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THE REACTION OF 3,3-DICHLOROALLYLTRIMETHYLSILANE WITH n-BUTYLITHIUM.

by

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THE REACTION OF 3,3-DICHLOROALLYLTRIMETHYLSILANE WITH n-BUTYLLITHIUM.

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SUMMARY

n-Butyllithium reacts with 3,3-dichloroallyltrimethylsilane to metalate the vinyl proton. Under the reaction conditions the Me₃SiCH₂C(Li)=CCl₂ formed undergoes β-elimination of LiCl to give Cl=CCH₂SiMe₃ whose subsequent reaction with n-butyllithium produces LiC=CCH₂SiMe₃. Addition of trimethylchlorosilane gives Me₃SiC=CCH₂SiMe₃. When two molar equivalents of n-butyllithium are used, further metalation of LiC=CCH₂SiMe₃ gives LiC=CCH(Li)SiMe₃. The action of N-bromosuccinimide on Me₃SiCH₂CH=CCl₂ resulted in formation of Me₃SiCH=CHCCl₂Br.

# National Science Foundation Graduate Fellow, 1973-1976.
INTRODUCTION.

In a recent investigation, we prepared the novel ambident allylic lithium reagent gem-chloro(trimethylsilyl)allyllithium, and studied its reactions with a variety of substrates.

Another trimethylsilyl-substituted allyllithium reagent which was of potential interest to us was II, and we report here concerning our attempts to prepare this reagent. Although they were unsuccessful, the route examined was of interest since it involved the reaction of n-butyllithium with a molecule which had three different potential sites at which the lithium reagent could attack.
RESULTS AND DISCUSSION.

The organosilicon compound which was chosen as a potential precursor for II was 3,3-dichloroallyltrimethylsilane, Me₃SiCH₂CH=CCl₂. This was readily prepared. The condensation of trichlorosilane with 1,1,3-trichloropropene by the method of Furuya and Sukawa² (eq. 1) gave Cl₃SiCH₂CH=CCl₂ whose methylation

$$\text{Cl}_2\text{C} = \text{CHCH}_2\text{Cl} + \text{HSiCl}_3 + \text{Et}_3\text{N} \xrightarrow{\text{CuCl}} \text{Cl}_3\text{SiCH}_2\text{CH}=\text{CCl}_2 + \text{Et}_3\text{NH}^+\text{Cl}^-$$

(1)

with methylmagnesium bromide produced the desired silane.

The hoped-for reaction of Me₃SiCH₂CH=CCl₂ with n-butyllithium is the one shown in eq. 2. Metalation α to a silyl group is a favorable process since silicon stabilizes an adjacent negative charge.³ In fact, trimethylsilylallyllithium, Li[Me₃SiCHCHCl₂], is readily prepared by reaction of allyltrimethylsilane with n-butyllithium.⁴,⁵ However, the two chlorine atoms in Me₃SiCH₂CH=CCl₂ also will have activating effects on the attack by n-butyllithium, and these will oppose the desired metalation process. On the one hand, they will enhance the acidity of the vinyl proton,

$$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CCl}_2 + n\text{-C}_4\text{H}_9\text{Li} \rightarrow \text{Li[Me}_3\text{SiCHCHCCl}_2] + n\text{-C}_4\text{H}_10$$

(2)

* The action of n-butyllithium on the isomeric Me₃SiCCl₂CH=CH₂ was reported in ref. 1.
making it more reactive toward a base; on the other hand, the two chlorine substituents will mutually enhance each other's reactivity toward lithium/chlorine exchange with an alkyl lithium. Thus \( \text{Me}_3\text{SiCH}_2\text{CH}=\text{CCl}_2 \) offers three potential sites for attack by \text{n-butyl}-lithium.

In the initial experiment, a molar equivalent of \text{n-butyl}-lithium in hexane was added to a solution of \( \text{Me}_3\text{SiCH}_2\text{CH}=\text{CCl}_2 \) in tetrahydrofuran (THF) which was cooled to \(-90\)°. After 30 min., an excess of trimethylchlorosilane was added to the reaction mixture. The products were an acetylenic silane, \(2,2,6,6\)-tetramethyl-2,6-disila-3-heptyne, \(\text{Me}_3\text{SiC}=\text{CCH}_2\text{SiMe}_3\), in 26\% yield, and \(2,2,6,6\)-tetramethyl-2,6-disila-3-chloro-3-heptene, \(\text{Me}_3\text{SiC(}\text{Cl})=\text{CCH}_2\text{SiMe}_3\), in 6\% yield. A 68\% recovery of the starting silane was realized.

Further experiments (Table 1) showed that longer reaction times or higher temperatures increase the yield of the acetylene. The last three experiments show roughly the same result, that just over one-half of the starting material is converted to the acetylene. Apparently, the conditions of the first experiment did not allow the reaction to go to completion.

The fact that about one-half of the starting material remains unreacted suggests that two molar equivalents of \text{n-butyl}-lithium are consumed per equivalent of substrate. However, doubling the amount of the lithium reagent caused more deprotonation of the substrate, and on reaction of the organolithium intermediates with trimethylchlorosilane, \(1,3,3\)-tris(trimethylsilyl)propyne, \(\text{Me}_3\text{SiC}=\text{CCH}(%\text{SiMe}_3)_2\), was formed in 19\% yield,
### TABLE 1. Reactions of 3,3-Dichloroallytrimethylsilane with One Molar Equivalent of *n*-Butyllithium. Trimethylchlorosilane Quench.

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<th>Reaction Temperature, °C</th>
<th>Reaction Time, min.</th>
<th>Relative Yields*</th>
<th>Me&lt;sub&gt;3&lt;/sub&gt;SiC=CH	ext{Me}-CH=CCl&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Me&lt;sub&gt;3&lt;/sub&gt;SiCH&lt;sub&gt;2&lt;/sub&gt;CH=CCl&lt;sub&gt;2&lt;/sub&gt;</th>
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</table>

\* Relative ratio determined by GLC.

\** Absolute yield determined by GLC (internal standard method).
in addition to Me₃SiC≡CCH₂SiMe₃ (37%). Such multiple substitution 
had been observed by West et al.⁶, who obtained the same tris-
(trimethylsilyl)propyne in a reaction of an excess of n-butyl-
lithium with propyne with subsequent addition of trimethyl-
chlorosilane.

These observations are explicable in terms of initial 
metalation of the vinyl proton of Me₃SiCH₂CH=CCl₂. Previous 
work reported by Köbrich and his coworkers⁷—⁹ is pertinent. Low 
temperature reactions of n-butyllithium with equimolar quantities 
of mono-, di-(cis- and trans-) and trichloroethylene were found 
to result in metalation of the vinylic hydrogens to give α-
chlorovinyllithium compounds (eq. 3). The stabilities of

\[
\begin{align*}
R_C\text{=C}H & + n-C_4H_9Li \rightarrow R_C\text{=C}Li + n-C_4H_{10} \\
(\text{R, R}’ = \text{H and/or Cl})
\end{align*}
\]

these products depended on their configuration. The least 
stable were those with vicinal chlorine and lithium substitu-
tion in trans relationship. These decomposed by trans-elimination 
to give an acetylene (eq. 4). In those cases where a chloro-

\[
\begin{align*}
R_C\text{=C}Li & \rightarrow RC\equiv CR’ + LiCl \\
(\text{R, R}’ = \text{H and/or Cl})
\end{align*}
\]

acetylene was produced, further reaction with n-butyllithium gave
alkynyllithium reagents. Such chemistry is involved in the
Me₃SiCH₂CH=CCl₂/n-C₄H₉Li interaction.

The initial step must be metalation (eq. 5). The product

\[
\begin{align*}
\text{Cl} & \quad \text{C=CH₂SiMe₃} & \quad \text{RLi} & \quad \text{Cl} \quad \text{C=CH₂SiMe₃} \\
\text{Cl} & \quad \text{C=CH₂SiMe₃} & \quad \text{C=CH₂SiMe₃} & \quad \text{RH}
\end{align*}
\]

undergoes trans-β-elimination of lithium chloride (eq. 6).

\[
\begin{align*}
\text{Cl} & \quad \text{C=CH₂SiMe₃} & \quad \text{Li} & \quad \text{Cl} \quad \text{C=CH₂SiMe₃} \\
\text{Cl} & \quad \text{C=CH₂SiMe₃} & \quad \text{ClC≡CCH₂SiMe₃} & \quad \text{LiCl}
\end{align*}
\]

The chloroacetylene produced reacts with n-butyllithium, giving
Li/Cl exchange (eq. 7). The reaction sequence (5,6,7) utilizes

\[
\begin{align*}
\text{ClC≡CCH₂SiMe₃} & \quad \text{C₄H₉Li} & \quad \text{LiC≡CCH₂SiMe₃} & \quad \text{C₄H₉Cl}
\end{align*}
\]

two molar equivalents of n-butyllithium per mol of Me₃SiCH₂CH=CCl₂.

If excess n-butyllithium is present, the alkynyllithium reagent
III undergoes further metalation to give the dilithium species
IV (eq. 8). Addition of trimethylchlorosilane to such reaction

\[
\begin{align*}
\text{LiC≡CCH₂SiMe₃} & \quad \text{C₄H₉Li} & \quad \text{LiC≡CCHSiMe₃} & \quad \text{C₄H₁₀}
\end{align*}
\]
mixtures results in formation of the silylation products of III
and IV, Me₃SiC≡CCH₂SiMe₃ and Me₃SiC≡CCH(SiMe₃)₂, respectively.
Since the initial lithium reagent produced (eq. 5) is only a transient species which undergoes rapid β-elimination of lithium chloride, it is clear why, as Table 1 shows, low reaction temperatures are not required. The first lithium reagent which persists, III, is stable at room temperature.

The small amount of 2,2,6,6-tetramethyl-2,6-disila-3-chloro-3-heptene formed in the Me₃SiCH₂CH=CCl₂/n-C₄H₉Li/Me₃SiCl reaction results from competitive Li/Cl exchange as shown in eq. 9.

\[
\begin{align*}
\text{Cl}-\text{C}=&\text{C}-\text{H} \\
\text{Cl}-\text{C}=&\text{C}-\text{H} + \text{n-C₄H₉Li} \\
\text{Li}-\text{C}=&\text{C}-\text{H} + \text{n-C₄H₉Cl} \\
\end{align*}
\]

Reagent V, an α-chlorovinyllithium species, is sufficiently stable for reaction with trimethylchlorosilane to take place, giving Me₃SiC(Cl)═CHCH₂SiMe₃. It is clear that the β-Cl effect on the acidity of a vinyl proton is greater than the α-silicon effect on the acidity of a methylene proton, and thus the desired chemistry (eq. 2) did not develop.

Our successful route to gem-chloro(trimethylsilyl)allyllithium involved the transmetalation reaction between Ph₃PbCH₂CH=C(Cl)SiMe₃ and n-butyllithium. The required organolead precursor was prepared by reaction of Ph₃PbMgBr with Me₃SiC(Cl)=CH-CH₂Cl. A similar route should, in principle, be applicable to the synthesis of Ph₃PbCH(SiMe₃)CH=CCl₂, VI, and via reaction of
Such a procedure also served well in the synthesis of gem-
dichloroallyllithium$^{10}$: 
\[
\text{CCl}_2=\text{CHCH}_2\text{Cl} + \text{Ph}_3\text{PbMgBr} \rightarrow \text{CCl}_2=\text{CH-}
\text{CH}_2\text{PbPh}_3 + n-\text{BuLi} \rightarrow \text{Li[CCl}_2\text{CHCH}_2].
\]
It is apparent that such transmetalation processes occur more readily than vinyl proton metalation β to a vinylic chlorine atom.

the latter with n-butyllithium, of Li[Me$_3$SiCHCHCCl$_2$]. This would require a suitable starting material for the preparation of the required lead compound. Allylic bromination of Me$_3$SiCH$_2$-CH=CCl$_2$ might provide a route Me$_3$SiCHBrCH=CCl$_2$, whose reaction with Ph$_3$PbMgBr then would be expected to give the desired VI. However, such allylic bromination of Me$_3$SiCH$_2$CH=CCl$_2$ could well proceed with allylic rearrangement, giving Me$_3$SiCH=CHCCl$_2$Br rather than the desired bromide. Indeed, Corriu et al.$^4$ had reported that allylic bromination of allyltriphelnylsilane with N-bromosuccinimide gave the rearranged bromide, Ph$_3$SiCH=CHCH$_2$Br. Nevertheless, we examined the allylic bromination of Me$_3$SiCH$_2$CH=CCl$_2$ with N-bromosuccinimide in carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide. This reaction gave a 91% yield of a monobromination product. The NMR and IR spectra of this product, however, showed it to be Me$_3$SiCH=CHCCl$_2$Br, rather than the desired Me$_3$SiCHBrCH=CCl$_2$. Presumably, rapid rearrangement of the initially formed radical, VII, to the more stable VIII took place before bromine atom abstraction occurred.

\[
\begin{align*}
\text{Me}_3\text{SiCHCH=CCl}_2 & \quad \text{Me}_3\text{SiCH=CHCCl}_2 \\
\text{VII} & \quad \text{VIII}
\end{align*}
\]
Such allyl radical rearrangements have been discussed in a
review by Walling.\textsuperscript{11}

It would appear that there is no easy route to \( \text{Li}[\text{Me}_3\text{SiCHCHCCl}_2] \).

**EXPERIMENTAL.**

**General Comments.** The "general comments" in the preceding paper\textsuperscript{1} are applicable.

**Preparation of 3,3-Dichloroallyltrichlorosilane and 3,3-Dichloroallyltrimethylsilane.**

\textbf{a}) \( \text{Cl}_3\text{SiCH}_2\text{CH}==\text{CCl}_2 \).

A two-liter, three-necked round-bottomed flask, equipped with a 500 ml pressure-equalizing addition funnel, a mechanical stirrer and a Claisen adapter fitted with a no-air stopper and a nitrogen inlet, was charged with 4.95 g (50 mmol) of CuCl, 139 ml (1.0 mol) of triethylamine (distilled from NaOH pellets) and 500 ml of diethyl ether. The addition funnel was topped with a no-air stopper and charged by syringe with 100.0 ml (1.0 mol) of 1,1,3-trichloropropene and 99.7 ml (1.0 mol) of trichlorosilane. The Claisen adapter was replaced with a reflux condenser topped with a nitrogen inlet tube and then the contents of the addition funnel were added dropwise during 80 min. while the reaction mixture was stirred and maintained at reflux. During the course of the addition the following color changes were observed: initially, olive green to colorless (after the first drops had been added) to yellow, then orange and, finally, brown. Subsequently, the addition funnel and the reflux condenser were
replaced by a glass stopper and a still head. About 400 ml of a trichlorosilane/diethyl ether mixture was distilled at 37°. The residue was transferred, under nitrogen, to a distillation flask and was trap-to-trap distilled at 0.03 mm, temperature to ~150°, into a receiver cooled with liquid nitrogen. The distillate was fractionally distilled at reduced pressure to give 85.0 g (35%) of Cl₃SiCH₂CH=CCl₂, bp 87-88.5° at 26 mm Hg. (Found: C, 14.99; H, 1.32. C₆H₃Cl₅Si calcd.: C, 14.74; H, 1.24). NMR (CCl₄): δ 2.49 (d, J = 8 Hz, 2H, CH₂) and 5.87 ppm (t, J = 8 Hz, 1H, =CH).

b) Me₃SiCH₂CH=CCl₂.

The reaction of 85.0 g (0.35 mol) of Cl₃SiCH₂CH=CCl₂ with methylmagnesium bromide in diethyl ether from 1.40 mol of magnesium, using standard Grignard alkylation procedure (non-hydrolytic work-up), gave 54.35 g (85%) of Me₃SiCH₂CH=CCl₂, bp 73-74° at 31 mm Hg, n°D 1.4604. (Found: C, 39.47; H, 6.63; Cl, 38.77. C₆H₁₂Cl₂Si calcd.: C, 39.35; H, 6.60; Cl, 38.71). NMR (CCl₄): δ 0.12 (s, 9H, Me₃Si), 1.65 (d, J=9 Hz, 2H, CH₂) and 5.85 (t, J = 9 Hz, 1H, =CH). IR(film): ν(C=Si) 1615 cm⁻¹.

Reaction of 3,3-Dichloroallyltrimethylsilane with n-Butyllithium.

A 500 ml, three-necked Morton flask, equipped with a mechanical stirrer, no-air stopper and a Claisen adapter fitted with a low-temperature thermometer and a nitrogen inlet tube, was charged with 2.874 g (15.7 mmol) of Me₃SiCH₂CH=CCl₂ dissolved in 250 ml of THF. The solution was cooled to -91° ± 2° C* and then
a 2.57 N solution of n-butyllithium (17.2 mmol) in hexane was added by syringe over a 15 min. period. The resulting clear, lavender solution was stirred at -90°C for 30 min. and then 2.60 ml (~20 mmol) of trimethylchlorosilane was added during a 2 min. period. The reaction mixture was stirred at -90°C for 30 min. The clear, colorless solution which resulted was allowed to warm slowly to room temperature and then was hydrolyzed to a dry end-point with saturated aqueous ammonium chloride. Filtration was followed by concentration of the filtrate at reduced pressure. GLC analysis of the residue (4 ft., 20% SE-30 at 110° and 6 ft. Carbowax at 110°) showed the presence of three components. These were isolated by GLC and were identified as starting material, Me₃SiCH₂CH=CCl₂, 10.7 mmol, 68% recovery (by IR and NMR); Me₃Si=CCCH₂SiMe₃, 4.08 mmol (26%), whose NMR spectrum [in CCl₄: δ0.17 (s, 18H, Me₃Si), and 1.52 ppm (s, 2H, CH₂)] matched that reported for this compound by West and Jones⁶; Me₃SiC(Cl)=CHCH₂SiMe₃, 0.94 mmol (6%), nD 1.4530 (lit.¹ nD 1.4529), whose NMR and IR spectra matched those of an authentic sample (cf. preceding paper¹).

The results of other 1:1 Me₃SiCH₂CH=CCl₂/n-BuLi/Me₃SiCl
reactions are given in Table 1.

A similar reaction was carried out in which 3.63 mmol of Me₃SiCH₂CH=CCl₂ in 200 ml of THF at 1°C was treated with 7.97 mmol of n-butyllithium in hexane. The caramel-colored reaction mixture was treated with 10 mmol of trimethylchlorosilane. Work-up as above, followed by GLC analysis and product isolation by GLC, showed the following compounds to be present: Me₃Si≡CCH₂-SiMe₃, 1.34 mmol (37%) and Me₃Si≡CCH(SiMe₃)₂, 0.69 mmol (19%), whose IR and NMR spectra matched the published spectra of this compound⁶,¹² [NMR (CCl₄): δ0.15 (s, 27H, Me₃Si) and 1.05 ppm (s, 1H, CH)].

Reaction of 3,3-Dichloroallyltrimethylsilane with N-Bromosuccinimide.

A 200 ml, three-necked Morton flask, equipped with a reflux condenser and a nitrogen inlet tube was charged with 8.898 g (48.6 mmol) of Me₃SiCH₂CH=CCl₂, 9.225 g (46.2 mmol) of N-bromosuccinimide, a spatula tip-ful of benzoyl peroxide and 100 ml of carbon tetrachloride. The mixture was stirred and heated at reflux for 5 hr., at which time iodide-starch paper was negative. The succinimide was filtered and the filtrate was trap-to-trap distilled (room temperature at 0.03 mm Hg). The distillate was concentrated (to 75°, 33 mmHg) and the residue was trap-to-trap distilled at 0.07 mm (heat gun), to give 11.6 g (91%) of Me₃SiCH=CHCCl₂Br, n²⁵D 1.5082 (Found: C, 27.95; H, 4.36; total halogen, 56.83; C₆H₁₁Cl₂BrSi calcd.: C, 27.50; H, 4.23; total halogen, 57.56). NMR (CCl₄): δ0.23 (s, 9H, Me₃Si), 4.03
(d, $J = 12\text{Hz}$, 1H, Si-CH=), 6.00 ppm (d, $J = 12\text{Hz}$, 1H, =CHCCl$_2$Br).

The NMR spectrum was almost superimposable with that of Me$_3$SiCH=CH- CBr$_3$.$^{13}$ IR(film): $\nu$ (C=C) 1605 sh, 1595 cm$^{-1}$.

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REFERENCES

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n-Butyllithium reacts with 3,3-dichloroallyltrimethylsilane to metatalate the vinyl proton. Under the reaction conditions the Me₃SiCH₂Z(Li)=CCl₂ formed undergoes β-elimination of LiCl to give CIC=CH₂SiMe₃ whose subsequent reaction with n-butyllithium produces LiC=CH₂SiMe₃. Addition of trimethylchlorosilane gives Me₃SiC=CH₂SiMe₃. When two molar equivalents of n-butyllithium are used, further metalation of LiC=CH₂SiMe₃ gives LiC=CH(Li)SiMe₃. The action of N-bromosuccinimide on Me₃SiCH=CH=CCl₂ resulted in formation of Me₃SiCH=CHCBrCl₂.