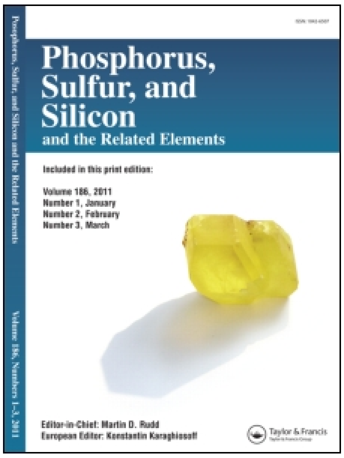

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# PREPARATION OF PENTAKIS(2,2,2-TRIFLUOROETHOXY) ARSORANE AND LITHIUM HEXAKIS(2,2,2-TRIFLUOROETHOXY) ARSENATE

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# PREPARATION OF PENTAKIS(2,2,2-TRIFLUOROETHOXY)ARSORANE AND LITHIUM HEXAKIS(2,2,2-TRIFLUOROETHOXY) ARSENATE

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Tris(2,2,2-trifluoroethyl) arsenite, **4**, has been synthesized from 2,2,2-trifluoroethanol and arsenic trichloride. When **4** was allowed to react with chlorine, pentakis(2,2,2-trifluoroethoxy)arsorane, **5**, resulted. This material reacted with lithium 2,2,2-trifluoroethoxide, **6**, to yield lithium hexakis(2,2,2-trifluoroethoxy) arsenate, **7**. A $^{75}$As NMR resonance was observed for this material.

Recently tetrakis(2,2,2-trifluoroethoxy)selenurane,[1] **1**, tetrakis(2,2,2-trifluoroethoxy)tellurane,[1] **2**, and pentakis(2,2,2-trifluoroethoxy)phosphorane,[2] **3**, were prepared. Variable temperature $^{19}$F NMR studies show that all undergo rapid intramolecular ligand reorganization at room temperature. In the case of **1** it was possible to slow this process on cooling. The other two compounds showed no change in their $^{19}$F NMR spectra over the temperature range investigated. All three substances added one equivalent of 2,2,2-trifluoroethoxide ion to give the appropriate ate complexes. It seemed of interest to extend these studies to include the corresponding arsenic analogues.

To this end tris(2,2,2-trifluoroethyl) arsenite, **4**, has been prepared from arsenic trichloride and 2,2,2-trifluoroethanol. It was thought that **4** would react with chlorine to give the unknown trialkoxydichloroarsorane. It was planned to allow this material to react with lithium 2,2,2-trifluoroethoxide[3] to give the arsorane, **5**. When the reaction mixture from the chlorination reaction was distilled, a material whose analysis corresponded to that of **5** was obtained. The mass spectrum of this material did not have a molecular ion derived from **5**. It did show an ion, $(CF_3CH_2O)_4As^+$, which is of course obtainable from **5**. The $^1$H, $^{13}$C and $^{19}$F NMR spectral data are all in agreement with those expected for **5**. Variable temperature $^{19}$F NMR studies showed no change over the temperature range investigated. These findings suggest that intramolecular ligand reorganization has a relatively low activation energy. This is not unexpected and it has been predicted.[4] Of course accidental identical chemical shift values for equatorial and apical trifluoromethyl groups cannot be excluded. A search for $^{75}$As NMR resonance was fruitless. $^{75}$As is a quadrupole nucleus, $I = \frac{3}{2}$, and its compounds are not expected to have detectable NMR resonances unless there is a high degree of electronic symmetry around the nucleus.[5]

$$\underset{\mathbf{4}}{(CF_3CH_2O)_3As} + Cl_2 \rightarrow \underset{\mathbf{5}}{(CF_3CH_2O)_5As} \xrightarrow[\mathbf{6}]{CF_3CH_2O^-} \underset{\mathbf{7}}{(CF_3CH_2O)_6As^-}$$

The mode of formation of **5** is not known. It may have formed by disproportionation of the expected mixed alkoxychloroarsorane.

Compound, **5**, was treated with 2 moles of lithium 2,2,2-trifluoroethoxide in ether. After removal of the solvent a white solid was obtained. The $^1$H, $^{19}$F and $^{13}$C NMR spectra of this material are all in agreement with the assigned structure, **7**. A $^{75}$As NMR resonance was found for this material at $\delta$ 190.3, relative to $AsF_6^-$. This resonance was broad and fine structure due to $^{19}$F coupling to $^{75}$As was not observed. The finding of such a resonance is what is expected for an octahedral ate complex.

## EXPERIMENTAL

$^1$H NMR spectra were recorded with Varian Models T-60 and FT-80 spectrometers. Chemical shift values are reported in parts per million relative to internal tetramethylsilane. $^{13}$C, $^{19}$F and $^{75}$As were recorded with a Varian Model FT-80 spectrometer equipped with a variable-temperature broad band probe. In all cases nuclei which are deshielded relative to their respective standard are assigned a positive chemical shift.

*Preparation of* **4**. To a stirred cooled, 0–5°C, solution of 32 g (0.32 mole) of triethylamine and 30 g (0.30 mole) of 2,2,2-trifluoroethanol in 400 ml of tetrahydrofuran was added 18.1 g (0.1 mole) of arsenic trichloride dropwise in an atmosphere of nitrogen over a period of 30 min. The mixture was allowed to warm to room temperature and it was stirred for two hours. After filtration under nitrogen, the filtrate was concentrated *in vacuo* and the residue was distilled, b.p. 38°C (0.45 mm) to give 27.9 g, 75% yield of **4**. Anal. Calcd. for C, 19.36; H 1.61. Found C, 19.36; H, 1.72. The $^1$H NMR, $CDCl_3$ solvent, had a quartet $\delta$ 4.26 ($^3J_{HCCF} = 8.5$ Hz). The $^{13}$C NMR, benzene-$d_6$ solvent had a quartet at $\delta$ 61.22 ($^3J_{CCF} = 36.4$ Hz) and a quartet at $\delta$ 124.34 ($^1J_{CF} = 277.4$ Hz). The $^{19}$F NMR, $CDCl_3$ solvent, had a triplet at $\delta$ $-82.22$ ($^3J_{HCCF} = 8.5$ Hz).

*Preparation of* **5**. Chlorine, ca. 1.5 g, was bubbled over 34 min. into 3.72 g of well-stirred **4** held at 0°C. After the addition of the chlorine, the mixture was stirred at 0°C for 1 hr and it was then allowed to warm to room temperature. The product was distilled, b.p. 54°C (0.1 mm) to give 3.47 g of **5**. Anal. Calcd. for C, 21.05; H, 1.75. Found C, 20.78; H, 1.8. The $^1$H NMR, $CDCl_3$ solvent, had a quartet at $\delta$ 4.29 ($^3J_{HCCF} = 8$ Hz). The $^{13}$C NMR, $CDCl_3$ solvent, had a quartet at $\delta$ 65.92 ($^3J_{CCF} = 36.5$ Hz) and another quartet at $\delta$ 124.3 ($^1H_{CF} = 277.6$ Hz). The $^{19}$F NMR, $CDCl_3$ solvent, had a triplet at $\delta$ $-82.76$ ($J_{HCCF} = 8$ Hz).

*Preparation of* **7**. Compound, **5**, 5.7 g (0.01 mole) in 10 ml of ether was added with stirring under nitrogen over a period of 30 min to a solution of lithium 2,2,2-trifluoroethoxide,[3] 3.12 g (0.029 mole) in 60 ml of ether. The mixture was stirred for 30 min and the solvent was removed to give a white solid. The $^1$H NMR, $CDCl_3$ solvent, had a quartet at $\delta$ 4.18 ($J_{HCCF} = 8.5$ Hz). The $^{19}$F NMR spectrum was recorded on a solution in $CD_2Cl_2$ which contained 12-crown-4. A triplet was found at $\delta$ $-75.58$ ($J_{FCCH} = 9.6$ Hz). The $^{13}$C of the same solution had a quartet at $\delta$ 63.39 ($J_{CCF} = 33.2$ Hz) and another at $\delta$ 126.34 ($J_{CF} = 279.2$ Hz). The $^{75}$As NMR spectrum on the same solution had a broad resonance at $\delta$ 190.3.

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