



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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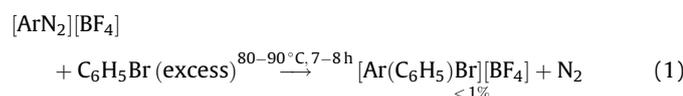
ABSTRACT

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 $R_F'BF_2 \cdot NMe$ ($R_F' = C_6F_5, C_3F_7C\equiv C$) 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^+ . $[4-CF_3C_6H_4(C_6F_5)Br][BF_4]$ 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 $[Z-C_nF_{2n+1}CF=CH(R_F)Br][BF_4]$.

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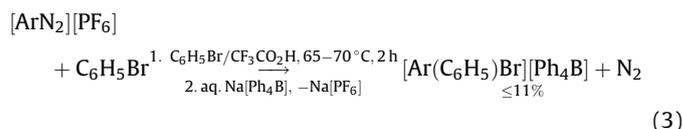
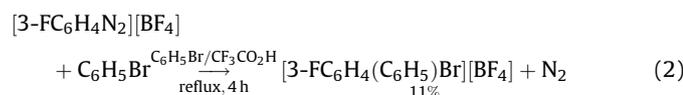
1. Introduction

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].



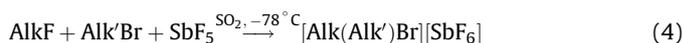
$Ar = 2-CH_3C_6H_4, 4-CH_3C_6H_4, 2,4-(CH_3)_2C_6H_3, 2\text{-naphthyl}, 4-ClC_6H_4, 4-C_2H_5OC(O)C_6H_4.$

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



$Ar = 2-CH_3C_6H_4, 4-CH_3C_6H_4$

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].



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



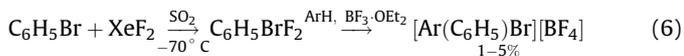
$Alk = CH_3, C_2H_5$

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].

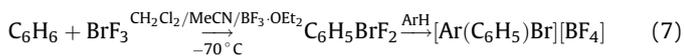
A more efficient route to asymmetrical bromonium salts is fluorine/organyl substitution in $RBrF_2$. The in situ formation of

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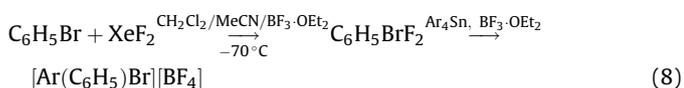
C₆H₅BrF₂ was proposed in reactions of C₆H₅Br with XeF₂ (Eqs. (6) and (8)), of C₆H₆ with BrF₃ (Eq. (7)), and of (C₆H₅)₂Hg with BrF₃ (Eq. (9)). Subsequently, the second aryl group was introduced by arenes [9,10], tetraarylstannanes [11], or diarylmercury [12] as arylating agents.



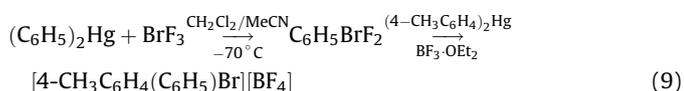
Ar = 4-FC₆H₄, 4-ClC₆H₄, 4-CH₃C₆H₄, 2-CH₃OC(O)C₆H₄



Ar = 4-FC₆H₄ (49%), 4-ClC₆H₄ (20–29%), 4-CH₃C₆H₄ (39%), 4-CH₃OC(O)C₆H₄ (27%)

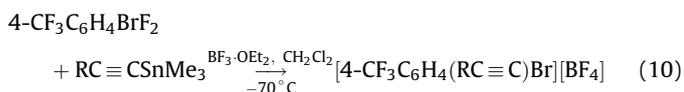


Ar = 4-CH₃C₆H₄ (55%), 4-CH₃OC₆H₄ (32%)



In a preceding paper [13] we have reported new routes to [(C₆F₅)₂Br][BF₄] 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 BrF₃ or [BrF₂]⁺ salts by two R_F groups under acidic conditions, e.g., by the reaction of perfluoroorganyldifluoroboranes, R_FBF₂, 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_FBF₃] with either BrF₃ or [BrF₂][SbF₆] in anhydrous HF (aHF). Despite of variations of temperature and stoichiometry of the reactants R_FBF₂ and BrF₃, we did not detect the intermediate R_FBrF₂ by ¹⁹F NMR spectroscopy and concluded that the F/R_F substitution in the intermediate bromane R_FBrF₂ proceeded faster than the formation of R_FBrF₂ from R_FBF₂ and BrF₃. The salt [(C₆F₅)₂Br][BF₄] was formed even from a reaction of C₆F₅BF₂ and BrF₃ 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 BrF₃ by a pentafluorophenyl group accelerates the subsequent F/C₆F₅ substitution step under formation of [(C₆F₅)₂Br]⁺ salts.

Concerning non-perfluorinated aryl difluorobromanes, only 3- and 4-CF₃C₆H₄BrF₂ are described in the literature. They were prepared in good to excellent isolated yields [14]. 4-CF₃C₆H₄BrF₂ 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-CF₃C₆H₄BrF₂ with C₈H₁₇C≡CSiMe₃ gave only a trace of the desired bromonium salt [15].



R = C₄H₉, (CH₃)₂CHCH₂, C₈H₁₇, cyclo-C₆H₁₁, (CH₃)₃C, (CH₃)₃Si (76–89%)

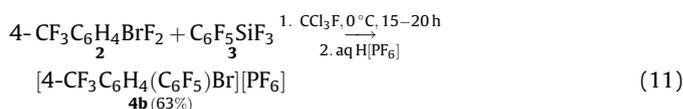
In the present paper we report the preparation of a representative series of asymmetrical bromonium salts [R_F(R'_F)Br]Y, where R'_F and R_F can represent a perfluoroorganyl group, by reaction of pentafluorophenyldifluorobromane (**1**) [16] and 4-trifluoromethylphenyldifluorobromane (**2**) [14] with two types of the organyl transfer

reagents of distinct Lewis acidity: aryltrifluorosilanes (Y = [SiF₅][−]) and per- or polyfluoroorganyldifluoroboranes (Y = [BF₄][−] or [R_FBF₃][−]).

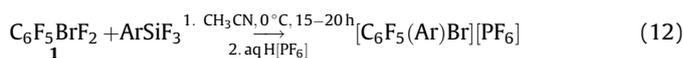
2. Results and discussion

2.1. Syntheses of asymmetrical bromonium salts using aryltrifluorosilanes

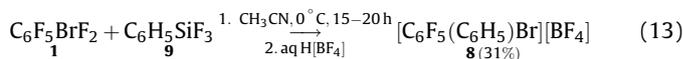
We have found that pentafluorophenyltrifluorosilane (**3**) easily reacted with bromane **2** in the weakly coordinating solvent CCl₃F to give 4-trifluoromethylphenyl(pentafluorophenyl)bromonium pentafluorosilicate (**4a**), which was converted into the thermally more stable hexafluorophosphate (**4b**) by metathesis with H[PF₆] in aqueous solution (Eq. (11)).



The attempt to prepare salt **4a** by the alternative route from bromane **1** and 4-trifluoromethylphenyltrifluorosilane (**5**) in CCl₃F, 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 CCl₃F. 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.



Ar = 4-CF₃C₆H₄ (**4b**) (67%), 4-FC₆H₄ (**7**) (57%)



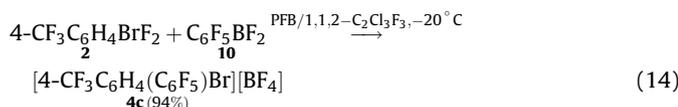
The differing results presented afore in reactions of 4-CF₃C₆H₄BrF₂ with C₆F₅SiF₃ compared to C₆F₅BrF₂ with 4-CF₃C₆H₄SiF₃ in weakly coordinating and coordinating solvents can be rationalized on basis of a stronger Br–F bond in C₆F₅BrF₂ than in 4-CF₃C₆H₄BrF₂ due to a higher bond polarity caused by the stronger electron-withdrawing C₆F₅ group and on a higher oxidizing property of [C₆F₅BrF₂]⁺ (simplified description of the polarized species) relative to [4-CF₃C₆H₄BrF₂]⁺. MeCN can moderate the oxidizing property of [C₆F₅BrF₂]⁺ by coordination.

2.2. Syntheses of asymmetrical bromonium salts using organyldifluoroboranes

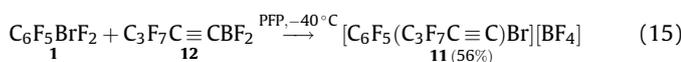
Perfluorinated organyldifluoroboranes are more acidic [17] and, in general, more easy to prepare [18–21] than the corresponding organyltrifluorosilanes. This situation allowed to study the preparation of asymmetrical bis(organyl)bromonium salts starting from arylidifluoroboranes. By this route we obtained 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)),

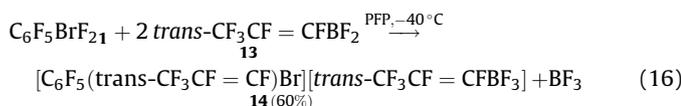
whereas the formation of [4-CF₃C₆H₄(C₆F₅)Br][SiF₅] (**4a**) using silane **3** took 15–20 h at 0 °C (Eq. (11))



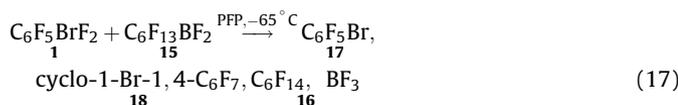
Perfluorinated pent-1-yn-1-yl(phenyl)bromonium tetrafluoroborate (**11**) was obtained by addition of heptafluoropent-1-yn-1-yldifluoroborane (**12**) to a cold solution of bromane **1** in PFP and was isolated as a white solid after removal of all volatiles in vacuum (Eq. (15))



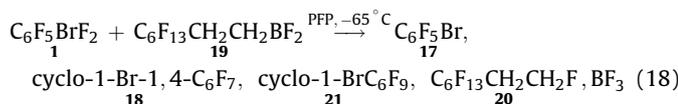
Under similar conditions, *trans*-pentafluoroprop-1-en-1-yldifluoroborane (**13**) reacted with bromane **1** to yield perfluorinated *trans*-prop-1-en-1-yl(phenyl)bromonium *trans*-pentafluoropropenyltrifluoroborate (**14**) (Eq. (16)). The configuration of the alkenyl moiety bonded to the bromine atom retended whereas in case of the previously reported formation of [(CF₃CF=CF)₂Br][CF₃CF=CFBF₃] from borane **13** and BrF₃ 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 BF₃ (F⁻-affinities 89.0 and 78.8 kcal/mol, respectively [17]) as discussed in Ref. [13].



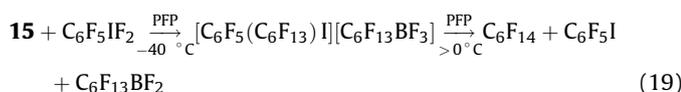
In contrast to the successful syntheses of salts **4c**, **11**, and **14**, the attempted preparation of the perfluorinated hex-1-yl(phenyl)bromonium salt failed. When a solution of perfluorohexyldifluoroborane (**15**) (2 equiv.) in PFP was added to a solution of C₆F₅BrF₂ in PFP at -65 °C, a mixture of perfluorohexane (**16**), bromopentafluorobenzene (**17**), 1-bromoheptafluorocyclohexa-1,4-diene (**18**), and non-consumed borane **15** was formed (Eq. (17))



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)).



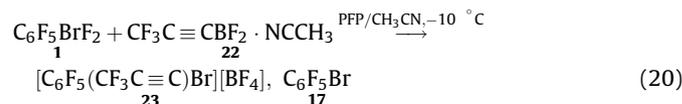
It should be noted that during the addition of the alkylboranes **15** and **19** to a solution of C₆F₅BrF₂, for a short time (10–20 s) a suspension was observed whose solid decomposed within 20–30 min to yield a colorless solution. Likely, this precipitate may be salt [Alk_F(C₆F₅)Br][XBF₃] (Alk_F = C₆F₁₃CH₂CH₂, X = F; Alk_F = C₆F₁₃, X = C₆F₁₃). Such salts are closely related to the iodonium salt [C₆F₁₃(C₆F₅)I][C₆F₁₃BF₃]. The latter was prepared from C₆F₁₃BF₂ and C₆F₅I₂ in PFP and decomposed above 0 °C (Eq. (19)) [22].



The formation of the minor products **18** and **21** in Eq. (18) can be assigned to a parallel reaction channel, the acid-assisted decom-

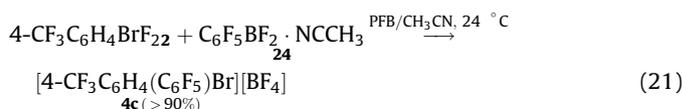
position of C₆F₅BrF₂ to C₆F₅Br and unsaturated cyclic bromo-containing compounds described in Ref. [23].

Furthermore, we investigated the influence of base Lewis acid adducts in case of organyldifluoroboranes-NCCH₃ on fluorine/organyl substitutions in ArBrF₂. The base adducts R_pBF₂·NCCH₃ are less acidic than the underlying boranes itself. We have found that bromane **1** reacted with the adduct CF₃C≡CBF₂·NCCH₃ (**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 C₆F₅Br (molar ratio **23**:**17** = 1:4) (Eq. (20))



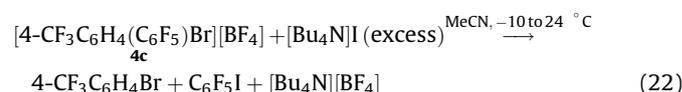
The formation of **17** was also observed in the synthesis of [(C₆F₅)₂Br][BF₄] from BrF₃ and (C₆F₅)_nBF_{3-n}·NCCH₃ (n = 1–3) [13,24]. Its amount was minimized when the reaction was performed at -70 °C, but it increased at higher temperatures (-20 to 25 °C). This phenomenon can be explained by fluoride abstraction from **1** under the action of a sufficient Lewis acid and following base coordination yielding [C₆F₅BrF·NCCH₃]Y which subsequently decomposed [24]

Contrary, the reaction of bromane **2** with adduct C₆F₅BF₂·NCCH₃ (**24**) gave salt **4c** in a high yield (Eq. (21)).

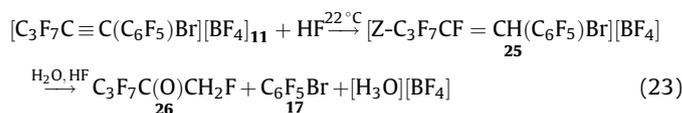


2.3. Prototypical reactivities of [R(R_F)Br][BF₄]

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 [(C₆F₅)₂Br]Y [24]. We present here some prototypical examples of their reactivity. When a solution of salt **4c** in MeCN was treated with [Bu₄N]I in MeCN, 4-bromobenzotrifluoride and iodopentafluorobenzene were formed in a 1:1 molar ratio besides [BF₄]⁻ and pentafluorobenzene (trace) (Eq. (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-octafluoropent-2-one (**26**) (Eq. (23)). Likely, that the formation of the latter product was caused by permeation of H₂O vapor passing through the 0.35 mm FEP wall during the long-term reaction.



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-

(85 mg, 0.32 mmol) in 1,1,2-C₂Cl₃F₃ (0.5 mL) and PFB (1.4 mL) and cooled to –20 °C. Then a cold (–20 °C) solution of C₆F₅BF₂ (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 CCl₃F (2 × 3 mL) at 15 °C and the solid was dried in vacuum at 20 °C to yield [4-CF₃C₆H₄(C₆F₅)Br][BF₄] (145 mg, 94%).

B. A solution of 4-CF₃C₆H₄BrF₂ (0.13 mmol) in CH₃CN (0.9 mL) was added in portions to a solution of C₆F₅BF₂ (0.13 mmol) in PFB (0.4 mL) and CH₃CN (1 mL). The solution was stirred at 24 °C for 10 min. The ¹⁹F NMR spectrum showed the formation of [4-CF₃C₆H₄(C₆F₅)Br][BF₄] in nearly quantitative yield besides traces of 4-CF₃C₆H₄Br and C₆F₅H.

[4-CF₃C₆H₄(C₆F₅)Br][BF₄] (**4c**). ¹H NMR (CH₃CN, 24 °C): δ 8.24 and 8.21, 7.98 and 7.96 (AA'BB', 4H). ¹¹B NMR (CH₃CN, 24 °C): δ –1.6 (s, Δν_{1/2} = 2 Hz, [BF₄][–]). ¹⁹F NMR (CH₃CN, 24 °C): δ –62.9 (s, 3F, CF₃), –131.0 (m, 2F, F^{2,6}), –141.6 (tt, ³J(F⁴, F^{3,5}) = 20 Hz, ⁴J(F⁴, F^{2,6}) = 7 Hz, 1F, F⁴), –156.1 (m, 2F, F^{3,5}), –149.9 (s, 4F, [BF₄][–]). ¹H NMR (PFB/1,1,2-C₂Cl₃F₃): δ 8.22 and 8.20, 7.88 and 7.84 (AA'BB', 4H). ¹¹B NMR (PFB/1,1,2-C₂Cl₃F₃): δ –2.1 (s, Δν_{1/2} = 5 Hz, [BF₄][–]). ¹⁹F NMR (PFB/1,1,2-C₂Cl₃F₃): δ –63.0 (s, 3F, CF₃), –130.3 (m, 2F, F^{2,6}), –140.8 (tt, ³J(F⁴, F^{3,5}) = 20 Hz, ⁴J(F⁴, F^{2,6}) = 7 Hz, 1F, F⁴), –156.7 (m, 2F, F^{3,5}), –145.3 (s, 4F, [BF₄][–]).

3.5.2. Preparation of [C₆F₅(C₃F₇C≡C)Br][BF₄] (**11**)

A 8-mm i.d. FEP trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of C₆F₅BrF₂ (57 mg, 0.20 mmol) in PFP (0.7 mL) and cooled to –40 °C. Then a cold (–40 °C) solution of C₃F₇C≡CBF₂ (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 CCl₃F (1 mL) at 15 °C and the solid was dried in vacuum at 20 °C to yield [C₆F₅(C₃F₇C≡C)Br][BF₄] (50 mg, 56%).

[C₆F₅(C₃F₇C≡C)Br][BF₄] (**11**). ¹¹B NMR (aHF, 0 °C): δ –2.1 (s, [BF₄][–]). ¹³C{¹⁹F} 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) (C₃F₇C≡C moiety), 146.0 and 145.7 (C⁴ and C^{2,6}), 139.7 (C^{3,5}), 101.0 (C¹) (C₆F₅ moiety). ¹⁹F 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) (C₃F₇C≡C moiety), –127.1 (m, 2F, F^{2,6}), –132.5 (tt, ³J(F⁴, F^{3,5}) = 19 Hz, ⁴J(F⁴, F^{2,6}) = 10 Hz, 1F, F⁴), –151.2 (m, 2F, F^{3,5}) (C₆F₅ moiety), –148.0 (s, 4F, [BF₄][–]). ¹⁹F 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) (C₃F₇C≡C moiety), –127.6 (m, 2F, F^{2,6}), –135.1 (tt, ³J(F⁴, F^{3,5}) = 19 Hz, ⁴J(F⁴, F^{2,6}) = 9 Hz, 1F, F⁴), –152.6 (m, 2F, F^{3,5}) (C₆F₅ moiety), –134.5 (s, 4F, [BF₄][–]).

3.5.3. Preparation of [C₆F₅(CF₃C≡C)Br][BF₄] (**23**)

A 11.7-mm i.d. PFA trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of CF₃C≡CBF₂·NCCH₃·NCCH₃ (0.20 mmol) in CH₃CN (1.5 mL) and cooled to –10 °C. Then a cold (–10 °C) solution of C₆F₅BrF₂ (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 ¹⁹F NMR spectrum showed signals of [C₆F₅(CF₃C≡C)Br][BF₄] (δ –50.2 (s, 3F, CF₃), –129.9 (m, 2F, F^{2,6}), –141.1 (tt, ³J(F⁴, F^{3,5}) = 20 Hz, ⁴J(F⁴, F^{2,6}) = 7 Hz, 1F, F⁴), –156.4 (m, 2F, F^{3,5}) (C₆F₅ moiety), –144.5 (s, 4F, [BF₄][–]), CF₃C≡CBF₂·NCCH₃, and C₆F₅Br in the ratio 1:3:4.

3.5.4. Preparation of [C₆F₅(trans-CF₃CF=CF)Br][trans-CF₃CF=CFBF₃] (**14**)

An 8-mm i.d. FEP trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of C₆F₅BrF₂ (45 mg, 0.15 mmol) in PFP (0.5 mL) and cooled to –40 °C. Then a cold (–45 °C) solution of trans-CF₃CF=CFBF₂ (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 ¹⁹F NMR spectrum (–10 °C) of the colorless mother liquor showed signals of [trans-CF₃CF=CFBF₃][–], C₆F₅Br, cyclo-1-Br-1,4-C₆F₇, cyclo-1-BrC₆F₉, and [C₆F₅(trans-CF₃CF=CF)Br]⁺ (resonances at –67.2 (dd, ³J(F³, F²) = 10 Hz, ⁴J(F³, F¹) = 19 Hz, 3F, F³), –109.7 (qd, ⁴J(F¹, F³) = 19 Hz, ³J(F¹, F²) = 131 Hz, 1F, F¹), –136.8 (d, ³J(F², F¹) = 131 Hz, 1F, F²), –127.1 (m, 2F, F^{2,6}), –134.6 (tt, ³J(F⁴, F^{3,5}) = 19 Hz, ⁴J(F⁴, F^{2,6}) = 10 Hz, 1F, F⁴), and –152.5 (m, 2F, F^{3,5}) ppm). All volatiles were removed in vacuum at –10 °C to yield the white salt [C₆F₅(trans-CF₃CF=CF)Br][trans-CF₃CF=CFBF₃] (57 mg).

[C₆F₅(trans-CF₃CF=CF)Br][trans-CF₃CF=CFBF₃] (**14**). ¹¹B NMR (CH₃CN, 24 °C): δ –0.5 (dq, ²J(B, F¹) = 26 Hz, ¹J(B, F) = 40 Hz, [trans-CF₃CF=CFBF₃][–]). ¹⁹F NMR (CH₃CN, –10 °C): δ –68.0 (dd, ³J(F³, F²) = 11 Hz, ⁴J(F³, F¹) = 19 Hz, 3F, F³), –109.4 (qdt, ⁴J(F¹, F³) = 19 Hz, ³J(F¹, F²) = 130 Hz, ⁵J(F¹, F^{2,6}) = 4 Hz, 1F, F¹), –140.9 (tqd, ⁶J(F², F^{2,6}) = 7 Hz, ³J(F², F³) = 11 Hz, ³J(F², F¹) = 130 Hz, 1F, F²), –128.8 (m, 2F, F^{2,6}), –137.9 (tt, ³J(F⁴, F^{3,5}) = 21 Hz, ⁴J(F⁴, F^{2,6}) = 8 Hz, 1F, F⁴), –154.3 (m, 2F, F^{3,5}) [trans-CF₃CF=CF(C₆F₅)Br]⁺; –66.9 (qdd, ⁵J(F³, BF₃) = 1 Hz, ³J(F³, F²) = 11 Hz, ⁴J(F³, F¹) = 23 Hz, 3F, F³), –156.0 (d, ³J(F¹, F²) = 130 Hz, 1F, F¹), –179.9 (d, ³J(F², F¹) = 130 Hz, 1F, F²), –143.4 (dq, ⁴J(BF₃, F²) = 8 Hz, ¹J(F, B) = 40 Hz, 3F, BF₃[–]) ([trans-CF₃CF=CFBF₃][–]).

3.5.5. Reaction of C₆F₅BrF₂ with C₆F₁₃BF₂

A solution of C₆F₅BrF₂ (60 mg, 0.21 mmol) in PFP (1.5 mL) was cooled to –65 °C and a cold (–65 °C) solution of C₆F₁₃BF₂ (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 ¹⁹F NMR spectrum (–60 °C) showed resonances of C₆F₁₃BF₂, C₆F₁₄, C₆F₅Br, and cyclo-1-Br-1,4-C₆F₇ (45:20:23:12) besides PFP.

3.5.6. Reaction of C₆F₅BrF₂ with C₆F₁₃CH₂CH₂BF₂

A solution of C₆F₅BrF₂ (0.31 mmol) in PFP (1.9 mL) was cooled to –63 °C and a cold (–62 °C) solution of C₆F₁₃CH₂CH₂BF₂ (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 ¹⁹F NMR spectrum (–60 °C) showed resonances of C₆F₁₃CH₂CH₂BF₂, C₆F₁₃CH₂CH₂F, C₆F₅Br, cyclo-1-Br-1,4-C₆F₇, cyclo-1-BrC₆F₉ and BF₃ (36:11:33:6:4:10) besides PFP. The ¹¹B NMR spectrum (–60 °C) contained signals of C₆F₁₃CH₂CH₂BF₂ (28.8 ppm) and BF₃ (9.7 ppm) (1:1).

3.6. Reactions of [R_F(R'_F)Br][BF₄]

3.6.1. Reaction of [C₆F₅(C₃F₇C≡C)Br][BF₄] (**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 (¹⁹F NMR) and new resonances of C₆F₅Br, C₃F₇C(O)CH₂F, [Z-C₃F₇CF=CH(C₆F₅)Br]⁺, and [BF₄][–] (1:1:2:4) were now present. The solution was extracted with cold (–20 °C) CCl₃F (0.5 mL). The extract contained C₆F₅Br and C₃F₇C(O)CH₂F whereas the salt [C₆F₅(Z-C₃F₇CF=CH)Br][BF₄] remained in the acid phase.

[C₆F₅(Z-C₃F₇CF=CH)Br][BF₄] (**25**). ¹H NMR (aHF, 24 °C): δ 7.94 (d, ³J(H¹, F²) = 21 Hz, 1H, H¹). ¹⁹F NMR (aHF, 24 °C): δ –80.3 (t, ⁴J(F⁵, F³) = 9 Hz, 3F, F⁵), –91.1 (m, 1F, F²), –117.6 (dq, ³J(F³, F²) = 13 Hz, ⁴J(F³, F⁵) = 9 Hz, 2F, F³), –125.8 (m, 2F, F⁴) (Z-C₃F₇CF=CH moiety), –129.1 (m, 2F, F^{2,6}), –136.3 (tt, ³J(F⁴, F^{3,5}) = 20 Hz, ⁴J(F⁴, F^{2,6}) = 9 Hz, 1F, F⁴), –153.8 (m, 2F, F^{3,5}) (C₆F₅ moiety), –151.0 (s, 4F, [BF₄][–]).

1H,1H-octafluoropentan-2-one (**26**). ^1H NMR (CCl_3F , 0°C): δ 5.30 (d, $^2J(\text{H}^1, \text{F}^1) = 46$ Hz, 2H, H^1). ^{19}F NMR (CCl_3F , 0°C): δ -81.2 (t, $^4J(\text{F}^5, \text{F}^3) = 9$ Hz, 3F, F^5), -122.9 (q, $^4J(\text{F}^3, \text{F}^5) = 9$ Hz, 2F, F^3), -127.8 (m, 2F, F^4), -237.2 (t, $^2J(\text{F}^1, \text{H}^1) = 46$ Hz, 1F, F^1). (cf. $\text{C}_4\text{F}_9\text{C}(\text{O})\text{CH}_2\text{F}$, lit [32], ^1H (CDCl_3): $\delta = 5.25$ (d, $^2J(\text{H}^1, \text{F}^1) = 45.8$ Hz, 2H, H^1). ^{19}F (CDCl_3): $\delta = -81.0$ (3F, F^6), -121.3 (2F, F^3), -123.1 (2F, F^4), -125.7 (2F, F^5), -237.0 (t, $^2J(\text{F}^1, \text{H}^1) = 45.8$ Hz, 1F, F^1)).

3.6.2. Reaction of $[(\text{CF}_3\text{C}\equiv\text{C})_2\text{Br}][\text{BF}_4]$ (**27**) with aHF

When a solution of **27** in aHF was kept at 0°C for 24 h a mixture of $[(\text{CF}_3\text{C}\equiv\text{C})_2\text{Br}][\text{BF}_4]$ and $[\text{Z}-\text{CF}_3\text{CF}=\text{CH}(\text{CF}_3\text{C}\equiv\text{C})\text{Br}][\text{BF}_4]$ (**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 $[(\text{Z}-\text{CF}_3\text{CF}=\text{CH})_2\text{Br}][\text{BF}_4]$ (**29**) (molar ratio **28**:**29** was 94:6 after 2 d and 64:36 after 9 d) besides minor unknown products.

$[\text{Z}-\text{CF}_3\text{CF}=\text{CH}(\text{CF}_3\text{C}\equiv\text{C})\text{Br}][\text{BF}_4]$ (**28**). ^1H NMR (aHF, 0°C): δ 7.88 (d, $^3J(\text{H}^1, \text{F}^2) = 20$ Hz, 1H, H^1). ^{11}B NMR (aHF, 0°C): δ -1.1 (s, $[\text{BF}_4]^-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (aHF, 0°C): δ 111.7 (q, $^1J(\text{C}-3, \text{F}-3) = 263$ Hz, C-3), 81.1 (q, $^2J(\text{C}-2, \text{F}-3) = 60$ Hz, C-2), 43.6 (q, $^3J(\text{C}-1, \text{F}-3) = 8$ Hz, C-1), 155.8 (d, $^1J(\text{C}^2, \text{F}^2) = 296$ Hz, q, $^2J(\text{C}^2, \text{F}^3) = 45$ Hz, C^2), 115.0 (d, $^2J(\text{C}^3, \text{F}^2) = 36$ Hz, q, $^1J(\text{C}^3, \text{F}^3) = 278$ Hz, C^3), 106.8 (d, $^2J(\text{C}^1, \text{F}^2) = 15$ Hz, q, $^3J(\text{C}^1, \text{F}^3) = 5$ Hz, C^1). ^{19}F NMR (aHF, 0°C): δ -52.4 (s, 3F, F-3), -70.1 (d, $^3J(\text{F}^3, \text{F}^2) = 9$ Hz, 3F, F^3), -93.2 (qd, $^3J(\text{F}^2, \text{F}^3) = 9$ Hz, $^3J(\text{F}^2, \text{H}^1) = 20$ Hz, 1F, F^2), -149.0 (s, 4F, $[\text{BF}_4]^-$).

$[(\text{Z}-\text{CF}_3\text{CF}=\text{CH})_2\text{Br}][\text{BF}_4]$ (**29**). ^1H NMR (aHF, 0°C): δ 7.44 (d, $^3J(\text{H}^1, \text{F}^2) = 20$ Hz, 1H, H^1). ^{11}B NMR (aHF, 0°C): δ -1.1 (s, $[\text{BF}_4]^-$). ^{19}F NMR (aHF, 0°C): δ -70.5 (d, $^3J(\text{F}^3, \text{F}^2) = 9$ Hz, 6F, F^3), -96.0 (qd, $^3J(\text{F}^2, \text{F}^3) = 10$ Hz, $^3J(\text{F}^2, \text{H}^1) = 22$ Hz, 2F, F^2), -149.0 (s, 4F, $[\text{BF}_4]^-$).

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

A cold (-10°C) solution of $[4-\text{CF}_3\text{C}_6\text{H}_4(\text{C}_6\text{F}_5)\text{Br}][\text{BF}_4]$ (0.06 mmol) in MeCN (1.2 mL) was poured into a cold (-15°C) solution of $[\text{Bu}_4\text{N}][\text{I}]$ (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 $4-\text{CF}_3\text{C}_6\text{H}_4\text{Br}$, $\text{C}_6\text{F}_5\text{I}$, $\text{C}_6\text{F}_5\text{H}$, and $[\text{BF}_4]^-$ 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, $\text{R}'\text{SiF}_3$ or $\text{R}'\text{BF}_2$, 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 $[\text{Ar}(\text{F})\text{Br}]^+$, 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 $[\text{C}_6\text{F}_5(\text{F})\text{Br}]^+$ in reactions of $\text{C}_6\text{F}_5\text{BrF}_2$ with ArSiF_3 ($\text{Ar} = \text{C}_6\text{H}_5$, $4-\text{FC}_6\text{H}_4$, $4-\text{CF}_3\text{C}_6\text{H}_4$). Per- and polyfluorinated alkylboranes $\text{R}'\text{BF}_2$ did not allow the isolation of perfluoroaryl(polyfluoroalkyl)bromonium salts. Instead, $\text{C}_6\text{F}_5\text{Br}$ and $\text{R}'\text{F}$ 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 $\text{C}\equiv\text{C}$ bond of the R'_{f} group.

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