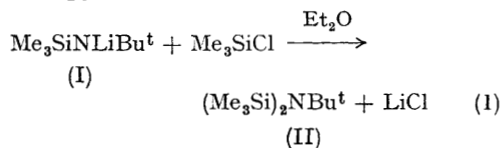


A Novel Metallation Reaction of *N*-Lithio-*t*-butylaminotrimethylsilane

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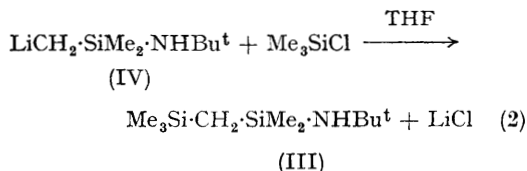
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N-LITHIO-*t*-BUTYLAMINOTRIMETHYLSILANE (I) has been prepared and couples normally with chlorotrimethylsilane in diethyl ether [reaction (1)] to give *N*-*t*-butylhexamethyldisilazane (II) (15%), a crystalline solid, m.p. 56–57°, characterised by elemental analysis, and infrared and n.m.r. spectroscopy.



We report that, in contrast to reaction (1), if tetrahydrofuran is used in place of diethyl ether, only traces of (II) are formed. The main product (29% yield) was the isomer of (II), (trimethylsilylmethyl)-*t*-butylaminodimethylsilane, $\text{Me}_3\text{SiCH}_2\cdot\text{SiMe}_2\cdot\text{NHBu}^\dagger$ (III). Evidence for structure (III) comprises (i) elemental analysis, (ii) infrared spectrum (ν_{NH} , 3490; $\nu_{\text{as}} \text{SiCH}_2\text{Si}$, 1050 cm^{-1} ; no $\nu_{\text{as}} \text{SiNSi}$), (iii) n.m.r. spectrum [singlets at τ 8.88 (Bu^\dagger); 9.89 (SiMe_2); 9.96 ($\text{SiMe}_3 + \text{NH}$); 10.22 (SiCH_2Si); in the ratio 9:6:10:2], (iv) hydrolytic degradation gave *t*-butylamine and 1,3-bis(trimethylsilylmethyl)-1,1,3,3-tetramethyldisiloxane, $(\text{Me}_3\text{Si}\cdot\text{CH}_2\cdot\text{SiMe}_2)_2\text{O}$.

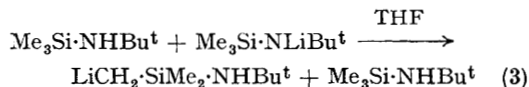
The surprising formation of (III) presumably involves the *C*-lithio-compound (IV) [reaction (2)].



Since diethylaminotrimethylsilane did not react with *n*-butyl-lithium in tetrahydrofuran (THF) under the same conditions, it is unlikely that direct

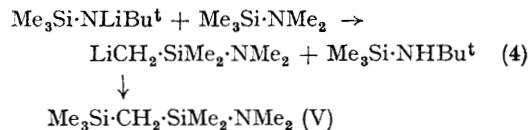
metallation of CH by butyl-lithium occurs in this case (*cf.* ref. 1); and the success of reaction (1) also indicates that *N*-lithiation is the first step.

We conclude that the *C*-lithio-derivative (IV) is produced from its isomer (I) in tetrahydrofuran (THF). Since unchanged *t*-butylaminotrimethylsilane was present in all our reaction mixtures, it is possible that this compound is metallated by its own *N*-lithium salt.



We attribute this transformation to the destabilisation of the anion of (I) relative to that of (IV) by the presence of the strongly electron-releasing *t*-butyl group adjacent to a negatively charged nitrogen atom. In agreement with this view, no reaction analogous to (3) was observed for the corresponding *N*-ethylamino-system.

If the intermolecular scheme (3) is correct, the reagent (I) might be expected to metallate SiCH_3 groups in other compounds, and we have observed such a reaction for dimethylaminotrimethylsilane [reaction (4)].



The compound (V) was the only product (26%) in spite of competition for the *N*-lithio-salt between $\text{Me}_3\text{SiNMe}_2$ and unreacted $\text{Me}_3\text{SiNHBu}^\dagger$.

The metallation reaction is not general for SiMe groups. The following compounds failed to react with reagent (I): $(\text{Me}_3\text{Si})_2\text{CH}_2$; Me_3SiPh ; $\text{EtSi}(\text{NMe}_2)_3$; $(\text{Me}_3\text{Si})_2\text{NET}$; $(\text{Me}_3\text{Si})_3\text{N}$.

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