



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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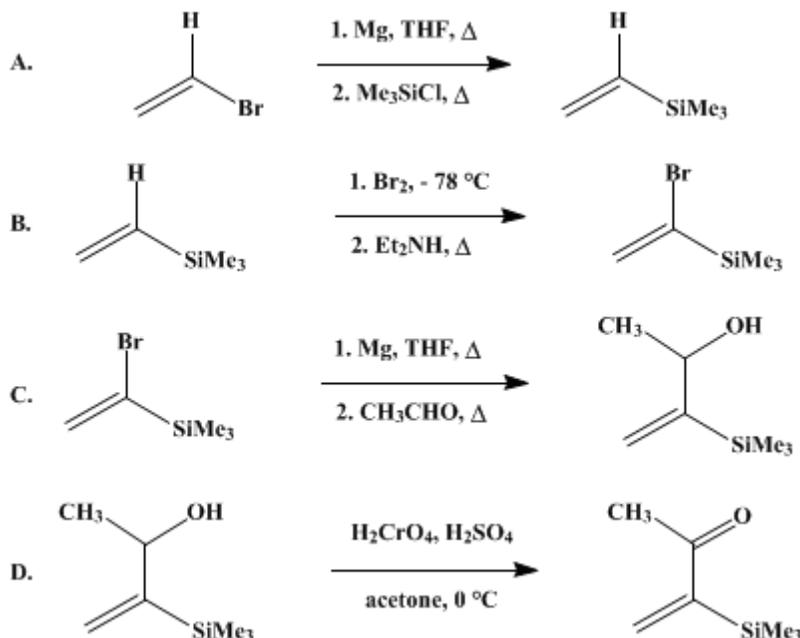
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*Organic Syntheses, Coll. Vol. 6, p.1033 (1988); Vol. 58, p.152 (1978).*

### 3-TRIMETHYLSILYL-3-BUTEN-2-ONE: A MICHAEL ACCEPTOR

#### [3-Buten-2-one, 3-(trimethylsilyl)-]



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Checked by William R. Baker and Robert M. Coates.

#### 1. Procedure

A. *Vinyltrimethylsilane* (**1**). A 2-l., three-necked, round-bottomed flask fitted with a mechanical stirrer, a reflux condenser, and a 500-ml., pressure-equalizing dropping funnel (Note 1) is charged with 26.4 g. (1.09 g.-atom) of magnesium turnings and 800 ml. of dry tetrahydrofuran (Note 2). A solution of 107 g. (70.5 ml., 1.00 mole) of vinyl bromide (Note 3) in 200 ml. of tetrahydrofuran is placed in the addition funnel and slowly added dropwise to the reaction vessel. After the reaction has begun (Note 4), the addition rate is regulated, maintaining a gentle reflux during the remainder of the addition period. The mixture is heated at reflux for an additional hour, and a solution of 108 g. (0.995 mole) of chlorotrimethylsilane (Note 5) in 100 ml. of tetrahydrofuran is added dropwise while the reaction is maintained at reflux with continued heating and stirring (Note 6). The suspension is stirred for another 2 hours under reflux, then cooled to room temperature and stirred overnight.

The condenser and dropping funnel are removed, and the flask is equipped for distillation with a 30.5-cm. Vigreux column. The distillate (b.p. 60–65°) is collected, transferred to a separatory funnel, and washed with 10–20 100-ml. portions of water (Note 7), yielding 67–78 g. (67–78%) of silane **1** as a colorless liquid containing small amounts of tetrahydrofuran (Note 8).

B. (1-Bromoethynyl)trimethylsilane (**2**). A 1-l., three-necked, round-bottomed flask equipped with a mechanical stirrer and a 250-ml. dropping funnel is charged with 89.8 g. (approximately 0.90 mole, (Note 8)) of silane **1**. The contents of the flask are stirred and cooled to –78°, and 168 g. (1.06 mole) of bromine is added dropwise over *ca.* 1 hour. The cooling bath is removed, and the red viscous mixture is warmed to room temperature. The flask is fitted with an efficient, water-cooled condenser, and 425 g. (600 ml., 5.82 moles) of diethylamine (Note 9) is cautiously (Note 10) added with continued stirring. After the addition is complete, the reaction mixture is heated at reflux for 12 hours, during which time a precipitate of diethylamine hydrochloride forms. The salts are separated from the cooled suspension by filtration and washed with several 300-ml. portions of diethyl ether. The ether filtrate is carefully

washed, first with 100-ml. portions of 10% hydrochloric acid until the aqueous layer remains acidic (pH *ca.* 2), then with 100 ml. of water and 200 ml. of saturated aqueous sodium chloride. The ether solution is dried with anhydrous magnesium sulfate, concentrated with a rotary evaporator, and distilled under reduced pressure through a 20.3-cm. Vigreux column, affording 104–110 g. (65–68%) of silane 2, b.p. 72–75° (120 mm.) (Note 11).

C. *3-Trimethylsilyl-3-buten-2-ol* (3). A 500-ml., three-necked, round-bottomed flask equipped with two 30.5-cm. Liebig condensers connected in series, a pressure-equalizing dropping funnel, and a magnetic stirrer is charged with 9.2 g. (0.38 g.-atom) of magnesium turnings and 100 ml. of tetrahydrofuran (Note 1) and (Note 2). About 2 g. of 1,2-dibromoethane is added, initiating the formation of the Grignard reagent. When the supernatant solution becomes warm and begins to reflux from reduction of 1,2-dibromoethane, a solution of 50 g. (0.28 mole) of silane 2 in 75 ml. of tetrahydrofuran is added dropwise to the stirred mixture at a rate that maintains gentle reflux. After the addition is complete, the reaction mixture is kept at reflux for an additional hour before freshly distilled acetaldehyde (25.0 g., 0.568 mole) is introduced. The temperature is maintained at reflux, and stirring is continued throughout the addition and for an additional hour. The flask is then fitted with a distillation head and heated until *ca.* 100 ml. of distillate has been collected. The reaction mixture is cooled (ice-water bath) and stirred, diluted with 100 ml. of ether, and hydrolyzed by addition of enough saturated ammonium chloride (approximately 50 ml.) to dissolve the thick, sticky precipitate. The salts are filtered and washed with ether, and the aqueous layer of the filtrate is extracted with three 150-ml. portions of ether. The combined ether layers are washed with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and concentrated by distillation at atmospheric pressure (Note 12), giving 48–55 g. of crude butenol 3 as a liquid that is used in the next step without further purification.

D. *3-Trimethylsilyl-3-buten-2-one* (4). A solution of 55 g. of crude butenol 3 in 100 ml. of acetone is placed in a 500-ml., three-necked, round-bottomed flask equipped with a mechanical stirrer and a 250-ml. dropping funnel. The reaction vessel is immersed in an ice-water bath, and 95 ml. of an aqueous solution containing chromium trioxide and sulfuric acid (Note 13) is added to the stirred acetone solution. After completion of the addition, 2-propanol is added to the reaction mixture until a green endpoint is reached, indicating consumption of excess oxidant. The contents are poured into 450 ml. of ether, 300 ml. of water are added, and the aqueous layer is saturated with sodium chloride. The layers are separated, and the aqueous solution is extracted with five 150-ml. portions of ether. The combined ether solutions are washed with two 150-ml. portions of saturated aqueous sodium chloride, dried with anhydrous magnesium sulfate, and concentrated by distillation at atmospheric pressure through a 30.5-cm. Vigreux column. Continued distillation under reduced pressure gives, after separation of a low boiling forerun, 14.7–15 g. (37–38%) of butenone 4 as a pale yellow liquid, b.p. 98–103° (100 mm.) (Note 14) and (Note 15).

## 2. Notes

1. The apparatus is flamed dry under an argon atmosphere and maintained under argon during the reaction.
2. The submitters purified the tetrahydrofuran by distillation from lithium aluminum hydride. The checkers used tetrahydrofuran that had been distilled from the sodium ketyl of benzophenone. (*Caution! See Org. Synth., Coll. Vol. 5, 976 (1973), for a warning regarding the purification of tetrahydrofuran.*)
3. Gaseous vinyl bromide is condensed in a 500-ml. flask cooled in an acetone–dry ice bath and diluted with 200 ml. of tetrahydrofuran. The submitters used vinyl bromide supplied by J. T. Baker Chemical Company; the checkers purchased this reagent from Linde Specialty Gases. Vinyl bromide is also available from Aldrich Chemical Company, Inc.
4. Approximately 70 ml. is added over a 20-minute period before formation of the Grignard reagent begins. The total addition time is *ca.* 1 hour.
5. The submitters used practical grade chlorotrimethylsilane purchased from PCR, Inc., which was distilled before use. Chlorotrimethylsilane from Aldrich Chemical Company, Inc., was employed by the checkers, both with and without prior distillation. Approximately the same yield was obtained in either case.
6. A white precipitate, presumed to be magnesium salts, is deposited as the solution of chlorotrimethylsilane is added.

7. The layers must be allowed to separate completely to avoid sizable mechanical losses. The submitters used 10 water extractions, whereas the checkers continued the extractions until the organic layer reached an approximately constant weight.
8. The  $^1\text{H}$  NMR spectrum of the product obtained by the checkers revealed the presence of  $6 \pm 2\%$  of tetrahydrofuran.
9. Diethylamine is available from Aldrich Chemical Company, Inc.
10. The reaction of the excess bromine with diethylamine is exothermic; consequently it may be necessary to moderate the reaction by cooling with an ice-water bath during the early stages of the addition.
11.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$  (multiplicity, coupling constant  $J$  in Hz., number of protons, assignment): 0.16 [s, 9H,  $\text{Si}(\text{CH}_3)_3$ ], 6.12 (d,  $J = 2$ , 1H, CH), 6.21 (d,  $J = 2$ , 1H, CH).
12. The checkers terminated the distillation when the head temperature reached  $44^\circ$ .
13. The oxidizing reagent is prepared as described in *Org. Synth., Coll. Vol. 5*, 866 (1973).
14. GC analysis of the product by the submitters on a 1.85-m. 3% silicone gum rubber (SE-30) column at  $25^\circ$  gave a single peak. Butenone 4 has the following  $^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ),  $\delta$  (multiplicity, coupling constant  $J$  in Hz., number of protons, assignment): 0.14 [s, 9H,  $\text{Si}(\text{CH}_3)_3$ ], 2.23 (s, 3H,  $\text{CH}_3$ ), 6.18 (d,  $J = 2$ , 1H, CH), 6.53 (d,  $J = 2$ , 1H, CH).
15. This material showed no tendency to deteriorate when stored under an argon atmosphere at  $-20^\circ$ .

### 3. Discussion

Butenone 4 has been obtained by Brook and Duff<sup>4</sup> from the reaction of 1-trimethylsilylvinylmagnesium bromide and acetic anhydride at  $-120^\circ$ . However, the product was a mixture of butenone 4 and a dimeric substance which apparently resulted from subsequent conjugate addition of the Grignard reagent to the ketone. The procedures in the present reaction sequence for the preparation of silane 1, silane 2, and 1-trimethylsilylvinylmagnesium bromide are based on those reported by Ottolenghi, Fridkin, and Zilkha.<sup>5</sup> Similarly, other 1-trimethylsilylvinyl ketones may be prepared by reaction of the appropriate aldehyde with 1-trimethylsilylvinylmagnesium bromide and subsequent oxidation with chromic acid. The 1-trimethylsilylvinyl ketones are remarkably stable and useful in a variety of conjugate addition reactions.<sup>6</sup>

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 6*, 666

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### References and Notes

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3. Department of Chemistry, Cornell University, Ithaca, New York 14853.
4. A. G. Brook and J. M. Duff, *Can. J. Chem.*, **51**, 2024 (1973).
5. A. Ottolenghi, M. Fridkin, and A. Zilkha, *Can. J. Chem.*, **41**, 2977 (1963).
6. R. K. Boeckman, Jr., D. M. Blum, and B. Ganem, *Org. Synth., Coll. Vol. 6*, 666 (1988).

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### Appendix

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

sodium ketyl of benzophenone

(1-Bromoethynyl)trimethylsilane

acetaldehyde (75-07-0)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether,  
diethyl ether (60-29-7)

acetic anhydride (108-24-7)

ammonium chloride (12125-02-9)

magnesium turnings (7439-95-4)

sodium chloride (7647-14-5)

bromine (7726-95-6)

acetone (67-64-1)

2-propanol (67-63-0)

chromic acid (7738-94-5)

1,2-dibromoethane (106-93-4)

diethylamine (109-89-7)

vinyl bromide (593-60-2)

magnesium sulfate (7487-88-9)

chromium trioxide (1333-82-0)

Tetrahydrofuran (109-99-9)

lithium aluminum hydride (16853-85-3)

diethylamine hydrochloride (660-68-4)

butenone (78-94-4)

argon (7440-37-1)

silane

CHLOROTRIMETHYLSILANE (75-77-4)

3-Trimethylsilyl-3-buten-2-one,  
3-Buten-2-one, 3-(trimethylsilyl)- (43209-86-5)

butenol

1-trimethylsilylvinylmagnesium bromide

Vinyltrimethylsilane (754-05-2)

3-Trimethylsilyl-3-buten-2-ol (66374-47-8)

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