



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

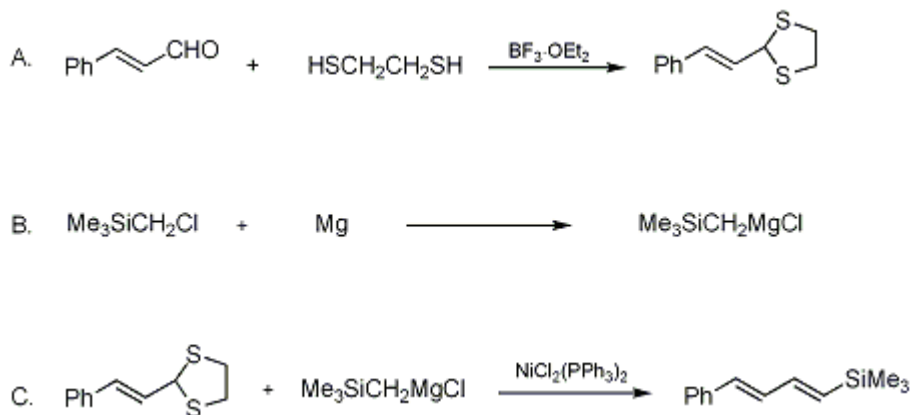
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.*

*Organic Syntheses, Coll. Vol. 9, p.727 (1998); Vol. 70, p.240 (1992).*

## NICKEL-CATALYZED SILYLOLEFINATION OF ALLYLIC DITHIOACETALS: (E,E)-TRIMETHYL(4-PHENYL-1,3-BUTADIENYL)SILANE

[Silane, trimethyl (4-phenyl-1,3-butadienyl)-, (E,E)-]



Submitted by Zhi-Jie Ni and Tien-Yau Luh<sup>1</sup>.

Checked by Shigeki Habaue and Hisashi Yamamoto.

### 1. Procedure

*CAUTION! 1,2-Ethanedithiol has a powerful stench. Steps A and C should be performed in a well-ventilated hood.*

A. *2-(2-Phenylethenyl)-1,3-dithiolane*. In a 1-L, round-bottomed flask equipped with a magnetic stirring bar are placed 26.8 g (0.2 mol) of freshly distilled (E)-3-phenyl-2-propenal and 20.1 g (0.21 mol) of 1,2-ethanedithiol in 400 mL of chloroform. To the stirred solution is added 10 mL (11.3 g, 0.080 mol) of boron trifluoride etherate in one portion. The mixture is stirred at room temperature for 2 hr. The chloroform solution is washed with two 100-mL portions of 10% aqueous sodium hydroxide. The aqueous layer is extracted twice with 100 mL of chloroform. The combined organic layers are washed twice with 200 mL of water, dried over anhydrous magnesium sulfate, and filtered. The filtrate is concentrated under reduced pressure to give 40.6 g (97%) of a white solid which is sufficiently pure for the next operation.

B. *(Trimethylsilyl)methylmagnesium chloride*. A 500-mL, three-necked, round-bottomed flask containing 5.2 g (0.22 g-atom) of magnesium turnings is equipped with a rubber septum, a reflux condenser, an addition funnel and a magnetic stirring bar. The system is flame-dried and flushed with nitrogen. A few crystals of iodine and 150 mL of anhydrous ether (Note 1) are introduced. As the contents of the flask are stirred, 25.8 g (0.21 mol) of (chloromethyl)trimethylsilane (Note 2) is added in small portions until the reaction begins, and then at such a rate as to maintain gentle refluxing of the ether. The addition requires about 30 min, after which the mixture is heated under reflux for an additional 30 min. The solution is cooled to room temperature and is used directly for the next reaction.

C. *(E,E)-Trimethyl(4-phenyl-1,3-butadienyl)silane*. In a 1-L, two-necked, round-bottomed flask fitted with a reflux condenser, rubber septum, and a magnetic stirring bar are placed 14.6 g (0.070 mol) of 2-(2-phenylethenyl)-1,3-dithiolane and 2.3 g (0.0035 mol) of dichlorobis(triphenylphosphine)nickel (Note 3). The flask is evacuated and flushed with nitrogen three times. To the above mixture is added 200 mL of anhydrous tetrahydrofuran (Note 4); then it is cooled in an ice bath. The ether solution of (trimethylsilyl)methylmagnesium chloride prepared above is introduced with a double-ended needle in

one portion (Note 5). The mixture is refluxed for 10 hr, cooled to room temperature, and treated with 200 mL of saturated ammonium chloride solution. The organic layer is separated and the aqueous layer is extracted with three, 200-mL portions of ether. The combined organic layers are washed twice with 100 mL of aqueous 10% sodium hydroxide solution and twice with 100 mL of brine. The organic solution is dried over anhydrous magnesium sulfate. The solvent is removed under reduced pressure and the residue is filtered through a short column packed with 30 g of silica gel (Note 6) and flushed under a positive nitrogen pressure with 300 mL of hexane. After evaporation of the solvent under reduced pressure, the yellowish residue is distilled to give 12.9 g (91%) of (E,E)-trimethylsilyl(4-phenyl-1,3-butadienyl)silane (Note 7) as a colorless liquid, bp 99–101°C (0.6 mm), which solidifies on standing, mp <37°C.

## 2. Notes

1. Ethyl ether is distilled from sodium-benzophenone ketyl before use.
2. (Chloromethyl)trimethylsilane, also available from Aldrich Chemical Company, Inc., was purchased from Wako Pure Chemical Industries, LTD. and used directly.
3. Dichlorobis(triphenylphosphine)nickel, also available from Aldrich Chemical Company, Inc., was purchased from Fluka AG, and used without further purification. The catalyst can also be prepared according to literature procedures.<sup>2,3</sup>
4. Tetrahydrofuran is distilled from sodium-benzophenone ketyl before use.
5. An excess of the Grignard reagent is required to maximize the yield; otherwise, the reaction is incomplete.
6. Silica gel (230–400 mesh) was purchased from E. Merck Co.
7. The spectral properties of the product are as follows: IR (neat)  $\text{cm}^{-1}$ : 3040, 1605, 1450, 1250, 1000, 870, 840, 730, 690;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.13 (s, 9 H,  $-\text{Si}(\text{CH}_3)_3$ ), 6.01 (d, 1 H,  $J = 17.6$ ,  $=\text{CHTMS}$ ), 6.58 (d, 1 H,  $J = 15.2$ ,  $\text{PhCH}=\text{C}$ ), 6.69 (dd, 1 H,  $J = 9.8$  and  $17.6$ ,  $=\text{CH}=\text{CHTMS}$ ), 6.83 (dd, 1 H,  $J = 9.8$  and  $15.2$ ,  $\text{PhCH}=\text{C}$ ), 7.20–7.40 (m, 5 H, aromatic) (The assignments for olefinic protons are based on simulation results);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-1.5$ , 126.7, 127.8, 128.7, 131.8, 133.0, 135.2, 137.4, 144.3; exact mass calcd for  $\text{C}_{13}\text{H}_{18}\text{Si}$ : 202.1178; found 202.1185.

## 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

Trimethyl(4-phenyl-1,3-butadienyl)silane can be prepared by the reaction of bis(trimethylsilyl)methylolithium with cinnamaldehyde<sup>4</sup> or 1,3-bis(trimethylsilyl)propenylolithium with benzaldehyde.<sup>5,6</sup> The reaction of 1-bromo-2-phenylthioethene with (E)-2-trimethylsilylethenylmagnesium bromide in the presence of a palladium catalyst gives the corresponding dienylyl sulfide which serves as a precursor for the preparation of butadienylylsilanes.<sup>7</sup> However, the starting materials in most of these syntheses are not readily available.

The procedure described here is based on a series of reports on the nickel-catalyzed coupling reactions of dithioacetals with Grignard reagents.<sup>8,9,10,11,12</sup> The method offers a new, very efficient and convenient route to the substituted butadienylylsilanes.<sup>8</sup> The starting materials are easily accessible and the operation is very simple. The reaction in general is highly stereoselective, if not stereospecific. The phenyl substituent can be replaced with simple alkyl groups and yields essentially remain unchanged.<sup>8</sup> The extension of this method to the synthesis of trienylylsilanes has proved successful.<sup>8</sup> Since vinylsilanes can be converted into  $\alpha,\beta$ -unsaturated aldehydes,<sup>13,14,15,16,17</sup> the combination of these latter procedures with the method described here can be used in the homologation of enals. (E)- $\beta$ -Arylvinylylsilanes are synthesized stereospecifically in a similar manner from benzylic dithioacetals.<sup>9</sup>

---

## References and Notes

1. Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong, and Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China.
  2. Cotton, F. A.; Faut, O. D.; Goodgame, D. M. L. *J. Am. Chem. Soc.* **1961**, 83, 344;
  3. Venanzi, L. M. *J. Chem. Soc.* **1958**, 719.
  4. Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. I* **1981**, 2415.
  5. Chan, T.-H.; Li, J.-S. *J. Chem. Soc., Chem. Commun.* **1982**, 969.
  6. Corriu, R.; Escudie, N.; Guerin, C. *J. Organometal. Chem.* **1984**, 264, 207.
  7. Fiandanese, V.; Marchese, G.; Mascolo, G.; Naso, F.; Ronzini, L. *Tetrahedron Lett.* **1988**, 29, 3705.
  8. Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1988**, 53, 5582.
  9. Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1988**, 53, 2129.
  10. Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1515,
  11. Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1011.
  12. Yang, P.-F.; Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1989**, 54, 2261.
  13. Chan, T. H.; Lau, P. W. K.; Mychajlowskij, W. *Tetrahedron Lett.* **1977**, 3317.
  14. Pillot, J. P.; Dunogues, J.; Calas, R. *Bull. Soc. Chim. Fr.* **1975**, 2143.
  15. Yamamoto, K.; Nunokawa, O.; Tsuji, J. *Synthesis* **1977**, 721.
  16. Yamamoto, K.; Yoshitake, J.; Nguyen Thi Qui; Tsuji, J. *Chem. Lett.* **1978**, 859.
  17. Yamamoto, K.; Ohta, M.; Tsuji, J. *Chem. Lett.* **1979**, 713.
- 

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

silica gel

brine

sodium-benzophenone ketyl

ether,  
ethyl ether (60-29-7)

ammonium chloride (12125-02-9)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

magnesium (7439-95-4)

nitrogen (7727-37-9)

benzaldehyde (100-52-7)

iodine (7553-56-2)

palladium (7440-05-3)

cinnamaldehyde

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

hexane (110-54-3)

boron trifluoride etherate (109-63-7)

1,2-ethanedithiol (540-63-6)

dichlorobis(triphenylphosphine)nickel (14264-16-5)

(chloromethyl)trimethylsilane (2344-80-1)

1-bromo-2-phenylthioethene

(E,E)-Trimethyl(4-phenyl-1,3-butadienyl)silane,  
Silane, trimethyl (4-phenyl-1,3-butadienyl)-, (E,E)- (70960-88-2)

2-(2-Phenylethenyl)-1,3-dithiolane (5616-58-0)

(E)-3-phenyl-2-propenal (104-55-2)

(Trimethylsilyl)methylmagnesium chloride

(E,E)-trimethylsilyl(4-phenyl-1,3-butadienyl)silane

Trimethyl(4-phenyl-1,3-butadienyl)silane

bis(trimethylsilyl)methylithium

(E)-2-trimethylsilylethenylmagnesium bromide

1,3-bis(trimethylsilyl)propenylithium