*Journal of Fluorine Chemistry*, *24* (1984) 457–465

Received: April 19, 1983; accepted: May 20, 1983

# SELECTIVE FORMATION AND REACTIVITY OF A STABLE CARBOCATION FORMED FROM PERFLUORINATED N,N'-DIMETHYL IMIDAZOLIDINE

H. BÜRGER, R. KÖPLIN and G. PAWELKE

Anorganische Chemie, FB 9, Universität-Gesamthochschule
D-5600 Wuppertal (F.R.G.)

## SUMMARY

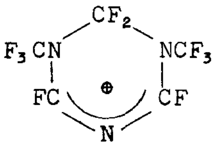
1,3-Bis(trifluoromethyl)-2,2,4,4,5,5-hexafluoro-imidazolidine (III) forms a stable 2-carbocation in $SbF_5$ solution. This cation reacts with $H_2O$ and $H_2S$ to yield the imidazolidine-2-one and -thione derivatives respectively. Selective halogen exchange in the 2-position is achieved by treatment of III with $BCl_3$ and $BBr_3$ to form the 2,2-dichloro and 2,2-dibromo derivatives. All compounds were characterised by NMR, IR, Raman and mass spectra.

## INTRODUCTION

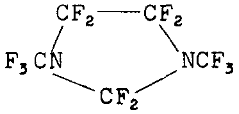
Recently we have shown that perfluorotrimethylamine $(CF_3)_3N$ (I), upon prolonged treatment with $SbF_5$, reacts to form the cyclic carbocation II which is obviously stabilized by charge delocalization [1]. This cation, which is also formed by trimerization of $CF_3NCF_2$ in $SbF_5$ and elimination of $CF_4$, suggests that the $CF_2$ group in the $>\overline{N}-CF_2-\overline{N}<$ fragment is more reactive towards Lewis acids than a terminal $NCF_3$ group. In order to evaluate this suggestion more thoroughly, we have synthesized another compound with this fragment, 1,3-bis(trifluoromethyl)-2,2,4,4,5,5-hexafluoro-imidazolidine (III), and studied its reactions with Lewis acids. (III) offers, in addition to the nitrogen atom, three different CF bonds which might be attacked in competitive reactions.

0022-1139/84/$3.00

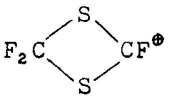
Related reactions of sulfur derivatives have been reported recently [2]. While $CF_2(SF_3)_2$ reacts with $AsF_5$ to form the cation $SF_3CF_2SF_2^+$, the cyclic tetrafluorodithietane yields the carbocation IV when treated with $SbF_5$.



(II)



(III)



(IV)

In the following we report on the reactions of III with Lewis acids and the characterization of the hitherto unknown compounds obtained in this study.

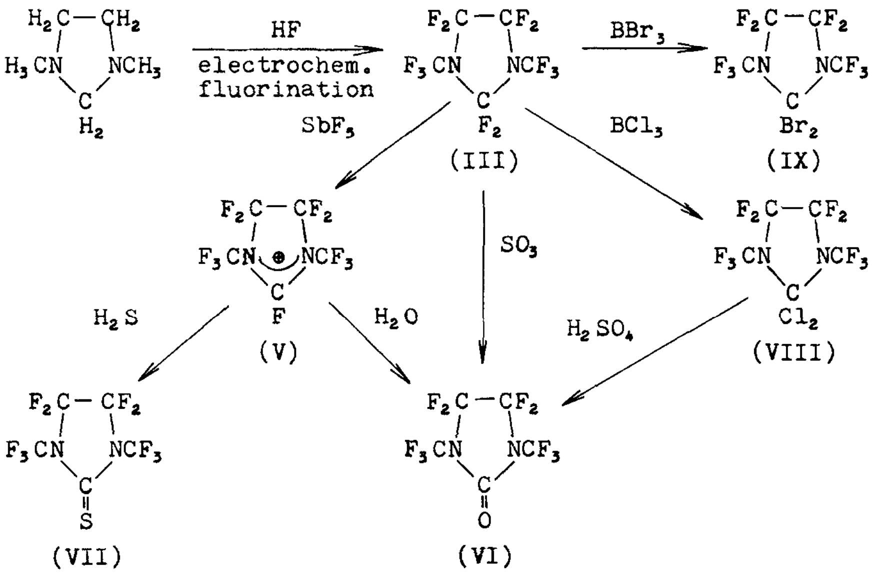
## RESULTS AND DISCUSSION

### Perfluoro-1,3-dimthylimidazolidine(III) and its reactions

III was first obtained as a by-product from the fluorination of $N(CH_3)_3$ with $CoF_3$ [3]. The electrochemical fluorination of 1,3-dimethylimidazolidine [4] under conditions similar to those described earlier [5] afforded substantial amounts of III, the yield being 26%. The $^{19}F$ NMR spectrum of our material, Table 1, agrees with that previously reported [3], though our boiling point is 56°C (cf.46°, Ref. [3]).

Excess of III and $SbF_5$, at room temperature, react within minutes to form V, which builds a solid, stable salt with the $Sb_2F_{11}^-$ anion. The structure of V follows from the $^{19}F$ NMR spectrum, Table 1, which proves the presence of three different F atoms in a 1 : 4 : 6 ratio. This cation readily reacts with $H_2O$ and $H_2S$ to form imidazolidine-2-one (VI) and 2-thione (VII) respectively.

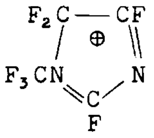
A somewhat different reactivity of III is revealed in its reactions with $BCl_3$ and $BBr_3$ at 140 and 100°C respectively. Though no ionic intermediates can be isolated, the 2-$CF_2$ group is converted, by halogen exchange, to $CCl_2$ (VIII) and $CBr_2$ fragments (IX) respectively. Treatment of VIII with concentrated sulfuric acid selectively cleaves the CCl bonds and provides an independent route to VI. Alternatively treatment of III with $SO_3$ for 24 hours at 140° affords VI in a 30% yield. Scheme (1) displays the above-mentioned reactions.



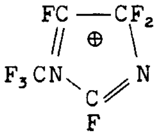
Scheme 1

From the constitution of the reaction products and the evaluation of $^{19}F$ NMR spectra recorded at different stages of the reactions, it can be concluded that $SbF_5$, $BCl_3$, $BBr_3$ and $SO_3$ selectively attack the $NCF_2N$ fragment while no reactivity of the $CF_2(C)$ and $CF_3(N)$ groups was indicated under the conditions employed. It is likely that the reactions with $SO_3$ and boron halides also proceed via a cationic intermediate.

The $Sb_2F_{11}^-$ salt of V is indefinitely stable at room temperature. The thermal decomposition of its solution in $SbF_5$ commences at 130°C, $CF_4$ being evolved slowly. At 150°, the decomposition proceeds rapidly. The $^{19}F$ NMR spectrum of the residue would not contradict the formation of the ions Xa and Xb, though convincing evidence is still lacking. Efforts to isolate and characterize further volatile decomposition products of V were so far unsuccessful.



Xa



Xb

Spectroscopic characterization

The $^{19}F$ and $^{13}C$ NMR spectra of III and V to IX are set out in Table 1. The $^{19}F$ spectra are of higher order, the $F_3CNCF_2CF_2NCF_3$ fragment giving rise to a $(A_3XX')_2$ spin system. The simulation of the poorly resolved $^{19}F$ NMR spectrum of IX permitted only the sum $^{4}J(\underline{F}_3CNC\underline{F}C) + {}^{5}J(\underline{F}_3CNCC\underline{F})$ to be determined accurately. The coupling constants of III were obtained from decoupling experiments. The $^{19}F$ NMR spectrum of V is displayed in Fig. 1.

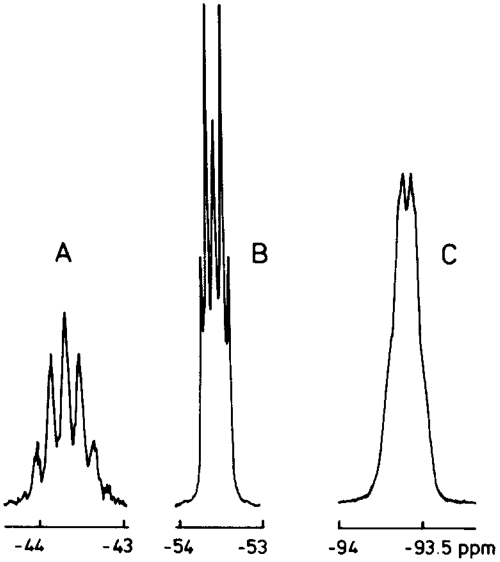


Fig. 1. $^{19}F$ NMR spectrum of V.

A : NC$\underline{F}$N; B : NC$\underline{F}_3$; C : NC$\underline{F}_2$C.

In the $^{13}C$ spectra only the 2-C atom shifts exhibit large and characteristic variations.

TABLE I

Physical properties and NMR spectra

| | III | V | VI | VII | VIII | IX |
|---|---|---|---|---|---|---|
| $bp_{760}$(°C) | 56 | - | 63 | 96 | 102 | 130 |
| mp (°C) | | | 10.5 | | | |
| $^{19}F$ NMR[a] | | | | | | |
| $\delta(NC\underline{F}_3)$[ppm] | -56.1[c] | -53.6[d] | -57.5[c] | -56.7[d] | -53.6[e] | -53.5[d] |
| $\delta(NC\underline{F}N)$[ppm] | -62.7 | -43.7 | - | - | - | - |
| $\delta(C\underline{F}_2C)$[ppm] | -92.6 | -93.6 | -96.1 | -94.8 | -91.7 | -92.1 |
| $^4J(C\underline{F}_2NC\underline{F}N)$[Hz] | 5.7 | < 1 [f] | | | | |
| $^4J(\underline{F}_3CNC\underline{F}N)$[Hz] | 7.9 | 14.8 | | | | |
| $^4J(\underline{F}_3CNC\underline{F}C)+{}^5J(\underline{F}_3CNCC\underline{F})$[Hz] | 7.2 | ~ 6.0 | 7.5 | 9.0 | 8.4 | 8.5 |
| $^{13}C$ NMR[b] | | | | | | |
| $\delta(N\underline{C}F_3)$[ppm] | 117.3[g] | | 117.3[h] | 117.8[h] | 118.8[h] | 118.3[h] |
| $\delta(N\underline{C}N)$[ppm] | 114.9 | | 137.4 | 164.6 | 94.1 | 45.0 |
| $\delta(\underline{C}CN)$[ppm] | 112.1 | | 112.0 | 113.4 | 112.9 | 111.6 |
| $^1J(N\underline{CF}_3)$[Hz] | 267.5 | | 269.2 | 269.7 | 269.0 | 269.0 |
| $^1J(N\underline{CF}N)$[Hz] | 258.3 | | - | - | - | - |
| $^1J(N\underline{CF}_2C)$[Hz] | 267.0 | | 270.8 | 271.5 | 268.2 | 269.0 |
| $^2J(N\underline{C}C\underline{F}_2)$[Hz] | 29.6 | | 29.3 | 29.5 | 29.8 | 29.8 |

[a] $\delta(^{19}F)$ against $CFCl_3$, positive sign = high frequency. [b] $\delta(^{13}C)$ against TMS, positive sign = high frequency. [c] Internal $CF_3COOH = -76.55$ ppm. [d] Internal $CF_3COOCH_3 = -76.2$ ppm. [e] Internal $(CF_3)_3N = -55.8$ ppm. [f] Structure unresolved, see text and figure 1. [g] External TMS. [h] Internal $CDCl_3 = 76.91$ ppm.

Gas phase infrared and liquid phase Raman spectra have been recorded of III and VI to IX. Diagnostic frequencies and their assignment are listed in Table 2.

TABLE II

Diagnostic vibrational frequencies [cm$^{-1}$] and relative intensities (IR/Raman)

| III | VI | VII | VIII | IX | Assignment |
|---|---|---|---|---|---|
| 1035 s/wp | - | - | 389 w/sp | 242 /sp | $\nu_s$ $CX_2$ |
| 1320 sh/- | - | - | 812 s/sh | 730 s/m | $\nu_{as} CX_2$ |
| 690 m/mp | - | - | 232 / m | 168 /mp | $\delta$ $CX_2$ |
| | 1858 s/mp | 1274 m/mp | | | $\nu$ C=O(S) |
| 774 -/sp | 748 m/sp | 750 w/sp | 744 w/sp | 745 sh/sp | $\delta_s$ $CF_3$ |
| 610 w/wp | 674 -/sp | 634 w/mp | 614 s/mp | 610 s/mp | $\delta$ $CF_2$ |

Except for the vibrations associated with the $NCX_2N$ fragment, X = F, Cl and Br, the spectra of III, VII and IX are similar. While in VI, $\nu$(CO) at 1858 cm$^{-1}$ is well isolated from all other fundamentals, the C = S stretching vibration at 1274 cm$^{-1}$ falls into the range of CF and skeletal stretching vibrations and, by coupling, causes major frequency and intensity changes.

The compounds III and VI to IX were examined by conventional EI mass spectrometry. The observed m/e values and the isotopic patterns confirm the constitution of the molecules. (M$^+$)ions were observed only for VI and VII, while III, VIII and IX fragmentate to form the (M-Halogen$^+$) ion. Table 3 gives a list of the strongest peaks (lightest isotopes) in the order of decreasing intensity.

TABLE 3

EI mass spectra in the order of decreasing intensity at 70 eV

| | m/e |
|---|---|
| (III) | 114($CF_3NCF^+$); 69($CF_3{}^+$); 164($CF_3CNCF_3{}^+$); 183($CF_3CFNCF_3{}^+$); 209($CF_3\overline{NCF_2CFNC}F^+$); 133($CF_3NCF_2{}^+$); 297($M-F^+$). |
| (VI) | 69($CF_3{}^+$); 114($CF_3NCF^+$); 92($CF_2NCO^+$); 164($CF_3NCCF_3{}^+$); 133($CF_3NCF_2{}^+$); 161($CF_3\overline{NCF_2C}O^+$); 50($CF_2{}^+$); 100($C_2F_4{}^+$); 275($M-F^+$); 294($M^+$). |
| (VII) | 69($CF_3{}^+$); 108($CF_3NCS^+$); 114($CF_3NCF^+$); 100($C_2F_4{}^+$); 164($CF_3NCCF_3{}^+$); 310($M^+$); 222($CF_3\overline{NCF_2CFNC}S^+$); 291($M-F^+$); 95($CF_3NC^+$). |
| (VIII) | 69($CF_3{}^+$); 100($C_2F_4{}^+$); 50($CF_2{}^+$); 114($CF_3NCF^+$); 164($CF_3NCCF_3{}^+$); 313($M-Cl^+$); 90($CF_2NCN^+$); 225($CF_3\overline{NCF_2CFNC}Cl^+$). |
| (IX) | 69($CF_3{}^+$); 100($C_2F_4{}^+$); 50($CF_2{}^+$); 114($CF_3NCF^+$); 164($CF_3NCCF_3{}^+$); 133($CF_3NCF_2{}^+$); 278($M-2Br^+$);357($M-Br^+$). |

## EXPERIMENTAL

Physical measurements were carried out as described [6]. Elemental analyses are by Mikroanalytisches Laboratorium Beller, Göttingen.

1,3-Bis(trifluoromethyl)-2,2,4,4,5,5-hexafluoro-imidazolidine(III) was prepared by electrochemical fluorination of 1,3-dimethyl-imidazolidine [4] according to the procedure described in Ref. [6] and purified by fractional distillation over a slit tube column, yield 26 %.

1,3-Bis(trifluoromethyl)-2,4,4,5,5-pentafluoro-imidazolidinium-undecafluoro-diantimonate(V) a) 50 g (0.23 mol) $SbF_5$ and 15 g (0.047 mol) III are condensed in a pyrex tube and shaken for several minutes at room temperature. A solution of V is obtained in quantitative yield. b) 11 g (0.051 mol) $SbF_5$ and 32 g (0.1 mol) III are heated in a pyrex tube to 80°C for several days. Then excess III is removed *in vacuo* whereby V is obtained quantitatively as a white powder.

1,3-Bis(trifluoromethyl)-4,4,5,5-tetrafluoro-imidazolidine-2-one(VI) a) To a solution of 0.047 mol V in $SbF_5$ were added 5 g (0.28 mol) $H_2O$, the vigorous reaction being controlled by cooling. Volatile reaction products were condensed on $P_4O_{10}$ and purified by fractional condensation in vacuo, yield 75 %. b) 3 g VIII and 20 ml concentrated $H_2SO_4$ were shaken at room temperature for 2 hours; after work-up yield 70 %. c) Stoichiometric quantities of III and $SO_3$ in a sealed 4 mm pyrex tube were heated to 140°C for 1 day. Volatile products were condensed on oleum, 30 % $SO_3$, and separated by fractional condensation, yield 30 %.
$C_5F_{10}N_2O$, mw 294.05. Required / found; % C, 20.40/20.62; % F, 64.61/64.40; % N, 9.59/9.44.

1,3-Bis(trifluoromethyl)-4,4,5,5-tetrafluoro-imidazolidine-2-thione(VII) 70 g (2.05 mol) $H_2S$ was condensed on a solution of V prepared from 50 g (0.23 mol) $SbF_5$ and 17 g (0.05 mol) III in a Hoke 150 ml stainless steel cylinder, and shaken at room temperature for several minutes. The volatile products were purified by fractional condensation, yield 30 %.
$C_5F_{10}N_2S$, mw 310.12. Required / found; % C, 19.35/19.72; % F, 61.26/60,6; % S, 10.34/10.79.

1,3-Bis(trifluoromethyl)-2,2-dichloro-4,4,5,5-tetrafluoro-imidazolidine(VIII) 18 g (0.051 mol) III and 9 g (0.077 mol) $BCl_3$ were reacted in a stainless steel cylinder for 4 days at 170°C. Volatile products were purified by fractional condensation in vacuo, yield 92 %.
$C_5Cl_2F_{10}N_2$, mw 348.96. Required / found; % C, 17.19/17.36; % Cl, 20.32/20.48; % F, 54.44/54.1; % N, 8.03/8.18.

1,3-Bis(trifluoromethyl)-2,2-dibromo-4,4,5,5-tetrafluoro-imidazolidine(IX) was prepared analogous to VIII from III and $BBr_3$, 4 days at 100°C, yield 40 %.
$C_5Br_2F_{10}N_2$, mw 437.87. Required / found; % C, 13.70 / 13.78; % Br, 36.50/36.28; % F, 43.39/43.0; % N, 6.40/6.26.

## ACKNOWLEDGEMENTS

We wish to thank the Bayer AG and the Fonds der Chemie for support.

## REFERENCES

1 H. Bürger, R. Köplin, G. Pawelke and C. Krüger, J.Fluorine Chem., 22 (1983) 175.

2 A Waterfeld and R. Mews, J. Fluorine Chem., 21 (1982) 5.

3 R.W. Rendell and B. Wright, Tetrahedron, 35 (1979) 2405.

4 C.H. Yoder and J.J. Zuckerman, J. Amer. Chem. Soc., 88 (1966) 4831.

5 H. Bürger, H. Niepel and G. Pawelke, J. Fluorine Chem., 15 (1980) 231.

6 H. Bürger, R. Eujen, H. Niepel and G. Pawelke, J.Fluorine Chem., 17 (1981) 65.