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The formation of oxygen-containing perfluorocyclohexadien -1-yliodine tetrafluorides

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Abstract

The electrophilic oxygenation of pentafluorophenyl iodo compounds $C_6F_5IF_n$ with iodine in different valencies (n = 0, 2, 4) using XeF₂-H₂O in HF allowed access to new organoiodine(V) compounds, namely isomeric oxopentafluorocyclohexadien-1-yliodine tetrafluorides, $C_6(O)F_5IF_4$. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

In 1996, we found that solutions of pentafluorobenzene derivatives (C_6F_5X) in HF formed oxopentafluorocyclohexadienes ($C_6(O)F_5X$) when treated with an equivalent amount of XeF₂ in the presence of 1–2 equivalents of water [1,2] (Scheme 1). The nature of potential reactive key intermediates such as Xe^{II}–oxygen compounds or HOF was discussed in [2]. *Formally*, this reaction can be described as an electrophilic oxygen atom is bonded to the C₆-skeleton. But *in reality* the reaction proceeded via hydroxyhexafluorocyclohexadienes as unstable intermediates. When the initial reaction steps are taken into account this process should be termed an electrophilic hydroxyfluorination.

When solutions of C_6F_5X in *anhydrous* hydrogen fluoride (aHF) reacted with XeF₂ in the absence of water, the addition of two fluorine atoms preferentially occurred to yield polyfluorinated cyclohexadienes C_6F_7X [3]. Using this method of fluorine addition, we recently prepared the previously unknown cycloalkenyliodine tetrafluorides from polyfluoroaryliodine tetrafluorides, as well as -aryliodine difluorides and -aryl iodides $C_6F_5IF_n$ (n = 0, 2, 4) [4]. When n = 0 or 2, the desired products were formed by two parallel reaction paths: the oxidative addition of fluorine to the iodine atom and the addition of fluorine to the perfluoroaryl group (Scheme 2).

Based on these experiences, we studied the electrophilic oxygenation of $C_6F_5IF_n$ (n = 0, 2, 4) with xenon diffuoride and H_2O in hydrogen fluoride as a promising route to oxygen—containing perfluorocyclohexadien-1-yliodine tetra-fluorides.

2. Results and discussion

The treatment of pentafluorophenyliodine tetrafluoride (1) in HF with XeF₂ (1.3 equivalent) and H₂O (1 equivalent) did not result in oxygenation of 1 at -25 °C, but warming to 12 °C caused the immediate evolution of xenon and the formation of 3-oxopentafluorocyclohexa-1,4-dien-1-yliodine tetrafluoride (2), 6-oxopentafluorocyclohexa-1,4-dien-1-yliodine tetrafluoride (3), 4,5-epoxypentafluorocyclohex-1-en-1-yliodine tetrafluoride (4), 3-oxo-4,5-epoxypentafluorocyclohexa-1,3-dien-1-yliodine tetrafluoride tetrafluoride (5), 5-oxopentafluorocyclohexa-1,3-dien-1-yliodine tetrafluoride (6), and 6-oxopentafluorocyclohexa-1,3-dien-1-yliodine tetrafluoride (7) (trace) in the ratio 2:3:4:5:6 = 76:6:6:6 in 77% overall yield (Scheme 3).

Oxygen-containing perfluorocycloalkenyliodine tetrafluorides 2–7 can be directly obtained from commercially available iodopentafluorobenzene (8) by in situ generation of 1. Thus, mixing of 8 with XeF₂ (2.6 equivalents) in HF at -20 °C and the subsequent addition of water (1.2 equivalents) and further

 $^{^{*}}$ Part 3 in the series "Electrophilic oxygenation with XeF₂–H₂O in hydrogen fluoride" [1].

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Scheme 1.



XeF₂ (1 equivalent) resulted in, after warming to 12–16 $^{\circ}$ C, the same products (Scheme 4).

To also extend the investigation to trivalent iodine compounds, we performed the electrophilic oxygenation of pentafluorophenyliodine difluoride (9) in two modified ways. When a solution of 9 in HF was treated with H₂O (1.3 equivalents) and XeF₂ (2.2 equivalents) at -30 °C, no gas evolution and reaction were observed, but upon warming from 5 to 20 °C, gas evolution occurred and compounds 2–7 were obtained in addition to C₆F₅IF₄ (1) (Scheme 5).

It is noteworthy that the conversion of **9** by XeF_2-H_2O in HF into products **1–7** was not inhibited by the addition of KF. Diminishing the acidity of HF by water as well as fluoride ions plays a less important role here than in the electrophilic fluorination with XeF_2 in aHF. For example, C_6F_6 did not react with XeF_2 in "basic" aHF, which contained KF, but was rapidly converted into 1,4- C_6F_8 in the absence of KF [10].

3. Conclusions

The ratio of 3-oxo- to 6-oxopentafluorocycloalkenes (2 + 5 + 6):(3 + 7) = 88:12 establishes that carbon atoms C-3 or C-5 of **1** are the predominant sites of reaction. This finding is very similar to the electrophilic oxygenation (hydroxyfluorination) of other pentafluorobenzene derivatives (C₆F₅X) bearing



electron-withdrawing substituents X = Cl, Br, CF₃, Me₃N⁺ [1], Xe⁺ [2].

Reactions of C_6F_5I or $C_6F_5IF_2$ with either XeF₂ in aHF or XeF₂–H₂O in HF yield organoiodine(V) tetrafluorides (mainly, cycloalkenyl derivatives). Although the relative contribution of routes A and B (Scheme 6) has not been determined, the exclusive formation of $C_6F_5I(OR)_2$ from C_6F_5I and the strong oxidants CF₃C(O)OOH or 100% HNO₃/(CF₃C(O))₂O (R = C(O)CF₃) [5,6] or (CF₃)₃COCl (R = OC(CF₃)₃) [7] allows one to assume the preference of route A over B at least for iodopentafluorobenzene.

4. Experimental details

The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (¹⁹F at 282.40 MHz) at 24 °C. The chemical shifts are referenced to CCl₃F (¹⁹F) [with C₆F₆ as secondary reference (-162.9 ppm)]. The molar composition of the reaction mixtures and the yields of products were determined by ¹⁹F NMR spectroscopy using the quantitative internal standard 1,1,2-trichlorotrifluoroethane (Merck).

 $C_6F_5IF_2$ was prepared by low-temperature fluorination of C_6F_5I in CCl_3F [8]. $C_6F_5IF_4$ was obtained by the reaction of IF_5 with $Bi(C_6F_5)_3$ in MeCN [9]. Iodopentafluorobenzene (Bristol Organics) was used as supplied.





Scheme 5.



All manipulations were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment under an atmosphere of dry argon.

4.1. Reaction of $C_6F_5IF_4$ (1) with XeF_2 and H_2O in HF

Pentafluorophenyliodine tetrafluoride (84 mg, 0.22 mmol) was suspended in aHF (2.5 mL) at -25 °C, and a cold (-25 °C) solution of water (4 mg, 0.22 mmol) in HF (0.5 mL) was added. The suspension was stirred for 5 min before XeF₂ (49 mg, 0.29 mmol) was added in one portion. The reaction mixture was allowed to warm to $-17 \,^{\circ}$ C over a 1 h period. When the reactor was placed in a 12 °C cold bath, gas evolution was observed. Stirring was continued for 1 h and the temperature was raised to 16 °C. The suspension was cooled to 0 $^{\circ}$ C and C₆F₆ (ca. 0.05 mL) was added to consume excess XeF₂. The reactor was maintained at 18-20 °C for 15 min. After cooling to -5 °C, the products were extracted with dichloromethane (1 mL). The ¹⁹F NMR spectrum showed the formation of 2 (0.13 mmol), 3 (0.01 mmol), 4 (0.01 mmol), 5 (0.01 mmol), and 6 (0.01 mmol) besides traces of 7, $C_6F_5IF_4$, and IF₅ (the amount of each was <0.01 mmol) (molar ratio 2:3:4:5:6 = 76:6:6:6:6).

3-Oxopentafluorocyclohexa-1,4-dien-1-yliodine tetrafluoride (2). ¹⁹F NMR (CH₂Cl₂): δ -6.8 (t ⁴*J*(IF₄, F⁶) = 18 Hz, d ⁴*J*(IF₄, F²) = 27 Hz, 4F, IF₄), -93.8 (m, 1F, F²), -99.7 (m, 2F, F^{6,6}), -133.3 (d ⁵*J*(F⁵, F²) = 5 Hz, d ³*J*(F⁵, F⁴) = 5 Hz, t ³*J*(F⁵, F⁶) = 23 Hz, 1F, F⁵), -152.5 (d ³*J*(F⁴, F⁵) = 5 Hz, d ⁴*J*(F⁴, F²) = 6 Hz, t ⁴*J*(F⁴, F⁶) = 10 Hz, 1F, F⁴).

6-Oxopentafluorocyclohexa-1,4-dien-1-yliodine tetrafluoride (3). ¹⁹F NMR (CH₂Cl₂): δ –9.7 (d ⁴*J*(IF₄, F²) = 24 Hz, 4F, IF₄), -107.8 (m, 1F, F²), -112.5 (d ³*J*(F³, F²) = 24 Hz, d ³*J*(F³, F⁴) = 22 Hz, d ⁴*J*(F³, F⁵) = 10 Hz, 2F, F^{3.3}), -144.8 (d ⁵*J*(F⁵, F²) = 3 Hz, d ³*J*(F⁵, F⁴) = 6 Hz, t ⁴*J*(F⁵, F³) = 10 Hz, 1F, F⁵), -146.4 (d ³*J*(F⁴, F⁵) = 6 Hz, d ⁴*J*(F⁴, F²) = 3 Hz, t ³*J*(F⁴, F³) = 22 Hz, 1F, F⁴). 4,5-Epoxypentafluorocyclohex-1-en-1-yliodine tetrafluoride (4). ¹⁹F NMR (CH₂Cl₂): δ -5.7 (d ⁴*J*(IF₄, F^{6A}) = 11 Hz, d ⁴*J*(F₄I, F^{6B}) = 24 Hz, d ⁴*J*(IF₄, F²) = 28 Hz, 4F, IF₄), -87.8 (m, d ²*J*(F^{6A}, F^{6B}) = 295 Hz, 1F, F^{6A}), -94.5 (m, 1F, F²), -110.2 (d ²*J*(F^{3A}, F^{3B}) = 302 Hz, d ³*J*(F^{3A}, F⁴) = 18 Hz, d ³*J*(F^{3A}, F²) = 29 Hz, 1F, F^{3A}), -114.2 (d ²*J*(F^{6B}, F^{6A}) = 295 Hz, 1F, F^{6B}), -123.5 (d, ²*J*(F^{3B}, F^{3A}) = 302 Hz, 1F, F^{3B}), -175.4 (d ³*J*(F⁵, F⁴) = 19 Hz, d ³*J*(F⁵, F^{6A}) = 19 Hz, d ³*J*(F⁵, F^{6B}) = 19 Hz, 1F, F⁵), -178.3 (m, 1F, F⁴).

3-Oxo-4,5-epoxypentafluorocyclohex-1-en-1-yliodine tetrafluoride (5). ¹⁹F NMR (CH₂Cl₂): δ -6.2 (d ⁴J(IF₄, F^{6A}) = 11 Hz, d ⁴J(IF₄, F^{6B}) = 24 Hz, d ⁴J(IF₄, F²) = 27 Hz, 4F, IF₄), -88.7 (d ²J(F^{6A}, F^{6B}) = 297 Hz, d ³J(F^{6A}, F⁵) = 18 Hz, quintet ⁴J(F^{6A}, IF₄) = 11 Hz, d ⁴J(F^{6A}, F²) = 10 Hz, 1F, F^{6A}), -90.5 (m, 1F, F²), -114.7 (m, 1F, F^{6B}), -173.9 (d ³J(F⁵, F⁴) = 18 Hz, d ³J(F⁵, F^{6A}) = 18 Hz, d ³J(F⁵, F^{6B}) = 18 Hz, 1F, F⁵), -174.8 (d ⁴J(F⁴, F²) = 10 Hz, d ³J(F⁴, F⁵) = 18 Hz, d ⁴J(F⁴, F^{6B}) = 2 Hz, 1F, F⁴).

5-Oxopentafluorocyclohexa-1,3-dien-1-yliodine tetrafluoride (6). ¹⁹F NMR (CH₂Cl₂): δ -8.7 (d ⁴J(IF₄, F²) = 26 Hz, t ⁴J(IF₄, F⁶) = 15 Hz, 4F, IF₄), -86.8 (m, 1F, F²), -97.7 (m, 2F, F^{6,6}),-128.9 (d ³J(F³, F²) = 5 Hz, t ⁴J(F³, F⁶) = 4 Hz, 1F, F³), -144.0 (d ⁴J(F⁴, F²) = 14 Hz, t ⁴J(F⁴, F⁶) = 8 Hz, 1F, F⁴).

6-Oxopentafluorocyclohexa-1,3-dien-1-yliodine tetrafluoride (7). ¹⁹F NMR (CH₂Cl₂): δ -11.1 (d ⁴*J*(IF₄, F²) = 22 Hz, 4F, IF₄), -90.4 (m, 1F, F²), -106.0 (d ⁵*J*(F⁵, F²) = 2 Hz, d ⁴*J*(F⁵, F³) = 12 Hz, d ³*J*(F⁵, F⁴) = 23 Hz, 2F, F^{5,5}), -133.9 (d ⁴*J*(F⁴, F²) = 23 Hz, t ³*J*(F⁴, F⁵) = 23 Hz, 1F, F⁴), -149.1 (d ³*J*(F³, F²) = 10 Hz, t ⁴*J*(F³, F⁵) = 12 Hz, 1F, F³).

4.2. Reaction of $C_6F_5I(8)$ with XeF_2 and H_2O in HF

Iodopentafluorobenzene (73 mg, 0.24 mmol) was dissolved in aHF (1.5 mL) at -30 °C and XeF₂ (107 mg, 0.63 mmol) was added in one portion. The colourless solution was stirred at -20 °C for 1 h before a cold (-25 °C) solution of water (5.5 mg, 0.30 mmol) in HF (0.5 mL) was added. After stirring at -24 to -20 °C for 15 min, a further portion of XeF₂ (48 mg, 0.28 mmol) was added and the solution was allowed to warm to -12 °C over a period of 1 h. A white suspension was formed. The reactor was placed in a 4 $^{\circ}$ C cold bath and warmed to 12 $^{\circ}$ C over a period of 1 h. The excess of XeF₂ was removed by reaction with C₆F₆ (ca. 0.05 mL). After cooling the suspension to -60 °C, the supernatant HF was decanted and residual HF was removed under vacuum at < 20 °C to yield a white solid product (81 mg). The ¹⁹F NMR spectrum of the reaction mixture in dichloromethane (1.5 mL) showed the formation of 1 (trace), 2 (0.15 mmol), 3 (0.01 mmol), 4 (0.01 mmol), 5 (0.01 mmol), 6 (0.01 mmol), and 7 (trace), besides IF₅ (0.01 mmol).

4.3. Reaction of $C_6F_5IF_2$ (9) with XeF_2 and H_2O in HF

Pentafluorophenyliodine difluoride (140 mg, 0.42 mmol) was cooled to -30 °C before a cold (-30 °C) solution of water (10 mg, 0.55 mmol) in HF (1.7 mL) was added. The solution was stirred for 5 min before XeF₂ (159 mg, 0.94 mmol) was added in one portion. The solution was stirred for an additional 5 min before the trap was placed in a 5 °C cold bath. Gas evolution occurred and a white suspension was formed. Finally, the reaction mixture was stirred at 15–20 °C for 1 h before being extracted with CH₂Cl₂ (1.5 mL) at -10 to -20 °C. The ¹⁹F NMR spectrum of the extract showed the formation of **1** (0.04 mmol), **2** (0.22 mmol), **3** (0.02 mmol), **4** (trace), **5** (trace), **6** (0.03 mmol), and **7** (0.01 mmol), in addition to IF₅ (0.04 mmol).

4.4. Reaction of $C_6F_5IF_2$ (9) with XeF_2 and $KF \cdot 2H_2O$ in HF

Pentafluorophenyliodine difluoride (65 mg, 0.20 mmol) was cooled to -25 °C and the cold (-25 °C) solution of KF·2H₂O (44 mg, 0.46 mmol) in HF (0.7 mL) was added. The solution was stirred for 5 min before XeF₂ (80 mg, 0.50 mmol) was added in one portion. The solution was stirred for an additional 5 min before the trap was placed in a bath at 1–3 °C. Gas evolution occurred and a white suspension was formed. After 15 min at 3 °C, the reaction mixture was stirred at 15–20 °C for 1 h prior to extraction with CH₂Cl₂ (0.8 mL) at 0 °C. The ¹⁹F

NMR spectrum of the extract showed the presence of 1 (0.02 mmol), 2 (0.11 mmol), 3 (0.01 mmol), 4 (trace), 5 (trace), 6 (0.01 mmol), and 7 (trace) (molar ratio 1:2:3:4:5:6:7 = 13:69:6:1:2:8:1; overall yield 80%), in addition to IF₅ (0.02 mmol).

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