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Contributions to the chemistry of bromine trifluoride
Part 3. Electronic influences on the fluorine–aryl substitution reaction of bromine trifluoride with monosubstituted phenyltrifluorosilanes

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Abstract

BrF_3 reacts with monosubstituted phenyltrifluorosilanes X-$C_6H_4SiF_3$ (X = H, *p*-Me, *p*-MeO, *m*-F, *p*-F, *m*-CF_3, *p*-CF_3) in equimolar reactions (CH_2Cl_2/MeCN solution, optimised reaction temperature) with three different patterns of products. Electron-rich aryl groups (X = H, *p*-Me, *p*-MeO) are only fluorinated, brominated and oxidised by BrF_3. Monofluorinated phenyltrifluorosilanes behave mainly like the electron-rich silanes, but additionally, in smaller amounts, (ca. 10%) disubstitution takes place on BrF_3 with formation of [(X-C_6H_4)$_2$Br] [SiF_5]. After metathesis the bromonium salts can be isolated as tetrafluoroborates or hexafluorophosphates. When X = *m*-CF_3 and *p*-CF_3, monosubstitution becomes the main reaction and X-$C_6H_4BrF_2$ can be isolated in good yields as first examples of hydrogen-containing phenylbromine difluorides. Their oxidation potential is high enough to oxidise I_2 to IF_5. Attempts to synthesise *p*-$CF_3C_6H_4BrCl_2$ were not successful.

Keywords: Bromine trifluoride; Fluorine–aryl substitution; Arylbromine difluorides; Diarylbromonium salts; Iodine pentafluoride; Arylbromine dichloride; NMR spectrometry; IR spectrometry

1. Introduction

Two stable classes of organobromine(III) compounds [1–3] are known: organobromine difluorides and its derivatives $RBrX_2$ and salts which contain diorganobromonium cations. Additionally bromonium ylids are discussed as intermediates [4,5]. The first polyvalent bromine(III) compound, diphenylenebromonium chloride was reported by Sandin and Hay [6] in 1952. Different synthetic routes to diarylbromonium salts were investigated by Nesmeyanov [7–10]. Martin et al. [11–13] isolated the first organic 10-Br-3 species, a dialkoxyarylbrominane. The first example of an isolated organobromine difluoride, $C_6F_5BrF_2$, was published by us in 1984 [14]. Until now no hydrogen-containing arylbromine difluorides $RBrF_2$ [difluoroarylbrominanes (10-Br-3)] could be isolated. From the literature it is known that Nesmeyanov assumed the intermediate formation of *p*-$FC_6H_4BrF_2$ when *p*-FC_6H_4Br was reacted with XeF_2 in SO_2 at −70°C [15] or when C_6H_5F underwent electrophilic substitution with BrF_3 in CH_2Cl_2 in the presence of MeCN and $BF_3 \cdot R_2O$ [16]. His assumption was established on the ^{19}F NMR spectrometric observation of a C-bonded *p*-fluorine atom at −108 ppm (CH_2Cl_2, −70°C), but no resonance for the BrF_2 group was reported. The positive result of the reaction of BrF_3 **1** with $C_6F_5SiF_3$ in CH_2Cl_2/MeCN encouraged us to prove the general use of that synthetic approach, especially for the synthesis of non-perfluorinated arylbromine difluorides X-$C_6H_4BrF_2$.

2. Results

Aryltrifluorosilanes X-$C_6H_4SiF_3$ **2** with substituents X = H, *p*-Me, *p*-MeO, *m*-F, *p*-F, *m*-CF_3 and *p*-CF_3 were investigated in equimolar reactions with BrF_3 in CH_2Cl_2/MeCN solution at low temperature. With X = *p*-Me **2b** and *p*-MeO **2c** the aryl transfer reagent **2** possessed more electron-rich aryl groups than in the reference silane **2a** (X = H). In the case of **2a**, **2b** and **2c** fluorination, bromination, (chlorination deriving from reaction with the solvent) and oxidation of the aryl group took place and no fluorine–aryl substitution products of **1**, whether X-$C_6H_4BrF_2$ **3** nor [(X-C_6H_4)$_2$Br] [SiF_5] **4** could be isolated or detected by ^{19}F NMR after the consumption of BrF_3.

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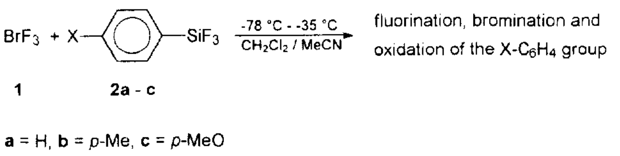
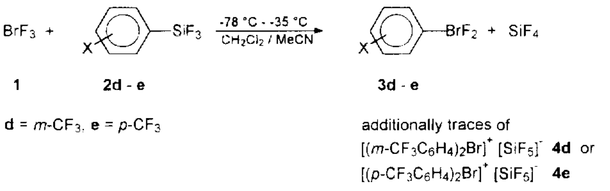
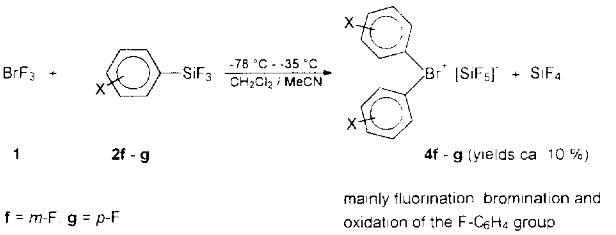


When the silanes **2d** (X = *m*-CF_3) and **2e** (X = *p*-CF_3) were reacted with **1** under the same conditions as **2a–c**, the fluorine–aryl substitution was successful. At approximately −55°C the reaction started as could be deduced from the evolution of SiF_4. The arylbromine difluorides X-$C_6H_4BrF_2$ **3d** and **3e** were isolated in 59.2 and 67.8% yield after purification.



When **1** was reacted with silanes **2f** (X = *m*-F) and **2g** (X = *p*-F) in a 1:1 reaction (CH_2Cl_2/MeCN, low temperature) fluorination, bromination and oxidation of the aromatic ring were the major reaction routes. By ^{19}F NMR no brominane **3** was detected. Only the disubstitution products, diarylbromonium pentafluorosilicates **4f** and **4g**, were observed by ^{19}F NMR and were isolated after metathesis as bromonium tetrafluoroborate **4j** or hexafluorophosphate **4k** (~10% yield).



$$\mathbf{4f} + [BF_4]^- \longrightarrow [(m\text{-}C_6H_4F)_2Br]^+ [BF_4]^- + [SiF_5]^-$$

4j

$$\mathbf{4g} + [PF_6]^- \longrightarrow [(p\text{-}C_6H_4F)_2Br]^+ [PF_6]^- + [SiF_5]^-$$

4k

This results does not explain the absence of **3f** and **3g**. In the past we were able to show that **3f** and **3g** are accessible by aimed reduction of the corresponding arylbromine tetrafluorides [17].

The co-product of fluorine–aryl substitutions SiF_4 was transformed to the $SiF_4 \cdot 2$ py adduct and identified by IR, elemental analysis and by its decomposition temperature [18].

3. Discussion

The nucleophilic fluorine–aryl substitution on **1** is influenced by the solvent. When the reaction was performed only in the solvent CH_2Cl_2 or in CCl_3F, a higher reaction temperature of −10°C was necessary. As a consequence of the elevated temperature, extensive oxidative decomposition took place relative to the desired substitution reaction. In the presence of MeCN, the reaction temperature could be lowered to ≤ −50°C and as a result, the oxidative decomposition was reduced and **3d–e** was obtained in good yields. In contrast to Nesmeyanov who investigated the formation of bromonium salts by electrophilic attack of **1** on aromatic compounds [19] or organometallics in acidic medium [9,10], we have found no change in yield when the stoichiometric ratio **1**:MeCN was varied in the range 1:0.4 to 1:2. The higher reaction temperature required with CCl_3F or CH_2Cl_2 can be attributed to the lack of activation by MeCN rather than to the lower solubility of **1** in those solvents. The presence of MeCN does increase the solubility of BrF_3 at low temperature, but more importantly contributes to the weakening of intermolecular fluorine-bridges in **1**. Additionally MeCN influences the dissociation equilibrium (polarisation) of BrF_3 and stabilises the electrophilic species of the dissociation (or polarisation) by base coordination.

$$2BrF_3 \rightleftarrows [BrF_2]^+_{MeCN} + [BrF_4]^-$$

Compound **2** is also influenced by MeCN. By coordination of MeCN with **2**, the polarity of the carbon–silicon bond increases, the bond is weakened, and consequently, the nucleophilicity of the aryl group in **2** is increased.

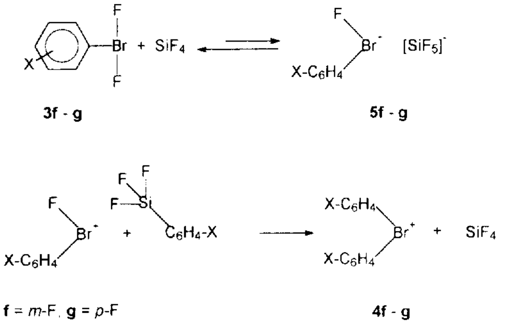
$$X\text{-}C_6H_4\text{-}SiF_3 + \text{base} \rightleftarrows X\text{-}C_6\overset{\delta-}{H_4} - \overset{\delta+}{SiF_3} \cdot \text{base}$$

In arylsilane **2a** the phenyl group is too electron-rich to preclude the electrophilic substitution of C–H bonds and the oxidation of the aromatic system by BrF_3. **2a** reacts with **1** at −78°C without considerable evolution of SiF_4. The introduction of one CF_3 group in a *m*- or *p*-position reduces the possibility of the reactions mentioned for **2a**. Similarly, the substituent fluorine influences the electron distribution of the σ-system of the aromatic ring. However, different from CF_3, fluorine delivers electron density to the π-system of the aryl group by back-bonding. Consequently the aryl group in **2f** and **2g** is more electron-rich than in **2d** and **2e** and fluorination, bromination and oxidation of the aromatic system proceed preferably to electrophilic attack at the ipso-carbon (difluorobromo desilylation). The products of C–H substitution and oxidation of the aromatic ring were not studied in detail. GC–MS analysis showed after hydrolysis a large variety of partially fluorinated, brominated and chlorinated (from reaction with CH_2Cl_2) species, mainly benzenes and in minor amounts cyclohexadienes and cyclohexenes.

The comparison of products from the reaction of **1** with **2d**–**2e** and **2f–2g** shows significant differences. Only very small amounts of fluorination, bromination and oxidation products of the aromatic ring were found for **2d** and **2e** in addition to 69.2 or 79.1% of crude BrF_3 monosubstitution products **3d–3e** and minor amounts (≤5%) of BrF_3 disubstitution products **4d** and **4e** (isolated after metathesis as [(*m*-

$CF_3C_6H_4)_2Br]$ $[BF_4]$ **4h** and $[(p\text{-}CF_3C_6H_4)_2Br]$ $[PF_6]$ **4i**). Whereas in the case of **2f** and **2g**, mainly fluorination, bromination, and oxidation products of the aromatic system were obtained besides small amounts (~10%) of BrF_3 disubstitution products **4f** and **4g** (isolated after metathesis as **4j** and **4k**).

The influence of the F- and CF_3-substituent on the formation of mono and disubstituted BrF_3 derivatives is mainly inductive. The formation of **4g** proceeds via **3g** and **5g**. The fluoride abstraction from **3g** is not favoured by resonance stabilisation of **5g**, because **3f** without a resonance contribution of fluorine in *m*-position of intermediate **5f** follows the same reaction path. In conclusion, the different influence of the F- and CF_3-substituents on the BrF_2 group in **3** is decisive for the final products and is caused by inductive interactions.



m- and *p*-Trifluoromethylphenylbromine difluoride possesses a lower fluoride donor ability to SiF_4 or the fluorosilanes **2** than the fluorophenylbromine difluorides. The abstraction of fluoride from **3** or the polarisation of the hypervalent F–Br–F bond in **3** by a Lewis-acid is necessary for the introduction of the second aryl group into **1**. Consequently one of the fluorine atoms of the BrF_2 group in **3f** and **3g** will be substituted faster than the first fluorine atom in **1**.

3d and **3e** are the first examples of non-perfluorinated arylbromine difluorides which could be isolated and characterised unambiguously. They are colourless solids which show, when heated in DTA experiments, an endothermic transition upon melting, followed by an exothermic decomposition at 152°C (**3d**) and 166°C (**3e**). Mild hydrolysis (addition of aqueous MeCN to the MeCN solution of **3**) is followed by a spontaneous redox reaction.

$$\underset{\mathbf{3d-e}}{\text{X-}C_6H_4BrF_2} + H_2O \xrightarrow[-2F^-\,-2H^+]{\text{MeCN}} (\text{X-}C_6H_4BrO)$$

$$\to \underset{\mathbf{6d-e}}{\text{X-}C_6H_4Br} + 0.5O_2$$

The hydrolysis products, F^- and H_3O^+ were determined quantitatively. Because of the fast oxidation of O^{2-}, it was not possible to determine the redox equivalent of $\text{X-}C_6H_4Br^{2+}$ by iodometry.

$$\underset{\mathbf{3d-e}}{\text{X-}C_6H_4BrF_2} + H_2O + {>}H^+ + {>}I^-$$

$$\xrightarrow[-2F^-]{} \underset{\mathbf{6d-e}}{\text{X-}C_6H_4Br} + 0.5O_2 + {>}H^+ + {>}I^-$$

In the ^{19}F NMR spectra the CF_3 and the BrF_2 groups give resonances of correct intensity in the range of −62 ppm. While the CF_3 resonance is a sharp singlet the BrF_2 singlet possesses a hwb of more than 10 Hz. In MeCN solution at 35°C the BrF_2 resonance in **3d** (−61.7 ppm) and in **3e** (−62.8 ppm) appears at a significantly lower frequency than in $C_6F_5BrF_2$ (**3l**) at −48.9 ppm [14]. The low frequency shift in **3d** and **3e** can be attributed to a larger negative charge on both hypervalent bonded fluorine atoms. It may be caused by the weaker C–Br bond and the smaller electron withdrawing effect of trifluoromethylphenyl groups compared with the pentafluorophenyl group.

Intense broad absorption bands at 550–480 cm^{-1} with maxima at 523 and 477 cm^{-1} in **3d** and 530–460 cm^{-1} in **3e** are characteristic for the valence vibrations of the BrF_2 group. Comparison with the reported values in solid BrF_3 (590, 570 $\nu_{as}(Br\text{-}F_{ax})$ and 480 cm^{-1} $\nu_s(Br\text{-}F_{ax})$ [20] shows a low wave number shift for $\nu_{as}(Br\text{-}F_{ax})$ from BrF_3 via **3l** (550 cm^{-1} [14]) to **3d** and **3e**.

3d and **3e** are strongly oxidising fluorinating agents which can be handled in organic solvents like MeCN or CH_2Cl_2. The strength of the fluorinating ability was demonstrated by the reaction of **3d–e** with I_2 in MeCN. At room temperature IF_5 is formed quantitatively in a fast reaction with $CF_3C_6H_4Br$ (**6d** and **6e**) as co-products.

$$5\,\mathbf{3d{-}e} + I_2 \xrightarrow[\text{r.t.}]{\text{MeCN}} 5\,\mathbf{6d{-}e} + 2IF_5$$

The oxidation potential of Br(III) in **3e** becomes obvious when **3e** is introduced into the metathesis reaction with Me_3SiCl in order to obtain $p\text{-}CF_3C_6H_4BrCl_2$. Below −10°C in a 1:1 reaction an equimolar mixture of **3e** and $p\text{-}CF_3C_6H_4Br$ **6e** and chlorine results. The 1:2 reaction ends with the total consumption of **3e** and Me_3SiCl and their conversion to **6e** and Me_3SiF.

$$p\text{-}CF_3C_6H_4BrF_2 + 1Me_3SiCl \to 0.5p\text{-}CF_3C_6H_4BrF_2$$

$$+ 0.5p\text{-}CF_3C_6H_4Br + Me_3SiF + 0.5Cl_2$$

$$p\text{-}CF_3C_6H_4BrF_2 + 2Me_3SiCl \to p\text{-}CF_3C_6H_4Br$$

$$+ 2Me_3SiF + Cl_2$$

4. Experimental details

All experiments were performed in FEP-PTFE or PFA-PTFE tube reactors or inliners under a dry Ar atmosphere. Solid products were handled under Ar in a stainless steel glovebox with the gas cleaning device Braun MB 100 G. BrF_3 was prepared from the elements at 0°C in a silica trap. After evaporation, the slightly yellow product was distilled and stored in a stainless steel sampling cylinder. The arylsilanes **2** were prepared from the corresponding bromobenzenes $\text{X-}C_6H_4Br$ **6** using Grignard reactions. Transformation to $\text{X-}C_6H_4SiCl_3$ with excess of $SiCl_4$ was followed by reaction with SbF_3. ^{19}F NMR measurements were performed in FEP inliners with Varian EM 360 L (56.45 MHz) and Bruker WP 80 SY (75.39 MHz) spectrometers ($T = 35°C$). Shift values are referred to CCl_3F using C_6F_6 as internal or SR standard [$\delta(C_6F_6) = -162.9$ ppm]. IR spectra were measured in KelF and paraffin suspensions (KBr windows) or in AgCl with the PE spectrometer 577.

*4.1. General procedure for the reaction of **1** with **2***

1 (1.71 g, 12.49 mmol) was frozen at −78°C. Under intensive magnetic stirring, cold CH_2Cl_2 (35 ml, −78°C) was added slowly. After dropwise addition of cold MeCN (1.30 ml, 24.88 mmol, −45°C), a slightly yellow solution resulted. Dry NaF (110 mg, 2.62 mmol) was added followed by the dropwise transfer (20 min) of a suspension of **2** (12.55 mmol in 6 ml CH_2Cl_2, −78°C, containing additionally 110 mg NaF). After 0.5 h at −78°C the temperature was raised to −55°C (evolution of SiF_4 in the case of **2d–e**) for 1 h and finally to −35°C for 2 h. Gas was pumped off before the suspension was filtered. The solid material was washed with CH_2Cl_2 or CCl_3F and dried in vacuum. The further treatment of the precipitate and the mother liquor depends upon the products.

*4.1.1. Isolation of **3d** and **3e** from the mother liquor*

The solvent was distilled off from the mother liquor at ≤ −30°C in vacuum. The resulting colourless to slightly yellow solid (crude **3d** 69.2%, crude **3e** 79.1%) was purified by repeated (3×) low temperature crystallisation (**3** was dissolved at r.t. in CCl_3F and crystallised at −78°C). Yield: 59.2% **3d**, 67.8% **3e**.

3d: ^{19}F NMR (MeCN) δ/ppm: −61.7 (s, b; 2F; BrF_2), −61.9 (s; 3F; CF_3); ^1H NMR (MeCN) δ/ppm: 7.22–8.30 (m; C_6H_4); IR (KelF) ν/cm^{-1}: 3080 (m), 1605 (w), 1475 (sh), 1425 (s), 1375 (m), 1320 (vs), (paraffin) 1305 (s), 1280 (s), 1172 (vs), 1140 (vs), 1090 (s), 1075 (s), 1054 (s), 992 (m), 933 (w), 920 (w), 905 (sh), 900 (m), 805 (s), 792 (vs), 690 (vs), 640 (w), 550–480 (vs), 523 (vs), 510 (sh), 477 (vs), 440 (m), 418 (w). DTA: 42°C (endothermic maximum), 152°C (exothermic maximum); $F_{hydr.}^{-}$ 14.57 (14.45%); neutralisation equivalent 131.96 (131.50 g/mol_{OH^-}).

3e: ^{19}F NMR (MeCN) δ/ppm: −62.8 (s, hwb = 11 Hz; 2F; BrF_2), −62.1 (s; 3F; CF_3); ^1H NMR (MeCN) δ/ppm: 7.91–8.38 (m; C_6H_4); IR (AgCl) ν/cm^{-1}: 3090 (m), 3050 (m), 1640 (w), 1585 (vs), 1470 (m), 1395 (s), 1315 (vs), 1290 (sh), 1200–1100 (vs, b), 1155 (vs), 1055 (s), 995 (s), 950 (m), 830 (vs), 820 (s), 770 (m), 715 (m), 685 (w), 620 (w), 580 (s), 530–460 (vs, b), 425 (m), 400 (m), 385 (m). DTA: 83°C (endothermic maximum), 166°C (exothermic maximum); $F_{hydr.}^{-}$ 14.28 (14.45%); neutralisation equivalent 124.21 (131.50 g/mol_{OH^-}).

*4.1.2. Isolation of **4h** and **4i** from the reaction of **1** with **2d** and **2e***

The precipitate was dissolved in water and treated with aqueous $H[PF_6]$ or $Na[BF_4]$ solution. Colourless solid precipitated. After separation, washing and drying the bromonium salts were characterised.

$[(m\text{-}CF_3C_6H_4)_2Br][BF_4]$ **4h**: 5.2% yield; ^{19}F NMR (MeCN) δ/ppm: −62.1 (s; 6F; CF_3), −149.4 (s; 4F; BF_4); ^1H NMR (MeCN δ/ppm: 7.79–8.36 (m; C_6H_4); mp 144°C (142–143°C [19]).

$[(p\text{-}CF_3C_6H_4)_2Br][PF_6]$ **4i**: 2.4% yield; ^{19}F NMR (MeCN) δ/ppm: −62.1 (s; 6F; CF_3), −70.7 (d, 707 Hz; 6F; PF_6); ^1H NMR (MeCN δ/ppm: 7.80–8.22 (m; C_6H_4); DTA: 168°C (endothermic maximum).

*4.1.3. Isolation of **4j** and **4k** from the reaction of **1** with **2f** and **2g***

A ^{19}F NMR sample of the precipitate (reaction of **1** with **2g**) established the presence of **4g** [δ/ppm: −104.6 (m; 2F; *p*-F); −139.8 (s, b; 5F; $[SiF_5]^-$)]. The precipitate was dissolved in water and treated with aqueous $H[PF_6]$ or $Na[BF_4]$ solution. Colourless solid precipitated. After separation, washing and drying the bromonium salts were characterised.

$[(m\text{-}FC_6H_4)_2Br][BF_4]$ **4j**: 10.7% yield; ^{19}F NMR (MeCN) δ/ppm: −104.00 (m; 2F; *m*-F), −150.01 (s; 4F; BF_4); ^1H NMR (MeCN δ/ppm: 7.48–7.98 (m; C_6H_4); mp 141–143°C (149–150°C [10]).

$[(p\text{-}FC_6H_4)_2Br][PF_6]$ **4k**: ~10% yield; ^{19}F NMR (MeCN) δ/ppm: −104.2 (m; 2F; *p*-F), −70.8 (d, 707 Hz; 6F; PF_6); ^1H NMR ($MeNO_2$) δ/ppm: 7.08–7.36 (m; 2H; *m*-C_6H_4), 8.11–8.32 (m; 2H; *o*-C_6H_4); DTA: 176°C (endothermic maximum).

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