Short Communications

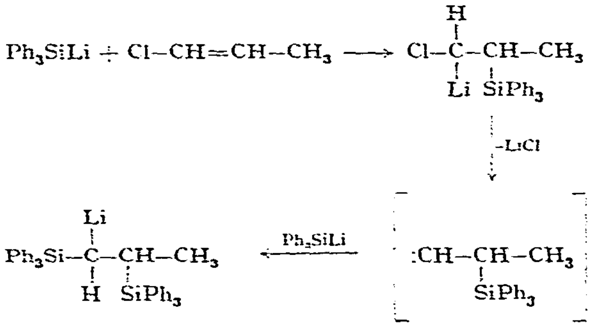
Reactions of triphenylsilyllithium with 1-chloropropene and 1-chloro-1-butene

The investigation of the reactions of triphenylsilyllithium with various organic halides[1,2] has now been extended to alkenyl chlorides. In the previous investigations it was found that primary chlorides, such as *n*-butyl chloride, reacted with triphenylsilyllithium yielding exclusively the coupling product, *n*-butyltriphenylsilane[1]. However, with polychloromethanes halogen-metal interconversion reactions occurred as evidenced by the formation of hexaphenyldisilane[2].

The reaction of 1-chloropropene with triphenylsilyllithium produced hexaphenyldisilane in yields of 13–15 %, but the 1-chloro-1-butene reaction did not give any hexaphenyldisilane. The major products from these reactions were 1,2-bis(triphenylsilyl)propane (45.5 %) and 1,2-bis(triphenylsilyl)butane (29.6 %), respectively.

1-Chloropropene reacted slowly with triphenylsilyllithium at a temperature below 0°, although at room temperature the reaction proceeded smoothly. 1-Chloro-1-butene was less reactive than 1-chloropropene and Color Test[3] I remained positive when an equimolar mixture was stirred at room temperature for 24 h.

From these reactions neither 1-(triphenylsilyl)propene nor 1-(triphenylsilyl)-1-butene were isolated. The absence of these compounds casts doubt on the possibility that 1-(triphenylsilyl)propene or 1-(triphenylsilyl)-1-butene might have been intermediates in the formation of 1,2-bis(triphenylsilyl)propane or 1,2-bis(triphenylsilyl)butane. 1,2-Bis(triphenylsilyl)propane was obtained in a 38.4 % yield from the reaction of 1-(triphenylsilyl)propene and triphenylsilyllithium after stirring for 22 h at room temperature and for 2 h at reflux.

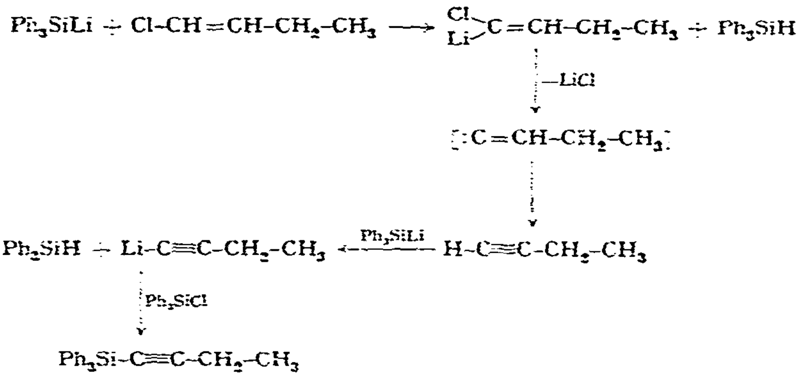


$$\mathrm{Ph_3SiLi + Cl{-}CH{=}CH{-}CH_3 \longrightarrow Cl{-}\underset{Li}{\overset{H}{C}}{-}\underset{SiPh_3}{CH}{-}CH_3 \xrightarrow{-LiCl} \left[:CH{-}\underset{SiPh_3}{CH}{-}CH_3\right] \xrightarrow{Ph_3SiLi} Ph_3Si{-}\underset{H}{\overset{Li}{C}}{-}\underset{SiPh_3}{CH}{-}CH_3}$$

The reaction might have proceeded by addition–elimination[4], followed by the coupling of triphenylsilyllithium and the resulting carbene intermediate[2,5].

When a mixture of 1-chloro-1-butene and triphenylsilyllithium was treated with chlorotriphenylsilane after 16 h of stirring, hexaphenyldisilane (15.1 %), triphenylsilane (13.0 %), 1-(triphenylsilyl)-1-butyne (7.4 %), and 1,2-bis(triphenylsilyl)butane (29.6 %) were isolated.

A mode of reaction which would lead to the formation of triphenylsilane and 1-(triphenylsilyl)-1-butyne might be as follows:



EXPERIMENTAL

Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. All melting points are uncorrected.

Reaction of triphenylsilyllithium with 1-chloropropene

(a) 1:1 Ratio. A solution of triphenylsilyllithium[6] (0.08 mole) was added dropwise to 6.1 g (0.08 mole) of 1-chloropropene at —60°. The reaction appeared to be slow at this temperature; therefore, the reaction mixture was allowed to warm to room temperature after 0.05 mole of triphenylsilyllithium had been added. The mixture was cooled again and the rest of the silyllithium compound was added. When the reaction mixture reached room temperature for the second time, Color Test I was positive. The reaction mixture was stirred for 1 h, at which time Color Test I was only faintly positive. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 2.80 g (13.5 %), was separated by filtration. The organic layer was dried with sodium sulfate and the solvent was removed. The residue was then chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 10.20 g (45.5 %) of 1,2-bis(triphenylsilyl)propane, m.p. 147.5–148.5°, after recrystallization from a benzene–petroleum ether (b.p. 60–70°) mixture. A mixed melting point with a sample obtained from the reaction of triphenylsilyllithium with 1-(triphenylsilyl)propene was not depressed and the infrared spectra were superimposable. (Found: C, 83.89; H, 6.31; Si, 10.03, 9.97. $C_{39}H_{36}Si_2$ calcd.: C, 83.51; H, 6.47; Si, 10.02 %.)

(b) 2:1 Ratio, followed by addition of chlorotriphenylsilane. A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 3.1 g (0.04 mole) of 1-chloropropene. The reaction mixture was cooled in an ice-salt bath during the addition and for an hour thereafter. Then it was allowed to come to room temperature. After a total of 2.5 h of reaction time, there was added 12 g (0.04 mole) of chlorotriphenylsilane in

50 ml of THF. The reaction mixture was worked up by the same procedure as in (*a*) after one h of stirring. The following compounds were obtained: hexaphenyldisilane, 7.10 g, and 1,2-bis(triphenylsilyl)propane, m.p. 148–148.5° (mixed m.p.), 10.55 g (47 %).

Preparation of 1-(triphenylsilyl)propene

(*a*) *From propenyllithium*[7] *and triphenylsilane.* A solution of propenyllithium (0.035 mole) was added to 9.10 g (0.035 mole) of triphenylsilane. Color Test I was positive at the end of the addition. It became negative after 4.5 h of stirring at room temperature. The reaction mixture was worked up to give a solid, which was then treated with methanol. Some insoluble material was separated by filtration. The mother liquor was cooled with ice to yield 9.60 g (91.5 %) of 1-(triphenylsilyl)propene, m.p. 55–60°. Several recrystallizations from methanol raised the melting point to 90.5–92°. The infrared spectra of the crude and pure products were identical, both showing characteristic double bond absorption bands at 6.20 (in chloroform) and 10.19 μ (in carbon disulfide).

(*b*) *From propenyllithium and chlorotriphenylsilane.* A solution of propenyllithium (0.035 mole) was added to 12 g (0.04 mole) of chlorotriphenylsilane in 50 ml of ether. The reaction was exothermic, but Color Test I was positive at the end of the addition. Color Test I became negative after 40 min of stirring. The reaction mixture was worked up to give 6.15 g (58.5 %) of crude 1-(triphenylsilyl)propene, m.p. 60–70°. Several recrystallizations from methanol gave a sample with a melting point of 87–90°. A mixed melting point with a sample obtained in (*a*) above was not depressed and the infrared spectra were superimposable. In addition, a small amount of 1-(triphenylsilyl)propyne, m.p. 115–116°, was isolated.

Reaction of triphenylsilyllithium with 1-(triphenylsilyl)propene

A solution of triphenylsilyllithium (0.008 mole) was added to 1.90 g (0.007 mole) of 1-(triphenylsilyl)propene. Color Test I was positive when the addition was completed. The reaction mixture was stirred for 22 h at room temperature and then for 2 h at reflux. It was worked up in the usual manner to give 1.50 g (38.4 %) of 1,2-bis(triphenylsilyl)propane, m.p. 148–148.5°, after recrystallization from a benzene–petroleum ether (b.p. 60–70°) mixture.

Reaction of triphenylsilyllithium with 1-chloro-1-butene

(*a*) *1:1 Ratio at room temperature.* A solution of triphenylsilyllithium (0.04 mole) was added over a period of 30 min to 2.23 g (0.04 mole) of 1-chloro-1-butene at room temperature. Color Test I was positive when the addition was completed. It remained positive at the end of 28 h of stirring at room temperature. The reaction mixture was worked up in the usual manner and the oily residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave an oil which solidified after two weeks of standing. The solid was recrystallized from petroleum ether (b.p. 60–70°) to give 2.55 g (22.2 %) of a product, possibly 1,2-bis(triphenylsilyl)butane, m.p. 137–139°. (Found: C, 83.69, 83.50; H, 6.44, 6.29; Si, 9.75, 9.64. $C_{40}H_{38}Si_2$ calcd.: C, 83.56; H, 6.67; Si, 9.77 %.)

Elution with carbon tetrachloride gave 1.55 g of a glassy polymeric material which failed to crystallize.

(*b*) *1:1 Ratio at reflux.* A solution of triphenylsilyllithium (0.04 mole) was added over a period of 30 min to 2.23 g (0.04 mole) of 1-chloro-1-butene. The color of the reaction mixture was a dark reddish-brown. The reaction mixture was refluxed for 1.5 h. A work-up by the same procedure as in (*a*) above gave 1,2-bis(triphenylsilyl) butane, 3.0 g (26.0 %), m.p. 136–137° (mixed m.p.). In addition, 1.70 g of a glassy polymeric material was isolated.

(*c*) *1:1 Ratio at room temperature, followed by addition of chlorotriphenylsilane.* A solution of triphenylsilyllithium (0.037 mole) was added to 2.23 g (0.04 mole) of 1-chloro-1-butene in 100 ml of THF. The reaction mixture was stirred for 16 h at room temperature before 6.5 g (0.022 mole) of chlorotriphenylsilane in 60 ml of THF was added. The reaction mixture changed from a deep reddish-brown to colorless within 1 h after the addition of chlorotriphenylsilane. Subsequent to hydrolysis, hexaphenyldisilane, 3.0 g (15.6 %), was separated by filtration. The organic layer was worked up in the usual manner and subsequently chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction a mixture of triphenylsilane and 1-(triphenylsilyl)-1-butyne. The mixture was treated with ethanol to give 0.85 g (7.4 %) of 1-(triphenylsilyl)-1-butyne, m.p. 86–88°. A mixed melting point with an authentic sample prepared from butynyllithium and chlorotriphenylsilane was not depressed. From the mother liquor there was obtained 1.25 g (13.0 %) of triphenylsilane which was identified by its infrared spectrum. Further elution with the same solvent gave an oil, which was treated with petroleum ether (b.p. 60–70°) to yield 2.55 g of 1,2-bis(triphenylsilyl)butane, m.p. 138–140° (mixed m.p.). Elution with carbon tetrachloride gave 1.55 g of an oil from which 0.60 g more of the same compound was obtained. The total yield of 1,2-bis(triphenylsilyl)butane was 3.15 g (29.6 %).

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