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REACTIONS OF SILYLPHOSPHINES AND SILYLARSINES WITH COVALENT HALIDES*

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SUMMARY

The reactions of $(CH_3)_3SiP(CH_3)_2$ and $(CH_3)_3SiAs(CH_3)_2$ with $SiCl_4$, SiF_4, SO_2Cl_2, and SO_2F_2 have been studied. The cleavage of the Si–P bond occurs more readily than the cleavage of the Si–As bond. The covalent halides containing oxygen give products that are harder to predict than do the nonoxygenated halides.

INTRODUCTION

In an earlier publication we reported that the cleavage of dimethyl(trimethylsilyl)phosphine and dimethyl(trimethylsilyl)arsine with nitrosyl chloride proceeded to give different types of products[1]. The reactions that accounted for the major products were as shown in eqns. (1) and (2).

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

$$(CH_3)_3SiP(CH_3)_2 + NOCl \rightarrow (CH_3)_3SiCl + (CH_3)_2PNO \quad (2)$$

The $(CH_3)_2PNO$ was not recovered but was assumed to undergo further reaction or decomposition. The present work was undertaken in order to determine whether cleavage of the Si–P and Si–As bonds by other covalent halides would also proceed by different major pathways and so give different types of products.

RESULTS AND DISCUSSION

It has been reported that dimethyl(trimethylsilyl)amine interacts with $SiCl_4$ to give quantitative yields of $(CH_3)_2NSiCl_3$ [2].

$$(CH_3)_3SiN(CH_3)_2 + SiCl_4 \rightarrow (CH_3)_3SiCl + (CH_3)_2NSiCl_3 \quad (3)$$

In this investigation it was found that the Si–P and Si–As species also interact with $SiCl_4$ to give analogous products:

$$(CH_3)_3SiP(CH_3)_2 + SiCl_4 \rightarrow (CH_3)_3SiCl + (CH_3)_2PSiCl_3 \quad (4)$$

$$(CH_3)_3SiAs(CH_3)_2 + SiCl_4 \rightarrow (CH_3)_3SiCl + (CH_3)_2AsSiCl_3 \quad (5)$$

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* Portions of this work are taken from a thesis to be submitted by Joseph E. Byrne in partial fulfillment of requirements for the Ph.D. degree.

In both cases the reactions were essentially complete. In the reaction with $(CH_3)_3SiP(CH_3)_2$ a white solid intermediate was noted and this suggested, perhaps, a reaction intermediate such as $[(CH_3)_3SiP(SiCl_3)(CH_3)_2]^+Cl^-$, similar to that observed in the reaction of triphenylphosphine with CCl_4[3].

The reactions of these silicon–Group V molecules with SiF_4 appear to be dependent on the Group V atom. It has previously been reported that SiF_4 interacts with $(C_2H_5)_3SiN(CH_3)_2$, at high temperature and pressure[4], as shown in eqn. (6).

$$(C_2H_5)_3SiN(CH_3)_2 + SiF_4 \xrightarrow[150^\circ]{20\ \text{atm}} (CH_3)_3NSiF_3 + (C_2H_5)_3SiF\ (95\%\ \text{yield}) \quad (6)$$

Under similar conditions the reaction of SiF_4 with $(CH_3)_3SiP(CH_3)_2$ and $(CH_3)_3SiAs(CH_3)_2$ proceeded to a much smaller extent. The amount of reaction in the $(CH_3)_3SiAs(CH_3)_2$ case was so slight that no evidence for the formation of $(CH_3)_2AsSiF_3$ was obtained. The reaction of SiF_4 with $(CH_3)_3SiP(CH_3)_2$ proceeded to a greater extent again, however, no $(CH_3)_2PSiF_3$ was observed. Small peaks observed in the NMR of the unreacted $(CH_3)_3SiP(CH_3)_2$ portion might be due to $(CH_3)_2PSiF_3$ but more likely are due to $(CH_3)_2PP(CH_3)_2$. These peaks appear as a 1/2/1 triplet in the area (1.03 ppm) and with the coupling constant (7 Hz) appropriate for $(CH_3)_2PP(CH_3)_2$ (lit.[5] chemical shift 1.06 ppm, coupling constant 7 Hz).

The previous reactions proceeded in the simple manner expected on the basis of prior experience with these cleavage reactions and the products observed were those expected in each case. When oxygen-containing covalent halides were used, however, the reactions immediately became much more complex and predictions of expected products became very difficult.

When SO_2Cl_2 was allowed to react with these silicon–Group V molecules the products varied greatly depending on the silicon–Group V species used. The reaction of $(C_2H_5)_2NSi(CH_3)_3$ with SO_2Cl_2 has been reported[6] [eqn. (7)]. In view of the products obtained the reaction can be considered to proceed via a two step process [eqns. (7a) and (7b)]:

$$2(C_2H_5)_2NSi(CH_3)_3 + SO_2Cl_2 \rightarrow 2(CH_3)_3SiCl + (C_2H_5)_2NSO_2N(C_2H_5)_2 \quad (7)$$

$$(C_2H_5)_2NSi(CH_3)_2 + SO_2Cl_2 \rightarrow (CH_3)_3SiCl + (C_2H_5)_2NSO_2Cl \quad (7a)$$

$$(C_2H_5)_2NSO_2Cl + (C_2H_5)_2NSi(CH_3)_3 \rightarrow (CH_3)_3SiCl + (C_2H_5)_2NSO_2N(C_2H_5)_2 \quad (7b)$$

In the Si–P reaction with SO_2Cl_2 as studied in the present work the reaction observed is shown in eqn. (8):

$$(CH_3)_3SiP(CH_3)_2 + SO_2Cl_2 \rightarrow (CH_3)_3SiCl + (CH_3)_2P(O)Cl + SO_2 \quad (8)$$

These products may be explained by assuming an initial step similar to that for $(C_2H_5)_2NSi(CH_3)_2$ [eqn. (9)] followed by decomposition to form $(CH_3)_2P(O)Cl$ and SO_2.

$$(CH_3)_3SiP(CH_3)_2 + SO_2Cl_2 \rightarrow (CH_3)_3SiCl + (CH_3)_2PSO_2Cl \quad (9)$$

The reaction of SO_2Cl_2 with $(CH_3)_3SiAs(CH_3)_2$ produced some $(CH_3)_3SiOSi(CH_3)_3$ [eqn. (10)], a product which was not observed in the preceeding reactions with $(CH_3)_3SiP(CH_3)_2$.

$$(CH_3)_3SiAs(CH_3)_2+SO_2Cl_2 \rightarrow (CH_3)_3SiCl+(CH_3)_3SiOSi(CH_3)_3+ +(CH_3)_2AsCl+SO_2 \qquad (10)$$

The nearly equal quantities of $(CH_3)_3SiCl$ and $(CH_3)_2AsCl$ found could be explained by a reaction pathway similar to that shown in eqn. (9) for the $(CH_3)_3SiP(CH_3)_2$ reaction. A second, minor, pathway would have to be postulated for the formation of the $(CH_3)_3SiOSi(CH_3)_3$ and for the formation of some $(CH_3)_2As$-containing products to account for the unrecovered $(CH_3)_2As$ groups. Such a situation was also observed in the reaction of NOCl with $(CH_3)_3SiAs(CH_3)_2$ in which the formation of $(CH_3)_3SiOSi(CH_3)_3$ again had to be accounted for[1]. As was discussed in the earlier work, it is difficult to postulate a satisfactory mechanism for this.

In view of the rather inert nature of SO_2F_2 it is not surprising that it failed to react with $(CH_3)_3SiAs(CH_3)_2$ since the Si–As species seems to be less reactive than the Si–P or Si–N species as was seen in the $SiCl_4$ and SiF_4 reactions. The reaction of SO_2F_2 with $(CH_3)_3SiP(CH_3)_2$ however, produced a rather large variety of products, not all of which could be identified. The major products obtained were $(CH_3)_3SiF$ and $(CH_3)_3SiOSi(CH_3)_3$. None of the $(CH_3)_2P$ groups were recovered. However, they probably were the cause of the large number of small peaks observed in the NMR spectrum. There was no evidence for $(CH_3)_2PP(CH_3)_2$ in the NMR spectrum and this probably eliminates the possible formation of $(CH_3)_2PF$ in the reaction since $(CH_3)_2PF$ has been reported[7] to undergo disproportionation into $(CH_3)_2PF_3$ and $(CH_3)_2PP(CH_3)_2$.

Since $(CH_3)_3SiP(CH_3)_2$ was found to be more reactive than $(CH_3)_3SiAs(CH_3)_2$ it was allowed to react with CF_3I. The reaction proceeded smoothly and good yields of both products were obtained [eqn. (11)]. There was no evidence for the formation of $(CH_3)_2PI$ or any other unexpected product.

$$(CH_3)_3SiP(CH_3)_2+CF_3I \rightarrow (CH_3)_3SiI+(CH_3)_2PCF_3 \qquad (11)$$

EXPERIMENTAL

Silicon tetrafluoride (99.6%), sulfuryl fluoride (99.5%), trifluoromethyl iodide (98%), silicon tetrachloride (98%) and sulfuryl chloride (practical) were used as commercially obtained (Matheson, P.C.R., Fisher). Dimethyl(trimethylsilyl)arsine[8] and dimethyl(trimethylsilyl)phosphine[1] were prepared as described in the literature. Their purity was verified by NMR and IR spectra. The IR spectrometer used was a Perkin–Elmer 457 and the NMR spectrometer was a Varian Associates A60 (upgraded with a Hi-Z 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.

SiCl$_4$

Reaction with $(CH_3)_3SiAs(CH_3)_2$. $(CH_3)_3SiAs(CH_3)_2$ (155 mg, 0.880 mmole) and $SiCl_4$ (161 mg, 0.947 mmole) and $(CH_3)_4Si$ (67.3 mg, 0.746 mmole) were condensed into an NMR tube which was then sealed. The NMR spectrum indicated that no reaction had occurred. The NMR tube was heated to 160° for 5 min and after this process the NMR spectrum again indicated that no reaction had occurred. After the NMR tube had remained at room temperature for eight months the NMR spectrum indicated the presence of only $(CH_3)_3SiCl$ (chem. shift: obs. −0.38 ppm, lit.[9] −0.42 ppm), and $(CH_3)_2AsSiCl_3$ (chem. shift: obs. −1.21 ppm, lit.[10] −1.22 ppm), and $(CH_3)_4Si$. Comparison of peak areas of $(CH_3)_3SiCl$ and $(CH_3)_2AsSiCl_3$ to peak area of the known amount of $(CH_3)_4Si$ indicated approximate yields for $(CH_3)_3SiCl$ and $(CH_3)_2AsSiCl_3$ of 100% and 90% respectively. The NMR tube was opened and the contents were separated by trap to trap distillation. The material that passed a −23° bath and remained in a −96° bath was confirmed by its IR spectrum[9] to be $(CH_3)_3$-SiCl. Excess HCl was added to the material that remained in the −23° bath. IR spectra identified $SiCl_4$ and $(CH_3)_2AsH$ as the principal products[12,13].

A small amount of solid also formed on the addition of excess HCl. Solid $[(CH_3)_2AsH_2]Cl$ along with $SiCl_4$ and $(CH_3)_2AsH$ are the expected products from the cleavage of $(CH_3)_2AsSiCl_3$ with HCl.

Reaction with $(CH_3)_3SiP(CH_3)_2$. $(CH_3)_3SiP(CH_3)_2$ (140 mg, 1.04 mmole), $SiCl_4$ (173 mg, 1.02 mmole), and $(CH_3)_4Si$ (66.1 mg, 0.733 mmole) were condensed into an NMR tube which was then sealed. On warming the tube to room temperature a white solid formed. The white solid slowly dissolved on shaking. The NMR spectrum indicated the presence of $(CH_3)_3SiCl$ (chem. shift: obs. −0.38 ppm, lit.[9] −0.42 ppm; 1.0 mmole) and $(CH_3)_2PSiCl_3$ (chem. shift: obs. −1.26 ppm, lit.[10] −1.26 ppm; 1.0 mmole).

In a separate experiment $(CH_3)_3SiP(CH_3)_2$ (45.1 mg, 0.336 mmole) and $SiCl_4$ (57.4 mg, 0.338 mmole) were allowed to react and the products were separated by trap to trap distillation. The material passing a −45° bath was shown by IR spectrum to be $(CH_3)_3SiCl$. Addition of excess HCl to the material held by the −45° bath produced $SiCl_4$, as evidenced by its IR spectrum, and a white solid. The white solid was stable on heating, as was a sample of $[(CH_3)_2PH_2]Cl$ prepared from $(CH_3)_2PH$ and HCl.

SiF_4

Reaction with $(CH_3)_3SiAs(CH_3)_2$. $(CH_3)_3SiAs(CH_3)_2$ (49.5 mg, 0.277 mmole) and SiF_4 (68.8 mg, 0.662 mmole) were condensed into a small heavy-walled tube (volume approx. 1.5 cm^3) and the tube was placed in an oil bath and heated to 160° for one-half hour. The tube was then opened and the contents were separated by trap to trap distillation. The material that passed a −34° bath was found to be SiF_4 [64.5 mg, 94% recovery. Molecular weight (Dumas): found 102; calcd. 104. Verified by IR spectrum[18]]. The IR spectrum of the small amount of material that passed a −78° bath indicated the presence of $(CH_3)_2AsH$ and $(CH_3)_3SiF$. The material that remained in the −78° bath was shown by IR to be a mixture of $(CH_3)_3SiAs(CH_3)_2$ and the hydrolysis product $(CH_3)_3SiOSi(CH_3)_3$.

Reaction with $(CH_3)_3SiP(CH_3)_2$. $(CH_3)_3SiP(CH_3)_2$ (120 mg, 0.896 mmole) and SiF_4 (90.1 mg, 0.855 mmole) were condensed into a glass reaction vessel (volume 1.8 ml) and held at 204° for 2.5 h. The contents of the vessel were then separated by trap to trap distillation. A blue-black residue remained in the reaction vessel. IR spectra of the material passing a −130° bath showed the material to be SiF_4 (66 mg, 0.64 mmole). The material passing a −63° bath was placed in an NMR tube with 0.885 mmole of C_6H_{12}. The NMR spectrum indicated the presence of $(CH_3)_3SiF$ (chem. shift: obs. doublet −0.15 ppm, lit.[9] −0.20 ppm; 0.35 mmole). The material which remained in the −63° bath was placed in an NMR tube with 0.898 mmole of

C_6H_{12}. The NMR spectrum indicated the presence of $(CH_3)_3SiP(CH_3)_2$ (chem. shift: obs. 2 doublets −0.97 and −0.09 ppm, lit.[14] −0.98 and −0.10 ppm; 0.30 mmole). Several small peaks were also observed which appeared to be a 1/2/1 triplet with a chemical shift of 1.03 ppm and a coupling constant of 7 Hz. In a separate reaction run at room temperature 96% of the original SiF_4 was recovered unchanged.

SO_2Cl_2

Reaction with $(CH_3)_3SiAs(CH_3)_2$. $(CH_3)_3SiAs(CH_3)_2$ (54.1 mg, 0.303 mmole) and SO_2Cl_2 (37.2 mg, 0.276 mmole) were condensed into a small tube attached to a vacuum line. A vigorous reaction ensued and a small amount of white solid formed. The volatile materials were separated by trap to trap distillation. The material that passed a −96° bath was shown to be SO_2 (16.5 mg, 0.258 mmole, 94% of original SO_2) by IR spectrum and molecular weight (Dumas method found 64.0; calcd. 64). IR spectra indicated the remaining mixture to be $(CH_3)_3SiCl$, $(CH_3)_3SiOSi(CH_3)_3$, and $(CH_3)_2AsCl$.

In a separate experiment $(CH_3)_3SiAs(CH_3)_2$ (53.9 mg, 0.302 mmole), SO_2Cl_2 (39.9 mg, 0.296 mmole), and $(CH_3)_4Si$ (115.7 mg, 1.283 mmole) were condensed into an NMR tube and the NMR spectrum taken. Analysis of the spectrum indicated the presence of the following materials: $(CH_3)_3SiCl$ (chem. shift: obs. −0.39 ppm, lit.[9] −0.42 ppm; 0.19 mmole, 64% of silyl groups); $(CH_3)_3SiOSi(CH_3)_3$ (chem. shift: obs. −0.06 ppm, lit.[9] −0.06 ppm; 0.054 mmole, 36% of silyl groups); $(CH_3)_2AsCl$ (chem. shift: obs. −1.59 ppm, lit.[1] −1.62 ppm; 0.21 mmole, 70% of $(CH_3)_2As$ groups). Several unidentifiable peaks were also observed at 2.87, 2.13, 2.03, and 0.98 ppm.

Reaction with $(CH_3)_3SiP(CH_3)_2$. $(CH_3)_3SiP(CH_3)_2$ (119 mg, 0.838 mmole), SO_2Cl_2 (135 mg, 0.996 mmole) and $(CH_3)_4Si$ (54 mg, 0.61 mmole) were condensed into an NMR tube. A reaction appeared to occur on mixing and the NMR spectrum indicated the presence of $(CH_3)_3SiCl$ (chem. shift: obs. −0.41 ppm, lit.[9] −0.42 ppm; 0.75 mmole) and $(CH_3)_2P(O)Cl$ (chem. shift; obs. doublet −1.99 ppm; lit.[1] −2.02 ppm; 0.70 mmole). The tube was opened and the contents separated by trap to trap distillation. The solid $(CH_3)_2P(O)Cl$ remained in the NMR tube. IR spectra indicated the volatile products to be SO_2[16] (0.480 mmole, 54%) and $(CH_3)_3SiCl$.

SO_2F_2

Reaction with $(CH_3)_3SiAs(CH_3)_2$. $(CH_3)_3SiAs(CH_3)_2$ (39.5 mg, 0.221 mmole) and SO_2F_2 (31.1 mg, 0.305 mmole) were condensed and then sealed into a small glass reaction vessel. After the mixture had been allowed to stand for three weeks the NMR spectrum showed no evidence of reaction. The vessel was then opened and the contents separated by trap to trap distillation. The material passing the −130° bath was shown by IR spectrum[15] to be SO_2F_2 (31.4 mg, 0.309 mmole). The material remaining in the −130° bath was shown by its IR spectrum to consist of $(CH_3)_3SiAs(CH_3)_2$ and its hydrolysis products $(CH_3)_3SiOSi(CH_3)_3$ and $(CH_3)_2AsH$.

Reaction with $(CH_3)_3SiP(CH_3)_2$. $(CH_3)_3SiP(CH_3)_2$ (208 mg, 1.54 mmole), SO_2F_2(156 mg, 1.54 mmole) and $(CH_3)_4Si$ (420 mg, 0.48 mmole) were condensed and sealed into an NMR tube. When the tube warmed to room temperature a white solid formed, which subsequently partially dissolved. An NMR spectrum of the mixture showed the presence of $(CH_3)_3SiF$ (chem. shift: obs. doublet −0.18 ppm, lit.[9] −0.20 ppm) and $(CH_3)_3SiOSi(CH_3)_3$ (chem. shift: obs. −0.06 ppm, lit.[9] −0.06

ppm) along with several other small unidentifiable peaks (−0.39 ppm and −1.08 ppm). On standing for 24 h the amount of white solid in the tube was substantially larger. The NMR tube was then placed in a bath at 114° for 1 h. Two immiscible liquid layers remained at the end of this time. The NMR spectrum now showed the presence of $(CH_3)_3SiF$ (chem. shift: obs. −0.18 ppm, lit.[9] −0.20 ppm; 0.72 mmole) and $(CH_3)_3SiOSi(CH_3)_3$ (chem. shift: obs. −0.06 ppm, lit.[9] −0.06 ppm; 0.25 mmole). Also present were a large number (ca. 20) of small unidentifiable peaks. The NMR tube was then opened and the volatile contents separated by trap to trap distillation. A white solid remained in the NMR tube. The material passing the −130° bath was shown by its IR spectrum to be SO_2F_2 (0.8 mmole). IR spectra confirmed the presence of $(CH_3)_3SiF$ and $(CH_3)_3SiOSi(CH_3)_3$ in the remaining material.

Reaction of $(CH_3)_3SiP(CH_3)_2$ with CF_3I

$(CH_3)_3SiP(CH_3)_2$ (276 mg., 2.06 mmole), CF_3I (400 mg, 2.04 mmole) and $(CH_3)_4Si$ (116 mg, 1.32 mmole) were condensed into an NMR tube. A white solid, which subsequently partially dissolved, formed on mixing. The NMR spectrum indicated the presence of $(CH_3)_3SiI$ (chem. shift: obs. −0.75 ppm, lit.[9] −0.78 ppm) and contained a doublet at −1.21 ppm consistent with that expected for $CF_3P(CH_3)_2$. Integration of the peak areas and comparison with the peak area for the known amount of $(CH_3)_4Si$ allowed a calculation of 1.80 mmole of $(CH_3)_3SiI$ (87% yield) and 1.76 mmole $(CH_3)_2PCF_3$ (86% yield). The tube was then opened and the presence of $(CH_3)_3SiI$ and $(CH_3)_2PCF_3$ was confirmed by infrared spectra[17,19]. The small amount of white solid which remained in the NMR tube was unidentified.

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