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Preliminary Communication

The preparation of *N,N*-dimethylaminomethyllithium

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With the advent of the potent metalating agent, n-butyllithium complexed with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA)[1,2], several new heteroatom-substituted methyllithium compounds have become available from the corresponding weakly acidic substituted methanes[3]. Obviously absent from this series of synthetically useful organo-

$$ZCH_3 + n\text{-}C_4H_9Li \cdot TMEDA \rightarrow ZCH_2Li \cdot TMEDA + C_4H_{10}$$
$$(Z = RS\text{-}, R_2P\text{-}, R_3Si\text{-})$$

metallic compounds are the *N,N*-dialkylaminomethyllithium compounds. Previous work has shown that although *N,N*-dialkylmethylamines undergo metalation with n-butyllithium·TMEDA[4] and t-butyllithium[5], the yields of desired products are very low even after extended reaction times.

We now report a high yield method for the preparation of the parent nitrogen-substituted organolithium compound, *N,N*-dimethylaminomethyllithium. The preparative route for this compound involves a transmetalation reaction between n-butyllithium·TMEDA and (*N,N*-dimethylaminomethyl)tributyltin.

$$(CH_3)_2NCH_2Sn(n\text{-}C_4H_9)_3 + n\text{-}C_4H_9Li{\cdot}TMEDA \xrightarrow{\text{hexane}} (CH_3)_2NCH_2Li{\cdot}TMEDA + (n\text{-}C_4H_9)_4Sn$$

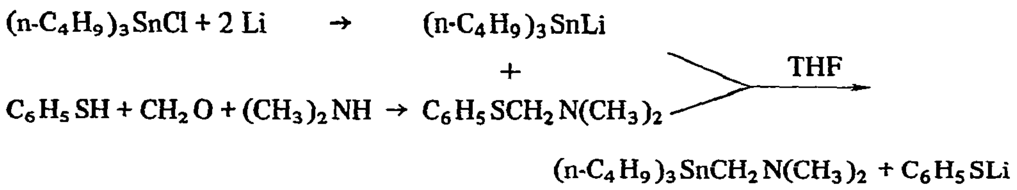
The metal interchange occurs rapidly at room temperature. The resulting *N,N*-dimethylaminomethyllithium·TMEDA complex has been derivatized by treatment of the reaction mixture with benzaldehyde to give (2-hydroxy-2-phenylethyl)dimethylamine.

$$(CH_3)_2NCH_2Li{\cdot}TMEDA + C_6H_5CHO \rightarrow \xrightarrow{H^+} (CH_3)_2NCH_2CH(OH)C_6H_5 \quad (86\%) + TMEDA$$

In a typical run, 10.4 g (0.03 mole) of (*N,N*-dimethylaminomethyl)tributyltin was added dropwise to 0.03 mole of $n\text{-}C_4H_9Li \cdot TMEDA$ complex dissolved in 30 ml of hexane at 0°. A precipitate formed immediately. After the reaction mixture had been stirred for one hour at room temperature, an aliquot was removed and hydrolyzed and the organic phase was analyzed by GLPC. No starting amine was detected, while tetrabutyltin was shown to be present.

The reaction mixture was then treated with 3.2 g (0.03 mole) of benzaldehyde which resulted in a rapid consumption of the insoluble material. Subsequent to 0.5 h of stirring, the reaction mixture was worked up in the usual manner to give 4.25 g (86%) of (2-hydroxy-2-phenylethyl)dimethylamine, b.p. 60–65°/0.1 mm (lit.[6] b.p. 123–126/11 mm) and 9.3 g (92%) of tetrabutyltin, b.p. 91–94°/0.1 mm. The amine was characterized by ^{1}H NMR spectral analysis with aromatic protons (5) at τ 2.75, methine proton (1, quartet, $J_{AX} = 9$ Hz, $J_{BX} = 4$ Hz) at τ 5.38, methylene protons (2, eight line pattern with $J_{AB} = 12$ Hz) at τ 7.56 and τ 7.8, and methyl protons (6, singlet) at τ 7.75. Mass spectral and elemental analysis data were in accord with the structure assignment. Quaternization of the amine with methyl iodide afforded the known methiodite, m.p. 226–227° (lit.[6] m.p. 225–226°).

This transmetalation route to *N,N*-dimethylaminomethyllithium, which is reminiscent of the method developed for the preparation of vinyllithium and related organolithium compounds[7], is particularly valuable since the starting organotin compound can be readily obtained by the reaction sequence outlined below. To a solution of 0.2 mole of tributyltinlithium in 150 ml of THF, prepared by the method of Tamborski and co-workers[8], was added 33.4 g (0.2 mole) of (*N,N*-dimethylaminomethyl)phenylsulfide. The reaction mixture was subsequently heated at 60° for two hours, cooled to room temperature, hydrolyzed, and worked up by a standard technique to give 48 g of (*N,N*-dimethylaminomethyl)tributyltin, b.p. 74–76°/0.04 mm. A ^{1}H NMR spectral analysis of the compound in $CDCl_3$ supported the structure assignment with signals centered at τ 7.53 ($SnCH_2$-N, $J(CH_2\text{-}^{117\text{-}119}Sn)$ *ca.* 23 Hz - not resolved) and τ 7.75 [$(CH_3)_2N$-] and ~τ 8.8 [$(C_4H_9)_3Sn$] in the correct area ratios. The methiodide salt of this compound melted at 168–169°. (Found: C, 39.0; H, 7.8; N, 2.9. Calcd.: C, 39.2; H, 7.75; N, 2.85%).



It should be pointed out that the precursory (dialkylaminomethyl)trialkyltin compounds can also be obtained from reactions of secondary amines with (α-halomethyl)-trialkyltins[9].

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