



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

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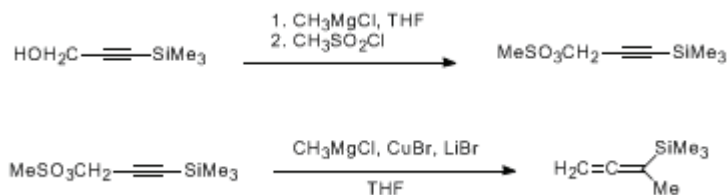
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## A GENERAL METHOD FOR THE SYNTHESIS OF ALLENYLSILANES: 1-METHYL-1-(TRIMETHYLSILYL)ALLENE

[Silane, trimethyl(1-methyl-1,2-propadienyl)-]



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### 1. Procedure

A 500-mL, three-necked, round-bottomed flask is equipped with a magnetic stirring bar, a rubber septum, a low-temperature thermometer, and a 250-mL pressure-equalizing dropping funnel fitted with a nitrogen inlet adapter (Note 1). The flask is charged with 30.0 g (0.234 mol) of 3-trimethylsilyl-2-propyn-1-ol (Note 2) and 230 mL of dry tetrahydrofuran (Note 3), and then cooled with an ice bath while 84 mL of a 2.8 M solution of methylmagnesium chloride in tetrahydrofuran (Note 4) is added at such a rate that the internal temperature does not rise above 10°C. Approximately 1.5 hr is required for the addition, after which time the gray solution is stirred at 0°C for 30 min, and then cooled below -70°C with a dry ice-acetone bath. Methanesulfonyl chloride (26.8 g, 0.234 mol) (Note 5) is added over 10 min via syringe, and after 30 min the cold bath is removed and the pale-yellow reaction mixture is allowed to warm to room temperature over 2 hr.

A 2-L, three-necked, round-bottomed flask equipped with a vacuum adapter and two glass stoppers (Note 1) is charged with 21.4 g (0.246 mol) of anhydrous lithium bromide and 35.3 g (0.246 mol) of anhydrous cuprous bromide (Note 6). The reaction vessel is evacuated and the contents are briefly heated with a Bunsen burner flame. After 30 min the vacuum is replaced by nitrogen and the apparatus is equipped with a mechanical stirrer and two rubber septa. Dry tetrahydrofuran (260 mL) (Note 3) is added, and the resulting green solution containing a small amount of undissolved solid is cooled with an ice bath while 84 mL of a 2.8 M solution of methylmagnesium chloride in tetrahydrofuran (Note 4) is added rapidly via syringe over 1–2 min. After 20 min of further stirring at 0°C, the reaction mixture appears as a viscous yellow-green suspension. The solution of the mesylate derivative of 3-trimethylsilyl-2-propyn-1-ol prepared above is now transferred via cannula over 45 min to the reaction mixture, which is cooled below -70°C with a dry ice-acetone bath. After 30 min, the cold bath is removed and the green reaction mixture is stirred at room temperature for 2 hr. The blue-gray mixture is then poured into a 2-L Erlenmeyer flask containing a magnetically stirred mixture of 400 mL of pentane, 200 mL of water, and 400 mL of saturated ammonium chloride solution. The organic phase is separated and washed successively with two 200-mL portions of saturated ammonium chloride solution, ten 1-L portions of water (Note 7), and 100 mL of saturated sodium chloride solution. The organic phase is dried over anhydrous sodium sulfate, and the drying agent is removed by filtration. The solvent is removed from the filtrate by atmospheric distillation through a 10-cm Vigreux column. The residual liquid is carefully distilled through a 12-cm column packed with glass helices to give 21.3–22.2 g, (72–75%) of 1-methyl-1-(trimethylsilyl)allene as a colorless liquid, bp 111°C (Note 8),(Note 9),(Note 10) (Note 11).

### 2. Notes

1. The apparatus is flame-dried at 20 mm pressure and then maintained under an atmosphere of nitrogen during the course of the reaction.

2. 3-Trimethylsilyl-2-propyn-1-ol was obtained from Petrarch Systems, Inc. and used as received. Alternatively, it can be prepared by the silylation of 2-propyn-1-ol.<sup>2</sup>
3. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately before use.
4. Methylmagnesium chloride in tetrahydrofuran was purchased from Aldrich Chemical Company, Inc.
5. Methanesulfonyl chloride was obtained from the Aldrich Chemical Company, Inc. and purified by distillation from phosphorus pentoxide before use.
6. Lithium bromide, obtained from Aldrich Chemical Company, Inc., and cuprous bromide, supplied by Fluka Chemical Corporation, were dried at 120°C (0.02 mm) for 8 hr before use. The checkers obtained lower yields (54–58%) with cuprous bromide that was supplied by other commercial sources.
7. This procedure conveniently removes tetrahydrofuran from the organic phase.
8. The submitters report bp 112–113°C and state that an additional 2.2 g (7%) of product, bp 54–56°C (90 mm), can be obtained by combining the distillation forerun with the pot residue and redistilling the mixture at reduced pressure.
9. The allenylsilane thus obtained was found by <sup>1</sup>H NMR analysis to be contaminated with 7–8% of 1-trimethylsilyl-1-butyne. This material is suitable for use in [3+2] annulations.<sup>3</sup> Efficient stirring during the formation of the mixed cuprate reagent is important in minimizing the amount of this impurity produced in the reaction.
10. The submitters note that if pure 1-methyl-1-(trimethylsilyl)allene is required, the mixture of allenylsilane and 1-trimethylsilyl-1-butyne is treated with 0.15 equiv of silver nitrate in 10:1 methanol–water at room temperature for 1 hr. Extraction with pentane and distillation furnishes the allenylsilane in 79% yield. Gas-chromatographic analysis (0.2-mm × 10.5-m methyl silicone-coated fused silica capillary column, split ratio 100:1, column pressure 20 psi, temperature 20°C) indicates that this material contains none of the acetylenic side product.
11. The product exhibits the following spectral properties: IR (neat) cm<sup>-1</sup>: 2955, 2920, 2900, 2860, 1935, 1440, 1400, 1250, 935, 880, 830, 805, 750, and 685; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ: 0.08 (s, 9 H), 1.67 (t, 3 H, *J* = 3.3), and 4.25 (q, 2 H, *J* = 3.3); <sup>13</sup>C NMR (67.9 MHz, CDCl<sub>3</sub>) δ: -2.1, 15.1, 67.3, 89.1, 209.1. The impurity, 1-trimethylsilyl-1-butyne, displays <sup>1</sup>H NMR peaks at 0.14 (s, 9 H), 1.15 (t, 3 H, *J* = 7), and 2.23 (q, 2 H, *J* = 7).

### 3. Discussion

Allenylsilanes serve as valuable three-carbon components in a general [3+2] annulation method for the synthesis of five-membered rings.<sup>4 5</sup> A variety of general synthetic approaches to allenylsilanes have recently been developed,<sup>6 7 8,9,10 11 12 13 14 15 16</sup> and a number of specialized routes to various specific functionalized derivatives<sup>17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39</sup> are available as well. The present procedure involves a modification of the general method of Vermeer,<sup>6</sup> which is the most widely applicable route to substituted allenylsilanes. Advantages of this approach include its efficiency, high regioselectivity, and utility in the synthesis of a variety of mono-, di-, and trisubstituted allenylsilane derivatives.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 347
- Org. Syn. Coll. Vol. 10, 165

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

sodium benzophenone ketyl

ammonium chloride (12125-02-9)

sodium chloride (7647-14-5)

silver nitrate (7761-88-8)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

cuprous bromide (7787-70-4)

Pentane (109-66-0)

Tetrahydrofuran (109-99-9)

Methanesulfonyl chloride (124-63-0)

2-propyn-1-ol (107-19-7)

3-Trimethylsilyl-2-propyn-1-ol (5272-36-6)

lithium bromide (7550-35-8)

phosphorus pentoxide (1314-56-3)

1-Methyl-1-(trimethylsilyl)allene,  
Silane, trimethyl(1-methyl-1,2-propadienyl)- (74542-82-8)

1-trimethylsilyl-1-butyne

methylmagnesium chloride (676-58-4)