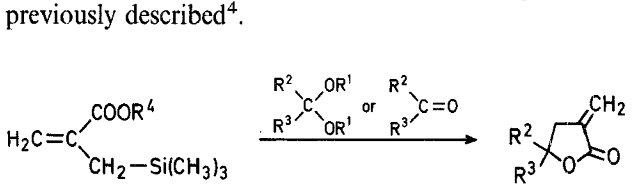
A Simple Synthesis of (2-Ethoxycarbonylallyl)-trimethylsilane, A Potential Synthon for the Synthesis of 2-Methylene-4-alkanolides

Akhtar Haider

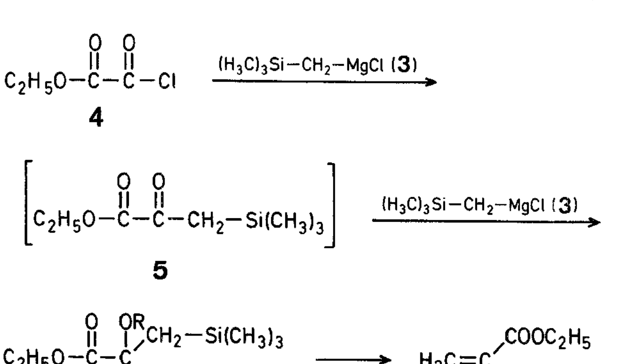
Institut de Chimie Organique, Universite de Lausanne, Rue de la Barre 2, CH-1005 Lausanne, Switzerland

In recent years, allylsilanes have attracted much attention as synthetic intermediates[1,2,3]. Thus, (2-ethoxycarbonylallyl)-trimethylsilane (**1**)[4] was proposed as synthon for synthesis of 2-methylene-4-alkanolides (**2**) which are associated with the antitumor properties of some natural products[5,6]. The synthesis of **1** from diethyl malonate in several steps has been previously described[4].



1 **2**

I report here a novel approach to this interesting allylsilane. The new method permits the preparation of **1** in good yield by a one-pot reaction of trimethylsilylmethylmagnesium chloride (**3**)[7,8] with ethoxalyl chloride (**4**); alternatively, product **1** can be prepared in higher yield by a related two-step procedure. Treatment of ethoxalyl chloride (**4**) with 2 equivalent of Grignard reagent **3**, at either room temperature or – 70 °C, gives **6** in good yield. The order of addition has no effect on the yield. *In situ* treatment of Grignard salt **6** with thionyl chloride[9] gives the allylsilane **1** in 53 % overall yield.



4 **5** **6** R = MgCl **7** R = H **1**

The reaction of an acyl chloride with **3** is known to produce trimethylsilylmethyl ketones[10,11,12]. Reaction of **4** with 1 equivalent of the Grignard reagent **3** leads to a 50/50 mixture of **4** and **6**. The mono-Grignard adduct, ethyl 3-trimethylsilyl-2-oxopropanoate (**5**), is not detected in this case. It is apparently more reactive than **4** and therefore reacts immediately with another molecule of **3** to give the salt **6**. Hydrolysis of Grignard salt **6** with a saturated solution of ammonium chloride produces the intermediate ethyl 2-hydroxy-2,2-bis[trimethylsilylmethyl]-acetate (**7**) in 83 % yield (based on **4**). When treated with 1 equivalent of potassium *t*-butoxide in ether (1 h, 0 °C) or with boron trifluoride ethyl etherate in dichloromethane (3 h, room temperature) the carbinol **7** is quantitatively converted into the allylsilane **1**.

Mass spectra were recorded on a Finnigan 1020 GC/MS spectrometer. I. R. spectra were determined on a Beckman IR 4230 spectrophotometer. ^{1}H-N.M.R. spectra were recorded on a Brucker 80-MHz spectrometer.

(2-Ethoxycarbonylallyl)-trimethylsilane (1):

To a stirred solution of trimethylsilylmethylmagnesium chloride [**3**; from chloromethyltrimethylsilane (4.0 g, 32.6 mmol) and magnesium (0.79 g, 32.6 mmol) in ether (30 ml)], a solution of ethoxalyl chloride (**4**; 2.22 g, 16.3 mmol) in ether (15 ml) is added slowly. After 3 h, the mixture is cooled in an ice bath and a solution of thionyl chloride (2 g, 16.8 mmol) in ether (15 ml) is added dropwise. The ice bath is removed and stirring is continued for 2 h at room temperature. Saturated ammonium chloride solution (40 ml) is added slowly. The aqueous mixture is extracted with ether (3 × 100 ml), the organic layers are washed with 1 normal sodium hydrogen carbonate solution (3 × 10 ml) and dried with magnesium sulfate. The solvent is evaporated and the residue distilled in vacuo; yield of **1**: 1.6 g (53 %); b.p. 50 °C/10 torr (Ref.[4], b.p. 35–40 °C/2 torr).

M.S. (E.I.): *m/e* = 186 (6.99 %); 185 (5.60); 171 (24.57); 143 (42.80); 141 (12.11); 127 (14.94); 117 (17.00); 103 (11.73); 98 (10.37); 83 (10.54); 74 (100); 68 (48.35); 59 (10.97).

I.R. (CH_2Cl_2): ν = 2960; 2905; 1710; 1628 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 5.97 (s, 1 H); 5.23 (s, 1 H); 4.20 (q, J = 7.0 Hz, 2 H); 1.80 (s, 2 H); 1.26 (t, J = 7.0 Hz, 3 H); 0.01 ppm (s, 9 H).

Ethyl 2-Hydroxy-2,2-bis[trimethylsilylmethyl]-acetate (7):

A solution of chloromethyltrimethylsilane (2.5 g, 20.4 mmol) in anhydrous ether (10 ml) is added dropwise to a stirred suspension of magnesium (0.5 g, 20.5 mmol) in anhydrous ether (30 ml) under a nitrogen atmosphere at room temperature. Gentle reflux occurs during the addition. After 3 h, a solution of ethoxalyl chloride (**4**; 1.4 g, 10.2 mmol) in ether (5 ml) is added slowly. The yellow-green mixture is stirred for 3 h, then quenched with ammonium chloride solution (1.1 g, in 30 ml water). The aqueous phase is extracted with ether (2 × 50 ml). The organic layer is dried with magnesium sulfate and evaporated. The residual crude product **7** is distilled in vacuo; yield: 2.41 g (85 %) b.p. 70 °C/0.1 torr.

$C_{12}H_{28}O_3Si_2$	calc.	C 52.22	H 10.23
(276.5)	found	52.32	10.22

M.S. (E.I.): *m/e* = 275 (M – 1, 0.03 %); 203 (21.82); 171 (11.75); 148 (48.99); 74 (100).

I.R. (CH_2Cl_2): ν = 3550; 2960; 2900; 1730; 1420; 1210; 1080; 1050; 1000; 940 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 4.2 (q, J = 7.0 Hz, 2 H); 3.1 (br. s, 1 H); 1.32 (t, J = 7.0 Hz, 3 H); 1.27 (s, 3 H); 0.03 ppm (s, 18 H).

(2-Ethoxycarbonylallyl)-trimethylsilane (1) from Compound 7:

Method A, using Potassium *t*-Butoxide: Potassium *t*-butoxide (220 mg, 1.96 mmol) is added to a solution of compound **7** (0.5 g, 1.8 mmol) in ether (15 ml) at 0 °C. After 1 h at room temperature, the mixture is diluted with ether (35 ml), washed with water (2 × 5 ml), and dried with magnesium sulfate. Evaporation of solvent gives the crude product **1** which is purified by distillation; yield: 290 mg (88.4 %).

Method B, using Boron Trifluoride: A solution of boron trifluoride diethyl etherate (0.3 ml, 2.38 mmol) in dry dichloromethane (2 ml) is added dropwise to a solution of compound **7** (0.552 g, 1.89 mmol) in dichloromethane (20 ml) at 0 °C. Stirring is continued for 30 min at 0 °C and 2.5 h at room temperature. The mixture is then washed with saturated sodium hydrogen carbonate solution (2 × 5 ml) and is dried with calcium chloride. Evaporation of solvent gives the pure allylsilane **1**; yield: 0.32 g (93.5 %).

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