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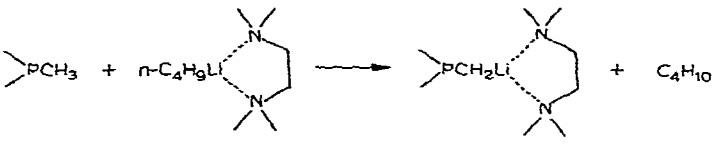
SHORT COMMUNICATION

Metalation of methylsilanes

It has been demonstrated recently that methylphosphines undergo relatively rapid reactions (1–24 h) with a metalating complex (I) comprised of equimolar quantities of n-butyllithium and N,N,N',N'-tetramethylethylenediamine (TMEDA) to give favorable yields (70–80%) of phosphinomethyllithium compounds[1].



(I)

The successful metalations of the very weakly acidic methylphosphines encouraged us to investigate the possibility of similarly employing (I) to convert methylsilanes to the corresponding silylmethyllithium compounds, a previously unknown process of theoretical interest.

Tetramethylsilane (TMS) and n-butyltrimethylsilane were chosen as model compounds for study and were contacted with equivalent amounts of (I) for 3 and 4 days, respectively. The formation of (trimethylsilyl)methyllithium from the reaction of (I) with tetramethylsilane was established by ^{1}H NMR spectral analysis* of the mixture, which exhibited signals centered at τ 9.6 (singlet, methyl) and 11.8 (singlet, methylene)[2]. A complex absorption pattern was present at τ 7.45–7.95 owing, in part, to the TMEDA protons.

Derivatization of a (I)/TMS metalation mixture with chlorotrimethylsilane afforded a 36% yield of bis(trimethylsilyl)methane, b.p. 132–136°, n_D^{20} 1.4150 [lit.[3] b.p. 132° (740 mm), n_D^{20} 1.4170]. A proton NMR spectral analysis of the compound confirmed the structure assignment (two singlets separated by an internal chemical shift of 0.29 ppm in the ratio of 9 : 1). The approximate chemical shifts of the methyl and methylene protons were τ 9.99 and 10.28, respectively, relative to a $CHCl_3$ lock signal.

In addition to the bis(trimethylsilyl)methane, some (18%) N,N,N'-trimethyl-N'-[(trimethylsilyl)methyl]ethylene diamine, $(CH_3)_2NCH_2CH_2N[CH_2Si(CH_3)_3]CH_3$ (II), was obtained, b.p. 188–192°. The amine exhibited ^{1}H NMR signals (singlets) in $CDCl_3$ centered at τ 7.64 (N–CH_2–CH_2–N), 7.92 (N–CH_3), 8.15 (N–CH_2–Si), and 9.96 [$Si(CH_3)_3$] in the correct area ratios. (Found: C, 56.6; H, 13.1; N, 13.7. $C_9H_{24}N_2Si$ calcd.: C, 57.4; H, 12.7; N, 14.9%.) A mass spectral analysis (at 70 e.v.) of the compound was consistent with the structure assignment, having an intense parent peak at m/e 188, intense *M*-15 (methyl) peak, and a base peak at m/e 130.

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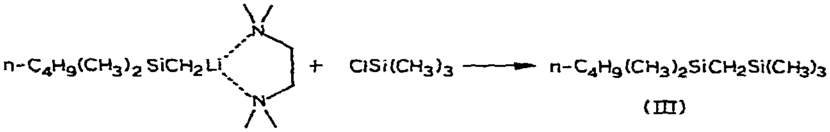
* The hexane solvent was removed *in vacuo* and replaced with dry benzene. The ^{1}H NMR spectral analysis was then made immediately on the resulting solution. The chemical shifts are referred to benzene which was the lock signal for the spectral determination.

Metalated n-butyltrimethylsilane was characterized qualitatively by treatment with trimethylchlorosilane to give the methylenedisilane (III) in 46% yield, b.p. 83°/18 mm, ^{1}H NMR signals were centered at τ 8.71 (β,γ-methylene), 9.14 (methyl), 9.48 (α-methylene), 9.98 and 10.00 (silylmethyl), and 10.28 (SiCH$_2$Si) in the correct area ratios. The amine (II) was also formed in an undetermined quantity as evidenced by ^{1}H NMR spectral analysis.



(III)

Further characterization of metalated n-butyltrimethylsilane was achieved by a mass spectral analysis of a deuterium oxide-quenched aliquot of the reaction mixture. From the 4-day, room temperature reaction, the recovered silane was found to contain 57.1% d_0, 42.6% d_1, and 0.3% d_2. These results are in agreement with the chlorosilane derivatization method and thereby demonstrate that the methylsilanes studied undergo metalation to the extent of *ca.* 40% during four days of contact at room temperature with the n-butyllithium/TMEDA complex.

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