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TRIS(TRIMETHYLSILYL)SILYLLITHIUM · 3 THF: A STABLE CRYSTALLINE SILYLLITHIUM REAGENT *

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Summary

A synthesis of crystalline tris(trimethylsilyl)silyllithium · 3 THF is described. This stable compound can be used in hydrocarbon solvents to give improved yields of coupling products.

Tris(trimethylsilyl)silyllithium is a useful reagent for the synthesis of a variety of polysilyl compounds, including acylsilanes [1],  $R\overset{\overset{O}{\|}}{C}Si(SiMe_3)_3$, which we have recently employed to synthesize "stable" solid [2] silaethylenes. However, its preparation as described originally [3,4] from tetrakis(trimethylsilyl)silane I, and methyllithium does not always result in high or reproducable yields. While all the reasons for this are possibly not known, impure and wet solvents, the presence of air, the purity of the starting material I, and the quality of the methyllithium are contributing factors.

The reagent is normally formed in THF as solvent, and we and Gilman et al. [3,4] have observed that this medium apparently facilitates side reactions such as silyl group abstraction (reforming I) or disproportionation during subsequent reactions. In addition, II in THF solution is unstable and slowly decomposes. These problems are avoided by the isolation of the silyllithium reagent II as a colourless crystalline solid containing three mole-equivalents of THF of solvation.

$$\underset{\text{(I)}}{(Me_3Si)_4Si} + MeLi \xrightarrow{THF} \underset{\text{(II)}}{(Me_3Si)_3SiLi} \cdot 3\ THF$$

The compound is reasonably soluble in hydrocarbon solvents, giving colourless

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* Dedicated by A.G.B. to Henry Gilman, friend and teacher, who, in one memorable year of association at Iowa State College, encouraged my development as a researcher and introduced me to the excitement and fascination of organosilicon chemistry.

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solutions in contrast to previous reports [4], and coupling reactions in such non-polar media are generally much cleaner and higher in yield. For example, while the coupling reaction of the silyllithium reagent as prepared in THF with pivaloyl chloride has never given more than 80% yield of the acylsilane, coupling of the new reagent, dissolved in pentane, with the acid chloride regularly gives 92—93% yields.

II is prepared from I essentially according to the Gilman procedure [3,4], using methyllithium-lithium bromide complex in ether. We have found it advantageous to follow the progress of the reaction by ^{1}H NMR spectroscopy, observing the disappearance of the signals of I at δ 0.23 ppm and methyllithium at —2.07 ppm, and the appearance of II at δ 0.07 ppm, since it is important to work the reaction up promptly on completion, in order to maximize the yield of II. Removal of the solvent yields a solid, crystallizable from pentane, which contains three molecules of THF as shown by the NMR intensities.

The THF probably remains coordinated to the reagent even on solution in hydrocarbons, as suggested by the lower than normal frequency of the ν_{asymm}(C—O—C) infrared absorption band (1051 cm^{-1} compared to 1072 cm^{-1} for free THF). However, some of the THF can be removed under reduced pressure. After 10 hours pumping of the solid at room temperature, NMR integrations showed that the amount of THF had been reduced to 2.5 mole-equivalents.

II has been characterized by its ^{1}H, ^{13}C, and ^{29}Si NMR absorptions and its infrared spectrum. As anticipated, the central silicon of II in C_6D_6 appears at much higher field (—185.4 ppm) than does the central silicon of I (—135.5 ppm). The $^1J(^{29}\text{Si}—^{13}\text{C})$ coupling constant of II, 39 ± 1 Hz, is considerably less than that previously reported [7] for simple alkyl silanes (e.g. Me_4Si = 50.3 Hz) but only somewhat smaller than the value of about 45.5 Hz observed for the Si—Me couplings in a large number of tris(trimethylsilyl)acylsilanes.

Experimental

All reactions were carried out on a vacuum line system under an atmosphere of dried argon. All solvents were carefully dried and were saturated with argon. NMR data is relative to TMS.

Tetrakis(trimethylsilyl)silane, I

This compound was prepared essentially as described by Gilman [6], except that only a 10% excess of Me_3SiCl and a 25% excess of lithium over $SiCl_4$ were employed. After stirring for 16 h under argon, filtration (use of a 3 cm bed of Celite 505 may facilitate this) gave a clear red-brown filtrate which was drowned in 10% hydrochloric acid and was extracted with ether. Removal of the ether gave a solid, which after recrystallization from acetone and washing with a little ethanol, gave pure I. Further purification of I by sublimation [6] was not necessary. ^{29}Si NMR (C_6D_6) (δ, ppm): —9.7 (Me_3Si), —135.5 ($(Me_3Si)_4$*Si*).

Tris(trimethylsilyl)silyllithium · 3 THF

To 59.09 g (0.18 mol) of I, pumped under vacuum for 12 h to remove air, was added 800 ml of THF. A solution of methyllithium-lithium bromide complex in ether (102 ml of 1.8 *M* solution (Alfa Inorganics)) was added over 3 h while stirring at room temperature. The reaction was followed by NMR and after 12 h the reaction was complete (absence of a ^{1}H NMR signal at δ 0.23 ppm) and the solvents were removed immediately using a vacuum distillation at room temperature. The solid residue was stirred for 2 h in 1.5 l pentane, and the resulting suspension was filtered under argon into another flask and cooled to −25°C in a refrigerator, yielding two crops totalling 79.9 g (92%) of II · 3 THF. Recrystallization from 1.5 l pentane containing 10 ml of THF gave pure material, which can be stored without decomposition under argon for months. However, on exposure to air the crystals rapidly and exothermally decompose. NMR: ^{1}H (cyclopentane): δ 0.08 ppm; (C_6H_6): 0.7 ppm. ^{13}C (C_6D_6): δ 7.0 ppm; $^1J(^{29}\text{Si}{-}^{13}\text{C}) = 39.1 \pm 1$ Hz. ^{29}Si (C_6D_6): −5.3 (Me_3Si), −185.4 ($(Me_3Si)_3$*Si*) ppm. IR (Nujol): 2940vs, 2887vs, 1460s, 1376m, 1339vw, 1243m, 1230vs, 1179vw, 1051vs (THF), 913m (THF), 892vs, 862s, 826vs, 740w, 727w, 666vs, 614vs cm^{-1}. M.W. Found (titration with acid): 478, 481. Calcd. for $C_{21}H_{51}Si_4O_3Li$: 471.

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