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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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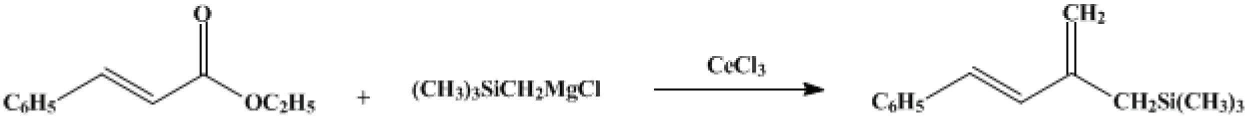
CONVERSION OF ESTERS TO ALLYLSILANES: TRIMETHYL(2-METHYLENE-4-PHENYL-3-BUTENYL)SILANE

[Silane, trimethyl (2-methylene-4-phenyl-3-butenyl)-]



Submitted by William H. Bunnelle and B. A. Narayanan[1].
Checked by Jürgen Fischer and Ekkehard Winterfeldt.

1. Procedure

A 1-L, three-necked, round-bottomed flask with mechanical stirrer and vacuum outlet (Note 1) is charged with powdered cerium (III) chloride ($CeCl_3 \cdot 7H_2O$, 52.92 g, 0.142 mol) (Note 2). The flask is immersed to the necks in an oil bath and evacuated to 0.2 mm. The solid is agitated by stirring as the flask is heated to 150°C for 2 hr. After the flask is cooled to room temperature, it is vented to the atmosphere and quickly purged with a stream of dry nitrogen for 2 min. At this stage, the flask is fitted with a low-temperature thermometer and a graduated 250-mL addition funnel containing 300 mL of dry tetrahydrofuran (THF) (Note 3), and capped with a rubber septum. Connection to a dry nitrogen line with a pressure relief bubbler is made via a needle through the septum. Tetrahydrofuran is run into the flask with good stirring, so that an even suspension results (Note 4). The white suspension is stirred at room temperature for 2 hr. Meanwhile, the addition funnel is charged with trimethylsilylmethylmagnesium chloride (Me_3SiCH_2MgCl, 1 *M* solution in ethyl ether, 142 mL, 0.142 mol) (Note 5) and (Note 6), transferred via stainless-steel cannula. The contents of the flask are cooled to −65°C with a dry ice/2-propanol bath, and the Grignard solution is added dropwise over a period of 40–50 min, so that the temperature of the reaction mixture remains below −60°C. The addition funnel is removed from the setup, with the septum/nitrogen inlet connected directly to the flask. After the cold mixture is stirred for 15 min more, ethyl cinnamate (10.32 g, 0.0586 mol) (Note 7) is added via syringe over a 2–3-min period. Stirring is continued as the flask is allowed to warm slowly to room temperature (Note 8). The off-white to beige reaction mixture is cooled to <5°C (ice-water bath) and quenched by the portionwise addition of chilled 1 *M* hydrochloric acid (200 mL), so that the internal temperature remains below 20°C (Note 9). The layers are separated, and the aqueous phase is extracted twice with ethyl ether (100 mL each). The combined organic layers are washed with saturated sodium bicarbonate solution (Note 10) and dried over sodium sulfate, and the solvents are removed at a rotary evaporator (25°C at 60 mm). The residual oil is transferred to a 100-mL, round-bottomed flask and distilled bulb-to-bulb (Note 11). The product (9.69–9.85 g, 76.5–78%) (Note 12) is collected at an air-bath temperature of 110–112°C, 0.20 mm.

2. Notes

1. The vacuum outlet should be packed with glass wool to prevent loss of significant quantities of cerium salt during the drying process. During some runs, cerium salts worked into the stirrer shaft bearing, causing it to bind. This problem could be avoided by placing a straight adapter tube between the bearing and the flask, to distance the bearing from the reaction mixture. The checkers found that sublimation of the cerium salt occurred in all their runs, but did not appear to affect the yield.
2. Cerium(III) chloride heptahydrate was purchased from Aldrich Chemical Company, Inc., and ground with a mortar and pestle just before use.
3. Tetrahydrofuran was freshly distilled under nitrogen from sodium and benzophenone. The (nominal) 250-mL funnel holds the entire volume of solvent.
4. On one occasion, when the solvent was added without stirring, the solid formed a hard cake on the bottom of the flask and resisted attempts to bring it into suspension. The full 2-hr "aging" period is necessary for best results.

5. This clear, pale-yellow solution was purchased from the Aldrich Chemical Company, Inc. The Grignard solution may be prepared from trimethylsilylmethyl chloride.[2] Take care to prevent air oxidation in opened bottles of the Grignard reagent—these solutions deteriorate rapidly, and older samples are unsuitable for the present procedure.

6. The prescribed quantity of Grignard reagent (and cerium salt) is 25% more than stoichiometric. This excess is required to ensure complete consumption of the ester.

7. Ethyl cinnamate was purchased from Eastman Kodak Company, and was distilled at 110–111°C/0.75 mm before use.

8. Warming takes approximately 3 hr. The reaction is complete by this time and can be worked up. Alternatively, the mixture may be stirred at room temperature for at least 12 hr (overnight) without any deleterious effect on yield.

9. If the reaction is allowed to become warm, substantial protodesilylation of the product takes place to give 3-methyl-1-phenyl-1,3-butadiene. The aqueous workup should be carried out rapidly to minimize this side reaction. The use of hydrochloric acid has a particular advantage since all of the salts dissolve, facilitating the extractions.

10. Some residual salts precipitate during this operation, but do not pose any handling difficulty.

11. Gas chromatographic analysis [0.53–mm i.d. × 10 m poly(dimethyl silicone) fused-silica column, temperature programmed from 140° to 220°C] indicates that this product is 98% pure, with < 1% 3-methyl-1-phenyl-1,3-butadiene and 1–2% of a less volatile, unidentified component. The checkers could obtain a very pure product by normal vacuum distillation. They found the impurities to be higher boiling compounds.

12. This material has the following spectral data: IR cm^{-1}: 3068, 1593, 872, 853, 838; ^{1}H NMR δ: 0.01 (s, 9 H), 1.80 (br, s, 2 H), 4.83 (br, s, 1 H), 5.00 (d, 1 H, $J = 1$), 6.45 (d, 1 H, $J = 16$), 6.77 (d, 1 H, $J = 16$), 7.1–7.4 (m, 5 H); ^{13}C NMR δ: −1.2, 22.2, 114.8, 126.4, 127.3, 128.6, 128.7, 132.0, 137.4, 143.8; MS (*m/e*, %): 216 (40%). 73 (100%).

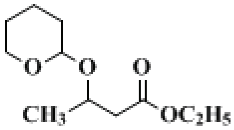
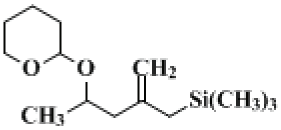
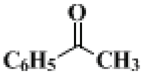
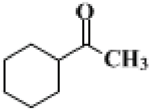
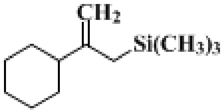
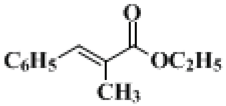
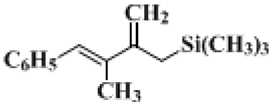
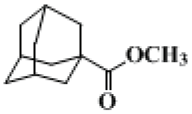
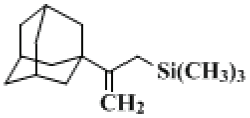
3. Discussion

Allylsilanes are exceptionally versatile compounds with a well-established function in organic synthesis.[3] [4] General methods for their preparation, then, are valuable. The method described here is effective for elaboration of esters to allylsilanes. The transformation is conceptually straightforward: twofold addition of a trimethylsilylmethyl metal species to the ester, followed by Peterson-type elimination from the resultant bis(trimethylsilylmethyl)carbinol, leads to the allylsilanes.

The Grignard reagent Me_3SiCH_2MgCl has been used to effect this conversion with simple, unbranched esters, but the yields are only moderate (∼50%) and the process fails completely for more sterically congested esters.[5] [6] [7] [8] In these cases, the α-silylketone intermediate resists further addition, instead suffering preferential enolization.[9] The use of organocerium reagents to circumvent this difficulty has been developed by two groups.[10,11] The reagent prepared from cerium(III) chloride and Me_3SiCH_2Li is quite effective for conversion of acid chlorides to allylsilanes, but does not react efficiently with esters.[10] Somewhat surprisingly in view of these results, a mixture of cerium(III) chloride with Me_3SiCH_2MgCl produces a powerful reagent for conversion of esters to allylsilanes in excellent yields.[11] Some examples, for reactions carried out on a 1-mmol scale, are collected in Table I.[11] Only the highly hindered methyl adamantanecarboxylate fails to react.

TABLE I

Ester	Allylsilane	Yield (%)
		95
		90[a]

		
		95
		77
		92
		0[b]

[a] Starting material and product each a 1 : 1 mixture of diastereoisomers.
[b] Starting material recovered quantitatively.

The protocol described above is a scaled-up modification of that reported earlier.[11] The title compound was prepared previously by a nickel-catalyzed cross-coupling,[12] and by the organocerium/acid chloride route.[10] The present procedure offers advantages in both convenience and yield compared to these other methods. Recently the method has been successfully applied to heteroatom-functionalized systems.[13]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 10, 200

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

Me_3SiCH_2Li

Me_3SiCH_2MgCl

hydrochloric acid (7647-01-0)

ethyl ether (60-29-7)

sodium bicarbonate (144-55-8)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

Benzophenone (119-61-9)

sodium (13966-32-0)

Ethyl cinnamate (103-36-6)

Tetrahydrofuran (109-99-9)

cerium (III) chloride,
cerium(III) chloride (7790-86-5)

methyl adamantanecarboxylate (711-01-3)

Trimethylsilylmethylmagnesium chloride (13170-43-9)

trimethylsilylmethyl chloride (2344-80-1)

Trimethyl(2-methylene-4-phenyl-3-butenyl)silane,
Silane, trimethyl (2-methylene-4-phenyl-3-butenyl)- (80814-92-2)

Cerium(III) chloride heptahydrate (18618-55-8)

3-methyl-1-phenyl-1,3-butadiene

bis(trimethylsilylmethyl)carbinol