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New types of asymmetrical bromonium salts $[R_F(R_F')Br]Y$ where R_F and/or R_F' represent perfluorinated aryl, alkenyl, and alkynyl groups

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ABSTRACT

A series of previously unknown asymmetrical fluorinated bis(aryl)bromonium, alkenyl(aryl)bromonium, and alkynyl(aryl)bromonium salts was prepared by reactions of $C_6F_5BrF_2$ or 4-$CF_3C_6H_4BrF_2$ with aryl group transfer reagents $Ar'SiF_3$ ($Ar' = C_6F_5$, 4-FC_6H_4, C_6H_5) or perfluoroorganyl group transfer reagents $R_F'BF_2$ ($R_F = C_6F_5$, *trans*-$CF_3CF{=}CF$, $C_3F_7C{\equiv}C$) preferentially in weakly coordinating solvents (CCl_3F, CCl_2FCClF_2, CH_2Cl_2, $CF_3CH_2CHF_2$ (PFP), $CF_3CH_2CF_2CH_3$ (PFB)). The presence of the base MeCN and the influence of the adducts $R_F'BF_2{\cdot}NCMe$ ($R_F = C_6F_5$, $CF_3C{\equiv}C$) on reactions aside to bromonium salt formation are discussed. Reactions of $C_6F_5BrF_2$ with $Alk_F'BF_2$ in PFP gave mainly C_6F_5Br and $Alk_F'F$ ($Alk_F' = C_6F_{13}$, $C_6F_{13}CH_2CH_2$), presumably, deriving from the unstable salts $[C_6F_5(Alk_F')Br]Y$ ($Y = [Alk_F'BF_3]^-$). Prototypical reactivities of selected bromonium salts were investigated with the nucleophile $I^-$and the electrophile H^+. $[4\text{-}CF_3C_6H_4(C_6F_5)Br][BF_4]$ showed the conversion into 4-$CF_3C_6H_4Br$ and C_6F_5I when reacted with $[Bu_4N]I$ in MeCN. Perfluoroalkynylbromonium salts $[C_nF_{2n+1}C{\equiv}C(R_F)Br][BF_4]$ slowly added HF when dissolved in aHF and formed $[Z\text{-}C_nF_{2n+1}CF{=}CH(R_F)Br][BF_4]$.

1. Introduction

Asymmetrical bis(aryl)bromonium salts were the first isolated and unambiguously characterized organic derivatives of bromine(III) (see reviews [1,2]). The first representatives were obtained in trace amounts by decomposition of benzenediazonium tetrafluoroborates in an excess of hot bromobenzene (Eq. (1)) [3–5].

$$[ArN_2][BF_4] + C_6H_5Br\,(\text{excess}) \xrightarrow{80-90\,^\circ C,\,7-8\,h} \underset{<1\%}{[Ar(C_6H_5)Br][BF_4]} + N_2 \quad (1)$$

Ar = 2-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 2,4-$(CH_3)_2C_6H_3$, 2-naphthyl, 4-ClC_6H_4, 4-$C_2H_5OC(O)C_6H_4$.

Decomposition of $[ArN_2][BF_4]$ in the presence of trifluoroacetic acid led to somewhat better results (Eqs. (2) and (3)) [6,7].

$$[3\text{-}FC_6H_4N_2][BF_4] + C_6H_5Br \xrightarrow[\text{reflux, 4 h}]{C_6H_5Br/CF_3CO_2H} \underset{11\%}{[3\text{-}FC_6H_4(C_6H_5)Br][BF_4]} + N_2 \quad (2)$$

$$[ArN_2][PF_6] + C_6H_5Br \xrightarrow[2.\ \text{aq. Na}[Ph_4B],\ -\text{Na}[PF_6]]{1.\ C_6H_5Br/CF_3CO_2H,\,65-70\,^\circ C,\,2\,h} \underset{\leq 11\%}{[Ar(C_6H_5)Br][Ph_4B]} + N_2 \quad (3)$$

Ar = 2-$CH_3C_6H_4$, 4-$CH_3C_6H_4$

It was assumed that these salts were formed via in situ generated aryl cations or structurally related electrophilic species which added to valence electron lone pairs of the bromine atom [2,3]. Later several bis(alkyl)bromonium (Eq. (4)) and alkyl(aryl)-bromonium salts (Eq. (5)) were prepared in solution by alkylation of alkyl bromides or aryl bromides with highly electrophilic carbocations [1,2].

$$AlkF + Alk'Br + SbF_5 \xrightarrow{SO_2,\,-78\,^\circ C} [Alk(Alk')Br][SbF_6] \quad (4)$$

Alk = CH_3, C_2H_5; Alk′ = CH_3, C_2H_5, $(CH_3)_2CH$

$$AlkF + C_6H_5Br + SbF_5 \xrightarrow{SO_2,\,-70\,^\circ C} [Alk(C_6H_5)Br][SbF_6] \quad (5)$$

Alk = CH_3, C_2H_5

In this context it is worth to mention, that the attempted methylation of the perfluorinated aryl bromide, 1,4-dibromotetrafluorobenzene, with CH_3F–SbF_5 in SO_2 failed [8].

A more efficient route to asymmetrical bromonium salts is fluorine/organyl substitution in $RBrF_2$. The in situ formation of

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$C_6H_5BrF_2$ was proposed in reactions of C_6H_5Br with XeF_2 (Eqs. (6) and (8)), of C_6H_6 with BrF_3 (Eq. (7)), and of $(C_6H_5)_2Hg$ with BrF_3 (Eq. (9)). Subsequently, the second aryl group was introduced by arenes [9,10], tetraarylstannanes [11], or diarylmercury [12] as arylating agents.

$$C_6H_5Br + XeF_2 \xrightarrow[-70\,^\circ C]{SO_2} C_6H_5BrF_2 \xrightarrow[1-5\%]{ArH,\ BF_3\cdot OEt_2} [Ar(C_6H_5)Br][BF_4] \quad (6)$$

Ar = 4-FC_6H_4, 4-ClC_6H_4, 4-$CH_3C_6H_4$, 2-$CH_3OC(O)C_6H_4$

$$C_6H_6 + BrF_3 \xrightarrow[-70\,^\circ C]{CH_2Cl_2/MeCN/BF_3\cdot OEt_2} C_6H_5BrF_2 \xrightarrow{ArH} [Ar(C_6H_5)Br][BF_4] \quad (7)$$

Ar = 4-FC_6H_4 (49%), 4-ClC_6H_4 (20–29%), 4-$CH_3C_6H_4$ (39%), 4-$CH_3OC(O)C_6H_4$ (27%)

$$C_6H_5Br + XeF_2 \xrightarrow[-70\,^\circ C]{CH_2Cl_2/MeCN/BF_3\cdot OEt_2} C_6H_5BrF_2 \xrightarrow{Ar_4Sn,\ BF_3\cdot OEt_2} [Ar(C_6H_5)Br][BF_4] \quad (8)$$

Ar = 4-$CH_3C_6H_4$ (55%), 4-$CH_3OC_6H_4$ (32%)

$$(C_6H_5)_2Hg + BrF_3 \xrightarrow[-70\,^\circ C]{CH_2Cl_2/MeCN} C_6H_5BrF_2 \xrightarrow[BF_3\cdot OEt_2]{(4-CH_3C_6H_4)_2Hg} [4\text{-}CH_3C_6H_4(C_6H_5)Br][BF_4] \quad (9)$$

In a preceeding paper [13] we have reported new routes to $[(C_6F_5)_2Br][BF_4]$ and the syntheses of previously unknown types of symmetrical $[(R_F)_2Br][Y]$ salts where R_F represents a perfluorinated alk-1-en-1-yl or alk-1-yn-1-yl group. The approach was based on the nucleophilic replacement of two fluorine atoms in BrF_3 or $[BrF_2]^+$ salts by two R_F groups under acidic conditions, e.g., by the reaction of perfluoroorganyldifluoroboranes, R_FBF_2, with bromine trifluoride in weakly coordinating solvents (wcs) like 1,1,1,3,3-pentafluoropropane (PFP) or 1,1,1,3,3-pentafluorobutane (PFB), or by the interaction of $K[R_FBF_3]$ with either BrF_3 or $[BrF_2][SbF_6]$ in anhydrous HF (aHF). Despite of variations of temperature and stoichiometry of the reactants R_FBF_2 and BrF_3, we did not detect the intermediate R_FBrF_2 by ^{19}F NMR spectroscopy and concluded that the F/R_F substitution in the intermediate bromane R_FBrF_2 proceeded faster than the formation of R_FBrF_2 from R_FBF_2 and BrF_3. The salt $[(C_6F_5)_2Br][BF_4]$ was formed even from a reaction of $C_6F_5BF_2$ and BrF_3 in a 1:1 molar ratio and in the presence of the base MeCN, which reduces the Lewis acidity of borane. In summary, the replacement of one fluorine atom in BrF_3 by a pentafluorophenyl group accelerates the subsequent F/C_6F_5 substitution step under formation of $[(C_6F_5)_2Br]^+$ salts.

Concerning non-perfluorinated aryl difluorobromanes, only 3- and 4-$CF_3C_6H_4BrF_2$ are described in the literature. They were prepared in good to excellent isolated yields [14]. 4-$CF_3C_6H_4BrF_2$ allowed the syntheses of alkynyl(aryl)bromonium tetrafluoroborates in reactions with alkynyltrimethylstannanes bearing electron-rich alkynyl groups under acidic conditions. The attempted reaction of 4-$CF_3C_6H_4BrF_2$ with $C_8H_{17}C{\equiv}CSiMe_3$ gave only a trace of the desired bromonium salt [15].

$$4\text{-}CF_3C_6H_4BrF_2 + RC{\equiv}CSnMe_3 \xrightarrow[-70\,^\circ C]{BF_3\cdot OEt_2,\ CH_2Cl_2} [4\text{-}CF_3C_6H_4(RC{\equiv}C)Br][BF_4] \quad (10)$$

R = C_4H_9, $(CH_3)_2CHCH_2$, C_8H_{17}, *cyclo*-C_6H_{11}, $(CH_3)_3C$, $(CH_3)_3Si$ (76–89%)

In the present paper we report the preparation of a representative series of asymmetrical bromonium salts $[R_F(R_F')Br]Y$, where R_F' and R_F can represent a perfluoroorganyl group, by reaction of pentafluorophenyldifluorobromane (**1**) [16] and 4-trifluoromethylphenyldifluorobromane (**2**) [14] with two types of the organyl transfer reagents of distinct Lewis acidity: aryltrifluorosilanes (Y = $[SiF_5]^-$) and per- or polyfluoroorganyldifluoroboranes (Y = $[BF_4]^-$ or $[R_F'BF_3]^-$).

2. Results and discussion

2.1. Syntheses of asymmetrical bromonium salts using aryltrifluorosilanes

We have found that pentafluorophenyltrifluorosilane (**3**) easily reacted with bromane **2** in the weakly coordinating solvent CCl_3F to give 4-trifluoromethylphenyl(pentafluorophenyl)bromonium pentafluorosilicate (**4a**), which was converted into the thermally more stable hexafluorophosphate (**4b**) by metathesis with $H[PF_6]$ in aqueous solution (Eq. (11)).

$$4\text{-}CF_3C_6H_4BrF_2 \ (\mathbf{2}) + C_6F_5SiF_3 \ (\mathbf{3}) \xrightarrow[2.\ aq\ H[PF_6]]{1.\ CCl_3F,\ 0\,^\circ C,\ 15-20\,h} [4\text{-}CF_3C_6H_4(C_6F_5)Br][PF_6] \ (\mathbf{4b}\ (63\%)) \quad (11)$$

The attempt to prepare salt **4a** by the alternative route from bromane **1** and 4-trifluoromethylphenyltrifluorosilane (**5**) in CCl_3F, led to a complex mixture without the target product. The same negative result was obtained in the reaction of **1** with 4-fluorophenyltrifluorosilane (**6**) in CCl_3F. Contrary results were obtained in the coordinating solvent MeCN. Salts 4-fluorophenyl(-pentafluorophenyl)bromonium hexafluorophosphate (**7**) and phenyl(pentafluorophenyl)bromonium tetrafluoroborate (**8**) could be synthesized on the route shown in Eqs. (12) and (13) in moderate to good yields.

$$C_6F_5BrF_2 \ (\mathbf{1}) + ArSiF_3 \xrightarrow[2.\ aq\ H[PF_6]]{1.\ CH_3CN,\ 0\,^\circ C,\ 15-20\,h} [C_6F_5(Ar)Br][PF_6] \quad (12)$$

Ar = 4-$CF_3C_6H_4$ (**4b**) (67%), 4-FC_6H_4 (**7**) (57%)

$$C_6F_5BrF_2 \ (\mathbf{1}) + C_6H_5SiF_3 \ (\mathbf{9}) \xrightarrow[2.\ aq\ H[BF_4]]{1.\ CH_3CN,\ 0\,^\circ C,\ 15-20\,h} [C_6F_5(C_6H_5)Br][BF_4] \ (\mathbf{8}\ (31\%)) \quad (13)$$

The differing results presented afore in reactions of 4-$CF_3C_6H_4BrF_2$ with $C_6F_5SiF_3$ compared to $C_6F_5BrF_2$ with 4-$CF_3C_6H_4SiF_3$ in weakly coordinating and coordinating solvents can be rationalized on basis of a stronger Br–F bond in $C_6F_5BrF_2$ than in 4-$CF_3C_6H_4BrF_2$ due to a higher bond polarity caused by the stronger electron-withdrawing C_6F_5 group and on a higher oxidizing property of $[C_6F_5BrF]^+$ (simplified description of the polarized species) relative to $[4\text{-}CF_3C_6H_4BrF]^+$. MeCN can moderate the oxidizing property of $[C_6F_5BrF]^+$ by coordination.

2.2. Syntheses of asymmetrical bromonium salts using organyldifluoroboranes

Perfluorinated organyldifluoroboranes are more acidic [17] and, in general, more easy to prepare [18–21] than the corresponding organyltrifluorosilanes. This situation allowed to study the preparation of asymmetrical bis(organyl)bromonium salts starting from aryldifluorobromanes. By this route we obtained amongst others the previously unknown perfluorinated alkenyl(aryl)- and alkynyl(aryl)bromonium salts. Attempts to synthesize per- and polyfluoroalkyl(pentafluorophenyl) bromonium salts failed.

The reaction of arylbromane **2** with pentafluorophenyldifluoroborane (**10**) was performed in PFB and 1,1,2-trichlorotrifluoroethane and gave 4-trifluoromethylphenyl(pentafluorophenyl) bromonium tetrafluoroborate (**4c**) in a high yield. Remarkably, the aryl group transfer was completed within 1 h at −20 °C (Eq. (14)),

whereas the formation of [4-$CF_3C_6H_4(C_6F_5)$Br][SiF_5] (**4a**) using silane **3** took 15–20 h at 0 °C (Eq. (11))

$$\underset{\mathbf{2}}{\text{4-CF}_3\text{C}_6\text{H}_4\text{BrF}_2} + \underset{\mathbf{10}}{\text{C}_6\text{F}_5\text{BF}_2} \xrightarrow{\text{PFB/1,1,2-C}_2\text{Cl}_3\text{F}_3,\,-20\,^\circ\text{C}} \underset{\mathbf{4c}\,(94\%)}{[\text{4-CF}_3\text{C}_6\text{H}_4(\text{C}_6\text{F}_5)\text{Br}][\text{BF}_4]} \quad (14)$$

Perfluorinated pent-1-yn-1-yl(phenyl)bromonium tetrafluoroborate (**11**) was obtained by addition of heptafluoropent-1-yn-1-yldifluoroborane (**12**) to a cold solution of bromane **1** in PFP and was isolated as a white solid after removal of all volatiles in vacuum (Eq. (15))

$$\underset{\mathbf{1}}{\text{C}_6\text{F}_5\text{BrF}_2} + \underset{\mathbf{12}}{\text{C}_3\text{F}_7\text{C}\equiv\text{CBF}_2} \xrightarrow{\text{PFP},\,-40\,^\circ\text{C}} \underset{\mathbf{11}\,(56\%)}{[\text{C}_6\text{F}_5(\text{C}_3\text{F}_7\text{C}\equiv\text{C})\text{Br}][\text{BF}_4]} \quad (15)$$

Under similar conditions, *trans*-pentafluoroprop-1-en-1-yldifluoroborane (**13**) reacted with bromane **1** to yield perfluorinated *trans*-prop-1-en-1-yl(phenyl)bromonium *trans*-pentafluoropropenyltrifluoroborate (**14**) (Eq. (16)). The configuration of the alkenyl moiety bonded to the bromine atom retended whereas in case of the previously reported formation of [$(CF_3CF{=}CF)_2$Br][$CF_3CF{=}CFBF_3$] from borane **13** and BrF_3 a partial conversion to the *cis*-isomer took place [13]. The nature of the counteranion depended on the higher fluoride affinity of borane **13** relative to that of BF_3 (F^--affinities 89.0 and 78.8 kcal/mol, respectively [17]) as discussed in Ref. [13].

$$\underset{\mathbf{1}}{\text{C}_6\text{F}_5\text{BrF}_2} + 2\,\textit{trans}\text{-}\underset{\mathbf{13}}{\text{CF}_3\text{CF}=\text{CFBF}_2} \xrightarrow{\text{PFP},\,-40\,^\circ\text{C}} \underset{\mathbf{14}\,(60\%)}{[\text{C}_6\text{F}_5(\text{trans-CF}_3\text{CF}=\text{CF})\text{Br}][\textit{trans}\text{-CF}_3\text{CF}=\text{CFBF}_3]} + \text{BF}_3 \quad (16)$$

In contrast to the successful syntheses of salts **4c**, **11**, and **14**, the attempted preparation of the perfluorinated hex-1-yl(phenyl)bromonium salt failed. When a solution of perfluorohexyldifluoroborane (**15**) (2 equiv.) in PFP was added to a solution of $C_6F_5BrF_2$ in PFP at −65 °C, a mixture of perfluorohexane (**16**), bromopentafluorobenzene (**17**), 1-bromoheptafluorocyclohexa-1,4-diene (**18**), and non-consumed borane **15** was formed (Eq. (17))

$$\underset{\mathbf{1}}{\text{C}_6\text{F}_5\text{BrF}_2} + \underset{\mathbf{15}}{\text{C}_6\text{F}_{13}\text{BF}_2} \xrightarrow{\text{PFP},\,-65\,^\circ\text{C}} \underset{\mathbf{17}}{\text{C}_6\text{F}_5\text{Br}},\ \underset{\mathbf{18}}{\text{cyclo-1-Br-1,4-C}_6\text{F}_7},\ \underset{\mathbf{16}}{\text{C}_6\text{F}_{14}},\ \text{BF}_3 \quad (17)$$

A similar result was obtained with the less acidic 1H,1H,2H,2H-tridecafluorooctyldifluoroborane (**19**) which was converted into 1H,1H,2H,2H-tetradecafluorooctane (**20**) (Eq. (18)).

$$\underset{\mathbf{1}}{\text{C}_6\text{F}_5\text{BrF}_2} + \underset{\mathbf{19}}{\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{BF}_2} \xrightarrow{\text{PFP},\,-65\,^\circ\text{C}} \underset{\mathbf{17}}{\text{C}_6\text{F}_5\text{Br}},\ \underset{\mathbf{18}}{\text{cyclo-1-Br-1,4-C}_6\text{F}_7},\ \underset{\mathbf{21}}{\text{cyclo-1-BrC}_6\text{F}_9},\ \underset{\mathbf{20}}{\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{F}},\ \text{BF}_3 \quad (18)$$

It should be noted that during the addition of the alkylboranes **15** and **19** to a solution of $C_6F_5BrF_2$, for a short time (10–20 s) a: suspension was observed whose solid decomposed within 20–30 min to yield a colorless solution. Likely, this precipitate may be salt [$Alk_F(C_6F_5)$Br][XBF_3] ($Alk_F = C_6F_{13}CH_2CH_2$, X = F; $Alk_F = C_6F_{13}$, $X = C_6F_{13}$). Such salts are closely related to the iodonium salt [$C_6F_{13}(C_6F_5)$I][$C_6F_{13}BF_3$]. The latter was prepared from $C_6F_{13}BF_2$ and $C_6F_5IF_2$ in PFP and decomposed above 0 °C (Eq. (19)) [22].

$$\mathbf{15} + \text{C}_6\text{F}_5\text{IF}_2 \xrightarrow[-40\,^\circ\text{C}]{\text{PFP}} [\text{C}_6\text{F}_5(\text{C}_6\text{F}_{13})\,\text{I}][\text{C}_6\text{F}_{13}\text{BF}_3] \xrightarrow[>0\,^\circ\text{C}]{\text{PFP}} \text{C}_6\text{F}_{14} + \text{C}_6\text{F}_5\text{I} + \text{C}_6\text{F}_{13}\text{BF}_2 \quad (19)$$

The formation of the minor products **18** and **21** in Eq. (18) can be assigned to a parallel reaction channel, the acid-assisted decomposition of $C_6F_5BrF_2$ to C_6F_5Br and unsaturated cyclic bromo-containing compounds described in Ref. [23].

Furthermore, we investigated the influence of base Lewis acid adducts of organyldifluoroboranes·$NCCH_3$ on fluorine/organyl substitutions in $ArBrF_2$. The base adducts $R_FBF_2{\cdot}NCCH_3$ are less acidic than the underlying boranes itself. We have found that bromane **1** reacted with the adduct $CF_3C{\equiv}CBF_2{\cdot}NCCH_3$ (**22**) (1 equiv.) in PFP/MeCN to yield trifluoroprop-1-yn-1-yl(pentafluorophenyl)bromonium tetrafluoroborate (**23**), but the conversion of **22** was incomplete and in particular the main product was C_6F_5Br (molar ratio **23:17** = 1:4) (Eq. (20))

$$\underset{\mathbf{1}}{\text{C}_6\text{F}_5\text{BrF}_2} + \text{CF}_3\text{C}\equiv\underset{\mathbf{22}}{\text{CBF}_2\cdot\text{NCCH}_3} \xrightarrow{\text{PFP/CH}_3\text{CN},\,-10\,^\circ\text{C}} \underset{\mathbf{23}}{[\text{C}_6\text{F}_5(\text{CF}_3\text{C}\equiv\text{C})\text{Br}][\text{BF}_4]},\ \underset{\mathbf{17}}{\text{C}_6\text{F}_5\text{Br}} \quad (20)$$

The formation of **17** was also observed in the synthesis of [$(C_6F_5)_2$Br][BF_4] from BrF_3 and $(C_6F_5)_nBF_{3-n}{\cdot}NCCH_3$ (n = 1–3) [13,24]. Its amount was minimized when the reaction was performed at −70 °C, but it increased at higher temperatures (−20 to 25 °C). This phenomenon can be explained by fluoride abstraction from **1** under the action of a sufficient Lewis acid and following base coordination yielding [$C_6F_5BrF{\cdot}NCCH_3$]Y which subsequently decomposed [24]

Contrary, the reaction of bromane **2** with adduct $C_6F_5BF_2{\cdot}NCCH_3$ (**24**) gave salt **4c** in a high yield (Eq. (21)).

$$\underset{\mathbf{2}}{\text{4-CF}_3\text{C}_6\text{H}_4\text{BrF}_2} + \underset{\mathbf{24}}{\text{C}_6\text{F}_5\text{BF}_2\cdot\text{NCCH}_3} \xrightarrow{\text{PFB/CH}_3\text{CN},\,24\,^\circ\text{C}} \underset{\mathbf{4c}\,(>90\%)}{[\text{4-CF}_3\text{C}_6\text{H}_4(\text{C}_6\text{F}_5)\text{Br}][\text{BF}_4]} \quad (21)$$

2.3. Prototypical reactivities of [$R(R_F')$Br][BF_4]

The reactivity of perfluorinated bis(organyl)bromonium salts [$R_F(R_F')$Br]Y is still not investigated [25] except of thermal decomposition and anion metathesis in case of [$(C_6F_5)_2$Br]Y [24]. We present here some prototypical examples of their reactivity. When a solution of salt **4c** in MeCN was treated with [Bu_4N]I in MeCN, 4-bromobenzotrifluoride and iodopentafluorobenzene were formed in a 1:1 molar ratio besides $[BF_4]^-$ and pentafluorobenzene (trace) (Eq. (22)).

$$\underset{\mathbf{4c}}{[\text{4-CF}_3\text{C}_6\text{H}_4(\text{C}_6\text{F}_5)\text{Br}][\text{BF}_4]} + [\text{Bu}_4\text{N}]\text{I (excess)} \xrightarrow{\text{MeCN},\,-10\text{ to }24\,^\circ\text{C}} \text{4-CF}_3\text{C}_6\text{H}_4\text{Br} + \text{C}_6\text{F}_5\text{I} + [\text{Bu}_4\text{N}][\text{BF}_4] \quad (22)$$

Another type of reactivity is the transformation of the polarizable triple bond in the perfluoroalkynyl moiety bonded to Br(III). Salt **11** underwent a slow HF addition in anhydrous HF at 24 °C yielding *Z*-1H-octafluoropent-1-en-1-yl(pentafluorophenyl)bromonium tetrafluoroborate (**25**) (38% conversion after 12 h). When the solution was kept for an additional 60 h at 24 °C, salt **11** was consumed completely and ca. 50% of salt **25** were converted into bromopentafluorobenzene and 1H,1H-octafluoropentan-2-one (**26**) (Eq. (23)). Likely, that the formation of the latter product was caused by permeation of H_2O vapor passing though the 0.35 mm FEP wall during the long-term reaction.

$$[\text{C}_3\text{F}_7\text{C}\equiv\text{C}(\text{C}_6\text{F}_5)\text{Br}][\text{BF}_4]_{\mathbf{11}} + \text{HF} \xrightarrow{22\,^\circ\text{C}} \underset{\mathbf{25}}{[\text{Z-C}_3\text{F}_7\text{CF}=\text{CH}(\text{C}_6\text{F}_5)\text{Br}][\text{BF}_4]} \xrightarrow{\text{H}_2\text{O, HF}} \underset{\mathbf{26}}{\text{C}_3\text{F}_7\text{C(O)CH}_2\text{F}} + \underset{\mathbf{17}}{\text{C}_6\text{F}_5\text{Br}} + [\text{H}_3\text{O}][\text{BF}_4] \quad (23)$$

HF addition across the triple bond occurred in a solution of bis(trifluoroprop-1-yn-1-yl)bromonium tetrafluoroborate (**27**) [13] in aHF. Here hydrogen fluoride was added to both alkynyl moieties to give in sequence *Z*-1H-trifluoroprop-1-en-1-yl(tri-

fluoroprop-1-yn-1-yl)bromonium tetrafluoroborate (**28**) and bis(*Z*-1H-trifluoroprop-1-en-1-yl)bromonium tetrafluoroborate (**29**) (Eqs. (24) and (25))

$$[(\underset{\mathbf{27}}{CF_3C\equiv C)_2Br}][BF_4] + HF \xrightarrow{25\ ^\circ C,\ 24\ h} [Z\text{-}CF_3CFCH(\underset{\mathbf{28}}{CF_3C\equiv CBr}][BF_4]\ (100\%) \quad (24)$$

$$[Z\text{-}CF_3CF=CH(CF_3C\equiv C)Br][BF_4] + HF \xrightarrow[(64\%\ \text{conversion})]{25\ ^\circ C,\ 9\ d} [(Z\text{-}CF_3CF=\underset{\mathbf{29}}{CH)_2Br}][BF_4] \quad (25)$$

3. Experimental

3.1. General

The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (300.13 MHz, ^{1}H; 282.40 MHz, ^{19}F; 96.29 MHz, ^{11}B; 75.47 MHz, ^{13}C). The chemical shifts are referenced to TMS (^{1}H, ^{13}C), CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)), and $BF_3{\cdot}OEt_2/CDCl_3$ (15%, v/v) (^{11}B), respectively. The composition of the reaction mixtures and the yields of products were determined by ^{19}F NMR spectroscopy using the internal integral standards C_6F_6 or PFB.

The products $C_6F_{13}CH_2CH_2F$ [26], *cyclo*-1-Br-1,4-C_6F_7, and *cyclo*-1-BrC_6F_9 [27] were identified by ^{19}F NMR spectroscopy.

As a convention for the presentation of the NMR spectral data the labelling of the carbon atoms and the attached fluorine (hydrogen) atoms in alkynyl groups is presented by hyphen, e.g., as C-3, F-3, or H-1, and that of the alkyl, alkenyl, and aryl moieties by superscripts, e.g., C^1, F^2, or H^3. The fluorine atoms F^2 at C^2 in $[R''C^2F{=}C^1F{-}X]$ compounds (X = B, Br) are specified by *cis* or *trans* relative to the position of X, e.g., F^{2trans}.

1,1,1,3,3-Pentafluoropropane (PFP) (Honeywell), 1,1,1,3,3-pentafluorobutane (PFB) (Solvay Fluor), CCl_3F (K11, Solvay Fluor), 1,1,2-trichlorotrifluoroethane (K113, Solvay Fluor) were stored over molecular sieves 3 Å, and $(C_2H_5)_2O$ (Baker) was stored over sodium before use. Acetonitrile (Baker) and dichloromethane (Baker) were purified and dried as described in Ref. [28]. Anhydrous HF (aHF) was stored over CoF_3. Boron trifluoride (Air Liquide), $[Bu_4N]I$ (Fluka) were used as supplied. Aryltrifluorosilanes $C_6H_5SiF_3$, 4-$CF_3C_6H_4SiF_3$, and 4-$FC_6H_4SiF_3$ were synthesized from the corresponding aryltrichlorosilanes and SbF_3 [29], $K[C_6F_{13}CH_2CH_2BF_3]$ [30], $[(CF_3C{\equiv}C)_2Br][BF_4]$ [13], $C_6F_5SiF_3$ [31], $C_6F_5BrF_2$ [16], 4-$CF_3C_6H_4BrF_2$ [14], and solutions of *trans*-$CF_3CF{=}CFBF_2$ [18], $CF_3C{\equiv}CBF_2$ [19], $C_3F_7C{\equiv}CBF_2$ [19], $C_6F_5BF_2$ [13], and $C_6F_{13}BF_2$ [13] in PFB or PFP were prepared as described.

All manipulations were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) or PFA (block copolymer of tetrafluoroethylene and perfluoroalkoxyethylene) equipment under an atmosphere of dry argon.

The solubility of 4-$CF_3C_6H_4BrF_2$ was determined to 0.27 mmol (71 mg) per mL of 1,1,2-$C_2Cl_3F_3$ and ≥0.44 mmol (≥116 mg) per mL of PFB (^{19}F NMR, 24 °C).

3.2. Preparation of $C_6F_{13}CH_2CH_2BF_2$ (19) in PFP

A 11.7-mm i.d. PFA trap was charged with $K[C_6F_{13}CH_2CH_2BF_3]$ (344 mg, 0.75 mmol), PFP (3 mL) and cooled to −25 °C. Boron trifluoride (5–7 mmol) was bubbled into the stirred suspension for 30 min. Excess of BF_3 was removed by flushing with dry argon (0 °C, 10 min). The suspension was centrifuged at 20 °C, the colorless mother liquor was decanted, the precipitate was washed with PFP (1 mL), and washing was combined with the mother liquor. The yield of $C_6F_{13}CH_2CH_2BF_2$ (0.63 mmol, 84%) was determined from the ^{19}F NMR spectrum using PFB as a quantitative integral reference.

$C_6F_{13}CH_2CH_2BF_2$ (**19**). ^{11}B NMR (PFP, 0 °C): δ 27.9 (s, $\Delta\nu_{1/2}$ = 218 Hz). ^{19}F NMR (PFP, 0 °C): δ −74.1 (s, $\Delta\nu_{1/2}$ = 183 Hz, 2F, BF_2), −80.3 (tt, $^3J(F^8, F^7)$ = 2 Hz, $^4J(F^8, F^6)$ = 10 Hz, 3F, F^8), −115.2 (m, 2F, F^3), −120.7 (m, 2F, F^5), −121.7 (m, 2F, F^6), −122.7 (m, 2F, F^4), −125.3 (m, 2F, F^7). (lit. [30] ^{1}H NMR (CH_2Cl_2, 24 °C): δ 1.5 (m, 2H, H^1), 0.5 (m, 2H, H^2). ^{11}B NMR (CH_2Cl_2, 24 °C): δ 27.5 (s, $\Delta\nu_{1/2}$ = 210 Hz). ^{19}F NMR (CH_2Cl_2, 24 °C): δ −73.8 (s, $\Delta\nu_{1/2}$ = 218 Hz, 2F, BF_2), −81.6 (tt, $^5J(F^8, F^5)$ = 3 Hz, $^4J(F^8, F^6)$ = 10 Hz, 3F, F^8), −116.6 (m, 2F, F^3), −122.5 (m, 2F, F^5), −123.5 (m, 2F, F^6), −124.2 (m, 2F, F^4), −126.8 (m, 2F, F^7)).

3.3. Preparation of $CF_3C{\equiv}CBF_2{\cdot}NCCH_3$ (22)

A cold (−15 °C) solution of CH_3CN (205 mg, 5.0 mmol) in CH_2Cl_2 (0.7 mL) was added with a syringe to a cold (−15 °C) solution of $CF_3C{\equiv}CBF_2$ (1.25 mmol) in PFB (6 mL). The solution was stirred at −15 °C for 10 min and evaporated to dryness in vacuum at 24 °C to give 132 mg (0.72 mmol, 57%) of $CF_3C{\equiv}CBF_2{\cdot}NCCH_3$.

$CF_3C{\equiv}CBF_2{\cdot}NCCH_3$ (**22**). ^{11}B NMR (CH_3CN, 24 °C): δ −3.6 (s, $\Delta\nu_{1/2}$ = 50 Hz, $BF_2{\cdot}NCCH_3$). ^{19}F NMR (CH_3CN, 24 °C): δ −50.2 (s, 3F, CF_3), −141.4 (s, $BF_2{\cdot}NCCH_3$).

3.4. Syntheses of asymmetrical bromonium salts with aryltrifluorosilanes

3.4.1. Preparation of the aryl(pentafluorophenyl)bromonium salts (8), (4b), and (7)

A cold (0 °C) solution of $ArSiF_3$ (1 mmol) in CH_3CN (2 mL) was added drop-wise to a cold (−10 °C) solution of $C_6F_5BrF_2$ (1 mmol) in CH_3CN (5 mL). The reaction solution was stirred at 0 °C for 15–20 h, all volatiles were removed in vacuum, and the residue was dissolved in water. In case of Ar = C_6H_5, the solution was treated with aqueous $H[BF_4]$, extracted with $CH_3NO_2/CHCl_3$ (3:1, v/v), and the solvent was evaporated. The residue was dissolved in a minimum volume of MeCN and poured into cold (0 °C) ether. The precipitated salt **8** was isolated in 31% yield. When Ar presented 4-$CF_3C_6H_4$ or 4-FC_6H_4, salts **4b** (67%) and **7** (57%) were precipitated by an analog procedure using aqueous $H[PF_6]$.

$[C_6H_5(C_6F_5)Br][BF_4]$ (**8**). ^{1}H NMR (CH_3CN): δ 8.13–7.65 (C_6H_5). ^{19}F NMR (CH_3CN): δ −130.2 (m, 2F, $F^{2,6}$), −140.8 (m, 1F, F^4), −154.8 (m, 2F, $F^{3,5}$), −149.4 (s, 4F, $[BF_4]^-$).

$[4\text{-}CF_3C_6H_4(C_6F_5)Br][PF_6]$ (**4b**). ^{1}H NMR (CH_3CN): δ 8.26 (m, 2H), 7.83 (m, 2H). ^{19}F NMR (CH_3CN): δ 62.3 (s, 3F, CF_3), −130.1 (m, 2F, $F^{2,6}$), −140.4 (m, 1F, F^4), −154.9 (m, 2F, $F^{3,5}$), −71.9 (d, ^1J(F, P) = 707 Hz, 6F, $[PF_6]^-$).

$[4\text{-}FC_6H_4(C_6F_5)Br][PF_6]$ (**7**). ^{1}H NMR (CH_3CN): δ 8.19 and 7.95, 7.56 and 7.26 (AA′BB′, 4H). ^{19}F NMR (CH_3CN): δ −101.8 (m, 1F, F^4), −130.7 (m, 2F, $F^{2,6}$), −140.9 (m, 1F, F^4), −155.0 (m, 2F, $F^{3,5}$), −71.4 (d, ^1J(F, P) = 706 Hz, 6F, $[PF_6]^-$).

3.4.2. Preparation of $[4\text{-}CF_3C_6H_4(C_6F_5)Br][PF_6]$ (4b)

A cold (0 °C) solution of $C_6F_5SiF_3$ (1 mmol) in CCl_3F (10 mL) was added drop-wise to a cold (−10 °C) solution of 4-$CF_3C_6H_4BrF_2$ (1 mmol) in CCl_3F (2 mL). The reaction solution was stirred at 0 °C for 15–20 h, all volatiles were removed in vacuum, and the residue was dissolved in water. Salt **4b** (63%) was precipitated by addition of aqueous $H[PF_6]$.

3.5. Syntheses of asymmetrical bromonium salts with organyldifluoroboranes

3.5.1. Preparation of $[4\text{-}CF_3C_6H_4(C_6F_5)Br][BF_4]$ (4c)

A 11.7-mm i.d. PFA trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of 4-$CF_3C_6H_4BrF_2$

(85 mg, 0.32 mmol) in 1,1,2-$C_2Cl_3F_3$ (0.5 mL) and PFB (1.4 mL) and cooled to −20 °C. Then a cold (−20 °C) solution of $C_6F_5BF_2$ (0.32 mmol) in PFB (0.4 mL) was added in portions. The colorless solution was stirred at −20 °C for 1 h and evaporated to dryness in vacuum at 20 °C. The residue was washed with CCl_3F (2 × 3 mL) at 15 °C and the solid was dried in vacuum at 20 °C to yield [4-$CF_3C_6H_4(C_6F_5)Br$][BF_4] (145 mg, 94%).

B. A solution of 4-$CF_3C_6H_4BrF_2$ (0.13 mmol) in CH_3CN (0.9 mL) was added in portions to a solution of $C_6F_5BF_2$ (0.13 mmol) in PFB (0.4 mL) and CH_3CN (1 mL). The solution was stirred at 24 °C for 10 min. The ^{19}F NMR spectrum showed the formation of [4-$CF_3C_6H_4(C_6F_5)Br$][BF_4] in nearly quantitative yield besides traces of 4-$CF_3C_6H_4Br$ and C_6F_5H.

[4-$CF_3C_6H_4(C_6F_5)Br$][BF_4] (**4c**). ^1H NMR (CH_3CN, 24 °C): δ 8.24 and 8.21, 7.98 and 7.96 (AA′BB′, 4H). ^{11}B NMR (CH_3CN, 24 °C): δ −1.6 (s, $\Delta\nu_{1/2}$ = 2 Hz, [BF_4]$^-$). ^{19}F NMR (CH_3CN, 24 °C): δ −62.9 (s, 3F, CF_3), −131.0 (m, 2F, $F^{2,6}$), −141.6 (tt, $^3J(F^4, F^{3,5})$ = 20 Hz, $^4J(F^4, F^{2,6})$ = 7 Hz, 1F, F^4), −156.1 (m, 2F, $F^{3,5}$), −149.9 (s, 4F, [BF_4]$^-$). ^1H NMR (PFB/1,1,2-$C_2Cl_3F_3$): δ 8.22 and 8.20, 7.88 and 7.84 (AA′BB′, 4H). ^{11}B NMR (PFB/1,1,2-$C_2Cl_3F_3$): δ −2.1 (s, $\Delta\nu_{1/2}$ = 5 Hz, [BF_4]$^-$). ^{19}F NMR (PFB/1,1,2-$C_2Cl_3F_3$): δ −63.0 (s, 3F, CF_3), −130.3 (m, 2F, $F^{2,6}$),−140.8 (tt, $^3J((F^4, F^{3,5})$ = 20 Hz, $^4J(F^4, F^{2,6})$ = 7 Hz, 1F, F^4), −156.7 (m, 2F, $F^{3,5}$), −145.3 (s, 4F, [BF_4]$^-$).

3.5.2. Preparation of [$C_6F_5(C_3F_7C{\equiv}C)Br$][$BF_4$] (11)

A 8-mm i.d. FEP trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of $C_6F_5BrF_2$ (57 mg, 0.20 mmol) in PFP (0.7 mL) and cooled to −40 °C. Then a cold (−40 °C) solution of $C_3F_7C{\equiv}CBF_2$ (0.22 mmol) in PFP (0.5 mL) was added in portions. After stirring at −40 °C for 2 h the colorless solution was evaporated to dryness in vacuum at 20 °C. The residue was washed with CCl_3F (1 mL) at 15 °C and the solid was dried in vacuum at 20 °C to yield [$C_6F_5(C_3F_7C{\equiv}C)Br$][$BF_4$] (50 mg, 56%).

[$C_6F_5(C_3F_7C{\equiv}C)Br$][$BF_4$] (**11**). ^{11}B NMR (aHF, 0 °C): δ −2.1 (s, [BF_4]$^-$). $^{13}C\{^{19}F\}$ NMR (aHF, 0 °C): δ 118.7 (C-5), 106.5 and 106.4 (C-3 and C-4), 81.3 (C-2), 50.6 (C-1) ($C_3F_7C{\equiv}C$ moiety), 146.0 and 145.7 (C^4 and $C^{2,6}$), 139.7 ($C^{3,5}$), 101.0 (C^1) (C_6F_5 moiety). ^{19}F NMR (aHF, 0 °C): δ −78.4 (t, ^4J(F-5, F-3) = 9 Hz, 3F, F-5), −101.3 (tq, ^3J(F-3, F-4) = 4 Hz, ^4J(F-3, F-5) = 9 Hz, 2F, F-3), −124.0 (t, ^3J(F-4, F-3) = 4 Hz, 2F, F-4) ($C_3F_7C{\equiv}C$ moiety), −127.1 (m, 2F, $F^{2,6}$), −132.5 (tt, $^3J(F^4, F^{3,5})$ = 19 Hz, $^4J(F^4, F^{2,6})$ = 10 Hz, 1F, F^4), −151.2 (m, 2F, $F^{3,5}$) (C_6F_5 moiety), −148.0 (s, 4F, [BF_4]$^-$). ^{19}F NMR (PFP, −40 °C): δ −79.0 (t, ^4J(F-5, F-3) = 9 Hz, 3F, F-5), −101.9 (tq, ^3J(F-3, F-4) = 4 Hz, ^4J(F-3, F-5) = 9 Hz, 2F, F-3), -124.8 (t, ^3J(F-4, F-3) = 4 Hz, 2F, F-4) ($C_3F_7C{\equiv}C$ moiety), −127.6 (m, 2F, $F^{2,6}$), −135.1 (tt, $^3J(F^4, F^{3,5})$ = 19 Hz, $^4J(F^4, F^{2,6})$ = 9 Hz, 1F, F^4), −152.6 (m, 2F, $F^{3,5}$) (C_6F_5 moiety), −134.5 (s, 4F, [BF_4]$^-$).

3.5.3. Preparation of [$C_6F_5(CF_3C{\equiv}C)Br$][BF_4] (23)

A 11.7-mm i.d. PFA trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of $CF_3C{\equiv}CBF_2{\cdot}NCCH_3{\cdot}NCCH_3$ (0.20 mmol) in CH_3CN (1.5 mL) and cooled to −10 °C. Then a cold (−10 °C) solution of $C_6F_5BrF_2$ (0.19 mmol) in PFP (2.5 mL) was added in portions. The yellow solution was stirred at −10 °C for 30 min and warmed to 24 °C. The ^{19}F NMR spectrum showed signals of [$C_6F_5(CF_3C{\equiv}C)Br$][BF_4] (δ −50.2 (s, 3F, CF_3), −129.9 (m, 2F, $F^{2,6}$),−141.1 (tt, $^3J(F^4, F^{3,5})$ = 20 Hz, $^4J(F^4, F^{2,6})$ = 7 Hz, 1F, F^4), −156.4 (m, 2F, $F^{3,5}$) (C_6F_5 moiety), −144.5 (s, 4F, [BF_4]$^-$), $CF_3C{\equiv}CBF_2{\cdot}NCCH_3$, and C_6F_5Br in the ratio 1:3:4.

3.5.4. Preparation of [C_6F_5(*trans*-$CF_3CF{=}CF)Br$][*trans*-$CF_3CF{=}CFBF_3$] (14)

An 8-mm i.d. FEP trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of $C_6F_5BrF_2$ (45 mg, 0.15 mmol) in PFP (0.5 mL) and cooled to −40 °C. Then a cold (−45 °C) solution of *trans*-$CF_3CF{=}CFBF_2$ (0.15 mmol) in PFP (0.8 mL) was added in portions. After 10–15 min a white suspension was formed. It was stirred at −40 °C for 2 h. The ^{19}F NMR spectrum (−10 °C) of the colorless mother liquor showed signals of [*trans*-$CF_3CF{=}CFBF_3$]$^-$, C_6F_5Br, *cyclo*-1-Br-1,4-C_6F_7, *cyclo*-1-BrC_6F_9, and [C_6F_5(*trans*-$CF_3CF{=}CF)Br$]$^+$ (resonances at −67.2 (dd, $^3J(F^3, F^2)$ = 10 Hz, $^4J(F^3, F^1)$ = 19 Hz, 3F, F^3), −109.7 (qd, $^4J(F^1, F^3)$ = 19 Hz, $^3J(F^1, F^2)$ = 131 Hz, 1F, F^1), −136.8 (d, $^3J(F^2, F^1)$ = 131 Hz, 1F, F^2), −127.1 (m, 2F, $F^{2,6}$), −134.6 (tt, $^3J(F^4, F^{3,5})$ = 19 Hz, $^4J(F^4, F^{2,6})$ = 10 Hz, 1F, F^4), and −152.5 (m, 2F, $F^{3,5}$) ppm). All volatiles were removed in vacuum at −10 °C to yield the white salt [C_6F_5(*trans*-$CF_3CF{=}CF)Br$][*trans*-$CF_3CF{=}CFBF_3$] (57 mg).

[C_6F_5(*trans*-$CF_3CF{=}CF)Br$][*trans*-$CF_3CF{=}CFBF_3$] (**14**). ^{11}B NMR (CH_3CN, 24 °C): δ −0.5 (dq, ^2J(B, F^1) = 26 Hz, ^1J(B, F) = 40 Hz, [*trans*-$CF_3CF{=}CFBF_3$]$^-$). ^{19}F NMR (CH_3CN, −10 °C): δ −68.0 (dd, $^3J(F^3, F^2)$ = 11 Hz, $^4J(F^3, F^1)$ = 19 Hz, 3F, F^3), −109.4 (qdt, $^4J(F^1, F^3)$ = 19 Hz, $^3J(F^1, F^2)$ = 130 Hz, $^5J(F^1, F^{2,6})$ = 4 Hz, 1F, F^1), −140.9 (tqd, $^6J(F^2, F^{2,6})$ = 7 Hz, $^3J(F^2, F^3)$ = 11 Hz, $^3J(F^2, F^1)$ = 130 Hz, 1F, F^2), −128.8 (m, 2F, $F^{2,6}$), −137.9 (tt, $^3J(F^4, F^{3,5})$ = 21 Hz, $^4J(F^4, F^{2,6})$ = 8 Hz, 1F, F^4), −154.3 (m, 2F, $F^{3,5}$) [*trans*-$CF_3CF{=}CF(C_6F_5)Br$]$^+$; −66.9 (qdd, $^5J(F^3, BF_3)$ = 1 Hz, $^3J(F^3, F^2)$ = 11 Hz, $^4J(F^3, F^1)$ = 23 Hz, 3F, F^3), −156.0 (d, $^3J(F^1, F^2)$ = 130 Hz, 1F, F^1), −179.9 (d, $^3J(F^2, F^1)$ = 130 Hz, 1F, F^2), −143.4 (dq, $^4J(BF_3, F^2)$ = 8 Hz, ^1J(F, B) = 40 Hz, 3F, BF_3^-) ([*trans*-$CF_3CF{=}CFBF_3$]$^-$).

3.5.5. Reaction of $C_6F_5BrF_2$ with $C_6F_{13}BF_2$

A solution of $C_6F_5BrF_2$ (60 mg, 0.21 mmol) in PFP (1.5 mL) was cooled to −65 °C and a cold (−65 °C) solution of $C_6F_{13}BF_2$ (0.45 mmol) in PFP (2 mL) was added in portions. The solution was stirred at −60 °C for 1 h. The initially formed yellow suspension became quickly (in 10–15 s) dark colored and after 20–30 min a colorless solution was formed. The ^{19}F NMR spectrum (−60 °C) showed resonances of $C_6F_{13}BF_2$, C_6F_{14}, C_6F_5Br, and *cyclo*-1-Br-1,4-C_6F_7 (45:20:23:12) besides PFP.

3.5.6. Reaction of $C_6F_5BrF_2$ with $C_6F_{13}CH_2CH_2BF_2$

A solution of $C_6F_5BrF_2$ (0.31 mmol) in PFP (1.9 mL) was cooled to −63 °C and a cold (−62 °C) solution of $C_6F_{13}CH_2CH_2BF_2$ (0.31 mmol) in PFP (1.5 mL) was added in portions within 3 min. The initially formed yellow suspension became quickly (in 20–30 s) dark colored and after 20–30 min a colorless solution was formed. The reaction mixture was stirred at −60 °C for 1 h. The ^{19}F NMR spectrum (−60 °C) showed resonances of $C_6F_{13}CH_2CH_2BF_2$, $C_6F_{13}CH_2CH_2F$, C_6F_5Br, *cyclo*-1-Br-1,4-C_6F_7, *cyclo*-1-BrC_6F_9 and BF_3 (36:11:33:6:4:10) besides PFP. The ^{11}B NMR spectrum (−60 °C) contained signals of $C_6F_{13}CH_2CH_2BF_2$ (28.8 ppm) and BF_3 (9.7 ppm) (1:1).

3.6. Reactions of [$R_F(R_F')Br$][BF_4]

3.6.1. Reaction of [$C_6F_5(C_3F_7C{\equiv}C)Br$][$BF_4$] (11) with aHF

A solution of salt **11** (50 mg) in aHF (0.6 mL) was kept at 22 °C in a FEP inliner. After 12 h, the conversion of **11** was 38% and after 72 h the signals of **11** had disappeared (^{19}F NMR) and new resonances of C_6F_5Br, $C_3F_7C(O)CH_2F$, [*Z*-$C_3F_7CF{=}CH(C_6F_5)Br$]$^+$, and [BF_4]$^-$(1:1:2:4) were now present. The solution was extracted with cold (−20 °C) CCl_3F (0.5 mL). The extract contained C_6F_5Br and $C_3F_7C(O)CH_2F$ whereas the salt [C_6F_5(*Z*-$C_3F_7CF{=}CH)Br$][BF_4] remained in the acid phase.

[C_6F_5(*Z*-$C_3F_7CF{=}CH)Br$][BF_4] (**25**). ^1H NMR (aHF, 24 °C): δ 7.94 (d, $^3J(H^1, F^2)$ = 21 Hz, 1H, H^1). ^{19}F NMR (aHF, 24 °C): δ −80.3 (t, $^4J(F^5, F^3)$ = 9 Hz, 3F, F^5), −91.1 (m, 1F, F^2), −117.6 (dq, $^3J(F^3, F^2)$ = 13 Hz, $^4J(F^3, F^5)$ = 9 Hz, 2F, F^3), −125.8 (m, 2F, F^4) (*Z*-$C_3F_7CF{=}CH$ moiety), −129.1 (m, 2F, $F^{2,6}$), −136.3 (tt, $^3J(F^4, F^{3,5})$ = 20 Hz, $^4J(F^4, F^{2,6})$ = 9 Hz, 1F, F^4), −153.8 (m, 2F, $F^{3,5}$) (C_6F_5 moiety), −151.0 (s, 4F, [BF_4]$^-$).

1H,1H-octafluoropentan-2-one (**26**). ^{1}H NMR (CCl_3F, 0 °C): δ 5.30 (d, $^{2}J(H^1, F^1)$ = 46 Hz, 2H, H^1). ^{19}F NMR (CCl_3F, 0 °C): δ −81.2 (t, $^{4}J(F^5, F^3)$ = 9 Hz, 3F, F^5), −122.9 (q, $^{4}J(F^3, F^5)$ = 9 Hz, 2F, F^3), −127.8 (m, 2F, F^4), −237.2 (t, $^{2}J(F^1, H^1)$ = 46 Hz, 1F, F^1). (cf. $C_4F_9C(O)CH_2F$, lit [32], ^{1}H ($CDCl_3$): δ = 5.25 (d $^{2}J(H^1, F^1)$ = 45.8 Hz, 2H, H^1). ^{19}F ($CDCl_3$): δ −81.0 (3F, F^6), −121.3 (2F, F^3), −123.1 (2F, F^4), −125.7 (2F, F^5), −237.0 (t $^{2}J(F^1, H^1)$ = 45.8 Hz, 1F, F^1)).

3.6.2. Reaction of [(CF$_3$C≡C)$_2$Br][BF$_4$] (27) with aHF

When a solution of **27** in aHF was kept at 0 °C for 24 h a mixture of $[(CF_3C{\equiv}C)_2Br][BF_4]$ and [*Z*-$CF_3CF{=}CH(CF_3C{\equiv}C)Br][BF_4]$ (**28**) (1:5) was formed. The conversion of **27**–**28** was completed at 25 °C within 24 h. Further maintaining at 25 °C led to the formation of $[(Z\text{-}CF_3CF{=}CH)_2Br][BF_4]$ (**29**) (molar ratio **28**:**29** was 94:6 after 2 d and 64:36 after 9 d) besides minor unknown products.

[*Z*-$CF_3CF{=}CH(CF_3C{\equiv}C)Br][BF_4]$ (**28**). ^{1}H NMR (aHF, 0 °C): δ 7.88 (d, $^{3}J(H^1, F^2)$ = 20 Hz, 1H, H^1). ^{11}B NMR (aHF, 0 °C): δ −1.1 (s, $[BF_4]^-$). $^{13}C\{^{1}H\}$ NMR (aHF, 0 °C): δ 111.7 (q, ^{1}J(C-3, F-3) = 263 Hz, C-3), 81.1 (q, ^{2}J(C-2, F-3) = 60 Hz, C-2), 43.6 (q, ^{3}J(C-1, F-3) = 8 Hz, C-1), 155.8 (d, $^{1}J(C^2, F^2)$ = 296 Hz, q, $^{2}J(C^2, F^3)$ = 45 Hz, C^2), 115.0 (d, $^{2}J(C^3, F^2)$ = 36 Hz, q, $^{1}J(C^3, F^3)$ = 278 Hz, C^3), 106.8 (d, $^{2}J(C^1, F^2)$ = 15 Hz, q, $^{3}J(C^1, F^3)$ = 5 Hz, C^1). ^{19}F NMR (aHF, 0 °C): δ −52.4 (s, 3F, F-3), −70.1 (d, $^{3}J(F^3, F^2)$ = 9 Hz, 3F, F^3), −93.2 (qd, $^{3}J(F^2, F^3)$ = 9 Hz, $^{3}J(F^2, H^1)$ = 20 Hz, 1F, F^2), −149.0 (s, 4F, $[BF_4]^-$).

[(*Z*-$CF_3CF{=}CH)_2Br][BF_4]$ (**29**). ^{1}H NMR (aHF, 0 °C): δ 7.44 (d, $^{3}J(H^1, F^2)$ = 20 Hz, 1H, H^1). ^{11}B NMR (aHF, 0 °C): δ −1.1 (s, $[BF_4]^-$). ^{19}F NMR (aHF, 0 °C): δ −70.5 (d, $^{3}J(F^3, F^2)$ = 9 Hz, 6F, F^3), −96.0 (qd, $^{3}J(F^2, F^3)$ = 10 Hz, $^{3}J(F^2, H^1)$ = 22 Hz, 2F, F^2), −149.0 (s, 4F, $[BF_4]^-$).

*3.6.3. Reaction of [4-CF$_3$C$_6$H$_4$(C$_6$F$_5$)Br][BF$_4$] (**4c**) with [Bu$_4$N]I in MeCN*

A cold (−10 °C) solution of $[4\text{-}CF_3C_6H_4(C_6F_5)Br][BF_4]$ (0.06 mmol) in MeCN (1.2 mL) was poured into a cold (−15 °C) solution of $[Bu_4N]I$ (229 mg, 0.62 mmol) in MeCN (0.8 mL). The brownish solution was stirred at −15 °C for 10 min and warmed to 24 °C. The ^{19}F NMR spectrum contained signals of 4-$CF_3C_6H_4Br$, C_6F_5I, C_6F_5H, and $[BF_4]^-$ in the molar ratio of 34:29:3:34.

4. Conclusions

The successful substitution of one fluorine atom in bromanes $ArBrF_2$ by organyl groups R′ (aryl, alkynyl, alkenyl, and alkyl groups) depends on the type of R′ reagents, $R'SiF_3$ or $R'BF_2$, their acidity, on the nucleophilicity of R′, on the type of solvent (weakly coordinating (wcs) or coordinating), on the oxidation strength of the polarized bromine derivative $[Ar(F)Br]^+$, and on the reducing strength of the reagent after interaction with the fluoride donor site of the bromane. Perfluorinated alkynyl, alkenyl, and aryl groups could be successfully used in F/R′ substitution reactions with $ArBrF_2$ in weakly coordinating solvents. Furthermore, it was shown, that MeCN weakens the oxidation strength of $[C_6F_5(F)Br]^+$ in reactions of $C_6F_5BrF_2$ with $ArSiF_3$ (Ar = C_6H_5, 4-FC_6H_4, 4-$CF_3C_6H_4$). Per- and polyfluorinated alkylboranes $R'BF_2$ did not allow the isolation of perfluoroaryl(polyfluoroalkyl)bromonium salts. Instead, C_6F_5Br and R′F were found as products of consecutive reactions. Bromonium cations showed two prototypical reactivities with a nucleophile and an electrophile at different centers (a) with the strongly reducing iodide ion reaction at Br^{III} and (b) with the super acid HF addition at the C≡C bond of the R_F' group.

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References

[1] G.A. Olah, Halonium Ions, Wiley, New York, 1975.
[2] G.A. Olah, K.K. Laali, Q. Wang, Onium Ions, Wiley, New York, 1998, pp. 246–268.
[3] A.N. Nesmeyanov, T.P. Tolstaya, L.S. Isaeva, Dokl. Akad. Nauk SSSR 104 (1955) 872–875, {Chem. Abstr 50 (1956) 11266}.
[4] A.N. Nesmeyanov, T.P. Tolstaya, L.S. Isaeva, Dokl. Akad. Nauk SSSR 117 (1957) 996–999, {Chem. Abstr 52 (1958) 8069)}.
[5] (a) A.N. Nesmeyanov, N.V. Kruglova, R.B. Maternikova, Zh. Obshch. Khim. 26 (1956) 2211–2218, {Chem. Abstr. 51 (1957) 4974};
(b) A.N. Nesmeyanov, N.V. Kruglova, R.B. Maternikova, J. Gen. Chem. U.S.S.R. 26 (1956) 2473–2478 (Engl. transl.).
[6] V.V. Grushin, I.I. Demkina, T.P. Tolstaya, M.V. Galakhov, V.I. Bakhmutov, Metallorg. Khim. 2 (1989) 727–736, {Chem. Abstr. 112 (1990) 198446}.
[7] G.A. Olah, T. Sakakibara, G. Asensio, J. Org. Chem. 43 (1978) 463–468.
[8] G.A. Olah, Y.K. Mo, E.G. Melby, H.C. Lin, J. Org. Chem. 38 (1973) 367–372.
[9] A.N. Nesmeyanov, I.N. Lisichkina, A.S. Kulikov, A.N. Vanchikov, T.P. Tolstaya, V.A. Chertkov, Dokl. Akad. Nauk SSSR 243 (1978) 1463–1467, {Chem. Abstr. 90 (1979) 151710}.
[10] A.N. Nesmeyanov, A.N. Vanchikov, I.N. Lisichkina, N.S. Khrushcheva, T.P. Tolstaya, Dokl. Akad. Nauk SSSR 254 (1980) 652–656, {Chem. Abstr. 94 (1981) 174489}.
[11] A.N. Nesmeyanov, A.N. Vanchikov, I.N. Lisichkina, V.V. Grushin, T.P. Tolstaya, Dokl. Akad. Nauk SSSR 255 (1980) 1386–1389, {Chem. Abstr. 95 (1981) 6664}.
[12] A.N. Nesmeyanov, A.N. Vanchikov, I.N. Lisichkina, V.V. Lazarev, T.P. Tolstaya, Dokl. Akad. Nauk SSSR 255 (1980) 1136–1140, {Chem. Abstr. 95 (1981) 24402}.
[13] H.-J. Frohn, V.V. Bardin, J. Fluorine Chem 131 (2010) 922–932.
[14] H.-J. Frohn, M. Giesen, J. Fluorine Chem. 89 (1998) 59–63.
[15] M. Ochiai, Y. Nishi, S. Goto, M. Shiro, H.-J. Frohn, J. Am. Chem. Soc. 125 (2003) 15304–15305.
[16] H.-J. Frohn, M. Giesen, J. Fluorine Chem. 24 (1984) 9–15.
[17] A. Abo-Amer, H.-J. Frohn, Chr. Steinberg, U. Westphal, J. Fluorine Chem. 127 (2006) 1311–1323.
[18] H.-J. Frohn, N.Yu. Adonin, V.V. Bardin, Z. Anorg. Allg. Chem. 629 (2003) 2499–2508.
[19] V.V. Bardin, N.Yu. Adonin, H.-J. Frohn, J. Fluorine Chem. 128 (2007) 699–702.
[20] V.V. Bardin, H.-J. Frohn, Main Group Met. Chem. 25 (2002) 589–613.
[21] H.-J. Frohn, V.V. Bardin, Z. Anorg. Allg. Chem. 629 (2003) 2465–2469.
[22] H.-J. Frohn, F. Bailly, V.V. Bardin, Mendeleev Commun. 19 (2009) 67–68.
[23] H.-J. Frohn, F. Bailly, D. Weiting, V.V. Bardin, J. Fluorine Chem. 130 (2009) 301–307.
[24] H.-J. Frohn, M. Giesen, D. Welting, G. Henkel, Eur. J. Solid State Inorg. Chem. 33 (1996) 841–853.
[25] H.-J. Frohn, M. Hirschberg, A. Wenda, V.V. Bardin, J. Fluorine Chem. 129 (2008) 459–473.
[26] V.A. Petrov, S. Swearingen, W. Hong, W.C. Petersen, J. Fluorine Chem. 109 (2001) 25–31.
[27] V.V. Bardin, J. Fluorine Chem. 89 (1998) 195–211.
[28] H.-J. Frohn, M.E. Hirschberg, R. Boese, D. Bläser, U. Flörke, Z. Anorg. Allg. Chem. 634 (2008) 2539–2550.
[29] V. Bazant, V. Chvalowsky, J. Rathousky, Organosilicon Compounds, vol. 2, no. 1, Publ. House of the Czechoslovak Acad. Sciences, Prague, 1965.
[30] A. Abo-Amer, N.Yu. Adonin, V.V. Bardin, P. Fritzen, H.-J. Frohn, Ch. Steinberg, J. Fluorine Chem. 125 (2004) 1771–1778.
[31] H.-J. Frohn, M. Giesen, A. Klose, A. Lewin, V.V. Bardin, J. Organomet. Chem. 506 (1996) 155–164.
[32] M.M. Chaabouni, A. Baklouti, J. Fluorine Chem. 47 (1990) 227–233.