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Journal of Fluorine Chemistry



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Thermal decomposition of 4-fluorobenzenediazonium perfluoroorganyl(fluoro)borates, $[4-FC_6H_4N_2]Y$ (Y = R_FBF₃ (R_F = C₆F₅, C₆F₁₃, *trans*-C₄F₉CF=CF, *cis*-C₆F₁₃CF=CF, CF₃C=C) and (C₆F₁₃)₂BF₂)



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ARTICLE INFO

Article history: Received 29 May 2013 Received in revised form 27 July 2013 Accepted 1 August 2013 Available online 14 August 2013

Keywords: Arenediazonium salts Thermal decomposition DSC analysis NMR spectroscopy

ABSTRACT

Heating of the neat salts $[4-FC_6H_4N_2][R_FBF_3]$ ($R_F = C_6F_5$, C_6F_{13} , trans- $C_4F_9CF=CF$, cis- $C_6F_{13}CF=CF$, $CF_3C\equivC$) or in solid mixtures with NaF gives the principal product $1,4-C_6F_2H_4$ besides R_FBF_2 or Na[R_FBF_3], respectively. Thermolysis of $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ in NaF results in $1,4-C_6F_2H_4$, Na[BF_4], Na[$(C_6F_{13})_2BF_2$], and a new type of product, the isomer Na[$C_6F_{13}CF(BF_3)C_5F_{11}$].

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1. Introduction

The Balz-Schiemann reaction is the classical method for replacing a diazonio group by fluorine. Typically, the reaction is performed by heating arenediazonium tetrafluoroborates, [ArN₂][BF₄], in an inert solid material or in an inert solvent and results in ArF, BF₃, and N₂. In some cases the thermolysis of diazonium salts with hexacoordinated fluoroanions, [ArN₂][XF₆] (X = P, As, Sb) or $[ArN_2]_2[SiF_6]$ etc. gives better yields of ArF. Overviews of known procedures, their modifications, the scope and limitation are compiled in fundamental monographs and reviews [1]. Despite a large number of publications on this topic, there are no data available on the thermal decomposition of arenediazonium organyl(fluoro)borates, $[ArN_2][R_nBF_{4-n}]$ (*n* = 1–4), or the related salts $[ArN_2][R_mXF_{6-m}]$ (X = P, As, Sb; m = 1-6). A priori two main reaction channels can be considered in case of $[ArN_2][R_nBF_{4-n}]$: (a) fluorodediazoniation of $[ArN_2][R_nBF_{4-n}]$ to fluoroarene and (b) replacement of the diazonio group by the organyl group R under formation of ArR.

During the last two decades we have elaborated convenient methods for the preparation of potassium perfluoroorganyltri-fluoroborates, $K[R_FBF_3]$, where R_F represents a perfluoroalkyl, perfluoroalkynyl, and perfluoroaryl group [2–7].

The availability of these salts allowed the preparation of a series of aryldiazonium perfluoroorganyltrifluoroborates and the investigation of their thermal decomposition products. We studied the thermolysis of 4-fluorobenzenediazonium perfluoroorganyl(fluoro) borate salts which allowed a convenient identification of the products by ¹⁹F NMR spectroscopy.

2. Results and discussion

4-Fluorobenzenediazonium perfluoroorganyl(fluoro)borates were prepared by anion metathesis of [4-FC₆H₄N₂][BF₄] with $K[R_FBF_3]$ or $K[(C_6F_{13})_2BF_2]$ in dry MeCN (Scheme 1).

The visually controlled thermal decomposition was performed in an NMR tube using 30–50 mg of the corresponding diazoniumborate salt. To test the experimental set up, the typical Balz-Schiemann reaction of [4-FC₆H₄N₂][BF₄] was performed. The neat salt [4-FC₆H₄N₂][BF₄] melted under decomposition at 158–160 °C (bath) giving 1,4-difluorobenzene in 86% yield. The new investigated organyltrifluoroborate salts, [4-FC₆H₄N₂][R_FBF₃], melted at 80– 100 °C and formed brown liquids which decomposed under bubbling of gas at 120–140 °C (R_F = C₆F₅, C₆F₁₃, *trans*-C₄F₉CF=CF) or 130–160 °C (*cis*-C₆F₁₃CF=CF). When R_F = C₆F₅, 1,4-C₆F₂H₄ and pentafluorophenyldifluoroborane (trace) were found besides pentafluoro-benzene and perfluorobiphenyl. The salt with R_F = C₆F₁₃ gave 1,4-C₆F₂H₄ (67%) and C₆F₁₃BF₂ (85%). Thermolysis of [4-FC₆H₄N₂][R_FBF₃] with R_F = *trans*-C₄F₉CF=CF and R_F = *cis*-C₆F₁₃CF=CF

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MeCN

84%

Scheme 1.

gave $C_6F_2H_4$ (Scheme 2) besides the corresponding boranes R_FBF_2 as main products.

Very often the thermal decomposition of arenediazonium salts is performed in inert solid materials (sand, CaF₂, etc.). This allows a good thermal control of the process and prevents a violent reaction. Usually, such a performance results in a better yield of the desired product. Although the thermolysis of [4-FC₆H₄N₂][R_FBF₃] gave 1,4- $C_6F_2H_4$ in high yields (Scheme 2), the pronounced hydrolytic sensibility of the co-product perfluoroorganyldifluoroborane leads to several by-products in minor quantity. To overcome this problem we performed the thermal decomposition of 4-fluorobenzenediazonium perfluoroorganyl(fluoro)borates in vigorously dried NaF. The solid matrix had no effect on the reaction route and allowed to trap the strong Lewis-acidic boranes as practically inert sodium perfluoroorganyl(fluoro)borates. For example, heating of [4- $FC_6H_4N_2][C_6F_5BF_3]$ in NaF gave 1,4- $C_6F_2H_4$, Na[$C_6F_5BF_3$], and Na[BF₄]. Thermolysis of $[4-FC_6H_4N_2][R_FBF_3]$ with $R_F = trans-$ C₄F₉CF=CF and *cis*-C₆F₁₃CF=CF in a perfluoroalkenyl moiety of the anion produced $1,4-C_6F_2H_4$ and the corresponding salt, Na[R_FBF₃], besides Na[BF₄]. Notably, the fluorodediazoniation of $[4-FC_6H_4N_2]$ [CF₃C=CBF₃] in NaF gave 1,4-C₆F₂H₄ only in a moderate yield of 51% whereas Na[CF₃C=CBF₃] and Na[BF₄] were formed in 9 and 76%, respectively (Scheme 3). Probably, the initially formed borane, CF₃C=CBF₂, underwent parallel reactions including C-B bond cleavage.

A specific feature was observed when $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ was thermalized. The neat borate melted at 130-140 °C with decomposition to yield 1,4-C₆F₂H₄, 6-difluoroborylperfluorododecane, C₆F₁₃CF(BF₂)C₅F₁₁, and some unidentified products. Unlike the thermolysis of [4-FC₆H₄N₂][C₆F₁₃BF₃] (Scheme 2) where

borane $C_6F_{13}BF_2$ resulted, borane $(C_6F_{13})_2BF$ was not observed when neat $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ was thermalized. However, heating of [4-FC₆H₄N₂][(C₆F₁₃)₂BF₂] with NaF resulted in 1,4- $C_6F_2H_4$, Na[(C_6F_{13})₂BF₂], Na[$C_6F_{13}CF(BF_3)C_5F_{11}$], and Na[BF₄]. The absence of bis(perfluoroalkyl)fluoroborane (with a higher fluoride affinity than $C_6F_{13}BF_2$) in the thermolysis without NaF can probably be explained by a fast isomerization of $(C_6F_{13})_2BF$ to $C_6F_{13}CF(BF_2)C_5F_{11}$ under the strong acidic reaction conditions (Scheme 4).

A selected series of [4-FC₆H₄N₂][R_FBF₃] salts was investigated by differential scanning calorimetry (DSC). For comparison, neat [4-FC₆H₄N₂][BF₄] showed an endothermal maximum at 160.6 °C (melting) which passes into an exothermal maximum at 162.6 °C (decomposition). In case of the neat salt $[4-FC_6H_4N_2][C_6F_5BF_3]$ melting and decomposition are more separated: melting at T_{max} = 98.0 °C (sharp endothermal peak) was followed by decomposition at T_{max} = 142.9 °C (broad exothermal peak). In case of perfluoroalkenyl- and perfluoroalkynyltrifluoroborate salts an endothermal process - presumably a phase transition - preceded melting. Melting and {decomposition} occurred at $T_{max} = 95.2$ $\{140.3\}$ °C $[4-FC_6H_4N_2][cis-C_6F_{13}CF=CFBF_3], 89.4 \{144.5\}$ °C [4-FC₆H₄N₂][*trans*-C₄F₉CF=CFBF₃], and 65.6 {102.7 and 105.7} °C $[4-FC_6H_4N_2]$ [CF₃C=CBF₃]/NaF (1:3, v/v). Notably, the DSC result of $[4-FC_6H_4N_2]$ [trans-C₄F₉CF=CFBF₃] mixed with NaF (1:3, v/v) did not distinct from the sample without NaF. The DSC result of $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ with melting at $T_{max} = 121.9 \degree C$ (endothermal effect) and the exothermal decomposition at T_{max} = 138.1 °C fitted well into the afore reported pattern.

The obtained data show distinctions and similarities between the parent fluoroborate salt [4-FC₆H₄N₂][BF₄] and the

 $[4-FC_6H_4N_2][C_6F_5BF_3] \longrightarrow 1, 4-C_6F_2H_4 + C_6F_5BF_2 + N_2 + C_6F_5H + (C_6F_5)_2$ 54% trace 24% 16% $[4-FC_{6}H_{4}N_{2}][C_{6}F_{13}BF_{3}] \longrightarrow 1, 4-C_{6}F_{2}H_{4} + C_{6}F_{13}BF_{2} + N_{2}$ 67% 85% $[4-FC_6H_4N_2][trans-C_4F_9CF=CFBF_3] \longrightarrow 1, 4-C_6F_2H_4 + trans-C_4F_9CF=CFBF_2 + N_2$ 80% 49% $[4-FC_6H_4N_2][\textit{cis-}C_6F_{13}CF=CFBF_3] \longrightarrow 1, 4-C_6F_2H_4 + \textit{cis-}C_6F_{13}CF=CFBF_2 + N_2 +$ 90% 5% cis-C₆F₁₃CF=CFH + C₆F₁₃C≡CF 4% 3%

Scheme 2.

$$\begin{array}{rcl} & & & & \\ & & & \\ \mbox{[4-FC}_6H_4N_2][C_6F_5BF_3] & \longrightarrow & 1,4-C_6F_2H_4 + Na[C_6F_5BF_3] + Na[BF_4] + N_2 \\ & & & & \\ & & & 79\% & 71\% & 11\% \end{array}$$

NaF

$$[4-FC_6H_4N_2][trans-C_4F_9CF=CFBF_3] \longrightarrow 1,4-C_6F_2H_4 + Na[trans-C_4F_9CF=CFBF_3] - 95\% \qquad 83\%$$

$$Na[cis-C_4F_9CF=CFBF_3] + Na[BF_4] + N_2$$

$$10\% \qquad 5\%$$

NaF
[4-FC₆H₄N₂][*cis*-C₆F₁₃CF=CFBF₃]
$$\longrightarrow$$
 1,4-C₆F₂H₄ + Na[*cis*-C₆F₁₃CF=CFBF₃] +
77% 65%
Na[*trans*-C₆F₁₃CF=CFBF₃] + C₆F₁₃C≡CF + Na[BF₄] + N₂
12% 3% 17%

NaF

$$[4-FC_6H_4N_2][CF_3C\equiv CBF_3] \longrightarrow 1, 4-C_6F_2H_4 + Na[CF_3C\equiv CBF_3] + Na[BF_4]$$

$$51\% \qquad 9\% \qquad 76\%$$

$$CF_3C\equiv CH + N_2$$

$$9\%$$

T = 160 - 170 °C

Scheme 3.

$$\begin{array}{cccc} & & & & & \\ \mbox{[4-FC}_6H_4N_2][(C_6F_{13})_2BF_2] & & & & & 1,4-C_6F_2H_4 + Na[(C_6F_{13})_2BF_2] + \\ & & & & & 25-200\ ^\circ C & 81\% & 39\% \\ & & & & & Na[C_6F_{13}CF(BF_3)C_5F_{11}] + Na[BF_4] + N_2 \\ & & & & & 33\% & 17\% \end{array}$$

Scheme 4.

organyltrifluoroborate derivatives 4-fluorobenzenediazonium perfluoroorganyl(fluoro)borates. While melting and decomposition practically coincided in case of [4-FC₆H₄N₂][BF₄], they are separated by 30–40 °C for [4-FC₆H₄N₂][R_FBF₃]. Generally, [4-FC₆H₄N₂][R_FBF₃] salts are less thermally stable than [4-FC₆H₄N₂][BF₄]. A high similarity consists in the products of thermal decomposition. In both cases the diazonio group is replaced by fluorine. Compound 1,4-C₆F₂H₄ is formed under liberation of BF₃ or R_FBF₂, respectively. No remarkable amount of FC₆H₄R_F (transfer of the weakly nucleophilic carbanion instead of fluoride) was detected.

Thermolysis of neat $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ offers an additional interesting result. Instead of elimination of the co-product $(C_6F_{13})_2BF$, its isomer $C_6F_{13}CF(BF_2)C_5F_{11}$ was formed. In the presence of NaF both fluoroboranes were trapped. The corresponding sodium salts Na[$(C_6F_{13})_2BF_2$] and Na[$C_6F_{13}CF(BF_3)C_5F_{11}$] were formed in comparable amounts. Likely that the isomerization of the strong Lewis acid $(C_6F_{13})_2BF$ to the less acidic $C_6F_{13}CF(BF_2)C_5F_{11}$ [8] proceeds via an intramolecular fluoride ion abstraction (cf. formation of $C_2F_5CF(BF_2)CF_3$ from $(C_2F_5)_2BF$ [9]).

3. Conclusion

The thermal decomposition of neat solid 4-fluorobenzenediazonium perfluoroorganyl(fluoro)borates proceeds similar to the classical Balz-Schiemann reaction under formation of 1,4-C₆F₂H₄, R_FBF₂ and N₂. When the decomposition occurs in the solid mixture with NaF, the borate Na[R_FBF₃] is formed instead of borane R_FBF₂ as co-product. The fluoride transfer in the fluorodediazotation reaction of [4-FC₆H₄N₂][R_FBF₃] proceeds at a lower temperature (30–40 °C) compared to the parent salt with the [BF₄]⁻ anion, despite the lower fluoride donor property of perfluoroorganyltrifluoroborate anions (cf. the gas phase fluoride affinity of the corresponding perfluoroorganyldifluoroboranes [12]). The thermolysis of $[4-FC_6H_4N_2][(R_F)_nBF_{4-n}]$ (n = 0-2) is no solid state reaction. It proceeds in the molten phase.

4. Experimental

4.1. General

The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (¹H at 300.13 MHz, ¹¹B at 96.29 MHz, ¹⁹F at 282.40 MHz). The chemical shifts are referenced to TMS (¹H), $BF_3 \cdot OEt_2/CDCl_3$ (15% v/v) (¹¹B), and CCl_3F (¹⁹F) [with C_6F_6 as a secondary reference (-162.9 ppm)]. The composition of the reaction mixtures and the yield of products were determined by ¹⁹F NMR spectroscopy using C₆F₆ as an internal standard for integration. DSC analyses were performed on a Netzsch 204 Phoenix instrument equipped with a CC220 controller; a TASC414/ 3A microprocessor system, and a personal computer. The solid samples (2-7 mg) were weighed in aluminum pans and closed by a pierced aluminum lid inside a glove box. The temperature difference between the sample and the empty reference pan with a pierced lid was measured choosing a temperature program of 10 K/min. The raw data were processed using the Netzsch Proteus Software Version 4.2.

The microscale thermolysis of neat $[4-FC_6H_4N_2][R_FBF_3]$ and $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ salts or mixture with NaF (1:3, v/v) was performed in a glass NMR tube (outer diameter 5 mm, length 178 mm under an atmosphere of dry Ar in the stirred silicone oil bath of a Büchi Melting Point B-510 device with rates of heating of 5 °C per min (25–90 °C) and 2 °C per min (90–170 °C).

Dichloromethane (Baker) was purified by treatment in sequence with H_2SO_4 , aqueous Na_2CO_3 , and water. After distillation over P_4O_{10} it was stored over molecular sieves 3 Å before use. Acetonitrile (Baker) was purified and dried as described in Ref. [10]. Salt $[4-FC_6H_4N_2][BF_4]$ was prepared by the general protocol [11] from $4-FC_6H_4NH_2$ (25.3 g, 227 mmol), 50% aq H[BF_4] (115 mL), and NaNO₂ (18.2 g, 262 mmol) in 67% yield and stored under an atmosphere of dry argon. Borates $K[C_6F_5BF_3]$ [2], $K[C_6F_{13}BF_3]$ [3], $K[trans-C_4F_9CF=CFBF_3]$ [4], $K[cis-C_6F_{13}CF=CFBF_3]$ [4], $K[CF_3C=CBF_3]$ [5] were prepared as described. Salt $K[(C_6F_{13})_2BF_2]$ [6] was prepared by a modified procedure (see 4.2). NaF was calcinated at 400 °C for 5 h in vacuum.

4.2. Preparation of $K[(C_6F_{13})_2BF_2]$

Salt K[(C₆F₁₃)₂B(OMe)₂] [6] (1.1 g, 1.46 mmol) was added to cold (0–5 °C) aHF (anhydrous HF, 4 mL) with stirring. Within a few hours the initially formed white suspension converted into a yellow solution which was stirred overnight at 20 °C. The solution was diluted with water (8 mL). The precipitate was filtered off and washed with water and finally dried in a vacuum desiccator over Sicapent[®] to yield K[(C₆F₁₃)₂BF₂] (796 mg, 75%).

4.3. Preparation of $[4-FC_6H_4N_2][R_FBF_3]$ and $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ salts

Syntheses were performed with 0.5 to 1.6 mmol of [4- $FC_6H_4N_2$][BF₄]. The solution of K[R_FBF₃] (1.1 equiv.) in MeCN (3–4 mL) was added to the stirred solution of [4- $FC_6H_4N_2$][BF₄] (1.0 equivalent) in MeCN (3–4 mL). The resulting suspension was stirred for 30–40 min and centrifuged. The yellow-brownish mother liquor was decanted. The solid residue was dried at 25 °C in vacuum and washed with dry ether (2× 10–20 mL). After removal of volatiles at 25 °C in vacuum, the flask was filled with argon and stored in a glove box under an atmosphere of dry argon.

 $[4-FC_6H_4N_2][C_6F_5BF_3]$ (yield 82%). ¹⁹F NMR (CH₃CN): δ -83.1 (tt, ⁴*J*(F⁴,H^{2,6}) = 4 Hz, ³*J*(F⁴,H^{3,5}) = 8 Hz, 1F, F⁴) (4-FC_6H_4N_2); -132.8

 $(tq(1:1:1:1), {}^{4}J(F_{3}B,F^{2,6}) = 11 Hz, {}^{1}J(F,B) = 43 Hz, 3F, BF_{3}), -134.9$ (m, 2F, F^{2,6}), -161.1 (t, {}^{3}J(F^{4},F^{3,5}) = 19 Hz, 1F, F^{4}), -165.4 (m, 2F, F^{3,5}) (C_{6}F_{5}BF_{3}). {}^{11}B NMR (CH_{3}CN): \delta 1.6 (q, {}^{1}J(B,F) = 43 Hz, BF_{3}).

 $\begin{array}{l} [4\text{-}\text{FC}_6\text{H}_4\text{N}_2][\text{C}_6\text{F}_{13}\text{B}\text{F}_3] \; (\text{yield } 77\%). \ ^{19}\text{F} \; \text{NMR}\; (\text{CH}_3\text{CN}): \; \delta \; -82.6 \\ (\text{tt}, \ ^4J(\text{F}^4,\text{H}^{2.6}) = 4\; \text{Hz}, \ ^3J(\text{F}^4,\text{H}^{3.5}) = 8\; \text{Hz}, \; 1\text{F}, \; \text{F}^4)\; (4\text{-}\text{FC}_6\text{H}_4\text{N}_2); \; -79.9 \\ (\text{tt}, \ \ ^3J(\text{F}^6,\text{F}^5) = 3\; \text{Hz}, \ \ ^4J(\text{F}^6,\text{F}^4) = 10\; \text{Hz}, \; 3\text{F}, \; \text{F}^6), \; -120.9 \; (\text{m}, \; \text{CF}_2), \\ -121.6 \; (\text{m}, \; \text{CF}_2), \; -122.4 \; (\text{m}, \; \text{CF}_2), \; -124.8 \; (\text{qtt}, \ \ ^3J(\text{F}^5,\text{F}^6) = 3\; \text{Hz}, \\ ^3J(\text{F}^5,\text{F}^4) = 8\; \text{Hz}, \ ^4J(\text{F}^5,\text{F}^3) = 13\; \text{Hz}, 2\text{F}, \text{F}^5), \; -132.2 \; (\text{m}, \; 2\text{F}, \text{F}^1), \; -151.1 \\ (\text{q}(1:1:1:1), \ ^1J(\text{F},\text{B}) = 41\; \text{Hz}, 3\text{F}, \text{B}F_3)(\text{C}_6\text{F}_{13}\text{B}\text{F}_3). \ ^{11}\text{B}\; \text{NMR}\; (\text{CH}_3\text{CN}): \\ \delta \; -0.7 \; (\text{tq}, \ ^2J(\text{B},\text{F}^1) = 20\; \text{Hz}, \ ^1J(\text{B},\text{F}) = 41\; \text{Hz}, \text{B}\text{F}_3). \end{array}$

 $\begin{array}{l} [4\text{-}FC_{6}H_{4}N_{2}][(C_{6}F_{13})_{2}BF_{2}] \ (\text{yield 84\%}). \ ^{19}F \ \text{NMR} \ (\text{CH}_{3}\text{CN}): \ \delta - 82.7 \\ (\text{tt}, \ ^{4}\!J(\text{F}^{4},\text{H}^{2,6}) = 4 \ \text{Hz}, \ ^{3}\!J(\text{F}^{4},\text{H}^{3,5}) = 8 \ \text{Hz}, 1\text{F}, \text{F}^{4}) \ (4\text{-}\text{FC}_{6}\text{H}_{4}N_{2}); \ -80.1 \ (\text{t}, \ ^{4}\!J(\text{F}^{6},\text{F}^{4}) = 10 \ \text{Hz}, 6\text{F}, \text{F}^{6}), \ -121.0 \ (\text{m}, 2\text{CF}_{2}), \ -121.7 \ (\text{m}, 4\text{CF}_{2}), \ -125.1 \\ (\text{m}, 4\text{F}, \text{F}^{5}), \ -130.4 \ (\text{m}, 4\text{F}, \text{F}^{1}), \ -172.5 \ (\text{q}(1:1:1:1), \ ^{1}\!J(\text{F},\text{B}) = 62 \ \text{Hz}, 2\text{F}, \\ BF_{2}) \ ((\text{C}_{6}\text{F}_{13})_{2}\text{BF}_{2}). \ ^{11}\text{B} \ \text{NMR} \ (\text{CH}_{3}\text{CN}): \ \delta \ 0.1 \ (\text{m}, \text{BF}_{2}). \end{array}$

[4-FC₆H₄N₂][CF₃C=CBF₃] (yield 78%). ¹⁹F NMR (CH₃CN): δ -82.9 (tt, ⁴*J*(F⁴,H^{2.6}) = 4 Hz, ³*J*(F⁴,H^{3.5}) = 8 Hz, 1F, F⁴) (4-FC₆H₄N₂); -47.8 (s, 3F, F³), -135.3 (q(1:1:1:1), ¹*J*(F,B) = 31 Hz, 3F, BF₃) (CF₃C=CBF₃). ¹¹B NMR (CH₃CN): δ -2.5 (q, ¹*J*(B,F) = 31 Hz, BF₃).

The ¹H NMR spectra of the above salts (in CH₃CN) contained resonances of the cation $[4-FC_6H_4N_2]^+$ at $\delta(H)$ 8.57 (dd, ³J(H²,H³) = 9.5 Hz, ⁴J(H²,F⁴) = 4.4 Hz, 2H, H^{2.6}), and 7.65 (dd, ³J(H³,H²) = 9.5 Hz, ³J(H³,F⁴) = 8 Hz, 2H, H^{3.5}) ppm.

4.4. Thermolysis of 4-fluorobenzenediazonium fluoroborate salts

The NMR tube was tightly connected with a cooled (-20 to -40 °C) trap filled with CH₂Cl₂ (0.5 mL) via an FEP tube. This trap allowed to follow the evolution of gas, e.g., N₂. The NMR tube was charged with the borate salt and immersed (3-4 cm) in the oil bath of the melting point device. After decomposition of the salt the NMR tube was quickly deposited into a cooling bath (-40 °C) for 5-10 min. The reaction products in the NMR tube were dissolved in CH₂Cl₂ (0.7 mL) at 25 °C, a defined quantity of C₆F₆ was added and the solution was analyzed by NMR spectroscopy. The cooled CH₂Cl₂ trap contained no fluoroorganics (¹⁹F NMR).

4.4.1. Thermolysis of $[4-FC_6H_4N_2][BF_4]$

The salt $[4-FC_6H_4N_2][BF_4]$ (44 mg, 0.20 mmol) melted accompanied by decomposition at 158–160 °C to give 1,4-difluorobenzene (0.17 mmol, 86%). BF₃ was not collected in the cooled CH₂Cl₂ trap under the experimental conditions.

4.4.2. Thermolysis of $[4-FC_6H_4N_2][C_6F_5BF_3]$

The salt $[4-FC_6H_4N_2][C_6F_5BF_3]$ (30 mg, 83 µmol) melted at 95–100 °C and formed a brown liquid phase which decomposed at 120–140 °C with bubbling. The ¹⁹F NMR spectrum of the residue

showed resonances of 1,4-C₆F₂H₄ (45 μ mol, 54%), C₆F₅H (20 μ mol, 24%), (C₆F₅)₂ (13 μ mol, 16%), and C₆F₅BF₂ (trace). The ¹¹B NMR spectrum contained a weak signal of C₆F₅BF₂ at 21.3 ppm [7e].

4.4.3. Thermolysis of $[4-FC_6H_4N_2][cis-C_6F_{13}CF=CFBF_3]$

The salt $[4-FC_6H_4N_2][cis-C_6F_{13}CF=CFBF_3]$ (47 mg, 82 µmol) melted at 90–95 °C and formed a brown liquid which decomposed at 130–150 °C with bubbling. The ¹⁹F NMR spectrum of the products in the NMR tube showed resonances of $1,4-C_6F_2H_4$ (74 µmol, 90%), $cis-C_6F_{13}CF=CFBF_2$ (14 µmol, 5%), $cis-C_6F_{13}CF=CFH$ (3 µmol, 4%), $C_6F_{13}C=CF$ (2 µmol, 3%), and unidentified compounds of minor quantity. The ¹¹B NMR spectrum showed the resonance of $cis-C_6F_{13}CF=CFBF_2$ at 14.8 ppm [13]. Washing with an aqueous solution of Na₂CO₃ and drying with K₂CO₃ led to the quantitative conversion of $cis-C_6F_{13}CF=CFBF_2$ to $cis-C_6F_{13}CF=CFH$. The other products were not changed.

 $cis-C_{6}F_{13}CF=CFH.$ ¹⁹F NMR (CH₂Cl₂): $\delta-81.4$ (m, 3F, F⁸), -119.8 (dt, ${}^{3}J(F^{3},F^{2}) = 14$ Hz, ${}^{4}J(F^{3},F^{5}) = 14$ Hz, 2F, F³), -122.5 (m, CF₂), -123.2 (m, CF₂), -125.5 (m, CF₂), -126.5 (m, 2F, F⁷), -151.3 (dd, {}^{3}J(F^{1},F^{2}) = 7 Hz, ${}^{2}J(F^{1},H^{1}) = 68$ Hz, 1F, F¹), -155.3 (m, 1F, F²).

 $C_6F_{13}C$ = CF. ¹⁹F NMR (CH₂Cl₂): δ −81.4 (m, 3F, F⁸), −97.4 (t, ⁴J(F³,F⁵) = 13 Hz, 2F, F³), −122 to −126.5 (3CF₂), −127.8 (m, 2F, F⁷), −189.4 (m, 1F, F¹).

4.4.4. Thermolysis of $[4-FC_6H_4N_2]$ [trans-C₄F₉CF=CFBF₃]

Melting of salt $[4-FC_6H_4N_2][trans-C_4F_9CF=CFBF_3]$ (44 mg, 93 µmol) at 80–90 °C resulted in a brown liquid which decomposed at 120–130 °C with bubbling. The ¹⁹F NMR spectrum of the products showed resonances of 1,4-C₆F₂H₄ (75 µmol, 80%), *trans*-C₄F₉CF=CFBF₂ (46 µmol, 49%), and minor unidentified compounds. In the ¹¹B NMR spectrum the resonance of *trans*-C₄F₉CF=CFBF₂ was detected at 13.6 ppm [13].

4.4.5. Thermolysis of [4-FC₆H₄N₂][C₆F₁₃BF₃]

The salt [4-FC₆H₄N₂][C₆F₁₃BF₃] (45 mg, 88 μ mol) melted at 110–115 °C and gave a brown liquid which decomposed at 120–130 °C with evolution of gas. The decomposition products were dissolved in CF₃CH₂CF₂CH₃ (PFB). The ¹⁹F NMR spectrum showed resonances of 1,4-C₆F₂H₄ (59 μ mol, 67%) and C₆F₁₃BF₂ (75 μ mol, 85%).

4.4.6. Thermolysis of $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$

When salt $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ (92 mg, 113 µmol) was heated melting and decomposition proceeded at 140–145 °C. The products were extracted with 1,1,1,3,3-pentafluorobutane (PFB). The ¹⁹F NMR spectrum showed resonances of 1,4-C₆F₂H₄ (89 µmol, 79%), C₆F₁₃CF(BF₂)C₅F₁₁ (31 µmol, 27%), and of unidentified compounds. The products C₆F₁₃BF₂, C₄F₉CF=CFBF₂ (*cis* and *trans*), 4-FC₆H₄C₆F₁₃, and 4-FC₆H₄CF=CFC₄F₉ were not detected (¹⁹F NMR).

 $C_6F_{13}CF(BF_2)C_5F_{11}$. ¹⁹F NMR (PFB): δ -79.9 (t, ⁴J(F¹,F³) = ⁴J(F¹²,F¹⁰) = 10 Hz, 6F, F^{1,12}), -116.8 (m, 2CF₂), -124.8 (m, 4F, F^{2,11}), -114.0 (d, ²J(F^{7A},F^{7B}) = 303 Hz, 1F^{7A}), -114.3 (d, ²J(F^{5A},F^{5B}) = 303 Hz, 1F^{5A}), -121 to -126 (2CF₂, 1F^{5B}, 1F^{7B}), -207.8 (m, 1F⁶).

4.5. Thermolysis of 4-fluorobenzenediazonium perfluoroorganylfluoroborates in NaF

The corresponding perfluoroorganyborate salts and vigorously dried NaF (1:3, v/v) were mixed in the glove box and loaded into an NMR tube. The NMR tube was immersed (3–4 cm) into the oil bath of the melting point device and heated to 160–170 °C within 5–7 min and kept at 169–170 °C for 1 min. After decomposition the NMR tube was quickly deposited into a cold (0 °C) bath for 5–10 min and the products were extracted with CH_2Cl_2 (0.8–1 mL) at

25 °C. The residue was washed with CH_2Cl_2 (2 × 1 mL), dried in vacuum and extracted with CH_3CN . Both extracts were analyzed by NMR spectroscopy.

4.5.1. Thermolysis of $[4-FC_6H_4N_2][C_6F_5BF_3]$ in NaF

Decomposition of $[4\text{-}FC_6H_4N_2][C_6F_5BF_3]$ (64 mg, 178 μ mol) in NaF (1:3, v/v) gave 1,4-C_6F_2H_4 (141 μ mol, 79%), (CH_2Cl_2 extract), Na[C_6F_5BF_3] (126 μ mol, 71%) and Na[BF_4] (20 μ mol, 11%) (CH_3CN extract) (19 F NMR).

4.5.2. Thermolysis of $[4-FC_6H_4N_2]$ [cis-C₆F₁₃CF=CFBF₃] in NaF

Decomposition of $[4-FC_6H_4N_2][cis-C_6F_{13}CF=CFBF_3]$ (47 mg, 82 µmol) in NaF (1:3, v/v) gave $1,4-C_6F_2H_4$ (63 µmol, 77%) and $C_6F_{13}C=CF$ (3 µmol, 3%) (CH₂Cl₂ extract) (¹⁹F NMR), Na[*cis*-C₆F₁₃CF=CFBF₃] (53 µmol, 65%), Na[*trans*-C₆F₁₃CF=CFBF₃] (10 µmol, 12%), and Na[BF₄] (14 µmol, 17%) (CH₃CN extract) (¹¹B, ¹⁹F NMR).

4.5.3. Thermolysis of $[4-FC_6H_4N_2]$ [trans- C_4F_9CF =CFBF₃] in NaF

Decomposition of $[4-FC_6H_4N_2][trans-C_4F_9CF=CFBF_3]$ (51 mg, 108 µmol) in NaF (1:3, v/v) gave $1,4-C_6F_2H_4$ (103 µmol, 95%) (CH₂Cl₂ extract) (¹⁹F NMR), Na[*trans*-C_4F_9CF=CFBF_3] (90 µmol, 83%), Na[*cis*-C_4F_9CF=CFBF_3] (11 µmol, 10%), and Na[BF_4] (6 µmol, 5%) (CH₃CN extract) (¹¹B, ¹⁹F NMR).

4.5.4. Thermolysis of $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ in NaF

A mixture of $[4-FC_6H_4N_2][(C_6F_{13})_2BF_2]$ (44 mg, 54 µmol) with NaF (1:3, v/v) was heated from 25 to 200 °C (bath) within 8 min and quickly cooled to 20 °C. The products were extracted with CH₃CN (0.7 mL). The extract contained 1,4-C₆F₂H₄ (44 µmol, 81%), Na[(C₆F₁₃)_2BF_2] (21 µmol, 39%), Na[C₆F₁₃CF(BF₃)C₅F₁₁] (18 µmol, 33%), and Na[BF₄] (9 µmol, 17%) (¹¹B, ¹⁹F NMR).

 $\begin{array}{l} Na[C_{6}F_{13}CF(BF_{3})C_{5}F_{11}] \,\,^{19}F \,\,NMR\,(CH_{3}CN).\,\delta-80.1\,(m,\,6F,\,F^{1,12}),\\ -119.7\,(m,\,2CF_{2}),\,-120.5\,(m,\,CF_{2}),\,-121.3\,(m,\,CF_{2}),\,-121.5\,(m,\,CF_{2}),\,-125.0\,(m,\,4F,\,F^{2,11}),\,-110.4\,(d,\,^{2}J(F^{7A},F^{7B})=304\,Hz,\,1F^{7A}),\\ -111.3\,(d,\,^{2}J(F^{7B},F^{7A})=304\,Hz,\,1F^{7B}),\,-110.4\,(d,\,^{2}J(F^{5A},F^{5B})=304\,Hz,\,1F^{5A}),\,-111.3\,(d,\,^{2}J(F^{5B},F^{5A})=304\,Hz,\,1F^{5B}),\,-208.7\,(m,\,1F^{6}),\,-143.9\,(q(1:1:1:1),\,^{1}J(F,B)=37\,Hz,\,BF_{3})\,(cf.\,with\,spectrum\,of\,M[C_{2}F_{5}CF(BF_{3})CF_{3}]\,[9]). \end{array}$

4.5.5. Thermolysis of $[4-FC_6H_4N_2][CF_3C \equiv CBF_3]$ in NaF

After decomposition of $[4-FC_6H_4N_2][CF_3C\equiv CBF_3]$ (48 mg, 169 µmol) in NaF (1:3/v/v) the products were extracted with CH₃CN (0.7 mL). The extract contained 1,4-C₆F₂H₄ (90 µmol, 51%), Na[CF₃C≡CBF₃] (16 µmol, 9%), CF₃C≡CH (16 µmol, 9%), and Na[BF₄] (129 µmol, 76%) besides few minor unidentified products (¹¹B, ¹⁹F NMR).

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