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PERFLUORINATED N-FLUOROIMINES

SYNTHESES AND REACTIONS WITH NUCLEOPHILIC REAGENTS

B. L. Dyatkin, K. N. Makarov and I. L. Knunyants
Institute of Organo-Element Compounds, Academy of Sciences, Moscow, USSR

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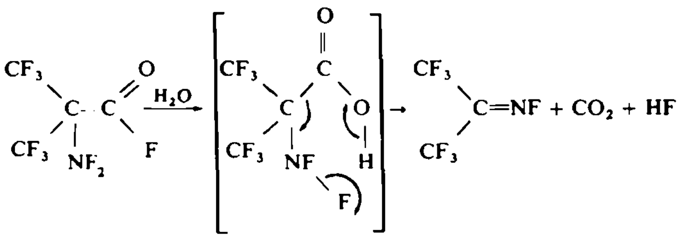
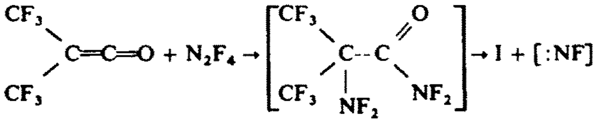
Abstract—Perfluorinated N-fluoroimines $R_fR'_fC{=}NF$, $R_fCF{=}NF$ and $R_fC(CN){=}NF$ were prepared and their reactions with some nucleophiles (amines, alcohols, water, diazomethane) leading to fluorinated diaziridines, N-fluoroiminoacids and their derivatives, gem.-alkoxy-N-fluoroamines and N-fluoroethyleneimines 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.[1–12] In 1965 Mitsch proposed a method of their synthesis by the reaction of perfluoroalkyl difluoroamines with ferrocene.[13] The use of iron pentacarbonyl in this reaction has been described recently.[14] 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[15] involves the decarboxylation of α-difluoroaminoperfluorocarboxylic acids, which occur by action of water on the corresponding acid halides, e.g.



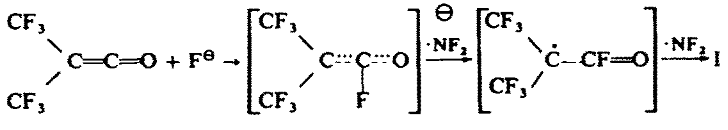
I II

The starting acid halides can be prepared from alkyl perfluorovinyl ethers and tetrafluorohydrazine.[16] α-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.[17] 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,[18] the reaction involves addition of a fluorine atom and difluoroamino group which is characteristic of the photochemical reactions of tetrafluorohydrazine with unsaturated compounds.[19] Soon after our work it was reported that bis-trifluoromethyl ketene reacts with tetrafluorohydrazine under UV irradiation in this manner, giving I.[20] Other homolytic addition reactions to $(CF_3)_2C{=}C{=}O$, e.g. that of NF_2OSO_2F, were described as well. It is quite possible that the conditions used by us may provide the addition of N_2F_4 to $(CF_3)_2C{=}C{=}O$ in accord with usual scheme, leading to α-difluoroaminohexafluoroisobutyric acid N,N-difluoroamide. This subsequently eliminates fluoroazene giving I.



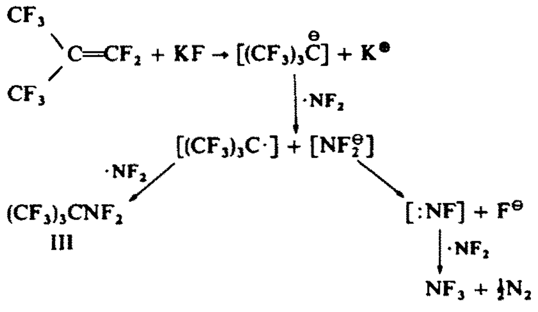
The possible generation of a fluorine atom by heating tetrafluorohydrazine can not be excluded.

It is likely however that the reaction may follow another path. Being a strong electrophile, bis-trifluoromethyl ketene forms the mesomeric carbanion **1** which is oxidized by difluoroamino radical to the radical **2**. The latter combines with difluoroamino radical affording I.



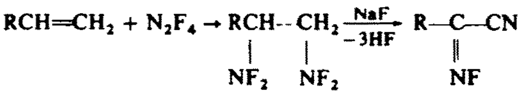
1 **2**

The ability of NF_2 to oxidize carbanions to the corresponding radicals has been demonstrated by a reaction of N_2F_4 with perfluoroisobutene (170°, autoclave), which is catalyzed by KF.[21]



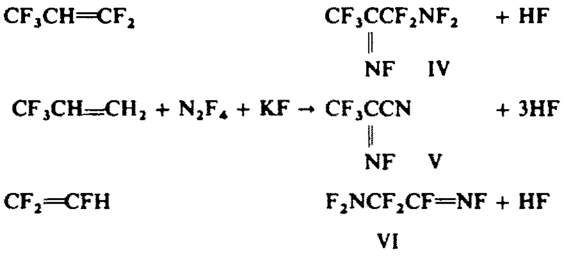
In the absence of KF, perfluoro-tert-butyl difluoroamine (III) does not form even at 220°. According to the scheme proposed, the difluoroamino radical is an electron acceptor i.e. an oxidant in the redox reaction, the difluoroamino anion generated eliminates fluoride ion giving fluorazene[22] and finally NF_3. Irreversible decay of difluoamino anion is probably the driving force of the reaction.

In 1966 Logothetis *et al.*[23] found a very convenient general method of synthesis of N-fluoroimines based on the reaction of N_2F_4 with olefines in the presence of NaF.



$$RCH{=}CH_2 + N_2F_4 \rightarrow \underset{NF_2}{RCH}-\underset{NF_2}{CH_2} \xrightarrow[-3HF]{NaF} R-\underset{NF}{\overset{\|}{C}}-CN$$

We have employed this reaction for hydrogen-containing fluoroolefines and obtained a number of perfluorinated N-fluoroimines:[24]



$$CF_3CH{=}CF_2 \qquad CF_3\underset{NF}{\overset{\|}{C}}CF_2NF_2 + HF \quad \text{IV}$$

$$CF_3CH{=}CH_2 + N_2F_4 + KF \rightarrow CF_3\underset{NF}{\overset{\|}{C}}CN + 3HF \quad \text{V}$$

$$CF_2{=}CFH \qquad F_2NCF_2CF{=}NF + HF \quad \text{VI}$$

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

$$CH_2{=}CHCl + N_2F_4 + KF \rightarrow \underset{\text{VII}}{NCCCl{=}NF} + \underset{\text{VIII}}{NCCF{=}NF}$$

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 α-ketoperfluoronitriles (5).

$$R_f-\underset{NF}{\overset{\|}{C}}-R'_f$$

3

a: $R_f = R'_f = CF_3$

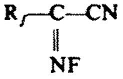
b: $R_f = CF_3$, $R'_f = CF_2NF_2$

$$R_f-\underset{NF}{\overset{\|}{C}}-F$$

4

a: $R_f = CF_3$[16]

b: $R_f = F_2NCF_2$



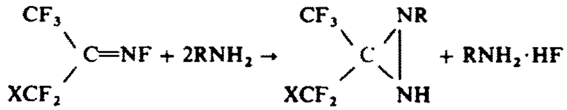
$$R_f-\underset{NF}{\overset{\|}{C}}-CN$$

5

$R_f = CF_3$

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°) with ammonia and primary amines giving bis-perfluoroalkyldiaziridines in high yield.[25]

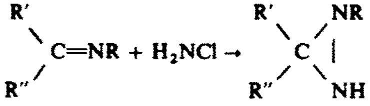


IX: $X = F, R = H$ XII: $X = NF_2, R = H$

X: $X = F, R = C_2H_5$ XIII: $X = NF_2, R = C_2H_5$

XI: $X = F, R = C_6H_5$

The reaction may be regarded as a modification of the Schmitz reaction.[26]



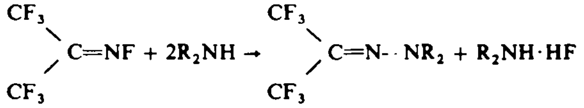
Diaziridines are of interest for studying the nitrogen inversion. The NMR F^{19} spectrum of XII reveals a distinct AB-system for the CF_2-group. The fluorine atoms of the CF_2 moiety may be magnetically non-equivalent when attached to an asymmetric carbon atom.[27] In a molecule like XII, asymmetry 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 H^1 spectrum of 1,1,3-trimethyl-3-benzyldiaziridine.[28]

TABLE 1. NMR F^{19} AND H^1 SPECTRA OF 3-TRIFLUOROMETHYL-3-(DIFLUOROAMINODIFLUOROMETHYL) DIAZIRIDINE (XII)

Group	ppm	Multiplicity	Hz
CF_3	−5·4	Septet	2·6
F_A	+31·9	Doublet of quartets with weak splitting of each line ($J \simeq 0·5$ Hz)	206 (A—B) 5·6 (A—CF_3)
F_B	+40·2	Doublet of quartets with splitting of each line to a doublet ($J = 2·4$ Hz)	206 (B—A) 4·8 (B—CF_3)
NF_2	−94·7	Broad signal	
NH	2·8	Broad signal	

The spectra were recorded at 56·4 MHz for F^{19} and at 60 MHz for H^1 with CF_3COOH and TMS as external standards, at 35°.

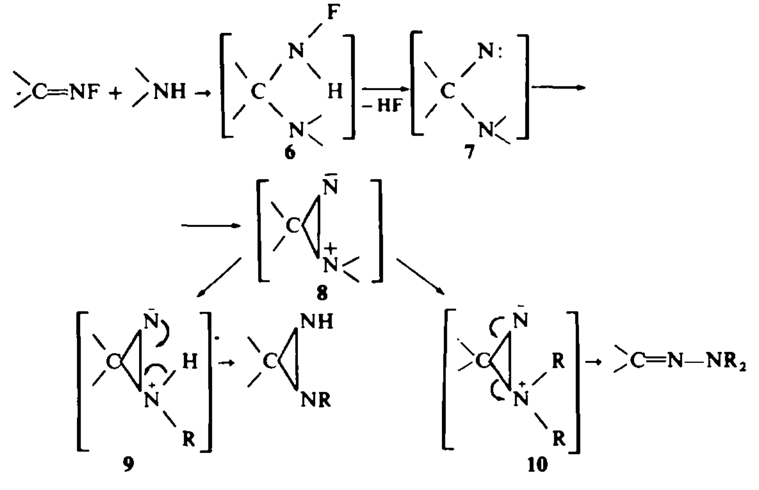
The interaction of N-fluoroimines of perfluoroketones with secondary amines also takes place very easily and leads to dialkylhydrazones of perfluoroketones:



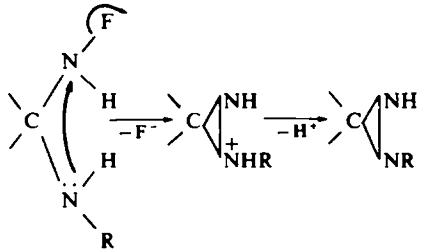
$$(CF_3)_2C{=}NF + 2R_2NH \rightarrow (CF_3)_2C{=}N{-}NR_2 + R_2NH\cdot HF$$

XIV: $R = C_2H_5$

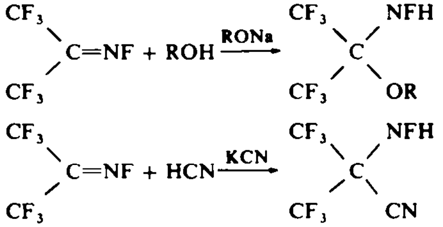
The formation of diaziridines and dialkylhydrazones in the reactions of N-fluoroimines of perfluoroketones with primary and secondary amines respectively may be described by the following general scheme:



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]



The suggestion of intermediate formation of **6** found some experimental confirmation 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]



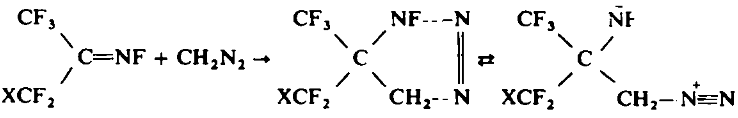
$$(CF_3)_2C{=}NF + ROH \xrightarrow{RONa} (CF_3)_2C(NFH)(OR)$$

XV R = C_2H_5

$$(CF_3)_2C{=}NF + HCN \xrightarrow{KCN} (CF_3)_2C(NFH)(CN)$$

XVI

N-Fluoroimines of perfluoroketones react readily with diazomethane at −50°. The reaction proceeds without evolution of nitrogen giving triazolines, which, unlike usual triazolines,[30, 31] could not be converted into their respective ethylenimines either photochemically or thermally. It was found however that such convertion may be realized smoothly by treatment with conc H_2SO_4, which can be explained by the transient existence of an open bipolar tautomeric form of triazolines **12**.* The IR spectrum of XVII shows the bands at 1569 cm^{-1} (N=N) and 2135 cm^{-1}, which may be attributed to N≡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.



11 **12**

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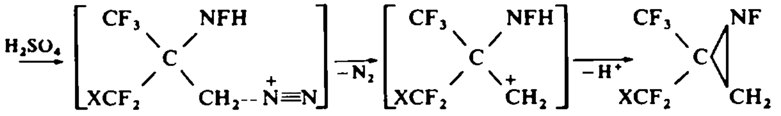
* Possible existence of a bipolar form of triazolines has been discussed by Baldwin *et al.*[32]

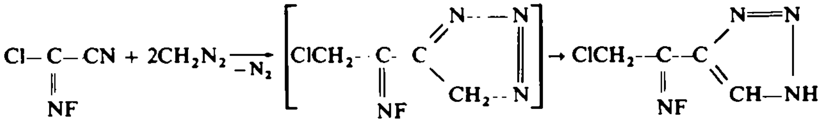


13

XIX: X = F
XX: X = NF_2

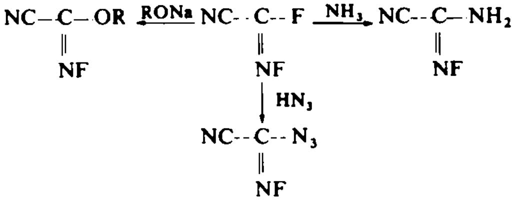
The N-fluoroethyleneimines obtained are quite stable towards conc H_2SO_4; they represent a new class of compounds and are of interest. The introduction of fluorine to a nitrogen atom increases essentially the nitrogen inversion barrier.[33]

The reaction observed between diazomethane and 1-cyano-N-fluoroformimidochloride (VII) is the following. One mole of CH_2N_2 reacts according to Nirenstein's scheme,[34] 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.



XXI

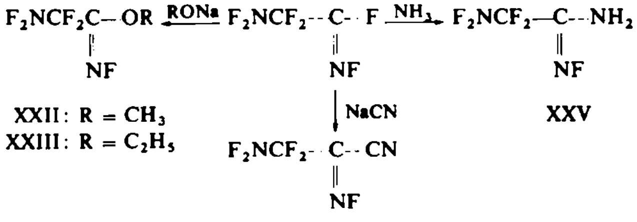
In reactions of N-fluoroimidifluorides with nucleophiles the substitution of the carbon-bonded F atom is typical. This property has been demonstrated earlier for a similar compound, 1-cyano-N-fluoroformimidofluoride.[23]



$$\mathrm{NC{-}\underset{\underset{\displaystyle NF}{\|}}{C}{-}OR} \xrightarrow{\mathrm{RONa}} \mathrm{NC{-}\underset{\underset{\displaystyle NF}{\|}}{C}{-}F} \xrightarrow{\mathrm{NH_3}} \mathrm{NC{-}\underset{\underset{\displaystyle NF}{\|}}{C}{-}NH_2}$$

$$\mathrm{NC{-}\underset{\underset{\displaystyle NF}{\|}}{C}{-}F} \xrightarrow{\mathrm{HN_3}} \mathrm{NC{-}\underset{\underset{\displaystyle NF}{\|}}{C}{-}N_3}$$

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



$$\mathrm{F_2NCF_2\underset{\underset{\displaystyle NF}{\|}}{C}{-}OR} \xrightarrow{\mathrm{RONa}} \mathrm{F_2NCF_2{-}\underset{\underset{\displaystyle NF}{\|}}{C}{-}F} \xrightarrow{\mathrm{NH_3}} \mathrm{F_2NCF_2{-}\underset{\underset{\displaystyle NF}{\|}}{C}{-}NH_2}$$

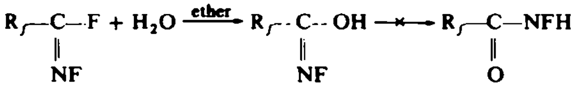
$$\mathrm{F_2NCF_2{-}\underset{\underset{\displaystyle NF}{\|}}{C}{-}F} \xrightarrow{\mathrm{NaCN}} \mathrm{F_2NCF_2{-}\underset{\underset{\displaystyle NF}{\|}}{C}{-}CN}$$

XXII: R = CH_3
XXIII: R = C_2H_5

XXV

XXIV

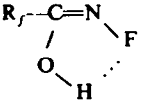
In all such reactions the resemblance to carboxylic acid fluorides is pronounced. The substitution products may be regarded as N-fluoroiminocarboxylic acid derivatives —esters, amides etc. Thus the hydrolysis of N-fluoroimidofluorides was of interest. The hydrolysis was carried out in ether at 20° for 40–50 hr. After treatment with KF and then with $MgSO_4$ to remove HF and H_2O, the ethereal solution was studied by NMR and IR spectroscopy (see Table 2). From the data obtained it may be assumed that the hydrogen bonds products of VI and $CF_3CF{=}NF$ are N-fluoroiminoacids rather than N-fluoroamides:[35]

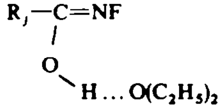


$$R_f\underset{\underset{NF}{\|}}{C}F + H_2O \xrightarrow{\text{ether}} R_f\underset{\underset{NF}{\|}}{C}OH \nrightarrow R_f\underset{\underset{O}{\|}}{C}NFH$$

XXVI: $R_f = F_2NCF_2$
XXVII: $R_f = CF_3$

For example in the F^{19} NMR spectrum of XXVI the signals at −94·0, approximately −32 and +32·9 ppm (from CF_3COOH as external standard) are observed corresponding to the NF_2, NF and CF_2 groupings. The NMR H^1 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 F^{19} is observed. These effects seem to be explained by both intra- and intermolecular hydrogen bond:

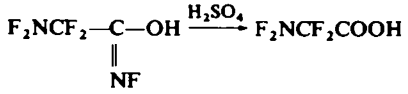




The hydrogen bond may be one of the factors causing stabilization of N-fluoroiminoacids. The second factor is apparently the reduced basisity of nitrogen due to the negative inductive effect of the F atom. We failed to obtain any evidence of the presence of isomeric N-fluoroamides. The NHF-grouping can be identified readily in the NMR F^{19} spectrum by the characteristic geminal spin–spin coupling constant J_{H-F} = 48–55 Hz, the signal being located relatively upfield e.g. for $C_2H_5OCONHF$ δ = +40·4 ppm from CF_3COOH.[36]

The hydrolysis of $R_fCF{=}NF$ leads finally to R_fCOOH. The formation of CF_3COOH from $CF_3CF{=}NF$ is noted earlier.[4] By treatment of VI with CH_3OH and H_2SO_4, 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 H_2SO_4 or in FSO_3H. Evidently, the electron-releasing substituents at the azomethine carbon atom, such as F, OH, OCH_3, increase the basicity of nitrogen and facilitate the hydrolysis.

The distillation of an etheral solution of XXVI, over conc H_2SO_4 for removal of ether resulted in considerable hydrolysis:



$$F_2NCF_2\underset{\underset{NF}{\|}}{C}OH \xrightarrow{H_2SO_4} F_2NCF_2COOH$$

The mixture of 46% XXVI and 54% F_2NCF_2COOH (NMR F^{19} 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 CH_3ONa), methyl difluoroaminodifluoroacetate was isolated as well.

Careful hydrolysis of $CF_3CF{=}NF$ (ether, 20°) leads also to N-fluoroiminoacid XXVII, as may be seen from Table 2.

TABLE 2

Hydrolysis of $F_2NCF_2CF(=NF)$									Hydrolysis of $CF_3CF(=NF)$							
Compounds	Chemical shifts in NMR F^{19}, ppm				Chem. shift OH PMR ppm	C=N cm^{-1}	C=O cm^{-1}	OH cm^{-1}	Compounds	Chemical shifts in NMR F^{19}, ppm			Chem. shift OH PMR ppm	C=N cm^{-1}	C=O cm^{-1}	OH cm^{-1}
	NF_2	NF	CF_2	CF						NF	CF_3	CF				
$F_2NCF_2CF{=}NF^a$	−99·2	−65·9	29·5	−2·1		1670			$CF_3CF{=}NF^b$	−54·6	−3·6	+7·1		1695		
$F_2NCF_2C(OH){=}NF$	−94·0	−32·7[c]	32·9		9·5[d]	1672		broad 3200	$CF_3C(OH){=}NF$	−26·5	+0·5		−10	1678		broad 3200
$F_2NCF_2C(OCH_3){=}NF$	−94·4	−37·2	31·3			1666			$CF_3C(OCH_3){=}NF$	−37·7	−6·2			1670		
F_2NCF_2COOH	−97·2		32·4				1780		CF_3COOH		−1·4[e]				1798	
$F_2NCF_2COOCH_3$	−96·2		31·4				1795		CF_3COOCH_3		−1·3				1803	

[a] All the chemical shifts in this Table are given to the same scale with CF_3COOH as external standard. NMR F^{19} of this compound was measured with $C_6H_5CF_3$ as internal standard. For the calculation we adopted $|\delta|\, CF_3COOH - |\delta|\, C_6H_5CF_3 = 14{\cdot}2$ ppm.

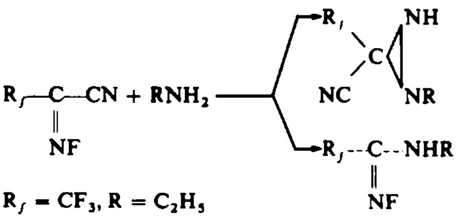
[b] NMR F^{19} of this compound was measured with $(CF_2)_4$ as internal standard. Recalculation was performed using the formula $\delta\,(CF_2)_4 - |\delta|\, CF_3COOH = 6{\cdot}0$ ppm.

[c] The chemical shift of the NF group varied from − 33·2 to − 19·9 ppm depending on the concentration of the compound in ether.

[d] The chemical shift of the OH group varied from 9·5 to 10·6 ppm.

[e] The chemical shift of the CF_3 group referenced to CF_3COOH as external standard.

The reactions of N-fluoroimines of α-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.

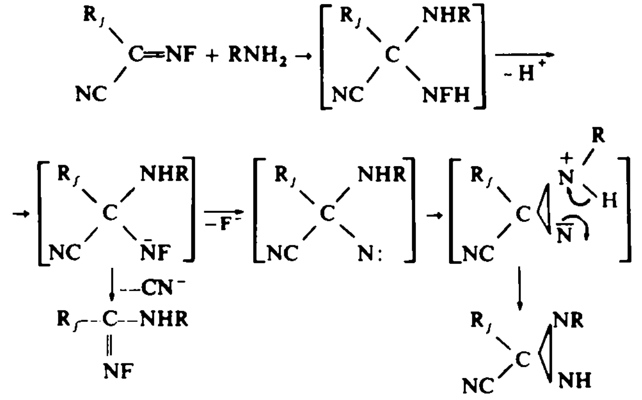


60% XXVIII

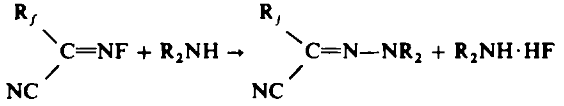
40% XXIX

$R_f = CF_3, R = C_2H_5$

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



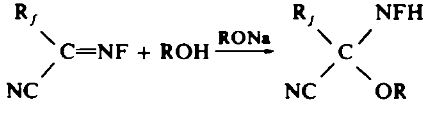
Reaction of $R_fC(CN)$=NF with secondary amines leads exclusively to dialkylhydrazones of α-ketoperflouronitriles:



$$R_f(NC)C{=}NF + R_2NH \rightarrow R_f(NC)C{=}N{-}NR_2 + R_2NH{\cdot}HF$$

$R_f = CF_3, R = C_2H_5$ XXX

In the presence of catalytic amounts of sodium alkoxides the addition of alcohols at the C=N takes place:

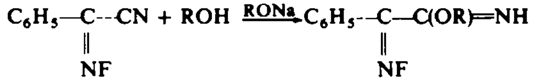


$$R_f(NC)C{=}NF + ROH \xrightarrow{RONa} R_f(NC)C(NFH)(OR)$$

XXXI

$R_f = CF_3, R = C_2H_5$

The NMR F^{19} and H^1 spectra of the adducts show the doublets with geminal spin–spin coupling constant $J_{H-F} = 55$ 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]



$$C_6H_5\text{—}\underset{\text{NF}}{\underset{\|}{C}}\text{—}CN + ROH \xrightarrow{RONa} C_6H_5\text{—}\underset{\text{NF}}{\underset{\|}{C}}\text{—}C(OR){=}NH$$

Probably, substitution of a phenyl group for a trifluoromethyl group increases the electrophility 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 56·4 MHz using CF_3COOH (TFA) as external or $C_6H_5CF_3$ (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.

α-Difluoroaminohexafluoroisobutyroyl flurodie (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 (23·6 g, 91%) bp 34–35°. (Found: C. 19·29; F. 68·52. C_4F_9NO requires: C. 19·29; F. 68·54%).

IR spectrum: ν_{max} 925. 975. 1020 (N--F); 1885 (C=O) cm^{-1} NMR F^{19} (BTF). ppm: doublet (J = 8·9 c/s) of triplets (J = 12·9 c/s) + 1·1 (CF_3), septet (J = 8·9 c/s) − 107·5 (COF), broad signal −99·7 (NF_2).

Hexafluoroacetone N-*fluoroimine* (II). I (28·0 g), H_2O (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).[15]

IR spectrum: ν_{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) +0·06, doublet (J = 9·7 c/s) of quartets (J = 6·5 c/s) + 3·7 (CF_3 in anti-position), broad signal − 108·6 (NF).

*Perfluoro-***tert***-butyldifluoroamine* (III). Perfluoroisobutene (8·0 g, 0·04 mole), tetrafluorohydrazine (0·09 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. $C_4F_{11}N$, mol. wt. 268·0 requires: C, 17·73; F, 77·11%, mol. wt. 271·0).

NMR F^{19} (BTF), ppm: triplet (J = 9·8 c/s) + 2·7 (CF_3), broad signal −96·5 (NF_2).

Difluoroaminopentafluoroacetone N-*fluoroimine* (IV). 2-Hydroperfluoropropene (17·6 g, 0·132 mole), tetrafluorohydrazine (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, 16·40; F, 70·00. $C_3F_8N_2$ requires: C, 16·68; F, 70·40%). IR spectrum: ν_{max} 910, 950, 990 (N—F); 1645 (C=N) cm^{-1} NMR F^{19} (BTF), ppm: multiplet + 40·0 (CF_2 of syn and anti isomers), doublet (J = 9·6 c/s) of multiplets + 2·3 (CF_3 of anti-isomer, CF_3 in respect to F), doublet (J = 28·6 c/s) of multiplets −0·9 (CF_3 of syn-isomer), broad signal −85·0 (NF_2 of syn- and anti-isomers), broad signal − 123·9 (NF of anti-isomer), broad signal − 126·5 (NF of syn-isomer).

Nitrile of perfluoropyruvic 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_3CN (40 ml) heated to 180° gave V (15·0 g, 71·5%), bp 8–10°. (Found: C, 25·85; F, 54·08%. $C_3F_4N_2$ requires: C, 25·73; F, 54·27%). IR spectrum: ν_{max} 960, 1030 (N--F); 1618 (C=N); 2250 (C≡N) cm^{-1}. NMR F^{19} (TFA). ppm: doublet (J = 12·2 c/s − 10·3 (CF_3), broad signal − 148·8 (NF).

Difluoroaminodifluoroacetic acid N-*fluoroimidofluoride* (VI). Trifluoroethylene (13·0 g, 0·158 mole) tetrafluorohydrazine (0·16 mole) and KF (35 g) in CH_3CN (30 ml) at 150° gave VI (25·4 g, 97%), bp −3– −2° (Found: C. 14·65: F. 69·24. $C_2F_4N_2$ requires: C. 14·47: F. 68·66%). IR spectrum: ν_{max} 860. 960. 1000 (N--F); 1670 (C=N) cm^{-1}. NMR F^{19} (BTF). ppm: doublet (J = 8·1 c/s) + 43·4 (CF_2), doublet (J = 35·4 c/s) of multiplets + 12·3 (CF), broad signal − 52·1 (NF) broad signal − 86·0 (NF_2).

1-*Cyano*-N-*fluoroformimidochloride* (VII) *and* 1-*cyano*-N-*fluoroformimidofluoride* (VIII). Vinyl chloride (9·37 g, 0·15 mole), tetrafluorohydrazine (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%).[23] VII, bp 46–48°. (Found: C, 22·83; F, 18·50. C_2FClN_2 requires: C. 22·52; F, 17·83%). IR spectrum: ν_{max} 928, 960, 987, 1135, 1170 (N--F); 1560 (C=N); 2245 (C≡N) cm^{-1}. NMR F^{19} (TFA), ppm: broad signal − 140·7 (NF).

3,3-*bis(Trifluoromethyl)diaziridine* (IX). 3·47 g (0·019 mole) II and 1 g (0·059 mole) NH_3 were allowed to react in a sealed ampoule for 10 hr at 20°. 3·23 g (94%) IX was obtained which was identified with an authentic sample[29] by means of GLC. (Found: C, 19·96; H, 1·21; F, 63·35. $C_3H_2F_6N_2$ 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 (0·039 mole)ethylamine were allowed to react in an ampoule for 3 hr at 20°. The reaction mixture was treated with H_2O, organic layer separated, dried over $MgSO_4$ and distilled giving X (3·51 g, 98%), bp 82–83°, n_D^{20} 1·3305, d_4^{20} 1·3629. (Found: C, 28·78; H, 3·02; F, 54·83; MR_D 31·60. $C_5H_6F_6N_2$ requires: C, 28·85; H, 2·91; F, 54·78%; MR_D 31·44). IR spectrum: ν_{max} 1408, 3236 cm^{-1}. NMR F^{19} (TFA) ppm: quartets (J = 8·7 c/s) −3·4 and −13·8 (CF_3). NMR H^1: triplet (J = 7·1 c/s) 1·2 (CH_3), quartet (J = 7·1 c/s) 2·9 (CH_2), 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°/42 mm. (Found: C, 42·20; H, 2·45; F, 44·53; N, 10·96. $C_9H_6F_6N_2$ requires: C, 42·18; H, 2·34; F, 44·57; N, 10·93%). IR spectrum: ν_{max} 1402, 3268 cm^{-1}.

3-*Trifluoromethyl-3-difluoroaminodifluoromethyldiaziridine* (XII). In the same manner IV (4·2 g, 0·0193 mole) and NH_3 (0·068 g, 0·04 mole) gave XII (3·45 g, 82·5%), bp 84–85°. n_D^{20} 1·3268. (Found: C, 16·97; H, 0·84; F, 62·35. $C_3H_2F_7N_2$ requires C, 16·87; H, 0·93; F, 62·48%). IR spectrum: ν_{max} 887, 930, 980, 1132 cm^{-1} (N—F); 1412, 3250, 3308 cm^{-1}.

1-*Ethyl-3-fluoromethyl-2-difluoroaminodifluoromethyldiaziridine* (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°, n_D^{20} 1·3412, d_4^{20} 1·4475.(Found: C, 24·85; H, 2·53; F, 55·12; MR_D 35·10. $C_5H_6F_7N_3$ requires C, 24·88; H, 2·49; F, 55·20%; MR_D 35·78). IR spectrum: ν_{max} 910, 935, 980, 1130 cm^{-1} (N—F); 1395, 3248, 3290 cm^{-1}.

Hexafluoroacetone N,N-*diethylhydrazone* (XIV). Analogously II (2·4 g, 0·0131 mole) and diethylamine (2·4 g, 0·033 mole) in CF_2Cl_2 (8 g) gave XIV (2·04 g, 66%), bp 67°/70 mm, n_D^{20} 1·3885, d_4^{20} 1·3695. (Found: C, 35·58; H, 4·20; F, 48·56; N, 11·81; MR_D 40·70. $C_7H_{10}F_6N_2$ requires: C, 35·60; H, 4·27; F, 48·27; N, 11·86%; MR_D 41·66). IR spectrum: ν_{max} 1600 cm^{-1} (C=N).

2-*Ethoxy-2-fluoroaminohexafluoropropane* (XV). II (3·0 g, 0·0164 mole), C_2H_5OH (3·16 g, 0·069 mole) and metallic Na (0·17 g) were allowed to react in an ampoule for 3 days at 20° giving XV (1·92 g, 51·3%), bp 93–94°, n_D^{20} 1·3280. (Found: C, 26·16; H, 2·58; F, 56·91; N, 6·73. $C_5H_6OF_7N$ requires: C, 26·21; H, 2·64; F, 58·05; N, 6·11%). IR spectrum: ν_{max} 878, 908, 956, 998, 1028 (N—F); 3300, 3410 cm^{-1} (N—H). NMR F^{19} (BTF), ppm: doublet (J = 50·7 c/s) of septets (J = 11·6 c/s) +77·4 (NFH), doublet (J = 11·6 c/s) +10·7 (CF_3). NMR H^1, ppm: triplet (J = 6·5 c/s) 1·3 (CH_3), quartet (J = 6·5 c/s) 4·0 (CH_2), 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°, n_D^{20} 1·3047. (Found: C, 22·48; H, 0·98; F, 62·90; N, 13·18. $C_4HF_7N_2$ requires: C, 22·85; H, 0·48; F, 63·33; N, 13·33%). IR spectrum: ν_{max} 910, 957, 1040 cm^{-1} (N—F); 2935, 3240 cm^{-1}. NMR F^{19} (BTF), ppm: doublet (J = 45·6 c/s) of septets (J = 10·5 c/s) +61·2 (NFH), doublet (J = 10·5 c/s) +6·9 (CF_3). NMR H^1, ppm doublet (J = 45·6 c/s) 11·4 (NHF).

1-*Fluoro*-5,5-*bis(trifluoromethyl)*-Δ^2-1,2,3-*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° 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° and the vacuum to 40 mm. At 2 mm the remaining reaction mass was transferred to a trap cooled to −78° giving XVII (2·08 g (37%)), a liquid product which solidified at −78°. IR spectrum: ν_{max} 878, 900, 935, 1005, 1032 (N—F); 1568 (N=N); 2135 (N≡N); 2873, 2973, 3020 cm^{-1} (C—H). NMR F^{19} (TFA), ppm: doublet (J = 11·3 c/s) −7·8 (CF_3), broad signal −41·3 (NF). NMR H^1, ppm: signal 4·6 (CH_2). Mass spectrum: 178 ($M^{\ddagger}$ −28, 36·4%), 159 (9·5%), 158 (11·3%), 128 (49·5%), 109 (12·5%), 78 (10·1%), 69 (100%), 33 (73·5%), 31 (20·6%), 28 (13·7%). The spectrum was obtained on a Varian CH-8 instrument at U = 71·0 eV.

1-*Fluoro*-2,2-*bis(trifluoromethyl)aziridine* (XIX). The ethereal soln of XVII obtained in a previous run was added dropwise carefully with periodic stirring to a reaction flask containing concentrated H_2SO_4, nitrogen evolution was observed. The reaction mixture was distilled at 19–20°/145 mm into a receiver cooled with dry ice, giving XIX (3·0 g, 38·5% basing on the starting II), bp 64–65°, n_D^{20} 1·2995. (Found: C, 24·36; H, 1·21; F, 67·45. $C_4H_2F_7N$ requires: C, 24·38; H, 1·02; F, 67·51%.) IR spectrum: ν_{max} 806, 873, 900, 968 (N—F); 3043, 3132 cm^{-1} (C—H). Detailed discussion of the NMR H^1 and F^{19} is available from.[33]

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

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* 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: ν_{max} 850, 870, 892, 940, 1040 (N—F), 1570 cm^{-1} (N=N). NMR F^{19} (TFA), ppm: +32·6 (CF_2), −7·2 (CF_3), broad signal −40·8 (NF) broad signal −92·8 (NF_2).

1-Fluoro-2-trifluoromethyl-2-difluoroiminodifluoromethylaziridine (XX).* Similarly to XIX an ethereal soln of XVIII was treated with concentrated H_2SO_4. The reaction mixture was distilled in vacuo (65 mm) into a trap cooled to −78°, giving XX (3·85 g, 43% basing on the starting IV), bp 27–33°/92 mm, n_D^{20} 1·3152. (Found: C, 21·05; H, 0·83; F, 65·55; N, 12·50. $C_4H_2F_8N_2$ requires: C, 20·87; H, 0·87; F, 66·08; N, 12·17%). IR spectrum: ν_{max} 870, 935, 962, 978, 1065 (N—F); 3042, 3133 cm^{-1} (C—H). Mass spectrum: 178 (28·4%), 159 (37·9%), 158 (21·8%), 128 (20·2%), 109 (37·5%), 69 (100%), 33 (80·0%).

1-H-4-(α-N-fluoroimino-β-chloro)ethyl-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.p. 70°/9 mm, which solidified at room temperature. (Found: C, 29·53; H, 2·30; F, 11·45; Cl, 20·14; N, 33·48. $C_4H_4FClN_4$ requires: C, 29·51; H, 2·46; F, 11·68; Cl, 21·85; N, 34·42%). IR spectrum: ν_{max} 850, 904, 938, 970, 993 (N—F); 1193, 1357, 1450, 1506, 1583, 1608 cm^{-1}. 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 (7·2 g, 0·043 mole), Na (0·1 g, 0·045 mole) and CH_3OH (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.p. 82–83°, n_D^{20} 1·3291. (Found: C, 20·30; H, 1·74; F, 52·07. $C_3H_3OF_5N_2$ requires: C, 20·23; H, 1·70; F, 53·35%). IR spectrum: ν_{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_2), 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, 0·045 mole) and C_2H_5OH (5 ml) gave XXIII (6·1 g, 73·4%), b.p. 102–103°, n_D^{20} 1·3380. IR spectrum: ν_{max} 830, 873, 930, 985, 1008 (N—F); 1663 cm^{-1} (C=N). NMR F^{19} (BTF), 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), NaCN (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.p. 38–40°. (Found: C, 20·75. $C_3F_5N_3$ requires: C, 20·79%). IR spectrum: ν_{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) +24·0 (CF_2), 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_2O, organic layer separated, dried over $MgSO_4$ and distilled, giving XXV (1·91 g, 65%), b.p. 74–75°/90 mm. IR spectrum: ν_{max} 830, 932, 980, 1000 (N—F); 1679 (C=N); 3365, 3420, 3510 cm^{-1} (N—H). NMR F^{19} (BTF), ppm: doublet (J = 4·3 c/s) +45·5 (CF_2), broad signal −21·8 (NF), broad signal −81·4 (NF_2).

Hydrolysis of $F_2NCF_2CF(=NF)$ (VI). VI (21 g), ether (30 ml) and H_2O (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.p. 80–85°, shown by GLC to be a mixture of 90% XXII and 10% $F_2NCF_2COOCH_3$. Yield 26% based on starting material.

Hydrolysis of $CF_3CF{=}NF$. Analogously, $CF_3CF{=}NF$ (5·25 g), ether (12 ml) and H_2O (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% $CF_3C(=NF)OCH_3$ and 47% CF_3COOCH_3 (GLC and NMR F^{19}).

2-Ethyl-3-trifluoromethyl-3-cyanodiaziridine (XXVIII) *and 1-aza-2-N-ethylaminoperfluoropropene* (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_2O, the organic layer separated, dried over $MgSO_4$ and investigated by spectroscopy. According to IR and NMR F^{19} data the

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* 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. $C_5H_6F_3N_3$ requires: C, 36·28; H, 3·62; F, 33·97%). IR spectrum: ν_{max} 1392, 1460; 2205 (C≡N); 3262 cm^{-1} (N–H). NMR F^{19} (TFA), ppm: singlet $-1{\cdot}7$ (CF_3). NMR H^1, ppm: triplet (J = 7·5 c/s), 1·2 (CH_3), quartet (J = 7·5 c/s) 2·7 (CH_2) broad signal 3·0 (NH). XXIX. IR spectrum: ν_{max} 800, 840, 888, 938 (N–F); 1660 (C=N); 3190 cm^{-1} (N–H). NMR F^{19} (TFA), ppm: doublet (J = 5·6 c/s) $-9{\cdot}4$ (CF_3), broad signal $-24{\cdot}8$ (NF).

Trifluoropyruvic acid nitrile N,N-diethylhydrazone (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 H_2O 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. $C_7H_{10}F_3N_3$ requires: C, 44·01; H, 5·24; F, 29·85%). IR spectrum: ν_{max} 1563 (C=N); 2198 cm^{-1} (C≡N). NMR F^{19} (TFA), ppm: singlet $-14{\cdot}8$ (CF_3). NMR H^1, ppm: triplet (J = 7·3 c/s) 1·3 (CH_3), quartet (J = 7·3 c/s) 3·7 (CH_2).

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 (0·09 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 H_2O, the organic layer separated, dried over $MgSO_4$ and investigated by spectroscopy. IR spectrum: ν_{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) +49·0 (NFH), doublet (J = 12·2 c/s) $-0{\cdot}4$ (CF_3). NMR H^1; ppm: triplet (J = 6·9 c/s) 1·3 (CH_3), quartet (J = 6·9 c/s) (CH_2) 2·9, doublet (J = 49·9 c/s) 9·2 (NFH).

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