

Silyl stabilized azanes: reactions of lithiumbis(trimethylsilyl)hydrazine with trialkyltin halides

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Received 15 August 2004; accepted 17 December 2004

Available online 7 February 2005

Abstract

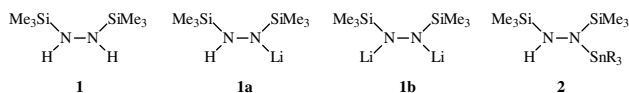
Lithium 1,2-bis(trimethylsilyl)hydrazine (**1a**) reacts with Me_3SnCl , Et_3SnBr and Bu_3SnCl to form bis(trimethylsilyl)(trimethylstannyl)hydrazine (**2a**), (triethylstannyl)bis(trimethylsilyl)hydrazine (**2b**) and (tributylstannyl)bis(trimethylsilyl)hydrazine (**2c**), respectively. Compounds **2a** and **2b** undergo disproportionation at room temperature to form bis(trimethylsilyl)bis(trimethylstannyl)hydrazine (**3a**) and bis(triethylstannyl)bis(trimethylsilyl)hydrazine (**3b**). In contrast, **2c** is highly stable and can withstand such a reaction up to 150 °C. The monostannylated products, **2a**, **2b** and **2c** do not get lithiated at NH and instead undergo transmetalation in their reaction with RLi or Li to form lithiumbis(trimethylsilyl)hydrazine (**1a**).

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Keywords: Bis(trimethylsilyl)hydrazine; Lithiumbis(trimethylsilyl)hydrazine; Trialkyltin halides; Disproportionation; Lithiation; Transmetalation

1. Introduction

Model compounds play an important role in synthetic chemistry as they help towards the syntheses, mechanistic behaviors and understanding of the properties of materials that are difficult to handle due to their high reactivity. Hydrazine is known to explode at higher temperatures to form ammonia and molecular nitrogen. Bis(trimethylsilyl)hydrazine, **1** [1] is a very stable model compound of hydrazine.



Lithiumbis(trimethylsilyl)hydrazine, **1a** [2] and dilithiumbis(trimethylsilyl)hydrazine, **1b** [3] have attracted the attention as model compounds of highly reactive LiN_2H_3 and $\text{Li}_2\text{N}_2\text{H}_2$ and their synthesis [4–6] and chemical reactions [3,5,6] have also been reported. If the lithium atom of lithiumbis(trimethylsilyl)hydrazine, **1a**, is substituted by an $-\text{SnR}_3$ group, the resulting (trialkylstannyl)bis(trimethylsilyl)hydrazine, **2**, would be endowed with two differentially reactive N–H and N–Sn bonds. As part of our study on silyl-nitrogen compounds [7–10], we report herein the reactions of lithiumbis(trimethylsilyl)hydrazine, $\text{Li}(\text{H})\text{N}_2(\text{SiMe}_3)_2$, **1a**, with trialkyltin halides.

2. Experimental

2.1. General comments

All investigations were carried out under vacuum and in the absence of air and moisture; glassware was also flame-dried under vacuum. Bis(trimethylsilyl)hydrazine

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[4,5], butyllithium [11], lithiumbis(trimethylsilyl)hydrazine [6] and trimethyltin chloride [12,13] were prepared as per reported procedure. Diethyl ether and tetrahydrofuran were dried over sodium benzophenoneketyl and the hydrocarbons were kept over sodium wire. NMR studies were recorded on a Jeol AL-300 MHz instrument, IR spectra on a Perkin–Elmer RX-I FT IR spectrometer and the mass spectra on a Varian MAT CH7 spectrometer or a Jeol Mstation JMS 700.

2.2. General procedure

Lithiumbis(trimethylsilyl)hydrazine (**1a**) (8.191 g, 45 mmol) was suspended in 30–40 ml of hexane (or Et₂O) and cooled to –80 °C. The required amounts of trialkylstannyl halides (45 mmol) dissolved in 15 ml hexane (or Et₂O) were added drop-wise and the reaction mixture was allowed to warm slowly to room temperature with stirring. It was then filtered to isolate LiX (X = Cl, Br). The ¹H NMR of a part of the filtrate was studied. The filtrate was carefully evacuated (up to 60 Torr at 25 °C) to remove the solvents and other volatile impurities and then fractionated to isolate and characterize the various products.

2.3. Reaction with Me₃SnCl

Reaction of **1a** with trimethyltin chloride in equimolar ratio at room temperature in tetrahydrofuran provided a mixture of bis(trimethylsilyl)(trimethylstannyl)hydrazine; **2a** and bis(trimethylsilyl)bis(trimethylstannyl)hydrazine; **3a** in the ratio 1:1. This ratio changed to 1:4 after 12 h at room temperature. Change of solvent to diethyl ether and lowering the temperature to –80 °C provided **2a** and **3a** in the ratio 4:1, while the same reaction in hexane at –80 °C resulted in exclusive formation of **2a**. Compound **2a** is stable at –80 °C, but as the reaction mixture comes to room temperature, it disproportionates slowly to **3a** and **1**. Careful fractional distillation provided **2a** at 100 °C/10^{–3} Torr and **3a** at 120 °C/10^{–3} Torr.

Compound **2a**: ¹H NMR (CDCl₃): δ 0.01 (s, 9H, Me₃Si), 0.02 (s, 9H, Me₃Si) and 0.21 (s, 9H, Me₃Sn); ²⁹Si NMR (¹H-decoupled)(CDCl₃): δ 3.65 (Me₃Si), 6.92 (Me₃Si); ¹¹⁹Sn NMR (¹H-decoupled)(CDCl₃): δ 65.53 (Me₃Sn). Mass spectrum (70 eV), *m/z* (assignment; %): 340 (M⁺; 21), 267 (M⁺ – SiMe₃; 3), 176 ((Me₃Si)₂N₂H₂⁺; 50), 120 (Sn⁺; 7), 102 (Me₃SiN₂H⁺; 3), 87 (Me₃SiN⁺; 2) and 73 (Me₃Si⁺; 100). Some characteristic IR bands (neat, cm^{–1}, s = strong, m = medium, sh = shoulder band): 3346m (ν N–H), 1070s (ν N–N), 835sh (ν Si₂–N₂), 760m (ν Si–N), 416s (ν Sn–N).

Compound **3a**: ¹H NMR (CDCl₃): δ 0.08 (s, 18H, 2SiMe₃) and 0.49 (s, 18H, 2SnMe₃); ²⁹Si NMR (¹H-decoupled)(CDCl₃): δ 5.54 (2SiMe₃); ¹¹⁹Sn NMR (¹H-decoupled): δ 87.75 (2SnMe₃). Mass spectrum (70 eV), *m/z* (assignment; %): 502 (M⁺; 12), 338 (M⁺ – SnMe₃;

9), 207 (Me₃SiNSn⁺; 20), 176 (2Me₃SiNH⁺; 41), 149 (Me₂Sn⁺; 9), 120 (Sn⁺; 5), 101 (Me₃SiN₂⁺; 3), 87 (Me₃SiN⁺; 2) and 73 (Me₃Si⁺; 100).

2.4. Reaction with Et₃SnBr

An equimolar reaction of **1a** with triethyltin bromide at –80 °C provided (triethylstannyl)bis(trimethylsilyl)hydrazine, **2b** in 90% yield. As the mixture is allowed to stand at room temperature for about 24 h, compound **2b** started disproportionating to bis(triethylstannyl)bis(trimethylsilyl)hydrazine, **3b** and bis(trimethylsilyl)hydrazine, **1**. Fractional distillation provided **2b** at 125 °C/10^{–3} Torr and **3b** at 140 °C/10^{–3} Torr.

Compound **2b**: ¹H NMR (CDCl₃): δ 0.02 (s, 9H, SiMe₃), 0.06 (s, 9H, SiMe₃) and 1.02 (t, 9H, 3CH₃–CH₂), 1.23 (q, 6H, 3CH₂–CH₃); ²⁹Si NMR (¹H-decoupled)(CDCl₃): δ 6.03 (SiMe₃), 8.29 (SiMe₃); ¹¹⁹Sn NMR (¹H-decoupled)(CDCl₃): δ 52.00 (SnEt₃). Mass spectrum (70 eV), *m/z* (assignment; %): 382 (M⁺; 20), 295 (M⁺ – Me₃Si; 1), 281 (M – Me₃SiN₂⁺; 3), 207 (Et₃Sn⁺; 26), 174 (Me₃SiNNSiMe₃⁺; 38), 159 (Me₃Si₂N₂⁺; 12), 149 (EtSn⁺; 16), 131 (Me₃Si₂⁺; 5), 116 (Me₄Si₂⁺; 2), 101 (Me₃SiN₂⁺; 2), 87 (Me₃SiN⁺; 5) and 73 (Me₃Si⁺; 100). Some characteristic IR bands (neat, cm^{–1}): 3345m (ν N–H), 1068s (ν N–N), 836sh (ν Si₂–N₂), 760m (ν Si–N), 427s (ν Sn–N).

Compound **3b**: ¹H NMR (CDCl₃): δ 0.09 (s, 18H, 2SiMe₃) and 1.03 (t, 18H, 6CH₃–CH₂), 1.35 (q, 12H, 6CH₂–CH₃); ²⁹Si NMR (¹H-decoupled)(CDCl₃): δ 6.55 (SiMe₃); ¹¹⁹Sn NMR (¹H-decoupled)(CDCl₃): δ 82.78 (SnEt₃). Mass spectrum (70 eV), *m/z* (assignment; %): 586 (M⁺; 9), 499 (M – Me₃Si⁺; 4), 380 (M – Et₃Sn⁺; 13), 207 (Et₃Sn⁺; 26), 176 ((Me₃Si)₂N₂H₂⁺; 27), 149 (EtSn⁺; 13), 132 (Me₃Si₂H⁺; 15), 118 (Me₄Si₂H₂⁺; 7), 101 (Me₃SiN₂⁺; 2), 87 (Me₃SiN⁺; 4) and 73 (Me₃Si⁺; 100).

2.5. Reaction with Bu₃SnCl

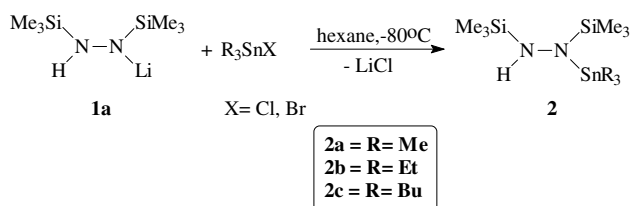
Reaction of **1a** with equimolar amount of tributyltin chloride at –80 °C or at room temperature provided (tributylstannyl)bis(trimethylsilyl)hydrazine, **2c** in almost 100% yield. Compound **2c** was distilled at 150 °C/10^{–3} Torr without any disproportionation. ¹H NMR (CDCl₃): δ 0.03 (s, 9H, SiMe₃), 0.07 (s, 9H, SiMe₃) and 1.12 (t, 9H, 3CH₃–CH₂–CH₂–CH₂), 1.46–1.69 (m, 18H, 3CH₃–CH₂–CH₂–CH₂); ²⁹Si NMR (¹H-decoupled)(CDCl₃): δ 4.17 (SiMe₃), 6.46 (SiMe₃); ¹¹⁹Sn NMR (¹H-decoupled)(CDCl₃): δ 45.32 (SnBu₃). Mass spectrum (70 eV), *m/z* (assignment; %): 466 (M⁺; 9), 409 (M⁺ – Bu; 7), 365 (M⁺ – Me₃SiN₂; 9), 290 (Bu₃Sn⁺; 8), 176 ((Me₃Si)₂N₂H₂⁺; 100), 161 ((Me₃Si)₂NH; 27), 146 (Me₆Si₂⁺; 21), 132 (Me₃Si₂H⁺; 70), 118 (Me₄Si₂⁺; 25), 101 (Me₃SiN₂⁺; 7), 88 (Me₃SiNH⁺; 8) and 73 (Me₃Si⁺; 82). Some characteristic IR bands (neat, cm^{–1}): 3343m

(ν N–H), 1071s (ν N–N), 869sh (ν Si₂–N₂), 765m (ν Si–N), 438s (ν Sn–N).

3. Results and discussion

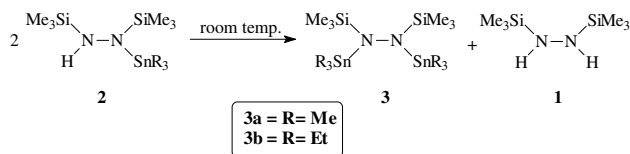
Lithiation of an isomeric mixture of symmetric and asymmetric bis(trimethylsilyl)hydrazine (BSH) with BuLi provides monolithiumbis(trimethylsilyl)hydrazine, **1a** [4–6]. This salt may act as a versatile reaction intermediate for the synthesis of (trialkylstannyl)bis(trimethylsilyl)hydrazine, **2**. Chemical reactions of compound **2** would be interesting as they involve two reactive centers (N–H and N–Sn) that are substantially different in their bond energies. When carefully studied, they may preferentially react with a variety of reagents involving cleavage of N–H or N–Sn bonds or both.

Reactions of **1a** with trialkyltin halides result in substitution products (trialkylstannyl)bis(trimethylsilyl)hydrazine (**2**).



These products are colorless liquids and can be distilled under vacuum of 10^{-3} Torr at different temperatures. These compounds have been fully characterized by multinuclear NMR, IR and mass spectral studies (see Section 2).

It has been observed that compounds **2a**, bis(trimethylsilyl)(trimethylstannyl)hydrazine and **2b**, (triethylstannyl)bis(trimethylsilyl)hydrazine undergo disproportionation reaction at room temperature to give bis(trialkylstannyl)bis(trimethylsilyl)hydrazine, **3** and bis(trimethylsilyl)hydrazine, **1**.



Interestingly, compound **2c**, (tributylstannyl)bis(trimethylsilyl)hydrazine is highly stable at room temperature. Deliberate increase of temperature to 150 °C for more than 30 min also did not disproportionate **2c**. With these observations in mind, investigations were carried out at different temperatures and in different organic solvents to study the stability of the monostannylated products, **2a**, **2b** and **2c**. All of them, in the absence of

any organic solvent, were found to be stable at low temperature (–25 °C) and could be stored for weeks. However, even at this temperature, addition of a few milliliters of organic solvent like hexane or tetrahydrofuran to **2a** or **2b** initiated the disproportionation. This did not happen in the case of **2c**. Additionally, as the system warmed up, the disproportionation increased. As the polarity of the solvent become higher the rate of disproportionation increases, the rate being the highest in tetrahydrofuran and the lowest in hexane. To evaluate the relative stability of these compounds, semi-quantitative life was calculated from the integrated intensities of the respective peaks of the reactants (**2a**, **2b**) and products (**3a**, **3b**) from the ¹H NMR spectra. This is shown in Table 1.

The quantity derived here is the time required for **2a** (or **2b**) to disproportionate to half of its concentration at room temperature (25 °C) and designated as $T_{1/2}$. Table 1 clearly shows that a change from methyl to ethyl group in –SnR₃ moiety has decreased the rate of disproportionation by more than six times and an *n*-butyl group made it completely stable. It is remarkable that the compound **2c**, (tributylstannyl)bis(trimethylsilyl)hydrazine can withstand a temperature of 150 °C without undergoing any disproportionation.

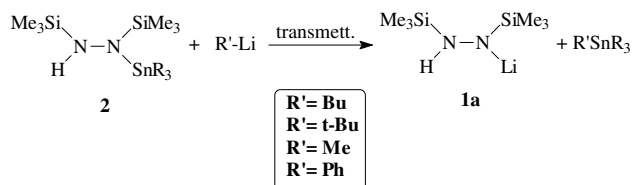
These observations indicate that, as the size of the chain of the alkyl group of the stannyl moiety increases, the stability of the monosubstituted product increases. Similar trends are observed in the reactions of trialkyl chlorosilanes with hydrazine in which the primary silylhydrazines (R₃SiN₂H₃; R = Me, Et, Pr) could not be isolated as they immediately underwent further disproportionation to bis(silyl)hydrazine [14–16]. However, if a bulky triphenylsilyl group is introduced, monosilylhydrazines are formed and their disproportionation occur only at 90 °C. Further, this class of monosilylated compounds, R₃SiN₂H₃ could be kinetically stabilized by the introduction of one or more bulky *tert*-butyl groups (for example; R = ^tBu₂F [17], ^tBu₂Me [18], ^tBu₂Ph [19] or ^tBu(*i*-Pr)₂ [19]). Thus the bulkiness of the alkyl group plays an important role in imparting stability to these classes of compounds.

Since compound **2** is endowed with two different reactive groups, it may be possible to lithiate the nitrogen atom of the N–H group to form lithium(trialkylstannyl)bis(trimethylsilyl)hydrazine, Li(SiMe₃)N–N(SiMe₃)(SnR₃) under appropriate reaction conditions. If both

Table 1
Observed $T_{1/2}$ of various (trialkylstannyl)bis(trimethylsilyl)hydrazines

2	SnR ₃	$T_{1/2}$ (h)	Temperature (°C)
2a	SnMe ₃	12	25
2b	SnEt ₃	78	25
2c	SnBu ₃	–	Stable at 150

these centers (i.e., N–H and N–Sn) were to react with lithiating reagent, then dilithiumbis(trimethylsilyl)hydrazine, **1b** would result. To check these possibilities, compound **2** was treated separately with BuLi, *t*-BuLi, MeLi, PhLi and Li powder at different temperatures (–25, 0, 25 °C) and in different organic solvents (*n*-hexane, THF, ether). Surprisingly, under all these conditions, compound **2** underwent transmetallation reaction to form **1a**, rather than the awaited lithiation of the nitrogen atom of N–H group.



4. Conclusions

Monolithiumbis(trimethylsilyl)hydrazine, **1a** on reaction with trialkylstannyl halide, R₃SnX (where R = Me, Et or Bu and X = Cl or Br) provides (trialkylstannyl) bis(trimethylsilyl)hydrazine, **2**. These monostannylated products show different rates of disproportionation that finds a direct correlation with the size of the alkyl group attached to the tin atom. The bulky nature of the alkyl group in (tributylstannyl)bis(trimethylsilyl)hydrazine makes it highly stable and it can withstand a temperature of 150 °C. The polarity of the reaction medium also controls the disproportionation reaction, the rate being the lowest in the least polar solvent like *n*-hexane. All these monostannylated products, on treatment with different lithiating reagents, undergo transmetallation reaction leading to lithiumbis(trimethylsilyl)hydrazine, **1a**

and in no case lithium(trialkylstannyl)bis(trimethylsilyl)hydrazine could be obtained.

Acknowledgments

We thank Council of Scientific and Industrial Research, New Delhi (India) for financial support.

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