Organic Syntheses

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). 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.

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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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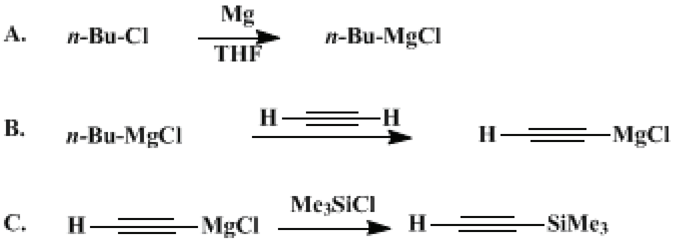
TRIMETHYLSILYLACETYLENE

[Silane, ethynyltrimethyl-]



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Checked by Dallas D. Crotts, Bruce E. Eaton, and Clayton H. Heathcock.

1. Procedure

A. *Butylmagnesium chloride.* A dry, 1-L, three-necked, round-bottomed flask is equipped with a sealed mechanical stirrer (Note 1), a 250-mL pressure-equalizing dropping funnel and a reflux condenser to the top of which is attached a T-piece connected at one end to a supply of dry nitrogen, and at the other to an oil or mercury bubbler. At the same time a dry, 2-L, three-necked, round-bottomed flask, fitted with a sealed mechanical stirrer and two swan-neck adapters, is prepared, with one adapter holding a gas inlet and a calcium chloride drying tube, and the other supporting a thermometer and a 1-L pressure-equalizing dropping funnel.

The 1-L flask is charged with magnesium turnings (39.6 g, 1.65 g-atom) (Note 2) and dry tetrahydrofuran (THF) (150 mL). The mixture is heated to reflux temperature under an atmosphere of dry nitrogen, and a crystal of iodine is added. The dropping funnel is filled with 1-chlorobutane (173 mL, 152.5 g, 1.65 mol) (Note 3) and a portion (15 mL) is added to the boiling THF mixture. The source of heat is removed. After the reaction has commenced, the THF begins to boil more vigorously and a further volume (400 mL) of THF is added to the reaction mixture. Then the remainder of the chlorobutane is added slowly at a rate sufficient to maintain the reaction under reflux. Finally, the reaction mixture is stirred and heated under reflux until all the magnesium has been consumed (0.5–1 hr).

B. *Ethynylmagnesium chloride.* While the butylmagnesium chloride is being prepared, the 2-L flask is filled with dry THF (500 mL), which is saturated by bubbling acetylene through it for 0.5–1 hr (Note 4). The warm (ca. 60°C) butylmagnesium chloride is rapidly poured under a liberal blanket of nitrogen into the 1-L dropping funnel, which is then flushed with nitrogen before being stoppered. The rapid flow of acetylene is maintained. The 2-L flask is cooled to −5°C in a dry ice–acetone bath, the acetylene is bubbled rapidly through the THF (Note 4), and the butylmagnesium chloride is added dropwise to the stirred reaction mixture at a rate sufficient to maintain the temperature below 20°C (Note 5). This addition requires 1 hr; then acetylene is bubbled through the reaction mixture for a further 0.5 hr. (The mixture cools to about 5°C during this period.) The acetylene supply is disconnected and replaced by dry nitrogen.

C. *Trimethylsilylacetylene.* A solution of chlorotrimethylsilane (152 mL, 130 g, 1.197 mol) (Note 6) in dry THF (100 mL) is placed in the 1-L dropping funnel and is added (20 min) to the cooled and stirred solution of ethynylmagnesium chloride at a rate sufficient to maintain a reaction temperature of about 15–20°C (Note 7). Finally, the dropping funnel is replaced by an efficient double-surface condenser and calcium chloride drying tube, and the reaction mixture is heated under reflux for 1 hr (Note 8). The reflux condenser is replaced by a distillation head and a double surface condenser is connected to a receiver flask which is cooled in an ice bath (Note 9). The reaction mixture is distilled under nitrogen with stirring until all the azeotrope of trimethylsilylacetylene and THF (700–800 mL, bp ca. 66°C) has distilled (Note 10) and (Note 11). The distillate is washed with ice–water portions (10 ×

500 mL) to remove the THF. Washing is continued until the organic layer stays constant in volume (Note 12). Distillation (Note 10) of the organic layer under an atmosphere of nitrogen through a short Vigreux column (Note 13) gives trimethylsilylacetylene, bp 50–52°C/760mm, n_D^{20} 1.391; (lit.[2,3,4] 53.5° C at 762 mm, n_D^{20} 1.3900; 52°C at 760 mm, n_D^{20} 1.3900; 52°C at 760 mm, n_D^{20} 1.3935) in yields ranging from 72.5 g (62%) to 87.5 g (75%) (Note 14) and (Note 15).

2. Notes

1. The checkers used an efficient magnetic stirrer.
2. The magnesium turnings for Grignard reactions were supplied by Fisons Scientific Apparatus, Loughborough. If less than 1.65 g-atom of magnesium is used, the final product will be contaminated with 1-chlorobutane.
3. It is essential that the 1-chlorobutane be free of 1-butanol. 1-Chlorobutane (Aldrich Chemical Company, Inc.) was purified by rapid passage through basic alumina (activity 1) before use.
4. Gaseous acetylene is introduced at the rate of about 20 L/hr and is purified by passage through a cold trap (−78°C), followed by bubbling through concentrated sulfuric acid and finally passage over sodium hydroxide pellets. These operations must be conducted in a well-ventilated fume hood. The checkers found that an insufficient acetylene flow rate in this and the next step results in the formation of butyltrimethylsilane and bis(trimethylsilyl)acetylene.
5. The temperature reaches 15°C after 0.5 hr, and 20°C after 0.8 hr. Ethynylmagnesium halides can rapidly disproportionate to bis(chloromagnesium)acetylene and acetylene at higher temperatures.[2] It is important to maintain the reaction mixture at or below 20°C and to have an excess of acetylene in order to prevent formation of the bis(magnesium chloride). The checkers found that the ethynylmagnesium chloride can be formed at 10–15°C, thus minimizing the problem.
6. Commercial chlorotrimethylsilane is distilled from quinoline under nitrogen.
7. It is important that the addition be done fairly rapidly. The checkers found that slow addition (2 hr at 20°C) resulted in significant disproportionation of the ethynylmagnesium chloride.
8. It is essential to have an efficient condenser during the reflux and distillation stages because the product, trimethylsilylacetylene, is extremely volatile.
9. The receiver must be cooled to avoid serious loss of volatile product.
10. The hot distillation apparatus should be allowed to cool under a nitrogen atmosphere before being dismantled.
11. The submitters distilled the azeotrope immediately after heating the mixture to reflux. If it is allowed to stand and cool, it sets solid with magnesium chloride and subsequent distillation results in appreciably lower yields.
12. The presence of residual THF in the final product is easily detected by the characteristic ^{1}H NMR signals at δ 1.85 (4 H) and 3.75 (4 H). The checkers found GLC to be more convenient than ^{1}H NMR for analysis at this point. Either a 6-m × 2-mm glass column of 3% OV-101 on WHP 80/100 with 30 mL/min He or a 15-m × 0.25-mm fused-silica capillary column of DB-5 (cross linked phenylsilicone) with 1 mL/min H_2 proved sufficient to resolve butane, trimethylsilylacetylene, butyltrimethylsilane, THF, 1-chlorobutane, and bis(trimethylsilyl)acetylene.
13. The checkers used an 18-in. Vigreux column, equipped with an adjustable reflux ratio takeoff. The final product can be contaminated with up to several percent butane unless careful distillation is carried out.
14. Trimethylsilylacetylene displayed the following spectroscopic properties: IR (CCl_4) cm^{-1}: 3280 (s) and 2050 (s); ^{1}H NMR: ($CDCl_3$, 250 MHz) δ: 0.18 (s, 9 H, CH_3), 2.36 (s, 1 H, ≡CH).
15. The submitters have carried out the preparation on twice the above scale with no reduction in yield.

3. Discussion

Trimethylsilylacetylene has been prepared by silylation of a variety of ethynyl metal derivatives.[2,3,4,5,6,7,8,9,10] The most useful methods are the silylation of ethynylmagnesium bromide[3,4,5] and chloride.[2,7,10] The use of ethynylmagnesium bromide has been reported to suffer from complicating side reactions,[2] and the results obtained in our hands were unreliable.

The present method is based on the silylation of ethynylmagnesium chloride as reported by Krüerke,[2] except that the Grignard reagent is prepared from 1-chlorobutane, rather than from the volatile (and therefore more difficult to manipulate) chloromethane. Although the preparation of ethynylmagnesium bromide is a well-established *Organic Syntheses* procedure,[11] the use of ethynylmagnesium chloride has received little attention.[5] It does not seem to be widely appreciated that butylmagnesium chloride is much more soluble in THF than ethylmagnesium bromide, and its use in Grignard ethynylations is strongly recommended. The preparation of ethynylmagnesium chloride essentially follows the *Organic Syntheses* procedure laid down for the bromide.[11]

Trimethylsilylacetylene is an extremely versatile (and potentially nucleophilic) two-carbon building block. Applications in organic synthesis have been well documented in the literature.[12,13,14]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 63
- Org. Syn. Coll. Vol. 8, 609

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

bis(chloromagnesium)acetylene

sulfuric acid (7664-93-9)

acetylene (74-86-2)

sodium hydroxide (1310-73-2)

magnesium,
magnesium turnings (7439-95-4)

nitrogen (7727-37-9)

chloromethane (74-87-3)

1-butanol (71-36-3)

iodine (7553-56-2)

1-chlorobutane,
chlorobutane (109-69-3)

Quinoline (91-22-5)

ethylmagnesium bromide (925-90-6)

chloride

Tetrahydrofuran,
THF (109-99-9)

ethynylmagnesium bromide

CHLOROTRIMETHYLSILANE (75-77-4)

bis(trimethylsilyl)acetylene (14630-40-1)

Trimethylsilylacetylene,
Silane, ethynyltrimethyl- (1066-54-2)

Ethynylmagnesium chloride

Butylmagnesium chloride (693-04-9)

butyltrimethylsilane (1000-49-3)