PERFLUORINATED N-FLUOROIMINES
SYNTHESES AND REACTIONS WITH NUCLEOPHILIC REAGENTS

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Abstract—Perfluorinated N-fluoroimines \( R_1R'_2C=NF \), \( R_1CF=NF \) and \( R_1C(CN)=NF \) were prepared and their reactions with some nucleophiles (amines, alcohols, water, diazomethane) leading to fluorinated diaziridines, N-fluoroiminoacids and their derivatives, gem.-alkoxy-N-fluoroamines and N-fluoroethyleneimines were investigated.

The syntheses and reactivity of compounds containing nitrogen-fluorine bond have been intensively studied during the last decade. N-Fluoroimine chemistry represents one of the lines of this novel area. The present work is concerned with the study of some perfluorinated N-fluoroimines, i.e. the substances where the N-fluoroimino group is attached to perfluoro alkyl radicals, the second substituent being the perfluoroalkyl radical, fluorine atom or cyanogroup. Earlier reports on such compounds were rather casual. In 1965 Mitsch proposed a method of their synthesis by the reaction of perfluoroalkyl difluoroamines with ferrocene. The use of iron pentacarbonyl in this reaction has been described recently. The procedure is quite general but is inconvenient preparatively and the starting perfluoroalkyl difluoroamines are not readily available (excepting vicinal bis-difluoroimino compounds). Another approach adopted by Bekker, Dyatkin and Knunyants involves the decarboxylation of \( \alpha \)-difluoroaminoperfluorocarboxylic acids, which occur by action of water on the corresponding acid halides, e.g.

\[
\begin{align*}
\text{CF}_3 & \quad \text{C} \quad \text{O} \\
\text{CF}_3 & \quad \text{C} \quad \text{F} \\
\text{CF}_3 & \quad \text{NF}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{CF}_3 & \quad \text{C} \quad \text{C} \quad \text{H}_2\text{O} \\
\text{CF}_3 & \quad \text{C} \quad \text{F} \\
\text{CF}_3 & \quad \text{NF} \\
\end{align*}
\]

\[
\begin{align*}
\text{CF}_3 & \quad \text{C} \quad \text{C} \quad \text{H}_2\text{O} \\
\text{CF}_3 & \quad \text{C} \quad \text{F} \\
\text{CF}_3 & \quad \text{NF} \\
\end{align*}
\]

\[
\begin{align*}
\text{CF}_3 & \quad \text{C} \quad \text{C} \quad \text{H}_2\text{O} \\
\text{CF}_3 & \quad \text{C} \quad \text{F} \\
\text{CF}_3 & \quad \text{NF} \\
\end{align*}
\]

The starting acid halides can be prepared from alkyl perfluorovinyl ethers and tetrafluorohydrazine. \( \alpha \)-Difluoroaminohexafluorisobutyryl fluoride (I) was obtained by us in nearly quantitative yield by the interaction of tetrafluorohydrazine and bis-trifluoromethyl ketene at 170° in an autoclave. Thus instead of addition of two difluoroamino groups to the \( C=C \) ketene bond, as is usually the case in the thermal reactions of tetrafluorohydrazine with olefines, the reaction involves addition of a fluorine atom and difluoroamino group which is characteristic of the photochemical
reactions of tetrafluorohydrazine with unsaturated compounds.\textsuperscript{19} Soon after our work it was reported that bis-trifluoromethyl ketene reacts with tetrafluorohydrazine under UV irradiation in this manner, giving I.\textsuperscript{20} Other homolytic addition reactions to (CF\textsubscript{3})\textsubscript{2}C═C═O, e.g. that of NF\textsubscript{2}OSO\textsubscript{2}F, were described as well. It is quite possible that the conditions used by us may provide the addition of N\textsubscript{2}F\textsubscript{4} to (CF\textsubscript{3})\textsubscript{2}C═C═O in accord with usual scheme, leading to α-difluoroaminohexafluoroisobutyric acid N,N-difluoroamide. This subsequently eliminates fluoroazene giving I.

\[
\begin{align*}
\text{CF}_3 & - \text{C} = \text{C} = \text{O} + \text{N}_2\text{F}_4 \rightarrow \begin{array}{c}
\text{CF}_3 \\
\text{CF}_3
\end{array} & - \begin{array}{c}
\text{C} - \text{C} = \text{O} \\
\text{NF}_2 \\
\text{NF}_2
\end{array} \rightarrow I + [:\text{NF}]
\end{align*}
\]

The possible generation of a fluorine atom by heating tetrafluorohydrazine can not be excluded.

It is likely however that the reaction may follow another path. Being a strong electrophile, bis-trifluoromethyl ketene forms the mesomeric carbanion I which is oxidized by difluoroamino radical to the radical 2. The latter combines with difluoroamino radical affording I.

\[
\begin{align*}
\text{CF}_3 & - \text{C} = \text{C} = \text{O} + \text{F}^\ominus \rightarrow \begin{array}{c}
\text{CF}_3 \\
\text{CF}_3
\end{array} & - \begin{array}{c}
\text{C} \cdots \text{C} = \text{O} \\
\text{F}
\end{array} \Theta \begin{array}{c}
\text{CF}_3 \\
\text{CF}_3
\end{array} & - \begin{array}{c}
\text{C} \\
\text{CF} = \text{O}
\end{array} & :\text{NF} \rightarrow I
\end{align*}
\]

The ability of NF\textsubscript{2} to oxidize carbanions to the corresponding radicals has been demonstrated by a reaction of N\textsubscript{2}F\textsubscript{4} with perfluoroisobutene (170°, autoclave), which is catalyzed by KF.\textsuperscript{21}

\[
\begin{align*}
\text{CF}_3 & - \text{C} = \text{CF}_2 + \text{KF} \rightarrow [(\text{CF}_3)_2\text{C}] + \text{K}^\ominus \\
\text{CF}_3 & - \cdot\text{NF}_2 \\
\cdot\text{NF}_2 & - [(\text{CF}_3)_2\text{C}] + [\text{NF}_2^\ominus ] \\
(\text{CF}_3)_2\text{CNF}_2 & \text{III} \\
\text{NF}_3 & \text{NF}_3 + \frac{1}{2}\text{N}_2
\end{align*}
\]

In the absence of KF, perfluoro-tert-butyl difluoroamine (III) does not form even at 220°. According to the scheme proposed, the difluoroamino radical is an electron acceptor i.e. an oxidant in the redox reaction, the difluoroamino anion generated eliminates fluoride ion giving fluoroazene\textsuperscript{22} and finally NF\textsubscript{3}. Irreversible decay of difluoroamino anion is probably the driving force of the reaction.

In 1966 Logothetis et al.\textsuperscript{23} found a very convenient general method of synthesis of N-fluoroimines based on the reaction of N\textsubscript{2}F\textsubscript{4} with olefines in the presence of NaF.
Perfluorinated N-fluoroimines

\[
\text{RCH} = \text{CH}_2 + \text{N}_2\text{F}_4 \rightarrow \text{RCH} = \text{CH}_2 \underset{\text{NaF}}{\text{+HF}} \rightarrow \text{R} - \text{C} - \text{CN} \rightarrow \text{NF}_2 \rightarrow \text{NF}_2 \rightarrow \text{NF}
\]

We have employed this reaction for hydrogen-containing fluoroolefins and obtained a number of perfluorinated N-fluoroimines:\(^{24}\)

\[
\begin{align*}
\text{CF}_3\text{CH} = \text{CF}_2 & \rightarrow \text{CF}_3\text{CCF}_3\text{NF}_2 + \text{HF} \\
& \rightarrow \text{NF} \quad \text{IV} \\
\text{CF}_3\text{CH} = \text{CH}_2 + \text{N}_2\text{F}_4 + \text{KF} & \rightarrow \text{CF}_3\text{CCN} + 3\text{HF} \\
& \rightarrow \text{NF} \quad \text{V} \\
\text{CF}_2 = \text{CFH} & \rightarrow \text{F}_2\text{NCF}_2\text{CF} = \text{NF} + \text{HF} \\
& \rightarrow \text{VI}
\end{align*}
\]

Vinyl chloride gives a mixture of N-fluorocyanoformimidochloride (VII) and fluoride (VIII).

\[
\text{CH}_2 = \text{CHCl} + \text{N}_2\text{F}_4 + \text{KF} \rightarrow \text{NCCl} = \text{NF} + \text{NCCF} = \text{NF}
\]

VII VIII

Thus we have examples of three types of perfluoroimines available for investigation: N-fluoroimines of perfluoroketones (3), N-fluoroimidofluorides of perfluorocarboxylic acids (4) and N-fluoroimines of \(\alpha\)-ketofluoroniol (5).

\[
R_1 - \text{C} - R'_1 \\
\quad | \\
NF \\
2 \\
\quad | \\
NF \quad \text{F} \\
3 \\
\quad | \\
NF \quad \text{CN} \\
4 \\
R_1 - \text{C} - \text{CN}
\]

a: \(R_1 = R'_1 = \text{CF}_3\)  

b: \(R_1 = \text{CF}_3, R'_1 = \text{CF}_2\text{NF}_2\)

N-Fluoroimines of all three types were found to have high reactivity towards nucleophilic agents, the reaction course depends on the nature of both imine and nucleophile.

N-Fluoroimines of perfluoroketones react very easily (at \(-78^\circ\)) with ammonia and primary amines giving bis-perfluoroalkyldiaziridines in high yield.\(^ {25}\)

\[
\text{CF}_3 \\
\quad \text{C} = \text{NF} + 2\text{RNH}_2 \rightarrow X\text{CF}_2 \rightarrow X\text{CF}_3 \quad \text{NR} \rightarrow \quad + \text{RNH}_2 \cdot \text{HF}
\]

IX: \(X = \text{F}, R = \text{H}\)  

XI: \(X = \text{F}, R = \text{C}_2\text{H}_5\)  

XII: \(X = \text{NF}_2, R = \text{H}\)  

XIII: \(X = \text{NF}_2, R = \text{C}_2\text{H}_5\)

The reaction may be regarded as a modification of the Schmitz reaction.\(^ {26}\)
Diaziridines are of interest for studying the nitrogen inversion. The NMR $^19$F spectrum of XII reveals a distinct AB-system for the CF$_2$-group. The fluorine atoms of the CF$_2$ moiety may be magnetically non-equivalent when attached to an asymmetric carbon atom. In a molecule like XII, asymmetry of the cyclic carbon atom arises in consequence of the trans-orientation of hydrogen atoms when the nitrogen inversion is rather slow. Similarly, the AB-system was observed for the CH$_2$ group in NMR $^1$H spectrum of 1,1,3-trimethyl-3-benzylidiaziridine.

<table>
<thead>
<tr>
<th>Group</th>
<th>ppm</th>
<th>Multiplicity</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$</td>
<td>-5.4</td>
<td>Septet</td>
<td>26</td>
</tr>
<tr>
<td>$F_A$</td>
<td>+31.9</td>
<td>Doublet of quartets with weak splitting of each line</td>
<td>5.6 (A--CF$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($J \approx 0.5$ Hz)</td>
<td></td>
</tr>
<tr>
<td>$F_B$</td>
<td>+40.2</td>
<td>Doublet of quartets with splitting of each line to a doublet</td>
<td>4.8 (B--CF$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($J = 2.4$ Hz)</td>
<td></td>
</tr>
<tr>
<td>NF$_2$</td>
<td>-94.7</td>
<td>Broad signal</td>
<td></td>
</tr>
<tr>
<td>NH</td>
<td>2.8</td>
<td>Broad signal</td>
<td></td>
</tr>
</tbody>
</table>

The spectra were recorded at 56.4 MHz for $^19$F and at 60 MHz for $^1$H with CF$_3$COOH and TMS as external standards, at 35°C.

The interaction of N-fluoroimines of perfluoroketones with secondary amines also takes place very easily and leads to dialkylhydrazones of perfluoroketones:

\[
\text{CF}_3\text{C}=\text{NF} + 2\text{R}_2\text{NH} \rightarrow \text{C} = \text{N} \cdot \text{NR}_2 + \text{R}_2\text{NH} \cdot \text{HF}
\]

The formation of diaziridines and dialkylhydrazones in the reactions of N-fluoroimines of perfluoroketones with primary and secondary amines respectively may be described by the following general scheme:
First addition of the amine takes place giving a geminal diamine 6 with an NFH-
group, then in the presence of a base (starting amine) the α-elimination of HF occurs
leading to an azene 7. The latter cyclizes to the bipolar ion 8 (see 29), which may
stabilize in two ways, depending on the presence or absence of a hydrogen atom at the
ammonium nitrogen. In the case of 9 the proton migrates to the negatively charged
nitrogen affording diaziridine, in the alternative case the cyclic species 10, isomerizes
to a linear structure giving hydrazone. Diaziridines formation can also be explained
by another scheme (Schmitz) via an intramolecular S_N2 substitution reaction:26

\[
\begin{align*}
\text{C}=\text{NF} + \text{ROH} & \rightarrow \text{C}=\text{NF} + \text{ROH} \rightarrow \text{C}=\text{NF} + \text{ROH} \\
\text{C}=\text{NF} + \text{HCN} & \rightarrow \text{C}=\text{NF} + \text{HCN} \\
\end{align*}
\]

The suggestion of intermediate formation of 6 found some experimental confirma-
tion by obtaining gem-alkoxy-N-fluoroamines XV and gem-cyano-N-fluoroamines
XVI from N-fluoroimines of type 3 and nucleophiles such as alcohols and hydrogen
cyanide in the presence of alkali metals alkoxides and cyanides respectively.25

N-Fluoroimines of perfluoroketones react readily with diazomethane at \(-50^\circ\). The
reaction proceeds without evolution of nitrogen giving triazolines, which, unlike
usual triazolines,\textsuperscript{30,31} could not be converted into their respective ethylenimines either
photochemically or thermally. It was found however that such conversion may be
realized smoothly by treatment with conc \(\text{H}_2\text{SO}_4\), which can be explained by the
transient existence of an open bipolar tautomeric form of triazolines 12.\textsuperscript{24} The IR
spectrum of XVII shows the bands at 1569 cm\(^{-1}\) (\(\text{N}=\text{N}\)) and 2135 cm\(^{-1}\), which may
be attributed to \(\text{N}=\text{N}\). Probably, after protonating the negatively charged NF-group,
the molecule is stabilized by elimination of nitrogen followed by an intramolecular
attack of carbonium 13 ion thus generated on the NFH-group.

\[
\begin{align*}
\text{C}=\text{NF} + \text{CH}_2\text{N}_2 & \rightarrow \text{C}=\text{NF} + \text{CH}_2\text{N}_2 \\
\text{C}=\text{NF} + \text{NC} & \rightarrow \text{C}=\text{NF} + \text{NC} \\
\end{align*}
\]

* Possible existence of a bipolar form of triazolines has been discussed by Baldwin \textit{et al.}\textsuperscript{32}
The N-fluoroethyleneimines obtained are quite stable towards conc H₂SO₄; they represent a new class of compounds and are of interest. The introduction of fluorine to a nitrogen atom increases essentially the nitrogen inversion barrier.

The reaction observed between diazomethane and 1-cyano-N-fluoroformimidochloride (VII) is the following. One mole of CH₂N₂ reacts according to Nirenstein's scheme, the second--according to 1,3-addition at the C≡N bond, 1-H-4-(α-N-fluoroimino-β-chloro)ethyl-1,2,3-triazole XXI being formed.

In reactions of N-fluoroimididifluorides with nucleophiles the substitution of the carbon-bonded F atom is typical. This property has been demonstrated earlier for a similar compound, 1-cyano-N-fluoroformimidofluoride.

N-Fluoroimidoperfluorocarboxylic acid fluorides react in the same way, eg.

In all such reactions the resemblance to carboxylic acid fluorides is pronounced. The substitution products may be regarded as N-fluoroiminocarboxylic acid derivatives --esters, amides etc. Thus the hydrolysis of N-fluoroimidofluorides was of interest. The hydrolysis was carried out in ether at 20° for 40-50 hr. After treatment with KF and then with MgSO₄ to remove HF and H₂O, the ethereal solution was studied by NMR and IR spectroscopy (see Table 2). From the data obtained it may be assumed
that the hydrolysis products of VI and CF₃CF=NF are N-fluoroiminoacids rather than N-fluoroamides:³⁵

\[
\begin{align*}
\text{R} && \text{C} && \text{F} & + \text{H}_2\text{O} & \xrightarrow{\text{ether}} & \text{R} && \text{C} && \text{OH} & \xrightarrow{\text{ether}} & \text{R} && \text{C} && \text{NFH} \\
\text{NF} & & & & & & \text{NF} & & & & & & \text{O}
\end{align*}
\]

XXVI: Rᵢ = F₂NCF₂
XXVII: Rᵢ = CF₃

For example in the F¹⁹ NMR spectrum of XXVI the signals at −94 ppm, approximately −32 and +329 ppm (from CF₃COOH as external standard) are observed corresponding to the NF₂, NF and CF₂ groupings. The NMR H¹ spectrum contains a signal at 9.5–10.6 ppm (from TMS as internal standard) depending on the concentration of XXVI in ether, a similar concentration effect for NF signal in NMR F¹⁹ is observed. These effects seem to be explained by both intra- and intermolecular hydrogen bond:

\[
\begin{align*}
\text{R} && \text{C} && \text{N} & \xrightarrow{\text{F}} & \text{O} \\
& & & & & \text{H} \\
& & & & & \text{H} \ldots \text{O(C}_2\text{H}_₅)₂
\end{align*}
\]

The hydrogen bond may be one of the factors causing stabilization of N-fluoroiminoacids. The second factor is apparently the reduced basicity of nitrogen due to the negative inductive effect of the F atom. We failed to obtain any evidence of the presence of isomeric N-fluoroamides. The NHF-grouping can be identified readily in the NMR F¹⁹ spectrum by the characteristic geminal spin–spin coupling constant \( J_{\text{H}-\text{F}} = 48–55 \) Hz, the signal being located relatively upfield e.g. for C₂H₅OCONHF \( \delta = +40–44 \) ppm from CF₃COOH.³⁶

The hydrolysis of RᵢCF=NF leads finally to RᵢCOOH. The formation of CF₃COOH from CF₃CF=NF is noted earlier.⁴ By treatment of VI with CH₃OH and H₂SO₄, methyldifluoroaminodifluoroacetate is obtained.³⁷ Therefore in the ethereal solutions of N-fluoroiminoacids obtained, the admixtures of the corresponding carboxylic acids are present. On the contrary, N-fluoroimines of perfluoroketones do not change at heating to 85° either in conc H₂SO₄ or in FSO₃H. Evidently, the electron-releasing substituents at the azomethine carbon atom, such as F, OH, OCH₃, increase the basicity of nitrogen and facilitate the hydrolysis.

The distillation of an ethereal solution of XXVI, over conc H₂SO₄ for removal of ether resulted in considerable hydrolysis:

\[
\begin{align*}
\text{F}_₂\text{NCF₂} && \text{C} && \text{OH} & \xrightarrow{\text{H}_2\text{SO}_₄} & \text{F}_₂\text{NCF₂} && \text{COOH} \\
\text{NF} & & & & & & \text{NF}
\end{align*}
\]

The mixture of 46% XXVI and 54% F₂NCF₂COOH (NMR F¹⁹ data) is obtained. Attempts to remove the ether in vacuo caused explosions.

Diazomethane treatment of an ethereal solution of XXVI gave the methyl ester of N-fluoroiminoacid (XXII) (obtained independently from VI and CH₃ONa), methyl difluoroaminodifluoroacetate was isolated as well.

Careful hydrolysis of CF₃CF=NF (ether, 20°) leads also to N-fluoroiminoacid XXVII, as may be seen from Table 2.
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Chemical shifts in NMR F&lt;sup&gt;19&lt;/sup&gt;, ppm</th>
<th>Chem. shift OH C≡N C≡O OH PMR cm&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Compounds</th>
<th>Chemical shifts in NMR F&lt;sup&gt;19&lt;/sup&gt;, ppm</th>
<th>Chem. shift OH C≡N C≡O OH PMR cm&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>F&lt;sub&gt;2&lt;/sub&gt;NCF&lt;sub&gt;2&lt;/sub&gt;CF(=NF)</td>
<td>-99.2 -65.9 29.5 -2.1 1670</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;CF(=NF)</td>
<td>-54.6 -3.6 +7.1 1695</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F&lt;sub&gt;2&lt;/sub&gt;NCF&lt;sub&gt;2&lt;/sub&gt;(OH)=NF</td>
<td>-94.0 -32.7 32.9 9.5&lt;sup&gt;a&lt;/sup&gt; 1672 broad CF&lt;sub&gt;3&lt;/sub&gt;(OH)=NF</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;(OH)=NF</td>
<td>-26.5 +0.5 -10 1678 broad 3200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F&lt;sub&gt;2&lt;/sub&gt;NCF&lt;sub&gt;2&lt;/sub&gt;(OCH₃)=NF</td>
<td>-94.4 -37.2 31.3 1666 CF&lt;sub&gt;3&lt;/sub&gt;(OCH₃)=NF</td>
<td>-37.7 - 6.2 1670</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F&lt;sub&gt;2&lt;/sub&gt;NCF&lt;sub&gt;2&lt;/sub&gt;COOH</td>
<td>-97.2 32.4 1780 CF&lt;sub&gt;3&lt;/sub&gt;COOH</td>
<td>-1.4&lt;sup&gt;a&lt;/sup&gt; 1798</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>F&lt;sub&gt;2&lt;/sub&gt;NCF&lt;sub&gt;2&lt;/sub&gt;COOCH₃</td>
<td>-96.2 31.4 1795 CF&lt;sub&gt;3&lt;/sub&gt;COOCH₃</td>
<td>-1.3 1803</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> All the chemical shifts in this Table are given to the same scale with CF<sub>3</sub>COOH as external standard. NMR F<sup>19</sup> of this compound was measured with C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> as internal standard. For the calculation we adopted |δ| CF<sub>3</sub>COOH = |δ| C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> = 142 ppm.

<sup>b</sup> NMR F<sup>19</sup> of this compound was measured with (CF<sub>3</sub>)<sub>4</sub> as internal standard. Recalculation was performed using the formula δ(CF<sub>3</sub>)<sub>4</sub> - δ(CF<sub>3</sub>COOH) = 60 ppm.

<sup>c</sup> The chemical shift of the NF group varied from -33.2 to -19.9 ppm depending on the concentration of the compound in ether.

<sup>d</sup> The chemical shift of the OH group varied from 9.5 to 10.6 ppm.

<sup>e</sup> The chemical shift of the CF<sub>3</sub> group referenced to CF<sub>3</sub>COOH as external standard.
The reactions of N-fluoroimines of \( \alpha \)-ketoperfluoronitriles with nucleophiles are more complex due to the dual character of the cyano-group which is capable to display pseudohalogen properties. Thus the reaction with primary amines gave both diaziridines and N-fluoroiminoacids N'-alkylamides, e.g.

\[
\begin{align*}
R,C(CN)=NF + RNH_2 & \rightarrow R,C-CN + RNH_2 + NF \\
R, & = CF_3, R = C_2H_5
\end{align*}
\]

The formation of both products may be explained by the general scheme:

\[
\begin{align*}
R,C(CN)=NF + RNH_2 & \rightarrow \left[ R,C-CN + RNH_2 + NF \right] \rightarrow \left[ R,C-CN + RNH_2 \right] \rightarrow \left[ R,C-CN + RNH_2 \right] \rightarrow \left[ R,C-CN + RNH_2 \right] \\
R, & = CF_3, R = C_2H_5
\end{align*}
\]

Reaction of \( R,C(CN)=NF \) with secondary amines leads exclusively to dialkylhydrazones of \( \alpha \)-ketoperfluoronitriles:

\[
\begin{align*}
R,C(CN)=NF + R_2NH & \rightarrow R,C-CN + R_2NH + HF \\
R, & = CF_3, R = C_2H_5
\end{align*}
\]

In the presence of catalytic amounts of sodium alkoxides the addition of alcohols at the \( C=\text{N} \) takes place:

\[
\begin{align*}
R,C(CN)=NF + ROH + Na & \rightarrow R,C-CN + ROH + NF \\
R, & = CF_3, R = C_2H_5
\end{align*}
\]

The NMR \( F^{19} \) and \( H^1 \) spectra of the adducts show the doublets with geminal spin-spin coupling constant \( J_{HF} = 55 \text{ Hz} \), characteristic of the NHF-group. It is interesting to compare this reaction with the previously described one of phenylcyano-N-fluoroformimine with alcohol in the presence of sodium alkoxide, conducted under similar conditions.\(^38\)
Probably, substitution of a phenyl group for a trifluoromethyl group increases the electrophilicity of the iminocarbon atom thus providing the formation of geminal alkoxy-N-fluoroamines.

**EXPERIMENTAL**

The NMR F\(^{19}\) spectra were recorded on a Hitachi H-60 Model spectrometer at an operating frequency 564 MHz using CF\(_3\)COOH (TFA) as external or C\(_6\)H\(_5\)CF\(_3\) (BTF) as internal standard. The NMR H\(^1\) spectra were recorded on a Perkin-Elmer R-12 Model instrument at 60 MHz with TMS as internal standard. IR spectra were obtained on UR-20 spectrometer. The absorption bands at 800-1100 cm\(^{-1}\) are conveniently assigned to N–F vibration.

\(\text{C,H,X}--\text{CN} + \text{ROH} \rightarrow \text{R}ONP\text{C,H}--\text{x}--\text{X}--\text{OH} \rightarrow \text{NH}\)

**a-Difluoromiminohexafluoroisobutyroyl fluoride (I).** Bistrifluoromethyl ketene (17.8 g, 0.1 mole) and tetrafluorohydrazine (0.2 mole) were heated to 170° for 24 hr in a 250 ml stainless steel autoclave. The reaction gave 1 (236 g 91%/), bp 34-35°. (Found: C, 19.29; F, 68.52. C\(_3\)F\(_7\)NO requires: C, 19.29; F, 68.54%).

IR spectrum: \(v_{\text{max}}\) 925.975.1020 (N–F); 1885 (C=O) cm\(^{-1}\).

NMR F\(^{19}\) (BTF), ppm: doublet (J = 89 c/s) of triplets (J = 129 c/s) + 1.1 (CF\(_3\)), septet (J = 89 c/s) - 107.5 (COF), broad signal - 99.7 (NF\(_3\)).

**Hexafluoroacetone N-fluoroimine (II).** 1 (280 g), H\(_2\)O (10 ml) and acetone (10 ml) were heated to 70° for 2 hr in a 100 ml autoclave to give II (15.5 g, 75%). The compound was identical with an authentic sample (GLC).

IR spectrum: \(v_{\text{max}}\) 948.1031 (N–F); 1652 (C=N) cm\(^{-1}\).

NMR F\(^{19}\) (BTF), ppm: doublet (J = 26.5 c/s) of quartets (J = 6.5 c/s) (CF\(_3\) in syn position) + 40.6, doublet (J = 97 c/s) of quartets (J = 65 c/s) + 3.7 (CF\(_3\) in anti-position), broad signal - 1086 (NF\(_3\)).

**Perfluoro-tat-buryldifluoroamine (III).** Pertfluoroisobutene (80 g, 0.04 mole), tetrafluorohydrazine (0.1 mole) and KF (5.3 g, 0.1 mole) were shaken in a 100 ml autoclave at 170° for 10 hr. The unreacted tetrafluorohydrazine was removed and the reaction product sublimated to an U-shaped tube cooled to -78°. III (8.3 g, 77%) was obtained as exceptionally volatile colourless solid melting in a sealed capillary at 27.5–29.5°, after which it resolidified and melted again at 33.5–36.5°. (Found: C, 17.56; F, 77.00. C\(_3\)F\(_6\)N requires: C, 17.73; F, 77.11%, mol. wt. 268.0 requires: C, 17.73; F, 77.11%, mol. wt. 268.0).

NMR F\(^{19}\) (BTF), ppm: triplet (J = 98 c/s) + 2.7 (CF\(_3\)).

**Dijluorominopentfluoroacetone N-fluoroimine (IV).** 2-Hydroperfluoropropene (176 g, 0.132 mole), tetratfluorohydrazine (0.132 mole) and KF (25 g) in acetonitrile (30 ml) were shaken in a 250 ml autoclave at 170° for 25 hr giving IV (21.7 g, 75%), bp 18-21° (GLC and NMR F\(^{19}\) gave the mixture of syn- and anti-isomers). (Found: C, 16.48; F, 70.40%. C\(_3\)F\(_7\) requires: C, 16.68; F, 70.40%).

IR spectrum: \(v_{\text{max}}\) 910.950.990 (N–F); 1645 (C=N) cm\(^{-1}\). NMR F\(^{19}\) (TFA), ppm: multiplet + 43.4 (CF\(_3\) of syn- and anti-isomers), doublet (J = 96 c/s) of multiplets + 2.3 (CF\(_3\) of anti-isomer, CF\(_3\) in respect to F), doublet (J = 81 c/s) of multiplets - 0.9 (CF\(_3\) of syn-isomer), broad signal - 85.0 (N\(_F\) of syn- and anti-isomers), broad signal - 123.9 (NF of anti-isomer), broad signal - 126.5 (NF of syn-isomer).

**Nitrile of perfluoroacrylic acid N-fluoroimine (V).** In the same manner 1,1,1-trifluoropropene (14.3 g, 0.15 mole), tetrafluorohydrazine (0.15 mole) and KF (50 g) in CH\(_3\)CN (40 ml) heated to 180° gave V (150 g, 71.5%), bp 8-10°. (Found: C, 25.85; F, 54.08%. C\(_3\)F\(_6\)N\(_2\) requires: C, 25.73; F, 54.27%).

IR spectrum: \(v_{\text{max}}\) 960.910.1030 (N–F); 1670 (C=N) cm\(^{-1}\). NMR F\(^{19}\) (TFA), ppm: doublet (J = 12.2 c/s - 10.3 (CF\(_3\)), broad signal - 148.8 (NF\(_3\)).

**Difluoroaminodifluorocetic acid N-fluoroimidofluoride (VI).** Trifluoroethylene (130 g, 0.158 mole), tetrafluorohydrazine (0.16 mole) and KF (35 g) in CH\(_3\)CN (30 ml) heated to 150° gave VI (25.4 g 97%), bp 3–5°. (Found: C, 14.65; F, 69.24. C\(_3\)F\(_6\)N\(_2\) requires: C, 14.47; F, 68.66%).

1-Cyano-N-fluoroformimidochloride (VII) and 1-cyano-N-fluoroformimidofluoride (VIII). Vinyl chloride (9.37 g, 0.15 mole) and KF (40 g) in benzonitrile (40 ml) heated to 150° gave VII (5.21 g, 34.7%) and VIII (4.87 g, 30.4%). VII, bp 46-48°. (Found: C, 22.83; F, 18.50. C\(_2\)F\(_3\)ClN\(_2\) requires: C, 22.52; F, 17.83%).
3,3-bis(Trifluoromethyl)diaziridine (IX). 3.47 g (0.019 mole) II and 1 g (0.009 mole) NH₃ were allowed to react in a sealed ampoule for 10 hr at 20°C. 3.23 g (94%) IX was obtained which was identified with an authentic sample by means of GLC. (Found: C, 19.96; H, 1.21; F, 63.55. C₃H₂F₃N₂ requires: C, 20.01; H, 1.12; F, 63.31%).

1-Ethyl-3,3-bis(trifluoromethyl)diaziridine (X). 3.15 g (0.0172 mole) II and 1.75 g (0.0039 mole) ethylamine were allowed to react in an ampoule for 3 hr at 20°C. The reaction mixture was treated with H₂O, organic layer separated, dried over MgSO₄ and distilled giving X (3.51 g, 98%). bp 82-83°C. nD 1.3305, d 1.3629. (Found: C, 28.78; H, 3.02; F, 54.83; MRg 35.60. C₃H₂F₃N₂ requires: C, 28.85; H, 2.94; F, 54.78%; MRg 35.78). IR spectrum: v max 1408, 1326 cm⁻¹. NMR F¹ (TFA) ppm: quartets (J = 8.7 c/s) -3.4 and -13.8 (CF₃). NMR H¹: triplet (J = 7.1 c/s) 1.2 (CH₂). quartet (J = 7.1 c/s) 2.9 (CH₂). broad signal 2.9 (NH).

1-Phenyl-3,3-bis(trifluoromethyl)diaziridine (XI). In the same manner II (2.25 g, 0.0123 mole) and aniline (3.0 g, 0.032 mole) gave 2.38 g (79.5%) XI. bp 74°C/42 mm. (Found: C, 42.20; H, 2.45; F, 44.32; N, 10.96. C₉H₆F₃N₂ requires: C, 42.18; H, 2.34; F, 44.57; N, 10.93%). IR spectrum: v max 1402, 3268 cm⁻¹.

3-Trifluoromethyl-3-difluoromethyldiaziridine (XII). In the same manner IV (4.2 g, 0.0193 mole) and NH₃ (0.068 g, 0.04 mole) gave XII (3.45 g, 82.5%). bp 84-85°C. nD 1.3268. (Found: C, 16.97; H, 0.98; F, 62.35. C₃H₂F₃N₂ requires: C, 16.87; H, 0.93; F, 62.38%). IR spectrum: v max 1412, 3250, 3308 cm⁻¹.

1-Ethyl-3-fluoromethyl-2-difluoromethyldiaziridine (XIII). IV (3.5 g, 0.0162 mole) and ethylamine (1.5 g, 0.032 mole) led to XIII (2.29 g, 71.6%). bp 99-101°C. nD 1.3412. d 1.4175. (Found: C, 24.85; H, 2.53; F, 55.12; MRg 35.10. C₃H₂F₃N₂ requires: C, 24.88; H, 2.49; F, 55.20%; MRg 35.78). IR spectrum: v max 910, 935, 980, 1130 cm⁻¹ (N--F); 1395, 3248, 3290 cm⁻¹.

Hexafluoroacetone N,N-diethylhydrazon (XIV). Analogously II (24 g, 0.131 mole) and dicthylamine (2.4 g, 0.033 mole) in CF₂Cl₂ (8 g) gave XIV (20.4 g, 66%). bp 67°C/70 mm, nD 1.3885. d 1.3695. (Found: C, 35.58; H, 4.20; F, 48.56; N, 11.81; MRg 407.0. C₁₀H₁₆F₁₈N₂ requires: C, 35.60; H, 4.27; F, 48.27; N, 11.86%). IR spectrum: v max 1600 cm⁻¹ (C=N).

2-Ethoxy-2-fluoroaminohexafluoropropane (XV). II (39 g, 0.0164 mole), C₂H₅OH (3.16 g, 0.069 mole) and metallic Na (0.17 g) were allowed to react in an ampoule for 3 days at 20°C giving XV (1.92 g, 51.3%). bp 93-94°C. nD 1.3280. (Found: C, 26.16; H, 2.58; F, 56.91; N, 6.73. C₁₀H₁₆F₁₈N₂ requires: C, 26.21; H, 2.54; F, 58.05; N, 6.11%). IR spectrum: v max 878, 903, 956, 998, 1028 (N--F); 3300, 3410 cm⁻¹ (I+- H). NMR F¹ (BTF) ppm: doublet (J = 50.7 c/s) of septets (J = 11.6 c/s) + 774 (NFH). doublet (J = 11.6 c/s) + 10.7 (CF₃). NMR H¹ ppm: triplet (J = 6.5 c/s) 1.3 (CH₂). quartet (J = 6.5 c/s) 4.0 (CH₂). doublet (J = 51.3 c/s) 8.9 (NFH).

2-Cyano-2-fluoroaminohexafluoropropane (XVI). Analogously II (4.05 g, 0.022 mole), HCN (2.1 g, 0.078 mole) and KCN (0.195 g) gave XVI (2.56 g, 55%). bp 83-84°C. nD 1.3280. (Found: C, 22.16; H, 2.58; F, 56.91; N, 6.73. C₁₀H₁₆F₁₈N₂ requires: C, 22.21; H, 2.49; F, 56.95; N, 6.73%). IR spectrum: v max 910, 957, 1040 (N--F); 2935, 3240 cm⁻¹ (C--H). NMR F¹ (BTF) ppm: doublet (J = 45.6 c/s) of septets (J = 10.5 c/s) + 61.2 (NFH). doublet (J = 10.5 c/s) + 69 (CF₃). NMR H¹ ppm: triplet (J = 6.5 c/s) 1.3 (CH₃). quartet (J = 6.5 c/s) 4.0 (CH₃). doublet (J = 51.3 c/s) 8.9 (NFH).

1-Fluoro-5,5-bis(trifluoromethyl)-1,2,3-triazoline. (XVII). An ethereal diazomethane soln was added dropwise with stirring to II (4.5 g, 0.0246 mole) in 5 ml ether, cooling to -50°C until the mixture became pale-yellow. The reaction proceeded without nitrogen evolution. A major part of ether evaporated at 100 mm Hg and while the ether evaporated the temperature of the bath was allowed to increase to +15°C and the vacuum to 40 mm. At 2 mm the remaining reaction mass was transferred to a trap cooled to -78°C giving XVII (2.08 g, 37%). a liquid product which solidified at -78°C. IR spectrum: v max 878, 900, 968, 1032, 1039, 1040 cm⁻¹ (N--F); 1568 (N=N); 2135 (Ng); 2873, 2973, 3020 cm⁻¹ (C--H). NMR F¹ (TFA) ppm: doublet (J = 11.3 c/s) -7.8 (CF₃). broad signal -41.3 (NFH). NMR H¹ ppm: signal 46 (CH₂). Mass spectrum: 178 (M+ - 28, 36.4%). 159 (9.5%). 158 (11.3%). 128 (49.5%). 109 (12.5%). 78 (10.1%). 69 (100%). 33 (75.3%). 28 (13.7%). The spectrum was obtained on a Varian CH-8 instrument at U = 710 eV.

1-Fluoro-2,2-bis(trifluoromethyl)diaziridine (XIX). The ethereal soln of XVII obtained in a previous run was added dropwise carefully with periodic stirring to a reaction flask containing concentrated H₂SO₄, nitrogen evolution was observed. The reaction mixture was distilled at 19-20°C/145 mm into a receiver cooled with dry ice, giving XIX (3.4 g, 38.5% based on the starting II), bp 64-65°C. nD 1.3295. (Found: C, 24.36; H, 1.21; F, 67.45. C₃H₂F₄N₂ requires: C, 24.38; H, 1.02; F, 67.51%). IR spectrum: v max 806, 873, 900, 968 (N--F). 3043, 3132 cm⁻¹ (C--H). Detailed discussion of the NMR H¹ and F¹ is available from.

1-Fluoro-5-trifluoromethyl-5-difluoroaminodifluoromethyl-1,2,3-triazoline (XVIII). Analogously an

* The detailed analysis of NMR spectra of XIII is in preparation.
ethereal diazomethane soln was added dropwise to IV (8.4 g, 0.039 mole) in 6 ml ether until the mixture became pale-yellow. A major part of ether was evaporated in vacuo and the remaining ethereal soln of XVIII was investigated by spectroscopic methods.Attempts at complete ether evaporation led to a vigorous decomposing. IR spectrum: $\nu_{max}$ 850, 870, 892, 940, 1040 (N=−F), 1570 cm$^{-1}$ (N=N). NMR F$^{19}$ (TFA), ppm: +32.6 (CF$_2$), −72 (CF$_3$), broad signal −40.8 (NF) broad signal −92.8 (NF$_2$).

1-Fluoro-2-trifluoromethyl-2-difluoromethylidifluoromethylaziridine (XX). Similar to XIX an ethereal soln of XVIII was treated with concentrated H$_2$SO$_4$. The reaction mixture was distilled in vacuo (65 mm) into a trap cooled to −78°, giving XX (3.85 g, 43% based on the starting IV), bp 27−33°/25 mm, n$^\circ$ 1.3152. (Found: C, 21.05; H, 0.83; F, 65.55; N, 12.50. C$_8$H$_3$F$_2$N$_2$ requires: C, 20.87; H, 0.87; F, 66.08; N, 12.17%). IR spectrum: $\nu_{max}$ 870, 935, 962, 978, 1065 (N=−F); 3042, 3133 cm$^{-1}$ (C=−H). Mass spectrum: 178 (28%), 159 (37-9%), 158 (21-8%), 128 (20-2%), 109 (37-5%), 69 (100%), 33 (80%).

1-H-4-(a,N-fluorozimino-b-chloroethyl)-1,2,3-triazol (XXI). Ethereal diazomethane soln was added dropwise at −78° to VII (4.57 g, 0.043 mole) in 3 ml ether. The mixture rapidly turned dark red and nitrogen evolution was observed. Ether was evaporated in vacuo, giving XXI (1.36 g, 19-5%) b. 70°/9 mm, which solidified at room temperature. (Found: C, 29-53; H, 2-30; F, 11-45; Cl, 20-14; N, 33-48. C$_8$H$_5$FClIN$_2$ requires: C, 29-51; H, 2-46; F, 11-68; Cl, 21-82; N, 34-42%). IR spectrum: $\nu_{max}$ 850, 904, 938, 970, 993 (N=−F); 1193, 1357, 1450, 1506, 1583, 1608 cm$^{-1}$ (C=−H). NMR F$^{19}$ (TFA), ppm: broad signal −112 (NF). NMR H$^1$, ppm: singlets 4-2 (CH$_2$), 7-9 (CH).

1-Aza-2-methoxy-3-difluoroaminoperfluoropropene (XXII). VI (7-9 g, 0.043 mole) and Na (0-1 g, 0.045 mole) and CH$_3$OH (5 ml) were allowed to react in a sealed ampoule for 10 hr at room temperature. The reaction mixture was treated with water, the organic layer separated, dried over MgSO$_4$ and distilled, giving XXII (6-53 g, 81%), b. 82−83°, n$^\circ$ 1.3291. (Found: C, 20-30; H, 1-74; F, 52-07. C$_5$H$_2$OF$_2$N$_2$ requires: C, 20-23; H, 1-70; F, 53-35%). IR spectrum: $\nu_{max}$ 850, 888, 933, 970, 992 (N=−F); 1666 cm$^{-1}$ (C=N). NMR F$^{19}$ (TFA), ppm: doublet (J = 5-3 c/s) + 30-7 (CF$_3$), broad signal −37-2 (NF), broad signal (NF$_2$) −94-5.

1-Aza-2-ethoxy-3-difluoroaminoperfluoropropene (XXIII). Analogously VI (7-2 g, 0.0043 mole), Na (0-1 g, 0.0045 mole) and C$_2$H$_4$OH (5 ml) gave XXIII (6-1 g, 73-4%), b. 102−103°, n$^\circ$ 1.3380. IR spectrum: $\nu_{max}$ 830, 873, 930, 985, 1008 (N=−F); 1663 cm$^{-1}$ (C=N). NMR F$^{19}$ (TFA), ppm: doublet (J = 4-8 c/s) + 40-3 (CF$_2$), broad signal −25-9 (NF), broad signal −81-2 (NF$_2$).

1-Aza-2-cyano-3-difluoroaminoperfluoropropene (XXIV). VI (4-5 g, 0.028 mole), NaN$_2$ (1-47 g, 0.03 mole) and THF (5 ml) were allowed to react in a sealed ampoule at 20° for 17 hr. The reaction mixture was washed with water, the organic layer separated, dried over CaCl$_2$ and distilled, giving XXIV (2-0 g, 42-5%), b. 38-40°. (Found: C, 20-75. C$_2$F$_2$N$_2$ requires: C, 20-79%). IR spectrum: $\nu_{max}$ 801, 930, 980, 1008 (N=−F); 1628 (C=N); 2306 cm$^{-1}$ (C=N). NMR F$^{19}$ (TFA), ppm: doublet (J = 6-3 c/s) + 240 (CF$_3$), broad signal −99-7 (NF$_2$), broad signal −161-6 (NF).

1-Aza-2-amino-3-difluoroaminoperfluoropropene (XXV). VI (3-0 g, 0.018 mole) and NH$_3$ (0-61 g, 0.036 mole) were allowed to react in an ampoule at 20° for 10 hr. The reaction mass was treated with H$_2$O, organic layer separated, dried over MgSO$_4$ and distilled, giving XXV (1-91 g, 65%), b. 74−75°/90 mm. IR spectrum: $\nu_{max}$ 830, 932, 980, 1000 (N=−F); 1679 (C=N); 3365, 3420, 3510 cm$^{-1}$ (N=−H). NMR F$^{19}$ (TFA), ppm: doublet (J = 4-3 c/s) + 45-5 (CF$_2$), broad signal −21-8 (NF), broad signal −81-4 (NF$_2$).

Hydrolysis of F$_2$NF$_2$CF (−NF) (VI). VI (21 g), ether (30 ml) and H$_2$O (3 ml) were shaken in a 50 ml autoclave for 40 hr at 20°. Unreacted VI (7-4 g) was distilled in a trap at −78°, the reaction mixture kept for a day over calcinated KF, then over MgSO$_4$ for one day, part of the ether was removed (about 10 ml) (at bath temperature as high as 50°). The remaining ethereal soln of XXVI was treated with diazomethane. Yield (4-11 g), b. 80−85°, shown by GLC to be a mixture of 90% XXII and 10% F$_2$NF$_2$COOCH$_3$. Yield 26%, based on starting material.

Hydrolysis of CF$_3$CF (−NF). Analogously, CF$_3$CF (−NF) (5-25 g), ether (12 ml) and H$_2$O (1 ml) were allowed to react at 20° for 40 hr. After partial removal of ether the reaction mixture was investigated by spectroscopy (Table 1). The ethereal soln of XXVII was treated with diazomethane and distilled at 48−52°. The mixture obtained contained 53% CF$_3$CF (−NF)OCH$_3$ and 47% CF$_3$COOCH$_3$ (GLC and NMR F$^{19}$).

2-Ethyl-3-trifluoromethyl-3-cyanodiaziridine (XXVIII) and 1-aza-2-N-ethyldifluoropropene (XXIX). V (9 g, 0.065 mole) was added to a reaction flask fitted with a dry-ice condenser and containing ethylamine (5-86 g, 0.13 mole) in 20 ml ether whilst stirring and cooling to −78°. The temperature was allowed to increase to room temperature over 1 hr. The reaction mixture was treated with H$_2$O, the organic layer separated, dried over MgSO$_4$ and investigated by spectroscopy. According to IR and NMR F$^{19}$ data the

* The detailed analysis of NMR spectra of XX is in preparation.
mixture consisted of 60%, XXVIII and 40%, XIX. Distillation at 31–53°/35 mm gave the mixture (5.58 g) of the same composition. XXVIII (32.3%) and XXIX (22.4%) were obtained. XXVIII was isolated by preparative chromatography (Varian aerograph - 1868-4), b.p. 45-46°/39 mm. (Found: C: 36.37; H: 3.69; F: 34.30. C₅H₄F₂N₂ requires: C: 36.28; H: 3.62; F: 33.97%). IR spectrum: \( \nu_{\text{max}} \) 1392, 1460, 2205 (C=3=N); 3262 cm\(^{-1}\) (N=H). NMR F\(^{19}\) (TFA), ppm: singlet -17 (CF₃). NMR H\(^1\), ppm: triplet (J = 7.5 c/s), 1/2 (CH₃). quartet (J = 7.5 c/s) 2/7 (CH₂) and broad signal 3.0 (NH). XXIX. IR spectrum: \( \nu_{\text{max}} \) 800, 840, 888, 938 (N=--; F); 1660 (C=C=N); 3190 cm\(^{-1}\) (N=--; H). NMR F\(^{19}\) (TFA), ppm: doublet (J = 5.6 c/s) -9.4 (CF₃), broad signal -24.8 (NF).

**Trifluoropyruvic acid nitrile N,N-diethyldihydrazone (XXX).** In a similar manner to the previous run, V (4.5 g, 0.0325 mole) was added into a reaction flask with diethylamine (4.75 g, 0.065 mole) and ether (15 ml). Work up with H₂O and ether removal gave XXX (3.92 g, 63%), b.p. 81-83°/10 mm. (Found: C: 43.64; H: 5.30; F: 29.08. C₅H₁₂F₂N₂ requires: C: 44.01; H: 5.24; F: 29.85%). IR spectrum: \( \nu_{\text{max}} \) 1563 (C=3=N); 2108 cm\(^{-1}\) (C=C=N). NMR F\(^{19}\) (TFA), ppm: singlet -14.8 (CF₃). NMR H\(^1\), ppm: triplet (J = 7.7 c/s) 1.3 (CH₃), quartet (J = 7.7 c/s) 3.7 (CH₂).

**α-N-Fluoroamino-α-ethoxyperfluoropropionitrile (XXXI).** The reaction flask fitted with a dry-ice reflux condenser and stirrer was cooled to -78° and charged with V (2.7 g, 0.0195 mole). Metallic Na (0.04 g, 0.004 mole) in 5 ml ethanol was gradually added at -78° for 30 min. After which the reaction flask was slowly heated to 20°. The reaction mass was washed with H₂O, the organic layer separated, dried over MgSO₄ and investigated by spectroscopy. IR spectrum: \( \nu_{\text{max}} \) 877, 911, 960, 1006 (N=--; F); 1632, 1670, 3140, 1730, 3240 cm\(^{-1}\). NMR F\(^{19}\) (TFA), ppm: doublet (J = 49.3 c/s) of quartets (J = 11.9 c/s) + 490 (NFH), doublet (J = 122 c/s) -0.4 (CF₃). NMR H\(^1\), ppm: triplet (J = 6.9 c/s) 1.3 (CH₃), quartet (J = 6.9 c/s) (CH₂) 2.9, doublet (J = 49.9 c/s) 9.2 (NFH).

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