Synthesis of Triphenylphosphonium Trichlorogermanate and Analogs. Preparation of Germylenes from Triphenylphosphonium Trichlorogermanate

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ABSTRACT

Triphenylphosphonium trichlorogermanate was prepared in quantitative yield by reducing germanium tetrachloride-triphenylphosphine (1:1) with tributyltin hydride in diethyl ether. Heating the phosphonium salt at 245°C gave $Ph_3P\text{-}GeCl_2$ in 90% recrystallized yield. Treatment of the phosphonium salt with $LiN(TMS)_2$ gave $Ge[N(TMS)_2]_2$ in 70–77% yield. Reaction of tin dichloride or zinc dichloride with triphenylphosphine and hydrogen chloride yielded tin and zinc analogs of triphenylphosphonium trichlorogermanate.

As part of a program aimed at developing synthetic methods based on divalent germanium and tin [1], we needed a stable and readily available compound that could serve as precursor to a variety of germylenes [2]. By modifying a literature procedure for the preparation of germanium dichloride, we synthesized triphenylphosphonium trichlorogermanate in excellent yield. This novel phosphonium salt was found to be a versatile intermediate, as it could be easily converted to $Ge[N(TMS)_2]_2$ or $Ph_3P\text{-}GeCl_2$. Furthermore, we prepared both the tin and zinc analogs of triphenylphosphonium trichlorogermanate and explored their reactions with aldehydes.
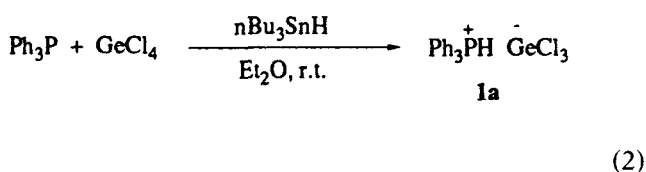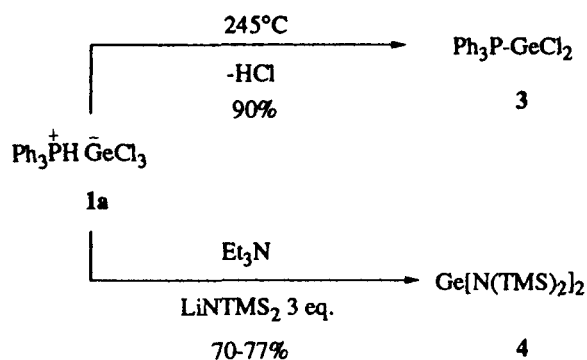
Germanium dichloride, most commonly used as a dioxane complex, can be prepared by several methods [3]. For large scale reactions, hydride reduction seems to be the most practical. Reduction of germanium tetrachloride with hydride generates trichlorogermane which undergoes α-elimination to form germanium dichloride (Equation 1). This reaction proceeds only in modest yield, however, due to side reactions initiated by the highly acidic trichlorogermane [4]. We hoped to improve this procedure by carrying out the reduction in the presence of base, which would serve to quench the acidic proton and simultaneously assist in the α-elimination reaction. This would be analogous to the reaction of base with chloroform to generate dichlorocarbene [5].

$$GeCl_4 \xrightarrow[\text{dioxane}]{\text{H}^-} \left[HGeCl_3 \right] \xrightarrow{\text{- HCl}} GeCl_2\text{-dioxane}$$
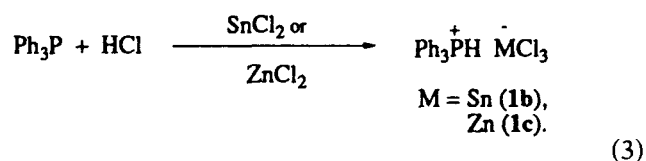
$$(1)$$
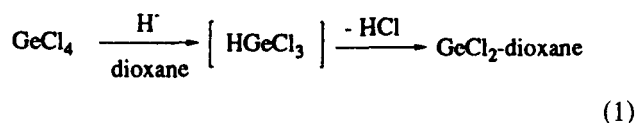
When tributyltin hydride was added to germanium tetrachloride in the presence of one equivalent of triphenylphosphine, a quantitative yield of white crystalline triphenylphosphonium trichlorogermanate (**1a**) precipitated from solution (Equation 2). The triphenylphosphonium salt was isolated by filtration and was either recrystallized or used directly in subsequent reactions. When the reaction was done on a 100 g scale, the product was obtained in greater than 90% recrystallized yield. Thus, triphenylphosphine is not only basic enough to form the desired phosphonium salt, but also removes the salt from solution, thereby avoiding side reactions.

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$$\underset{\substack{\text{Ph}_3\overset{+}{\text{P}}\text{H } \overset{-}{\text{Ge}}\text{Cl}_3 \\ \textbf{1a}}}{} \quad \begin{array}{c} \xrightarrow[\substack{-\text{HCl} \\ 90\%}]{245°\text{C}} \quad \underset{\textbf{3}}{\text{Ph}_3\text{P-GeCl}_2} \\[3em] \xrightarrow[\substack{\text{LiNTMS}_2 \text{ 3 eq.} \\ 70\text{-}77\%}]{\text{Et}_3\text{N}} \quad \underset{\textbf{4}}{\text{Ge}[\text{N(TMS)}_2]_2} \end{array}$$

$$\text{Ph}_3\text{P} + \text{GeCl}_4 \xrightarrow[\text{Et}_2\text{O, r.t.}]{n\text{Bu}_3\text{SnH}} \underset{\textbf{1a}}{\text{Ph}_3\overset{+}{\text{P}}\text{H } \overset{-}{\text{Ge}}\text{Cl}_3}$$
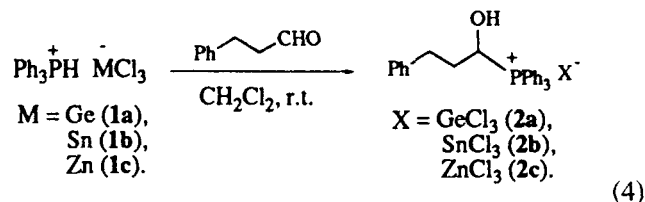
(2)

If phosphonium salt (**1a**) is heated [6] under vacuum at 245°C for 15 minutes, it loses hydrogen chloride and forms the known germanium dichloride triphenylphosphine complex **3** in 90% recrystallized yield (Scheme 1) [7]. Furthermore, triphenylphosphonium trichlorogermanate can be converted to bis-amido germanium (II) compound **4** by either of two methods [8]. This transformation can be accomplished directly by the addition of **1a** to three equivalents of lithium hexamethyldisilazane; distillation affords the purified amide **4** in ca. 50% yield [9]. Alternatively, phosphonium salt **1a** can be converted to a triethylammonium salt in situ and then treated with three equivalents of lithium hexamethyldisilazane. In the latter procedure, the yield of germanium amide **4** is improved to 70–77%.

Analogs of triphenylphosphonium trichlorogermanate can also be prepared. For example, addition of tin dichloride or zinc dichloride to an ethereal solution of triphenylphosphine and hydrogen chloride yields the corresponding phosphonium salts in high yield (Equation 3) [10]. The compounds **1a–c** were readily identified via NMR and IR spectroscopy as well as elemental analysis.

$$\text{Ph}_3\text{P} + \text{HCl} \xrightarrow[\text{ZnCl}_2]{\text{SnCl}_2 \text{ or}} \text{Ph}_3\overset{+}{\text{P}}\text{H } \overset{-}{\text{M}}\text{Cl}_3$$

M = Sn (**1b**),
Zn (**1c**).

(3)

Addition of compounds **1a–c** to hydrocinnamaldehyde yielded 1-hydroxy triphenylphosphonium salts **2a–c** irrespective of the counterion (Equation 4). Thus, triphenylphosphine readily adds

to aldehydes under anhydrous, acidic conditions and is more nucleophilic than either trichlorogermanate or trichlorostannate [11].

$$\underset{\substack{M = \text{Ge (1a)}, \\ \text{Sn (1b)}, \\ \text{Zn (1c)}.}}{\text{Ph}_3\overset{+}{\text{P}}\text{H } \overset{-}{\text{M}}\text{Cl}_3} \xrightarrow[\text{CH}_2\text{Cl}_2, \text{ r.t.}]{\text{Ph}\diagdown\diagup\text{CHO}} \underset{\substack{X = \text{GeCl}_3 \text{ (2a)}, \\ \text{SnCl}_3 \text{ (2b)}, \\ \text{ZnCl}_3 \text{ (2c)}.}}{\text{Ph}\diagup\diagdown\diagup\underset{\overset{+}{\text{PPh}_3}}{\overset{\text{OH}}{|}}\text{ X}^-}$$

(4)

EXPERIMENTAL

^{1}H NMR spectra were recorded at 400 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 75 MHz. ^{31}P NMR spectra were recorded at 160 MHz. All infrared spectra were obtained on a Perkin Elmer Model 283 IR. C, H, N analyses were obtained for all new compounds from G. D. Searle, Skokie, IL.

Synthesis of Ph$_3$PHGeCl$_3$

A solution of Bu$_3$SnH (111 g, 0.381 mol) in ethyl ether (150 mL) was slowly added to a stirred mixture of GeCl$_4$ (81.7 g, 0.381 mol) and Ph$_3$P (100 g, 0.381 mol) in ethyl ether (400 mL) at room temperature. After 15 minutes, the suspension was allowed to settle, then the ether was removed via cannula. The remaining solid was recrystallized by dissolving it in CH$_2$Cl$_2$ (150 mL) and then adding diethyl ether (50 mL). After 6 hours at $-30°$C, the supernatant liquid was removed via cannula and the remaining solid was washed with ether (3X, 50 mL). The solid was then dried in vacuo to yield 154.9 g (92%) of triphenylphosphonium trichlorogermanate. ^{1}H NMR (CDCl$_3$): δ 10.1 (d, 1 H, $^1J_{PH}$ = 535 Hz), 7.90–7.75 (m, 9 H), 7.66–7.60 (m, 6 H); ^{13}C NMR (CDCl$_3$): δ 135.27 (d, $^4J_{PC}$ = 2.7 Hz), 134.21 (d, J_{PC} = 11.2 Hz), 130.31 (d, J_{PC} = 13.3 Hz), 115.72 (d, $^1J_{PC}$ = 86.9 Hz); ^{31}P (CDCl$_3$): δ 3.2 (d, $^1J_{PH}$ = 545 Hz); IR (CHCl$_3$, cm^{-1}) 3060 (W), 3000 (M), 2940 (W), 2400 (W), 2380 (M), 1590 (M), 1480 (W), 1440 (M), 1110 (S), 870 (M). Elemental analysis expected: C, 48.89; H 3.65. Found: C, 48.82; H, 3.64.

Synthesis of Ph$_3$PHSnCl$_3$

Diethyl ether (5 mL) and hydrogen chloride (1.0 mL, 1.0 mmol, 1 M in ethyl ether) was added to a suspension of tin dichloride (0.19 g, 1.0 mmol) in THF (ca. 1 mL). A solution of triphenylphosphine (0.26 g, 1.0 mmol) in diethyl ether (5 mL) was added to the resulting clear solution. The reaction becomes cloudy, forming an oil that quickly turns solid. The solid is isolated by filtration and recrystallized with CH$_2$Cl$_2$:Et$_2$O to give 0.44 g (90%) of triphenylphosphonium trichlorostannate. ^{1}H NMR (CDCl$_3$): δ 10.4 (d, 1 H, $^1J_{PH}$ = 545 Hz), 7.92–7.87 (m, 6 H), 7.8–7.67 (m, 3 H), 7.61–7.63 (m, 6 H); ^{13}C NMR

(CDCl$_3$): δ 135.12 (d, $^4J_{PC}$ = 3.1 Hz), 134.43 (d, J_{PC} = 11.1 Hz), 130.21 (d, J_{PC} = 13.3 Hz), 117.33 (d, $^1J_{PC}$ = 86.8 Hz); ^{31}P NMR (CDCl$_3$): δ 2.89 (d, $^1J_{PH}$ = 543 Hz); IR (CHCl$_3$, cm^{-1}) 3000 (M), 2920 (W), 2380 (W), 1590 (W), 1430 (M), 1110 (S), 1000 (W), 860 (M). Elemental analysis expected: C, 44.27; H, 3.30. Found: C, 44.18; H, 3.30.

Synthesis of Ph$_3$PHZnCl$_3$

Prepared in a manner similar to Ph$_3$PHSnCl$_3$. ^{1}H NMR (CD$_2$Cl$_2$): δ 9.69 (d, 1 H, $^1J_{PH}$ = 532 Hz), 7.85–7.78 (m, 9 H), 7.76–7.61 (m, 6 H); ^{13}C NMR (CD$_2$Cl$_2$): δ 135.70 (d, $^4J_{PC}$ = 2.9 Hz), 134.76 (d, J_{PC} = 11.2 Hz), 130.78 (d, J_{PC} = 13.5 Hz), 116.39 (d, $^1J_{PC}$ = 87.3 Hz); ^{31}P NMR (CD$_2$Cl$_2$): δ 6.63 (d, $^1J_{PH}$ = 530 Hz); IR (CH$_2$Cl$_2$, cm^{-1}) 2920 (M), 2860 (W), 2320 (W), 1590 (W), 1100 (S), 860 (M). Elemental analysis expected: C, 49.70; H, 3.71. Found: C, 49.53; H, 3.66.

Synthesis of Ph$_3$P-GeCl$_2$ [10]

A 50 ml round bottom flask was charged with triphenylphosphonium trichlorogermanate (4.40 g, 10.0 mmol) under nitrogen. The flask was put under vacuo, placed in a sand bath, and then heated at 245°C for 40 minutes. As it was heated, the trichlorogermanate first melted to a clear liquid, then became yellowish green. Upon cooling, a white solid formed (4.0 g). This solid was recrystallized from a minimum amount of methylene chloride and diethyl ether to give 3.75 g (91%) of triphenylphosphine germanium dichloride complex. ^{1}H NMR (CDCl$_3$): δ 7.6–7.5 (m). Elemental analysis expected: C, 53.28; H, 3.73. Found: C, 53.31; H, 3.74.

Synthesis of Ge[N(TMS)$_2$]$_2$ [2]

Et$_3$N (22.9 g, 31.5 mL, 226 mmol) was slowly added to a solution of triphenylphosphonium trichlorogermanate (25.0 g, 56.5 mmol) in CH$_2$Cl$_2$ (200 mL) at 0°C. The reaction mixture was allowed to warm to room temperature, stirred for 90 minutes, and then concentrated at reduced pressure. The oil was washed with hexane (5 × 50 mL) to remove the triphenylphosphine. The oil was dissolved in THF (125 mL), cooled to 0°C, and treated with a solution of LiN(TMS)$_2$ (26.76 g, 160 mmol) in THF (125 mL). After 1 hour, the THF was removed in vacuo and hexane (2X, 100 mL) was added. After 30 minutes, the hexane solution was transferred via cannula to a Schlenk flask and the volatiles were removed in vacuo to yield a dark oil. The oil was then purified by Kugelrohr distillation to yield Ge[N(TMS)$_2$]$_2$ as a pale yellow solid (70–77%). ^{1}H NMR (CDCl$_3$): δ 0.3 (s).

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[9] Bis-amidogermanium (II) compound **4** is very sensitive to water and oxygen. If this reaction is performed under an atmosphere of "high purity" nitrogen supplied from a cylinder, the yield can plummet to 10%. If the nitrogen atmosphere is obtained from a liquid nitrogen dewar, reproducibly good yields are obtained. For methods on purifying cylinder nitrogen, see D. F. Shriver, M. A. Drezdzon: *The Manipulation of Air-Sensitive Compounds*, 2nd ed., Wiley Interscience, New York (1986).

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