Electrophilic Oxygenation with XeF$_2$ - H$_2$O in Hydrogen Fluoride, Part 1. Oxygenation of [C$_6$F$_5$Xe]$^+$ [AsF$_6$]$^-$ and Epoxidation of Fluorinated Cycloalkenylxenon(II) Salts

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Dedicated to Prof. Dr. M. Herberhold on the occasion of his 60th birthday

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Xenon Difluoride, (Pentafluorophenyl)xenon(II), (Pentafluoro-1,4-cyclohexadien-3-on-1-yl)xenon(II), (Pentafluoro-4,5-epoxy cyclohexen-3-on-1-yl)xenon(II), Electrophilic Oxygenation

XeF$_2$ and H$_2$O react with [C$_6$F$_5$Xe]$^+$ [AsF$_6$]$^-$ in HF without Xe-C bond cleavage under formation of the cyclohexadienone compound [3-O-1,4-C$_6$F$_5$Xe]$^+$ [AsF$_6$]$^-$ The FC=CF moiety in this diene is epoxidised with the same reagent. The cyclohexadiene compound [1,4-C$_6$F$_5$Xe]$^+$ [AsF$_6$]$^-$ could also be epoxidised under the same conditions.

Introduction

The fluorination of organic compounds with xenon difluoride is well documented [1]. Reactions of XeF$_2$ with aromatic, polyfluoroaromatic and unsaturated substrates in the presence of Lewis acids (HF, BF$_3$, SbF$_5$ or NbF$_5$) usually lead to fluoro-deprotonation of C-H bonds, or two fluorine atoms are added to C-C double bonds. When alkenes react with XeF$_2$, methanol and HF or BF$_3$ - OEt$_2$, fluoromethylation of the C-C double bond takes place [2]. In the last case the intermediate formation of unstable [FXeOME] or related species was postulated rather than the formation of hypofluorite MeOF. To our knowledge, the reactivity of the system XeF$_2$ - H$_2$O in HF towards organic substrates has not yet been investigated.

Recently we have published the first preparation of (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) and (nonafluorocyclohexen-1-yl)xenon(II) hexafluorarsenates by fluorination of (pentafluoro phenyl)xenon(II) hexafluorarsenates 1 with xenon difluoride in anhydrous HF [3]. Until now this reaction is the only example of a transformation of the organic moiety bonded to xenon without C-Xe bond cleavage.

From electrostatic arguments it can be expected that the positively charged xenon atom in the [C$_6$F$_5$Xe]$^+$ cation should make the interaction of the pentafluorophenyl group with electrophiles more difficult or should inhibit it.

In the course of our systematic investigations in organoxenon chemistry, the interaction of arylxenon(II) salt 1 with the system XeF$_2$ - H$_2$O in HF was studied [4].

Results and Discussion

Treatment of (pentafluorophenyl)xenon(II) hexafluoroarsenate 1 with a slight excess of xenon difluoride and water in HF leads to the formation of two new organoxenon(II) compounds, (pentafluoro-1,4-cyclohexadien-3-on-1-yl)xenon(II) hexafluoroarsenate 2, together with a small amount of (pentafluoro-4,5-epoxy cyclohexen-3-on-1-yl) xenon(II) hexafluoroarsenate 3. The latter substance is the only fluoroorganylxenon(II) product when the reaction mixture is treated with an additional equivalent of XeF$_2$ and water at room temperature, but the epoxyhexenone 3 did not undergo any further reaction when treated with an excess of xenon difluoride and water.

The success of the preparation of the dieneone 2 from 1 depends strongly on the reaction conditions. 2 was obtained by addition of xenon difluoride to

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a solution of 1 and $\text{H}_2\text{O}$ in HF at $-10^\circ\text{C}$ or, alternatively, by addition of a freshly prepared solution of $\text{XeF}_2$ in HF containing $\text{H}_2\text{O}$ to a solution of 1 in anhydrous HF at $-10^\circ\text{C}$. In both cases the resulting reaction mixture was subsequently warmed to ambient temperature. When a solution of $\text{XeF}_2$ and $\text{H}_2\text{O}$ (2 equivalent) in HF was maintained at $-10^\circ\text{C}$ for 1 h, gas slowly evolved. After the completion of the gas evolution and disappearance of $\text{XeF}_2$ resonances in the $\text{^19F}$ NMR spectrum no reaction had taken place with $[\text{C}6\text{F}5\text{Xe}]^+$ $[\text{AsF}_6]^-$. But when a new portion of $\text{XeF}_2$ was added, the conversion of 1 into dienone 2 proceeded.

\[
\text{F} \quad \text{Xe}^+ [\text{AsF}_6]^- + \text{XeF}_2 + \text{H}_2\text{O} \quad \text{HF} \quad \text{Xe}^+ [\text{AsF}_6]^- \quad \text{XeF}_2 + \text{H}_2\text{O} \quad \text{Xe}^+ [\text{AsF}_6]^- \quad \text{XeF}_2 + \text{H}_2\text{O} \quad \text{Xe}^+ [\text{AsF}_6]^- 
\]

It should be noted that the solution of $\text{XeF}_2$ in HF is unstable in the presence of water. At $-40^\circ\text{C}$ decomposition proceeds slowly, and after 22 h the volume of evolved gas is ca. 86% of the theoretically expected amount of $\text{Xe}^0$. Simultaneously with the gas evolution the intensity of the $\text{XeF}_2$ resonance in the $\text{^19F}$ NMR spectrum is diminished. The resulting solution displays a correspondingly decreased oxygenation reactivity. When the solution is allowed to react with 1 (0.66 equivalent with respect to 1 equivalent of the initial amount of $\text{XeF}_2$), only approximately 20% of 1 is converted into the dienone 2. Nevertheless, nearly total conversion of $[\text{C}6\text{F}5\text{Xe}]^+$ $[\text{AsF}_6]^{-}$ is achieved by the introduction of a new portion of $\text{XeF}_2$ into the solution. No fluorination (addition of fluorine atoms) of the pentafluorophenyl ring of 1, or of the C=C double bonds of 2 was observed.

The results allow assumptions about the nature of the reactive species in this new oxygenation reaction. The intermediate may be $\text{HOF}$, $\text{H}_2\text{O}_2$ (or their protonated forms $[\text{H}_2\text{OF}]^+$ and $[\text{H}_2\text{O}_2]^+$), or electrophilic xenon-oxygen species. Hydrolysis of xenon difluoride in water proceeds via the intermediate formation of $\text{H}_2\text{O}_2$ [5]. The reaction of $[\text{XeF}]^+ [\text{MF}_6]^- (\text{M} = \text{Sb, As})$ with water in HF at $-60^\circ\text{C}$ yields the salt $[\text{H}_2\text{OF}]^+ [\text{MF}_6]^- [6]$. Interaction of this salt with an excess of water gives the $[\text{H}_2\text{O}_2]^{+}$ cation. However, 1 does not react with 30 or 90% $\text{H}_2\text{O}_2$ in HF at room temperature either in the presence of a Lewis acid (NbF$_5$) nor without one. After addition of xenon difluoride to the solution containing 30% $\text{H}_2\text{O}_2$, the formation of 2 was observed. Salts of the monofluorooxonium cation $[\text{H}_2\text{OF}]^{+}$ and $\text{HOF}$ are stable in HF at $-40^\circ\text{C}$ [6]. If these oxyfluorides would be the reactive intermediates, the formation of 2 from 1 should be expected after consumption of $\text{XeF}_2$ at least at $-40^\circ\text{C}$. But this was not observed. It seems more probable that the key reactive species is an unstable xenon-oxygen containing intermediate like $[\text{HOXe}]^+ \cdot [\text{FHF}]^-$, or a structurally related oxidant which reacts as an "HO" equivalent. The situation may be compared with reactions of the cation $[\text{FXe}]^+$ which is the equivalent of "F" in many chemical processes.

\[
\text{F} \quad \text{Xe}^+ [\text{AsF}_6]^- + \text{XeF}_2 + \text{H}_2\text{O} \quad \text{HF} \quad \text{Xe}^+ [\text{AsF}_6]^- \quad \text{XeF}_2 + \text{H}_2\text{O} \quad \text{Xe}^+ [\text{AsF}_6]^- \quad \text{XeF}_2 + \text{H}_2\text{O} \quad \text{Xe}^+ [\text{AsF}_6]^- 
\]

The similarity of both electrophilic oxidative processes was demonstrated by the fluorination of 1 with $\text{XeF}_2$ - HF (without water) [3] and by the epoxidation of the (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) salt 4 [3] to (heptafluoro-4,5-epoxycyclohexen-1-yl)xenon(II) hexafluoroarsenate 5 (in the presence of $\text{H}_2\text{O}$). The inertness of the FC=CXe+ moieties in all alkenylxenon(II) salts 2, 3 and 5 as well as in (nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenate 6 toward reactions with $\text{XeF}_2$ - $\text{H}_2\text{O}$ in HF is noteworthy.
The new alkenylxenon(II) derivatives 2, 3, and 5 are stable at room temperature as solids as well as in HF solution. Fast decomposition was observed when epoxihexene 3 was dissolved in MeCN at -10 to 20 °C. For reliable identification, 2 was converted into the known 1-bromopentafluoro-1,4-cyclohexadien-3-one 7 by the reaction with NaBr. Previously such regioselective replacement of xenon by bromine was performed on diene 4 [3] and 1 [7].

The 19F NMR spectrum of diene 2 in HF displays resonances at -88.9 (F-2), -96.7 (F-6,6), -130.2 (F-5), and -147.2 (F-4) ppm. The signal of atom F-2 shows satellites due to 19F-129Xe coupling \[^3J(19F-2)(129Xe) = 70.0 \text{ Hz}\]. The other J(FF) values are 3.5 (2,4), 5.8 (2,5), 8.3 (2,6), <1 (4,5), 8.9 (4,6) and 22.6 (5,6) Hz. The 19F NMR spectrum of epoxihexene 3 (HF, -10 °C) exhibits resonances at -82.3 (F-2), -95.1 (F-6A), -101.2 (F-6B), -166.3 (F-5), and -168.7 (F-4) ppm; \[^3J(19F-2)(129Xe) = 73.9 \text{ Hz}\], \(^{129Xe}(FF) = 9.0 \text{ (2,4), 8.4 (2,6A), 9.0 (2,6B), 18.1 (4,5), 4 (4,6B), 17.3 (5,6A), 14.0 (5,6B), 284 (6A, 6B) Hz}\]. A similar, but more complex spectrum is found for epoxihexene 5: The resonances of the fluorine atoms are located at -84.8 (F-2), -95.1 (F-6A), -101.0 (F-6B), -107.1 (F-3A), -119.4 (F-3B), -166.2 (F-5) and -170.5 (F-4) ppm; \[^3J(19F-2)(129Xe) = 74.0 \text{ Hz}\], \(^{129Xe}(FF) = 25.5 \text{ (2,3A), 20.3 (2,3B), 9 (2,4), 8.5 (2,6), 299 (3A,3B), 15.8 (3A,4), 11.5 (3B,4), 3.5 (3B,5), 15 (4,5), 16.5 (5,6A), 13 (5,6B), 281 (6A, 6B) Hz}\]. All 19F NMR spectra contain also the very broad resonance of the AsF6\(^{-}\) anion centred at -65 to -68 ppm.

The 129Xe NMR spectra of the alkenylxenon(II) hexafluoroarsenates 2, 3 and 5 as measured in HF (-10 °C) show doublets at -2352.4, -2336.5 and 2321.1 ppm, respectively. The corresponding coupling constants \(^3J(129Xe)(19F-2)\) are 70.5 ± 1.5, 72.0 ± 1.5 and 71.4 ± 0.6 Hz. The comparison of these \(\delta(129Xe)\) and \(J(19F)(129Xe)\) values with those of diene 4 \(\delta(129Xe) = -2348.5 \text{ ppm}, \quad ^3J(129Xe)(19F-2) = 68.1 \text{ Hz}\) and (nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenane 6 \(\delta(129Xe) = -2294.6 \text{ ppm}, \quad ^3J(129Xe)(19F-2) = 69.7 ± 1.1 \text{ Hz}\) in HF [3] shows that the replacement of two fluorine atoms in position 3 by oxygen affects the 129Xe chemical shift only slightly, while the epoxidation of the FC=CF moiety of diene 4 and diene 2 leads to a more remarkable high-frequency shift of the 129Xe resonances.

**Experimental**

The NMR spectra were measured on Bruker spectrometers: WP 80 SY 19F at 75.40 and 129Xe at 22.17 MHz and DRX 500 129Xe at 138.87 MHz (CaF\(_6\) internal and XeF\(_2\)/HF external references). The chemical shifts \(\delta(19F)\) were related to CFCl\(_3\) \(\delta(19F)\) (\(\delta(19F) = -162.9 \text{ ppm}\)).

The salt [CaF\(_6\)Xe\(^{19}\)]\(^{+}\) [AsF\(_6\)\(^{-}\)] 1 was prepared as described previously [8], HF was freshly distilled from ca. 5% SbF\(_5\) - HF solution using a PTFE-FEP equipment. All experiments were performed in FEP tubes.

**Reaction of [CaF\(_6\)Xe\(^{19}\)]\(^{+}\) [AsF\(_6\)\(^{-}\)] 1 with XeF\(_2\) - H\(_2\)O in HF**

Method A. A solution of 1 (160 mg, 0.328 mmol) in HF (1 ml) was cooled to -10 °C and water (14 mg, 0.777 mmol) was introduced. Xenon difluoride (97 mg, 0.574 mmol) was added in portions. After each addition the reactor was kept at room temperature till completion of xenon evolusion. Finally the reaction mixture was kept at 20 - 22 °C for 20 min. The 19F NMR spectrum showed the complete conversion of 1 into 2 and 3 (traces). The excess of XeF\(_2\) was destroyed by addition of CaF\(_6\), which underwent electrophilic oxygenation in the presence of H\(_2\)O (see part 2). After evaporation of HF and of the volatile by-products in vacuum the residue was washed with cold CH\(_2\)Cl\(_2\) and dried in vacuum. 151 mg (91 %) of colourless solid 2 were isolated.

Method B. Xenon difluoride (17 mg, 0.100 mmol) was dissolved at -20 °C in 0.2 ml HF containing 5 mg (0.277 mmol) of H\(_2\)O. This solution was immediately transferred to the solution of 1 (50 mg, 0.102 mmol) in HF (0.1 ml), and the resulting solution was kept at 20 - 22 °C for 10 min. The conversion of 1 into diene 2 was ca. 20 % (19F NMR). The addition of the next portion of XeF\(_2\) (total amount 34 mg, 0.201 mmol) led to the formation of 2 and 3 (1 : 0.4, mol), some residual 1 being left in traces.

Method C. Water (12 mg, 0.666 mmol) was added to the solution of XeF\(_2\) (70 mg, 0.414 mmol) in HF (0.15 ml) at -40 °C. No reaction was observed within 20 min (19F NMR). Gas evolution proceeded when this solution was warmed to -10 °C. After 1 h the resonance of XeF\(_2\) disappeared in the 19F NMR spectrum. After dissolution of 1 (80 mg, 0.164 mmol) no reaction was detected during 12 h at 20 - 22 °C. When a new portion of XeF\(_2\) (43 mg,
0.254 mmol) was added, dienone 2 and traces of 1 and 3 were formed.

Method D. A solution of XeF₂ (48 mg, 0.284 mmol) and H₂O (10 mg, 0.556 mmol) in HF (0.2 ml) was kept at -40 °C for 22 h. The measured volume of the evolved gas was 5.5 ml (86 % of the theoretical amount of Xe²⁰).

The ¹⁹F NMR spectrum showed only a residual amount of XeF₂. 1 (92 mg, 0.189 mmol) was added and the resulting solution was warmed to ambient temperature. After 3 - 5 min the reaction was complete and give a mixture of 1 and 2 (10 : 3, mol).

Method E. The solution of 1 (80 mg, 0.164 mmol) and H₂O (6 mg, 0.330 mmol) in HF (0.1 ml) was treated with XeF₂ (90 mg, 0.532 mmol) as described above (method A) to give 3 (61 mg, 72 % yield) as a glassy colourless solid after removing the excess XeF₂ with C₆F₆ and evaporation of the volatile products in a vacuum at room temperature.

Method F. The solution of 1 (50 mg, 0.102 mmol) and H₂O (15 mg, 0.816 mmol) in HF (0.15 ml) was kept at room temperature for 7 d. No reaction took place, and the chemical shifts in the ¹⁹F NMR spectrum were the same as in anhydrous HF. Addition of XeF₂ (21 mg, 0.124 mmol) caused gas evolution with complete consumption of xenon difluoride and ca. 50 % conversion of 1 to diene 2.

**Epoxidation of diene 4**

1 (90 mg, 0.184 mmol) was fluorinated with XeF₂ (36 mg, 0.213 mmol) in anhydrous HF (0.2 ml) as described in [3] to give 4 and a residual amount of 1 (86 : 14, mol). This solution was treated with H₂O (7 mg, 0.389 mmol) and XeF₂ (30 mg, 0.177 mmol) to yield 5, 6 and 4 (74, 11 and 15 mol %, respectively, determined by ¹⁹F NMR).

**Interaction of (nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenate 6 with XeF₂ - H₂O in HF**

A solution of 6 [3] (112 mg, 0.199 mmol) and XeF₂ (35 mg, 0.207 mmol) in HF (0.2 ml) was treated with water (5 mg, 0.278 mmol) at -5 °C. Gas evolution was complete within 10 min, but 6 did not react within 12 h at room temperature.

**Interaction of 1 with H₂O₂ in HF**

Method A. The solution of 1 (50 mg, 0.102 mmol) in HF (1.2 ml) was mixed with a solution of 30 % H₂O₂ (17 mg, 0.150 mmol of H₂O₂) in HF (0.07 ml) at -60 °C. No reaction was observed after 1 h at room temperature. Addition of NbF₅ (50 mg, 0.266 mmol) did not induce a reaction within 7 d at 20 - 22 °C. Treatment of the reaction mixture with XeF₂ (25 mg, 0.148 mmol) gave 1 and 2 (molar ratio 1 : 1, determined by ¹⁹F NMR).

Method B. 1 (75 mg, 0.154 mmol) was added to a solution of 90 % H₂O₂ (20 mg, 0.55 mmol of H₂O₂) in HF (0.1 ml) at -78 °C and then kept at room temperature for 1 h. No reaction of 1 was observed (¹⁹F NMR). Addition of NbF₅ (55 mg, 0.292 mmol) caused slow gas evolution (presumably oxygen), but arylxenon(II) salt 1 remained unchanged for 3 d.

**Reaction of 2 with NaBr**

A solution of 2 obtained from 1 (80 mg, 0.164 mmol) and XeF₂ (43 mg, 0.254 mmol) in HF (0.2 ml) was treated with dry NaBr (48 mg, 0.466 mmol) at -15 °C. When the gas evolution was complete, dichloromethane was added, and HF was evaporated at room temperature. The liquid phase was separated, the solid was washed with CH₂Cl₂ and the combined extracts analysed by ¹⁹F NMR spectrometry. The spectra indicated the formation of 1-bromopentafluoro-1,4-cyclohexadien-3-one 7 [9] (quantitative yield) (C₆H₅CF₃ as internal reference).

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