Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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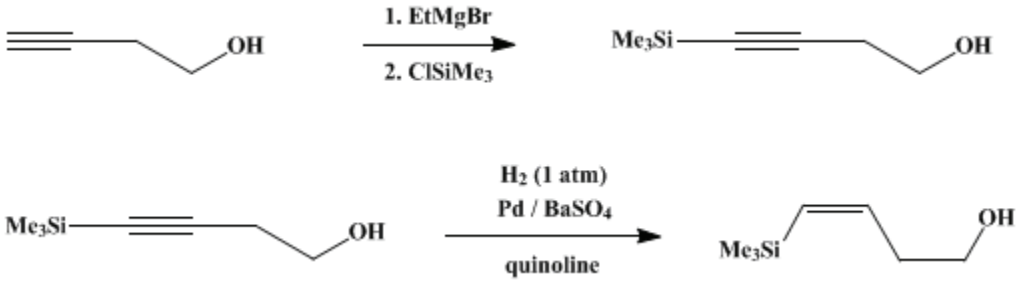
Organic Syntheses, Coll. Vol. 8, p.609 (1993); Vol. 68, p.182 (1990).

(*Z*)-4-(TRIMETHYLSILYL)-3-BUTEN-1-OL

[3-Buten-1-ol, 4-(trimethylsilyl)-, (*Z*)-]



Submitted by Larry E. Overman, Mark J. Brown, and Stephen F. McCann[1].
Checked by Ronald C. Newbold and Andrew S. Kende.

1. Procedure

A. *Preparation of 4-(trimethylsilyl)-3-butyn-1-ol*. A flame-dried, three-necked, 2-L, round-bottomed flask is fitted with a 1-L pressure-equalizing addition funnel, a mechanical stirrer, and a nitrogen inlet. The flask is flushed with dry nitrogen and charged with 3-butyn-1-ol (Note 1) (freshly distilled, 31.4 g, 0.448 mol) and 900 mL of anhydrous tetrahydrofuran (Note 2). The stirred solution is cooled to 0°C under nitrogen and to it is added over 1 hr a solution of ethylmagnesium bromide in tetrahydrofuran (493 mL of 2.0 *M* solution, 0.986 mol) (Note 1). The resulting heterogeneous mixture is rapidly stirred at 0°C for 1 hr, allowed to warm to room temperature for 1 hr, and then recooled to 0°C. To this mixture is slowly added over 30 min with rapid stirring freshly distilled (Note 3) chlorotrimethylsilane (125 mL, 0.986 mol). The mixture is stirred for 1 hr at 0°C and allowed to warm to room temperature over 1–2 hr. The entire reaction mixture is poured slowly with rapid stirring into a 4-L Erlenmeyer flask that contains 1 L of ice-cold 3 *M* hydrochloric acid, and is stirred at 25°C for an additional 2 hr. The organic phase is separated and the aqueous phase is extracted with three 200-mL portions of ether.

The combined organic phases are washed with two 200-mL portions of water, four 200-mL portions of saturated sodium bicarbonate solution, and two 200-mL portions of saturated sodium chloride. The organic phase is dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure at room temperature using a rotary evaporator. The crude product is distilled through a short-path distillation apparatus under reduced pressure to give 45.2 g (0.318 mol, 71% yield) of 4-(trimethylsilyl)-3-butyn-1-ol, bp 78–79°C (10 mm), as a colorless liquid (Note 4) and (Note 5).

B. *Preparation of (Z)-4-(trimethylsilyl)-3-buten-1-ol*. A dry, 250-mL, round-bottomed flask with a stirring bar is charged with 8.84 g (0.062 mol) of 4-(trimethylsilyl)-3-butyn-1-ol, 0.4 g of 5% palladium on barium sulfate (Note 6), 0.45 g of synthetic quinoline (Note 7), and 78 mL of methanol. The flask is placed in a hydrogenation apparatus equipped with a gas burette, and the stirred mixture is thoroughly purged with nitrogen. The nitrogen is then replaced by hydrogen and the reaction mixture is stirred at atmospheric pressure and room temperature until 1.46 L (0.065 mol) of hydrogen is consumed. The flask is flushed with nitrogen and the solution is filtered through a thick pad of Celite. The filtrate is concentrated on a rotary evaporator at room temperature to afford 10–15 mL of an oil, which is diluted with 150 mL of ether. The ether solution is thoroughly washed once with 200 mL of ice-cold 0.2 *M* sulfuric acid, then once with 20 mL of 5% sodium bicarbonate solution. The ether layer is dried over anhydrous magnesium sulfate, filtered, and concentrated to yield 8.4 g (0.058 mol) of the crude buten-1-ol (Note 8). Short-path distillation under reduced pressure gives 7.60 g (0.0527 mol, 85% yield) of (*Z*)-4-(trimethylsilyl)-3-buten-1-ol, bp 95–100°C (25 mm) as a colorless liquid (Note 9) and (Note 10).

2. Notes

1. The reagents, 3-butyn-1-ol and 2.0 *M* ethylmagnesium bromide in tetrahydrofuran, were purchased from Aldrich Chemical Company, Inc. The ethylmagnesium bromide concentration can be easily checked by titration with menthol using 1,10-phenanthroline as indicator.[2]
2. Tetrahydrofuran was distilled from sodium and benzophenone under a nitrogen atmosphere.
3. Chlorotrimethylsilane was purchased from Aldrich Chemical Company, Inc., and was distilled from calcium hydride under an atmosphere of nitrogen immediately prior to use.
4. The product, 4-(trimethylsilyl)-3-butyn-2-ol, shows the following proton NMR spectrum at 300 MHz in $CDCl_3$ δ: 0.03 (s, 9 H, $SiCH_3$), 1.8 (broad s, 1 H, OH), 2.47 (t, 2 H, CH_2), 3.67 (m, 2 H, CH_2OH); and infrared spectrum (neat) cm^{-1}: 3350 (very broad), 2178, 1250, 1031, 894, 842, 760.
5. Similar yields can be obtained in this silylation by using the chloromagnesium salt (from butylmagnesium chloride) as described in *Org. Synth., Coll. Vol. VIII* **1993**, 606.
6. The 5% palladium on barium sulfate was purchased from Engelhard Industries, Newark, NJ.
7. Synthetic quinoline was purchased from Aldrich Chemical Company, Inc. and was distilled prior to use.
8. The proton NMR spectrum of the crude buten-1-ol was essentially identical to that of the distilled product, except for traces of solvent. This crude silylbuten-1-ol was of sufficient purity for the tetrahydropyridine synthesis described in the next procedure.
9. Distilled product showed a proton NMR at 250 MHz in $CDCl_3$ as follows δ: 0.14 (s, 9 H, $SiCH_3$), 1.61 (broad s, 1 H, OH), 2.37–2.46 (m, 2 H, CH_2CH_2OH), 3.68 (broadened t, 2 H, J = 6.5, CH_2OH), 5.66–5.71 (dt, 1 H, J = 14.1, J = 1.2, $Me_3SiCH{=}CHR$), 6.29 (overlapping dt, 1 H, J = 14.1, J = 7.1, $R_3SiCH{=}CHR$). Gas chromatographic analysis using a 25-m 5% methylphenylsilicone column showed that this sample was a 92:8 mixture of *Z* and *E* isomers and contained <2% of other impurities.
10. The submitters report that *Z*-4-(trimethylsilyl)-3-buten-1-ol of >98% isomeric purity can be obtained in ca. 60% overall yield by a more lengthy sequence involving hydroalumination–protonolysis[3] of the tetrahydropyranyl (THP) ether of 4-(trimethylsilyl)-3-butyn-1-ol[4] followed by cleavage[5] of the THP ether with pyridinium *p*-toluenesulfonate in methanol. This sequence is less convenient for the tetrahydropyridine synthesis described in the next procedure, since the isomeric purity of the vinylsilane is not important for the cyclization reaction.[6]

3. Discussion

The direct silylation of 3-butyn-1-ol follows the Danheiser modification[7] of the Westmuze–Vermeer[8] method. The subsequent semihydrogenation is a modification[9] of the Lindlar procedure and yields the *Z*-alkene isomer in >90% isomeric purity.

Another *Organic Syntheses* procedure[10] illustrates one[6] of the uses of the four-carbon organosilane intermediates described in this preparation.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 358

References and Notes

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

tetrahydropyranyl (THP) ether of 4-(trimethylsilyl)-3-butyn-1-ol

THP ether

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

methanol (67-56-1)

ether (60-29-7)

hydrogen (1333-74-0)

sodium bicarbonate (144-55-8)

sodium chloride (7647-14-5)

nitrogen (7727-37-9)

barium sulfate (7727-43-7)

Benzophenone (119-61-9)

sodium (13966-32-0)

palladium (7440-05-3)

Quinoline (91-22-5)

menthol (15356-60-2)

ethylmagnesium bromide (925-90-6)

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

calcium hydride (7789-78-8)

3-butyn-1-ol (927-74-2)

1,10-phenanthroline (66-71-7)

CHLOROTRIMETHYLSILANE (75-77-4)

TETRAHYDROPYRIDINE

vinylsilane (7291-09-0)

(Z)-4-(Trimethylsilyl)-3-buten-1-ol,
3-Buten-1-ol, 4-(trimethylsilyl)-, (Z)-,
Z-4-(trimethylsilyl)-3-buten-1-ol (87682-77-7)

Butylmagnesium chloride (693-04-9)

4-(trimethylsilyl)-3-butyn-1-ol (2117-12-6)

4-(trimethylsilyl)-3-butyn-2-ol (6999-19-5)

pyridinium p-toluenesulfonate