



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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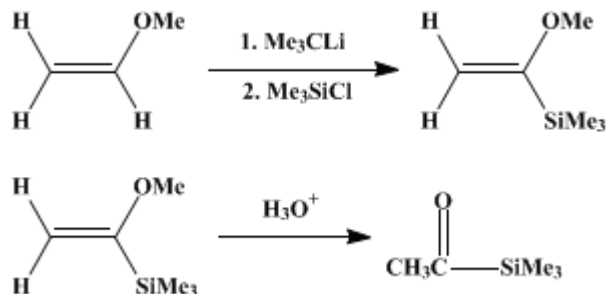
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ACETYLTRIMETHYLSILANE

[Silane, acetyltrimethyl-]



Submitted by John A. Soderquist¹

Checked by Edward D. White III and James D. White.

1. Procedure

Caution! tert-Butyllithium is extremely pyrophoric and must not be allowed to come into contact with the atmosphere. This reagent should only be handled by individuals trained in its proper and safe use. It is recommended that transfers be carried out by using a 20-mL or smaller glass syringe filled to no more than 2/3 capacity, or by cannula. For a discussion of procedures for handling air-sensitive reagents, see Aldrich Technical Bulletin AL-134. [Note added August 2009]. (Note 1)

A dry (Note 2), 2-L, round-bottomed flask containing a magnetic stirring bar and equipped with a rubber septum inlet is flushed with dry nitrogen and charged with 450 mL of purified tetrahydrofuran (Note 3). After the contents of the flask are cooled using a dry ice-acetone bath, 72 g (1.2 mol) of methyl vinyl ether is distilled into the flask from a commercial cylinder (Note 4). The septum is replaced, under a positive pressure of nitrogen gas, with a 500-mL, pressure-equalizing addition funnel equipped with a rubber septum inlet. The stirred contents of the flask are continuously cooled while 1.0 mol of tert-butyllithium in pentane solution (*Caution! Solutions of this reagent are pyrophoric and extreme care should be exercised when carrying out this manipulation!*) (Note 5) is transferred to the addition funnel and subsequently added to the mixture dropwise over ca. 1.5 hr. The resulting yellow slurry is allowed to warm slowly to 0°C over ca. 3 hr (Note 6). With the addition of dry ice to the bath, the near-colorless solution is recooled to ca. -78°C and 84.6 g (0.78 mol) of chlorotrimethylsilane (Note 7) is transferred to the addition funnel and subsequently added dropwise to the stirred mixture. The cold bath is removed and, after the mixture has reached room temperature, is allowed to stir for an additional 1 hr (Note 8). The contents of the flask are carefully poured into a 2-L separatory funnel which contains ca. 400 g of ice and ca. 200 mL of saturated ammonium chloride solution (Note 9). After separation of the aqueous layer, the organic solution is washed with water (12 × 250 mL) (Note 10), dried over anhydrous potassium carbonate, filtered, and distilled to give 89–95 g (88–94%) of 1-(methoxyvinyl)trimethylsilane (bp 102–104°C, 760 mm), n_D^{20} 1.4173 (Note 11) and (Note 12).

A 50-mL, round-bottomed flask is charged with 65 g (0.50 mol) of 1-(methoxyvinyl)trimethylsilane and 300 mL of a 4:1 v/v mixture of acetone and 1.0 M aqueous hydrochloric acid (Note 13). After the pale-yellow-green solution is stirred for 1 hr at room temperature, it is transferred to a 1-L separatory funnel and 150 mL each of water and diethyl ether are added. After separation, the aqueous layer is washed with diethyl ether (2 × 50 mL), and these extracts are combined with the organic material. The ethereal solution is washed with water (3 × 300 mL), dried over anhydrous magnesium sulfate, filtered, and distilled to give 45–48 g (78–83%) of acetyltrimethylsilane (bp 112°C, 760 mm), n_D^{20} 1.4125 (lit.² 1.4113) (Note 14) and (Note 15).

2. Notes

1. For a detailed description of the general techniques used in the handling of air-sensitive solutions, consult ³. Alternatively, a useful pamphlet describing these techniques is available from Aldrich Chemical Company, Inc., on request.

2. All of the glassware used in the preparation of 1-(methoxyvinyl)trimethylsilane was dried for at least 4 hr at 110°C, assembled hot, and allowed to cool under a nitrogen atmosphere.

3. Reagent-grade **tetrahydrofuran** (Aldrich Chemical Company, Inc.) was distilled under a **nitrogen** atmosphere from sodium/benzophenone prior to use.

4. Commercial cylinders of **methyl vinyl ether** were obtained from Matheson Gas Products, East Rutherford, NJ, and were fitted with a standard needle-valve regulator adapted to connect to a 24-in. 16-gauge syringe needle (Aldrich Chemical Company, Inc.). Unwanted, nonvolatile impurities from the cylinder were removed by employing a second flask, which was empty and septum-sealed, between the cylinder and the cold reaction flask. The gaseous reagent is transferred, through the needle, into the empty flask and through a double-ended needle (Aldrich Chemical Company, Inc.) into the reaction flask. The weight of the added **methyl vinyl ether** was periodically determined from the difference between the initial tare weight of the flask plus the contents and the total weight at each new weighing. However, the amount of this reagent added can be varied by at least $\pm 10\%$ without significantly affecting the product yield.

5. This reagent was obtained either from Aldrich Chemical Company, Inc., or Lithium Corporation of America, Bessemer City, NC. A technical data sheet is available from the suppliers. Solutions of ca. 2 M were titrimetrically analyzed for active alkyl lithium by the tosylhydrazone method.⁴ It is advisable to make certain that the organolithium reagent to be used was prepared in **pentane** solution. This evaluation can be easily accomplished by the gas-chromatographic analysis of the organic layer obtained from the hydrolysis, under a **nitrogen** atmosphere, of the **tert-butyllithium** solution to be used. **Isobutane** and **pentane** should comprise essentially all of the volatile material observed. Recently, from the latter supplier, we found that the solvent used was a petroleum distillate that contained some higher-boiling components. As a consequence, the distillative isolation of the product was more difficult and the yield was lower (i.e., 80%).

6. The slow warm-up is accomplished conveniently by the removal of the solid dry ice from the cold bath. This process minimizes the formation of acetylenic byproducts. The warm-up period can vary with the amount of coolant used. We have consistently obtained good results using sufficient coolant to match the liquid level of the reaction mixture.

7. **Chlorotrimethylsilane** was purchased from Petrarch, Inc., Levittown, PA and was distilled from **calcium hydride** prior to use.

8. **Lithium chloride** precipitates during the warm-up procedure.

9. *Caution! The reaction mixture contains low boiling components and care must be exercised to prevent product loss.*

10. This procedure effectively removes the **tetrahydrofuran**, thus simplifying the distillative isolation of the product. This operation must be done carefully to prevent the loss of product.

11. A Nester–Faust Model NFT-50 annular spinning-band distillation unit was used to obtain the reported product yields in >99% Chemical purity by gas-chromatographic analysis (Perkin–Elmer Model Sigma 1B Instrument using a 6-ft \times 1/8-in. 5% SE-30 on silylated Chromosorb W column). Lower product yields (84–86%) of similar chemical purity were obtained using a 200-mm column packed with glass helices.

12. This product gave a satisfactory combustion analysis for $C_6H_{14}OSi$ and exhibited the following spectroscopic data: 1H NMR ($CDCl_3$) δ : 0.09 (s, 9 H), 3.50 (s, 3 H), 4.28 (d, 1 H, $J = 2.0$), 4.59 (d, 1 H, $J = 2.0$); ^{13}C NMR ($CDCl_3$) δ : -2.3 (Si–CH₃), 54.0 (OCH₃), 93.3 (C-2), 170.1 (C-1); IR (film) cm^{-1} : 1590 (C=C); 1257 (TMS); 1227, 1050 (C=C–OR); MS: m/z 130 (6%), 115 (20%), 89 (47%), 73 (100%), 59 (29%), 44 (11%), 42 (15%).

13. Exposure to direct sunlight was routinely avoided because of the known photochemical reactivity of acylsilanes.⁵

14. Distillation and gas-chromatographic analysis of this compound was carried out as described in (Note 11).

15. This product gave a satisfactory combustion analysis for $C_5H_{12}OSi$ and exhibited the following spectroscopic data: 1H NMR ($CDCl_3$) δ : 0.09 (s, 9 H), 2.16 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ : -3.5 (Si–CH₃), 35.2 (CH₃), 246.8 (C=O); IR (film) cm^{-1} : 1645 (C=O); MS: m/z 116 (13%), 101 (11%), 73 (100%), 59 (6%), 44 (34%), 42 (15%). The ultraviolet spectrum of this material in **cyclohexane** solution exhibits absorbances at 381, 365, 356, and 344 nm with molar extinction coefficients of 91, 123, 97, and 60, respectively. In addition, shorter-wavelength shoulders are observed. For a detailed discussion of the spectroscopic properties of acylsilanes, consult ⁶.

3. Discussion

Acylsilanes have been known since 1957, when Brook described the synthesis of **benzoyltriphenylsilane**.⁷ Their unique reactivity has made them very useful reagents for organic syntheses.⁸ The simplest known member of this class of compounds, **acetyltrimethylsilane**, has been prepared from the oxidation of **1-trimethylsilylethanol**,⁶ the hydrolysis of **2-methyl-2-trimethylsilyl-1,3-dithiane**,² the silylation–hydrolysis of **N-acetylimidazole**,⁹ the lithiation–silylation–hydrolysis of **ethyl vinyl ether**,¹⁰ the pyrolysis of **2,4,4-trimethyl-2-trimethylsilyl-1,3-oxathiolane 3,3-dioxide**,¹¹ and the silylation of

acid chlorides.¹²

The present preparation¹³ utilizes the simple deprotonation of methyl vinyl ether first reported by Baldwin and co-workers to obtain 1-(methoxyvinyl)lithium,¹⁴ which functions as a very useful reagent for nucleophilic acylation.¹⁵ After detailed studies of the processes involved, this approach has been applied to the syntheses of a number of acyl derivatives of silicon, germanium, and tin.¹⁶ This procedure also overcomes the hydrolysis problems encountered in a previous study.¹⁰ The vinyl ether approach to such acylmetalloids has been demonstrated to provide access to systems that cannot be prepared using other acyl anion equivalents.¹⁷ In the present case, the simple two-step process from commercially available reagents gives the highest reported overall yield of pure acetyltrimethylsilane from chlorotrimethylsilane (69–78%). Moreover, the reaction sequence can be scaled up or down without encountering difficulties.

References and Notes

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17. Soderquist, J. A.; Hassner, A. *J. Org. Chem.* **1980**, *45*, 541. See also ¹⁶.

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

1-(methoxyvinyl)lithium
potassium carbonate (584-08-7)
hydrochloric acid (7647-01-0)
diethyl ether (60-29-7)
ammonium chloride (12125-02-9)
nitrogen (7727-37-9)
cyclohexane (110-82-7)
acetone (67-64-1)
Pentane (109-66-0)
magnesium sulfate (7487-88-9)
Tetrahydrofuran (109-99-9)
Lithium chloride (7447-41-8)
methyl vinyl ether (9003-09-2)
ethyl vinyl ether (109-92-2)

calcium hydride (7789-78-8)

isobutane (75-28-5)

CHLOROTRIMETHYLSILANE (75-77-4)

Acetyltrimethylsilane,
Silane, acetyltrimethyl- (13411-48-8)

1-(methoxyvinyl) trimethylsilane,
1-(methoxyvinyl)trimethylsilane (79678-01-6)

benzoyltriphenylsilane

2,4,4-trimethyl-2-trimethylsilyl-1,3-oxathiolane 3,3-dioxide

tert-Butyllithium (594-19-4)

N-acetylimidazole (2466-76-4)

1-trimethylsilylethanol (13246-39-4)

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