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IMPROVEMENTS IN THE PREPARATION AND USE OF [TRIS(TRIMETHYLSILYL)METHYL]LITHIUM

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Summary

Improvements in the preparation and use of [tris(trimethylsilyl)methyl]lithium are described.

Introduction

There is increasing interest in the use of the $(Me_3Si)_3C$ ("trisyl") group as a ligand, and this is normally attached to metal or metalloid centres by use of [tris(trimethylsilyl)methyl]lithium. This reagent is usually made by metallation of $(Me_3Si)_3CH$ by MeLi in a mixture of diethyl ether and tetrahydrofuran (THF) as originally described [1]. In that procedure, after addition of $(Me_3Si)_3CH$ in THF to MeLi in Et_2O the solution is refluxed for 6 h. We have found that if the Et_2O is removed after the mixing of the reagents only 2 h refluxing is then needed, and yields of $(Me_3Si)_3CLi$ of over 90% are usually obtained *.

Additional points which may assist those using the lithium reagent are as follows:
(i) We now usually use MeLi prepared from MeCl, rather than MeBr as originally described [1]. However in coupling with metal or metalloid halides, MX_x, with X = Cl, Br, or I, it is often advisable to use MeX containing the same halogen, otherwise halogen exchange may occur between the metal halide and the lithium halide and cause complications.
(ii) Determination of the yield of $(Me_3Si)_3CLi$ has been simplified by using ^1H NMR spectroscopy to measure the $(Me_3Si)_4C/(Me_3Si)_3CH$ ratio in the mixture obtained by treatment of a sample of the solution with Me_3SiCl.
(iii) Since the presence of residual MeLi can sometimes cause complications (see, for example, ref. 3), it is often helpful to destroy this species by addition of a little

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* For simplicity we represent the lithium compound as $(Me_3Si)_3CLi$, although in the solid state the actual formula is $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ [2], and the dialkyllithiate ion is probably also present in solution in THF.

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Me_3SiOMe or Me_3SiOEt. These react rapidly with MeLi but are unaffected by $(Me_3Si)_3CLi$, and they or their coupling or hydrolysis products can be readily evaporated off with the solvent during work up.

Experimental

A typical procedure is as follows: A 1.8 *M* solution of MeLi (0.081 mol) (prepared from methyl chloride) in diethyl ether (45 cm^3) was added with stirring under nitrogen to a solution of tris(trimethylsilyl)methane (17.4 g, 0.075 mol) in THF (120 cm^3). The diethyl ether was then distilled off, and the residual solution was boiled under reflux under nitrogen. The progress of the reaction was monitored as described below, and after 2 h about 95% of the $(Me_3Si)_3CH$ had been converted into $(Me_3Si)_3CLi$.

For the monitoring, samples (0.5 cm^3) of the solution were removed from time to time, and added to Me_3SiCl (0.5 cm^3) in a small open dish, which was then heated gently to drive off all the solvent and residual Me_3SiCl. The residue was extracted with CCl_4 and the solution was filtered and its ^1H NMR spectrum determined. The relative heights of the signals from the Me groups of $(Me_3Si)_4C$ (δ 0.23 ppm) and $(Me_3Si)_3CH$ (δ 0.10 ppm) then (after allowance for the different number of protons in the two compounds) gave the $(Me_3Si)_4C/(Me_3Si)_3CH$ ratio, and thus the degree of conversion of the $(Me_3Si)_3CH$ into $(Me_3Si)_3CLi$.

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