

REACTIONS OF TRIPHENYLSILYLLITHIUM WITH SOME DICHLOROPROPENES

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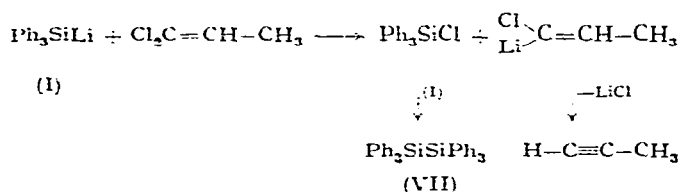
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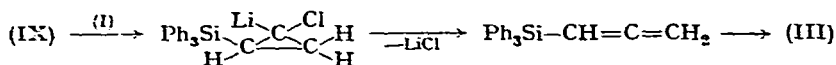
Recently, it has been reported from this laboratory that the reactions of triphenylsilyllithium (I) with 1-chloropropene and 1-bromopropene revealed not only a significant difference in the mode of the reactions of (I) toward these two compounds but also the possibility of formation of carbene intermediates^{1,2}. Thus, in the case of 1-bromopropene, vinylcarbene has been suggested as a probable intermediate which would lead to the formation of 1,3-bis(triphenylsilyl)propene (II), 1-(triphenylsilyl)propyne (III), 1,3-bis(triphenylsilyl)propyne (IV), and tris(triphenylsilyl)propadiene (V). The first step was visualized as an abstraction of a γ -hydrogen by propenyl-lithium or by (I), followed by γ -elimination of lithium bromide.

The reaction of 1,1-dichloropropene with (I) was found to resemble quite closely the 1-bromopropene reaction. When a large excess of (I) was added to 1,1-dichloropropene and the mixture subsequently treated with chlorotriphenylsilane, (IV) and (V) were obtained in addition to (III), triphenylsilane (VI), and hexaphenyldisilane (VII). When chlorotriphenylsilane was not added, the major products were (III) (26.2%), (VI) (16.4%), and (VII) (52.5%).

It has been demonstrated that (III) reacts with (I) to give (IV), (V), and 1,2-bis(triphenylsilyl)propene². Hexaphenyldisilane (VII) was formed as a result of the halogen-metal interconversion reaction²:



A possibility that (III) and (VI) might have resulted from propyne through metalation and coupling between propynyllithium and (VI) was ruled out, since the reaction of the latter two compounds yielded (III) to the extent of only 2-3%. The competition of propynyllithium with triphenylsilyllithium in the reaction toward chlorotriphenylsilane is unfavorable, in view of the fact that the reaction of 1-chloropropyne, which was formed indirectly by the action of phenyllithium upon 1,2-dichloropropene⁴, with (I) gave (III) (11.7%) and (VII) (73.9%)⁵. Moreover, in this reaction there exists a possibility that (III) could be formed by an addition-elimination mechanism⁵. The formation of 1-chloropropyne might reasonably be expected from the reaction of 1,1-dichloropropene with (I) through the abstraction of an olefinic hydrogen and the subsequent elimination of lithium chloride.



Since an olefinic hydrogen of the cyclopropene system is fairly acidic⁸, (IX) would be expected to undergo a metalation reaction with (I). Proton shift may occur within the 1-chlorocyclopropenyl anion⁹ and the negative charge would distribute itself over the ring. Elimination of lithium chloride would be difficult because of high strain involved on the part of the ring. Addition of triphenylsilane to the anion followed by ring opening and elimination of lithium chloride or abstraction of a proton from the solvent, would give (III) or (VIII).

The reaction of (I) with 1,3-dichloropropene in a 1:1 ratio gave a 9.7% yield of (VII) and a 75% yield of a mixture of 1-(triphenylsilyl)-3-chloropropene (X), m.p. 105–107.5°, and 1-chloro-3-(triphenylsilyl)propene (XI), m.p. 112.5–115.5°. The ratio of (X) to (XI) was approximately 5 to 4 judging from the NMR spectrum of a typical mixture. The separation of these two compounds was difficult and only small amounts of each were obtained in pure form after working up the mixture by a combination of chromatography and fractional recrystallizations from *n*-propanol.

Compounds (X) and (XI) were identified by NMR (Table 1) and infrared (Table 2) spectra. The NMR spectra are quite similar to each other: (X), multiplets centered at 4.15 and 7.48; (XI), multiplet centered at 4.22 and doublet at 7.70 τ . The structure

TABLE I
NUCLEAR MAGNETIC RESONANCE DATA
(τ -Values)^a

Compounds	Olefinic Hydrogens			-CH ₂ -	-CH ₃
Ph ₃ Si-CH=CH-CH ₂ -Cl	4.15 (m) ^b			7.48 (m)	
Ph ₃ Si-CH ₂ -CH=CH-Cl	4.22 (m)			7.70 (d)	
Ph ₃ Si-CH ₂ -CCl=CH ₂		5.04 (d)	5.16 (q)	7.23 (d)	
Ph ₃ Si-CH ₂ -CH=CH ₂	4.16 (m)	5.00 (m)	5.25 (d)	7.64 (d) ^c	
Ph ₃ Si-CH ₂ -CH=CH-SiPh ₃	3.84 (m)			7.33 (d)	
(Ph ₃ Si) ₂ CH-CH=CH-SiPh ₃	4.00 (m)			6.50 (q)	
Ph ₃ Si-CH=C(CH ₃)-SiPh ₃	2.77 (q)				8.17 (d)
Ph ₃ Si-C(CH ₃)=CH ₂	4.06 (m)	4.56 (m)			8.05 (t)
Ph ₃ Si-C(=CH ₂)-CH ₂ -CH ₃	4.03 (m)	4.49 (m)		7.76 (q) ^c	9.01 (t)
(Ph ₃ Si) ₂ C=C=CH-SiPh ₃			5.75 (s)		

^a Run at 60 Mc in CDCl₃ using tetramethylsilane as the internal standard.

^b s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

^c Each peak is further divided into triplets.

inferred from these data, and from comparison with the spectra of compounds such as allyltriphenylsilane, 1,3-bis(triphenylsilyl)propene (II), and 1,3,3-tris(triphenylsilyl)propene (XII), is a 1,3-disubstituted propene. The infrared spectrum of (X) is very similar to those of (1-triphenylsilyl)propene and 1-(triphenylsilyl)-1-butene, suggesting (X) to be 1-(triphenylsilyl)-3-chloropropene. The infrared spectrum of (XI), however, is shown to be similar to that of (VIII). A reasonable conclusion would be that (XI) is 1-chloro-3-(triphenylsilyl)propene.

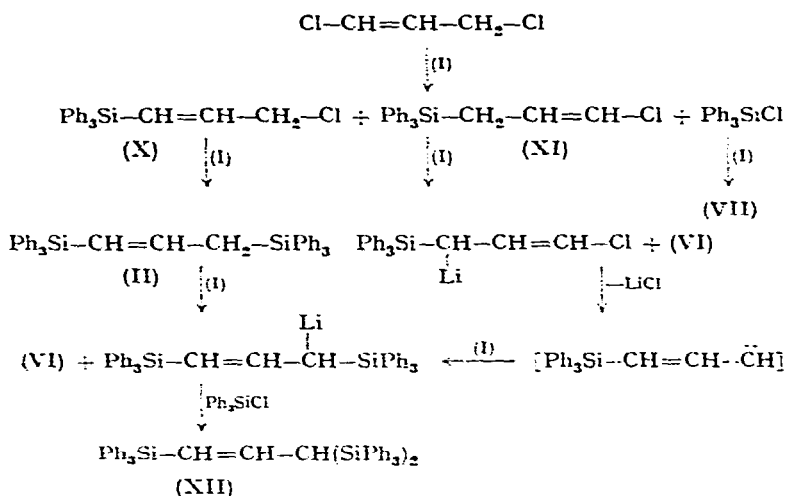
TABLE 2
INFRARED ABSORPTION SPECTRA OF TRIPHENYLSILYL-SUBSTITUTED PROPENES AND BUTENES

Compounds	Characteristic absorption bands									
$\text{Ph}_3\text{Si}-\text{CH}=\text{CH}-\text{CH}_2-\text{Cl}$	6.17 (m) ^a	7.56 (s)	8.87 (m)	10.05 (s)	...	12.51 (m)	13.41 (m)
$\text{Ph}_3\text{Si}-\text{CH}_2-\text{CH}=\text{CH}-\text{Cl}$	6.19 (w)	...	8.62 (m)	...	10.70 (m)	12.00 (s)	12.70 (m)
$\text{Ph}_3\text{Si}-\text{CH}_2-\text{C}(\text{Cl})=\text{CH}_2$	6.18 (s)	...	8.35 (m)	...	10.72 (m)	11.64 (s)	12.95 (s)
$\text{Ph}_3\text{Si}-\text{CH}=\text{CH}-\text{CH}_3$	6.20 (s)	...	8.11 (w)	10.19 (s)	13.10 (s)
$\text{Ph}_3\text{Si}-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$	6.45 (s)	10.15 (m)	...	11.31 (w)	12.75 (w)
$\text{Ph}_3\text{Si}-\text{C}(\text{CH}_3)=\text{CH}_2$	10.75 (s)
$\text{Ph}_3\text{Si}-\text{C}(=\text{CH}_2)-\text{CH}_2-\text{CH}_3$	6.22 (vw)	10.75 (s)	11.53 (w)

^a Letters in parentheses indicate the relative intensities of absorption bands: s = strong; m = medium; w = weak; vw = very weak

The addition of 2 equivalents of (I) to 1,3-dichloropropene gave a 31.0% yield of (II) in addition to a 12.5% yield of (VII). The yield of (II) increased to 50.5% when 3 equivalents of (I) were used. Treatment of a mixture of (X) and (XI) with 2 equivalents of (I) yielded (II) (57.7%) and (VI) (96.2% based on the mixture). When an equimolar mixture of (I) and (II) was stirred for 24 hours and chlorotriphenylsilane subsequently added, (XII) was isolated in a 34.6% yield.

These results suggest the following reaction paths:



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 1,1-dichloropropene

(a). *At -60°. (1). 2:1 Ratio.* A solution of triphenylsilyllithium¹⁰ (0.08 mole) was added over a period of 1 h to 4.45 g (0.04 mole) of 1,1-dichloropropene in 50 ml of ether at -60°. The reaction mixture was allowed to warm to room temperature, whereupon Color Test I¹¹ was negative. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 14.5 g (70%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave a trace amount of triphenylsilane and 1-(triphenylsilyl)propene, both of which were identified by comparison of their infrared spectra with those of authentic samples. Elution with carbon tetrachloride gave also a trace of 2-chloro-3-(triphenylsilyl)propene and tris(triphenylsilyl)propadiene. These two compounds were also identified by their infrared spectra.

In a second experiment reverse addition was employed. The work-up gave hexaphenyldisilane (77.6%), triphenylsilane (4.8%), 1-(triphenylsilyl)propene (0.5%), and 2-chloro-3-(triphenylsilyl)propene (0.7%).

(2). *3:1 Ratio.* A solution of triphenylsilyllithium was added dropwise over a period of 1.25 h to 2.78 g (0.025 mole) of 1,1-dichloropropene in 50 ml of ether at

-60°. When 0.06 mole of triphenylsilyllithium had been added, Color Test I became positive. The reaction mixture was allowed to warm to room temperature and an additional 0.02 mole of triphenylsilyllithium was added. Color Test I remained positive after 3 h of stirring. Chlorotriphenylsilane in ether was added dropwise. When 0.01 mole had been added, Color Test I became negative. The reaction mixture was worked up by the same procedure as in (1). The following compounds were isolated: hexaphenyldisilane, 13.5 g; triphenylsilane, 1.50 g (23.1% based on 1,1-dichloropropene); and 1-(triphenylsilyl)propyne, 0.30 g (4.0%). The last compound was identified by a mixed melting point determination with an authentic sample.

(b). *At room temperature. (1). 1:2 Ratio.* A solution of triphenylsilyllithium (0.05 mole) was added dropwise over a period of 1 h to 11.1 g (0.10 mole) of 1,1-dichloropropene in 150 ml of ether at room temperature. After being stirred for 30 min, the reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 8.90 g (68.7%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) gave in the first fraction 0.45 g (3.5%) of triphenylsilane. Further elution with the same solvent gave in the second fraction 0.70 g (4.2%) of 2-chloro-3-(triphenylsilyl)propene, m.p. 97-99°, after recrystallization from methanol. A mixed melting point with a sample obtained from the reaction of triphenylsilyllithium with 2,3-dichloropropene was not depressed. The infrared and NMR spectra were identical. Elution was continued with petroleum ether (b.p. 60-70°), whereupon 1-(triphenylsilyl)propyne, 0.85 g (5.7%), m.p. 115.5-116.5° (mixed m.p.), was isolated as the last product.

(2). *2:1 Ratio.* A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 2 h 20 min to 5.34 g (0.048 mole) of 1,1-dichloropropene in 125 ml of ether. Color Test I was negative when the addition was complete. The reaction mixture was worked up by the same procedure as in (1) to give hexaphenyldisilane, 11.80 g (57.0%); triphenylsilane, 2.10 g (16.9% based on 1,1-dichloropropene); and 1-(triphenylsilyl)propyne, 2.85 g (20.0% based on 1,1-dichloropropene).

In a second experiment the addition of chlorotriphenylsilane, 9.4 g (0.032 mole), followed after the reaction mixture had been stirred for 4 h. Hexaphenyldisilane was obtained in a yield of 14.5 g (70%), but the yield of the other two products remained essentially the same: triphenylsilane, 2.20 g (18.8%); and 1-(triphenylsilyl)propyne, 2.35 g (18.5%). Chlorotriphenylsilane was recovered as triphenylsilanol in an 81.5% yield.

(3). *2.5:1 Ratio.* A solution of triphenylsilyllithium was added dropwise to 3.34 g (0.03 mole) of 1,1-dichloropropene in 100 ml of ether. When 0.07 mole of triphenylsilyllithium had been added, Color Test I was negative, but it became positive when 0.075 mole had been added. After being stirred for 30 min, the reaction mixture was worked up by the same procedure as in (1). The following compounds were isolated: hexaphenyldisilane, 10.2 g (52.5%); triphenylsilane, 3.20 g (16.4% based on 1,1-dichloropropene); 1-(triphenylsilyl)propyne, 2.35 g (26.2% based on 1,1-dichloropropene).

(4). *3:1 Ratio, followed by addition of chlorotriphenylsilane.* A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 3 h to 2.78 g (0.025 mole) of 1,1-dichloropropene in 100 ml of tetrahydrofuran (THF). The color of the reaction mixture changed from white to a reddish-brown during the last third of the addition.

After 3 h of stirring, chlorotriphenylsilane (10.0 g, 0.033 mole) in 30 ml of THF was added. The reaction mixture was stirred for 1.5 h before it was worked up by the same procedure as in (1). The following compounds were isolated: hexaphenyldisilane, 12.50 g (60.2%); triphenylsilane, 5.05 g (77.7% based on 1,1-dichloropropene, 24.3% based on triphenylsilyllithium); 1-(triphenylsilyl)propyne, 3.10 g (41.6% based on 1,1-dichloropropene); 1,2-bis(triphenylsilyl)propene, 0.75 g (5.4%); and tris(triphenylsilyl)propadiene, 1.20 g (5.9%). In addition, there was 1.05 g of a material with a melting range of 145–200° which was mainly a mixture of the last two compounds. 1,2-Bis(triphenylsilyl)propene and tris(triphenylsilyl)propadiene were identified by mixed melting points and a comparison of infrared spectra with those of the samples obtained from the reaction of triphenylsilyllithium with 1-(triphenylsilyl)propyne².

Reaction of triphenylsilyllithium with 1,3-dichloropropene

(a). 1:1 Ratio. A solution of triphenylsilyllithium (0.04 mole) was added dropwise over a period of 2.5 h to 4.45 g (0.04 mole) of 1,3-dichloropropene in 100 ml of THF. Color Test I was negative immediately after this addition. After 1 h of stirring the reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 1.00 g (9.7%), 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 10.05 g (75.0%) of a mixture of two isomers, possibly 1-(triphenylsilyl)-3-chloropropene (X) and 1-chloro-3-(triphenylsilyl)propene (XI). (Found: Si, 8.41, 8.33. C₂₁H₁₉ClSi calcd.: Si, 8.39%.)

Separation of the two isomers proved to be very difficult. Recrystallization of the mixture from ethanol afforded a sample with a melting point of 87–89°. When the mixture was chromatographed on alumina, the first fraction eluted with petroleum ether (b.p. 60–70°) gave a sample with a melting point of 87–96°. Repeated recrystallizations from *n*-propanol gave a small amount (less than 0.1 g) of (X) with a melting point of 105–107.5°.

The very last fractions eluted with petroleum ether (b.p. 60–70°), after 1000 ml of the eluant, gave a sample which was rich in the other component, m.p. 89–106°. Repeated recrystallizations from *n*-propanol gave (XI) (less than 0.1 g), m.p. 112.5–115.5°.

When the infrared spectra of (X) and (XI) (see Table 2) were combined, the resulting spectrum was superimposable with that of a typical mixture. Thus, the mixture consisted of these two isomers.

The NMR spectra of (X) and (XI) (see Table 1) were very similar, both indicating the presence of a methylene group and olefinic hydrogens.

The combined information of the infrared and NMR spectra suggested (X) to be 1-(triphenylsilyl)-3-chloropropene and (XI) to be 1-chloro-3-(triphenylsilyl)propene.

(b). 2:1 Ratio. A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 4.45 g (0.04 mole) of 1,3-dichloropropene in 100 ml of THF. The reaction mixture was cooled by an ice bath during the addition. Color Test I was slightly positive when the addition was completed. Subsequent to hydrolysis, hexaphenyldisilane, 2.60 g (12.5%), was separated by filtration. The residue obtained after the work-up of the organic layer was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 6.90 g (31.0%) of 1,3-bis(triphenylsilyl)propene, m.p. 157–158.5°, after recrystallization from an ethyl acetate–ethanol mixture. A mixed melting point with a dehydrated product of 1,3-bis(triphenylsilyl)-2-propanol was not depressed.

(c). *3:1 Ratio*. A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 2 h to 2.78 g (0.025 mole) of 1,3-dichloropropene in 100 ml of THF. The reaction mixture was a deep reddish-black. Color Test I was positive when the addition was complete. It became only weakly positive after 4 h of stirring. Subsequent to hydrolysis, hexaphenyldisilane, 0.87 g (6.7%), was separated by filtration. The residue obtained after a work-up of the organic layer was chromatographed on alumina. The early fractions eluted with petroleum ether (b.p. 60–70°) were rechromatographed to give 5.00 g (77.0% of theoretical) of triphenylsilane, 0.15 g (1.8%) of tetraphenylsilane, m.p. 228–234° (mixed m.p.), and 0.40 g of 1,3-bis(triphenylsilyl)propene, m.p. 156–158° (mixed m.p.).

The original chromatography was continued. Elution with petroleum ether (b.p. 60–70°) gave 3.25 g of 1,3-bis(triphenylsilyl)propene. Elution with carbon tetrachloride gave 3.40 g of the same compound and a fair amount of non-crystallizing polymeric oil. The combined yield of 1,3-bis(triphenylsilyl)propene was 7.05 g (50.5%).

Reaction of triphenylsilyllithium with a mixture of 1-(triphenylsilyl)-3-chloropropene (X) and 1-chloro-3-(triphenylsilyl)propene (XI)

A solution of triphenylsilyllithium (0.04 mole) was added dropwise over a period of 1 h to 6.70 g (0.02 mole) of the mixture obtained in (a) above in 70 ml of THF. The solution immediately turned a reddish-brown, indicating that metalation was taking place as soon as the coupling product was formed. The color became a deep reddish-black at the end of the addition. Color Test I was positive. After stirring for 1 h the reaction mixture was hydrolyzed with dilute acid. No hexaphenyldisilane was obtained. The organic layer was worked up in the usual manner. The compounds isolated were: triphenylsilane, 5.00 g (96.2% of theoretical); and 1,3-bis(triphenylsilyl)propene, 6.45 g (57.7%), m.p. 155.5–159.5° (mixed m.p.). In addition, there was some non-crystallizing, glassy, polymeric material.

Reaction of phenyllithium with a mixture of 1-(triphenylsilyl)-3-chloropropene (X) and 1-chloro-3-(triphenylsilyl)propene (XI)

An ethereal solution of phenyllithium was added to 6.70 g (0.02 mole) of a mixture of (X) and (XI) in 50 ml of THF. Immediately a purple color developed with evolution of some heat. Color Test I was negative after the addition was completed. The reaction mixture was worked up in the usual manner after 1 h of stirring, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60–70°) gave the following compounds: the starting material, 1.85 g (27.6% recovery); tetraphenylsilane, 0.15 g (2.2%); and 3-(triphenylsilyl)propyne, 0.64 g (10.7%), m.p. 89–91°, after recrystallization from *n*-propanol. The latter compound was identified by its infrared spectrum; 3.02 ($\text{—C}\equiv\text{C—H}$) and 4.75 μ ($\text{—C}\equiv\text{C—}$). Elution with carbon tetrachloride gave a fair amount of non-crystallizing polymeric oil.

Reaction of triphenylsilyllithium with 1,3-bis(triphenylsilyl)propene, followed by addition of chlorotriphenylsilane.

A solution of triphenylsilyllithium (0.02 mole) was added over a period of 15 min to 5.35 g (0.0096 mole) of 1,3-bis(triphenylsilyl)propene in 50 ml of THF. A deep reddish color developed. After stirring for 24 h, there was added 7.20 g (0.024 mole) of chlorotriphenylsilane in 50 ml of ether. The color of the reaction mixture faded gradually

and completely over a period of 11 h. The mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 3.45 g (33.3%), was separated by filtration. The residue obtained after a work-up of the organic layer was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 1.80 g (34.6%) of triphenylsilane. Further elution with carbon tetrachloride gave an oil, which was treated with a mixture of petroleum ether (b.p. 60–70°) and methanol to give 5.65 g (34.6%) of 1,3,3-tris(triphenylsilyl)propene, m.p. 165–166.5°, after two recrystallizations from an ethyl acetate–methanol mixture. (Found: C, 83.91, 83.81; H, 5.80, 5.74; Si, 10.29, 10.27. $C_{57}H_{48}Si_3$ calcd.: C, 83.78; H, 5.92; Si, 10.31%.)

The NMR spectrum supports the proposed structure (see Table 1).

Reaction of triphenylsilyllithium with 2,3-dichloropropene

(a). *1:1 Ratio*. A solution of triphenylsilyllithium (0.03 mole) was added dropwise over a period of 1 h 15 min to 3.30 g (0.03 mole) of 2,3-dichloropropene in 100 ml of THF. The reaction mixture was a light brown. It was stirred for 3 h. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 2.20 g (28.3%), 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 0.85 g (10.9%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave a partially solidified oil, which was treated with a petroleum ether (b.p. 60–70°)–methanol mixture. 2-Chloro-3-(triphenylsilyl)propene (VIII), m.p. 99–100°, crystallized out. The mother liquor was concentrated and more of (VIII) was isolated. The filtrate was again concentrated to give a material with a melting range of 78–95°. It was recrystallized twice from methanol to give pure (VIII). The total yield of (VIII) was 1.95 g (19.5%). From the third filtrate there was obtained 0.10 g of 1-(triphenylsilyl)propyne, m.p. 114–115° (mixed m.p.). Further elution with the same solvent gave 0.60 g of 1-(triphenylsilyl)propyne. The combined yield was 0.70 g (7.8%).

The melting point of (VIII) was raised to 101–102° after two recrystallizations from methanol. The infrared spectrum (see Table 2) showed the characteristic absorption bands for a double bond at 6.18 and 10.72 μ . Other characteristic bands for the compound were: 11.64 μ (a possible chlorine bond attached to an unsaturated carbon) and 12.95 μ (a possible methylene group).

The NMR spectrum indicated the presence of a methylene group and terminal vinyl hydrogens (see Table 1).

(b). *2:1 Ratio, followed by addition of chlorotriphenylsilane*. A solution of triphenylsilyllithium (0.05 mole) was added dropwise over a period of 30 min to 2.75 g (0.025 mole) of 2,3-dichloropropene in 100 ml of ether. Color Test I was slightly positive and the color of the reaction mixture was a reddish-brown. After 20 min of stirring, 7.5 g (0.025 mole) of chlorotriphenylsilane in ether was added. The reaction mixture was stirred for 1 h. It was worked up by the same procedure as in (a) above. The compounds isolated were: hexaphenyldisilane, 4.50 g (34.7%); triphenylsilane, 3.10 g (47.7%); 1-(triphenylsilyl)propyne, 1.55 g (20.8%); a mixture of 1-(triphenylsilyl)propyne and compound (VIII), 1.0 g; and tris(triphenylsilyl)propadiene, 0.55 g (2.7%). The last compound was identified by a mixed melting point determination with the compound obtained from the reaction of triphenylsilyllithium with 1-(triphenylsilyl)propyne followed by addition of chlorotriphenylsilane.

(c). *8:3 Ratio, followed by addition of chlorotriphenylsilane.* A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 3 h 15 min to 3.30 g (0.03 mole) of 2,3-dichloropropene in 100 ml of THF. Color Test I was weakly positive and the color of the reaction mixture was a dark reddish-brown. After 2 h 45 min of stirring, 10.4 g (0.035 mole) of chlorotriphenylsilane in 30 ml of THF was added. The stirring was continued for another hour before the reaction mixture was worked up by the same procedure as in (a). The compounds isolated were: hexaphenyldisilane, 0.25 g (3.3%); triphenylsilane, 9.65 g (46.4%); 1-(triphenylsilyl)propyne, 0.85 g (9.5%); 1,2-bis(triphenylsilyl)propene, 0.90 g (5.4%); 1,3-bis(triphenylsilyl)propyne, 0.75 g (4.5%); and tris(triphenylsilyl)propadiene, 4.40 g (18.0%). The last three compounds were identified by mixed melting points and a comparison of their infrared spectra with those of the respective compounds obtained from the reaction of triphenylsilyllithium with 1-(triphenylsilyl)propyne followed by the addition of chlorotriphenylsilane.

Reaction of triphenylsilyllithium with 2-chloro-3-(triphenylsilyl)propene (VIII)

A solution of triphenylsilyllithium (0.005 mole) was added dropwise over a period of 15 min to 1.60 g (0.0048 mole) of (VIII) in 50 ml of THF. A purple color developed immediately. During the first few h of stirring the purple color faded to light orange. After stirring for a total of 7.5 h the reaction mixture was worked up in the usual manner. The compounds isolated were: triphenylsilane, 0.80 g (64.1%), and 1-(triphenylsilyl)propyne, 0.90 g (62.9%).

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SUMMARY

Reactions of triphenylsilyllithium with 1,1-dichloropropene, 2,3-dichloropropene, and 1,3-dichloropropene were investigated. The reactions of the first two compounds gave identical products: hexaphenyldisilane, triphenylsilane, 2-chloro-3-(triphenylsilyl)propene, and 1-(triphenylsilyl)propyne. The reaction of 2-chloro-3-(triphenylsilyl)propene and triphenylsilyllithium resulted in the formation of equal amounts of triphenylsilane and 1-(triphenylsilyl)propyne. Triphenylsilyllithium reacted with 1,3-dichloropropene in a 1:1 ratio to give hexaphenyldisilane, 1-(triphenylsilyl)-3-chloropropene, and 1-chloro-3-(triphenylsilyl)propene. The latter two compounds reacted further with triphenylsilyllithium yielding 1,3-bis(triphenylsilyl)propene. Possible mechanisms of the reactions are discussed.

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