

Distinct reactivities of *cis*- and *trans*-R_FCF=CFBF₂ towards XeF₂ and the first synthesis of a [*trans*-R_FCF=CFXe]⁺ salt

 Hermann-Josef Frohn^{a*} and Vadim V. Bardin^b
^a Department of Chemistry, Inorganic Chemistry, University of Duisburg-Essen, D-47048 Duisburg, Germany.

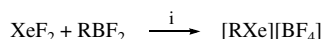
Fax: +49 203 379 2231; e-mail: h-j.frohn@uni-due.de

^b N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation

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The competitive reaction of C₄F₉CF=CFBF₂ (*cis*:*trans* = 1.2:1) with XeF₂ demonstrated for the first time a remarkably lower reaction rate of the *trans* isomer with respect to the *cis* isomer in the xenoborylation reaction (formation of the [C₄F₉CF=CFXe]⁺ cation with a *cis*:*trans* ratio of 2.5 to 4:1) and allowed us to develop reaction conditions for the syntheses of [*trans*-C₄F₉CF=CFXe]⁺ salts.

We have developed a widely applicable method to synthesise organoxenonium(II) salts [RXe][Y]. Using the reaction of XeF₂ with (organo)difluoroboranes RBF₂, we were able to prepare a representative series of organoxenonium salts with R = aryl, alkenyl and alkynyl groups following Scheme 1.^{1–4}



Scheme 1 Conditions: i, CH₂Cl₂, 1,1,1,3,3-pentafluoropropane (PFP), or SO₂FCl, –65 to –30 °C.

However, the reactivity of alk-1-enyldifluoroboranes XCF=CFBF₂ towards XeF₂ diverged from the pattern described in Scheme 1. When X was F, *cis*-C_nF_{2n+1} (*n* = 1, 2) and *trans*-H, the corresponding alkenylxenon(II) salts were formed. In case of X = *trans*-C_nF_{2n+1} (*n* = 1, 4), the perfluoroalkenyldifluoroborane starting compound was slowly consumed, but no organoxenonium salts were detected among the reaction products.² This was surprising because the *trans* configuration was realised in the structurally related perfluorocyclohexa-1,4-dien-1-yl-xenonium and perfluorocyclohex-1-enylxenonium salts, which were obtained by the oxidative fluorine addition to [C₆F₅Xe][Y] as relatively stable compounds.⁵ Furthermore, the closely related reaction of *trans*-CF₃CF=CFBF₂ with other hypervalent F–E–F moieties such as in 4-FC₆H₄IF₂ yielded smoothly the corresponding iodonium salt [(4-FC₆H₄)(*trans*-CF₃CF=CF)I][BF₄].⁶ We have assumed that the formation of [*trans*-XCF=CFXe][Y] from *trans*-XCF=CFBF₂ and XeF₂ is sterically hindered when X represents a bulky substituent (perfluoroalkyl group). In such cases, competitive side-processes (oxidative fluorination *etc.*) became predominant.²

The relative rate of xenoborylation [the formal replacement of the difluoroboryl group by xenon(+)] of *cis*- and *trans*-perfluoroalk-1-enyldifluoroboranes can be estimated by reacting an equimolar mixture of both isomers with XeF₂. For this competitive reaction, we prepared a solution of C₄F₉CF=CFBF₂ (*cis*:*trans* = 1.2:1) (**1**) in CH₂Cl₂,[†] and treated it with a solution of xenon difluoride in 1,1,1,3,3-pentafluoropropane (PFP) at –35 to –40 °C. After 1 h, the mixture of *cis*-perfluorohex-1-enylxenon(II) (*cis*-**2**) and *trans*-perfluorohex-1-enylxenon(II) (*trans*-**2**) salts (molar ratio of 4:1) was precipitated, and a white solid was isolated. The opposite order of mixing the reagents, the addition of **1** to XeF₂ in PFP, gave a mixture of *cis*-**2** and

trans-**2** in the molar ratio 2.5:1[‡] (Scheme 2). The way how the ratio of isomers in the product depends on the order of mixing shows that, in case of a local excess of the borane starting material, *trans*-C₄F₉CF=CFBF₂ is faster consumed in a by-reaction competing with xenoborylation than the *cis* isomer.

[†] A solution of *cis*-**1** and *trans*-**1** was prepared in a quantitative yield by bubbling BF₃ (in an excess) into a cold (–45 °C) stirred suspension of K[C₄F₉CF=CFBF₃] (*cis*:*trans* = 1.3:1)⁸ in CH₂Cl₂ or PFP and subsequent decantation of the mother liquor from insoluble K[BF₄]. The NMR spectra of *trans*-**1** coincided with the reported one.^{2,9}

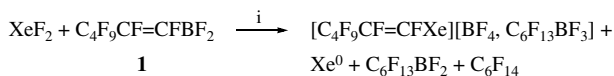
cis-**1**: ¹¹B NMR (PFP, 0 °C) δ: 19.3 (br. s). ¹⁹F NMR (PFP, 0 °C) δ: –79.9 [tt, 3F, F(6), ³J_{F(6)–F(5)} 2 Hz, ⁴J_{F(6)–F(4)} 10 Hz], –82.3 (s, 2F, BF₂), –115.0 [m, 2F, F(3)], –122.2 [m, 2F, F(4)], –122.4 [m, F, F(2)], –124.8 [m, 2F, F(5)], –145.1 [m, 1F, F(1)].

[‡] A cold (5 °C) solution of XeF₂ (160 mg, 0.95 mmol) in PFP (1.5 ml) was added to a cold (–40 °C) stirred solution of *cis*-**1** (0.33 mmol) and *trans*-**1** (0.27 mmol) in CH₂Cl₂ (1.5 ml). A white suspension was formed and stirred at –35 °C for 1 h, the mother liquor was decanted, the solid residue was washed with cold (–30 °C) PFP (1.5 ml) and dried in a vacuum at –25 °C for 30 min to give a white solid mixture of **2** (55 mg) (*cis*:*trans* = 4:1) ([BF₄][–]: [C₆F₁₃BF₃][–] = 1:3). The mother liquor contained *cis*-C₄F₉CF=CFH (0.03 mmol), *trans*-C₄F₉CF=CFH (0.08 mmol), C₆F₁₃BF₂ (0.08 mmol), C₆F₁₄ (0.11 mmol), CH₂FCl and CHF₂Cl (¹⁹F NMR). Similarly, **2** (144 mg) (*cis*:*trans* = 2.5:1) ([BF₄][–]: [C₆F₁₃BF₃][–] = 2:1) was obtained by the addition of *cis*-**1** (0.31 mmol) and *trans*-**1** (0.26 mmol) in PFP (2 ml) to XeF₂ (113 mg, 0.66 mmol) in PFP (1 ml). Salts *trans*-**2** ([BF₄][–]: [C₆F₁₃BF₃][–] = 15:85) (110 mg) were obtained by the addition of *trans*-**1** (0.77 mmol) in PFP (2.5 ml) to XeF₂ (135 mg, 0.79 mmol) in PFP (2 ml) at –40 °C and working up after stirring for 4 h (88% conversion of *trans*-**1**; the yields of C₆F₁₃BF₂ and C₆F₁₄ were 0.08 and 0.20 mmol, respectively).

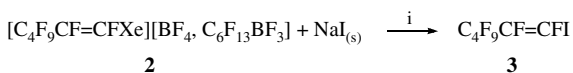
2: ¹⁹F NMR (aHF, –20 °C) δ: –71.8 [dd*, 1F, F(1), ³J_{F(1)–F(2)} 72 Hz, ²J_{F(1)–Xe} 146 Hz], 79.4 [t, 3F, F(6), ⁴J_{F(6)–F(4)} 10 Hz], –112.6 [tdd*, 2F, F(3), ⁴J_{F(3)–F(5)} 13 Hz, ³J_{F(3)–F(2)} 13 Hz, ⁴J_{F(3)–Xe} 53 Hz], –117.7 [dd*, 1F, F(2), ³J_{F(2)–F(1)} 72 Hz, ³J_{F(2)–Xe} 180 Hz], –120.6 [m, 2F, F(4)], –124.2 [m, 2F, F(5)] (*cis*-**2**); –79.5 [t, 3F, F(6), ⁴J_{F(6)–F(4)} 10 Hz], –86.9 [tdd*, 1F, F(1), ⁴J_{F(1)–F(3)} 25 Hz, ³J_{F(1)–F(2)} 123 Hz, ²J_{F(1)–Xe} 161 Hz], –114.6 [ddt, 2F, F(3), ⁴J_{F(3)–F(1)} 25 Hz, ³J_{F(3)–F(2)} 12 Hz, ⁴J_{F(3)–F(5)} 12 Hz], –121.4 [m, 2F, F(4)], –124.4 [m, 2F, F(5)], –133.1 [d, 1F, F(2), ³J_{F(2)–F(1)} 123 Hz] (*trans*-**2**); –79.6 [t, 3F, F(6), ⁴J_{F(6)–F(4)} 10 Hz], –120.1 (m, CF₂), –120.9 (m, CF₂), –121.6 (m, CF₂), –124.4 [m, 2F, F(5)], –132.2 [m, 2F, F(1)], –147.7 (br. s, BF₃) ([C₆F₁₃BF₃][–]), 147.7 (br. s) ([BF₄][–]). ¹²⁹Xe NMR (aHF, –20 °C) δ: –3413 [ddt, ²J_{Xe–F(1)} 148 Hz, ³J_{Xe–F(2)} 183 Hz, ⁴J_{Xe–F(3)} 55 Hz] (*cis*-**2**); –3495 [dd, ²J_{Xe–F(1)} 162 Hz, ³J_{Xe–F(2)} 50 Hz] (*trans*-**2**). ¹¹B NMR (aHF, –20 °C) δ: –0.6 (br. s, [C₆F₁₃BF₃][–]), –2.2 (s, [BF₄][–]).

The procedure where a Lewis acid (borane) was added to the fluorobase (XeF_2) allowed to obtain *trans*-perfluoroalk-1-enyl-xenonium salts for the first time.

The composition of the *cis/trans* mixture of **2** was unambiguously proved by multinuclear magnetic resonance spectroscopy[§] and by conversion to corresponding 1-iodoperfluorohex-1-enes using NaI in aHF⁷ (Scheme 3).[¶]



Scheme 2 Conditions: i, CH_2Cl_2 or PFP, -35°C , 1–1.5 h.



Scheme 3 Conditions: i, aHF, -60°C .

[§] The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (^{19}F at 282.40 MHz, ^{129}Xe at 83.46 MHz). The chemical shifts were referenced to CCl_3F (^{19}F) [with C_6F_6 as a secondary reference, δ : 162.9] and XeOF_4 (^{129}Xe) [with XeF_2 as a secondary reference, $\text{XeF}_2/\text{MeCN}/24^\circ\text{C}$ ($c \rightarrow 0$), δ : -1813.28]. As a convention, the multiplicities of the ^{19}F NMR signals caused by couplings with the ^{129}Xe nucleus (satellites) are denoted by (*).

[¶] Anhydrous NaI (in an excess) was added to a cold (-60°C) stirred solution of **2** (*cis:trans* = 4:1) in aHF (0.7 ml) and caused immediate gas evolution and a pink colouration. The products were extracted with cold (-60°C) CH_2Cl_2 (0.5 ml). The ^{19}F NMR spectrum showed the quantitative conversion of **2** to $\text{C}_4\text{F}_9\text{CF}=\text{CFI}$ **3**.

3: ^{19}F NMR (CH_2Cl_2 , -20°C) δ : -81.8 [t, 3F, F(6), $^4J_{\text{F}(6)-\text{F}(4)}$ 10 Hz], -82.7 [d, 1F, F(1), $^3J_{\text{F}(1)-\text{F}(2)}$ 7 Hz], -114.8 [td, 2F, F(3), $^4J_{\text{F}(3)-\text{F}(5)}$ 12 Hz, $^3J_{\text{F}(3)-\text{F}(2)}$ 12 Hz], -124.4 [m, 2F, F(4)], -127.4 [m, 2F, F(5)], -130.1 [m, 1F, F(2)] (*cis-3*); -81.9 [t, 3F, F(6), $^4J_{\text{F}(6)-\text{F}(4)}$ 9 Hz], -107.4 [ttd, 1F, F(1), $^5J_{\text{F}(1)-\text{F}(4)}$ 6 Hz, $^4J_{\text{F}(1)-\text{F}(3)}$ 26 Hz, $^3J_{\text{F}(1)-\text{F}(2)}$ 150 Hz], -118.0 [m, 2F, F(3)], -125.7 [m, 2F, F(4)], -127.5 [m, 2F, F(5)], -146.2 [d, 1F, F(2), $^3J_{\text{F}(2)-\text{F}(1)}$ 150 Hz] (*trans-3*)¹⁰ (*cis:trans* = 4:1).

This result demonstrated that $[\text{trans-R}_\text{F}\text{CF}=\text{CFXe}][\text{Y}]$ salts are principally accessible to xenoborylation. Thus, we changed our earlier applied conditions for the reaction of *trans-1* with XeF_2 ² and were able to isolate individual salt *trans-2*. In case of *trans-R}_\text{F}\text{CF}=\text{CFBF}_2, a diminished rate of xenoborylation is combined with a larger relative contribution of by-reactions, mainly oxidative fluorination reactions with polarised XeF_2 .² For comparison, both boranes, *cis*- and *trans*- $\text{ClCF}=\text{CFBF}_2$, with the sterically less demanding substituent Cl underwent xenoborylation with equal rates.² The replacement of the α -fluorine atom in $\text{CF}_2=\text{CFBF}_2$ by the more bulky CF_3 group did not affect the rate of xenoborylation.³*

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