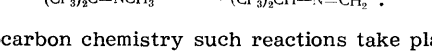
Selective reactions of fluorine-containing imines made it possible to achieve the synthesis of a large number of the compounds under consideration via functional transformations with retention of the C=N bond. For example, hexafluoroacetone azine combines smoothly with nucleophiles via one of the C=N bonds and is converted into hydrazones, while on interaction with trialkyl phosphites or tertiary phosphines the primary product isomerises into a phosphazo-compound[115–117]:



Hexafluoroacetone alkenylimines interact with nucleophiles via the 1,4-addition mechanism[118,119]:

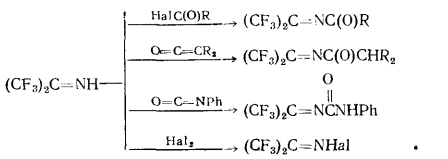


In contrast to their non-fluorinated analogues, hexafluoroacetone alkylimines undergo the imine–imine prototropic shifts extremely readily even in the presence of triethylamine[120]:

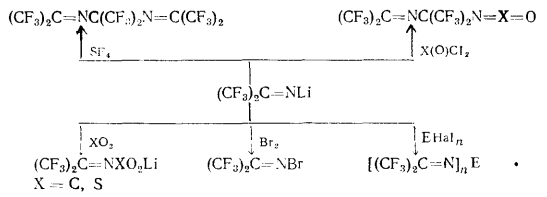


In the hydrocarbon chemistry such reactions take place at a low rate only in the presence of extremely strong bases.

Hexafluoroacetone imine and hydrazone are precursors of a large number of fluorine-containing imines. They have been involved in acylation by acyl halides[60], ketens[19,73,121], and isocyanates[17,60]; the substitutional halogenation of hexafluoroacetone imine has been achieved in the presence of alkali metal fluorides[122]:



Hexafluoroacetone *N*-lithioimine proved to be more reactive in reactions with various electrophiles. On intense cooling. this compound is smoothly brominated[19], forms addition products with sulphur dioxide or carbon dioxide[123], forms substitution products on reaction with chlorotrimethylsilane, phosphorus trichloride, arsenic trichloride, sulphur dichloride, boron halides, sulphene chlorides, and sulphinyl chlorides[124], and sulphur tetrafluoride[125]:



Instances of the conversion of fluorine-containing oximes into imines are known. For example, hexafluoroacetone dichlorophosphorylimine has been obtained by the reaction of hexafluoroacetone oxime nitrite with phosphorus trichloride[126]:

$$(CF_3)_2C{=}NONO \xrightarrow{PCl_3} (CF_3)_2C{=}NP(O)Cl_2 \ .$$

Reactions involving the fluorination of amines, amides, imines, iminoesters, amidines, and guanidine and its derivatives by elemental fluorine as well as the reactions of unsaturated compounds with tetrafluorohydrazine, chlorodifluoroamine, and difluoroamine are widely used in the synthesis of *N*-fluoroimines with a fluorinated hydrocarbon group. In combination with the dehydrofluorination, reductive dehalogenation, and homolytic decomposition reactions of the substances formed, the above processes made it possible to devise a large number of specific methods for the synthesis of *N*-fluoroimines of different structure, which have been examined in detail in a number of communications[8-10, 127-129].

The reactions of electrophiles with nitriles have been used recently for the synthesis of *N*-halogenoimines. For example, halogenofluorosulphates react with the nitriles of perfluorocarboxylic acids under mild conditions[130]; on heating in the presence of a strong inorganic acid, polyfluoroalkyl hypochlorites add to nitriles[131]:

$$R_F{-}C{\equiv}N + HalOSO_2F \rightarrow R_F{-}C\!\!<\!\!\begin{matrix}NHal\\OSO_2F\end{matrix} \ ;$$

$$R_F{=}CF_3,\ NO_2CF_2,\ (NO_2)_2CF,\ n\text{-}C_3F_7 \ .$$

$$R_F{-}C{\equiv}N + ClOCH_2(CF_2)_4H \xrightarrow[110-115^\circ]{H^+} R_F{-}C\!\!<\!\!\begin{matrix}NCl\\OCH_2(CF_2)_4H\end{matrix} \ .$$

There are comparatively few data on homolytic reactions leading to fluorine-containing imines. At the same time the possibility, in principle, of employing for these purposes reactions based on the properties of carbenes and carbenoid species as well as the high tendency of the N–Hal bonds in halogenoimines towards homolysis have been demonstrated; the prospects of the synthesis of fluorine-containing imines via the pyrolytic reactions of fluorine- and nitrogen-containing unsaturated compounds have been assessed.

Thus bis(trifluoromethyl)diazomethane alkylates hexafluoroacetone imine fairly smoothly[132] and its pyrolysis in the presence of alkanes leads to hexafluoroacetone hydrazones[133] in a mixture with other substances:

$$(CF_3)_2CN_2 \begin{cases} \xrightarrow{HN{=}C(CF_3)_2} (CF_3)_2CHN{=}C(CF_3)_2 \\ \xrightarrow{\Delta,HR} (CF_3)_2C{=}NNHR \end{cases} .$$

Thermal reactions of bis(trifluoromethyl)diazirine lead to hexafluoroacetone azine[134], while heating in the presence of alkanes results in the formation of hexafluoroacetone alkylimines[133]:

$$(CF_3)_2C\!\!<\!\!\begin{matrix}N\\N\end{matrix} \begin{cases} \xrightarrow{\Delta} (CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \\ \xrightarrow{HR,165^\circ} (CF_3)_2C{=}NR \end{cases} .$$

Isonitriles react smoothly with perfluoroalkyl iodides to form fluorine-containing iodocarbonylimines[135]:

$$RN{=}C + IR_F \rightarrow RN{=}C\!\!<\!\!\begin{matrix}R_F\\I\end{matrix} \ .$$

Many cyclic fluorine-containing imines have been obtained in reactions involving [1 + 4]-cycloaddition of isonitriles to fluorine-containing unsaturated compounds (see below).

It has been shown that *N*-halogenoimines are converted under the conditions of photolysis into the corresponding azines[19]; in the presence of metallic mercury, these compounds readily condense with sulphene chlorides and acyl chlorides[136]:

$$(CF_3)_2C{=}NHal \begin{cases} \xrightarrow[Hal=Br]{h\nu} (CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \\ \xrightarrow[Hg]{HalX} (CF_3)_2C{=}NX \end{cases} ;$$

$$X = SCF_3,\ C(O)CF_3 \ .$$

The pyrolysis of hexafluoroacetone azine with alkanes or alkenes[137,138] leads to mixtures of substances containing hexafluoroacetone hydrazones:

$$(CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \begin{cases} \xrightarrow{(CH_3)_2C{=}C(CH_3)_2} \\ \xrightarrow{HR} \begin{cases} \rightarrow (CF_3)_2C{=}NNHC(CF_3)_2CH_2C(CH_3)_2 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad CH_3 \\ \rightarrow (CF_3)_2C{=}NNHC(CF_3)_2R \end{cases} \end{cases} .$$

When hexafluoroisopropylideneiminoxybis(trifluoromethyl)amine was heated with polyfluoroethylenes, the products of the insertion of an alkene in both N–O bonds were obtained[139]:

$$(CF_3)_2C{=}NON(CF_3)_2 \xrightarrow{CF_2{=}CFX} (CF_3)_2C{=}NCF_2CFXON(CF_3)_2 +$$

$$+ (CF_3)_2C{=}NOCF_2CFXN(CF_3)_2 \ ;$$

$$X = F, Cl \ .$$

The above data indicate the extremely wide variety of the methods of synthesis of polyfluorinated imines. They are formed as a result of anionotropic, cationotropic, and homolytic reactions, concerted and stepwise electrocyclic processes, and cycloaddition–decomposition reactions.

The formation of extremely stable intermediates, which are converted into the final imines as a result of severe stepwise or mild concerted processes, is characteristic of the majority of the methods. As fluorine atoms of polyfluoroalkyl groups accumulate at the C=N bond of the intermediate, the efficiency of the stepwise processes falls and that of the concerted processes increases. This apparently reflects a common feature of fluorine-containing imines—a marked increase of strain in the latter with increase of the number of fluorine atoms and polyfluoroalkyl groups at the C=N bond.

III. CERTAIN PHYSICOCHEMICAL PROPERTIES

The physicochemical properties of fluorine-containing imines have been little investigated. A broad set of characteristics has been established only for isolated compounds among *N*-fluoromines of practical importance[8]. For the remaining compounds, the boiling points and in certain cases the refractive indices and densities are known. The majority of the fluorine-containing imines have been characterised by their infrared spectra [ν(C=N)] and their ^{19}F and ^{1}H NMR spectra. The thermodynamic parameters have been determined only for certain *N*-fluoroimines; in a number of instances the geometrical parameters of the molecules of these compounds have been calculated[8].

The characteristics of the physicochemical properties of the compounds considered have been expressed most strikingly in the series of perfluoroketone imines whose parameters are partly compiled in the Table. It follows from the data presented that, in contrast to their hydrocarbon analogues,

fluorine-containing imines are relatively low-boiling liquids, while certain perfluoroimines are gases under the usual conditions. Low boiling points are characteristic even of amines with mobile hydrogen atoms in the molecule, which indicate extremely weak forces of dipole–dipole interactions, a low energy of the intermolecular $n\pi$ interactions, and a weak hydrogen bond between the molecules of fluorine-containing imines in the liquid state. These findings are correlated with the sharp decrease of the basicity and the "amphoteric" properties of the imine after the introduction of fluorine atoms or polyfluoroalkyl groups at the C=N bond.

The boiling points and spectroscopic parameters of the imines $(CF_3)_2C{=}N{-}R$.[19,59,74,122,140]

R	B.p., °C	ν(C = N), cm^{-1}	$\delta[(CF_3)_2C=N]$, p.p.m.*	
			syn-	*anti-*
H	16—16.5	1670	—2.9	—1.1
F	—10—-8	1620	—12.9	—9.7
Cl	—	1630	—9.0	—7.4
Br	49.5—50	1650	—6.6	—5.6
OH	72—73	—	—10.9	—8.8
OCH_3	—	—	—11.4	—9.2
NH_2	95.5—96.0	1600	—13.4	—12.0
NHC_6H_5	—	1664	—15.8	—8.7
$N(CH_3)_2$	—	—	—24.4	—12.7
$N{=}C(CF_3)_2$	67—67.5	1660	—11.5	—7.8
CH_3	34—35	1705	—11.3	—5.2
C_6H_5	135—137	1680	—16.6	—8.6
iso-C_3F_7	—	1750	—11.6	—5.2
SCF_3	51.3	1655	—	
$Si(CH_3)_3$	84.7	1770	—	
$C(O)CH_3$	85	1735	—5.7	
$C(O)CF_3$	45	1750	—8.1	
$S(O)CF_3$	86.7	1675	—	
$S(O)C_6H_5$	41(0.05 mm)	1600	—13.2	
$SO_2C_6H_5$	100(5.0 mm)	1750	—3.9	

*Relative to CF_3COOH.

It is noteworthy that the reduced basicity and weak "amphoteric" properties of fluorine-containing imines are responsible for their increased stability and their much smaller tendency towards oligomeric transformations than for the non-fluorinated analogues. This is the reason for the existence under the usual conditions of the fluorine-containing analogues of many aliphatic imines of the hydrocarbon series, which are unknown in their free state.

The high volatility of perfluoroketone hydrazones and especially their oximes, which are fairly strong acids, must be regarded as extremely interesting[141]. This can be explained by the weak *s* character of the hybrid state of the orbitals not only of the *p* electrons of the imine nitrogen but also of the *p* electrons of the heteroatom linked to the imino-group, which is possible only in the presence of additional many-centre molecular orbitals in the CNO and CNN triads of fluorine-containing imines. Data indicating the extremely high stability and the relative ease of formation of the oximes and hydrazones of fluorocarbonyl compounds compared with fluorine-containing azomethines are consistent with this finding.

The analysis of the vibrational spectra of fluorine-containing imines leads to a similar conclusion. Judging from these characteristics, the imine bond in the compounds considered is more sensitive to various effects of substituents than in the molecules of the hydrocarbon analogues. Thus the stretching vibration frequencies of the C=N bond in fluorine-containing imines are manifested in the region from 1770 cm^{-1} for hexafluoroacetone trimethylsilylimine (see Table) to 1553 cm^{-1} for the *N*-fluoroimine of the dinitrile of mesoxalic acid[8]. The corresponding range for the imines of the hydrocarbon series is from 1680 to 1600 cm^{-1}.[1] Even for the monosubstituted hexafluoroacetone anils, the stretching vibration frequency of the C=N bond varies from 1698 to 1592 cm^{-1} depending on the nature and position of the substituent in the benzene ring[140].

When the dependence of the vibrational spectra of fluorine-containing imines on structure is considered (see Table), it is striking that only in the presence of a pair of *p* electrons in the substituent at the imine nitrogen (*N*-halogenomines, oximes, hydrazones, azines, sulphenylimines, and sulphinylimines) are the vibrations of the C=N bond manifested in the region characteristic of the hydrocarbon analogues and the degree of displacement of this band towards lower energies is correlated with the increase of the overlap integral of the orbitals of the valence electrons of the imine nitrogen and the substituent. In the absence of substituents with a pair of *p* electrons, the energy of the stretching vibrations of the C=N bond of the fluorine-containing imine is much higher than in the hydrocarbon analogues and increases with enhancement of the electron withdrawing effects of the substituent at the imine nitrogen.

The dependence of the ^{19}F NMR spectra of hexafluoroacetone imines on structure is unusual (see Table). Substituents at the imine nitrogen having *p* electrons diminish the shielding of the fluorine nuclei of the CF_3 group in parallel with the increase of the overlap integral of the orbitals of the imine nitrogen and the substituent of this type. Analogous effects are introduced by other substituents of the *+E* type, which has been shown particularly clearly in the series of hexafluoroacetone anils[140] and in this case too a shift of the stretching vibration bands of the C=N bond towards lower energies has been observed simultaneously with diminution of the shielding of the fluorine nuclei. Such a complex dependence is possible only for the "acetylenic" type of π overlap via the C=N bond in the compounds considered, which is fully consistent with their enhanced electrophilic properties.

Additional information about the compounds considered is provided by the results of the study for the dynamics of the ^{19}F NMR spectra[142]. Two groups of signals due to non-equivalent polyfluoroalkyl groups usually appear in the spectra of imines of fluorine-containing symmetrical ketones having a fairly rigid C=N bond [14,19,59,122,140]. The study of the temperature variation of the spectra makes it possible to discover the energy barrier to the *Z*/*E* transition[14,59,74,143], which consitutes a quantitative measure of the rigidity of the imine linkage.

The energy barriers of the *Z*/*E* transitions ($\Delta G''$) have now been estimated for *N*-perfluoroisopropyldifluorocarbonylimine[1] (approximately 11 kcal mol^{-1}), hexafluoroacetone perfluoroisopropylimine[14] (13.4 kcal mol^{-1}), and hexafluoroacetone anils[74] (14.35–15.45 kcal mol^{-1}). According to the results of Dowson et al.[143], $\Delta G''$ for aliphatic hexafluoroacetone imines varies from 12.0 to 20.5 kcal mol^{-1} depending on the degree of branching of the alkyl group. Presumably the rigidity of the C=N bond in these compounds is determined by the hyperconjugation of the alkyl substituent. Thus hexafluoroacetone methylimine is distinguished by the maximum energy barrier to *Z*/*E* isomerisation (20.5 kcal mol^{-1}). For compounds with a secondary alkyl group (isopropyl and α-hydrohexafluoroisopropyl), the $\Delta G''$ are 17.5 and 18.5 kcal mol^{-1} respectively, while the values for compounds with a "tertiary" alkyl group (t-butyl, perfluoroisopropyl, and α-chlorohexafluoroisopropyl) are 12.0–13.7 kcal mol^{-1}.

Thus the C=N bond in perfluoroketone imines is much less rigid than in the imines of the hydrocarbon series, where the $\Delta G''$ are greater than 25 kcal mol^{-1} even for aliphatic

representatives[1,142]. The greatest increase of the rigidity of the imine bond in the compounds considered is apparently attained as a result of hyperconjugation effects; the barrier to the *Z*/*E* isomerisation of perfluoroketone imines is increased by substituents with positive mesomeric contributions and possibly substituents with a high *p*-electron density.

At the same time compounds are known among perfluoroketone imines for which the *Z*/*E* transformations are achieved under the usual conditions and even at −60 °C. Judging from the ^{19}F NMR spectra, the acylimines[19], perfluoroacylimines[24,144], sulphinylimines[58], and sulphonylimines[23] of perfluoroketones belong to compounds of this class.

IV. THE REACTIVITY OF FLUORINE-CONTAINING IMINES

As unsaturated compounds with "amphoteric" properties, the non-fluorinated imines readily interact with electrophiles and nucleophiles. Under anhydrous conditions, they are readily protonated by acids with formation of iminium salts, interact with halogens and alkylating and nitrosating reagents, combine with alcohols, thiols, and amines, and react with organometallic compounds. Iminium salts interact particularly readily with nucleophiles.

As unsaturated compounds of the electron-donating type, imines enter into certain pericyclic reactions, particularly the [2 + 1]-, [2 + 2]-, and [2 + 3]-cycloaddition reactions. Azomethines, iminium salts, and acylimines are most reactive in these processes; compounds of the last type also possess dienophilic properties. The coordination-unsaturated character of the imine bond determines many isomeric and tautomeric transformations of imines of the hydrocarbon series.

The reactivity of the fluorine-containing imines differs significantly from that of their non-fluorinated analogues. The differences are considered below in relation to reactions with electrophiles and nucleophiles and also cycloaddition reactions.

1. Reactions with Electrophiles

In most cases polyfluorinated imines are weak or even extremely weak bases. Under anhydrous conditions, they are therefore frequently indifferent to acids and do not manifest properties due to the formation of iminium salts. Only the hydrazones of fluorine-containing aldehydes and ketones are apparently protonated by strong acids, as shown by the electrophilic cooperative effect of sulphuric acid in the dimerisation of hexafluoroacetone dimethylhydrazone described by Wright and Zollinger[53]:

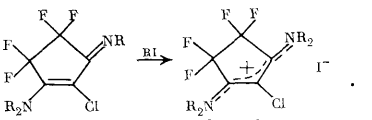
$$(CF_3)_2C{=}N{-}N(CH_3)_2 + (CH_3)_2\overset{+}{N}(H){-}N{=}C(CF_3)_2 \xrightarrow{-H^+} \begin{matrix}(CF_3)_2C{-}N{-}N(CH_3)_2\\ |\quad\quad |\\ H\quad\quad (CH_3)_2N{-}N{-}C(CF_3)_2\end{matrix}$$

There are also data concerning the acid-catalysed reactions of partly fluorinated *N*-fluoroimines, which are attributed to the cleavage of the N–F bond by protic and Lewis acids[8]. Fully fluorinated *N*-fluoroimines do not interact even with sulphuric and fluorosulphonic acids[10]. Perfluoroketone perfluoroacylimines are indifferent to anhydrous acids on heating, which is used in their purification[50,61].

At the same time aqueous solutions of acids decompose fluorine-containing imines[85,86,89,96,99,101], which makes it possible to regard these compounds as convenient precursors of carbonyl and other compounds, for example[99]:

$$CF_3{-}\underset{\|}{\underset{NH}{C}}{-}\underset{|}{\underset{NH_2}{CF}}{=}\underset{|}{\underset{NH_2}{C}}{-}CF_3 \xrightarrow{H_2O,\ H^+} CF_3C\underset{O}{\overset{\|}{C}}FH\underset{O}{\overset{\|}{C}}CF_3$$

In view of their low basicity and weak nucleophilic properties, the alkylation of fluorine-containing imines has been hardly investigated. An example of such a reaction is provided only by the interaction of cyclic iminoenamines with alkyl iodides[93], where the alkylation is promoted by the additional stabilisation of the iminium ion by dialkylaminovinyl groups:



Among the halogens, only gaseous fluorine adds to the C=N bond of fluorine-containing imines. Thus perfluoroderivatives of saturated amines are isolated together with the perfluoro-derivatives of *N*-fluoroimines in the fluorination of nitriles and various imines in the gaseous and solid phases[8]. Chlorine fluoride, which readily adds to the C=N bond in *N*-fluorodihalogenocarbonylimines[8] and hexafluoroacetone perfluoroacylimines, have similar properties[144]:

$$(CF_3)_2C{=}NC(O)R_F \xrightarrow{FCl} (CF_3)_2CFN\begin{matrix}C(O)\,R_F\\ Cl\end{matrix};$$
$$R_F = CF_3,\ C_2F_5 .$$

It is noteworthy that exhaustive fluorination of imines frequently takes place in the presence of alkali metal fluorides, the most active of which is CsF. Thus hexafluoroacetone imine has been converted into the *N*-fluoroimine on fluorination in the presence of KF and into the perfluoroisopropyldifluoroamine in the presence of CsF.[122] In the presence of CsF, hexafluoroacetone *N*-fluoroimine combines with chlorine fluoride[8]:

$$(CF_3)_2C{=}NF \xrightarrow[CsF]{F{-}X} (CF_3)_2CFNF{-}X;$$
$$X = F,\ Cl .$$

The chlorination and bromination of fluorine-containing imines do not usually take place in the absence of a catalyst. Only the interaction of bromine with hexafluoroacetone alkenylimines, leading to 1,4-addition products, has been described[119]:

$$(CF_3)_2C{=}N{-}CH{=}CRR' \xrightarrow{Br_2} (CF_3)_2CBrN{=}CHCBrRR';$$
$$R = Me,\ iso\text{-}C_3F_7,\ Ph;\ R' = H,\ Me .$$

However, many reactions of the compounds considered with halogens and other electrophiles have been achieved in the presence of bases. The interaction of perfluoroketone oximes and polyfluoroalkylhydroamoyl halides with chlorine in pyridine leads to nitrosoperhalogenoalkanes[141,145] (the Piloti reaction):

$$\begin{matrix}R_F\\ X\end{matrix}\!\!>\!C{=}NOH \xrightarrow[C_5H_5N]{Cl_2} \begin{matrix}R_F\\ X\end{matrix}\!\!>\!\underset{Cl}{C}{-}NO .$$

On chlorination in the presence of CsF and bromination in the presence of KF, perfluoroketine imines have been converted into the corresponding halogenoimines[122] (see above).

Chloropentafluoroacetone imine interacts smoothly with oxalyl chloride in pyridine, which leads to 1,2-dichloropentafluoroisopropyl isocyanate[146]:

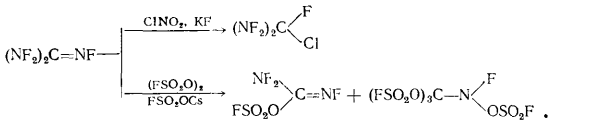
$$\begin{matrix}ClF_2C\\ F_3C\end{matrix}\!\!>\!C{=}NH \xrightarrow[C_5H_5N]{ClC(O)C(O)Cl} \begin{matrix}ClF_2C\\ F_3C\end{matrix}\!\!>\!CCl{-}N{=}C{=}O .$$

Hexafluoroacetone imine interacts with sulphur tetrafluoride[147] and thionyl fluoride[148] in the presence of caesium fluoride as the catalyst; in the presence of KF, hexafluoroacetone imine reacts with carbonyl fluoride[146]:

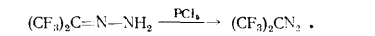
$$(CF_3)_2C{=}NH \begin{cases}\xrightarrow{SF_4,\ CsF} (CF_3)_2CF{-}N{=}SF_2\\ \xrightarrow[100^\circ]{SOF_2,\ CsF,} (CF_3)_2CF{-}N{=}S{=}O\\ \xrightarrow{COF_2,\ KF} (CF_3)_2CF{-}N{=}C{=}O\end{cases}$$

In the absence of catalysts, such reactions can be achieved only when the explosive hexafluoroacetone lithioimine is used (see above).

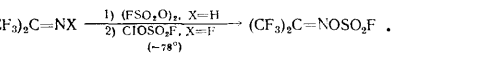
The interactions of pentafluoroguanidine with nitryl chloride catalysed by KF [149] and with peroxodisulphuryl difluoride in the presence of caesium fluorosulphate[150] have been described:



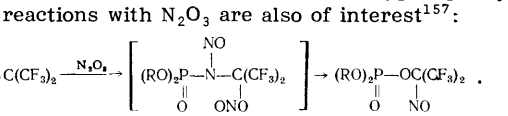
Non-catalysed reactions of electrophiles with fluorine-containing imines are also known. Thus hexafluoroacetone hydrazone is oxidised to bis(trifluoromethyl)-diazomethane on treatment with PCl_5:[60]



Substitutional fluorosulphonation of hexafluoroacetone imine by peroxodisulphuryl difluoride[151] and the reactions of halogenofluorosulphates with pentafluoroguanidine[152,153] and hexafluoroacetone fluoroimine[154] take place readily:

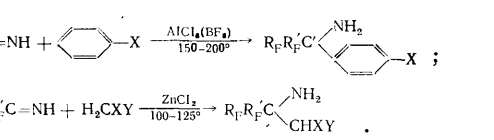


Hexafluoroacetone imine reacts with boron halides under mild conditions[155,156]:



The transformations of hexafluoroacetone dialkoxyphosphoryl-imines in the reactions with N_2O_3 are also of interest[157]:

The reactions of perfluoroketone imines with aromatic compounds or CH acids in the presence of Lewis acids apparently proceed via an electrophilic mechanism[158]:



It is evident from the data presented that fluorine-containing imines possess an unusual ability to interact with electrophiles. The protonation, alkylation, acylation, and electrophilic reactions, which take place readily with the non-fluorinated analogues and usually proceed via three-centre transition states, are not characteristic of these compounds. Fluorine-containing imines interact fairly vigorously only with reagents capable of electrophilic addition via a four-centre transition state (nitrosating agents, boron halides, and probably halogenofluorosulphates). Analogous behaviour is to some extent characteristic also of the reactions of electrophiles with polyfluoroalkenes[159].

The available data also show that, as fluorine or polyfluoroalkyl groups accumulate at the imine bond, its ability to interact with electrophiles is sharply reduced. At the same time there is an increase of the probability of the reaction of fluorine-containing imines with electrophiles via a nucleophilic mechanism, which is also characteristic of polyfluoroalkenes[160]. The above finding suggests that one may expect an appreciable expansion of the range of reactions of fluorine-containing imines with electrophiles, many of which may acquire applied importance.

2. Reactions with Nucleophiles

In terms of the character of their reactivity with respect to nucleophiles, the fluorine-containing imines known at present can be divided into two groups. *N*-Polyfluoroalkyl-substituted mono- and di-fluorocarbonylimines, polyfluoroalkylhydroxamoyl fluorides, and certain *N*-fluoroimines should be included in the first group. All these compounds form predominantly or exclusively products of the substitution of the fluorine atom and the carbon atom of the imine group on interaction with nucleophiles of the type H–X. Numerous examples of reactions of this type have been published in a book[5] and in a review[6].

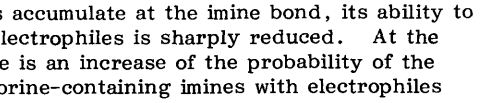
This character of the reactivity of the fluorine-containing imines of the first group is apparently associated with the increased asymmetry of the π orbital of the C=N bond due to the effects of the fluorine atom; this results in the elimination of the possibility of the concerted addition of the nucleophile and the process takes place in a stepwise manner.

The absence of direct correlations between the nucleophilic properties of the reactants and the conditions of their reactions with *N*-trifluoromethyldifluorocarbonylimine (pentafluoro-2-azapropene) may be quoted in support of these ideas[6]. Proof of the impossibility of concerted reactions of compounds of this type has been obtained in a study of the interaction of polyfluoroalkylhydroxamoyl halides with triethylamine[161–165] where nitrile oxides should have been formed as a result of the concerted dehydrohalogenation. It was shown in the above studies that the mode of reaction depends little on the structure of the polyfluoroalkyl group and is determined exclusively by the nature of the halogen at the C=N bond. Thus, whereas the interaction of hydroxamoyl fluorides with triethylamine leads to oligomers under any conditions in the presence of dipolarophiles and in their absence[162], i.e.

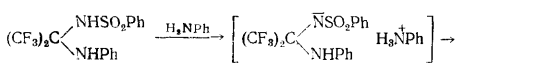
the corresponding hydroxamoyl chlorides and particularly hydroxamoyl bromides are converted by triethylamine under mild conditions into the corresponding nitrile oxides, detected by the presence of the [2 + 3]-cycloaddition products[163–165].

Acyl-, sulphinyl-, and sulphonyl-imines should be included in the second group of fluorine-containing imines, which react with nucleophiles to form addition products. Polyfluoroketone sulphonylimines have been most widely investigated in reactions with nucleophiles[166–173].

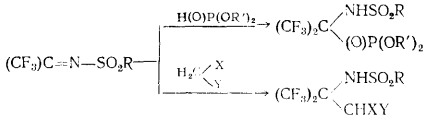
It has been shown[166–168] that polyfluoroketone methane- and benzenesulphonylimines interact vigorously with proton-containing nucleophiles and in many instances such reactions can be carried out unambiguously only in dilute solutions with cooling and slow introduction of the nucleophile into the reaction medium. Under optimum conditions, the reactions with aliphatic alcohols, α,β-unsaturated alcohols, ethylene chlorohydrin, and phenol (0–20 °C), thiols (−40 °C), amines (−50 to −40 °C), carboxylic acid amides (including their fluoro-derivatives), urea, and sulphonamides (50–60 °C) take place almost quantitatively:



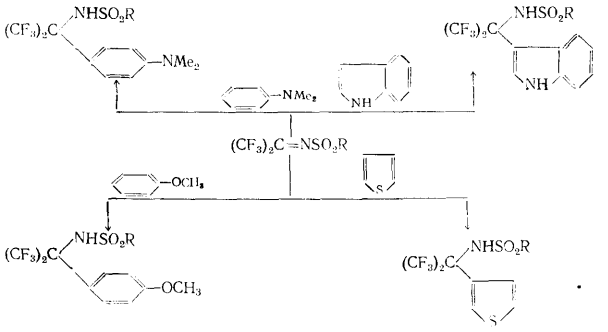
Polyfluoroketone sulphonylimines interact particularly vigorously with fairly strong bases. In this case there is a possibility of side reactions due to the appearance of an excess of the base in the reaction medium[166,167]:



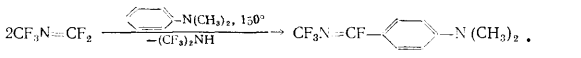
The reactions of polyfluoroketone sulphonylimines with PH and CH acids such as dialkyl phosphites (20 °C),[169] malonic and acetoacetic esters, and acetylacetone (20–50 °C) take place under mild conditions in the absence of catalysts[170]:



The π-electron-donating aromatic compounds, namely *N*,*N*-dimethylaniline (−40 °C),[171] indole (20 °C),[172] and anisole and thiophen (50–60 °C),[171,173] are unusually readily alkylated by polyfluoroketone sulphonylimines. The alkylation takes place regiospecifically at the site of maximum π-electron density in the ring:

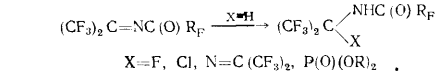


In all these reactions polyfluoroketone sulphonylimines behave as "mild" π-acids, which has been confirmed by the method of competing reactions[168]. This feature is responsible for the concerted mechanism of the addition reaction, which constitutes a significant difference between the sulphonylimines and the imines of the first group, for which many of the reactions described above either do not occur or require extremely severe conditions, for example[174]:

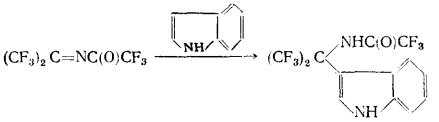


Hexafluoroacetone perfluoroacylimines, sulphinylimines, dialkoxyphosphorylimines, and acylimines, which are similar to sulphonylimines as regards the conditions of their reactions with nucleophiles, are distinguished by an extremely low energy barrier to *Z*/*E* transformations.

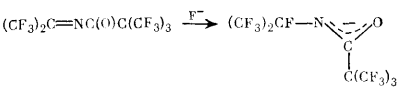
Hexafluoroacetone perfluoroacylimines are apparently even stronger π-acids than sulphonylimines. Together with the usual nucleophiles[24,108], they combine under mild conditions with hydrogen halides[144], hexafluoroacetone imine[73], and dialkyl phosphites[175] in the absence of catalysts:



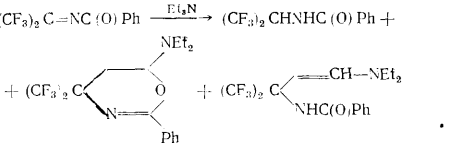
Hexafluoroacetone trifluoroacetylimine alkylates indole exothermically (on cooling)[172]:



A single example of the interaction of acylimines with the fluoride ion is known. It has been shown[106] that hexafluoroacetone perfluoropivaloylimine combines with caesium fluoride in an exothermic reaction, forming a salt stable up to 130 °C:



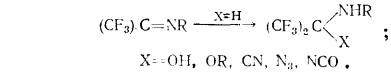
According to the available data, hexafluoroacetone sulphonylimines react exothermically with alcohols, thiols, and amines[58], while hexafluoroacetone dialkoxyphosphorylimines undergo exothermic reactions with water and alcohols[57]. At 20 °C alcohols, amines, and sulphonamides add to trifluoroacetaldehyde sulphonylimines[176]. Polyfluoroketone acylimines are highly reactive in reactions with alcohols thiols, amines, and acid amides[20,56]. The electrophilic properties of hexafluoroacetone acylimines are so pronounced that they are capable of "abstracting" a hydride anion from a triethylamine molecule[177]:



Other fluorine-containing imines are less reactive with respect to nucleophiles: polyfluoroketone imines unsubstituted at the nitrogen atom, aliphatic polyfluorinated azomethines, anils, hydrazones, azines, and *N*-fluoroimines. They constitute, as it were, an intermediate group of imines between difluoro- or fluoro-carbonylimines, on the one hand, and sulphonyl- or acyl-imines, on the other.

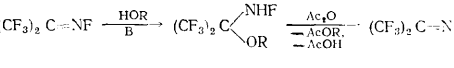
All these compounds combine vigorously with highly basic nucleophiles such as ammonia, amines, and hydrazines in the absence of catalysts, which has been demonstrated in relation to the reaction of hexafluoroacetone imines and anils[17,19,26,53,140], perfluoroguanidines, perfluoroamidines, and perfluoroketone *N*-fluoroimines[8,10], as well as hexafluoroacetone azine[115]. Thiols add to hexafluoroacetone anils[140] and alkenylimines[119] in the absence of catalysts and without heating. The conditions governing the interaction with hydroxy-compounds depend greatly on the nucleophilic properties of the latter and the electrophilic properties of the imine.

Thus hexafluoroacetone imine and its *N*-alkyl and *N*-aryl derivatives combine with lower alcohols on moderate heating or in the presence of catalysts without heating[17,26,78,140]. In the presence of basic catalysts, HCN, HN_3, HNCO, and acid alcohols interact with hexafluoroacetone imine[19,120]:



The addition is favoured by protophilic solvents capable of forming non-solvated anionoid species. Analogous features are characteristic also of the series of *N*-fluoroimines[8,10].

Even powerful electrophiles such as pentafluoroguanidine and pentafluoroamidines, which readily combine with lower alcohols, interact with weakly basic hydroxy-compounds only in the presence of nucleophilic catalysts[178,179]. Weaker electrophiles, for example polyfluoroketone *N*-fluoroimines, react even with aliphatic alcohols only in the presence of bases, forming adducts which are readily decomposed[8,10]:



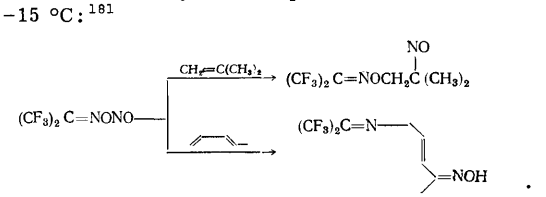
The extremely strong influence of steric factors on the conditions and even the possibility of the addition of the reactant to the C=N bond, characteristic also of the imines of the hydrocarbon series, must be regarded as a characteristic feature of the properties of the intermediate group of fluorine-containing imines, apart from the marked dependence of the conditions in their reactions with nucleophiles on the basicity of the latter. The increase of the bulk of the substituent at the imine nitrogen atom or at the nucleophilic centre of the reactant leads to a sharp alteration of the reaction parameters, so that in many instances even highly basic amines do not form adducts with fluorine-containing imines.

The next characteristic feature is that many of the fluorine-containing imines of this group are distinguished by an increased tendency towards the stepwise combination with nucleophiles. This determines the optimum conditions for their reactions with nucleophiles, the possibility of achieving the reactions with electrophiles with nucleophilic cooperation discussed above, and many unusual reactions of *N*-fluoroimines involving the formation of aza-anions[8]. In this respect the imines of the intermediate group, as it were, manifest the properties of difluoro- and fluoro-carbonylimines with the difference that they give rise to addition products instead of substitution products.

Thus a broad spectrum of the reactivities of the test compounds has been manifested in fluorine-containing imine–nucleophile systems: ranging from typical stepwise reactions to extremely mild concerted reactions. In the reactions of the first type one of the aspects of the reactivity of the dichlorocarbonylimines known in the hydrocarbon series is thrown into sharp contrast and is enhanced, while in the second type the unusual chemistry of iminium compounds is strongly manifested. At the same time the analogies noted above must be regarded as superficial. In reality the study of fluorine-containing imines as electrophiles led to the discovery of the most effective precursors of aza-anions, the strongest of the known "soft" π-acids, and a multiplicity of compounds with intermediate properties.

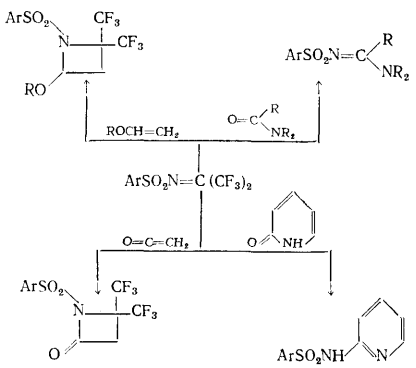
3. Cycloaddition Reactions

Various representatives of fluorine-containing imines have been investigated to unequal extents in cycloaddition reactions. Fluorine-containing oximes and their derivatives have not apparently been involved in cycloaddition hitherto. It has only been shown that in some of their reactions with unsaturated compounds, where one might have expected the formation of cyclic [2 + 2]- and [4 + 2]-adducts, acyclic substances were obtained. This happens on heating under severe conditions mixtures of hexafluoroisopropylideneiminoxy-*N*,*N*-bis(trifluoromethyl)amine with polyfluoroalkenes[139] (see above). The nitrite of hexafluoroacetone oxime interacts analogously with polyfluoroalkenes at 180–190 °C [180] and with ethylenic compounds and 1,3-dienes at −50 to −15 °C:[181]



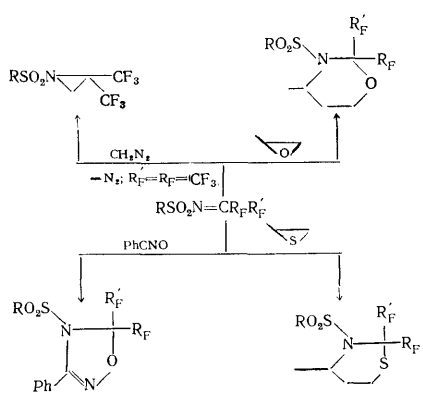
It may be that the many-centre π orbital of the derivative of the fluorine-containing oxime has no common symmetry elements with the π orbitals of alkenes and 1,3-dienes, i.e. the concerted [2 + 2]- and [4 + 2]-cycloaddition reactions are in this case prohibited.

Fluorine-containing azomethines are somewhat more reactive in cycloaddition processes than their hydrocarbon analogues and the tendency of these compounds towards cyclisation increases sharply with enhancement of the electron-accepting properties of the substituent at the imine nitrogen atom. Among the compounds of this series, polyfluoroketone sulphonylimines are the most reactive. It has been shown for hexafluoroacetone toluene-*p*-sulphonylimine that, under the conditions of intense cooling they react with keten and alkyl vinyl ethers to form cyclic [2 + 2]- adducts[21,22]. Hexafluoroacetone benzenesulphonylimine reacts vigorously with carboxamides via the cycloaddition–decomposition mechanism[182]:

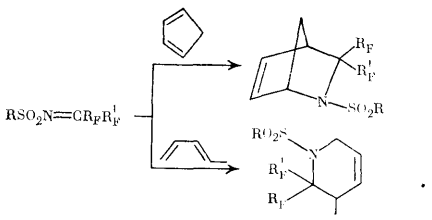


These data show that, as regards their tendency towards [2 + 2]-cycloaddition, fluorine-containing sulphonylimines have no equals in organic chemistry.

Polyfluoroketone sulphonylimines are extremely reactive also in [3 + 2]-cycloaddition. Their interaction with diazoalkanes takes place even at −60 °C and is accompanied by the elimination of nitrogen[168], which is characteristic of reactions of diazoalkanes controlled by the lowest unoccupied molecular orbitals (LUMO) of the imine and proceeds via a symmetrical transition state. Hexafluoroacetone benzenesulphonylimine readily interacts with benzonitrile oxide apparently via a stepwise pathway[161]. Polyfluoroketone sulphonylimines enter smoothly, under conditions typical for concerted reactions, into [3 + 2]-cycloaddition with oxirans and thi-irans[183,184]:

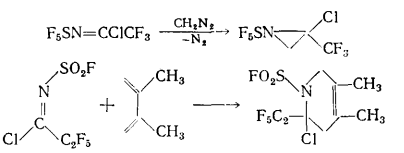


The [4 + 2]-cycloaddition of polyfluoroketone sulphonylimines takes place under unusually mild conditions[166]. They react smoothly with cyclopentadiene only with intense cooling (to −50 °C). *cis,trans*-Piperylene also enters into the reaction at a reduced temperature:

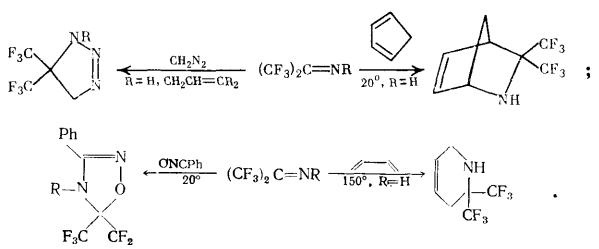


However, α,β-unsaturated aldehydes and ketones could not be involved in cycloaddition with polyfluoroketone sulphonylimines. The properties of polyfluoroketone sulphonylimines in [2 + 2]- and [4 + 2]-cycloaddition reactions described above are unusual and must be regarded as an exceptional case from the standpoint of the Woodward–Hoffman rules.

Other examples of the cycloaddition of highly electrophilic fluorine-containing imines are known. For example, trifluoroacetaldehyde toluene-*p*-sulphonylimine[37] readily forms a cyclic [4 + 2]-adduct with 2,3-dimethylbutadiene. Limiting cases of an unusually high tendency towards cycloaddition are known among fluorine-containing imines of other types, including halogenocarbonylimines[186,187]:



As the electron-withdrawing effects of the substituent and the imine nitrogen atom in fluorine-containing azomethines are reduced, their capacity for [2 + 2]-cycloaddition falls sharply. Thus hexafluoroacetone imine interacts with isobutene on heating above 200 °C to form a product of the "ene" reaction[188]. The reactivity in the [3 + 2]- and [4 + 2]-cycloaddition processes is reduced to a somewhat lesser extent[19,188–191]:



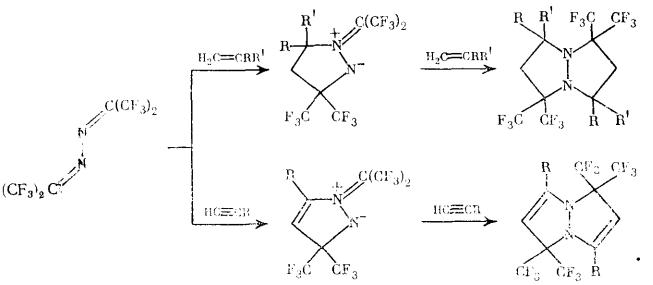
Attention should be drawn to the fact that diazomethane enters into these reactions as a 1,3-dipole[188,190] and not as a carbene precursor.

N-Fluoroimines are usually more reactive in cycloaddition reactions than fluorine-containing alkyl- and aryl-imines. They form fairly smoothly cyclic [3 + 2]- and [4 + 2]-adducts with diazomethane and 1,3-dienes respectively. Some of the compounds of this series, for example, perfluoroguanidines and amidines, are actually more reactive in [4 + 2]-cycloaddition reactions than polyfluoroketone sulphonylimines. However, in contrast to sulphonylimines, these compounds also give rise to [3 + 2]-cycloaddition products on reaction with diazomethane[8].

Fluorine containing hydrazones have been scarcely investigated in cycloaddition reactions. At the same time the spontaneous or acid-catalysed dimerisation of hexafluoroacetone *N*,*N*-dimethylhydrazone[53] (see above) under mild conditions constitutes important evidence indicating their capacity for cyclisation.

The pericyclic reactions of fluorine-containing azines and especially hexafluoroacetone azine occupy a special place in the chemistry of fluorine-containing imines. Attempts to involve this compound in [1 + 2]-cycloaddition lead either to the cleavage of the imine bond[109]:

or to products of the transformations of the primary cyclic [1 + 2]-adducts[55,116–119,192] (see above). Only keten[114] and diazomethane[115] could be involved in the reaction via the C=N bond with formation of cyclic [2 + 2]- and [3 + 2]-adducts respectively (see above). In other numerous reactions of hexafluoroacetone azine with unsaturated compounds, 1,5-diazabicyclo[3.3.0]octanes and 1,5-diazabicyclo[3.3.0]-octa-2,6-dienes are usually produced with the intermediate formation of cyclic azomethine-imines (see the communications by Tipping and co-workers[193,194] and Burger and co-workers[195,196] and the references quoted therein):



Thus the interaction of hexafluoroacetone azine with unsaturated compounds takes place as a two-stage cross [2 + 3]-cycloaddition. Ethylene, acetylene, monoalkyl- and monoaryl-substituted ethylenes and acetylenes, geminal dialkyl- and diaryl-ethylenes, alkyl vinyl ethers, alkoxyacetylenes, ynamines, certain cyclic alkenes, 1,3-dienes, acrylates, propiolates, etc. react with hexafluoroacetone azine via this pathway.

The intermediate azomethine-imines proved to be fairly stable in reactions of hexafluoroacetone azine with geminal dialkylethylenes, 1,3-dienes, alkoxyacetylenes, ynamines, etc. These compounds were isolated, their structure was demonstrated by spectroscopic methods and X-ray diffraction studies[193,196–200], and their properties were investigated. The intermediate products of these reactions served as precursors of 1,5-diazabicyclo[3.3.0]oct-2-enes, hexafluoroacetone alkenylhydrazones, and fluorine- and nitrogen-containing heterocycles (1,2-diazepines, pyrazoles, pyrazolines, pyrimidines, pyridine and triazine derivatives, etc.)[191–212].

The study of the pericyclic reactions of hexafluoroacetone azine enriched organic chemistry in new examples of intramolecular 1,3-, 1,4-, and cascade proton shifts, unusual 1,4-sigmatropic transitions of the CF_3 group, and examples of unusual intramolecular electrocyclic reactions. However, the observed characteristic features of the reactivity of azines as 1,3-dipolar systems of atoms realised in the C=N=N=C four-centre fragment must be regarded as the most important outcome of the study of hexafluoroacetone azine. The observed charactersitics of its reactions with unsaturated compounds reflect the features of [2 + 3]-cycloaddition reactions of the LUMO-controlled type and are important in synthetic organic chemistry.

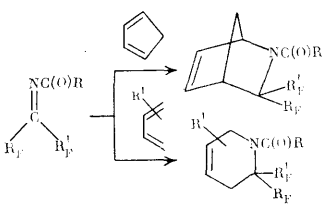
The studies of pericyclic reactions of fluorine-containing keten imines led to new advances in the chemistry of imines[11]. Their capacity for cycloaddition is greater than that of the known non-fluorinated triarylketen imines and, like the fluorine-containing azomethimes, increases appreciably as the

electron withdrawing effects of the substituents at the imine nitrogen atom become more pronounced. In contrast to triarylketen imines, fluorine-containing keten imines react exclusively at the imine bond in the [2 + 2]- and [3 + 2]-cycloaddition reactions with alkyl vinyl ethers, acetylenes, octafluoroisobutene, diazomethane, and nitrones. The dimerisation of fluorine-containing keten imines takes place analogously with nucleophilic cooperation by "soft" bases. Only dimerisation in the presence of "hard" bases and the epimerisation of these compounds involve the carbon–carbon bond. Thus the fluoroalkyl substituents in the cumulated C=C=N system exhibit more pronounced activating effects on the imine bond than on the carbon–carbon bond. The activating effects of perfluoroalkyl groups diminish the electron-donating properties of the imine group and hence the reactions controlled by the highest occupied molecular orbitals, characteristic of hydrocarbon keten imines, are replaced by the LUMO-controlled processes in the case of the fluorine-containing keten imines.

The appearance of unusual properties in the series of *N*-arylbis(trifluoromethyl)keten imines, where the imine group is linked to a conjugated system, proved to be an interesting consequence of the activating effect of the perfluoroalkyl groups. The primary pericyclic reactions are accompanied in this case by electrocyclic reactions involving aromatic systems. Formally both types of processes take place as [1 + 4]-cycloaddition in the presence of a carbenoid species and as [2 + 4]-cycloaddition in reactions with electron-donating alkenes or acetylenes. These mild reactions led to the prospect of the synthesis of hitherto inaccessible fluorine-containing derivatives of indole and quinoline and, in principle, they can be used also to synthesise other fluorine- and nitrogen-containing heterocycles[11].

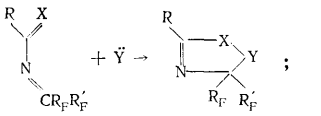
A large group of fluorine-containing imines, widely investigated in cycloaddition reactions, comprises the acyl-, thioacyl-, and iminoacyl-imines of polyfluoroketones. In contrast to azines, where the rigidity of the N–N bond prevents the formation of a four-centre π orbital in the molecule, free rotation of the acyl group at the nitrogen atom of the C=N bond is characteristic of compounds of this type, which creates conditions for the manifestation of the reactivity of both the isolated imine group and the conjugated C=N–C=X system.

The properties due to the isolated C=N bond have been investigated only in relation to the reactions involving the [4 + 2]-cycloaddition of cyclopentadiene and acyclic 1,3-dienes to polyfluoroketone acetyl- and perfluoroacyl-imines[213,214]:



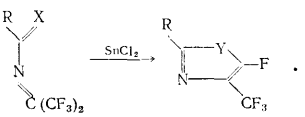
Perfluoroacylimines proved to be particularly reactive in these reactions. Cyclic adducts with cyclopentadiene can be isolated only when the reaction is carried out with intense cooling; perfluoroacylimines react at reduced temperatures even with acyclic 1,3-dienes. Hexafluoroacetone acetylimine enters into these reactions at room temperature.

The properties of polyfluoroketone acyl-, thioacyl-, and iminoacyl-imines as four-centre conjugated systems have been investigated much more widely. Carbenes, carbenoid species, and carbene precursors interact vigorously with these compounds via the [1 + 4]-cycloaddition mechanism:

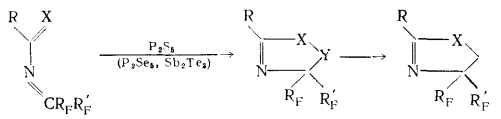


X=O, S, NH, NR, NAr; Y=CH_2, CCl_2, $C(OMe)_2$, C=NR, $P(OR)_3$.

Diazomethane[21], dichloro- and dimethoxy-carbenes and complexes of carbenes with chromium pentacarbonyl[83,109,212–217], isonitriles[83,216–220], and trialkyl phosphites[73,87,221–224] were made to undergo this reaction. Stannous chloride reacts similarly to carbonoid species, but the primary adduct decomposes and 1,3-azoles are formed[225,226]:

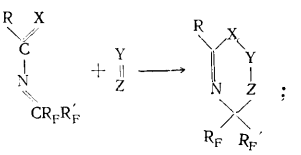


The affinity of acyl-, thioacyl-, and iminoacyl-imines for sulphur, selenium, and tellurium atoms proved to be unusually high. When the imines are heated with phosphorus pentasulphide or pentaselenide and antimony telluride, cyclic [1 + 4]-adducts are formed and then undergo a further exchange reaction[79,82,227–229]:



Y=S, Se, Te.

Reactions involving the [2 + 4]-cycloaddition of unsaturated compounds to acyl-, thioacyl-, and iminoacyl-imines of polyfluoroketones take place in most cases under extremely mild conditions. Electron-donating alkenes[21], alkyl vinyl ethers[21,230], keten[21,231], sulphenes and alkoxyacetylenes[232], aromatic aldehydes[233,234], α,β-unsaturated aldehydes[214,235], carboxylic acid nitriles[234], cyanamides[84], various alkenyl cyanides[214,236,237], and sulphoxides[238] undergo these reactions:



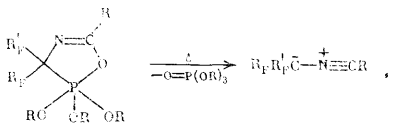
X=O, S, NH, NR, NAr.

The dienophilic properties of the compounds enumerated usually become more marked with enhancement of their electron-donating properties, which indicates the operation of LUMO-controlled mechanisms of these reactions.

Among the heterodienes of the series considered, the maximum activity is shown by perfluoroacylimines, which form cyclic [1 + 4]- and [2 + 4]-adducts as a rule under the conditions of intense cooling. These compounds must be regarded as the most reactive heterodienes among those known at present in organic chemistry.

The studies of the pericyclic reactions of polyfluoroketone acylimines enriched organic chemistry in many new examples of sigmatropic transformations and electrocyclic reactions, apart from the reactions discussed above. The cyclic

[1 + 4]-adducts of acylimines with phosphites, whose pyrolysis leads to highly reactive fluorine-containing nitrile-ylides, proved to be particularly interesting[239,240]:



A unique feature of these 1,3-dipoles is their unusually high capacity for [2 + 3]-cycloaddition not only to electron-donating unsaturated compounds but also to the C=N bond in nitrogen-containing heterocycles with formation of fluorine- and nitrogen-containing condensed systems.

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Numerous fluorine-containing analogues of imines of all known types have now been investigated on a fairly broad scale. These compounds proved in most cases to have more strained structures compared with their hydrocarbon analogues, which is the reason for their higher stability, the unique combination of their properties, and the specific features of the optimum conditions and pathways leading to their formation.

The introduction of fluorine and fluoroalkyl groups at the C=N bond usually suppresses the amphoteric character of the imines and imparts to them pronounced electrophilic properties, which depend in an unusually marked manner on the nature and positions of the fluorine-containing and other substituents at the imine bond. The effects resulting from the effect of the substituents at the highly polarisable C=N bond lead in this instance either to its marked inactivation or to a sharp increase of its ability to be involved in stepwise or concerted reactions. The chemistry of fluorine-containing imines therefore involves contrasting features. It is particularly rich in examples of extremely reactive and unreactive compounds with a C=N bond.

The above feature of the properties of fluorine-containing imines suggests that these compounds are ideal objects for theoretical studies. Comparative investigation of fluorine-containing imines and their non-fluorinated analogues at the electronic level constitutes at present one of the promising approaches to the creation of general molecular orbital models of organic compounds and their reactions.

Fluorine-containing azomethines, which reproduce many of the properties of non-fluorinated iminium salts, are of particular theoretical interest. The availability, stability, physicochemical properties convenient for investigations, and high reactivity suggest that the use of individual representatives of these compounds in the modelling of numerous biochemical reactions, involving the formation and metabolism of biogenic Schiff bases, is likely to be promising. Presumably more extensive studies of the steric effects and of the stereochemistry of reactions involving fluorine-containing imines will exert a fruitful influence on the understanding of the chemical nature of many processes involving vital activity.

The applied aspects of fluorine-containing imines have been associated for a long time only with the chemistry of the highly strained energy rich *N*-fluoroimines. However, during the last decade there has been a sharp increase of interest in various fluorine-containing imines as precursors of a wide variety of acyclic and alicyclic fluorine- and nitrogen-containing compounds. The data already accumulated at the present time suggest that fluoroimines can be usefully employed for the introduction of polyfluoroalkyl groups into a wide variety of specific structures, which leads to the possibility of their application in the syntheses of physiologically active substances and technically important products and also for the preparation of highly valuable materials. All these factors show that the advances achieved at the present time in the study of fluorine-containing imines constitute only the beginning of the development of an extremely rich field of the chemistry of organofluorine compounds with an electrophilic C=N bond.

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