REACTIONS OF TRIPHENYLSILYLLITHIUM WITH 1-BROMOPROPENE AND 1-(TRIPHENYLSILYL)PROPYNE

HENRY GILMAN AND DAN AOKI
Chemical Laboratory of Iowa State University, Ames, Iowa (U.S.A.)

(Received December 16th, 1963)

A significant difference in the behavior of organic chlorides and bromides toward triphenylsilyllithium (I) has been noted[1,2]. Thus, primary chlorides such as *n*-butyl chloride reacted with (I) exclusively by a coupling reaction[2,*]. The bromides, on the other hand, reacted predominantly by halogen–metal interconversion which led to the formation of hexaphenyldisilane (II) as a result of the secondary coupling reaction of (I) and bromotriphenylsilane[1,2].

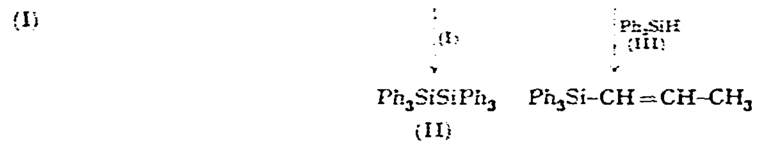
Although the initial attack of (I) on polychloromethanes and polybromomethanes was by halogen–metal interconversion, some of the secondary reactions involved appeared to be different[4]. Organolithium compounds show dissimilarities in their reactions toward methylene chloride and methylene bromide. *n*-Butyllithium reacted with methylene chloride by metalation[5], while with methylene bromide it underwent halogen–metal interconversion[6].

The reactions of 1-chloropropene and 1-chloro-1-butene with (I) gave 1,2-bis(triphenylsilyl)propane and 1,2-bis(triphenylsilyl)butane, respectively, as major products[7]. The reaction of 1-bromopropene and *n*-butyllithium yielded 1-phenyl-2-butyn-1-ol in a 75% yield upon the addition of benzaldehyde[8].

It is perhaps not surprising that a large yield (70%) of (II) was obtained from the reaction of 1-bromopropene and (I) in view of the fact that the bromides in general undergo halogen–metal interconversion reactions readily with (I). It is surprising, however, that seven other compounds were isolated from the same reaction. These compounds and their yields are listed in Table 1.

1,2-Bis(triphenylsilyl)propane was probably formed by the same mechanism as in its formation from the 1-chloropropene reaction[7]; that is, an addition–elimination reaction followed by a coupling between the resulting carbene and (I).

The formation of 1-(triphenylsilyl)propene was likely the result of the reaction of triphenylsilane (III) with propenyllithium[7], which would be formed from the halogen–metal interconversion reaction.



$$\begin{tikzcd}[column sep=small] \underset{\text{(I)}}{Ph_3SiLi} + Br\text{–}CH{=}CH\text{–}CH_3 \arrow[r] & Ph_3SiBr \arrow[d, dashed, "\text{(I)}"] + & Li\text{–}CH{=}CH\text{–}CH_3 \arrow[d, dashed, "Ph_3SiH \ \text{(III)}"] \\ & \underset{\text{(II)}}{Ph_3SiSiPh_3} & Ph_3Si\text{–}CH{=}CH\text{–}CH_3 \end{tikzcd}$$

---

[*] Some exceptions have been noted: isobutyl chloride gave a small amount of hexaphenyldisilane in addition to a 62% yield of the coupling product, whereas neopentyl chloride yielded hexaphenyldisilane in a 64% yield[3].

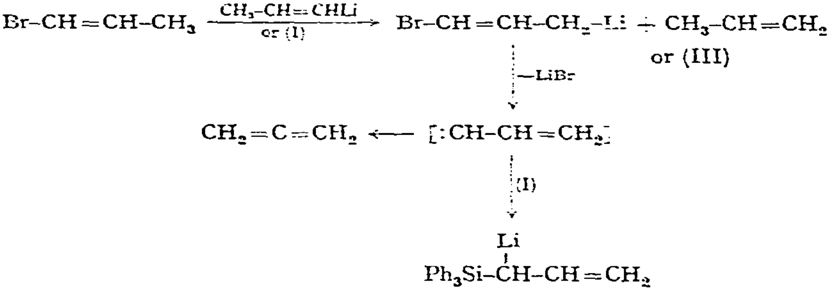
TABLE 1

PRODUCTS[a] FROM THE REACTION OF Ph_3SiLi (I) WITH 1-BROMOPROPENE OTHER THAN HEXAPHENYLDISILANE (II)

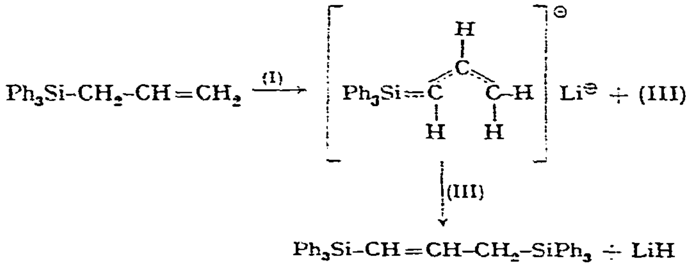
Compounds	*No Ph_3SiCl added,* %	*Ph_3SiCl added,* %
Triphenylsilane	?[b]	13.5
1,2-Bis(triphenylsilyl)propane	6.8[c]	7.7
1-(Triphenylsilyl)propene	11.0	6.7
1,3-Bis(triphenylsilyl)propene	—	2.2
1-(Triphenylsilyl)propyne	7.1	15.3
1,3-Bis(triphenylsilyl)propyne	7.2	4.3
Tris(triphenylsilyl)propadiene	0.2	6.4

[a] Not all the compounds were isolated from a single run.
[b] The presence of triphenylsilane was shown by the infrared spectrum, but the yield could not be calculated because the compound could not be obtained in a pure state.
[c] Values are the highest yields obtained.

Propenyllithium, however, seemed to be unstable under the reaction conditions, as evidenced by the fact that the yield of 1-(triphenylsilyl)propene did not increase by the addition of chlorotriphenylsilane (IV). Since all the other products seem to have a common intermediate, propenyllithium as well as (I) may have participated in the formation of this intermediate compound. The abstraction of a γ-hydrogen from 1-bromopropene by propenyllithium or by (I) and subsequent elimination of lithium bromide would give a vinylcarbene, which either rearranges to propadiene or reacts with (I) to form a metalated allyltriphenylsilane:



The anion of the metalated allyltriphenylsilane exists as a resonance hybrid of the structure as shown below[9,10]. When a mixture of (I) and allyltriphenylsilane was stirred at room temperature for 22 h, 1,3-bis(triphenylsilyl)propene was obtained in a 40% yield.

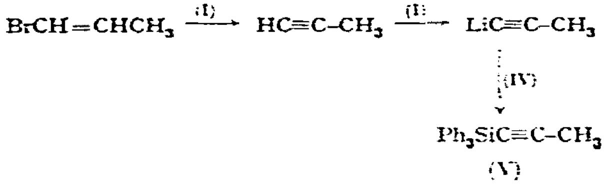


Probably, vinylcarbene rearranges to allene within a short period of time so that there may be little chance for (I) to react with it to form the metalated allyltriphenylsilane, hence a very low yield of 1,3-bis(triphenylsilyl)propene and no allyltriphenylsilane were obtained. Vinylcarbene may also form cyclopropene[11], although no derivative of cyclopropene was isolated.

The allene may then be metalated by (I):

$$CH_2{=}C{=}CH_2 \xrightarrow{(I)} Li\text{–}CH{=}C{=}CH_2 + (III)$$

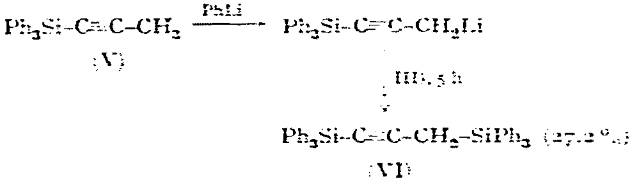
Since the resulting allenyllithium is a vinyllithium type compound, it would be expected to couple with (III) to give (triphenylsilyl)propadiene, which may rearrange to the more stable 1-(triphenylsilyl)propyne (V) prior to or after hydrolysis. The formation of (V) could also be accounted for by the following simple sequence:



$$\begin{tikzcd} BrCH{=}CHCH_3 \arrow[r, "(I)"] & HC{\equiv}C\text{–}CH_3 \arrow[r, "(I)"] & LiC{\equiv}C\text{–}CH_3 \arrow[d, dashed, "(IV)"] \\ & & \underset{(V)}{Ph_3SiC{\equiv}C\text{–}CH_3} \end{tikzcd}$$

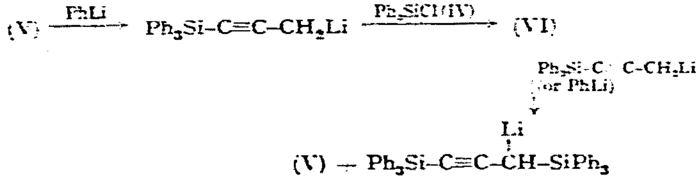
The addition of chlorotriphenylsilane (IV) would then lead to an increased yield of (V).

1-(Triphenylsilyl)propadiene and/or (V) can undergo further metalation–coupling reactions to give 1,3-bis(triphenylsilyl)propyne (VI) and tris(triphenylsilyl)propadiene (VII). To verify the last phase of the reactions, (V) was allowed to react with (I). When an equimolar mixture was stirred at room temperature for 5 h, there was obtained (III) (51.3 %), (V) (18.4 %), (VI) (29.9 %), and 1,2-bis(triphenylsilyl)propene (VIII) (18.5 %). When phenyllithium was used as a metalating agent and subsequently (III) was added, (VI) was isolated in a 27.2 % yield:



$$\begin{tikzcd} \underset{(V)}{Ph_3Si\text{–}C{\equiv}C\text{–}CH_3} \arrow[r, "PhLi"] & Ph_3Si\text{–}C{\equiv}C\text{–}CH_2Li \arrow[d, dashed, "(III)\text{, 5 h}"] \\ & \underset{(VI)}{Ph_3Si\text{–}C{\equiv}C\text{–}CH_2\text{–}SiPh_3} \ (27.2\ \%) \end{tikzcd}$$

When chlorotriphenylsilane (IV) was used as a derivatizing agent, (VII) (22.5 %) and (VI) (12.6 %) were isolated. The fact that the starting material, (V), was recovered in a larger yield from the reaction using chlorotriphenylsilane (IV) than in the case of triphenylsilane (III) addition, 32.5 % vs 17.2 %, suggests that the metalated (V) as well as unreacted phenyllithium metalated (VI) as soon as it was formed.



$$\begin{tikzcd} (V) \arrow[r, "PhLi"] & Ph_3Si\text{–}C{\equiv}C\text{–}CH_2Li \arrow[r, "Ph_3SiCl\,(IV)"] & (VI) \arrow[d, dashed, "Ph_3Si\text{–}C{\equiv}C\text{–}CH_2Li\ (or\ PhLi)"] \\ & & (V) + Ph_3Si\text{–}C{\equiv}C\text{–}\overset{Li}{CH}\text{–}SiPh_3 \end{tikzcd}$$

The 1,3-bis(triphenylsilyl)propyne anion undoubtedly exists as a resonance hybrid:

$$[\mathrm{Ph_3Si{-}C{\equiv}C{-}\overset{\ominus}{C}H{-}SiPh_3} \longleftrightarrow \mathrm{Ph_3Si{-}\overset{\ominus}{C}{=}C{=}CH{-}SiPh_3}]$$

Chlorotriphenylsilane (IV) couples with the allenic form, which provides better spatial arrangement for three bulky triphenylsilyl groups than the acetylenic form as seen from molecular models.

The metalation reaction of (VI) by (I) was virtually complete as evidenced by the isolation of a small amount (2.9%) of (II) when (IV) was added. In the case of (V), (II) was obtained in a 15.8% yield, which was a measure of unreacted (I).

$$\mathrm{(VI)} \xrightarrow[3.5\ h]{(I)} \xrightarrow[3.0\ h]{(IV)} \mathrm{(II)}\ (2.9\%) + \mathrm{(III)}\ (88.5\%)$$

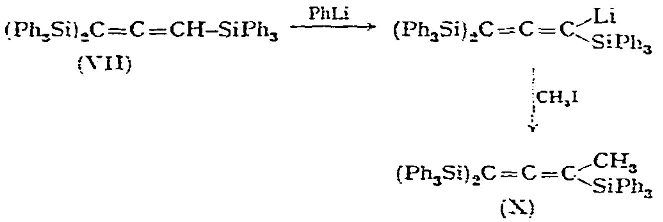
$$+ \underset{\mathrm{(VII)}}{\mathrm{(Ph_3Si)_2C{=}C{=}CH{-}SiPh_3}}\ (50.8\%)$$

$$+ \underset{\mathrm{(IX)}}{\mathrm{(Ph_3Si)_2C{=}C{=}C(SiPh_3)_2}}\ \text{(trace)}$$

Tris(triphenylsilyl)propadiene (VII) was identified by physical and chemical evidence. The elementary analysis and molecular weight determination were compatible with the formula. Its infrared spectrum showed a strong absorption band at 5.30 μ. The usual allenic absorption bands appear[12] at or near 5.0 μ. Synthesis of several triphenylsilyl-substituted allenes revealed that the position of bands shifted from 5.23 μ for 2,4-bis(triphenylsilyl)-2,3-pentadiene to 5.49 μ for tetrakis(triphenylsilyl)propadiene (IX). The reason for this shift might be the increased number of participating *d*-orbitals of the silicon atoms for partial bond formation; thereby reducing allenic bond character.

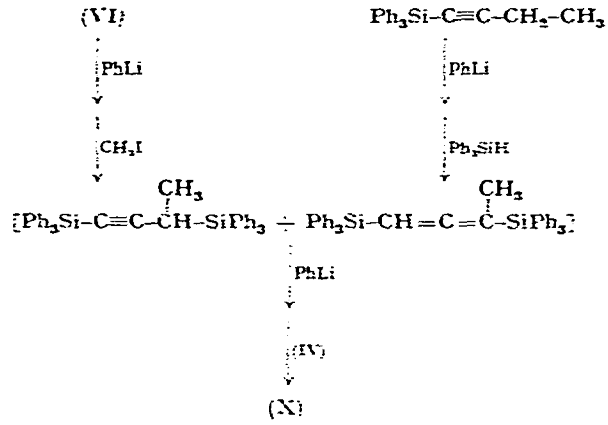
The NMR spectrum of (VII) showed a resonance peak at 5.75 τ, which is characteristic for an allenic hydrogen[13]. The replacement of the allenic proton by deuterium through metalation and hydrolysis with deuterium oxide resulted in the disappearance of the peak at 5.75 τ in its NMR spectrum.

The allene (VII) was metalated by phenyllithium and subsequently treated with (IV). The tetra-substituted allene (IX) was obtained in a 16.7% yield. The NMR spectrum showed only signals due to phenyl hydrogens. When methyl iodide was used to derivatize the metalated (VII), the reaction proceeded smoothly and 1,1,3-tris(triphenylsilyl)-1,2-butadiene (X) was obtained in a 67% yield.



$$\underset{\mathrm{(VII)}}{\mathrm{(Ph_3Si)_2C{=}C{=}CH{-}SiPh_3}} \xrightarrow{\mathrm{PhLi}} \mathrm{(Ph_3Si)_2C{=}C{=}C}\begin{cases}\mathrm{Li}\\ \mathrm{SiPh_3}\end{cases} \xrightarrow{\mathrm{CH_3I}} \underset{\mathrm{(X)}}{\mathrm{(Ph_3Si)_2C{=}C{=}C}\begin{cases}\mathrm{CH_3}\\ \mathrm{SiPh_3}\end{cases}}$$

The allene (X) was also synthesized by the following sequence of reactions:



The reaction of (V) and (I) had an important side reaction. It is the addition of (I) to the triple bond[7]. 1,2-Bis(triphenylsilyl)propene (VIII) was obtained in a yield of 18.5 %. The NMR spectrum was compatible with the structure, showing a doublet at 8.17 τ for terminal methyl hydrogens and a quartet at 2.77 τ for an olefinic hydrogen. The reaction mixture was hydrolyzed with deuterium oxide in hope of isolating deuterated (VIII). The attempt, however, failed. This indicates that the metalated (VIII) is unstable under the conditions employed and it must be protonated prior to hydrolysis.

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-bromopropene

(a) 1:1 Ratio

A solution of triphenylsilyllithium[14] (0.05 mole) was added dropwise over a period of 50 minutes to 6.06 g (0.05 mole) of 1-bromopropene in 100 ml of ether at room temperature. Color Test I[15] was negative after the addition. The reaction mixture was stirred for 4 h. Subsequent to hydrolysis 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 1.65 g (11.0 %) of 1-(triphenylsilyl)propene, m.p. 90.5–92°, after recrystallization from methanol. A mixed melting point with an authentic sample prepared from propenyllithium and chlorotriphenylsilane[7] was not depressed and the infrared spectra were superimposable. Further elution with the same solvent gave in the second fraction 1.05 g (7.1 %) of 1-(triphenylsilyl)propyne, m.p. 115.5–116°, after recrystallization from methanol. A mixed melting point with an authentic sample was not depressed. Elution with carbon tetrachloride gave 0.25 g (1.8 %) of 1,3-bis(triphenylsilyl)propene, identified by a mixed melting point determination with a sample obtained from the reaction of triphenylsilyllithium with 1,3-dichloropropene[16] and by a comparison of infrared spectra, as well as a trace amount of tris(triphenylsilyl)propadiene, identified by comparison of its infrared spectrum with that of the sample obtained from the reaction of triphenylsilyllithium with 1-(triphenylsilyl)propyne.

(*b*) *4:3 Ratio, followed by addition of chlorotriphenylsilane*

A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 2 h to 7.28 g (0.06 mole) of 1-bromopropene in 200 ml of ether. Color Test I was faintly positive when the addition was completed. After 1 h of stirring there was added 15 g (0.05 mole) of chlorotriphenylsilane in 150 ml of ether. The reaction mixture was stirred for 2.5 h before it was worked up by the same procedure as in (*a*). The following compounds were isolated: hexaphenyldisilane, 15.0 g (72.5 %); triphenylsilane, 1.35 g (6.5 % based on triphenylsilyllithium); 1-(triphenylsilyl)propyne, 2.75 g (15.3 % based on 1-bromopropene); 1-(triphenylsilyl)propene, 1.20 g (6.7 % based on 1-bromopropene); 1,2-bis(triphenylsilyl)propane, 0.10 g (0.3 %), identified by comparison of its infrared spectrum with that of an authentic sample; and tris(triphenylsilyl)propadiene, 1.80 g (3.7 %), m.p. 186.5–188.5° (mixed m.p.).

(*c*) *8:5 Ratio, followed by addition of chlorotriphenylsilane*

A solution of triphenylsilyllithium (0.08 mole) was added to 6.06 g (0.05 mole) of 1-bromopropene in 100 ml of ether at room temperature. Color Test I was positive even after 5 h of stirring. Chlorotriphenylsilane was added until the color test became negative. This process required about 0.02 mole of chlorotriphenylsilane. An excess of 0.01 mole of chlorotriphenylsilane was added. The reaction mixture was worked up by the same procedure as in (*a*). The following compounds were isolated: hexaphenyldisilane, 15.20 g; a mixture of triphenylsilane and 1-(triphenylsilyl)propene, 1.75 g; 1-(triphenylsilyl)propyne, 1.0 g (6.6 %); 1,2-bis(triphenylsilyl)propane, 2.15 g (7.7 %); 1,3-bis(triphenylsilyl)propene, 0.40 g (1.4 %); 1,3-bis(triphenylsilyl)propyne, 0.30 g (1.1 %); and tris(triphenylsilyl)propadiene, 2.60 g (6.4 %).

(*d*) *3:1 Ratio*

A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 1 h to 3.03 g (0.025 mole) of 1-bromopropene in 100 ml of ether at 30–35°. Color Test I was positive at the end of this addition. It remained positive after 2 h of stirring. The reaction mixture was worked up by the same procedure as in (*a*). The following compounds were isolated: hexaphenyldisilane, 1.90 g (9.2 %); triphenylsilane, 10.45 g (50.2 %); 1,2-bis(triphenylsilyl)propane, 0.95 g (6.8 %), identified by a mixed melting point with an authentic sample[7]; and 1,3-bis(triphenylsilyl)propyne, 1.0 g (7.2 %).

In another run, chlorotriphenylsilane (10.2 g, 0.034 mole) was added after the mixture was stirred 1 h and 40 min. The yield of hexaphenyldisilane was 19.50 g. The other products were triphenylsilane, 2.35 g (36.2 % based on 1-bromopropene); 1,2-bis(triphenylsilyl)propane, 0.45 g (3.2 %); 1,3-bis(triphenylsilyl)propene, 0.30 g (2.2 %); 1,3-bis(triphenylsilyl)propyne, 0.60 g (4.3 %); and a compound with a melting point of 186–189°. The last compound has not been identified, but the infrared spectrum indicated the presence of a double bond.

Reaction of triphenylsilyllithium with 1-triphenylsilylpropyne

(a) Without addition of chlorotriphenylsilane

A solution of triphenylsilyllithium (0.03 mole) was added dropwise over a period of 20 min to 9.25 g (0.031 mole) of 1-(triphenylsilyl)propyne in 70 ml of tetrahydrofuran (THF). The reaction mixture was stirred for 5 h at room temperature during which time Color Test I remained positive. A work-up in the usual manner gave a solid residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 4.0 g (51.3 %) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave in the second fraction 1.70 g (18.4 % recovery) of the starting material. Still further elution with the same solvent gave in the third fraction 3.20 g (18.5 %) of 1,2-bis(triphenylsilyl)-propene, m.p. 147–149°, after several recrystallizations from an ethyl acetate–methanol mixture. (Found: C, 83.89, 83.77; H, 6.23, 6.43; Si, 10.05, 9.84. $C_{33}H_{34}Si_2$ calcd.: C, 83.81; H, 6.13; Si, 10.05 %.)

The NMR spectrum was in agreement with the proposed structure, showing a doublet at 8.17 τ and a quartet at 2.77 τ. The infrared spectrum, however, did not show any absorption band corresponding to a double bond.

Elution with carbon tetrachloride gave an oil which was treated with petroleum ether (b.p. 60–70°) to give 4.10 g of 1,3-bis(triphenylsilyl)propyne, m.p. 127–128.5°, after recrystallization from an ethyl acetate–methanol mixture. The mother liquor was concentrated and an additional 1.05 g of the same compound crystallized out. The total yield was 5.15 g (29.9 %). (Found: C, 84.35, 84.31; H, 5.91, 5.77; Si, 9.97, 9.95. $C_{39}H_{32}Si_2$ calcd.: C, 84.12; H, 5.79; Si, 10.09 %.)

The infrared spectrum showed a characteristic triple bond absorption band at 4.60 μ.

(b) Followed by addition of chlorotriphenylsilane

(1) *In a mixture of ether and THF.* A solution of triphenylsilyllithium (0.03 mole) was added dropwise to 9.0 g (0.03 mole) of 1-(triphenylsilyl)propyne in 70 ml of ether at room temperature. A deep reddish-brown color developed. After 5 h of stirring there was added 9.0 g (0.03 mole) of chlorotriphenylsilane in ether. The color of the reaction mixture faded to light yellow. The reaction mixture was hydrolyzed with dilute acid after 1 h of stirring. Hexaphenyldisilane, 2.45 g (15.8 %), 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 the following compounds: triphenylsilane, 4.25 g (54.5 %); 1-(triphenylsilyl)propyne, [illegible] and 1,2-bis(triphenylsilyl)propene, 2.15 g (14.6 %) [illegible] from an ethyl acetate–methanol mixture. (Found: C, 84.09, 84.01; H, 5.86, 5.73; Si, 10.21, 10.20; mol. wt. Rast, 764. $C_{57}H_{46}Si_3$ calcd.: C, 83.97; H, 5.69; Si, 10.34 %; mol. wt., 815.21.)

The infrared spectrum showed a characteristic allenic absorption band at 5.30 μ. The NMR spectrum supported the proposed structure showing a single peak at 5.75 τ.

From the mother liquor after separation of tris(triphenylsilyl)propadiene there was obtained 0.90 g (5.4%) of 1,3-bis(triphenylsilyl)propyne, m.p. 126–127.5° (mixed m.p.).

(2) *In THF*. A solution of triphenylsilyllithium (0.03 mole) was added dropwise to 9.10 g (0.03 mole) of 1-(triphenylsilyl)propyne in 50 ml of THF. After 5.5 h of stirring there was added 10.0 g (0.033 mole) of chlorotriphenylsilane in 50 ml of THF. Color Test I was positive prior to this addition. The reaction mixture was hydrolyzed with dilute acid after 1 h of stirring. The organic layer was dried with sodium sulfate. The solvent was removed. When the oily residue was treated with petroleum ether (b.p. 60–70°) there appeared a fairly large amount (6.10 g) of precipitate which was filtered off. The melting point of this precipitate was 177–182°. It was raised to 186–188° after recrystallization from an ethyl acetate–methanol mixture. A mixed melting point with tris(triphenylsilyl)propadiene was not depressed.

The mother liquor was poured onto an alumina column for chromatography. The following compounds were isolated: triphenylsilane, 2.00 g (25.2%); 1-(triphenylsilyl)propyne 0.90 g (9.9% recovery); 1,2-bis(triphenylsilyl)propene, 3.00 g (18.0%); tris(triphenylsilyl)propadiene, 1.85 g; and 1,3-bis(triphenylsilyl)propyne, 1.60 g (9.5%). The combined yield of tris(triphenylsilyl)propadiene was 7.95 g (32.1%).

Reaction of phenyllithium with 1-(triphenylsilyl)propyne

(*a*) *Followed by addition of triphenylsilane*

A solution of phenyllithium (0.03 mole) was added dropwise over a period of 15 min to 9.0 g (0.03 mole) of 1-(triphenylsilyl)propyne in 50 ml of THF. The reaction mixture became slightly warm during this addition. After 5 h of stirring at room temperature, during which time Color Test I became negative, there was added 7.8 g (0.03 mole) of triphenylsilane in 60 ml of THF. The reaction mixture was stirred for another 5 h. The solution was a dark reddish-brown. A work-up in the usual manner left an oily residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 5.45 g (69.9% recovery) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave in the second fraction a mixture of tetraphenylsilane and 1-(triphenylsilyl)propyne. Fractional recrystallization of this mixture from petroleum ether (b.p. 60–70°) gave 0.75 g (9.6%) of tetraphenylsilane and 1.25 g (13.9% recovery) of 1-(triphenylsilyl)propyne. Both compounds were identified by mixed melting points with authentic samples.

Further elution with carbon tetrachloride gave an oil which upon treatment with petroleum ether (b.p. 60–70°) yielded 4.55 g (27.2%) of 1,3-bis(triphenylsilyl)propyne, m.p. 126–127.5° (mixed m.p.).

In another run, a mixture of phenyllithium and 1-(triphenylsilyl)propyne was stirred for 16 h before triphenylsilane was added. The solution was then stirred for another 24 h. The following compounds were isolated: triphenylsilane, 4.60 g (54.1% recovery); tetraphenylsilane, 1.11 g (11.0%); 1-(triphenylsilyl)propyne, 1.45 g (17.2% recovery); and 1,3-bis(triphenylsilyl)propyne, 5.30 g (31.7%).

(*b*) *Followed by addition of chlorotriphenylsilane*

A solution of phenyllithium (0.02 mole) was added slowly to 6.0 g (0.02 mole) of 1-(triphenylsilyl)propyne in 50 ml of THF. After stirring for 7 h there was added

6.30 g (0.021 mole) of chlorotriphenylsilane in 50 ml of ether. The reaction mixture was stirred for another 1.5 h. It was worked up in the usual manner and subsequently chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.77 g (11.5%) of tetraphenylsilane and 1.95 g (32.5% recovery) of 1-(triphenylsilyl)propyne. Further elution with carbon tetrachloride gave an oil which upon treatment with petroleum ether (b.p. 60–70°) yielded 3.67 g (22.5%) of tris(triphenylsilyl)propadiene, m.p. 186–188° (mixed m.p.). The mother liquor was concentrated and there crystallized out 1.40 g (12.6%) of 1,3-bis(triphenylsilyl)propyne, m.p. 127–128° (mixed m.p.).

Reaction of triphenylsilyllithium with tris(triphenylsilyl)propadiene

(a) Without addition of chlorotriphenylsilane

A solution of triphenylsilyllithium (0.013 mole) was added to 5.8 g (0.0071 mole) of tris(triphenylsilyl)propadiene in a mixture of 50 ml of ether and 50 ml of THF at room temperature. After 3 h of stirring Color Test I was only faintly positive. The reaction mixture was worked up by the usual procedure after a total stirring of 5 h. The residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 2.35 g (69.5%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with carbon tetrachloride gave an oil which was treated with petroleum ether (b.p. 60–70°) to yield 5.15 g (88.8%) of the starting material, tris(triphenylsilyl)propadiene.

(b) Followed by addition of chlorotriphenylsilane

A solution of triphenylsilyllithium (0.0135 mole) was added slowly to 5.6 g (0.0069 mole) of tris(triphenylsilyl)propadiene in 77 ml of THF at room temperature. Color Test I was positive after 3.5 h of stirring. The reaction mixture was stirred for a total of 6 h before 4.0 g (0.013 mole) of chlorotriphenylsilane in 40 ml of THF was added. After being stirred for an additional 3.5 h, the reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 2.20 g (31.4%), was separated by filtration. A work-up of the organic layer left a solid residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 1.85 g (52.6%) of triphenylsilane. Further elution with carbon tetrachloride gave an oil which upon treatment with petroleum ether (b.p. 60–70°) gave 4.25 g (76.0%) of the starting material. However, this material contained some tetrakis(triphenylsilyl)propadiene as evidenced by the presence of an additional absorption band at 5.5 μ in its infrared spectrum, although the melting point was 186.5–188.5° (mixed m.p.). From the mother liquor there was isolated 0.20 g (2.7%) of crude tetrakis(triphenylsilyl)propadiene, m.p. 418–440°.

Reaction of phenyllithium with tris(triphenylsilyl)propadiene

(a) Followed by addition of chlorotriphenylsilane

An ethereal solution of phenyllithium (0.01 mole) was added to 6.0 g (0.00736 mole) of tris(triphenylsilyl)propadiene in 60 ml of THF. The reaction mixture became slightly warm. Color Test I was negative after 1.5 h of stirring. A solution of 3.3 g (0.011 mole) of chlorotriphenylsilane in 30 ml of THF was added after a total of 4 h of stirring. The reaction mixture was stirred for another 23 h, during which time the color of the solution changed from light clear brown to yellow. A work-up in the usual manner gave an oily residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.40 g (11.9 %) of tetraphenylsilane which was identified by a mixed melting point determination with an authentic sample. Further elution with carbon tetrachloride gave an oil in three fractions which were treated separately with petroleum ether (b.p. 60–70°). From the first fraction there was obtained 0.15 g of pure starting material. When the second fraction was treated with petroleum ether (b.p. 60–70°), there precipitated out 0.55 g of a material, melting above 305°, which was recrystallized from an ethyl acetate–methanol mixture to give 0.35 g of tetrakis(triphenylsilyl)propadiene, m.p. 442–448°. The mother liquor was concentrated and some petroleum ether (b.p. 60–70°) was replaced with ethyl acetate. Upon the addition of cold methanol there precipitated out 2.65 g of a material melting at 183–203°. Fractional recrystallization from an ethyl acetate–methanol mixture gave 0.85 g of pure starting material and 0.17 g of tetrakis(triphenylsilyl)propadiene, m.p. 448–452°. The third fraction gave, after similar treatment to the above, 0.55 g of tetrakis(triphenylsilyl)propadiene, m.p. 418–452°. The total yield of the starting material recovered in pure form was 1.0 g (16.7 %). Tetrakis(triphenylsilyl)propadiene was obtained in a yield of 1.07 g (13.5 %). (Found: C, 83.25, 83.05; H, 5.67, 5.50; Si, 10.25, 10.25; mol. wt., 1058, 990. $C_{75}H_{60}Si_4$ calcd.: C, 83.90; H, 5.63; Si, 10.47 %; mol. wt., 1073.6.)

The infrared spectrum showed a very intense band at 5.49 μ which was attributable to the allenic bond. Other characteristic bands appeared at 12.00 and 12.18 μ. The NMR spectrum showed only the absorption signals of the aromatic hydrogens, thus supporting the structure of a tetrasubstituted allene.

(b) *Followed by addition of methyl iodide*

A solution of phenyllithium (0.01 mole) was added slowly to 2.20 g (0.0027 mole) of tris(triphenylsilyl)propadiene in 50 ml of THF. After a stirring of 3.25 h at room temperature there was added 1.8 g (0.0127 mole) of methyl iodide in 10 ml of THF. Some heat was evolved and the reaction mixture became colorless. After 1 h of stirring the reaction mixture was worked up in the usual manner, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60–70°) did not give any product. Elution with carbon tetrachloride gave a solid product which was recrystallized from petroleum ether (b.p. 60–70°) to give 1.70 g (67 %) of 1,1,3-tris(triphenylsilyl)-1,2-butadiene, m.p. 196–198°. (Found: C, 82.51, 82.34; H, 6.06, 5.97; Si, 10.22, 10.12. $C_{58}H_{48}Si_3$ calcd.: C, 84.00; H, 5.83; Si, 10.16 %.)

The infrared spectrum showed a very intense allenic absorption band at 5.34 μ. A band at 7.36 μ was very likely due to the methyl group present.

(c) *Followed by addition of deuterium oxide**

A solution of phenyllithium (0.01 mole) was added to 2.0 g (0.0025 mole) of tris(triphenylsilyl)propadiene in 60 ml of THF. After a stirring of 3 h there was added 0.8 ml (0.04 mole) of deuterium oxide. Some ether was added. The organic layer was washed twice with water and dried with sodium sulfate. The solvent was removed. The residue was treated with petroleum ether (b.p. 60–70°) and methanol to give

---

* Deuterium oxide was kindly provided by Dr. R. W. KING of Iowa State University.

1.75 g (87.5 %) of deuterated tris(triphenylsilyl)propadiene, m.p. 187–189°, after recrystallization from an ethyl acetate–methanol mixture. The mixed melting point of the non-deuterated and the deuterated compounds was not depressed. Their infrared spectra were identical, except that a peak at 13.80 μ was missing in the spectrum of the deuterated compound. The NMR spectrum showed no signal at 5.75 τ, indicating that the compound was deuterated completely.

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

A solution of triphenylsilyllithium (0.01 mole) was added slowly over a period of 15 min to 5.2 g (0.0093 mole) of 1,3-bis(triphenylsilyl)propyne in 50 ml of THF. A deep reddish-brown color developed almost immediately after this addition. After a stirring of 3.5 h at room temperature there was added 3.5 g (0.012 mole) of chlorotriphenylsilane in 30 ml of THF. The solution was decolorized almost immediately without evolving any heat. The reaction mixture was hydrolyzed with dilute acid after an additional stirring of 3 h. A small amount, 0.15 g (2.9 %), of hexaphenyldisilane was separated by filtration. The organic layer was worked up by the usual procedure and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 2.30 g (88.5 %) of triphenylsilane, which was identified by its infrared spectrum. Elution with carbon tetrachloride gave an oil, which upon treatment with petroleum ether (b.p. 60–70°) yielded a total of 3.85 g (50.8 %) of tris(triphenylsilyl)propadiene, m.p. 187–188.5°, after recrystallization from an ethyl acetate–methanol mixture. From the mother liquor there was obtained 0.12 g of a high melting material, m.p. 441–600°(+), part of which was tetrakis(triphenylsilyl)propadiene as indicated by the presence of an absorption band at 5.50 μ in its infrared spectrum.

Reaction of phenyllithium with 1,3-bis(triphenylsilyl)propyne

(a) Followed by addition of chlorotriphenylsilane

A solution of phenyllithium (0.01 mole) was added slowly over a period of 15 min to 5.60 g (0.01 mole) of 1,3-bis(triphenylsilyl)propyne in 50 ml of THF at room temperature. Immediately a reddish color developed and the solution became warm. The reaction mixture was stirred for 3 h, during which time its color became a very dark reddish-brown. Color Test I was, however, negative. A solution of 3.30 g (0.011 mole) of chlorotriphenylsilane in 30 ml of THF was added. The color of the reaction mixture changed slowly from dark to light orange. After 2 h of stirring one gram more of chlorotriphenylsilane was added and the stirring was continued for another 3 h. The reaction mixture was then worked up and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.40 g (11.9 %) of tetraphenylsilane, which was identified by a mixed melting point determination with an authentic sample. Further elution with carbon tetrachloride gave an oil, which upon treatment with petroleum ether (b.p. 60–70°) yielded 3.45 g (42.4 %) of tris(triphenylsilyl)propadiene, m.p. 187–189°, after recrystallization from an ethyl acetate–methanol mixture. This compound was identified by a mixed melting point determination and by a comparison of the infrared spectra. The mother liquor was concentrated and there was isolated 1.55 g (27.7 %) of the starting material, 1,3-bis(triphenylsilyl)propyne.

In addition, a trace amount of tetrakis(triphenylsilyl)propadiene, identified by its infrared spectrum, was formed.

(b) *Followed by addition of methyl iodide*

(*1*) *2:1 Ratio.* A solution of phenyllithium (0.01 mole) was added rapidly to 2.50 g (0.0045 mole) of 1,3-bis(triphenylsilyl)propyne in 50 ml of THF. The solution immediately became reddish-black and evolved some heat. After one hour's stirring there was added 1.80 g (0.0127 mole) of methyl iodide in 10 ml of THF. The reaction mixture was worked up in the usual manner after 1 h of stirring. The residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 0.13 g (8.6 %) of tetraphenylsilane. Further elution with the same solvent gave in the second fraction 0.08 g (3.1 %) of a compound with a melting point of 166–167° after recrystallization from petroleum ether (b.p. 60–70°). The infrared spectrum of this compound was very similar to that of 2,4-bis(triphenylsilyl)-2,3-pentadiene, which was obtained from the reaction of phenyllithium with a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene followed by the addition of methyl iodide. Further elution with carbon tetrachloride gave an oil, which upon treatment with petroleum ether (b.p. 60–70°) gave 0.95 g of a material with a melting point of 131–135°. Recrystallization from an ethyl acetate–methanol mixture failed to give a pure product. The infrared spectrum showed characteristic bands at 4.65 (strong), 5.25 (weak), 10.75, 11.32 and 12.80 μ. The material may have been a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene. From the mother liquor there was obtained an additional 0.35 g of the mixture. The total yield of the mixture was 1.30 g (50.8 %).

(*2*) *1:1 Ratio.* A solution of phenyllithium (0.01 mole) was added slowly to 5.10 g (0.0092 mole) of 1,3-bis(triphenylsilyl)propyne in 70 ml of THF. The reaction mixture was stirred for 20 h at room temperature before 1.80 g (0.0127 mole) of methyl iodide in 15 ml of THF was added. After being stirred for 2 h, the reaction mixture was worked up by the same procedure as in (1). Tetraphenylsilane was not isolated. The yield of the mixture was 3.05 g (58 %). The infrared spectrum of the mixture showed characteristic bands (in carbon disulfide solution) at 5.22, 7.32, 7.36, 10.30, 10.60 (very weak), 10.98, 11.85 (weak), and 13.76 μ. The analysis of these bands indicated that the following compounds were present in the mixture: 1,3-bis(triphenylsilyl)-1-butyne (7.32, 10.30, 10.98); 1,3-bis(triphenylsilyl)-1,2-butadiene (5.22, 7.36, 10.60, 13.76); 1,3-bis(triphenylsilyl)-3-methyl-1-butyne (7.36, 11.84); and possibly the starting material (7.32, 13.76). Three recrystallizations of this mixture gave a material with a melting point of 133–135°. It was predominantly 1,3-bis(triphenylsilyl)-1-butyne, the major contaminant being the starting material (13.33, 13.76). 1,3-Bis(triphenylsilyl)-1-butyne was obtained from the reaction of phenyllithium with 1-(triphenylsilyl)-1-butyne followed by the addition of triphenylsilane, m.p. 135–136.5°.

Reaction of triphenylsilyllithium with 1-(triphenylsilyl)-1-butyne

A solution of triphenylsilyllithium (0.03 mole) was added to 7.35 g (0.0235 mole) of 1-(triphenylsilyl)-1-butyne in 70 ml of THF. The reaction mixture was stirred for 40.5 h at room temperature. Its color remained a dark reddish-brown. The reaction mixture was worked up in the usual manner and the black residue obtained was treated with petroleum ether (b.p. 60–70°). A solid material, 0.80 g, m.p. 190–220°, was separated by filtration. It was recrystallized from an ethyl acetate–ethanol mixture, 0.60 g, m.p. 197–225°. The mother liquor was poured onto an alumina column. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 3.35 g (43.0 %) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave a partially solidified oil in several fractions from which the following compounds were isolated: tetraphenylsilane, 0.35 g (4.4 %), m.p. 230–233° (mixed m.p.); 1-(triphenylsilyl)-1-butyne, 0.20 g (2.7 % recovery); a compound obtained from the reaction of triphenylsilyllithium with 1-bromo-1-butene, 0.15 g, m.p. 221–223°; and a compound, possibly 1,2-bis(triphenylsilyl)-1-butene, 0.20 g (2 %), m.p. 134–137°, whose infrared spectrum showed a moderately strong absorption band at 6.25 μ, suggesting the presence of a double bond. Elution with carbon tetrachloride gave 3.90 g of an oil from which there was isolated 0.15 g (1.8 %) of crude 1,3-bis(triphenylsilyl)-1-butyne, m.p. 128–133°, which was identified by a comparison of infrared spectra.

Reaction of phenyllithium with 1-(triphenylsilyl)-1-butyne

(*a*) *Followed by addition of triphenylsilane*

An ethereal solution of phenyllithium (0.034 mole) was added slowly to 9.35 g (0.030 mole) of 1-(triphenylsilyl)-1-butyne in 100 ml of THF. The reaction mixture was stirred for 20 h at room temperature before 9.40 g (0.036 mole) of triphenylsilane in 30 ml of THF was added. After being stirred for another 20 h, the reaction mixture was hydrolyzed with dilute acid. An insoluble material, 3.70 g, was separated by filtration. It was identified as tetraphenylsilane, m.p. 231–233.5° (mixed m.p.). The organic layer was worked up in the usual manner and the residue was treated with petroleum ether (b.p. 60–70°). The precipitate was filtered off. It was identified as tetraphenylsilane, 1.35 g. The mother liquor was poured onto an alumina column. Elution with petroleum ether (b.p. 60–70°) gave 7.65 g (81.4 % recovery) of triphenylsilane, identified by its infrared spectrum, and 0.40 g of tetraphenylsilane. The combined yield of tetraphenylsilane was 5.45 g (47.6 % based on phenyllithium). In addition, there was isolated 0.20 g (1.3 %) of crude starting material.

Elution with carbon tetrachloride gave an oil in two fractions, both of which were treated separately with a mixture of petroleum ether (b.p. 60–70°) and methanol. The first fraction gave 1.45 g (11.7 %) of a material with a melting range of 128.5–136°. The infrared spectrum showed characteristic absorption bands at 4.64, 5.23, 7.35, 10.30, 10.68, 10.99 and 13.79 μ. This material was possibly a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene. The second fraction yielded 0.55 g (3.2 %) of what was possibly 1,3-bis(triphenylsilyl)-1-butyne, m.p. 135–136.5°. The infrared spectrum showed characteristic bands at 4.64 (–C≡C–), 10.30, and 10.99 μ. (Found: C, 84.44, 84.24; H, 5.86, 5.76; Si, 9.67, 9.64. $C_{40}H_{34}Si_2$ calcd.: C, 84.16; H, 6.00; Si, 9.84 %.)

(*b*) *Followed by addition of methyl iodide*

An ethereal solution of phenyllithium (0.015 mole) was added to 3.15 g (0.01 mole) of 1-(triphenylsilyl)-1-butyne in 50 ml of THF. The reaction mixture was stirred for 19 h before 2.25 g (0.016 mole) of methyl iodide in 30 ml of ether was added. The reaction mixture went from light brown to colorless with the evolution of some heat. It was hydrolyzed with dilute acid after 1.75 h of stirring. Tetraphenylsilane, 1.15 g, was separated by filtration. The organic layer was worked up in the usual manner leaving an oily residue, which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave an oil which was treated with methanol. The insoluble material was filtered off and identified as tetraphenylsilane, 0.25 g, m.p. 231–234° (mixed m.p.). The combined yield of tetraphenylsilane was 1.40 g [41.6% based on 1-(triphenylsilyl)-1-butyne]. From the mother liquor there was obtained 0.10 g (3.1%) of what was possibly 1-(triphenylsilyl)-3-methyl-1-butyne, m.p. 79–81°. The infrared spectrum showed characteristic bands at 4.60 (–C≡C–), 7.65, 10.38, and 12.11 μ.

Reaction of phenyllithium with a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene followed by aditdion of methyl iodide

The starting mixture was obtained from two sources: (1) from the reaction of phenyllithium with 1,3-bis(triphenylsilyl)propyne followed by the addition of methyl iodide; (2) from the reaction of phenyllithium with 1-(triphenylsilyl)-1-butyne followed by the addition of triphenylsilane.

An ethereal solution of phenyllithium (0.01 mole) was added to 3.15 g (0.0055 mole) of a mixture of 1,3-bis(triphenylsilyl)-1-butyne and 1,3-bis(triphenylsilyl)-1,2-butadiene in 60 ml of THF. The reaction mixture was stirred for 3 h before 1.8 g (0.0127 mole) of methyl iodide in 15 ml of ether was added. The reaction mixture went from orange-brown to colorless upon the addition of methyl iodide. After 2 h of stirring the reaction mixture was worked up in the usual manner, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.10 g of tetraphenylsilane, m.p. 229–232° (mixed m.p.). Elution with carbon tetrachloride gave an oil which was treated with petroleum ether (b.p. 60–70°) to give 1.90 g of a solid, m.p. 140–162°. Recrystallization from a mixture of ethyl acetate and methanol yielded 1.15 g (35.8%) of crude 2,4-bis(triphenylsilyl)-2,3-pentadiene, m.p. 165–170°. Another recrystallization from the same solvent produced 0.90 g (28.0%) and raised the melting point to 174–175°. The infrared spectrum showed the characteristic allenic absorption band at 5.23 μ. (Found: C, 84.51, 84.31; H, 6.00, 5.94; Si, 9.64, 9.64. $C_{41}H_{36}Si_2$ calcd.: C, 84.19; H, 6.20; Si, 9.61%.)

From the filtrate and from the original mother liquor there was obtained a material, 1.60 g (50%), which melted in the range of 135–145°. An attempt to purify by recrystallization failed. The infrared spectrum of this material showed characteristic bands at 4.61, 4.68, 5.22, 7.36, 10.10(?), 10.34 (very weak), 11.00 (broad and very weak), and 11.84 μ. Analysis of these bands indicated that this material was a mixture of 1,3-bis(triphenylsilyl)-1-butyne (trace, 4.61?, 10.34, 11.00), 2,4-bis(triphenylsilyl)-2,3-pentadiene (5.22, 7.37, 10.10, 11.03), and possibly 1,3-bis(triphenylsilyl)-3-methyl-1-butyne (4.68, 7.36, 11.84).

Reaction of triphenylsilyllithium with allyltriphenylsilane

A solution of triphenylsilyllithium (0.02 mole) was added to 6.0 g (0.02 mole) of allyltriphenylsilane in 30 ml of THF. After being stirred for 22 h at room temperature, the reaction mixture was worked up in the usual manner and the residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 1.50 g (29%) of triphenylsilane, which was identified by its infrared spectrum. Further elution with the same solvent gave in the second fraction 0.55 g (0.2 %) of allyltriphenylsilane, the starting material. Following elution with carbon tetrachloride there was obtained 4.45 g (40.0 %) of 1,3-bis(triphenylsilyl)-propene, m.p. 158–159.5°, after recrystallization from petroleum ether (b.p. 60–70°). This compound was identical with a dehydration product of 1,3-bis(triphenylsilyl)-2-propanol. It was also identical with a product obtained from a reaction of triphenylsilyllithium with 1,3-dichloropropene in a 2:1 ratio.

ACKNOWLEDGEMENTS

The NMR spectra were kindly furnished by Dr. R. W. King, and the infrared spectra were provided through the courtesy of Mrs. Ikue Ogawa of Iowa State University. This research was supported in part by the United States Air Force under Contract AF 33(616)-6463 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

SUMMARY

1-Bromopropene reacted with triphenylsilyllithium yielding hexaphenyldisilane as the major product. However, seven other compounds were isolated as by-products. The reaction of 1-(triphenylsilyl)propyne, one of the by-products, with triphenylsilyllithium was investigated. The major products were 1,2-bis(triphenylsilyl)propene and 1,3-bis(triphenylsilyl)propyne. When chlorotriphenylsilane was added to the above reaction mixture, an additional product, tris(triphenylsilyl)propadiene, was isolated. By metalation–coupling reactions three other triphenylsilyl-substituted allenes were synthesized: 2,4-bis(triphenylsilyl)-2,3-pentadiene, 1,1,3-tris(triphenylsilyl)-1,2-butadiene, and tetrakis(triphenylsilyl)propadiene. Allyltriphenylsilane reacted with triphenylsilyllithium in a similar manner to give 1,3-bis(triphenylsilyl)-propene.

REFERENCES

1 H. Gilman, D. Aoki and D. Wittenberg, *J. Am. Chem. Soc.*, 81 (1959) 1107.
2 H. Gilman and D. Aoki, *J. Org. Chem.*, 24 (1959) 426.
3 H. Gilman and G. Dappen, unpublished results.
4 H. Gilman and D. Aoki, *Chem. Ind. (London)*, (1960) 1165; *J. Organometal. Chem.*, 1 (1964) 449.
5 G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, 81 (1959) 4996.
6 W. T. Miller, Jr. and C. S. Y. Kim, *J. Am. Chem. Soc.*, 81 (1959) 5008.
7 H. Gilman and D. Aoki, submitted for publication.
8 D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, 80 (1958) 1922.
9 E. J. Lanpher, *J. Am. Chem. Soc.*, 79 (1957) 5578.
10 H. F. Herbrandson and D. S. Mooney, *J. Am. Chem. Soc.*, 79 (1957) 5809.
11 G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, 83 (1961) 2015.
12 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London, 1954, p. 61.
13 L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, New York, 1959, p. 61.
14 H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, 80 (1958) 608.
15 H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, 47 (1925) 2002.
16 H. Gilman and D. Aoki, unpublished studies.