REACTIONS OF ORGANOSILICON–GROUP V COMPOUNDS WITH NITROSYL CHLORIDE*

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SUMMARY

The reactions of $(CH_3)_3SiN(CH_3)_2$, $(CH_3)_3SiP(CH_3)_2$, and $(CH_3)_3SiAs(CH_3)_2$ with NOCl have been studied. The products observed are, respectively: $(CH_3)_3SiCl$ and $(CH_3)_2NNO$; $(CH_3)_3SiOSi(CH_3)_3$, N_2O, NO, N_2, $(CH_3)_3SiCl$, $(CH_3)_2P(O)Cl$, and a glassy solid; $(CH_3)_3SiOSi(CH_3)_3$, N_2O, and $(CH_3)_2AsCl$.

Covalent halides, such as BX_3 and HX, have been extensively used to cleave the bond between the Si and Group V atoms in species such as dimethyl(trimethylsilyl)amine[1] $[(CH_3)_3SiN(CH_3)_2]$ and dimethyl(trimethylsilyl)arsine[2] $[(CH_3)_3SiAs(CH_3)_2]$. Studies with optically active Si–N molecules have shown that these cleavage reactions proceed with inversion of configuration in almost all cases[3,4]. These inversion reactions have been rationalized by the mechanism indicated in eqn. 1 in which attack on N by an electrophile, A (such as B or H), is followed by displacement of R_2NA from Si by X^-.

$$R_3SiNR_2 + AX \rightarrow [R_3Si\overset{+}{N}(A)R_2]X^- \rightarrow R_3SiX + R_2NA \qquad (1)$$
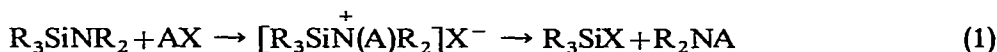
In the few cases where inversion of configuration does not occur, the reactions have been rationalized by the mechanism indicated in eqn. 2 involving a four-centered process.

$$R_3SiNR_2 + AX \rightarrow R_3SiNR_2 \rightarrow R_3Si\underset{X}{\overset{N}{<}}{}^{R_2}A \rightarrow R_3SiX + R_2NA \qquad (2)$$
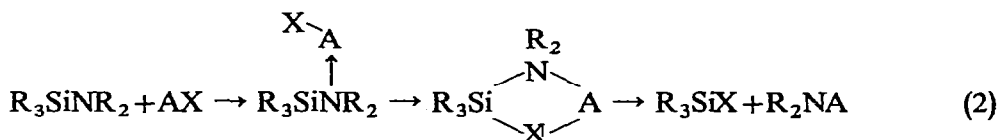
Both mechanisms predict the formation of the Si–X bond. This has indeed been the case for all reactions thus far reported. This work, however, reports for the first time reactions in which R_2MX (M = P or As) will be formed in preference to the R_3SiX species.


When nitrosyl chloride (NOCl) was allowed to react with $(CH_3)_3SiN(CH_3)_2$, the products obtained were trimethylsilyl chloride $[(CH_3)_3SiCl]$ and dimethyl-nitrosamine $[(CH_3)_2NNO]$. The products were exactly those expected based on the known products of other reactions of this type[5] and can be simply explained by the inversion mechanism mentioned previously.

$$(CH_3)_3SiN(CH_3)_2 + NOCl \rightarrow [(CH_3)_3Si\overset{\overset{O}{N}}{N}(CH_3)_2]Cl^- \rightarrow$$
$$(CH_3)_3SiCl + (CH_3)_2NNO \quad (3)$$
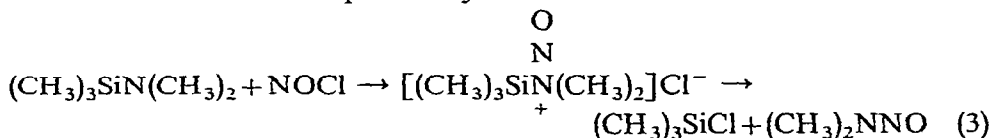
Nitrosyl chloride is an appreciably polar molecule[6] and therefore the formation of the nucleophile, Cl^-, should occur rather easily.

Previously reported cleavage reactions[2,7] involving R_3SiAsR_2 species are all explainable on the basis of a similar mechanism and all, as expected, result in the formation of R_3SiX. The reaction of NOCl with $(CH_3)_3SiAs(CH_3)_2$ does not yield $(CH_3)_3SiCl$ and $(CH_3)_2AsNO$ but was found instead to give nitrous oxide (N_2O), hexamethyldisiloxane $[(CH_3)_3SiOSi(CH_3)_3]$, and dimethylchloroarsine $[(CH_3)_2-AsCl]$ (eqn. 4).

$$(CH_3)_3SiAs(CH_3)_2 + NOCl \rightarrow (CH_3)_3SiOSi(CH_3)_3 + N_2O + (CH_3)_2AsCl \quad (4)$$
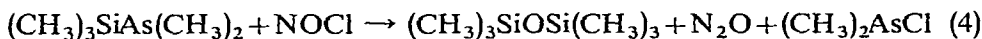
This is the first reported case in which the halogen does not become attached to the silicon. The exact type of mechanism used in the preceding reaction, therefore, would not be applicable in this case. A satisfactory mechanism is difficult to postulate. If the reaction were to proceed by the type of mechanism indicated in eqn. 3, $(CH_3)_3$-SiNO would be displaced and would then be postulated to decompose to form $[(CH_3)_3Si]_2O$ and N_2O. Both the decomposition and displacement of $(CH_3)_3SiNO$ are difficult to justify. If the reaction were to proceed by the type of mechanism indicated in eqn. 2 involving a four-centered process, the chlorine would go to the arsenic and the nitrogen would go to the silicon. On cleavage $(CH_3)_3SiNO$ would first be formed and would then be postulated to decompose to form $[(CH_3)_3Si]_2O$ and N_2O. These assumptions are again difficult to justify; therefore, the reasons for the reversal of products [i.e., $(CH_3)_2AsCl$ rather than $(CH_3)_3SiCl$] are not fully understood at this time.

Whereas the reaction of NOCl with $(CH_3)_3SiN(CH_3)_2$ or $(CH_3)_3SiAs(CH_3)_2$ can be written in a fairly simple manner, the reaction of NOCl with $(CH_3)_3SiP(CH_3)_2$ is much more complex. A large variety of products are obtained including $(CH_3)_3SiCl$, $(CH_3)_3SiOSi(CH_3)_3$, $(CH_3)_2P(O)Cl$, N_2O, NO, N_2, and an unidentified glassy solid. The most important of the large variety of products obtained can be accounted for by assuming that the reaction proceeds in two ways.

One path would follow eqn. 3 for the reaction of $(CH_3)_3SiN(CH_3)_2$ and could be written as shown in eqn. 5. Since most of the original $(CH_3)_2P$ groups must remain

$$(CH_3)_3SiP(CH_3)_2 + NOCl \rightarrow [(CH_3)_3Si\overset{+}{P}(NO)(CH_3)_2]Cl^- \rightarrow$$
$$(CH_3)_3SiCl + (CH_3)_2PNO \quad (5)$$
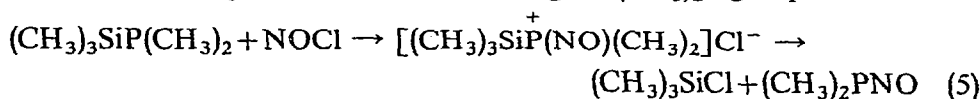
in the glassy solid, the $(CH_3)_2PNO$ would have to undergo further reaction or decomposition to form the solid. Since the majority of the $(CH_3)_3Si$ groups were recovered as $(CH_3)_3SiCl$, this would indicate that eqn. 5 would be the major pathway.

The other path would be similar to the path followed by the reaction of $(CH_3)_3SiAs-(CH_3)_2$ and would account for the formation of $(CH_3)_2PCl$, $[(CH_3)_3Si]_2O$, and N_2O. The $(CH_3)_2PCl$, being an excellent oxygen acceptor, would then pick up oxygen from a donor in the mixture to form the observed $(CH_3)_2P(O)Cl$. Since less $(CH_3)_2P(O)Cl$ was recovered than expected on the basis of the amount of $(CH_3)_3SiOSi(CH_3)_3$ obtained, some of this would also have to be postulated to react or decompose to form a portion of the glassy solid. The addition of $AgNO_3$ to a portion of the glassy solid gave a white precipitate thereby indicating the probable presence of chlorine in the solid as would be expected if $(CH_3)_2P(O)Cl$ were one of the materials that reacted to form the solid. Thus it appears that $(CH_3)_3SiP(CH_3)_2$ reacts with NOCl in a manner intermediate to the reaction of $(CH_3)_3SiN(CH_3)_2$ and $(CH_3)_3SiAs(CH_3)_2$, but more similar to that of $(CH_3)_3SiN(CH_3)_2$, with NOCl.

EXPERIMENTAL

Nitrosyl chloride (NOCl) was used as commercially obtained (Matheson, 97%). Dimethyl(trimethylsilyl)amine[8] (b.p. found 85–86°, lit. 86°) and dimethyl-(trimethylsilyl)arsine[3] (mol.wt. found 176.5, calcd. 178.8) were prepared as described in the literature. Dimethyl(trimethylsilyl)phosphine was prepared in the same manner as $(CH_3)_3SiAs(CH_3)_2$ with the exception that phenyllithium (C_6H_5Li) was used in place of n-butyllithium (C_4H_7Li) in order to facilitate purification. Its purity was verified by NMR and molecular weight (Dumas method found 136.0; calcd. 134.2).

Reaction with $(CH_3)_3SiN(CH_3)_2$

Excess NOCl was bubbled through $(CH_3)_3SiN(CH_3)_2$ (8.111 g, 0.06748 mole). An exothermic reaction occurred. After the evolution of heat had ceased, distillation of the products gave $(CH_3)_3SiCl$ (5.592 g, 74.5% yield; n_D^{20} 1.3883, lit.[9] 1.3885) and $(CH_3)_2NNO$ (3.731 g, 72.5% yield) (Found: C, 32.62; H, 8.12. $C_2H_6N_2O$ calcd.: C, 32.42; H, 8.17%.) The structure was confirmed by infrared spectrum[10].

Reaction with $(CH_3)_3SiAs(CH_3)_2$

Nitrosyl chloride (24.4 mg, 0.373 mmole) and $(CH_3)_3SiAs(CH_3)_2$ (48.5 mg, 0.368 mmole) were distilled into a small tube attached to a vacuum line. The tube was then slowly allowed to warm from $-196°$ to room temperature and subsequently returned to $-196°$. The process was repeated several times, and the volatile materials were then separated by trap-to-trap distillation on the vacuum line. Material that passed a $-134°$ bath was shown by infrared to be N_2O (7.7 mg, 97.5% yield). The material that remained in the trap at $-134°$ was shown by NMR to consist of $(CH_3)_3$-$SiOSi(CH_3)_3$ (chem. shift -0.06 ppm, lit.[11] -0.06 ppm) and $(CH_3)_2AsCl$ [chem. shift -1.63 ppm, chem. shift of $(CH_3)_2AsCl$ prepared by a literature[12] method -1.62 ppm] in an approximately 1 to 2 mole ratio. These could not be separated by trap-to-trap distillation. Therefore, Cl_2 (0.368 mmole) was distilled in to react with the volatile $(CH_3)_2AsCl$ in order to form nonvolatile $(CH_3)_2AsCl_3$. The volatile $(CH_3)_3SiOSi-(CH_3)_3$ (21.9 mg, 73% yield) was then recovered. The nonvolatile $(CH_3)_2AsCl_3$ was then heated and CH_3Cl was shown by infrared to be evolved as is expected on heating this material[13].

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

Nitrosyl chloride (0.1031 g, 1.58 mmole) and $(CH_3)_3SiP(CH_3)_2$ (0.1708 g, 1.27 mmole) were distilled into a small tube attached to a vacuum line. The tube was then allowed to warm from $-196°$ to $-36°$, held there for $\frac{1}{2}$ h, and then allowed to warm to room temperature. A small amount of noncondensable gas (shown by mass spec. to be N_2), a clear liquid, and a white solid were observed as products at this point. A small amount of excess NOCl was recovered when the products were separated by trap-to-trap distillation. Material that passed a $-134°$ bath was shown by infrared to be a mixture of nitric oxide (NO) and nitrous oxide (N_2O) (a mixed molecular weight determination allowed an estimation of 0.29 mmole N_2O and 0.14 mmole NO). Material held by a $-112°$ bath was shown by infrared and NMR to be $(CH_3)_3SiCl$ [0.923 mmole, 77% of $(CH_3)_3Si$ groups, chem. shift -0.38 ppm, lit.[11] -0.42 ppm, Dumas mol.wt. of isolated product 109.0, calcd. 108.6] and [$(CH_3)_3SiOSi(CH_3)_3$ (0.138 mmole, 23% of $(CH_3)_3Si$ groups, chem. shift -0.06 ppm, lit.[11] -0.06 ppm]. On heating the white solid, a portion sublimed and was shown by NMR (chem. shift -2.02 ppm, chem. shift of a sample prepared according to literature techniques[14] -2.02 ppm) and melting point (66.5–68°, lit.[14] 66.5–68.4°) to be $(CH_3)_3P(O)Cl$ (0.1 mmole). The remainder of the solid was an unidentifiable amber viscous liquid that cooled to a glass. After dissolving the glassy solid in HNO_3, treatment with $AgNO_3$ gave a white precipitate which dissolved on the addition of NH_3.

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