

Preparation of Bistrifluoromethylamino-derivatives of Phosphorus(III) and Arsenic(III)

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BISTRIFLUOROMETHYLAMINO-DERIVATIVES of mercury,¹ sulphur,² selenium,³ and boron⁴ are already known. Very recently three such derivatives of phosphorus(v), $(\text{CF}_3)_2\text{NPF}_3\text{Cl}$, $(\text{CF}_3)_2\text{NPF}_2\text{Cl}_2$, and $(\text{CF}_3)_2\text{NPF}_2\text{O}$ were prepared in this laboratory.⁵ The first two were made by the interaction of $(\text{CF}_3)_2\text{NCl}$ with PF_3 and PF_2Cl respectively and the last by controlled hydrolysis of the dichloro-compound. We have now examined the analogous reaction of $(\text{CF}_3)_2\text{NCl}$ with $(\text{CF}_3)_3\text{P}$ and $(\text{CF}_3)_3\text{As}$. With equimolar quantities of reactants the tris-phosphine yields $(\text{CF}_3)_2\text{NP}(\text{CF}_3)_2$ in high yield (b.p. 51°), CF_3Cl being eliminated. This in turn undergoes further stepwise reaction with $(\text{CF}_3)_2\text{NCl}$, giving $[(\text{CF}_3)_2\text{N}]_2\text{PCF}_3$ (b.p. 92.5°) and $[(\text{CF}_3)_2\text{N}]_3\text{P}$ (b.p. 135°). These are all stable liquids at room temperature and have been characterised by analysis and by infrared and n.m.r. spectroscopy. Their mass spectra show the presence of molecular ions.

A number of reactions of these substances are being studied. The first, $(\text{CF}_3)_2\text{NP}(\text{CF}_3)_2$ yields a white sublimable crystalline solid with chlorine, for which the formula $(\text{CF}_3)_2\text{NP}(\text{CF}_3)_2\text{Cl}_2$ has been

established. All of the compounds are readily hydrolysed by dilute alkali, CF_3 being eliminated as CF_3H and the $(\text{CF}_3)_2\text{N}$ group completely broken down.

A similar reaction occurs between $(\text{CF}_3)_2\text{NCl}$ and $(\text{CF}_3)_3\text{As}$; CF_3Cl is eliminated and, by a stepwise reaction $(\text{CF}_3)_2\text{NAs}(\text{CF}_3)_2$ (b.p. 70°) and $[(\text{CF}_3)_2\text{N}]_2\text{AsCF}_3$ (b.p. 109°) are formed. So far we have been unsuccessful in preparing the tris compound $[(\text{CF}_3)_2\text{N}]_3\text{As}$. Considerable amounts of $\text{CF}_3\text{N}=\text{CF}_2$ are formed in this case. Reaction between $(\text{CF}_3)_3\text{Sb}$ and $(\text{CF}_3)_2\text{NCl}$ is likewise different, the main products isolated being $\text{CF}_3\text{N}=\text{CF}_2$, CF_3Cl , and SbF_3 . It seems reasonable to suppose that an unstable quinquivalent derivative of the Group V element is an intermediate in all of these reactions. The only clear evidence so far obtained to support this hypothesis is the formation of a white 1:1 adduct from $(\text{CF}_3)_2\text{NI}$ and $[(\text{CF}_3)_2\text{N}]_2\text{AsCF}_3$. It was, however unstable and evolved $\text{CF}_3\text{N}=\text{CF}_2$.

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