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SYNTHESIS OF TRIMETHYLSILYLBIS(TRIFLUOROMETHYL) PHOSPHINE AND ARSINE BY EXCHANGE REACTIONS*

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Abstract—The exchange reactions of $(CH_3)_3SiM(CH_3)_2$ (M = N, P, As) with $(CF_3)_2M'H$(M'= P, As) were studied. The exchange of the two phosphine compounds produced $(CH_3)_3SiP(CF_3)_2$. In reactions where $(CH_3)_3SiAs(CF_3)_2$ formed it was found to slowly decompose.

INTRODUCTION

In earlier publications[1, 2] we reported the results of studies of the reactions of silylphosphines and silylarsines with covalent halides. The results were difficult to interpret since the silylphosphine reactions generally gave very different products than did the silylarsine reactions.

$$2(CH_3)_3SiAs(CH_3)_2 + 2NOCl \rightarrow (CH_3)_3SiOSi(CH_3)_3 + N_2O + 2(CH_3)_2AsCl \quad (1)$$

$$(CH_3)_3SiP(CH_3)_2 + NOCl \rightarrow (CH_3)_3SiCl + (CH_3)_2P(O)Cl + [Me_3Si]_2O + N_2 + N_2O + NO + \text{unidentified solid.} \quad (2)$$

We therefore decided to synthesize substituted silylphosphines and arsines so that their reactions with covalent halides could later be studied.

RESULTS AND DISCUSSION

Exchange reactions between $(CH_3)_3SiM(CH_3)_2$ (M = N, P, As) and $(CF_3)_2M'H$ (M' = P, As) were tried in order to prepare the desired $(CH_3)_3SiP(CF_3)_2$ and $(CF_3)_3SiAs(CF_3)_2$. The products observed in the reactions of $(CF_3)_2PH$ with the silicon-group V compounds are given below:

$$(CH_3)_3SiN(CH_3)_2 + (CF_3)_2PH \rightarrow (CH_3)_3SiF + \text{black solid} \quad (3)$$

$$(CH_3)_3SiP(CH_3)_2 + (CF_3)_2PH \rightarrow (CH_3)_2PH + (CH_3)_3SiP(CF_3)_2 \quad (4)$$

$$(CH_3)_3SiAs(CH_3)_2 + (CF_3)_2PH \xrightarrow[\Delta]{} (CH_3)_3SiF + (CH_3)_2AsP(CF_3)_2 + \cdots \quad (5)$$

The reaction indicated in Eqn (3) was very vigorous and there was no evidence for the formation of any $(CH_3)_3SiP(CF_3)_2$. Low temperature PMR studies, which are not available to the authors, would be useful to see if these vigorous reactions could be moderated and evidence for the initial formation of $(CH_3)_3SiM(CF_3)_2$ obtained. The presence of $(CH_3)_3SiF$ in the products of this and other reactions leads one to suspect initial formation of $(CH_3)_3SiM(CF_3)_2$ followed by a rapid β-elimination or a base catalyzed decomposition under the conditions of the reaction. Such a β-elimination has been reported to occur with $(CH_3)_3SiN(CF_3)_2$[3].

$$(CH_3)_3SiN(CF_3)_2 \rightarrow (CH_3)_3SiF + CF_3N{=}CF_2. \quad (6)$$

There was, however, no evidence for the formation of any $CF_3P{=}CF_2$ or $CF_3As{=}CF_2$.

The reaction indicated by Eqn (4) occurred rapidly and gave nearly quantitative yields of stable products.

The reaction indicated by Eqn (5) did not occur at room temperature. It was necessary to heat the reactants to 113° before products were formed. There was no evidence for the formation of any $(CH_3)_3SiP(CF_3)_2$.

When $(CF_3)_2AsH$ was allowed to react with the silicon-group V molecules the following was observed:

$$(CH_3)_3SiN(CH_3)_2 + (CF_3)_2AsH \rightarrow (CH_3)_3SiF + \text{black solid} \quad (7)$$

$$(CH_3)_3SiP(CH_3)_2 + (CF_3)_2AsH \rightarrow (CH_3)_3SiAs(CF_3)_2 + (CH_3)_2PH \quad (8)$$

$$(CH_3)_3SiAs(CF_3)_2 + (CH_3)_2PH \rightarrow (CH_3)_3SiF + (CH_3)_2PAs(CF_3)_2 + \text{brown solid} \quad (8a)$$

$$(CH_3)_3SiAs(CH_3)_2 + (CF_3)_2AsH \rightarrow (CH_3)_3SiAs(CF_3)_2 + (CH_3)_2AsH \quad (9)$$

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$$(CH_3)_3SiAs(CF_3)_2 + (CH_3)_2AsH \rightarrow (CH_3)_3SiF + (CF_3)_2AsAs(CH_3)_2 + \text{unidentified material.} \quad (9a)$$

If the desired $(CH_3)_3SiAs(CF_3)_2$ is obtained in the reaction indicated by Eqn (7) a subsequent decomposition must occur.

The reactions indicated by Eqns (8) and (9) both occurred to give the desired products which then slowly disappeared.

EXPERIMENTAL

Bis(trifluoromethyl)phosphine[4], bis(trifluoromethyl)arsine[4], dimethyl(trimethylsilyl)amine[5], dimethyl(trimethylsilyl)phosphine[1], and dimethyl(trimethylsilyl)arsine[6], were prepared as described in the literature. Their purity was verified by NMR and i.r. spectra. The i.r. spectrometer used was a Perkin-Elmer 457 and the NMR spectrometer was a Varian Associates A60 (upgraded with a HiZ kit). The NMR was used to determine concentrations by placing a known amount of $(CH_3)_4Si$ in the sample tube and comparing peak area of the known amount of $(CH_3)_4Si$ with peak area of the substance being studied.

$(CF_3)_2PH$

Reaction with $(CH_3)_3SiN(CH_3)_2$. $(CH_3)_3SiN(CH_3)_2$ (68·3 mg, 0·584 m-mole), $(CF_3)_2PH$ (105·7 mg, 0·622 m-mole) and $(CH_3)_4Si$ (40·1 mg, 0·456 m-mole) were condensed into an NMR tube which was then sealed. On warming to room temperature heat was evolved and a vigorous reaction occurred. This mixture separated into two layers. Analysis of the PMR spectrum indicated 0·577 m-mole of $(CH_3)_3SiF$ (99% $(CH_3)_3Si$ groups) (doublet, chemical shift observed −0·19 ppm, literature[7] −0·20 ppm) and an unidentified triplet at −2·98 ppm. On standing the contents of the NMR tube transformed to a black solid and an amber liquid, but the spectrum remained unchanged. The NMR tube was opened and the volatile material was shown by i.r. to consist of $(CH_3)_3SiF$ and $(CH_3)_4Si$.

Reaction with $(CH_3)_3SiP(CH_3)_2$. $(CH_3)_3SiP(CH_3)_2$ (71·5 mg, 0·533 m-mole), $(CF_3)_2PH$ (91·2 mg, 0·546 m-mole) and $(CH_3)_4Si$ (42·3 mg, 0·482 m-mole) were condensed into an NMR tube which was then sealed. When the tube had warmed to room temperature a PMR spectrum indicated the presence of $(CH_3)_2PH$ (0·52 m-mole; chemical shift observed, PH; −3·15 ppm, CH_3; −1·07 ppm, literature[8] PH; −3·13 ppm, CH_3; −1·06 ppm) and $(CH_3)_3SiP(CF_3)_2$ (0·52 m-mole; doublet of septets, chemical shift observed −0·44 ppm, literature[9] −0·42 ppm). The spectrum was unchanged after 16 hr. The NMR tube was opened and the contents were fractionated in a high vacuum line. The presence of $(CH_3)_2PH$[10] and $(CH_3)_3SiP(CF_3)_2$[9] was confirmed by their i.r. spectra.

Reaction with $(CH_3)_3SiAs(CH_3)_2$. $(CH_3)_3SiAs(CH_3)_2$ (79·9 mg, 0·449 m-mole), $(CF_3)_2PH$ (84·3 mg, 0·491 m-mole) and $(CH_3)_4Si$ (48·4 mg, 0·550 m-mole) were condensed into an NMR tube which was then sealed. A PMR spectrum taken after the tube had been standing at room temperature for 2 hr showed only the original reactants. The tube was then heated at 113° for 2 hr and the PMR spectrum indicated the formation of some $(CH_3)_3SiF$. After 3 hr of heating, the PMR spectrum indicated that no $(CH_3)_3SiAs(CH_3)_2$ remained and that $(CH_3)_3SiF$, $(CH_3)_2AsP(CF_3)_2$ along with an unidentified peak at 1·08 ppm were formed. After 19 hr of heating, the amount of $(CH_3)_2AsP(CF_3)_2$ was increased and the peak at 1·08 ppm became several peaks. Three days of heating did not further change the spectrum which then showed $(CH_3)_3SiF$ (0·447 m-mole, doublet chemical shift observed −0·17 ppm, literature[7] −0·20 ppm) and $(CH_3)_2AsP(CF_3)_2$ (0·178 m-mole, doublet of septets, chemical shift observed −1·36 ppm, ${}^3J_{HP}$ = 10·6 c/s, ${}^5J_{HF}$ = 0·6 c/s, literature[11] −1·46 ppm, the poor agreement between the literature and experimental chemical shift values for these and other $(CH_3)_2MM'(CF_3)_2$ derivatives is felt to be due to solvent effects in the complex mixtures, ${}^3J_{HP}$ = 11 c/s, ${}^5J_{HF}$ = 0·7 c/s, and several unidentified peaks at −0·90 and −0·98 ppm along with a broad multiplet centered at −1·1 ppm. Similar results were obtained in a separate reaction.

$(CF_3)_2AsH$

Reaction with $(CH_3)_3SiN(CH_3)_2$. $(CH_3)_3SiN(CH_3)_2$ (67·5 mg, 0·577 m-mole), $(CF_3)_2AsH$ (126 mg, 0·589 m-mole) and $(CH_3)_4Si$ (40·3 mg, 0·458 m-mole) were condensed into an NMR tube which was then sealed. On warming the tube to room temperature an immediate reaction occurred and the solution separated into two layers. The PMR spectrum indicated the presence of $(CH_3)_3SiF$ (0·486 m-mole, doublet chemical shift observed −0·17 ppm, literature −0·20 ppm) and a number of small peaks at −0·80, −1·63, −2·34, −2·82, −2·90, −3·00, −3·10 and −3·12 ppm. On standing, much of the liquid in the tube changed to a black solid.

Reaction with $(CH_3)_3SiP(CH_3)_2$. $(CH_3)_3SiP(CH_3)_2$ (133 mg, 0·99 m-mole), $(CF_3)_2AsH$ (254 mg, 1·19 m-mole) and $(CH_3)_4Si$ (39·4 mg, 0·448 m-mole) were condensed into an NMR tube which was then sealed. A PMR spectrum of the mixture showed the presence of $(CH_3)_2PH$ and $(CH_3)_3SiAs(CF_3)_2$ (0·96 m-mole, chemical shift observed −0·47 ppm; see reaction with $(CH_3)_3SiAs(CH_3)_2$ below for identification of $(CH_3)_3SiAs(CF_3)_2$). A PMR spectrum taken 2 hr later showed a decrease in the amount of $(CH_3)_3SiAs(CF_3)_2$ and the formation of some $(CH_3)_3SiF$ and $(CH_3)_2PAs(CF_3)_2$. A PMR spectrum taken 24 hr later showed no $(CH_3)_3SiAs(CF_3)_2$, no $(CH_3)_2PH$, 0·92 m-mole of $(CH_3)_3SiF$ (doublet, chemical shift observed −0·18 ppm, literature −0·20 ppm), and some $(CH_3)_2PAs(CF_3)_2$ (doublet of septets, chemical shift observed −1·44 ppm, literature[11] −1·54 ppm). On standing, most of the mixture in the NMR tube converted to a brown solid.

Reaction with $(CH_3)_3SiAs(CH_3)_2$. $(CH_3)_3SiAs(CH_3)_2$ (168·3 mg, 0·946 m-mole), $(CF_3)_2AsH$ (212·3 mg, 0·988 m-mole) and $(CH_3)_4Si$ (85·7 mg, 0·974 m-mole) were condensed into an NMR tube which was then sealed. Successive PMR spectra of the mixture indicated a slow reaction (about 1 hr for completion), first forming $(CH_3)_3SiAs(CF_3)_2$ (chemical shift observed −0·47 ppm) and $(CH_3)_2AsH$ (chemical shift observed CH_3 doublet −1·00 ppm, H septet −2·45 ppm, literature[12] CH_3 doublet −0·98 ppm, H septet −2·44 ppm) which then disappeared and left final products of $(CH_3)_3SiF$ (1·04 m-mole, doublet chemical shift observed −0·18 ppm, literature −0·20 ppm) and $(CH_3)_2AsAs(CF_3)_2$ (0·575 m-mole, septet, chemical shift observed −1·38 ppm, ${}^5J_{HF}$ = 0·6 c/s, literature[11] −1·50 ppm, ${}^5J_{HF}$ = 0·6 c/s). Small unidentified peaks remained at −1·03, −1·05, −1·11 and −1·13 ppm.

In a separate reaction the NMR tube was immersed in liquid nitrogen when a PMR spectrum showed $(CH_3)_2AsH$ and $(CH_3)_3SiAs(CF_3)_2$ (peak at −0·47 ppm) to be the principal products. The NMR tube was opened and the mixture fractionated in a high vacuum line. The fraction (held by −78°, pass −36°) containing the material believed to be $(CH_3)_3SiAs(CF_3)_2$ was placed in a NMR tube with HCl and $(CH_3)_4Si$. A PMR spectrum of the mixture indicated the presence of $(CH_3)_3SiCl$ (chemical shift observed −0·38 ppm, literature[7] −0·42 ppm) and $(CF_3)_2AsH$ (septet, chemical shift observed −5·33 ppm, chemical shift of a sample prepared by the literature method −5·28 ppm). The tube was then opened and the presence of $(CH_3)_3SiCl$ and $(CF_3)_2AsH$ were confirmed by i.r. spectra. Since $(CH_3)_3SiCl$ and $(CF_3)_2AsH$ are the expected cleavage products of $(CH_3)_3SiAs(CF_3)_2$ by HCl, this confirmed the $(CH_3)_3SiAs(CF_3)_2$ as having a PMR peak at −0·47 ppm. The $(CH_3)_3SiAs(CF_3)_2$ could not be obtained in a pure state since it slowly decomposed during fractionation.

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