Reactions of Lithium Hydridosilylamides with Carbonyl Compounds and Mixtures of Carbonyl Compounds and Chlorotrimethylsilane

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The lithium hydridosilylamides $\text{Me}_2(\text{H})\text{SiN}(\text{Li})\text{R}$ (1: $\text{R} = \text{CMe}_3$, 2: $\text{R} = \text{SiMe}_3$) were allowed to react either with the non-enolizable carbonyl compounds $\text{CH}_2=\text{C}(\text{Me})\text{CHO}$, $\text{PhCHO}$ and $\text{Ph}_2\text{CO}$ followed by trapping with chlorotrimethylsilane (A), or with mixtures of these carbonyl compounds and chlorotrimethylsilane (B). In the second case the course of the reactions is determined by the carbonyl compound. The composition of the reaction mixtures is nearly the same according to A and B.

Main products in the reactions with the aldehydes are the corresponding imines $\text{R}'\text{CH}=\text{NR}$ ($\text{R}' = \text{CH}_2=\text{C}(\text{Me})$, $\text{Ph}$) 3, 4, 8, 9 formed by addition of the hydridosilylamides to the C=O group of the aldehydes and subsequent LiOSiMe$_2$H elimination. Partial hydrosilylation of the aldehydes by the hydridosilanolate followed by the trimethylsilylation yields the alkoxydisiloxanes $\text{R}'\text{CH}_2\text{OSiMe}_2\text{OSiMe}_3$ 6, 11. In some cases 2 partially reacts under hydrosilylation to give the alkoxydisilazanes $\text{R}'\text{CH}_2\text{OSiMe}_2\text{NHSiMe}_3$ 7, 12.

The hydrosilylation is the preferred reaction of 1 and 2 with benzophenone. The compounds $\text{Ph}_2\text{CHO}\text{SiMe}_2\text{NHR}$ 13, 14 are obtained. This difference in the reaction behaviour of 1 and 2 towards the aldehydes and benzophenone is mainly due to steric reasons. Depending on the conditions the imines $\text{Ph}_2\text{C}=\text{NR}$ 20, 21 may be formed. $\text{Ph}_2\text{CHO}\text{SiMe}_2\text{OSiMe}_3$ (22) is a secondary product of imine formation.

In all reactions of 1 and 2 with the carbonyl compounds the corresponding alkoxy silanes $\text{R}'\text{CH}_2\text{OSiMe}_3$ (5: $\text{R}' = \text{CH}_2=\text{C}(\text{Me})$, 6: $\text{R}' = \text{Ph}$) and $\text{Ph}_2\text{CHO}\text{SiMe}_3$ (15) are generated.

Compounds resulting from a reaction of 1 and 2 with chlorotrimethylsilane are produced to minor extent, but only if the molar ratio of amide to carbonyl compounds is not greater than one. The formation of a silanimine intermediate in reaction according to B is not observed.

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