# A Simple and Convenient Route to Arylxenon(II) Tetrafluoroborates

H.-J. Frohn[a], H. Franke[a], and V. V. Bardin[b]

[a]Fachgebiet Anorganische Chemie, Gerhard-Mercator-Universität Duisburg,
Lotharstr. 1, D-47048 Duisburg, Germany
[b]Institute of Organic Chemistry, 630090 Novosibirsk, Russia

Reprint requests to Prof. Dr. H.-J. Frohn.
Fax: (+49) 203 379 2231. E-mail: frohn@uni-duisburg.de

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An improved synthesis of arylxenon(II) salts is reported. The series of fluoro-containing arylxenon(II) tetrafluoroborates (aryl = $C_6F_5$, 2,3,4,5-$C_6HF_4$, 3,4,5-$C_6H_2F_3$ and 3,5-$C_6H_3F_2$) are prepared by the reaction of xenon difluoride with the corresponding aryldifluoroboranes. The salts $[C_6F_5Xe]$ $[BF_4]$ and $[2,3,4,5\text{-}C_6HF_4Xe]$ $[BF_4]$ are long-term stable in anhydrous HF (aHF) solution at rt, while $[3,4,5\text{-}C_6H_2F_3Xe]$ $[BF_4]$ and $[3,5\text{-}C_6H_3F_2Xe]$ $[BF_4]$ are converted into 1,2,3,5-tetrafluorobenzene and 1,3,5-trifluorobenzene, respectively, within a few hours.

## Introduction

In 1989 the first preparation of arylxenon(II) salts, pentafluorophenylxenon(II) pentafluorophenyl(fluoro)borates, by reaction of tris(pentafluorophenyl)borane and xenon difluoride was reported [1, 2].

$$(C_6F_5)_3B + XeF_2 \xrightarrow[-40^\circ C]{CH_2Cl_2 \text{ or } MeCN} [C_6F_5Xe]\,[(C_6F_5)_nBF_{4-n}] \qquad (1)$$

Later this procedure was extended to some other arylxenon(II) salts [3 - 6]. However, the preparation and purification of boranes with electron-withdrawing substituents in the aryl group is a delicate process owing to the high tendency for tetraarylborate formation and the moisture-sensitivity of the boranes. A disadvantage of the traditional synthetic approach is the presence of nucleophilic arylfluoroborate anions in combination with the electrophilic arylxenon(II) cation. This fact makes it neccessary to convert arylxenon(II) arylfluoroborates into salts with less nucleophilic anions like $[AsF_6]^-$ in order to increase the thermal stability. Furthermore, it should be mentioned, that only one third of the aryl groups Ar is transferred to $Xe^{(II)}$ (eq. (2)).

$$Ar_3B + XeF_2 \xrightarrow{CH_2Cl_2} [ArXe][Ar_2BF_2] \qquad (2)$$

The alternative pathway to [ArXe] $[OS(O)_2CF_3]$ by reaction of ArH with $XeF_2$ in the $CF_3C(O)OH$ - $CF_3S(O)_2OH$ - $CCl_3F$ system at –40 °C resulted in low yields of arylxenon(II) compounds and, in many cases, in the non-regiospecific replacement of hydrogen by xenon(II) [7].

We have elaborated a new reaction sequence for the preparation of organoxenon(II) tetrafluoroborates based on the interaction of xenon difluoride with organyldifluoroboranes generated *in situ* from the corresponding potassium aryltrifluoroborates and boron trifluoride in an inert solvent [8]. We present now the fruitful application of aryldifluoroboranes for the synthesis of some fluoro-containing arylxenon(II) tetrafluoroborates. Most of the aryl groups under investigation have the presence of hydrogen atom(s) in *ortho*-position(s) in common.

## Results and Discussion

The general procedure of the improved synthesis consists of the sequential defluoridation of K $[ArBF_3]$ by $BF_3$ in $CH_2Cl_2$ at -40 to -50 °C, the separation of the dichloromethane solution of $ArBF_2$ from solid K $[BF_4]$ followed by the reaction of the aryldifluoroborane with $XeF_2$ which results in the precipitation of the desired arylxenon(II) tetrafluoroborate.

$$K[ArBF_3] \xrightarrow[-40 \text{ to } -50^\circ C, CH_2Cl_2]{+BF_3, -K[BF_4]} ArBF_2 \xrightarrow[CH_2Cl_2]{+XeF_2} [ArXe][BF_4] \qquad (3)$$

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Pentafluorophenylxenon(II) (**1**), 2,3,4,5-tetrafluorophenylxenon(II) (**2**), 3,4,5-trifluorophenylxenon(II) (**3**), and 3,5-difluorophenylxenon(II) (**4**) tetrafluoroborates were prepared in high yields. It should be mentioned that aryldichloroboranes can also be used as starting materials. For instance, salt **1** was obtained by the reaction of an excess of xenon difluoride with a mixture of $C_6F_5BCl_2$ and $C_6F_5BF_2$.

$$1\,(C_6F_5BCl_2 + C_6F_5BF_2) + 1.9\,XeF_2 \xrightarrow{CH_2Cl_2} [C_6F_5Xe]\,[BF_4] + Cl_2 + Xe \qquad (4)$$

However, the use of chloroboranes has no advantage over the substrates $Ar_3B$ or $C_6F_5BF_2$ because 50 % of xenon difluoride is lost in a preceeding redox reaction.

**1** and the new hydrogen-containing arylxenon compounds **2**, **3** and **4** are white solids. The latter show reduced stability with diminishing number of fluorine atoms in the aromatic moiety. Indeed, **1** and **2** did not decompose at rt in a dry argon atmosphere over one year. Compound **3** remained unchanged at least for 4 d whereas **4** underwent total decomposition within a few hours under the same conditions. The suspensions of the arylxenon tetrafluoroborates **3** and **4** (no *ortho*-fluorine atoms) in dichloromethane showed the lowest thermal stability. Both salts are converted completely into 1,2,3,5-tetrafluorobenzene (**5**) or 1,3,5-trifluorobenzene (**6**), respectively, within a few hours.

The fluoro-containing arylxenon(II) tetrafluoroborates **1** - **4** are soluble in basic MeCN as well as in strong anhydrous acids. The solution of **1** in MeCN slowly decomposes at rt similarly to the corresponding hexafluoroarsenate [6] to give mainly $C_6HF_5$, $(C_6F_5)_2$ and traces of $C_6F_6$ after 23 d. The decomposition of the trifluorophenylxenon salt **3** was complete within 18 h under the same conditions yielding a complex mixture which contains 1,2,3,5-tetrafluorobenzene. **4** remained unchanged in an $CD_3CN$ - EtCN solution at –60 °C for 7 h, but was converted into 1,3,5-trifluorobenzene (**6**) at –30°C.

Solutions of the tetra- and pentafluorophenylxenon(II) salts **2** and **1** in acidic media were significantly more stable than in basic media. No changes of these salts were detected in the anhydrous HF (aHF) solutions at rt during 13 - 16 d. The solution of the related $[C_6F_5Xe]\,[AsF_6]$ salt in HOTf could be stored for four years at rt without decomposition. In contrast to the stability of arylxenon(II) salts with fluorine in *ortho*-position, **3** was converted in aHF quantitatively into tetrafluorobenzene **5** within 12 h. It should be emphasized that the total decomposition of **3** in HOTf solution at rt resulted in the formation of a mixture of **5** and 3,4,5-trifluorophenyl triflate (**7**) (18 : 82).

Table I. Preparation of $[ArXe]\,[BF_4]$.

| $ArBF_2$, mmol | $CH_2Cl_2$, ml | $XeF_2$, mmol | $[ArXe]\,[BF_4]$, yield in mmol (%) |
|---|---|---|---|
| $C_6F_5BF_2$, 1.40 | 3 | 1.50 | 1.26 (90) |
| $C_6F_5BF_2 + C_6F_5BCl_2$ (21 : 79), 0.50 | 2 | 0.93 | 0.29 (58) |
| 2,3,4,5-$C_6F_4HBF_2$, 1.23 | 2.5 | 1.26 | 1.03 (84) |
| 3,4,5-$C_6F_3H_2BF_2$, 1.95 | 4 | 1.97 | 1.58 (81) |
| 3,5-$C_6F_2H_3BF_2$, 1.53 | 10 | 1.38 | 0.57 (41) |

$$\underset{\mathbf{3}}{[3,4,5\text{-}C_6H_2F_3Xe]\,[BF_4]} \xrightarrow[rt]{aHF\ or\ CH_2Cl_2} \underset{\mathbf{5}}{1,2,3,5\text{-}C_6H_2F_4} + BF_3 + Xe \qquad (5)$$

$$\underset{\mathbf{3}}{[3,4,5\text{-}C_6H_2F_3Xe]\,[BF_4]} \xrightarrow[-BF_3,\,-Xe]{CF_3S(O)_2OH} \underset{\mathbf{5}}{1,2,3,5\text{-}C_6H_2F_4} + \underset{\mathbf{7}}{3,4,5\text{-}C_6H_2F_3OS(O)_2CF_3} \qquad (6)$$

The aHF solution of **4** was the least stable in this series and conversion of **4** into trifluorobenzene **6** proceeded already at -30 °C.

$$\underset{\mathbf{4}}{[3,5\text{-}C_6H_3F_2Xe]\,[BF_4]} \xrightarrow[0°C\ or\ rt]{aHF\ or\ CH_2Cl_2} \underset{\mathbf{6}}{1,3,5\text{-}C_6H_3F_3} + BF_3 + Xe \qquad (7)$$

These experimental results show the clear interdependence between the presence of carbon-bonded fluorine atoms in the $[BF_4]^-$ salts of arylxenon cations and the thermal stability and reactivity towards strong acids with weakly nucleophilic anions. The influence of the electronic structure in partially fluorinated arylxenon(II) cations on their reactivity will be discussed elsewhere.

Table II. NMR spectra of [ArXe] [$BF_4$].

| Ar | Solvent | T [°C] | δ(H) | δ(F) [a]<br>F-2 | <br>F-3 | <br>F-4 | <br>F-5 | <br>F-6 | δ(Xe) |
|---|---|---|---|---|---|---|---|---|---|
| $C_6F_5$ | HF | −10 | | −123.26 | −151.53 | −137.85 | −151.53 | −123.26 | −3940.6 |
| | | | J [Hz]: (2,3) 11, (2,4) 6, (2,6) 6[c], (3,4) 19, (3,5) 5[c], (F-2,Xe) 58.6; 59.3[b], (F-3,Xe) 18 | | | | | | |
| $C_6F_5$ | MeCN | −30 | | −125.48 | −155.04 | −142.26 | −155.04 | −125.48 | −3785.8 |
| | | | J [Hz]: (2,4) 4, (3,4) 20, (F-2,Xe) 68; 67[b] | | | | | | |
| 2,3,4,5-$C_6HF_4$ | HF | −10 | 8.70 | −120.20 | −143.25 | −140.60 | −127.57 | | −3840.6 |
| | | | J [Hz]: (2,3) 15, (2,4) 7, (2,6) 4, (3,4) 18, (3,5) 5, (3,6) 3, (4,5) 18, (4,6) 7, (F-2,Xe) 54.8; 54.7 [b], (H-6,Xe) 14.3[b] | | | | | | |
| 2,3,4,5-$C_6HF_4$ [d] | HF | −10 | 8.65 | −119.94 | −143.35 | −140.90 | −127.82 | | −3836.3 |
| | | | J [Hz]: (3,4) 16, (4,5) 16, (F-2,Xe) 55.5 [b], (H-6,Xe) 16[b] | | | | | | |
| 2,3,4,5-$C_6HF_4$ | MeCN | −30 | 8.11 | −122.54 | −147.29 | −144.35 | −132.12 | | −3712.2 |
| | | | J [Hz]: (2,3) 18, (2,4) 8, (2,5) 5, (2,6) 5, (3,4) 19, (3,5) 9, (4,5) 20, (4,6) 7, (5,6) 9, (F-2,Xe) 63.4; 63.1[b] | | | | | | |
| 3,4,5-$C_6H_2F_3$ | HF | −10 | 8.54 | | −120.87 | −147.15 | −120.87 | | −3704.4 |
| | | | J [Hz]: (2,3) 5, (2,4) 5, (3,4) 18, (H-2, Xe) 17.6[b] | | | | | | |
| 3,4,5-$C_6H_2F_3$ | MeCN | −30 | 8.05 | | −125.89 | −150.37 | −125.89 | | −3606.6 |
| | | | J [Hz]: (2,3) 6, (3,4) 19 | | | | | | |
| 3,5-$C_6H_3F_2$ | HF, | −60 | 8.46 (H-2,6)<br>8.06 (H-4), | | −96.59 | | −96.59<br>J [Hz]: (Xe, H-2,6) 19.4 | | −3708.0 |
| 3,5-$C_6H_3F_2$ | [e] | −60 | 7.94 (H-2,6),<br>7.59 (H-4) | | −101.42 | | −101.42<br>J [Hz]: unresolved signal | | −3605.8 |

[a] $^{19}F$ resonances of the anion $[BF_4]^-$ were located at −148.71 (**1**), −148.03 (**2**), −147.56 (**3**) in acetonitrile solution, at −149.43 [e] (**4**) ppm, and at −148.09 (**1**), −148.50 (**2**), −148.16 (**3**) and −148.31 (**4**) ppm in aHF solution; [b] From $^{129}Xe$ NMR spectrum; [c] Apparent constant; [d] Counteranion $[AsF_6]^-$; [e] In $CD_3CN$ - EtCN (1 : 3).

## Experimental

NMR spectra were measured on Bruker spectrometers WP 80 SY ($^1H$ at 80.13 MHz and $^{19}F$ at 75.39 MHz) and AVANCE DRX 500 ($^1H$ at 500.13 MHz, $^{19}F$ at 470.59 MHz and $^{129}Xe$ at 138.34 MHz) with TMS ($^1H$), $CCl_3F$ ($^{19}F$), and $XeOF_4$ ($^{129}Xe$) as references. The IR spectra were measured on the Bruker IFS 66 spectrometer in polyethylene pellets. GC-MS analysis was performed with the Hewlett Packard HP G 1800A instrument.

Preparations of K [$ArBF_3$] and $ArBF_2$ (Ar = $C_6F_5$, 2,3,4,5-$C_6HF_4$, 3,4,5-$C_6H_2F_3$ and 3,5-$C_6H_3F_2$) were recently described [8]. The yield of aryldifluoroboranes was determined from the $^{19}F$ NMR spectra of the solutions in dichloromethane using 1,1,2-trichlorotrifluoroethane as quantitative internal reference.

Anhydrous HF was electrolytically dried and trifluoromethanesulfonic acid was distilled before use. All manipulations with arylxenon(II) salts were carried out in a dry argon atmosphere in FEP traps. For NMR measurements FEP inliners were used.

*Preparation of arylxenon(II) tetrafluoroborates (general procedure)*

Xenon difluoride was added portionwise to the stirred solution of the aryldifluoroborane in dichloromethane at −40 to −50 °C. After 1 - 2 h the suspension was warmed slowly to rt. After centrifugation the mother liquor was decanted and the arylxenon(II) tetrafluoroborate was washed with several portions of $CH_2Cl_2$ and finally dried in vacuum at rt (Table I). Salt **4** was isolated at $\leq$ -40 °C.

The reaction of a mixture (21 : 79) of $C_6F_5BF_2$ and $C_6F_5BCl_2$ with $XeF_2$ was performed in a similar manner.

NMR spectra are presented in Table II.

Pentafluorophenylxenon(II) tetrafluoroborate **1**. IR: 441, 433, 381, 349, 308, 278, 224, 203, 132, 116 $cm^{-1}$.

Elemental analysis for $C_6BF_9Xe$ (385.15 g/mol)

Calcd C 18.7 F 44.4 %,
Found C 19.4 F 44.3 %.

2,3,4,5-Tetrafluorophenylxenon(II) tetrafluoroborate **2**. IR: 434, 384, 359, 338, 321, 292, 282, 212, 194, 168, 148, 117 $cm^{-1}$.

Elemental analysis for $C_6HBF_8Xe$ (367.91 g/mol)

Calcd C 19.6 H 0.27 F 41.3 %,
Found C 18.6 H 0.23 F 42.0 %.

*Stability of [ArXe] [BF₄] solutions in acids*

A. [2,3,4,5-$C_6HF_4Xe$] [$BF_4$] (0.10 mmol) was dissolved in aHF (0.2 ml) and kept at rt for 16 d. No changes were detected ($^{19}$F NMR).

B. A solution of [3,4,5-$C_6H_2F_3Xe$] [$BF_4$] (0.13 mmol) in aHF (0.3 ml) was kept at rt for 12 h. Quantitative conversion of **3** into 1,2,3,5-tetrafluorobenzene was observed ($^{19}$F NMR).

C. [3,4,5-$C_6H_2F_3Xe$] [$BF_4$] (0.07 mmol) was dissolved in HOTf (0.1 ml) at -60 °C and kept at rt. The conversion of **3** was *ca.* 50 % after 1.5 h and complete after 16 h. The formation of 1,2,3,5-tetrafluorobenzene and 3,4,5-$C_6H_2F_3OS(O)_2CF_3$ as the only aromatic compounds was confirmed by $^{19}$F NMR. The reaction mixture was poured onto ice, the products were extracted with dichloromethane and the extracts were dried with $MgSO_4$. The $^{19}$F NMR spectrum showed the presence of 1,2,3,5-tetrafluorobenzene and 3,4,5-$C_6H_2F_3OS(O)_2CF_3$ (18 : 82) (quantitative total yield). The latter compound was characterized by the $^{19}$F resonances at -130.6 (F-3,5), -159.6 (F-4) and -73.0 ($OSO_2CF_3$) ppm [*J*, Hz: (2,3) 7.2, (2,4) 5.5 and (3,4) 20.3] and the $^1$H resonance at 7.07 ppm. The mass spectrum of the mixture contained the molecular ions *m/z* 150 [1,2,3,5-$C_6H_2F_4$]$^+$ and 280 [3,4,5-$C_6H_2F_3OS(O)_2CF_3$]$^+$.

D. A solution of [3,5-$C_6H_3F_2Xe$] [$BF_4$] (0.14 mmol) in aHF (1 ml) was kept at -30 °C for 13 h. It showed the formation of trifluorobenzene **6** (64 % conversion of **4**). At 0 °C the decomposition of **4** into **6**, Xe and $BF_3$ was complete within a few hours ($^{19}$F NMR).

*Stability of [ArXe][BF₄] solutions in MeCN or EtCN-MeCN*

A. An acetonitrile solution of **1** was kept at rt and showed 60 % conversion after 13 d and total conversion after 23 d ($^{19}$ F NMR). Products were $C_6HF_5$, $(C_6F_5)_2$ (10 : 1), $C_6F_6$ (traces) besides an unidentified compound $C_6F_5X$ [$\delta$(F): -143.38 (F-2,6), -153.10 (F-4) and -161.26 (F-3,5) ppm)]. The broad resonance at *ca.* -149 ppm was assigned to fluorine bonded to boron, presumably $[BF_4]^-$.

B. A solution of [3,4,5-$C_6H_2F_3Xe$] [$BF_4$] (0.08 mmol) in MeCN (0.25 ml) was kept at rt for 18 h. The $^{19}$F NMR spectrum confirmed the total decomposition of **3** and the formation of 1,2,3,5-tetrafluorobenzene (yield 14 %) besides a number of unidentified products.

C. Compound [3,5-$C_6H_3F_2Xe$] [$BF_4$] (0.14 mmol) was dissolved in EtCN - $CD_3CN$ (3 : 1) (0.5 ml) at -60 °C. No changes were observed within 7 h at this temperature, but warming to -30 °C caused the quantitative decomposition of **4** and the formation of 1,3,5-trifluorobenzene as the main aromatic product ($^{19}$F NMR).

*Stability of [ArXe][BF₄] in CH₂Cl₂ suspensions*

A. A suspension of [3,4,5-$C_6H_2F_3Xe$] [$BF_4$] (0.08 mmol) in $CH_2Cl_2$ (0.25 ml) was agitated at rt for 5 d. The $^{19}$F NMR spectrum showed the total decomposition of salt **3** and the formation of 1,2,3,5-tetrafluorobenzene besides traces of unidentified products.

B. Compound [3,5-$C_6H_3F_2Xe$] [$BF_4$] (0.14 mmol) was suspended in $CH_2Cl_2$ (0.5 ml) at -60 °C and agitated at rt. The quantitative conversion of **4** into 1,3,5-trifluorobenzene was observed within 2 h ($^{19}$F NMR).

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