

spectrum obtained from the simple adding-up of the spectra from pure PDGA and PLGA-PLP(II) complex while the dotted line (b) represents the ideal CD spectrum obtained from the simple adding-up of the spectra from pure PLGA and PDGA-PLP(II) complex on the assumption that no interaction occurs between pure PGA and PGA-PLP(II) complex in view of Eq. (1). When compared to the solid line exhibiting the actual CD spectrum for the ternary system obtained from simultaneous mixing of PDGA(2), PLGA(2), and PLP(II)(1) solutions, the spectrum (a) appears to be more similar to the actual curve, implying that the PLP(II) having a left-handed helix forms the interpolymer complex more favorably with PLGA having a right-handed helix. Consequently, the selective complexation of PLP(II) with PLGA has been confirmed again.

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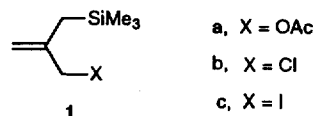
Convenient Synthesis of 2-(Chloromethyl)-3-(trimethylsilyl)propene and Allylsilane Based Bifunctional Reagents

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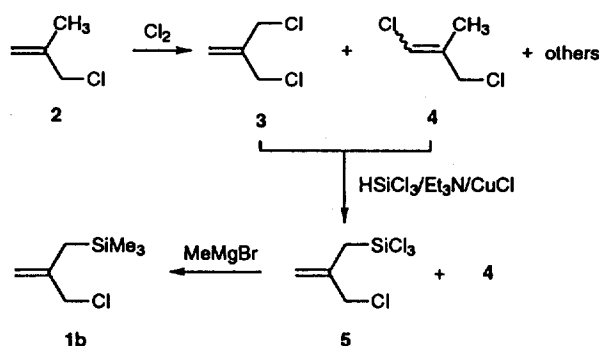
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Allylsilane based bifunctional reagents like **1** have been extensively employed in organic synthesis as valuable annulating agents.¹ Various synthetic methods of the reagents have been developed.² Recently Trost and coworker prepared 2-(chloromethyl)-3-(trimethylsilyl)propene (**1b**) using 3-chloro-2-chloromethylpropene (**3**), from which they synthesized the acetate **1a**, one of the most versatile [3+2] annulating agent.^{2d} We found that the chloride **1b** could be prepared from a mixture of the chlorination products of methallyl chloride, instead of very expensive dichloride **3**.



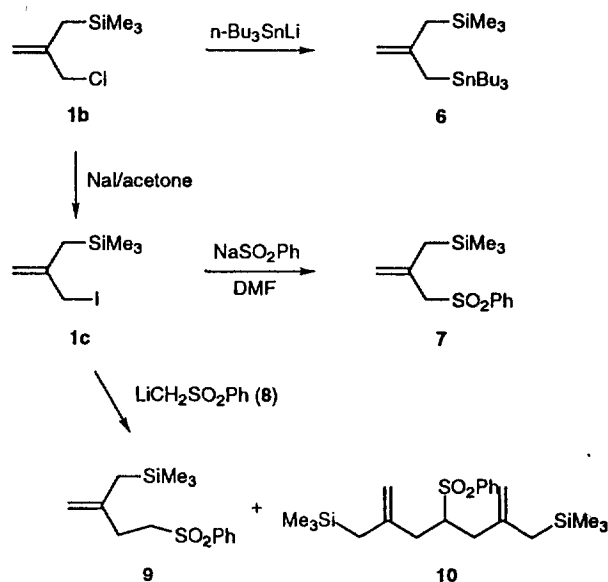
Chlorination of methallyl chloride (**2**) with molecular chlorine was reported to afford 34% of **3** along with a little isomeric dichlorides **4** and 1,2,3-trichloro-2-methylpropane.³ However, when we performed the reaction under the similar conditions a mixture of **3** and **4** was obtained in 60-70% yield, and the ratio of the products was *ca.* 40:60. It is difficult to separate by distillation since the boiling points of them are close to each other. When the mixture of **3** and **4** was treated with trichlorosilane and triethylamine in the presence of a catalytic amount of cuprous chloride gave only monosilyl product **5**. Surprisingly, **4** was remained intact under the reaction condition. The product **5** could be easily isolated from the unreacted **4** by distillation. Reaction of **5** with 3.5 equiv of methylmagnesium bromide in ether at -78°C provided **1b** in 90% yield.



Having found a facile and large scale preparation of the chloride **1b** from inexpensive commercially available mate-

rials, we decided to synthesize some bifunctional reagents which might have wide synthetic utilities.

The reaction of the chloride **1b** with (tributylstannyl)-lithium in THF at room temperature afforded 3-(tributylstannyl)-2-(trimethylsilylmethyl)propene (**6**) in 79% yield. The bimetallic reagent **6**, having allylstannane and allylsilane moieties,⁴ should be a versatile intermediate like 2-stannyl-3-silylpropene.⁵ 2-(Phenylsulfonylmethyl)-3-(trimethylsilyl)propene **7**, used as a 2-(trimethylsilylmethyl)allyl anion,⁶ was prepared by warming (100 °C) of a DMF solution of **1c** with sodium benzenesulfonate. The iodide **1c** was obtained from the transhalogenation of the chloride **1b** with NaI in refluxing acetone.⁷ The reaction of the iodide **1c** with the carbanion **8** derived from methyl phenyl sulfone gave another sulfone-containing allylsilane **9** (48%) along with the bisallylsilane **10** (10%). Presumably, the bisallylsilane **10** arises from the reaction of the anion derived from the initially formed



9 with the iodide **1c**. By slow addition of the anion **8** to **1c** in THF, the formation ratio of **9** over **10** was improved, however, the formation of **10** could not be completely suppressed.

In summary, an inexpensive and facile synthesis of the chloride **1b** provides direct access to several allylsilane based bifunctional reagents. Synthetic applications of the reagents are currently being explored in our laboratory.

Experimental

¹H NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer using chloroform as an internal standard. ¹³C NMR spectra were obtained on a Varian Gemini-200 spectrometer with CDCl_3 as solvent and internal reference. Low resolution mass spectra were recorded on a JEOL JMS-AX 505 WA mass spectrometer with a 70 eV ionization potential. Melting and boiling points are uncorrected.

Chlorination of methallyl chloride. Methallyl chloride (214 g, 2.54 mol) was placed in a 500 mL, 3-neck flask fitted with a gas inlet tube, an outlet tube, and a thermometer reaching below the level of the liquid. Chlorine was passed into the stirred chloride at a rate to maintain the

temperature at 15–20 °C, the flask being surrounded by an ice-water bath. The chlorination was continued until methallyl chloride was consumed completely as indicated by ¹H NMR spectra of the reaction mixture; this required about 4 hours. After chlorination was complete, the reaction mixture was poured into cold water. The organic phase was washed with water and dried over Na_2SO_4 . The crude products were distilled using a column of 30 cm length and 2.5 cm diameter filled with glass beads. Distillation (52–55 °C/30 mmHg) provided a mixture of **3** and **4** (210 g, 65%). The intensities of the peaks in the ¹H NMR spectrum show a ratio of isomers of 42 : 58. **3**: ¹H NMR (CDCl_3 , 200 MHz) δ 4.21 (4H, s), 5.34 (2H, s). **4** (a mixture of E and Z isomers): ¹H NMR δ 1.87 (CH_3), 4.22 (CH_2), 5.97, 6.23 (CH).

Preparation of 2-(chloromethyl)-3-(trichlorosilyl)propene (5) from the mixture of dichlorides 3 and 4. A solution of freshly distilled trichlorosilane (27 mL, 36.2 g, 0.27 mol) and a mixture of **3** and **4** [83 g, it contained 34 g (0.27 mol) of **3**] in anhydrous ether (70 mL) was added to a solution of triethylamine (38 mL, 27.6 g, 0.27 mol) in anhydrous ether (200 mL) containing cuprous chloride (0.2 g, 2 mmol) over a period of 2 h. The reaction mixture was stirred at room temperature for 16 h and then filtered under nitrogen. Ether was removed, the residue was distilled at reduced pressure (29 mmHg) to afford 42 g of the unreacted **4** (53–55 °C) and 43 g (71%) of **5** (99–102 °C). The boiling point of **4** (E and Z) is 128–130 °C at atmospheric pressure (cf. the boiling point of **3** is 138 °C). **5**: ¹H NMR δ 2.55 (2H, s), 4.13 (2H, s), 5.15 (1H, s), 5.35 (1H, s).

2-(Chloromethyl)-3-(trimethylsilyl)propene (1b). To a solution of **5** (34 g, 0.15 mol) in ether (150 mL) was added a solution of methylmagnesium bromide in ether (175 mL of a 3 M solution, 0.52 mol). The mixture was stirred at –78 °C for 1 h and then at room temperature for 12 h. The reaction mixture was poured into an ice-cooled solution of sat. aq. NH_4Cl (400 mL), the ether layer was separated, and the aqueous layer was extracted with ether (100 mL \times 2). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. Distillation of the residue afforded 21.6 g (90%) of **1b**: bp 75 °C/31 mmHg (lit.^{2d} bp 158 °C/760 mmHg); ¹H NMR δ 0.05 (9H, s), 1.69 (2H, s), 3.97 (2H, s), 4.76 (1H, s), 5.01 (1H, s).

3-(Tributylstannyl)-2-(trimethylsilylmethyl)propene (6). To a solution of lithium diisopropylamide prepared from diisopropylamine (0.8 mL, 5.7 mmol) in THF (5 mL) and butyllithium (3.2 mL of 1.6 M hexane solution) at 0 °C, tributyltin hydride (1.3 mL, 4.8 mmol) was added. After 30 min stirring, the resulting (tributylstannyl)lithium was cooled to –23 °C, treated with **1b** (0.81 g, 4.9 mmol), and then kept at 25 °C for 10 h. The reaction mixture was poured into ice water and extracted with ether (20 mL \times 3). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. Purification by Kugelrohr distillation under reduced pressure gave 1.61 g (79%) of **6** as a colorless oil: bp 132–135 °C/0.4 mmHg; ¹H NMR δ 0.05 (9H, s), 0.8–1.6 (27H, m), 1.43 (2H, s), 1.73 (2H, s), 4.20 (1H, s), 4.37 (1H, s); ¹³C NMR δ –0.80, 9.95, 14.2, 18.0, 22.2, 27.9, 29.6, 103.3, 148.0.

2-(Iodomethyl)-3-(trimethylsilyl)propene (1c). To an acetone (105 mL) solution of NaI (18 g, 0.12 mol) was added 14.7 g (0.09 mol) of **1b**. The mixture was heated to

boil for 3 h. The mixture was cooled to room temperature, treated with sat. aq $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL), and washed with brine (100 mL \times 2). Purification by distillation in the dark (25 °C, 0.2 mmHg, trapped at -78 °C) afforded 20.0 g (87%) of **1c**: ^1H NMR δ 0.05 (9H, s), 1.73 (2H, s), 3.88 (2H, s), 4.70 (1H, s), 5.12 (1H, s).

2-(Phenylsulfonylmethyl)-3-(trimethylsilyl)propene (7). Sodium benzenesulfinate (2.03 g, 14.0 mmol) was added to a DMF (15 mL) solution of **1c** (3.01 g, 11.7 mmol) at room temperature. The mixture was heated at 100 °C for 4 h, and then allowed to cool to room temperature. To the mixture, brine (50 mL) was added, and extracted with ether (50 mL \times 3). The combined ether extracts were washed with water, dried over Na_2SO_4 , filtered, and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2) to give 2.98 g (95%) of **7**: mp 55-57 °C; ^1H NMR δ 0.01 (9H, s), 1.72 (2H, s), 3.71 (2H, s), 4.55 (1H, br), 4.78 (1H, br), 7.50-7.69 (3H, m), 7.85-7.90 (2H, m); ^{13}C NMR δ -1.38, 26.33, 64.70, 117.47, 128.52, 128.82, 133.54, 135.11, 138.19.

4-Phenylsulfonyl-2-(trimethylsilylmethyl)-1-butene (9). To a solution of methyl phenyl sulfone (5.8 g, 41 mmol) in THF (100 mL) was added a solution of *n*-butyllithium in hexane (1.6 M, 26 mL, 42 mmol) at 0 °C. After 1 h stirring, **1c** (9.5 g, 37 mmol) in THF (10 mL) was added. The solution was stirred at room temperature for 3 h. Saturated ammonium chloride (150 mL) was added and extracted with ether (50 mL \times 4). The combined extracts were washed with water, dried (Na_2SO_4), evaporated, and chromatographed on silica gel (hexane : ether = 5 : 1) to afford 5.55 g (48%) of **9** and 1.51 g (10%) of **10**.

9: ^1H NMR δ -0.04 (9H, s), 1.46 (2H, s), 2.29-2.37 (2H, m), 3.18-3.26 (2H, m), 4.54-4.56 (2H, m), 7.58-7.68 (3H, m), 7.91-7.95 (2H, m); ^{13}C NMR δ -1.63, 26.67, 30.58, 54.69, 108.43, 127.88, 129.13, 133.56, 138.79, 143.22; MS *m/e* 282 (M^+ , 1), 267 (3), 141 (44), 73 (100%). **10:** ^1H NMR δ -0.05 (18H, s), 1.33 (2H, d, $J=13.4$ Hz), 1.44 (2H, d, $J=13.4$ Hz), 2.18 (2H, dd, $J=7.6, 15.0$ Hz), 2.57 (2H, dd, $J=5.0, 15.0$ Hz), 3.28-3.42 (1H, m), 4.56 (2H, s), 4.61 (2H, s), 7.50-7.68 (3H,

m), 7.85-7.90 (2H, m); ^{13}C NMR δ -1.63, 25.93, 37.07, 60.97, 110.86, 128.63, 128.90, 133.43, 138.22, 142.54; MS *m/e* 408 (M^+ , 7), 393 (11), 321 (8), 267 (55), 73 (100%).

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