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), (CF₃)₂NPF₃Cl, (CF₃)₂ NPF₂Cl₂, and (CF₃)₂NPF₂O were prepared in this laboratory.⁵ The first two were made by the interaction of (CF₃)₂NCl with PF₃ and PF₂Cl respectively and the last by controlled hydrolysis of the dichlorocompound. We have now examined the analogous reaction of (CF₃)₂NCl with (CF₃)₃P and (CF₃)₃As. With equimolar quantities of reactants the trisphosphine yields (CF₃)₂NP(CF₃)₂ in high yield (b.p. 51°), CF₃Cl being eliminated. This in turn undergoes further stepwise reaction $(CF_3)_2NCl$, giving $[(CF_3)_2N]_2PCF_3$ (b.p. 92.5°) and $[(CF_3)_2\mathrm{N}]_3\mathrm{P}$ (b.p. $135^\circ).$ 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, $(CF_3)_2NP(CF_3)_2$ yields a white sublimable crystalline solid with chlorine, for which the formula $(CF_3)_2NP(CF_3)_2Cl_2$ has been

established. All of the compounds are readily hydrolysed by dilute alkali, CF_3 being eliminated as CF_3H and the $(CF_3)_2N$ group completely broken down.

A similar reaction occurs between (CF₃)₂NCl and (CF₃)₃As; CF₃Cl is eliminated and, by a stepwise $(CF_3)_2NAs(CF_3)_2$ (b.p. 70°) [(CF₃)₂N]₂AsCF₃ (b.p. 109°) are formed. So far we have been unsuccessful in preparing the tris compound [(CF₃)₂N]₃As. Considerable amounts of CF₃N=CF₂ are formed in this case. Reaction between (CF₃)₃Sb and (CF₃)₂NCl is likewise different, the main products isolated being CF₃N=CF₂, CF₃Cl, and SbF₃. It seems reasonable to suppose that an unstable quinquevalent 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 (CF₃)₂NI and [(CF₃)₂N]₂AsCF₃. It was, however unstable and evolved $CF_3N = CF_2$.

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