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Journal of Fluorine Chemistry 89 (1998) 111–115

JOURNAL OF FLUORINE CHEMISTRY

New reactions of perfluorinated *N*-fluoroalkanimines

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Accepted 24 October 1997

Abstract

N-fluoroalkanimines of the type $R_fCF{=}N{-}F$ undergo fluoride catalyzed dimerization and rearrangement in a polar solvent into the corresponding diaziridines. They also undergo nucleophilic substitutions to $(CF_3)_2CF(R_f)C{=}N{-}F$ by reaction with hexafluoropropene (HFP) in the presence of CsF. These *N*-fluoroimines react with SbF_5 giving the corresponding aza-alkenes as a result of a Beckmann rearrangement.

Keywords: Fluoride; Diaziridines; *N*-fluoroalkanimines

1. Introduction

Despite the fact that a variety of *N*-fluoroimines are known, the chemistry of this important class of organofluorine compounds is mostly represented by the reactions of $CF_2{=}N{-}F$ [1,2], $CF_3(X)C{=}N{-}F$ (X = F, NF_2, CN) [3], perfluoroguanidine [4] and $(CF_3)_2C{=}N{-}F$ [3,4]. Data about the reactivity of higher *N*-fluoroalkanimines are rare in the literature, mostly due to the complicated and unselective methods for their preparation. The recent availability of compounds of the type $R_fCF{=}N{-}F$ from $(R_f)_2NF$ [5,6] provided an opportunity to investigate their reactivity.

$$(R_f)_3N \xrightarrow[-R_fF]{SbF_5} R_fN{=}CFR'_f \xrightarrow{F_2/CsF} (R_f)_2NF$$

$$\xrightarrow[-R_fF]{SbF_5} +R'_fCF{=}NF$$

2. Experimental

2.1. General

Volatile compounds were handled in a Pyrex vacuum line. Amounts were determined by PVT measurements or direct weighing. Infrared spectra were recorded on a Perkin-Elmer Model 1430 instrument with data station (liquid film, KCl). GLC analyses were done on a Perkin-Elmer 8500 instrument using acid washed chromasorb coated with 5% Halocarbon K-352. Purity of all new compounds was greater than 95%. Mass spectra were recorded on Hewlett-Packard 5985B spectrometer at 70 ev for both EI and CI (CH_4). Samples were introduced by direct gas injection. ^{19}F NMR spectra were recorded on an IBM NR 200 AF instrument with $CFCl_3$ as an internal reference in $CDCl_3$. Boiling points were determined by Sivoloboff's method and are uncorrected. Compound **15** was identified by comparison with an authentic sample.

2.2. Reagents

N-fluoroimines $C_3F_7CF{=}NF$ **1**, $C_5F_{11}CF{=}NF$ **2**, imines $C_4F_9O{-}N{=}C(F)C_3F_7$ **7** and $CF_3(CF_2Cl)CFO{-}N{=}C(F){-}C_3F_7$ **8** were prepared by literature methods [5,6]. Acetonitrile was distilled twice over P_4O_{10} and stored over CaH_2. Cesium fluoride was dried with a Bunsen burner and then pulverized in a dry box before use. All other chemicals were purchased from commercial sources and used as received.

Caution! Many *N*-fluoro compounds are known to be powerful explosives. We had no problems during the preparation and handling of the *N*-fluoroimines and diaziridines, but the potential instability of these compounds and their derivatives should be kept in mind. The preparation and reaction of these materials should be done on a small scale.

2.3. Dimerization of N-fluoroimines 1 and 2

In a 100 ml flask containing a suspension of dry CsF (2 mmol) in 20 ml of CH_3CN, imines **1** or **2** (5–8 mmol) were

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0022-1139/98/$19.00
PII S0022-1139(98)00096-7

added by vacuum transfer. The reaction mixture was warmed to 22°C over 10 min and was kept at this temperature with stirring for 3 days. The contents of the flask were then poured into water, and the organic layer was separated and dried over P_4O_{10} for 1 h. The volatile materials were then removed under vacuum.

3: Yield 86%; clear glass at −196°C; IR 1396 (m), 1360 (m), 1234 (vs), 1142 (s), 1055 (s), 1055 (w), 964 (m), 872 (m), 750 (m) cm^{-1}; MS *m/z* 467 (70, MH^+); ^{19}F NMR $CF_3^ACF_2^GCF_2^GCF^CF^DNN(F)^TCF^ECF_2^FCF_2^GCF_3^B$ A −81.20 (3F, dt), B −81.55 (3F, t), C −98.00 and D −98.63 (2F, typical AB pattern), E −144.2 (1F, m), F −121.2 (2F, m), G −125.6 (2F, m), −126.0 (2F, m), −126.5 (2F, m), I −7.2 (1F, m) ppm; $J_{A-G}=J_{B-F}=10.0$, $J_{C-D}\simeq 210$ Hz, other coupling constants not readily determined.

4: Yield 90%, clear glass at −196°C; IR 1387 (m), 1360 (m), 1210 (vs), 1146 (s), 1107 (w), 812 (w), 730 (m) cm^{-1}; MS *m/z* 667 (90, MH^+); ^{19}F NMR $CF_3^A(CF_2)_4^ECF^BF^CNN(F)^FCF^D(CF_2)_4^ECF_3$A. A −81.3 (6F, q), B −97.6 and C −100.0 (2F, typical AB pattern), D −143.8 (1F, m), E −120.2 (4F, m), −121.7 (2F, m), −122.2 (2F, m), −123.3 (2F, m), −124.7 (2F, m), −126.6 (4F, m), F −7.2 1F, dm) ppm; $J_{B-C}\simeq 210$ Hz, other coupling constants not readily determined.

2.4. Reactions with hexafluoropropylene

These reactions and some characteristic data for the products are summarized in Table 1. The reactions were carried out as above and the products were similarly isolated. In the case of imines **1** and **2** a slightly exothermic reaction was observed when the reaction was warmed to 22°C. For compounds **5**, **6**, **9**, and **10**, other J_{F-F} spin–spin couplings were present but their values could not be readily determined without decoupling experiments, which were not undertaken.

5: IR 1638 (w), 1622 (w), 1344 (m), 1301 (vs), 1249 (vs), 1140 (s), 1137 (s), 984 (vs), 955 (m), 830 (m), 740 (m) cm^{-1}; ^{19}F NMR $CF_3^ACF_2^DCF_2^C[(CF_3)_2^BCF^E]C{=}N{-}F^F$ A −80.4 (3F, t), B −73.6 (6F, d), C −108.3 (2F, dm), D −124.1 (2F, d), E −183.3 (1F, m), F +66.3 (1F, m) ppm; $J_{A-C}=10$, $J_{C-E}=34$, $J_{B-F}=26$, $J_{D-E}=17$ Hz.

6: IR 1624 (w), 1360 (m), 1330 (s), 1241 (vs), 1205 (vs), 1149 (vs), 1003 (m), 981 (m), 954 (m), 742 (m), 717 (m), 710 (m), 525 (m) cm^{-1}; ^{19}F NMR $CF_3^ACF_2^GCF_2^ECF_2^DCF_2^C[(CF_3)_2^BCF^F]{-}C{=}N{-}F^I$ A −81.3 (3F, t), B −75.5 (6F, d), C −107.4 (2F, br s), D −119.6 (2F, m), E −122.2 (2F, m), G −126.8 (2F, m), F −183.2 (1F, m), I +66.2 (1F, br m) ppm; $J_{B-I}=27$, $J_{C-F}=33$, $J_{A-E}=11$ Hz.

9: IR 1556–1524 (w), 1348(m), 1302 (m), 1238 (vs), 1141 (m), 982 (m), 943 (m), 899 (m), 743 (m), 728 (m) cm^{-1}; ^{19}F NMR $CF_3^CCF_2^KCF_2^ICF_2^DON{=}C[CF^J(CF_3)_2^A]{-}CF_2^FCF_2^GCF_3^B$ A −73.1 (6F, s), B −80.1 (3F, t), C −81.5 (3F, t), D −88.9 (2F, t), F −107.8 (2F, dm), G −123.9 (2F, d), I −125.5 (2F, q), K −127.1 (2F, m), L −182.4 (1F, m) ppm; $J_{C-I}=10$, $J_{B-F}=9$, $J_{F-L}=36$, $J_{G-L}=16$, $J_{D-K}=11$ Hz.

10: IR 1639 (w), 1356 (w), 1301 (m), 1243 (vs), 1103 (s), 1057 (m), 957 (m), 842 (m), 742 (m) cm^{-1}; ^{19}F NMR $CF_3^C(CF^AF^BCl)CF^ION{=}C[CF^K(CF_3)_2^E]CF_2^FCF_2^GCF_3^D$ A −65.4 and B −66.5 (2F, typical AB pattern), C −75.8 (3F, t), D −80.3 (3F, t), E −73 (6F, s), F −107.7 (2F, dm), G −124.1 (2F, d), I −134.4 (1F, m), K −186.7 (1F, tm) ppm; $J_{A-B}\simeq 184$, $J_{A-B}=J_{C-I}=10$, $J_{K-F}=27$, $J_{K-G}=15$ Hz.

2.5. Isomerization of 3, 5 and 6 under action of SbF_5

To a weighed amount of SbF_5 in a 5-ml sample tube fitted with a Teflon-glass valve, the *N*-fluorocompound was slowly added at 22°C (*Caution!* A highly exothermic reaction was observed at 22°C in the case of **3**, which underwent isomerization to **15** [7] (see Section 3). Isomerization of **5** and **6** was complete at 100°C (2–2.5 h). The reaction products were worked up as described above. Ratio of reactants, b.p. and the yields of products are given in Table 2.

11: IR 1771 (s), 1354 (m), 1306 (vs), 1253 (s), 1146 (s), 986 (s), 868 (w), 820 (w) cm^{-1}; ^{19}F NMR $(CF_3)_2^BCF^ECF^F{=}NCF_2^CCF_2^DCF_3^A$ A −81.45 (3F, t), B −74.87 (6F, t), C −93.88 (2F, dq), D −188.45 (1F, m), E −129.60 (2F, s), F −13.92 (1F, m) ppm; $J_{C-E}=19$, $J_{B-E}=J_{B-F}=7$, $J_{A-C}=8$, $J_{E-F}=18$ Hz, other coupling constants not readily determined.

Table 1
Reaction of imines **1**, **2**, **7** and **8** with HFP

Imine[a]	HFP[a]	CsF[a]	MeCN (ml)	Temp. (°C)	Time (h)	Product (yield %)	b.p. (°C)	MS $(MH)^+$ (int. %)
1 (8)	8.5	3	8	22–30	2	**5** (98)	87–88	384 (71)
2 (8.4)	9	3	10	22–30	2.5	**6** (87)	134–135	484 (100)
7 (2)	2.1	1	5	22	2	**9** (95)	168–169	600 (40)
8 (1)	1.2	3	5	22	2	**10** (70)	159–160	566 (100) 568 (63)

[a]mmol.

Table 2
Isomerization of *N*-fluoro Derivatives **3**, **5** and **6** by SbF_5

N–F[a]	SbF_5[a]	Temp. (°C)	Time (h)	Product (yield %)	b.p. (°C)	MS MH^+ (int. %)
3 (2)	0.5	exotherm	0.15	**15** (84)	–	–
5 (4.2)	0.5	100	0.5	**11** (80)	84–85	384 (71)
6 (2)	0.3	100	3	**12** (85)	126–127	484 (15)

[a]mmol.

12: IR 1780 (s), 1352 (m), 1310 (m), 1250 (s), 1140 (s), 979 (s), 868 (w), 800 (m) cm^{-1}; ^{19}F NMR $(CF_3)_2{}^BCF^I CF^K{=}NCF_2{}^CCF_2{}^DCF_2{}^FCF_2{}^GCF_3{}^A$ A −81.64 (3F, t), B −74.95 (6F, t), C −93.05 (2F, dt), D −123.48 (2F, m), F −125.52 (2F, m), G −126.90 (2F, m), I −182.55 (1F, d-hept.), K −14.05 (1F, m) ppm; $J_{K-I}=19$, $J_{B-I}=J_{B-K}=8$, $J_{C-K}=19$, $J_{C-F}=8$ Hz, other coupling constants not readily determined.

3. Results and discussion

3.1. Reactions with nucleophiles

Despite the fact that higher perfluoroazaalkenes do not dimerize by reaction with metal fluorides, [8] *N*-fluoroimines **1** and **2** react with CsF in a polar solvent giving the corresponding diaziridines **3** and **4**.

$$C_3F_7CF{=}N\text{-}F \xrightarrow[22°C]{CsF/MeCN} C_4F_9\text{-}\overline{N\text{-}N(F)\text{-}CF}\text{-}C_3F_7$$
1 **3**

$$C_5F_{11}CF{=}N\text{-}F \xrightarrow[22°C]{CsF/MeCN} C_6F_{13}\text{-}\overline{N\text{-}N(F)\text{-}CF}\text{-}C_5F_{11}$$
2 **4**

This reaction is related to the cyclodimerization of F–N=C(X)NF_2 [4] and CF_2=N–F [1]. In the latter case, the linear dimer $CF_3N(F)CF{=}NF$ can be isolated and shown to undergo cyclization, indicating that the linear dimer is an intermediate to the cyclodimer. The formation of **3** and **4** probably proceed similarly but the uncyclized dimers were not observed under these conditions. The diaziridines **3** and **4** were characterized by ^{19}F NMR, IR and MS. Their IR spectra exhibit strong absorptions near 1400 cm^{-1}, which is characteristic for perfluoro-1-methyldiaziridine (1435 cm^{-1}) [1,2] and perfluoro-2,3-dialkyloxaziridines (1412–1418 cm^{-1}) [9,10]. The CI mass spectra exhibit intense parent $(MH)^+$ ions for each of the compounds. The ^{19}F NMR, while quite complex, provide definitive proof of structure. As in the case of perfluoro-2,3-dialkyloxaziridines [9,10], the high inversion barrier of the nitrogen is responsible for the magnetic nonequivalence of the fluorines in the CF_2 group attached to nitrogen. The chemical shifts of these fluorines [−98.0; −98.6 (**3**); −97.60, −100.0 (**4**) ppm], the magnitude of ^2J (210 Hz), and the chemical shift of the single fluorine attached to carbon and nitrogen [−144.21, −7.25 (**3**); −143,83, −7.15 (**4**) ppm] are comparable to that found for perfluoro-2,3-dialkyloxaziridines and perfluoro-1-methyldiaziridine.

Like other *N*-fluoroimine, compounds **1** and **2** are extremely reactive towards nucleophiles. For example, reaction of these compounds with HFP in the presence of CsF is slightly exothermic and results in the formation of compounds **5** and **6** in a high yield (Table 2). The reaction of **1** and **2** with the perfluoroisopropyl anion from HFP is a somewhat fortuitous reaction. One might have expected the only products to be **3** and **4** but clearly the rate of the reaction with the $(CF_3)_2CF^-$ anion is competitive with excess HFP.

$$\mathbf{1} + HFP \xrightarrow[22°C]{CsF/MeCN} \begin{matrix} C_3F_7 \\ \diagdown \\ C{=}N \\ \diagup \quad \diagdown \\ (CF_3)_2CF \quad F \end{matrix} \qquad \mathbf{5}$$

$$\mathbf{2} + HFP \xrightarrow[22°C]{CsF/MeCN} \begin{matrix} C_5F_{11} \\ \diagdown \\ C{=}N \\ \diagup \quad \diagdown \\ (CF_3)_2CF \quad F \end{matrix} \qquad \mathbf{6}$$

The reaction of *N*-alkylimines with HFP in the presence of metal fluorides is well known [8,11,12] and polyfluorinated *N*-alkoxyimines, like the *N*-fluoroimines and aza-alkenes, can also be reactive. Reaction between HFP and imines **7** and **8** takes place at room temperature resulting in the formation of compounds **9** and **10** in high yield:

$$C_4F_9O\text{–}N{=}CFC_3F_7 + HFP$$
7

$$\xrightarrow[22°C,\ 2h]{MeCN,\ CsF} C_4F_9O\text{–}N{=}C(i\text{-}C_3F_7)C_3F_7$$
9

$$CF_3(CF_2Cl)CFO\text{–}N{=}CFC_3F_7$$
8

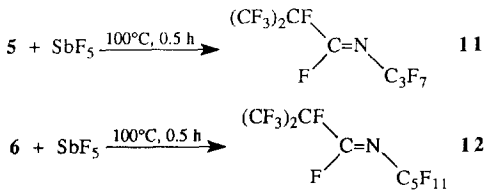
$$\xrightarrow[22°C,\ 2h]{MeCN,\ CsF} CF_3(CF_2Cl)CFO\text{–}N{=}C(i\text{-}C_3F_7)C_3F_7$$
10

Compounds **9** and **10** exhibit weak absorptions in the IR spectra near 1640 cm^{-1} assignable to the (C=N). The CI mass spectra exhibit parent $(MH)^+$ ions of high intensity. The ^{19}F NMR spectra of compounds **5** and **6** show the expected number of different resonances in each case with appropriate relative areas. The chemical shifts of the N–F

groups [+66.33 (**5**), +66.20 (**6**) ppm] are in good agreement with the values for *N*-fluoroimines of polyfluoroketones [13]. The large value of coupling constant between the fluorine attached to nitrogen and the CF_3 groups of *i*-C_3F_7 ($^5J = 27$ Hz) indicates that they are *syn* and the geometry of the starting imine is unchanged. The same is true for compound **6**. Another typical feature for the NMR spectra of **9**, **10** and **5, 6** is the large size of the ^4J coupling constant between single fluorine in $(CF_3)_2CF$ and the gem-difluoromethylene group. In all cases, it is within the range 27–36 Hz. For **9** and **10**, the two possible structural isomers cannot be readily assigned. We assume the geometry of the starting imine (alkoxy group *anti* to C_3F_7) is maintained.

3.2. Reaction with SbF_5

In contrast to the *N*-fluoroimine of hexafluoroacetone which reacts with SbF_5 exothermically [5], compounds **5** and **6** do not interact with antimony pentafluoride at 22°C. However at elevated temperature, both undergo isomerization into the aza-alkenes **11** and **12** (Table 3).

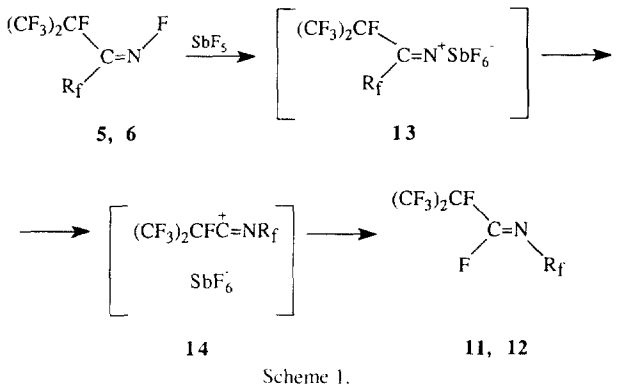


According to the ^{19}F NMR both **11** and **12** are exclusively the *anti*-isomers [^4J coupling constants between CF_2N– and the vinyl fluorine are 19 Hz in both cases, cf. Ref. [14]]. This fact indicates that the reaction is stereospecific and only the substituent trans to the N–F fragment migrates to nitrogen. This reaction probably proceeds according to the mechanism proposed for the Beckmann rearrangement [15], which includes heterolysis of the N–F bond by SbF_5, resulting in the azacation intermediate **13**. Then 1,2 migration of the perfluoroalkyl group leads to the formation of the more stable carbocation **14**. Abstraction of a fluoride anion by cation **14** gives the final product (Scheme 1).

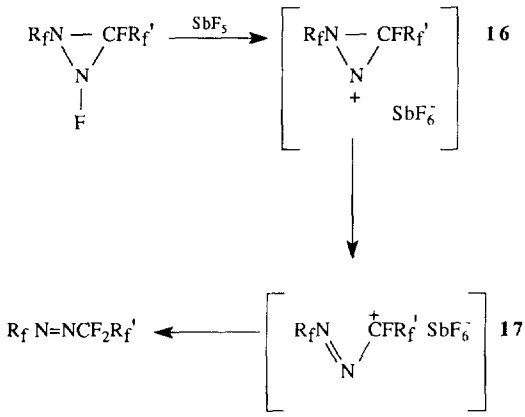
Diaziridine **3** can also be isomerized by SbF_5. This reaction is exothermic and produces the diazo compound **15**.

$$\mathbf{3} + SbF_5 \xrightarrow{\text{exotherm.}} C_4F_9N{=}NC_4F_9 \quad \mathbf{15}$$

This type of isomerization has been observed before for perfluoro-1,2-dimethyldiaziridine under action of BF_3 [Q.C. Mir, D.D. DesMarteau, unpublished results] or the fluorinated metal surface of the autoclave [1]. The mechanism of the reaction probably involves, as in the case of imines **5** and **6**, the generation of an intermediate azacation **16**, which has the possibility to isomerize into carbocation **17** due to ring opening (Scheme 2).



Scheme 1.



Scheme 2.

4. Conclusion

Perfluoro *N*-fluoroalkanimines containing large perfluoroalkyl groups exhibit the same reactivity as simple imines like $CF_2{=}NF$, when polar solvents are used for reactions with fluoride ion and with other nucleophiles. Clearly 1,1-difluoromethanimines, such as $CF_2{=}NF$ and $CF_2{=}NCF_3$, are more reactive but higher alkanimines exhibit the characteristic reactivity with nucleophiles of the polar C=N– bond in perfluorinated systems.

Acknowledgements

The financial support of this research by Ausimont is gratefully acknowledged.

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