



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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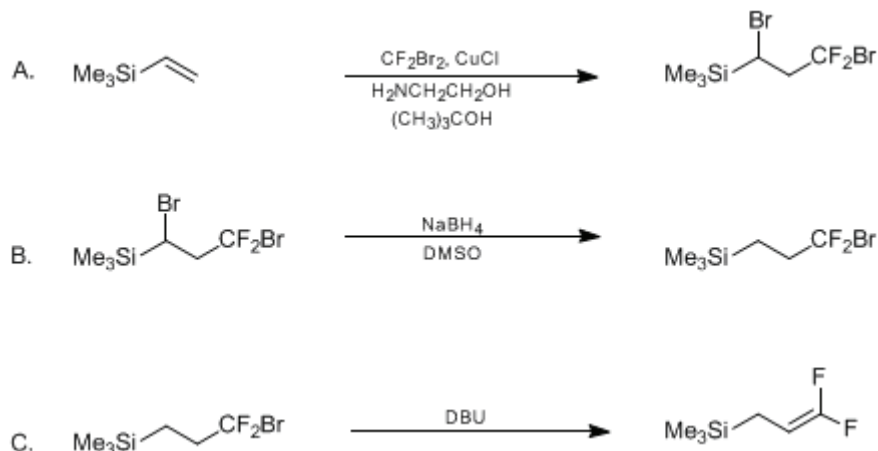
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*September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## (3,3-DIFLUOROALLYL)TRIMETHYLSILANE

### [Silane, (3,3-difluoro-2-propenyl)trimethyl-]



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### 1. Procedure

A. *(1,3-Dibromo-3,3-difluoropropyl)trimethylsilane* (Note 1). A 250-mL pressure tube (Note 2) equipped with a magnetic stirring bar is charged with vinyltrimethylsilane (20 g, 30.8 mL, 0.20 mol), ethanolamine (6.11 g, 6.04 mL, 0.10 mol), dibromodifluoromethane (83.9 g, 36.5 mL, 0.4 mol), copper (I) chloride (0.18 g, 1.8 mmol), and tert-butyl alcohol (15 mL) (Note 3) and (Note 4). The tube is sealed and stirred for 20 hr in an oil bath at 90°C (Note 5). The reaction mixture is combined with that from another run at the same scale and diluted with 40 mL of hexane (the mixture separates into a cloudy supernatant and a brown resin). The hexane layer is separated and the resinous precipitate extracted with two 20-mL portions of hexane. The combined solutions are filtered through a bed of silica gel on a 60-mL fritted glass funnel and the resulting clear filtrate is concentrated by rotary evaporation using a water aspirator. The crude material is fractionally distilled to afford 71.9–78.3 g (58–61%) of the dibromide as a colorless oil, bp 78–79°C (12 mm) [lit.<sup>2</sup> bp 95°C (25 mm)] (Note 6).

B. *(3-Bromo-3,3-difluoropropyl)trimethylsilane*. A 1-L, four-necked flask is equipped with a mechanical stirrer, thermometer, Claisen adapter, septum inlet, reflux condenser (the top of which is connected to a calcium chloride drying tube), and a solid addition funnel. The flask is charged with (1,3-dibromo-3,3-difluoropropyl)trimethylsilane (78.3 g, 0.25 mol), and anhydrous dimethyl sulfoxide (200 mL), and the solid addition funnel is charged with sodium borohydride (11.5 g, 0.30 mol) (Note 7) and (Note 8). The stirred solution is warmed to 80°C, and sodium borohydride is added at a rate sufficient to maintain a reaction temperature of 80–90°C (Note 9). Toward the end of the addition, an additional portion of dimethyl sulfoxide (200 mL) is added via syringe to lower the viscosity of the reaction mixture. After the addition is complete, the mixture is cooled in an ice-water bath, diluted with 100 mL of pentane, and cautiously quenched with 12 M hydrochloric acid until no further gas evolution occurs. The mixture is transferred to a separatory funnel and washed with three 100-mL portions of 5% brine. The pentane extract is dried over calcium chloride and the solvent removed through a 15-cm Vigreux column. Further fractionation yields 41.5 g (72%) of 3-bromo-3,3-difluoropropyltrimethylsilane, bp 139–141°C (Note 10).

C. *(3,3-Difluoroallyl)trimethylsilane*. A 100-mL, three-necked, round-bottomed flask is equipped with a magnetic stirrer, short-path distillation head, and an electric heating mantle. The flask is charged with 30.99 g (0.13 mol) of (3-bromo-3,3-difluoropropyl)trimethylsilane and 29.1 g (0.19 mol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Note 11). Stirring and gradual heating are begun and the

reaction mixture becomes thick with precipitate (Note 12). The product distilling from the mixture is collected from 80–100°C giving 11.88 g of colorless liquid.

Additional product is obtained by extractive workup of the residue. The cooled residue is acidified by adding 50 mL of 3 N hydrochloric acid and the resulting solution is extracted with 50 mL of pentane. The pentane layer is washed with 2 × 50 mL of water, dried over sodium sulfate, filtered and concentrated at 35°C under ca. 30 mm vacuum. The remaining liquid is distilled using a short-path distillation head to afford an additional 1.77 g of product (bp 86–95°C). The combined product, weighing 13.65 g (70% yield), has a purity of 85–90% based on NMR and capillary GC analysis (Note 13).

## 2. Notes

1. This procedure is based on a report by Burton and Kehoe.<sup>3</sup>
2. An Ace Model # 8648-83 tube with a FETFE O-ring was used.
3. Vinyltrimethylsilane, ethanolamine, copper(I) chloride (98+% ACS reagent grade), and dibromodifluoromethane were obtained from Aldrich Chemical Company, Inc. tert-Butyl alcohol was obtained from Fisher Scientific Company.
4. Dibromodifluoromethane (bp 22°C) was chilled and handled as a liquid.
5. The bottom third of the tube was immersed. The reaction mixture changed color from blue-green to brown during this period.
6. This material is 95–98% pure by GLC analysis (20% DC 200 on 80-100 mesh Chromosorb P, 4' × 0.25" column, 200°C). The presence of a lower-boiling impurity, 3-bromo-3,3-difluoro-1-propenyltrimethylsilane, does not affect the yield of the subsequent steps.
7. Dimethyl sulfoxide (99+% anhydrous grade) and sodium borohydride were purchased from Aldrich Chemical Company, Inc.
8. Other polar aprotic solvents (HMPA, DMPU) were used successfully in place of DMSO in small-scale runs.
9. Shortly after starting the addition, the exothermic reaction causes an increase in temperature, and external heating is discontinued. Care should be taken not to add the sodium borohydride too rapidly, as temperatures above 92°C have resulted in the formation of an over-reduced product, 3,3-difluoropropyltrimethylsilane. It is advisable to have an ice bath available in case the reaction requires external cooling.
10. This compound has the following spectral properties: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ: 0.02 (s, 9 H, Me<sub>3</sub>Si), 0.72–0.83 (m, 2 H, H-1), 2.14–2.38 (m, 2 H, H-2); <sup>13</sup>C NMR δ: –1.94 (Me<sub>3</sub>Si), 10.8 (C-1), 40.0 (t, C-2, J = 22.6), 125.4 (t, J = 307, CF<sub>2</sub>Br).
11. The 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Aldrich Chemical Company, Inc.
12. On a smaller scale the reaction was run in a round-bottomed flask and the product isolated at this stage by direct distillation of the reaction mixture through a short-path distillation head.
13. This product has the following spectroscopic properties: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ: 0.00 (s, 9 H, Me<sub>3</sub>Si), 1.2 (dt, <sup>3</sup>J<sub>HH</sub> = 8.9, <sup>4</sup>J<sub>FH</sub> = 1.5, 2 H, CH<sub>2</sub>), 4.1 (dtd, <sup>3</sup>J<sub>FH</sub> (trans) = 25.2, <sup>3</sup>J<sub>HH</sub> = 8.9, <sup>3</sup>J<sub>FH</sub> (cis) = 2.7, 1 H, =CH); <sup>13</sup>C NMR δ: –2.25 (Me<sub>3</sub>Si), 10.8 (unresolved m, CH<sub>2</sub>), 74.6 (t, <sup>2</sup>J<sub>FC</sub> = 23.0, =CH), 156.3 (dd, <sup>1</sup>J<sub>FC</sub> = 284, CF<sub>2</sub>); IR (film) cm<sup>-1</sup>: 1740 s (C=CF<sub>2</sub>). The <sup>1</sup>H NMR and IR data are consistent with those previously reported.<sup>4</sup>

## 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

Radical addition of dibromodifluoromethane to alkenes followed by sodium borohydride reduction is a convenient two-step method for the introduction of the difluoromethyl group.<sup>5</sup> Either one or both carbon-bromine bonds in the intermediate dibromides may be reduced, depending on the reaction conditions. In the case of acyclic dibromodifluoromethane-alkene adducts, the reduction occurs

*regioselectively* to yield the relatively inaccessible bromodifluoromethyl-substituted alkanes. The latter are potential building blocks for other fluorinated compounds. For example, they may be dehydrohalogenated to 1,1-difluoroalkenes; an example of this methodology is illustrated in this synthesis of (3,3-difluoroallyl)trimethylsilane.

(3,3-Difluoroallyl)trimethylsilane was first prepared in low yield from the high-temperature reaction of vinyltrimethylsilane with chlorodifluoromethane.<sup>6</sup> An improved synthesis involving the insertion of difluorocarbene into the requisite  $\beta$ -silyl ylide has been reported.<sup>4</sup> Although the yield is excellent, the reaction consumes a mole of the valuable Wittig reagent (it forms the phosphonium salt which must be recycled) in generating difluorocarbene from chlorodifluoromethane. Other (3,3-difluoroallyl)silanes have been synthesized via the  $S_N2'$  reactions of silyl anions with 3,3,3-trifluoropropenes.<sup>7</sup>

(3,3-Difluoroallyl)silanes are of interest as carbon-carbon bond forming building blocks in organofluorine chemistry.<sup>4,7,8</sup>

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## References and Notes

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## Appendix

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

brine

HMPA

DMPU

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

sodium sulfate (7757-82-6)

copper(I) chloride (7758-89-6)

Pentane (109-66-0)

ethanolamine (141-43-5)

hexane (110-54-3)

dimethyl sulfoxide,  
DMSO (67-68-5)

tert-butyl alcohol (75-65-0)

sodium borohydride (16940-66-2)

1,8-diazabicyclo[5.4.0]undec-7-ene (6674-22-2)

(3,3-Difluoroallyl)trimethylsilane,  
Silane, (3,3-difluoro-2-propenyl)trimethyl- (40207-81-6)

(1,3-Dibromo-3,3-difluoropropyl)trimethylsilane (671-80-7)

Vinyltrimethylsilane (754-05-2)

dibromodifluoromethane (75-61-6)

(3-Bromo-3,3-difluoropropyl)trimethylsilane,  
3-bromo-3,3-difluoropropyltrimethylsilane (134134-62-6)

3-bromo-3,3-difluoro-1-propenyltrimethylsilane

3,3-difluoropropyltrimethylsilane

chlorodifluoromethane (75-45-6)