A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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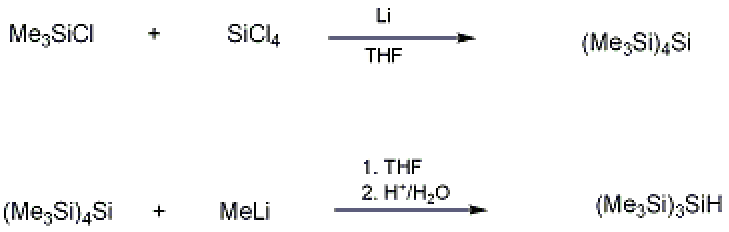
TRIS(TRIMETHYLSILYL)SILANE

[Trisilane, 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)-]



Submitted by Joachim Dickhaut and Bernd Giese[1].
Checked by George A. O'Doherty and Leo A. Paquette.

1. Procedure

Lithium powder (7.55 g, 1.07 mol) is placed in a 500-mL, four-necked flask equipped with a condenser, mechanical stirrer, dropping funnel, and low-temperature thermometer (Note 1) and (Note 2). The apparatus is carefully flushed several times with nitrogen followed by the addition of 50 mL of anhydrous tetrahydrofuran (THF). The reaction flask is cooled to approximately −60°C in a dry ice-acetone bath, and a mixture of freshly distilled (from CaH_2) chlorotrimethylsilane (54.8 mL, 47.1 g, 0.43 mol) and tetrachlorosilane (Note 3) (10.1 mL, 15.0 g, 0.09 mol) in 140 mL of anhydrous THF is added over 1 hr by dropping funnel so that the temperature of the reaction mixture never exceeds −30°C. After addition is complete, stirring is continued for 0.5 hr with cooling (Note 4). The gold-brown suspension is allowed to warm to room temperature and stirred for 12 hr, during which time the color becomes more intense (Note 5). The thermometer is removed and the mixture is heated to reflux for 2 hr to destroy the remaining chlorotrimethylsilane. After the condenser is cooled to room temperature, it is replaced with a nitrogen bubbler and gas inlet. Methyllithium-lithium bromide complex (66 mL, 99 mmol, 1.5 M in ether) is added over 3 hr to the grey-brown mixture with vigorous stirring (Note 6). During the addition a continuous stream of nitrogen is bubbled through the reaction mixture. After the reaction mixture is stirred for an additional 16 hr at room temperature, it acquires a greenish tint. Hydrolysis is carried out by the careful addition of the reaction mixture to 400 mL of ice-cold 2 N hydrochloric acid. [*CAUTION: The solid residue may be highly pyrophoric. The checkers blanketed the flask with argon prior to the introduction of ether (100 mL) and poured the vigorously stirred slurry into the cold hydrochloric acid. This rinse procedure was repeated twice more.*] The aqueous phase is extracted four times with 200-mL portions of pentane, the combined organic phases are dried over magnesium sulfate and the solvents removed under reduced pressure. Distillation under reduced pressure (1 mm, 38°C) affords 13.4–17.2 g of the product as a clear oil (60–77% yield).

2. Notes

1. The checkers used a three-necked flask having one arm equipped with a Claisen head.
2. All reagents were purchased from Fluka Chemical Corporation, except the methyllithium-lithium bromide complex, which was purchased from Aldrich Chemical Company, Inc., and were used without further purification. The lithium powder can be weighed in air; however, the use of a dust mask is recommended.
3. As tetrachlorosilane smokes strongly when exposed to air, introduction to the addition funnel is best carried out using a syringe.
4. If the temperature falls below −60°C, the mixture may solidify, but returns to a liquid upon warming.
5. The synthesis should be carried out over three days, stirring the mixture overnight. The stirring times reported should be considered a minimum, and need not be followed exactly.
6. A clean dropping funnel should be used for the addition of the methyllithium solution, and should be filled with rigorous exclusion of air. It is simpler to employ a syringe pump, and replace the dropping funnel with a septum. In this case the stream of nitrogen can be introduced by a needle through the

septum.

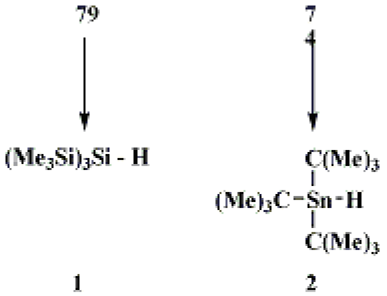
Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

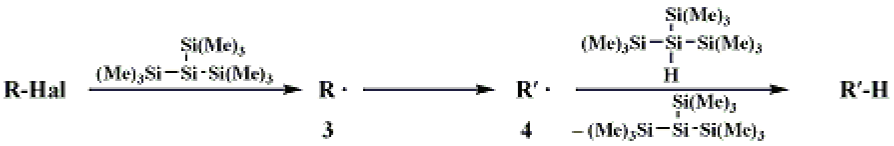
3. Discussion

Tris(trimethylsilyl)silane **1** can be substituted for toxic stannanes like tributyl-stannane **2** in organic syntheses which involve radicals,[2] because: a) silyl radicals are as efficient as stannyl radicals in the radical-forming step,[3] and b) the Si-H bond strength in tris(trimethylsilyl)silane **1** is only slightly higher than the Si-H bond strength in tributylstannane **2**.[4]

Bond energy (kcal/mol):



Thus, heating a mixture of an organic bromide or iodide with equimolar amounts of silane **1** and catalytic amounts of a radical initiator like azobisisobutyronitrile gives organic radicals **3** that can undergo addition, cyclization or rearrangement reactions[2] (**3** → **4**) before hydrogen abstraction[5] yields the product.



Tris(trimethylsilyl)silane **1**is a mediator in this reaction. In contrast to the reported method,[6] the synthesis described in this procedure gives silane **1** in high yields in a one-pot reaction.

References and Notes

1. Institute of Organic Chemistry, University of Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

hydrochloric acid (7647-01-0)

ether (60-29-7)

hydrogen (1333-74-0)

nitrogen (7727-37-9)

Pentane (109-66-0)

lithium (7439-93-2)

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

Methyllithium (917-54-4)

argon (7440-37-1)

tributylstannane,
tributyl-stannane (688-73-3)

tetrachlorosilane (10026-04-7)

CHLOROTRIMETHYLSILANE (75-77-4)

Methyllithium-lithium bromide (332360-06-2)

azobisisobutyronitrile (78-67-1)

Tris(trimethylsilyl)silane,
Trisilane, 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)- (1873-77-4)