

Synthesis and characterization of sodium bis(trimethylstannyl) amide and bis(trimethylsilyl) bis(trimethylstannyl)-phospha-tetrazene

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Abstract

Sodium bis(trimethylstannyl)amide $\text{NaN}(\text{SnMe}_3)_2$, isolated by the reaction of trimethylstannyldiethylamine with sodium amide, reacts with tris(trimethylsilyl)hydrazino-dichloro-phosphine to form bis(trimethylsilyl)bis(trimethylstannyl)-2-phospha-2-tetrazene, $(\text{Me}_3\text{Si})_2\text{N}=\text{N}=\text{P}=\text{N}(\text{SnMe}_3)_2$. Both the molecules have been isolated and characterized. © 1997 Elsevier Science S.A.

Keywords: Sodium bis(trimethylstannyl)amide; Bis(trimethylsilyl)bis(trimethylstannyl)-2-phospha-2-tetrazene; Synthesis; Characterization

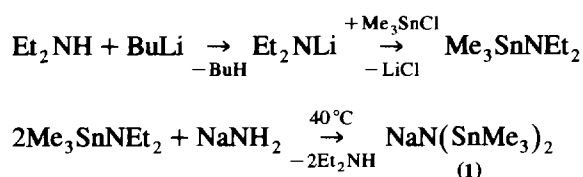
1. Introduction

Lithium bis(trimethylsilyl)amide [1] and other alkali metal bis(silyl)amides [1–4] are well known synthetic intermediates and have been used extensively as ligand transfer reagents, as low coordinative environment reagents, as alkali metal transfer agents and as reagents for introducing covalent character in inorganic systems [1–4]. However, a similar molecule with stannyl moiety in place of silyl is not reported in the literature. With this in view, an attempt has been made to synthesize sodium bis(trimethylstannyl)amide $\text{NaN}(\text{SnMe}_3)_2$ and use it as a ligand transfer reagent to synthesize bis(trimethylsilyl)bis(trimethylstannyl)-2-phospha-2-tetrazene $(\text{Me}_3\text{Si})_2\text{N}=\text{N}=\text{P}=\text{N}(\text{SnMe}_3)_2$.

2. Results and discussion

Trimethylstannyldiethylamine, $\text{Me}_3\text{SnNEt}_2$, formed by the reaction of lithium diethylamide with chlorotrimethylstannane, reacts with sodium amide in the ratio 2:1 in benzene at 40°C to provide a white crystalline solid, sodium bis(trimethylstannyl)amide,

$\text{NaN}(\text{SnMe}_3)_2$ (1), subliming at 55°C/10⁻³ torr. It is also purified by crystallization from diethyl ether at low temperatures.



Compound (1) was found to be soluble in solvents like benzene, toluene, n-hexane, diethyl ether, tetrahydrofuran, etc. It is sensitive to hydrolysis. In sunlight, it turns yellowish slowly but shows no noticeable decomposition.

The ¹H NMR of (1) in benzene (n-hexane) shows a singlet at 0.20 (0.15) ppm due to stannyl protons. The presence of stannyl group is supported by tin satellites at 55 and 57 Hz due respectively to $J(^1\text{H}-^{117}\text{Sn})$ and $J(^1\text{H}-^{119}\text{Sn})$. The ¹¹⁹Sn NMR of (1) in deuterated benzene (C₆D₆) shows a signal at 464.4 ppm. This signal is characteristic of tetrahedral tin(IV) [5]. The mass spectrum of (1) shows a molecular ion with relatively low intensity (5%, 70 eV) at *m/z* 365 and the observed isotopic pattern agrees with that calculated for C₆C₁₈NNaSn₂ (Fig. 1). Besides important fragments at 328 (Me₆Sn₂)⁺, 202 (NaNSnMe₃)⁺, 187 (NaNSnMe₂)⁺ and 165 (Me₃Sn)⁺, a valuable

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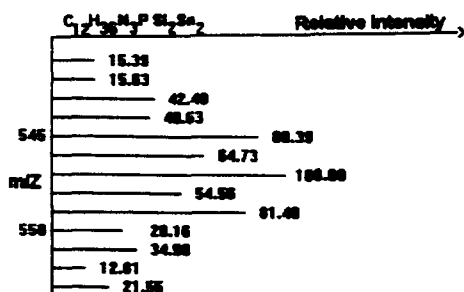


Fig. 2. Observed isotopic pattern of molecular ion in $C_{12}H_{36}N_3PSi_2Sn_2$.

This indicates the possibility of symmetric arrangement of groups in (2), that is $(Me_3Sn)(Me_3Si)N-N=P-N(SiMe_3)(SnMe_3)$ under the conditions.

3. Experimental

3.1. General comments

All investigations were carried out in the absence of air and moisture on a vacuum line connected to a dry nitrogen supply system. Trimethylstannyldiethylamine [11], n-butyl lithium [12], lithium tris(trimethylsilyl)hydrazine [13], tris(trimethylsilyl)hydrazinodichloro-phosphine [6] were prepared as reported. 1H NMR measurements were recorded on Varian EM 390 and ^{31}P , ^{29}Si , ^{119}Sn NMR on Bruker FT NMR 300 MHz. Mass spectra were run on GC mass spectrometer Model 705-205 + (VG). 1H NMR δ (ppm) in benzene (Et_2O): $(Me_3Si)_2N_2H_2$, 0.12 (0.07); $(Me_3Si)_3N_2H$, 0.13, 0.11 (2:1) (0.09); $(Me_3Si)_3N_2Li$, 0.25 (0.19); $(Me_3Si)_3N_2PCl_2$, 0.38, 0.20d (0.44, 0.28d) (1:2); Me_3SnNEt_2 , 0.13 (0.17); Me_3SnCl , 0.23 (0.60).

3.2. Preparation of sodium bis(trimethylstannyl)amide (1)

Trimethylstannyldiethylamine (4.72 g, 20 mmol) in 10 ml of benzene was added to sodium amide (0.409 g, 10 mmol) suspended in 10 ml of benzene. The reaction mixture was stirred at room temperature for one day. Its 1H NMR showed a very weak signal at 0.20 ppm attributed to the formation of the bis(stannyl)amide and a strong signal at 0.15 ppm due to unreacted Me_3SnNEt_2 . The reaction mixture was then stirred for a further 3 days at room temperature after which the 1H NMR showed incomplete reaction. The temperature of the reaction mixture was then raised to 40°C and kept at this temperature for four days. 1H NMR of the supernatant liquid showed the absence of Me_3SnNEt_2 signal at 0.15 ppm. The solution showed a signal at 0.20 ppm due to $NaN(SnMe_3)_2$, a triplet at 0.99 ppm and a quartet at 2.41 ppm due to Et_2NH .

After completion of the reaction at 40°C, the reaction mixture was filtered. The filtrate was then evacuated to give a white powder. It was purified by sublimation into a cooled glass boat at 55°C/ 10^{-3} torr. It was then crystallized from n-hexane at low temperatures. It decomposes without melting on heating at 110°C. Anal. Found: C, 18.98; H, 4.75; Sn, 51.10. $C_6H_{18}NNaSn_2$ Calc.: C, 19.75; H, 4.94, Sn, 51.12%.

1H NMR in benzene (n-hexane) (iTMS) δ (ppm) 0.20 (0.15) [18 H, $(Me_3Sn)_2$] $J(^{117}Sn-^1H)$ and $J(^{119}Sn-^1H)$ at 55 and 57 Hz.

^{119}Sn NMR in C_6D_6 (eTMT) 464.4 ppm.

Mass spectrum (70 eV) m/z (assignment; relative intensity %): 365 [(m)⁺; 5], 350 [(m-Me)⁺; 10], 328 [$(Me_6Sn)_2^+$; 30], 217 [$(Me_4SnNNa)^+$; 9], 202 [$(Me_3SnNNa)^+$; 10], 188 [$(Me_3SnNa)^+$; 10], 179 [$(Me_3SnN)^+$; 45], 165 [$(Me_3Sn)^+$; 40], 150 [$(Me_2Sn)^+$; 21], 97 [$(Me_4NNA)^+$; 68], 82 [$(Me_3NNA)^+$; 29], 57 [$(C_4H_9)^+$; 100].

3.3. Preparation of trimethylsilyl-bis(trimethylstannyl)amine $(Me_3Sn)_2NSiMe_3$

Chlorotrimethylsilane (1.080 g, 10 mmol) was added to sodium bis(trimethylstannyl)amide (3.65 g, 10 mmol) in 20 ml benzene in a round bottom flask. The mixture was stirred for 2 h. The clear solution was decanted and its 1H NMR was taken. The spectrum showed the absence of signals due to $NaN(SnMe_3)_2$ (0.20 ppm) as well as Me_3SiCl (0.21 ppm). The clear solution was evacuated under high vacuum to get a sticky mass. 1H NMR $(Me_3Sn)_2N(SiMe_3)$ δ (ppm) in benzene (n-pentane): 0.24 (0.25) [18 H, Me_3Sn] and 0.22 (0.07) [9 H, Me_3Si]. The Me_3Sn signals are supported by the side bands at 55 and 57 Hz.

3.4. Preparation of tris(trimethylstannyl)amine $(Me_3Sn)_3N$

Chlorotrimethylstannane (2.575 g, 5 mmol) solution in 10 ml benzene was added dropwise to a solution of $NaN(SnMe_3)_2$ (1.855 g, 5 mmol) taken in 20 ml benzene. The reaction mixture was stirred overnight and then filtered to remove a white precipitate of NaCl. The solution was found to contain only one signal at 0.23 ppm. It was evacuated to get a crystalline mass. 1H NMR in benzene (n-pentane) δ (ppm): 0.23 (0.18) [27 H, $3Me_3Sn$]. This signal has side bands at 55 and 57 Hz.

3.5. Preparation of bis(trimethylsilyl)bis(trimethylstannyl)-phospha-tetrazene $(Me_3Si)_2N-N=P-N(SnMe_3)_2$

Sodium bis(trimethylstannyl)amide $NaN(SnMe_3)_2$ (7.290 g, 20 mmol) was dissolved in ether (30 ml) and added dropwise to a solution of $(Me_3Si)_3N_2PCl_2$

(6.980 g, 20 mmol) in ether (25 ml) at -78°C . The colourless solution was stirred at -78°C and then allowed to warm up to -30°C and stirred for 4 h at this temperature. A white precipitate appeared due to formation of NaCl. A sample of this colourless decantate at -30°C showed a signal at 167.13 ppm in ^{31}P NMR. ^1H NMR of this solution showed three major signals at 0.42 (Me_3Si), 0.20 ($2\text{Me}_3\text{Si}$) and 0.23 ppm ($2\text{Me}_3\text{Sn}$). The NMR is indicative of an intermediate phosphine, $(\text{Me}_3\text{Si})_2\text{N}-\text{N}(\text{SiMe}_3)-\text{P}(\text{Cl})-\text{N}(\text{SnMe}_3)_2$. The reaction mixture was then allowed to come to room temperature, when it started acquiring a greenish yellow colour. It was then stirred at room temperature for 24 h and filtered to remove NaCl. The greenish yellow filtrate was evacuated and ^1H NMR of the trapped liquid contained a signal at 0.40 ppm due to Me_3SiCl which underwent hydrolysis to give a signal at 0.06 ppm due to $(\text{Me}_3\text{Si})_2\text{O}$. The residual yellowish semi-solid was evacuated and then heated at $65-70^{\circ}\text{C}/10^{-3}$ torr to obtain a light yellow sublimate (4.90 g, 45% yield). The sublimate could be recrystallized from *n*-pentane at low temperatures (m.p. 52°C). The compound is soluble in common organic solvents. It is stable at room temperature but sensitive to air and moisture. Anal. Found: C, 26.16; H, 6.21; N, 7.44. $\text{C}_{12}\text{H}_{36}\text{N}_3\text{PSi}_2\text{Sn}_2$ Calc.: C, 26.35; H, 6.59; N, 7.69%.

^1H NMR in benzene δ (ppm) 0.40 (18 H, $2\text{Me}_3\text{Sn}$), $J(^{117}\text{Sn}-^1\text{H})$ and $J(^{119}\text{Sn}-^1\text{H})$ at 55 and 57 Hz, 0.16 (18 H, $2\text{Me}_3\text{Si}$).

^{29}Si NMR in C_6D_6 (eTMS) 7.42 ppm.

^{119}Sn NMR in C_6D_6 (eTMT) 463.7 ppm.

^{31}P NMR in C_6D_6 (e H_3PO_4) 301.26 ppm.

Acknowledgements

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References

- [1] D.H. Harris, M.F. Lappert, *J. Organomet. Chem. Libr.* 2 (1976) 13.
- [2] U. Wannagat, H. Niederprüm, *Chem. Ber.* 94 (1961) 1540.
- [3] N. Wiberg, G. Fischer, H. Bachhuber, *Chem. Ber.* 107 (1974) 1456.
- [4] N. Wiberg, *Adv. Organomet. Chem.* 23 (1984) 131.
- [5] M. Nadvornik, J. Holecek, K. Handlir, A. Lycka, *J. Organomet. Chem.* 275 (1984) 43.
- [6] S.K. Vasisht, T.P. Kaur, K. Usha, J. Kaushal, K. Bandhu, *Phosphorus, Sulfur and Silicon* 107 (1995) 189.
- [7] N. Wiberg, *Adv. Organomet. Chem.* 24 (1985) 179.
- [8] S.K. Vasisht, M. Sood, P.K. Verma, T. Kaur, K. Usha, *Phosphorus, Sulfur and Silicon* 47 (1990) 349.
- [9] O.J. Scherer, W. Glässel, *Chem. Ber.* 110 (1977) 3874.
- [10] E. Niecke, W. Flick, *Angew. Chem., Int. Ed. Engl.* 12 (1973) 585.
- [11] C.M. Wright, E.L. Muetterties, *Inorg. Synth.* 10 (1967) 137.
- [12] H. Gilman, J.A. Beel, C.G. Brannen, M.W. Bullock, G.E. Dunn, L.S. Miller, *J. Am. Chem. Soc.* 71 (1949) 1499.
- [13] N. Wiberg, E. Weinberg, W.Ch. Joo, *Chem. Ber.* 107 (1974) 1764.