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## NEW SYNTHESIS OF IF<sub>5</sub>O

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### SUMMARY

Phosphorus trifluoride oxide readily replaces two fluorine ligands in IF<sub>7</sub> for a doubly bonded oxygen atom, thereby providing a new and convenient synthesis for IF<sub>5</sub>O. Attempts to extend this method to the syntheses of either IF<sub>3</sub>O<sub>2</sub> or IFO<sub>3</sub> were unsuccessful due to competing deoxygenation reactions of the iodine oxyfluoride precursors. Furthermore, PF<sub>3</sub>O does not undergo fluorine-oxygen exchange with the NF<sub>4</sub><sup>+</sup> cation.

### INTRODUCTION

Recent work from our laboratory on fluorine-oxygen exchange reactions has shown that the nitrate ion is an excellent reagent for replacing two fluorine ligands by one doubly bonded oxygen atom in compounds such as BrF<sub>5</sub> [1, 2], XeF<sub>6</sub> [3], XeOF<sub>4</sub> [4], ClF<sub>5</sub>, ClF<sub>3</sub> and ClF [5], and IF<sub>5</sub> [6]. However, IF<sub>7</sub> did not yield IF<sub>5</sub>O but resulted in the formation of IF<sub>5</sub> and half a mol of oxygen [6]. This was unexpected since IF<sub>7</sub> is known to undergo fluorine-oxygen exchange with either silica at 100°C [7] or Cab-O-Sil [8], Pyrex [9, 10], I<sub>2</sub>O<sub>5</sub> [10] or small amounts of water [9, 10] at ambient temperature. Recently, it was shown that PF<sub>3</sub>O is also an effective reagent for accomplishing fluorine-oxygen exchange in XeF<sub>6</sub>, UF<sub>6</sub>, ClF<sub>5</sub>, and BrF<sub>5</sub> [11]. It was, therefore, interesting to examine whether IF<sub>7</sub> and PF<sub>3</sub>O undergo a fluorine-oxygen exchange reaction or are subject to deoxygenation as in the IF<sub>7</sub>-NO<sub>3</sub><sup>-</sup> case [6].

### EXPERIMENTAL

Volatile materials were handled in a stainless steel vacuum line equipped with Teflon-FEP U-traps, stainless steel bellows-seal valves, and a Heise Bourdon tube-type gauge [12].

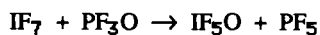
All reactions were carried out either in stainless steel containers or sapphire tubes. Infrared spectra were recorded on a Perkin Elmer Model 283 spectrometer using a 5-cm path length Teflon cell with AgCl windows for gases, and AgCl disks, pressed in an Econo press (Barnes Engineering Co.), for solids. Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser. Literature methods were used for the syntheses of IF<sub>7</sub> [8], PF<sub>3</sub>O [13], IF<sub>3</sub>O<sub>2</sub> [14], and NF<sub>4</sub>BF<sub>4</sub> [15].

### Synthesis of IF<sub>5</sub>O

A 30 ml stainless steel cylinder was passivated first with ClF<sub>3</sub> and then with PF<sub>3</sub>O. After evacuation and cooling to -196°C, the cylinder was loaded successively with IF<sub>7</sub> (1.04 mmol) and PF<sub>3</sub>O (1.10 mmol) and allowed to warm to room temperature. After five days the volatile products were removed and separated by fractional condensation in U-traps cooled to -78, -126, and -196°C. Only a small amount of non-condensable gas was observed, presumably O<sub>2</sub>. The -196°C trap contained PF<sub>5</sub> (1.03 mmol) and PF<sub>3</sub>O (0.07 mmol). The -78°C trap contained IF<sub>5</sub> (0.08 mmol), while the -126°C trap contained IF<sub>5</sub>O (0.91 mmol, 88% yield based on IF<sub>7</sub>).

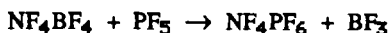
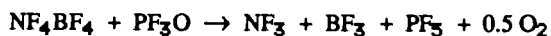
## RESULTS AND DISCUSSION

Iodine heptafluoride and PF<sub>3</sub>O readily undergo a fluorine-oxygen exchange reaction according to:



The reaction proceeds at room temperature and produces IF<sub>5</sub>O in a yield of about 90%. In addition to IF<sub>5</sub>O, small amounts of IF<sub>5</sub> and oxygen are formed due to some decomposition of IF<sub>5</sub>O. Use of an excess of PF<sub>3</sub>O does not result in further fluorine-oxygen exchange and the formation of either IF<sub>3</sub>O<sub>2</sub> or FIO<sub>3</sub>. This was confirmed by an examination of the IF<sub>5</sub>O-PF<sub>3</sub>O and the IF<sub>3</sub>O<sub>2</sub>-PF<sub>3</sub>O systems. At room temperature, no fluorine-oxygen exchange was observed, while at elevated temperatures the iodine oxyfluoride starting materials underwent deoxygenation rather than fluorine-oxygen exchange with PF<sub>3</sub>O.

Attempts to achieve fluorine-oxygen exchange in NF<sub>4</sub>BF<sub>4</sub> with PF<sub>3</sub>O did not produce any NF<sub>3</sub>O. Instead, the NF<sub>4</sub>BF<sub>4</sub> fluorinated the PF<sub>3</sub>O to PF<sub>5</sub> and oxygen, followed by a partial displacement reaction of BF<sub>4</sub><sup>-</sup> by PF<sub>5</sub>.



This result is not surprising in view of the previous findings that (+V) nitrogen exhibits a maximum coordination number of four toward fluorine [16] and  $\text{PF}_5$  can displace  $\text{BF}_3$  from  $\text{NF}_4\text{BF}_4$  [17].

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