Silyl-nitrogen compounds: Part VI-Reactions of lithium tris (trimethylsilyl)hydrazine with non-metallic halides

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Lithium tris(trimethylsilyl)hydrazine (Me₃Si)₂N-N(SiMe₃)Li (1) reacts with non-metallic halides EXₙ to form bis (trimethylsilyl)hydrazino in derivatives [(Me₃Si)₃N₂1₂EXₙ-2 where E=B, X=F, n=3; E=C, X=Br, n=4; E=Si, X=Cl, n=4 and E=P, X=Cl, n=5. Non-metallic monohydrazino derivatives (Me₃Si)₃N₂EXₙ-1 are formed in cases of BF₃, Me₂SiCl₂, PCl₃, PBr₃, AsCl₃ and Et₂NAsCl₂.

Materials and Methods
All investigations were carried out in an inert and moisture-free atmosphere on a vacuum line. All glassware was also flame-dried under vacuum. Tris(trimethylsilyl) hydrazine³, lithium tris (trimethylsilyl)hydrazine⁴ and butyllithium⁵ were prepared as reported in literature. NMR measurements were recorded on Varian EM 390k and Brucker FT-NMR 300 MHz instruments. Mass spectrum was recorded on VG analytical 11-2505-70s and elemental analysis on a Carto Erba Strumentazione (Italy) Elemental analyser Model 1106. The ¹H NMR of Me₃Si protons (ppm) in benzene (Et₂O/hexane) showed the signals: (Me₃Si)₂N₂H₂, 0.12(0.07); (Me₃Si)₂N₂H₃, 0.13, 0.11(2:1), 0.09; Li(SiMe₃)₂N⁻N(SiMe₃)₂, 0.25(0.19); (Me₃Si)₂NH, 0.09(0.05), Me₃SiCl, 0.20(0.37), Me₃SiBr, 0.34(0.50).

General procedure
Lithium tris(trimethylsilyl) hydrazine (1) (20 mmol, 5.25g), dissolved in 40 ml n-hexane (Et₂O), was added dropwise. The reaction mixture was then slowly allowed to come to room temperature. The spectrum ¹H NMR of the reaction mixture was recorded to monitor the progress of the reaction. The reaction mixture was filtered and the residue dried in vacuo. The filtrate was evaporated to remove solvents and other volatile compounds up to 60 torr at room temperature. The residue (R) was then distilled or sublimed or crystallised to isolate pure products. The yields of pure products, obtained in significant amount, are based on amounts isolated whereas those of unseparable mixtures or very small amounts of compounds are calculated from the ¹H NMR integrated ratios after adding a known amount of cyclohexane or toluene as standard.

The compounds along with their analytical data are listed in Table 1

Results and Discussion
It is already reported that CC₄ reacts with lithium tris (trimethylsilyl) hydrazine¹ (1) or dilithium bis(trimethylsilyl) hydrazine² to form bis(trimethylsilyl)amino- carbonimidochloride.

However, carbon tetrabromide behave differently and undergoes dihydrazidation in its reaction with (1). Bis {tris(trimethylsilyl)hydrazino} - dibromomethane (2) is formed as a white solid subliming at 80°C/10⁻³torr.
Table I — Analytical data of silylated non-metallic hydrazines

<table>
<thead>
<tr>
<th>Reactants (molar ratio)</th>
<th>Compound</th>
<th>Yield (%)</th>
<th>S.P. (°C/10^3 torr)</th>
<th>Found (calcd. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1):Exn*</td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>2:1</td>
<td>[(Me3Si)N2]2CBr2, (2)</td>
<td>74</td>
<td>80</td>
<td>33.9</td>
</tr>
<tr>
<td>1:1</td>
<td>(Me3Si)N-N(SiMe3)(BF2), (3)</td>
<td>59</td>
<td>60</td>
<td>35.9</td>
</tr>
<tr>
<td>2:1</td>
<td>[(Me3Si)N2]2BF, (4)</td>
<td>44</td>
<td>75</td>
<td>41.0</td>
</tr>
<tr>
<td>1:1</td>
<td>(Me3Si)N-N(SiMe3)(SiMe2Cl), (5)</td>
<td>55</td>
<td>55</td>
<td>37.9</td>
</tr>
<tr>
<td>2:1</td>
<td>[(Me3Si)N2]2SiCl2, (6)</td>
<td>51</td>
<td>80</td>
<td>35.7</td>
</tr>
<tr>
<td>1:1</td>
<td>(Me3Si)N-N(SiMe3)PCl2**, (7)</td>
<td>79</td>
<td>110</td>
<td>29.2</td>
</tr>
<tr>
<td>1:1</td>
<td>(Me3Si)N-N(SiMe3)PBr2**, (8)</td>
<td>75</td>
<td>100(d)</td>
<td>22.9</td>
</tr>
<tr>
<td>1:1</td>
<td>(Me3Si)N-N(SiMe3)AsCl2, (9)</td>
<td>77</td>
<td>115</td>
<td>26.9</td>
</tr>
<tr>
<td>1:1</td>
<td>(Me3Si)N-N(SiMe3)AsBr2, (10)</td>
<td>60</td>
<td>110(d)</td>
<td>21.9</td>
</tr>
<tr>
<td>1:1</td>
<td>(Me3Si)N-N(SiMe3)(Et2NAsCl), (11)</td>
<td>85</td>
<td>140(d)</td>
<td>35.8</td>
</tr>
<tr>
<td>2:1</td>
<td>[(Me3Si)3N2]PCl3**, (12)</td>
<td>56</td>
<td>95(d)</td>
<td>33.5</td>
</tr>
</tbody>
</table>

* Exn represents element halide.
** Analysis of P agreed with theoretical values
(d) means decomposition before sublimation

The 1H NMR spectrum of (2) in n-hexane gives just one signal at δ0.17 for all the silyl protons while in benzene it shows two signals at δ0.22 and 0.26 with relative areas in the ratio 2:1 due to 2[(Me3Si)N2], 2[Me3SiN] and CBr2 groups, respectively. The mass spectrum (70eV) gives molecular ion peak at M/e+666. Major fragments are observed at M/e+ 513(m-Me3SiBr) and 247([Me3Si]3N2)+ and 73(Me3Si)+.

The Lewis acid boron trifluoride interacts with base (1) in equivalent amounts to give a non-metallic hydrazine(Me3Si)N-N(SiMe3)BF2(3) which is stable and does not undergo the expected elimination of Me3SiBF2 or Me3SiF, Eq.(iii)
Compounds (3) is a white solid subliming at 60°C/10⁻³ torr. Its ¹H NMR spectrum in ether(benzene) shows two peaks with relative areas of 2:1 at δ 0.17(0.13), and 0.26(0.21). The signal at δ0.26(0.21) is a triplet with J(H,F) = 0.9 Hz. Its ²⁹Si NMR(¹H decoupled) spectrum in C₆D₆ gives resonance signals at δ9.29 and 12.58 with relative areas of 2:1. The ¹¹B NMR(¹H decoupled) spectrum in C₆D₆ shows a signal at δ 1.00 indicating three-coordinated boron. ¹⁹F NMR spectrum in C₆D₆ gives a resonance signal at δ-27.0 indicating fluorine attached to three- coordinated boron.

In mass spectrum (70eV), molecular ion peak is observed at M/e+ 296. Other prominent fragments are observed at 204(m-Me₃SiF), 176(Me₆Si₂BF), 117(Me₃SiNBF), 103(Me₃SiBF). The base peak is observed at M/e+150 which corresponds to (Me₃Si=N=NBF₂).

The reaction of BF₃ with (1) in the ratio 1:2 provides a non metallic dihyrazino derivative (4). It has been observed that B-F bond in (4) in quite strong and all attempts to synthesize pentasila-bor-pentazene (Me₃Si)₂N-N=B-N(SiMe₃)-N(SiMe₃) by the elimination of Me₃SiF on heating up to 110°C/10⁻³ torr. failed.

Compound (4) is a white solid subliming at 75°C/10⁻³ torr. The ¹H NMR spectrum of (4) in (CD₂O) (benzene) shows signals at δ 0.20 (0.28) [ d; J(H,F) = 1.0 Hz, 2(Me₃Si₂N] and 0.37(0.38) [ s,2 Me₃SiN]. ²⁹Si NMR (¹H decoupled) spectrum in C₆D₆ has resonances at δ 87.87 and 7.90(4:2). The ¹¹B NMR (δ=8.24) and ¹⁹F NMR(δ-93) spectra are characteristic of 3-coordinated boron with fluorine bonded to it. The mass spectrum has a very small molecular ion peak at M/e+ 524 but shows characteristic fragments at 505 (m-F), 432(m-Me₃SiF), 247[(Me₃Si₂N]², 176[(Me₃Si₂BF]² and 73(Me₃Si)².

The reaction of Me₂SiCl₂ with dilithium bis(trimethylsilyl)hydrazine is reported to give a mixture of products with a small yield of tetrazadisilacyclohexane. Reaction of (1) with Me₂SiCl₂ has been carried out to find if it could provide a higher yield of tetrazadisilacyclohexane or form a simple hydrazine which may then eliminate Me₃SiCl to act as a source of silamine, =Si=N-. However, it has been observed that hydrazine derivative (5) is formed which unlike a similar tetrazene derivative, does not lose Me₃SiCl up to its sublimation temperature of 55°C/10⁻³ torr.

The ¹H NMR spectrum (5) in n-hexane(benzene) shows resonances at δ 0.20(0.23), 0.27(0.27) and 0.47(0.53) with relative areas of 6:3:2 due to (Me₃Si)₂N, Me₃SiN, Me₃SiCl protons, respectively. The ²⁹Si-NMR (¹H decoupled) spectrum in C₆D₆ gives signals at δ 11.98, 12.10 and 16.32 in 2:1 ratio corresponding to (Me₃Si)₂N, Me₃SiN and Me₃SiCl respectively. Mass spectrum shows a molecular ion peak at M/e+ 340.

Silicon (IV) chloride is a stronger lewis acid compared to Me₂SiCl₂. It reacts with (1) to form a dihydrazino derivative (6) which sublimes at 80°C/10⁻³ torr.

The reaction of PX₃(X=Cl or Br) with dilithium bis(trimethylsilyl)hydrazine is known to give an intermediate phosphazene which undergoes easy polymerisation. Similarly, lithium tris(trimethylsilyl)tetrazene is known to combine with PX₃ to form intermediate aminophosphanes (Me₃Si)₂NPX₂ which decompose slowly at room temperature to form phosphazene polymer (Me₃SiNPX)n. The reaction of (1) with PX₃ leads to a substituted product dihalotris(trimethylsilyl)hydrazinophosphine which has been very useful as a starting material for synthesis of long chain phosphazenes.
Their NMR spectra (Table-2) are characteristic of structures (7) and (8). The $^{31}$P NMR spectrum is characteristic of 3-coordinated P(III). Mass spectrum of (7) shows $M/e^+$ at 348 and of (8) at 438. Both show fragment characteristic of (m-X)$_2$+, (Me$_3$Si)$_3$N$_2$+, As$_3$+ and halogens.

Arsenic (III) derivatives asX$_2$Y (where X=Y=Cl or Br and X=Cl, Y=Et$_2$N) react with (1) to form hydrazino As(III) derivatives.

The compounds (9), (10), (11) are very stable and do not undergo loss of halosilane even up to 100-130$^\circ$C/10$^{-3}$ torr. Consequently, these molecules do not act as a source of arsazenes,-As=N-. Their NMR spectra are typical of their structures (Table 2). Their mass spectra show molecular ion peak in each case. Besides, prominent fragments characteristic of (m-Me$_3$Si)$_2$+, (m-Me$_3$SiX)$_2$+, [(Me$_3$Si)$_3$N]$_2$+, As$_3$+, Me$_3$Si$_2$+ are observed in each case.

Phosphorous (V) chloride may behave as an oxidising agent. In its reaction with (1), it is expected that an initial loss of LiCl could lead to tetrachlorotrismethylhydrazinophosphorane which may lose Me$_3$SiCl to form phosphorus (V) azene. However, the reaction proceeds in 2:1 ratio to give bis(hydrazino) trichlorophosphorane (12).

Compounds (12) which is a white solid decomposes before its sublimation temperature. The $^1$H NMR spectrum of (12) in n-hexane(benzene) shows signals at 80.32(0.19), [d, $J_{H-P}$ = 0.9Hz] and 0.52(0.35) due to (Me$_3$Si)$_2$N, Me$_3$SiN groups, respectively. The $^{29}$Si NMR (1H decoupled) spectrum in C$_6$D$_6$ shows signals at 8 19.68 and 13.49 due to Me$_3$SiN and (Me$_3$Si)$_2$N groups, respectively. The $^{31}$P NMR (1H decoupled) spectrum in C$_6$D$_6$ shows signals at 8 -70.20 indicating five-coordinated P(V).

The results indicate that non-metallic hydrazines are quite stable and do not undergo easy elimination of halosilane at higher temperature in vacuum. Higher non-metallic halides prefer to form bis-hydrazino derivatives, whereas, the lower ones tend to form monohydrazino derivatives. Boron (III) fluoride forms both mono and bis derivatives.

**Acknowledgement**

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**References**