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A Convenient Two-Step Preparation of Monodeuteriated Tetramethylsilane

Short Communication

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Purified partially mono-deuteriated *TMS* was synthesized by preparing lithiomethyltrimethylsilane from chloromethyltrimethylsilane and reaction of the former with deuteriated water. Using this reference deuterium chemical shifts in parts per million can be reported with respect to [^{2}H] resonance frequency of internal *TMS* in deuterium nmr spectroscopy.

(Keywords: [^{2}H] *TMS, synthesis; Lithiomethyltrimethylsilane)*

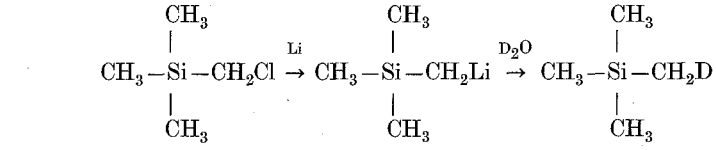
Eine einfache zweistufige Synthese von monodeuteriertem Tetramethylsilan (Kurze Mitteilung)

Es wird die Synthese von partiell monodeuteriertem *TMS* beschrieben. Dazu wurde Monochlormethyltrimethylsilan in Lithiomethyltrimethylsilan übergeführt und dieses mit D_2O weiter zum Zielprodukt umgesetzt.

The positions of proton resonances in a NMR spectrum are measured relative to the resonance position of the twelve equivalent protons of an arbitrary reference substance tetramethylsilane[1]. In a previous report we reported the preparation of tritiated *TMS* in a similar manner for referencing ^{3}H NMR spectra and calculated the *Larmor* frequency ratio for the ghost referencing procedure[2]. Using the stable isotope deuterium, we now report the preparation of partially deuteriated *TMS* in a two step synthesis. Regardless of referencing ^{3}H NMR spectra, for deuterium chemical shifts in ^{2}H NMR spectra the actual use of the material routinely would obviously be possible.

Deuterium chemical shifts, in parts per million, are essentially the same as those of the analogous ^{1}H isotope and so far has been reported

with respect to broad signal of fully deuteriated *TMS*[3]. Partially deuteriated *TMS* could not be prepared by simple exchange methods and it is prepared by the route shown below:



Preparation of Lithiomethyltrimethylsilane[4,6]

In a 50 ml, three-necked flask fitted with a mercury-sealed stirrer, a dropping funnel, and a double surface condenser, there were placed *n*-pentane (10 ml), lithium foil (280 mg) (preparation of thin lithium foil is described in Ref.[5]). After heating to reflux, chloromethyltrimethylsilane (1.25 g) was gradually added over a two hour period with vigorous stirring, giving a purple coloured solution. On refluxing for additional ten hours, reaction continued and the solution became deep purple in colour. The coloured material, however, settled to the bottom on standing overnight, leaving a water-white organic layer. The reaction mixture was then filtered through sintered glass to remove the precipitated lithium chloride along with unreacted lithium metal. The solvent was removed by vacuum distillation from filtrate to obtain a white solid product. Finally the solid was sublimed at 110 °C under a pressure of 10^{-5} mm (using a diffusion pump) and so obtained as pure white crystals of lithiomethyltrimethylsilane in the cooler parts of the sublimation apparatus: the solid was collected, m. p. 112 °C, yield 700 mg.

Preparation of Deuteriated Tetramethylsilane

Lithiomethyltrimethylsilane (70 mg) was placed in a tube and the tube was capped. The reaction vessel was cooled at 0 °C and a mixture of deuterium oxide (0.5 ml) and CH_3OD (0.5 ml) was added by a refrigerated syringe. The reaction tube was left 0.5 h in ice and dilute HCl (1 ml) was added and the mixture was stirred at 0 °C for 15 min. $CDCl_3$ (3 ml) was added, and the lower phase was withdrawn and dried (Na_2SO_4). This solution was then placed in a NMR tube and ^{1}H NMR spectrum was recorded by a T-60 MHz NMR spectrometer. The spectrum showed a single line at 0.00 ppm corresponding to *TMS*'s proton resonances (no ordinary *TMS* had been added to the sample). [A small peak at 7.3 ppm indicates the solvent used ($CDCl_3$)]. The molecular ion of deuteriated *TMS* ($M^+ = 89$) was measured with an A.E.I. MS 12 mass spectrometer indicating the synthesis of partially mono-deuteriated *TMS*. The yield of the reaction was calculated to be 96%.

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