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<tr>
<td><strong>Author(s)</strong></td>
<td>Shinokubo, Hiroshi</td>
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Studies on Sequential Carbon-Carbon Bond Formation Reaction Using Silyldihalomethylithium

Hiroshi Shinokubo

1998
Studies on Sequential Carbon-Carbon Bond Formation Reaction Using Silyldihalomethylolithium

Hiroshi Shinokubo

1998
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Introduction and General Summary

Organic synthesis as a powerful art and methodology has been applied to the construction of manifold compounds. It opens up new avenues of research in medicinal and agricultural chemistry to develop alternative and better synthetic methods. In modern organic synthetic chemistry, it has been an obviously challenging target to achieve high degree of chemo-, regio-, and stereoselectivity in the reaction. In addition, it should be also important to pursue high efficiency in the construction of increasingly complex molecules. In order to attain this aim, a promising strategy is the one-pot reaction in which multiple carbon-carbon bonds are formed and several components are coupled in a single operation. Pharmaceuticals and agrochemicals are rarely prepared in a single process and are usually produced via an elaborate chain of separate reaction steps. In a one-pot reaction, however, solvents for the reaction and wastes created at the workup and purification stages can be reduced more efficiently than when each reaction step is carried out separately. Nowadays, various types of one-pot reactions have been explored. The key to the success of a one-pot reaction is to design carefully the reaction sequence so that the first step creates the conditions to set up the next reaction stage.

Rearrangement of a silyl group from carbon to oxygen, the Brook rearrangement for example, is driven by the affinity of silicon with negatively charged oxygen and produces a carbanionic species which could react with some electrophile to form a carbon-carbon bond (Scheme 1). This type of rearrangement of a silyl group can be used as the key step to prepare the next carbon-carbon formation reaction in a one-pot reaction. Thus, addition of a silicon containing carbanion to a carbonyl compound or epoxide would provide an oxyanion with concomitant formation of the first carbon-carbon bond and then would reproduce a carbanion which could undergo the next carbon-carbon bond formation via migration of the silicon atom. Actually, the sequential carbon-carbon bond formation reaction (tandem reaction) triggered by the anionic rearrangement of a silyl group from carbon to oxygen has recently attracted the attention of many chemists and has been regarded as a new
synthetic methodology for construction of organic molecules. Several examples of this type of tandem carbon-carbon bond formation reactions are reviewed as follows.

**Scheme 1**

![Scheme 1 Diagram](image)

Matsuda *et al.* have reported that 1,4-rearrangement of a silyl group occurred in the reaction of lithiated trimethylsilylacetonitrile with epoxides and the resultant carbanion added to another epoxide to afford \( \alpha \)-(1-hydroxyalkyl)-\( \gamma \)-lactones after hydrolytic workup.

**Scheme 2**

![Scheme 2 Diagram](image)

Ito and Murakami have reported that ((2,6-dimethylphenylimino)(trialkylsilyl)methyl)lithium in the reaction with aldehydes served as a synthetic equivalent of a carbonyl dianion via an anionic rearrangement of the trialkylsilyl group from the imino carbon to oxygen.

**Scheme 3**

![Scheme 3 Diagram](image)

A regiospecific generation of cyclic silyl enol ethers was conducted through the Brook
rearrangement followed by trapping of γ-siloxyallyllithium with iodomethane (Scheme 4). 5d

**Scheme 4**

\[
\begin{array}{c}
\text{HO-SiMe}_2\text{Ph} & \xrightarrow{n-\text{BuLi}} & \text{LiO-SiMe}_2\text{Ph} & \xrightarrow{\text{CH}_3\text{I}} & \text{OSiMe}_2\text{Ph} \\
\end{array}
\]

Some tandem carbon-carbon bond formation reactions using acylsilanes via the Brook rearrangement have been developed. 5e, h For example, a cyclopentanone derivative was formed in the reaction of α,β-unsaturated acylsilane with a lithium enolate of 3-methyl-2-butane (Scheme 5).

**Scheme 5**

\[
\begin{array}{c}
\end{array}
\]

Some silicone-induced cascade reactions initiated by the reaction of 1-lithio-1-trialkylsilyldithioacetal with epoxide were reported (Scheme 6). 5f, g Very recently, Smith III employed this type of sequential reaction using a dithio compound in a five-component coupling reaction (Scheme 7). 5i

**Scheme 6**

\[
\begin{array}{c}
\end{array}
\]
As shown above, the silicon migration-induced cascade reaction has now become a powerful synthetic method. In this thesis, these types of sequential carbon-carbon bond formation reactions using silyldihalomethylolithium will be focused on in Chapter 1 to Chapter 4. The starting silicon-substituted dihalomethylolithium is readily available by treatment of trialkylsilyldihalomethane with lithium diisopropylamide at \(-78^\circ C\). It is a kind of lithium carbenoid which is generally thermally unstable at a higher temperature than \(-90^\circ C\) and not easy to handle. This silyldihalomethylolithium is, however, stable below \(-40^\circ C\) owing to the stabilizing ability of the \(\alpha\)-carbanion by the silicon atom through \((p-\sigma^*)\pi\)-conjugation. Thus, utilization of silyldihalomethylolithium as a synthetic intermediate is fairly easy.

In Chapter 1, anionic 1,3-rearrangement of the trialkylsilyl group in the \(\beta\)-oxido silane derived from tert-butyldimethylsilyldihalomethylolithium and aldehydes or ketones is described. Although the Peterson olefin formation reaction via 1,2-elimination of \(\beta\)-oxidosilanes is generally rapid, no 1,1-
dihaloalkene was formed in this case.

**Scheme 9**

\[
\text{t-BuMe}_2\text{SiClBr}_2 + \text{PhCHO} \rightarrow \text{PhLi}_2\text{OSiMe}_2\text{t-BuClBr} \rightarrow \text{PhLi}_2\text{OSiMe}_2\text{t-BuClBr}
\]

One-pot synthesis of \( R^1\text{CH}(\text{OSiMe}_2\text{t-Bu})CX_2\text{CH(OH)}R^2 \) (X=Cl, Br) by sequential addition of two different aldehydes (\( R^1\text{CHO} \) and \( R^2\text{CHO} \)) starting from tert-butyldimethylsilyldihalomethyllithium was achieved. Use of HMPA as a co-solvent was the key to controlling the reaction. Only in the case of HMPA, a three-component coupled product was obtained along with a minimal amount of a diol derivative \( R^1\text{CH}(\text{OSiMe}_2\text{t-Bu})CX_2\text{CH(OH)}R^1 \) which was yielded from tert-butyldimethylsilyldihalomethyllithium with two equivalents of the first aldehyde (\( R^1\text{CHO} \)).

**Scheme 10**

\[
\text{t-BuMe}_2\text{SiClCH}_2\text{Cl} + \text{RCHO} \rightarrow \text{R}^1\text{Li}_2\text{OSiMe}_2\text{t-BuCl} \rightarrow \text{R}^2\text{CHO} + \text{R}^1\text{Li}_2\text{OSiMe}_2\text{t-BuCl}
\]

This type of rearrangement of a silyl group was also observed in the reaction of tert-butyldimethylsilyldihalomethyllithium with epoxide. The sequential reaction was carried out as shown in Scheme 11.

**Scheme 11**

\[
\text{SiClLiX}_2 + \text{O} \rightarrow \text{SiLiX}_2 + \text{HMPA} \rightarrow \text{Electrophile} \rightarrow \text{SiLiX}_2 + \text{O}
\]

\( Si = \text{t-BuMe}_2\text{Si} \)

Chapter 2 further deals with the similar type of silicon-induced cascade carbon-carbon bond formation reaction as discussed in Chapter 1. Treatment of alkyl benzoate, formate, or trifluoroacetates with tert-butyldimethylsilyldihalomethyllithium gave alkyl tert-butyldimethylsilyl mixed acetals in good yields via anionic 1,3-rearrangement of a silyl group from carbon to a negatively charged oxygen atom.
High degree of asymmetric induction was observed in the reaction of esters of a chiral secondary alcohol with silyldihalomethyllithium. In this reaction, a planar $sp^2$ carbon of an ester carbonyl group was converted into a tetrahedral $sp^3$ carbon center.

Scheme 13

One-pot synthesis of a three-component coupling product $R^1C(OR^2)(OSiMe_2-t-Bu)CX_2E'$ ($X=\text{Cl, Br}$) by sequential addition of an ester ($R^1C_2R^2$) and the second electrophile was achieved starting from tert-butyldimethylsilyldihalomethyllithium in the presence of HMPA as a co-solvent.

Scheme 14

The reaction of the mixed acetals thus obtained with allylsilane$^{12}$ in the presence of Lewis acid afforded allylated ethers in good yields.

A formation of $\alpha$-silylketones$^{13}$ and acylsilanes$^{14}$ from aldehydes and ketones with silyldibromomethyllithium is described in Chapter 3. An addition of benzaldehyde to an ethereal solution of tert-butyldimethylsilyldibromomethyllithium provided an $\alpha$-bromo-$\alpha$-silyl ketone via 1,2-hydride migration$^{15}$ under the departure of bromide in the intermediary $\beta$-oxidesilane. Surprisingly, the use of ketone instead of aldehyde afforded an $\alpha$-bromoacylsilane through a bromo silyl epoxide intermediate. In this case, an addition of TMEDA increased the yield of the product.
Further treatment of the α-bromo-α-silyl ketone with butyllithium afforded a lithium enolate¹⁶ which provided β-hydroxy-α-silyl ketone upon treatment with aldehyde in ether. The enolate gave α,β-unsaturated ketone or monosilyl ether of 2-acyl-1,3-diol in THF instead of ether via a lithium enolate resulted from the anionic 1,3-rearrangement of the silyl group³ from carbon to oxygen.

The use of isopropylmagnesium bromide in place of butyllithium also resulted in a formation of the corresponding magnesium enolate¹⁶ which gave β-hydroxy-α-silylalkyl ketone in high yield upon treatment with aldehydes.
Treatment of 2-(allyldimethylsiloxy)-1,1-dibromoalkane, which was easily prepared by the sequential reaction of (allyldimethylsilyl)dibromomethyllithium with aldehyde (Scheme 18) described in Chapter 1, with tributyltin hydride in the presence of a catalytic amount of triethylborane\(^{17}\) afforded 1-oxa-2-silacycloheptane derivative selectively in good yield via a \(7\text{-}\text{endo}\) mode radical cyclization reaction.\(^{18}\) On the other hand, cyclization of vinyldimethylsiloxy derivative resulted in a formation of 3-methyl-1-oxa-2-silacyclopentane selectively through a \(5\text{-}\text{exo}\) mode cyclization. (Scheme 19)

\begin{center}
\textbf{Scheme 18}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{scheme18}
\end{center}

\begin{center}
\textbf{Scheme 19}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{scheme19}
\end{center}

A nucleophilic addition of allyl- or vinyldiphenylsilanol\(^{19}\) to ethyl vinyl ether in the presence of \textit{N}-iodosuccinimide\(^{20}, 21\) provided 1-(allyldiphenylsiloxy)- or 1-(diphenylvinylsiloxy)-1-ethoxy-2-iodoethane in good yield, which was also converted into a seven-membered or a five-membered ring product upon treatment with tributyltin hydride.

\begin{center}
\textbf{Scheme 20}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{scheme20}
\end{center}
Allylsilanol can be regarded as a synthon of allyl alcohol through oxidative cleavage\textsuperscript{22} of the Si-C bond. In the case of allylic alcohol, the radical cyclization of iodoether derived from allyl alcohol afforded only a five-membered cyclic ether\textsuperscript{23} which was further converted into a branched alkenol selectively upon treatment with allyltrimethylsilane in the presence of titanium tetrachloride. In contrast, in the case of allylsilanol, cyclization of the iodo silyl ether followed by subsequent allylation and oxidation provided a linear alkenol exclusively. Therefore, two isomeric branched and linear alkenols could be prepared selectively by the choice of allyl alcohol or allylsilanol with alkyl vinyl ether.

\textbf{Scheme 21}

\textit{Allyl alcohol}
References and Notes


4. Tandem transformations initiated by the migration of a silyl group have been reviewed. Jankowski, P.; Raubo, P.; Wicha, J. Synlett. 1994, 985.


### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>Bp</td>
<td>boiling point</td>
</tr>
<tr>
<td>bs</td>
<td>broad singlet</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>ca.</td>
<td>circa (about)</td>
</tr>
<tr>
<td>calcld</td>
<td>calculated</td>
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<tr>
<td>Co.</td>
<td>company</td>
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<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>DIBAL-H</td>
<td>diisobutylaluminum hydride</td>
</tr>
<tr>
<td>DME</td>
<td>dimethoxyethane</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>ee</td>
<td>enantiomeric excess</td>
</tr>
<tr>
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<td>edition</td>
</tr>
<tr>
<td>equiv</td>
<td>equivalent</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>et al.</td>
<td>et alii (and others)</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>HMPA</td>
<td>hexamethylphosphoric triamide</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz (s⁻¹)</td>
</tr>
<tr>
<td>ibid</td>
<td>ibidem (in the same space)</td>
</tr>
<tr>
<td>IR</td>
<td>infrared (spectrum)</td>
</tr>
<tr>
<td>LAH</td>
<td>lithium aluminum hydride</td>
</tr>
<tr>
<td>LDA</td>
<td>lithium diisopropylamide</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>mCPBA</td>
<td>m-chloroperbenzoic acid</td>
</tr>
<tr>
<td>M</td>
<td>molar (1 M = 1 mol dm⁻³)</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>min</td>
<td>minute(s)</td>
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<tr>
<td>ml</td>
<td>1 ml = 1 cm³</td>
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<tr>
<td>mmol</td>
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<tr>
<td>Mp</td>
<td>melting point</td>
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<tr>
<td>NMR</td>
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<tr>
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<td>reference</td>
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<tr>
<td>Rf</td>
<td>relative mobility</td>
</tr>
<tr>
<td>r.t.</td>
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</tr>
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<td>temp</td>
<td>temperature</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>Torr</td>
<td>1 Torr = 133.322 Pa</td>
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<tr>
<td>TMEDA</td>
<td>N,N,N',N'-tetramethylethylenediamine</td>
</tr>
<tr>
<td>TBAF</td>
<td>tetra-n-butyrammonium fluoride</td>
</tr>
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Instrumentation and Materials

Distillation of the products was performed by the use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. Melting points were obtained on a Yanako MP-50929 melting point apparatus and are uncorrected. $^1$H NMR (300 MHz) and $^{13}$C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer, CDCl$_3$ was used as a solvent unless otherwise noted, and chemical shifts being given in $\delta$ value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merk Silica-gel 60F$_{254}$. Column chromatography was done with silica-gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification, however aldehydes were distilled and stocked under argon. Dichloromethane, DMF and DMSO was dried with molecular sieves 4A. Toluene, benzene, hexane, and diethyl ether were dried over slices of sodium. Dimethoxyethane (DME) was distilled from sodium benzophenone ketyl and stored over slices of sodium. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use.
One-pot synthesis of $R^1CH(OSiMe_2-t-Bu)CX_2CH(OH)R^2$ ($X=\text{Cl, Br}$) by successive addition of two different aldehydes ($R^1\text{CHO}$ and $R^2\text{CHO}$) has been achieved starting from tert-butyldimethylsilyldihalomethylithium. Treatment of a THF solution of the title carbanion ($X=\text{Cl}$) with $p$-MeOC$_6$H$_4\text{CHO}$ or $n$-BuCHO followed by an addition of HMPA and benzaldehyde gave the corresponding 1,3-diol monosilyl ether in 83% or 45% yield, respectively. The use of oxirane in place of aldehyde as the first electrophile followed by addition of benzaldehyde provided 1,4-diol monosilyl ether.
(1) Reaction of tert-butyldimethylsilyldihalomethyllithium with aldehydes followed by 1,3-rearrangement of silyl group from carbon to oxide.

Intramolecular 1,2-rearrangement of silicon from carbon to negatively charged oxygen is well known as Brook rearrangement\(^1\) and many examples have been reported\(^2\) for the construction of organic molecules. In contrast, 1,3-rearrangement of silicon from carbon to β-oxyanion is rare since olefin formation via 1,2-elimination of β-oxidosilanes is rapid. The author has found a synthetic method for formation of two carbon-carbon bonds in one-pot based on organosilicon chemistry which involves an unprecedented 1,3-rearrangement of silicon.\(^3\), \(^4\), \(^5\)

tert-Butyl(dibromomethyl)dimethylsilane (1a)\(^6\) was deprotonated by treatment with lithium diisopropylamide in DME-THF (2:1) at \(-78^\circ\text{C}\) to give tert-butyldimethylsilyldibromomethyl-lithium (2a). Treatment of 2a with benzaldehyde (2.4 eq) lead to 1,3-diol monosilyl ether 5 (1:2 adduct, 72% yield) via the intermediacy of lithium carbenoid 4 along with 1:1 adduct (PhCH(OSiMe\(_2\)-t-Bu)CHBr\(_2\), 6, 22%) (Scheme 1). This was a surprising result since the β-oxidosilane 3, by analogy with the examples of Me\(_3\)SiCH(Li)Cl\(^7\) and Me\(_3\)SiC(Li)(SR)\(_2\),\(^8\) would have been expected to eliminate lithium bromide or lithium tert-butyldimethylsilanoloxide to give α,β-epoxy silane or alkene rather than 1,3-diol monosilyl ether 5 (Scheme 2).

**Scheme 1**

\[
\begin{align*}
\text{t-BuMe}_2\text{SiCHBr}_2 & \xrightarrow{\text{LDA}} \text{t-BuMe}_2\text{SiCBr}_2 \quad \text{PhCHO} \quad \text{PhCHO} \\
& \quad \text{1:2 adduct, 72% yield} \quad \text{1:1 adduct, 22%}
\end{align*}
\]
The distribution of the products (1:1 adduct to 1:2 adduct) depends heavily on the nature of the substituent on the silicon. The respective dibromomethylsilane and the yields of the corresponding products (1:1 adduct and 1:2 adduct) in the reaction of $R_3SiClLiBr_2$ (1.2 mmol) with PhCHO (1.0 mmol) in THF were as follows: $Me_3SiClBr_2$, 10% 29%, 0%; $t-BuMe_2SiClBr_2$, 68%, 22%; $i-Pr_3SiClBr_2$, 18%, 25%; Ph$_2$Me$SiClBr_2$, 36%, 49%; Ph$_3$SiClBr$_2$, 18%, 74%. Thus, Ph$_3$SiClBr$_2$ was the best reagent for the preparation of 1,3-diol monosilyl ether (PhCH(OSiR$_3$)CBr$_2$CH(OH)Ph). The rate of rearrangement was also sensitive to the reaction solvent. In ether, instead of DME-THF, rearrangement of silicon (3 → 4) did not proceed and the reaction of tert-butyldimethylsilyldibromomethyl lithium (2a) with benzaldehyde gave an adduct PhCH(OH)CBr$_2$(SiMe$_2$-t-Bu), 7 in 77% yield after workup (1 N HCl-ether). Addition of methanol (10 eq) before workup to the reaction mixture provided the rearranged product 6 in 87% yield. In the same way, the reaction between 2a and heptanal, cinnamaldehyde, or acetophenone provided the corresponding rearranged silyl ether R$_1$R$_2$C(OSiMe$_2$-t-Bu)CBr$_2$ in 71%, 75% or 65% yield, respectively, by the addition of methanol before workup. Rearrangement by an addition of methanol might proceed as follows: (1) Protonation of 3 by methanol gives 7 and lithium methoxide, (2) lithium methoxide can deprotonate 7 to regenerate 3 and an equilibrium mixture of 3 and lithium methoxide is obtained, (3) equilibration shifts via C→O rearrangement of silyl group to form dibromoalkyllithium 4, and (4) finally protonation of 4 by methanol affords the rearranged product 6 (Scheme 3). This assumption was supported by the following two facts. The use of MeOD gave PhCH(OSiMe$_2$-t-Bu)CDBr$_2$. When the carbinol 7 (0.5 mmol) was treated with a catalytic amount of CH$_3$OLi (0.1 mmol) in ether (3 ml)-methanol (5.0 mmol), the carbinol was
transformed rapidly to the alkoxy-isilane 6 in 90% yield.

**Scheme 3**

\[
\begin{align*}
\text{Ph} & \quad \text{SiMe}_2\text{t-Bu} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{OLi} & \quad \text{Ph} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{SiMe}_2\text{t-Bu} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
+ \quad \text{CH}_3\text{OH} & \quad \text{Ph} \\
\text{SiMe}_2\text{t-Bu} & \quad \text{Ph} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{CH}_3\text{OLi} & \quad \text{CH}_3\text{OH} \\
\end{align*}
\]

A crossover experiment was conducted to demonstrate the intramolecularity of the migration process. Upon treatment of a mixture of 7 and 8 with a catalytic amount of CH$_3$OLi in Et$_2$O-MeOH at -78 °C for 1 h, only two products (6 and 9) were isolated. No crossover products could be observed (Scheme 4).

**Scheme 4**

\[
\begin{align*}
\text{Ph} & \quad \text{SiMe}_2\text{t-Bu} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{Si} & \quad \text{n-Bu} \\
\text{Li} & \quad \text{Ph} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{SiMe}_2\text{t-Bu} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{Si} & \quad \text{Pr}_3 \\
\text{Li} & \quad \text{Ph} \\
\text{Et}_2\text{O} / \text{CH}_3\text{OH} & \quad \text{Et}_2\text{O} / \text{CH}_3\text{OH} \\
-78 ^\circ \text{C} & \quad 1 \text{ h} \\
\text{Ph} & \quad \text{SiMe}_2\text{t-Bu} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{H} & \quad \text{H} \\
\text{CH}_3\text{OLi} & \quad \text{CH}_3\text{OLi} \\
\text{OH} & \quad \text{OH} \\
\end{align*}
\]

Treatment of 6 with lithium diisopropylamide in THF provided carbanion 4 which reacted with an electrophile such as methyl iodide, allyl bromide, benzaldehyde, pentanal, or cyclohexanone to give the corresponding adduct in 97% (10a), 97% (10b), 95% (5), 85% (10c), or 70% (10d) yield, respectively (Scheme 5).

**Scheme 5**

\[
\begin{align*}
\text{Ph} & \quad \text{SiMe}_2\text{t-Bu} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{OLi} & \quad \text{LDA} \\
\text{THF} & \quad \text{THF} \\
\text{Ph} & \quad \text{SiMe}_2\text{t-Bu} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{Li} & \quad \text{Electrophile} \\
\end{align*}
\]

Then we turned our attention toward one-pot synthesis of 10 by successive addition of two different electrophiles to tert-butyldimethylsilyldibromomethyl lithium (2a). It was anticipated that an addition of DME and second electrophile to the reaction mixture of 2a and benzaldehyde in
ether would provide 10 in one-pot. However, an addition of DME and methyl iodide or 4-methoxybenzaldehyde as a second electrophile gave no desired product and only 6 was isolated in 50–55% yield. An addition of HMPA instead of DME afforded an adduct 10 (E'=Me) in 53% yield upon successive treatment with Mel as the second electrophile. Fortunately, tert-butyldimethylsilyldichloromethyl lithium (2b), generated from tert-butyl(dichloromethyl)dimethylsilane (1b) and LDA, proved to be more effective than dibromo analogue 2a for the purpose. In this case, the migration of silicon in the adduct 11, derived from 2b and aldehyde such as PhCHO, PhCH=CHCHO, or n-BuCHO, did not proceed in THF. An addition of HMPA to the reaction mixture, however, caused the rearrangement providing a carbanion which reacted with various second electrophiles effectively (Table 1).

Table 1. One-pot synthesis of RCH(OSiMe2-t-Bu)CCl2E' from 1b

<table>
<thead>
<tr>
<th>R</th>
<th>Electrophile</th>
<th>E'</th>
<th>Yield of 12 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Ph</td>
<td>MeI</td>
<td>Me</td>
</tr>
<tr>
<td>b</td>
<td>Ph</td>
<td>CH2=CHCH2Br</td>
<td>CH2=CHCH2</td>
</tr>
<tr>
<td>c</td>
<td>PhCH=CH</td>
<td>MeI</td>
<td>Me</td>
</tr>
<tr>
<td>d</td>
<td>n-Pr</td>
<td>CH2=CHCH2Br</td>
<td>CH2=CHCH2</td>
</tr>
<tr>
<td>e</td>
<td>4-MeO-C6H4</td>
<td>PhCHO</td>
<td>PhCH(OH)</td>
</tr>
<tr>
<td>f</td>
<td>PhCH=CH</td>
<td>PhCHO</td>
<td>PhCH(OH)</td>
</tr>
<tr>
<td>g</td>
<td>n-Bu</td>
<td>PhCHO</td>
<td>PhCH(OH)</td>
</tr>
</tbody>
</table>

a) The products consist of two monosilyl ethers such as PhCH(OH)CCl2CH(OSiMe2-t-Bu)C6H4-p-OMe and PhCH(OSiMe2-t-Bu)CCl2CH(OH)C6H4-p-OMe. Each isomer was a mixture of two diastereomers ((1R*,3R*):(1R*,3S*) = 4:6 or 1:1).

Dichlorides 12 were easily reduced by n-Bu3SnH-Et3B13 to give the corresponding
methylene compounds. For instance, treatment of 12a (0.6 mmol) with n-Bu₃SnH (1.75 mmol) in the presence of Et₃B (0.7 mmol) in hexane at 80 °C afforded PhCH(OSiMe₂-t-Bu)CH₂CH₃ in 97% yield which was converted into 1-phenyl-1-propanol (13) by treatment with n-Bu₄NF. Thus, tert-butyldimethylsilyldichloromethyllithium can be regarded as a synthon of dichloromethylene dianion (CCl₂^-) or methylene dianion (CH₂^-) (Scheme 6).¹⁴

Scheme 6

\[
\begin{align*}
\text{OSiMe}_2\text{t-Bu} & \quad \text{OSiMe}_2\text{t-Bu} \\
\text{Ph} & \quad \text{OH}
\end{align*}
\]

1. "CH₃

n-Bu₃SnH - Et₃B \quad n-Bu₄NF

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
12a & \quad 13
\end{align*}
\]

(2) Reaction of tert-butyldimethylsilyldihalomethyllithium with oxiranes followed by 1,4-rearrangement of silyl group from carbon to oxide.

The new method described in Section (1) was applied to the reaction with oxiranes. Treatment of 2-phenyloxirane (14a) with tert-butyldimethylsilylbromomethyllithium (2a) in ether at -40 °C¹⁵ provided 3,3-dibromo-3-tert-butyldimethylsilyl-1-phenyl-1-propanol (16a) in 32% yield. Other oxiranes such as 14b or 14c also gave the corresponding alcohol 16b or 16c in 51% or 80% yield, respectively (Scheme 6). The reaction did not proceed at -78 °C in contrast to the one with aldehyde which reacted easily at that temperature. Di-substituted oxiranes such as 1,2-epoxycyclopentane and 2-methoxymethyl-3-phenyloxirane did not react with 2a and oxiranes were recovered unchanged even after prolonged reaction period. 2-Phenylloxetane and 2-methoxy-methyloxolane were also recovered upon treatment with 2a.

Scheme 7

\[
\begin{align*}
t-\text{BuMe}_2\text{SiCBr}_2 & \quad 14 \\
\text{Li} & \quad \text{Et}_2\text{O} \\
\text{Si} = t-\text{BuMe}_2\text{Si}
\end{align*}
\]

Then we studied the 1,4-rearrangement¹⁶ of silyl group from carbon to oxide in the adduct
and found that the rate of the rearrangement depended heavily on the reaction solvent as in the case of the adduct 3 generated from 2a and aldehyde. In ether, migration did not take place. However, change of the solvent from ether to THF facilitated the 1,4-rearrangement of silyl group. For instance, treatment of 1,2-epoxypropane with 2a in THF at -40 °C gave 1,1-dibromo-1-deuterio-3-tert-butyldimethylsiloxybutane in 83% yield (81% D) after quenching with MeOD. Various oxiranes provided the corresponding products as shown in Table 2. Among them, ethylene oxide gave the best results and the reaction with 2a afforded 3,3-dibromo-1-siloxypropane almost quantitatively. t-Butyldimethylsilyldichloromethylithium (2b) reacted with oxiranes equally effectively as 2a.

Table 2. Reaction of tert-butyldimethylsilyldihalomethyllithium 2 with oxiranes in THF

<table>
<thead>
<tr>
<th>X</th>
<th>R</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Br CH₃</td>
<td>83 (81%D)⁹⁹</td>
</tr>
<tr>
<td>b</td>
<td>Br H</td>
<td>98</td>
</tr>
<tr>
<td>c</td>
<td>Br Ph</td>
<td>65</td>
</tr>
<tr>
<td>d</td>
<td>Br CH₂=CH</td>
<td>63</td>
</tr>
<tr>
<td>e</td>
<td>Cl CH₃</td>
<td>80</td>
</tr>
<tr>
<td>f</td>
<td>Cl H</td>
<td>96</td>
</tr>
<tr>
<td>g</td>
<td>Cl Ph</td>
<td>62 (83%D)⁹⁹</td>
</tr>
<tr>
<td>h</td>
<td>Cl ClCH₂</td>
<td>78</td>
</tr>
</tbody>
</table>

a) MeOD was used instead of MeOH
Dihaloalkyllithium 18, regenerated by 1,4-rearrangement of silyl group in THF in the presence of HMPA smoothly reacted with second electrophiles to give the corresponding adducts in good yields. The representative results are summarized in Table 3. The use of isopropyl formate afforded 2,2-dichloro-4-siloxybutanal.

Table 3. One-pot synthesis of RCH(OSiMe₂-t-Bu)CH₂CX₂E' from 2

<table>
<thead>
<tr>
<th>X</th>
<th>R</th>
<th>Electrophile</th>
<th>E'</th>
<th>Yield of 19 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Br</td>
<td>CH₃I</td>
<td>CH₃</td>
<td>60</td>
</tr>
<tr>
<td>b</td>
<td>Cl</td>
<td>CH₃I</td>
<td>CH₃</td>
<td>68</td>
</tr>
<tr>
<td>c</td>
<td>Cl</td>
<td>CH₃I</td>
<td>PhCH(OH)</td>
<td>65</td>
</tr>
<tr>
<td>d</td>
<td>Cl</td>
<td>H</td>
<td>CH₃I</td>
<td>80</td>
</tr>
<tr>
<td>e</td>
<td>Cl</td>
<td>H</td>
<td>HCOOiPr</td>
<td>56</td>
</tr>
</tbody>
</table>

Finally, we examined the relative reaction rate between 1,3-rearrangement and 1,4-rearrangement. A catalytic amount of tert-BuOK was added to a mixture of 7 and 16a (7:16a = 1:1) in CD₃OD. The reaction mixture was monitored by ¹H NMR (PhCH vs PhCH(OSi)). Whereas 1,3-rearrangement completed within 5 min, 1,4-rearrangement was slow and took 30 min to complete (Figure 1).
Figure 1

\[ \text{Ph} \text{Br}_3 \text{Si} + \text{Ph} \text{Br}_3 \text{Si} \xrightarrow{t-\text{BuOK}} \text{CD}_3\text{OD} \rightarrow \text{Ph} \text{Br}_3 \text{Si}^{\text{OSi}} \text{D} + \text{Ph} \text{Br}_3 \text{Si}^{\text{OSi}} \text{Br}_3 \text{Si} \]

\( Si = t-\text{BuMe}_2\text{Si} \)

![Graph showing conversion over time for 1,4- and 1,3-rearrangements.](image-url)

- △ - 1,4-Rearrangement
- ⧫ - 1,3-Rearrangement

Time (min)
Experimental

*tert*-Butyl(dibromomethyl)dimethylsilane (1a): Bp 60 °C (1 Torr); IR (neat) 2926, 2856, 1464, 1364, 1252, 839, 824, 779 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.25 (s, 6H), 1.02 (s, 9H), 5.27 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) –6.84, 17.94, 27.30, 34.11. Found: C, 29.22; H, 5.76%. Calcd for C\(_7\)H\(_{16}\)Br\(_2\)Si: C, 29.18; H, 5.60%.

*tert*-Butyl(dichloromethyl)dimethylsilane (1b): Bp 70 °C (20 Torr); IR (CH\(_2\)Cl\(_2\)) 2930, 2856, 1465, 1365, 1264, 832, 785, 740, 701 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.21 (s, 6H), 1.00 (s, 9H), 5.41 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) –7.95, 17.42, 26.97, 62.27. Analytically pure sample could not be obtained because of its sublimation character.

General Procedure for the Reaction of *tert*-Butyldimethylsilyldibromomethyl lithium (2a) with aldehydes. An ethereal solution (2 ml) of *tert*-butyl(dibromomethyl)dimethylsilane (0.29 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in Et\(_2\)O (3 ml) at –78 °C under argon atmosphere. After the mixture was stirred for 1 h at –78 °C, benzaldehyde (0.13 g, 1.2 mmol) in Et\(_2\)O (1 ml) was added and the reaction mixture was stirred for 20 min at –78 °C. The mixture was quenched with methanol (1 ml). Extractive workup (1M HCl and hexane) followed by purification by silica-gel column chromatography gave 1,1-dibromo-2-(*tert*-butyldimethylsiloxy)-2-phenylethane (6) in 87% yield: Bp 90 °C (1.0 Torr); IR (neat) 2926, 2852, 1455, 1362, 1255, 1135, 1094, 857, 836, 778, 699 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.13 (s, 3H), 0.15 (s, 3H), 0.91 (s, 9H), 4.94 (d, \(J = 5.3\) Hz, 1H), 5.63 (d, \(J = 5.3\) Hz, 1H), 7.30–7.45 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) –4.94, –4.68, 18.25, 25.69, 51.56, 79.90, 127.48, 128.07, 128.61, 139.75. Found: C, 42.78; H, 5.79%. Calcd for C\(_{14}\)H\(_{22}\)Br\(_2\)OSi: C, 42.65; H, 5.62%.

2,2-Dibromo-2-(*tert*-butyldimethylsilyl)-1-phenylethanol (7): Bp 110 °C (0.5 Torr); IR (neat) 3546, 3448, 2956, 2854, 1464, 1365, 1250, 1027, 821, 712 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.35
2,2-Dibromo-1-(tert-butyldimethylsiloxy)-1-phenylpropane (10a): A THF (2 ml) solution of 2,2-dibromo-1-(tert-butyldimethylsiloxy)-1-phenylethane (6, 0.39 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in THF (3 ml) at -78 ºC. After the mixture was stirred for 15 min, methyl iodide (0.09 ml, 1.5 mmol) in THF (1 ml) was added and the reaction mixture was stirred for 1 h at -78 ºC. Extractive workup followed by silica-gel column chromatography gave title compound 10a (0.40 g) in 97% yield; Bp 90 ºC (1.0 torr); IR (neat) 2926, 2854, 1454, 1255, 1099, 1071, 858, 777, 700 cm⁻¹; ¹H NMR (CDCl₃) δ -0.26 (s, 3H), 0.15 (s, 3H), 0.91 (s, 9H), 2.40 (s, 3H), 4.92 (s, 1H), 7.30–7.55 (m, 5H); ¹³C NMR (CDCl₃) δ -5.12, -4.65, 18.20, 25.73, 35.60, 72.78, 83.80, 127.40, 128.48, 129.23, 138.64. Found: C, 43.90; H, 6.02%. Calcd for C₁₅H₂₄Br₂O₂Si: C, 44.13; H, 5.93%.

4,4-Dibromo-5-(tert-butyldimethylsiloxy)-5-phenyl-1-pentene (10b): Bp 105 ºC (1.0 Torr); IR (neat) 3078, 3028, 2926, 2854, 1643, 1455, 1361, 1257, 1098, 923, 855, 777, 700 cm⁻¹; ¹H NMR (CDCl₃) δ -0.29 (s, 3H), 0.14 (s, 3H), 0.92 (s, 9H), 3.00 (ddt, J = 15.0, 6.6, 1.3 Hz, 1H), 3.08 (ddt, J = 15.0, 6.6, 1.3 Hz, 1H), 4.98 (s, 1H), 5.20 (ddt, J = 16.8, 1.7, 1.3 Hz, 1H), 5.29 (ddt, J = 10.2, 1.7, 1.3 Hz, 1H), 6.08 (ddt, J = 16.8, 10.2, 6.6 Hz, 1H), 7.30–7.60 (m, 5H); ¹³C NMR (CDCl₃) δ -5.06, -4.57, 18.20, 25.75, 48.50, 79.13, 83.29, 119.65, 127.39, 128.55, 129.58, 133.93, 138.59. Found: C, 46.73; H, 6.01%. Calcd for C₁₇H₂₆Br₂O₂Si: C, 47.02; H, 6.03.

(1R*,3R*)-2,2-Dibromo-1,3-diphenyl-3-(tert-butyldimethylsiloxy)propanol (5): Mp 92.0–93.0 ºC; IR (CH₂Cl₂) 3550, 3432, 3028, 2926, 2852, 1471, 1454, 1389, 1264, 1199, 1099, 1070, 837, 737, 700 cm⁻¹; ¹H NMR (CDCl₃) δ -0.24 (s, 3H), 0.21 (s, 3H), 0.95 (s, 9H), 4.55 (bd, J = 2.8 Hz, 1H), 5.08 (d, J = 2.8 Hz, 1H), 5.40 (s, 1H), 7.30–7.70 (m, 10H); ¹³C NMR (CDCl₃) δ
-5.34, -4.82, 18.11, 25.69, 77.32, 80.93, 84.01, 127.11, 127.63, 128.60, 128.90, 129.80, 137.78, 138.70. Found: C, 50.63; H, 5.63%. Calcd for C$_{21}$H$_{28}$Br$_2$O$_2$Si: C, 50.41; H, 5.64%.

\[ (IR^{*},3S^{*})-2,2\text{-Dibromo-1,3-diphenyl-3-}(\text{tert\text{-}butyldimethylsiloxy})\text{propanol (5')}: \]
\[ \text{M p} \]
120–121 °C; IR (CH$_2$Cl$_2$) 3542, 3050, 2926, 2854, 1454, 1265, 1113, 863, 838, 732, 701 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ –0.29 (s, 3H), 0.17 (s, 3H), 0.96 (s, 9H), 3.10 (d, $J = 5.4$ Hz, 1H), 4.53 (d, $J = 5.4$ Hz, 1H), 5.27 (s, 1H), 7.30–7.75 (m, 10H); $^{13}$C NMR (CDCl$_3$) $\delta$ –4.91, –4.28, 18.27, 25.83, 78.65, 81.35, 85.94, 127.33, 127.59, 128.74, 129.43, 138.61, 138.85. Found: C, 50.24; H, 5.64%. Calcd for C$_{21}$H$_{28}$Br$_2$O$_2$Si: C, 50.41; H, 5.64%. The physical and spectral data of 5 and 5’ were identical with those of the respective authentic sample.$^{18}$

\[ (IR^{*},3R^{*})-2,2\text{-Dibromo-1-phenyl-1-}(\text{tert\text{-}butyldimethylsiloxy})\text{-3-heptanol (10e)}: \]
\[ \text{Bp} \]
115 °C (0.5 Torr); IR (neat) 3464, 2952, 2854, 1459, 1379, 1255, 1200, 1098, 1072, 867, 838, 778, 699 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ –0.28 (s, 3H), 0.14 (s, 3H), 0.89 (s, 9H), 0.92 (t, $J = 7.3$ Hz, 3H), 1.10–2.20 (m, 6H), 3.36 (bs, 1H), 3.81 (bs, 1H), 5.23 (s, 1H), 7.30–7.60 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ –5.34, –4.80, 14.04, 18.07, 22.52, 25.65, 28.09, 34.92, 75.70, 82.07, 84.95, 127.37, 128.67, 129.79, 138.19. Found: C, 47.75; H, 6.74%. Calcd for C$_{19}$H$_{32}$Br$_2$O$_2$Si: C, 47.51; H, 6.71%.

\[ (IR^{*},3S^{*})-2,2\text{-Dibromo-1-phenyl-1-}(\text{tert\text{-}butyldimethylsiloxy})\text{-3-heptanol (10e')}: \]
\[ \text{Bp} \]
115 °C (0.5 Torr); IR (neat) 3464, 3446, 3030, 2926, 2859, 1459, 1362, 1253, 1120, 838, 777, 699 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ –0.31 (s, 3H), 0.13 (s, 3H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.95 (s, 9H), 1.20–2.20 (m, 7H), 3.23 (t, $J = 10.0$ Hz, 1H), 5.19 (s, 1H), 7.30–7.65 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ –5.04, –4.39, 14.03, 18.22, 22.58, 25.78, 28.10, 34.65, 76.79, 80.19, 90.42, 127.48, 128.46, 129.26, 138.56. Found: C, 47.68; H, 6.72%. Calcd for C$_{19}$H$_{32}$Br$_2$O$_2$Si: C, 47.51; H, 6.71%.

The assignment of the stereochemistry of 10e and 10e’ is based on NOE experiments.
1-((tert-Butyldimethylsiloxy)-2,2-dibromo-2-(1-hydroxycyclohexyl)-1-phenylpropane (10d): Mp 100-101 °C; IR (CH₂Cl₂) 3474, 2930, 2856, 1452, 1265, 1051, 837, 738, 701 cm⁻¹; ¹H NMR (CDCl₃) δ –0.46 (s, 3H), 0.09 (s, 3H), 0.92 (s, 9H), 1.10–2.30 (m, 10H), 3.97 (bs, 1H), 5.28 (s, 1H), 7.30–7.80 (m, 5H); ¹³C NMR (CDCl₃) δ –4.74, –4.05, 18.04, 21.76, 22.24, 25.55, 25.81, 31.50, 35.50, 79.56, 80.98, 126.90, 128.88, 131.07, 138.96. Found: C, 48.84; H, 6.81%. Calcd for C₂₀H₃₂Br₂O₂Si: C, 48.79; H, 6.55%.

General Procedure for One-pot Synthesis of 12 (RCH(OSiMe₂-t-Bu)CCI₂E') from 1b. A THF (2 ml) solution of tert-butyl(dichloromethyl)dimethylsilane (1b, 0.24 g, 1.2 mmol) was added to a solution of lithium diisopropylamide (1.4 mmol) in THF (3 ml) at –78 °C under argon atmosphere. After the mixture was stirred for 1 h at –78 °C, benzaldehyde (0.11 g, 1.0 mmol) in THF (1 ml) was added and the reaction mixture was stirred for 20 min at –78 °C. Methyl iodide (1.5 mmol) in THF (1 ml) and then HMPA (0.24 ml, 1.4 mmol) in THF (1 ml) were added successively to the reaction mixture and the resulting mixture was allowed to warm to room temperature over 5 h. Extractive workup (1M HCl and hexane) followed by purification by silica-gel column chromatography gave 1-((tert-butyldimethylsiloxy)-2,2-dichloro-1-phenylpropane 12a (0.23 g) in 71% yield. When aldehydes were used as the second electrophile, the reaction mixture was allowed to warm to –20 °C and kept there for 1 h before workup. 12a: Bp 90 °C (1.0 Torr); IR (neat) 2928, 2884, 2854, 1455, 1375, 1254, 1105, 1076, 861, 836, 777, 699 cm⁻¹; ¹H NMR (CDCl₃) δ –0.21 (5, 3H), 0.12 (s, 3H), 0.90 (s, 9H), 2.04 (s, 3H), 4.92 (s, 1H), 5.19 (dd, J = 17.1, 1.4 Hz, 1H), 5.27 (dd, J = 10.2, 1.4 Hz, 1H).

5-((tert-Butyldimethylsiloxy)-4,4-dichloro-5-phenyl-1-pentene (12b): Bp 95 °C (1.0 Torr); IR (neat) 3080, 2950, 2854, 1644, 1455, 1254, 1105, 930, 858, 837, 777, 699 cm⁻¹; ¹H NMR (CDCl₃) δ –0.24 (s, 3H), 0.11 (s, 3H), 0.90 (s, 9H), 2.83 (dd, J = 14.7, 6.7 Hz, 1H), 2.97 (dd, J = 14.7, 6.7 Hz, 1H), 4.96 (s, 1H), 5.19 (dd, J = 17.1, 1.4 Hz, 1H), 5.27 (dd, J = 10.2, 1.4 Hz, 1H), 29.
6.05 (ddt, \(J = 17.1, 10.2, 6.7\) Hz, 1H), 7.30–7.40 (m, 3H), 7.45–7.55 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) -5.15, -4.66, 18.16, 25.69, 46.31, 82.49, 95.04, 120.03, 127.44, 128.49, 129.32, 131.80, 138.32.

Found: C, 59.32; H, 7.60%. Calcd for C\(_{17}\)H\(_{26}\)Cl\(_2\)O\(_2\): C, 59.12; H, 7.59%.

\((E)\)-3-(tert-Butyldimethylsiloxy)-4,4-dichloro-1-phenyl-1-pentene (12c): Bp 100 °C (1.0 Torr); IR (neat) 3010, 2928, 2854, 1650, 1460, 1253, 1130, 1073, 968, 873, 836, 777, 748, 691 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.08 (s, 3H), 0.16 (s, 3H), 0.94 (s, 9H), 2.08 (d, \(J = 6.8\) Hz, 1H), 6.31 (dd, \(J = 15.9, 6.8\) Hz, 1H), 6.68 (d, \(J = 15.9\) Hz, 1H), 7.27–7.55 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) -4.84, -3.99, 18.22, 25.77, 32.19, 81.64, 91.88, 126.70, 128.09, 128.65, 134.42, 136.23.

Found: C, 59.36; H, 7.88%. Calcd for C\(_{17}\)H\(_{26}\)Cl\(_2\)O\(_2\): C, 59.12; H, 7.59%.

5-(tert-Butyldimethylsiloxy)-4,4-dichloro-1-octene (12d): Bp 65 °C (1.0 Torr); IR (neat) 2956, 2856, 1464, 1362, 1257, 1146, 1104, 924, 835, 775 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.12 (s, 3H), 0.15 (s, 3H), 0.92 (s, 9H), 0.94 (t, \(J = 7.3\) Hz, 3H), 1.20–2.05 (m, 4H), 2.80–3.00 (m, 2H), 3.90 (dd, \(J = 7.0, 2.6\) Hz, 1H), 5.22 (dq, \(J = 17.0, 1.7\) Hz, 1H), 5.27 (dq, \(J = 10.2, 1.7\) Hz, 1H), 6.03 (ddt, \(J = 17.0, 10.2, 6.8\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) -3.98, -3.60, 14.17, 18.43, 26.02, 35.95, 46.75, 80.81, 96.27, 119.86, 131.92. Found: C, 53.83; H, 9.29%. Calcd for C\(_{14}\)H\(_{28}\)Cl\(_2\)O\(_2\): C, 54.01; H, 9.06%.

\((IR^*,3R^*)\)-2,2-Dichloro-1-(4-methoxyphenyl)-3-phenyl-1,3-propanediol: 1,3-Diol monosilyl ether 12e was converted into diol with saturated aqueous KF in the presence of a catalytic amount of n-Bu\(_4\)NF in THF and two diastereomers of diol were separated by silica-gel column chromatography. IR (neat) 3382, 2954, 2930, 1710, 1611, 1513, 1250, 1177, 1066, 1032, 832, 731, 700 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.04 (bs, 1H), 3.12 (bs, 1H), 3.82 (s, 3H), 5.05 (s, 1H), 5.07 (s, 1H), 6.90 (d, \(J = 8.8\) Hz, 2H), 7.35–7.60 (m, 7H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 55.22, 78.92, 79.23, 98.49, 113.20, 127.71, 127.80, 128.80, 128.90, 129.20, 129.93, 130.15, 137.15, 154.97. Found: C, 58.87;
H, 4.94%. Calcd for C₁₆H₁₆O₃Cl₂: C, 58.73; H, 4.93%.

\((IR^*,3S^*)-2,2\)-Dichloro-1-(4-methoxyphenyl)-3-phenyl-1,3-propanediol: Bp 110 °C (0.5 Torr); IR (neat) 3388, 2954, 2930, 1707, 1611, 1514, 1252, 1178, 1035, 860, 829, 730, 700 cm⁻¹; \(^1\)H NMR (CDCl₃) \(\delta\) 3.57 (bs, 1H), 3.69 (bs, 1H), 3.82 (s, 3H), 5.27 (s, 1H), 5.30 (s, 1H), 6.91 (d, \(J = 8.9\) Hz, 2H), 7.35–7.60 (m, 7H); \(^1\)C NMR (CDCl₃) \(\delta\) 55.21, 78.87, 79.17, 95.02, 113.10, 127.68, 127.78, 128.80, 128.87, 129.08, 130.04, 130.23, 137.02, 159.85. Found: C, 58.50; H, 4.96%. Calcd for C₁₆H₁₆O₃Cl₂: C, 58.73; H, 4.93%.

\((IR^*,3R^*)-2,2\)-Dichloro-1-phenyl-1,3-heptanediol: Bp 90 °C (0.2 Torr); IR (neat) 3838, 3820, 2956, 2860, 1492, 1455, 1379, 1191, 1089, 1063, 859, 702 cm⁻¹; \(^1\)H NMR (CDCl₃) \(\delta\) 0.90 (t, \(J = 7.3\) Hz, 3H), 1.20–2.15 (m, 6H), 2.26 (d, \(J = 9.3\) Hz, 1H), 3.38 (d, \(J = 3.5\) Hz, 1H), 3.66 (dt, \(J = 9.3, 1.9\) Hz, 1H), 5.31 (d, \(J = 3.5\) Hz, 1H), 7.35–7.65 (m, 5H); \(^1\)C NMR (CDCl₃) \(\delta\) 13.94, 22.46, 27.82, 32.15, 77.52, 79.50, 100.33, 127.74, 127.84, 128.70, 136.91. Found: C, 56.05; H, 6.58%. Calcd for C₁₃H₁₈Cl₂O₂: C, 56.33; H, 6.55%.

\((IR^*,3S^*)-2,2\)-Dichloro-1-phenyl-1,3-heptanediol: IR (neat) 3364, 2954, 2858, 1495, 1455, 1380, 1201, 1123, 1089, 1054, 971, 857, 756, 698 cm⁻¹; \(^1\)H NMR (CDCl₃) \(\delta\) 2.57 (d, \(J = 6.5\) Hz, 1H), 3.07 (d, \(J = 4.3\) Hz, 1H), 4.47 (t, \(J = 6.5\) Hz, 1H), 5.34 (d, \(J = 4.3\) Hz, 1H), 6.50 (dd, \(J = 16.0, 6.5\) Hz, 1H), 6.74 (d, \(J = 16.0\) Hz, 1H), 7.25–7.65 (m, 10H); \(^1\)C NMR (CDCl₃) \(\delta\) 78.01,

\((E)-(IR^*,3R^*)-2,2\)-Dichloro-1,5-diphenyl-4-pentene-1,3-diol: IR (Nujol) 3458, 1455, 1198, 1118, 1064, 1046, 966, 906, 835, 737, 700 cm⁻¹; \(^1\)H NMR (CDCl₃) \(\delta\) 2.57 (d, \(J = 6.5\) Hz, 1H), 3.07 (d, \(J = 4.3\) Hz, 1H), 4.47 (t, \(J = 6.5\) Hz, 1H), 5.34 (d, \(J = 4.3\) Hz, 1H), 6.50 (dd, \(J = 16.0, 6.5\) Hz, 1H), 6.74 (d, \(J = 16.0\) Hz, 1H), 7.25–7.65 (m, 10H); \(^1\)C NMR (CDCl₃) \(\delta\) 78.01,
79.10, 98.83, 124.98, 126.69, 126.86, 126.95, 127.86, 128.06, 128.28, 128.55, 128.73, 129.04, 135.47, 135.81, 136.76. Found: C, 62.93; H, 5.06%. Calcd for C_{17}H_{16}Cl_{2}O_{2}: C, 63.17; H, 4.99%.

\((E)-(IR^{*},3S^{*})\)-2,2-Dichloro-1,5-diphenyl-4-pentene-1,3-diol: IR (neat) 3306, 3028, 2920, 1719, 1638, 1493, 1452, 1201, 1123, 1044, 966, 909, 866, 746, 696 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 2.97 (bs, 1H), 3.27 (bs, 1H), 4.88 (bd, \(J = 6.0\) Hz, 1H), 5.33 (s, 1H), 6.53 (dd, \(J = 15.9, 6.0\) Hz, 1H), 6.83 (d, \(J = 15.9\) Hz, 1H), 7.25–7.65 (m, 10H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 77.63, 78.65, 95.85, 124.69, 126.76, 126.86, 127.70, 127.84, 128.26, 128.34, 128.59, 128.70, 128.81, 129.03, 135.32, 135.95, 136.93. Found: C, 62.88; H, 4.98%. Calcd for C\(_{17}\)H\(_{16}\)Cl\(_2\)O\(_2\): C, 63.17; H, 4.99%.

Reduction of Dichloride 12a with \(n\)-Bu\(_3\)SnH-Et\(_3\)B. A hexane solution of Et\(_3\)B (0.96 M, 0.73 ml, 0.7 mmol) was added to a solution of 12a (186 mg, 0.6 mmol) and \(n\)-Bu\(_3\)SnH (0.47 ml, 1.75 mmol) in hexane (5 ml). The mixture was heated at 80 °C for 24 h. The resulting mixture was concentrated in vacuo and the residual oil was diluted with dichloromethane (20 ml). Potassium fluoride (1.0 g) and saturated aqueous potassium fluoride (1.0 ml) were added, and the resulting mixture was stirred at 25 °C for 15 h. The reaction mixture was filtered and filtrate was concentrated. Purification of the residual oil by silica-gel column chromatography gave 1-phenyl-1-tert-butyldimethylsiloxypropane (0.15 g) in 97% yield.

3,3-Dibromo-3-(tert-butyldimethylsilyl)-1-phenyl-1-propanol (16a): IR (neat) 3562, 3426, 2958, 2928, 2884, 2856, 1465, 1253, 1039, 835, 820, 776, 761, 698, 668 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.30 (s, 3H), 0.32 (s, 3H), 1.06 (s, 9H), 2.80 (dd, \(J = 15.3, 2.7\) Hz, 1H), 2.87 (dd, \(J = 15.3, 6.3\) Hz, 1H), 2.98 (d, \(J = 2.4\) Hz, 1H), 5.54 (ddd, \(J = 6.3, 2.7, 2.4\) Hz, 1H), 7.25–7.50 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) -5.87, 19.59, 28.46, 55.05, 67.89, 73.70, 125.80, 127.55, 128.68, 144.30. Found: C, 44.13; H, 5.93%. Calcd for C\(_{15}\)H\(_{24}\)OBr\(_2\)Si: C, 44.29; H, 5.95%.
**4,4-Dibromo-4-(tert-butyldimethylsilyl)-2-butanol (16b):** Bp 100 °C (1 Torr); IR (neat) 3390, 2960, 2896, 2858, 1465, 1366, 1253, 1073, 930, 836, 776, 668 cm⁻¹; \(^1\)H NMR (CDCl₃) δ 0.307 (s, 3H), 0.314 (s, 3H), 1.081 (s, 9H), 1.31 (d, \(J = 6.3\) Hz, 3H), 2.53 (dd, \(J = 15.3, 2.7\) Hz, 1H), 2.60 (dd, \(J = 15.3, 5.7\) Hz, 1H), 2.64 (d, \(J = 2.7\) Hz, 1H), 4.59 (m, 1H); \(^1\)C NMR (CDCl₃) δ -5.95, 19.54, 24.06, 28.43, 53.90, 68.11, 68.59. Found: C, 34.67; H, 6.53%. Calcd for C₁₀H₂₂Br₂OSi: C, 34.70; H, 6.41%.

**4,4-Dibromo-4-(tert-butyldimethylsilyl)-1-methoxy-2-butanol (16c):** Bp 95 °C (0.5 Torr); IR (neat) 3426, 2928, 2884, 2856, 1465, 1253, 1195, 1126, 1086, 934, 835, 775, 667 cm⁻¹; \(^1\)H NMR (CDCl₃) δ 0.32 (s, 6H), 1.08 (s, 9H), 2.59 (dd, \(J = 15.5, 4.8\) Hz, 1H), 2.65 (dd, \(J = 15.5, 3.6\) Hz, 1H), 2.74 (d, \(J = 3.3\) Hz, 1H), 3.438 (s, 3H), 3.442 (dd, \(J = 9.6, 7.2\) Hz, 1H), 3.57 (dd, \(J = 9.6, 3.9\) Hz, 1H), 4.54 (m, 1H); \(^1\)C NMR (CDCl₃) δ -5.93, -5.83, 19.53, 28.44, 49.35, 59.09, 67.60, 70.40, 76.55. Found: C, 35.36; H, 6.58%. Calcd for C₁₁H₂₄Br₂O₂Si: C, 35.12; H, 6.43%.

**General Procedure for the Reaction of Silyldihalomethyllithium 2 with Oxirane.** A reaction of tert-butyldimethylsilyldibromomethyllithium (2a) with styrene oxide is representative. A THF (2 ml) solution of tert-butyl(dibromomethyl)dimethylsilane (1a, 0.29 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in THF (3 mJ) at -78 °C. After the mixture was stirred for 1 h at -78 °C, styrene oxide (0.14 g, 1.2 mmol) in THF (1 ml) was added and the mixture was warmed to -40 °C over 1 h. The resulting mixture was quenched with methanol and stirred another 10 min at room temperature. Extractive workup (1M HCl and hexane) followed by purification by silica-gel column chromatography gave 1,1-dibromo-3-(tert-butyldimethylsiloxy)-3-phenylpropane (17c, 0.27 g) in 65 % yield: Bp 135 °C (1.0 Torr); IR (neat) 2948, 2928, 2884, 2854, 1471, 1456, 1362, 1255, 1156, 1089, 1002, 929, 837, 777, 699, 615 cm⁻¹; \(^1\)H NMR (CDCl₃) δ -0.24 (s, 3H), 0.05 (s, 3H), 0.86 (s, 9H), 2.55 (ddd, \(J = 14.5, 9.2, 4.0\) Hz, 1H), 2.79 (ddd, \(J = 14.5, 9.2, 4.0\) Hz, 1H), 4.87 (dd, \(J = 9.2, 3.5\) Hz, 1H), 5.69 (dd, \(J = 9.8, 4.0\) Hz, 1H), 7.20–7.35 (m, 5H); \(^1\)C NMR (CDCl₃) δ -4.96, -4.47, 18.08, 25.79, 42.91, 56.18, 73.62,
126.07, 127.83, 128.44, 143.14. Found: C, 44.00; H, 5.94%. Calcd for C\textsubscript{15}H\textsubscript{24}Br\textsubscript{2}O\textsubscript{2}Si: C, 44.13; H, 5.93%.

**1,1-Dibromo-3-(tert-butyldimethylsiloxy)butane (17a):** Bp 90°C (1.0 Torr); IR (neat) 2952, 2926, 2886, 2854, 1463, 1375, 1256, 1135, 1046, 967, 836, 775, 683 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\textsubscript{3}) \(\delta\) 0.08 (s, 3H), 0.11 (s, 3H), 0.89 (s, 9H), 1.18 (d, \(J = 6.0\) Hz, 3H), 2.41 (ddd, \(J = 14.4, 10.2, 3.0\) Hz, 1H), 2.54 (ddd, \(J = 14.4, 9.0, 3.6\) Hz, 1H), 4.00 (ddq, \(J = 3.0, 9.0, 6.0\) Hz, 1H), 5.72 (dd, \(J = 10.2, 3.6\) Hz, 1H); \(^{13}\)C NMR (CDCl\textsubscript{3}) \(\delta\) -4.90, -4.27, 17.84, 23.33, 25.73, 43.38, 55.06, 67.04. Found: C, 34.99; H, 6.56%. Calcd for C\textsubscript{10}H\textsubscript{22}Br\textsubscript{2}O\textsubscript{2}Si: C, 34.70; H, 6.41%.

**1,1-Dibromo-3-(tert-butyldimethylsiloxy)propane (17b):** Bp 80°C (1 Torr); IR (neat) 2952, 2926, 2856, 1471, 1387, 1256, 1161, 1104, 932, 836, 777, 686 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\textsubscript{3}) \(\delta\) 0.07 (s, 6H), 0.90 (s, 9H), 2.58 (dt, \(J = 6.6, 5.7\) Hz, 2H), 3.72 (t, \(J = 5.7\) Hz, 2H), 5.84 (t, \(J = 6.6\) Hz, 1H); \(^{13}\)C NMR (CDCl\textsubscript{3}) \(\delta\) -5.60, 18.14, 25.76, 43.16, 48.13, 60.70. Found: C, 32.82; H, 6.01%. Calcd for C\textsubscript{9}H\textsubscript{20}Br\textsubscript{2}O\textsubscript{2}Si: C, 32.55; H, 6.07%.

**5,5-Dibromo-3-(tert-butyldimethylsiloxy)-1-pentene (17d):** Bp 90°C (1 Torr); IR (neat) 3078, 3008, 2952, 2928, 2884, 2856, 1645, 1463, 1419, 1362, 1253, 1086, 923, 836, 776, 680, 562 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\textsubscript{3}) \(\delta\) 0.05 (s, 3H), 0.10 (s, 3H), 0.90 (s, 9H), 2.46 (ddd, \(J = 14.4, 9.3, 3.9\) Hz, 1H), 2.61 (ddd, \(J = 14.4, 9.0, 4.5\) Hz, 1H), 4.25 (m, 1H), 5.13 (d, \(J = 10.2\) Hz, 1H), 5.24 (d, \(J = 17.1\) Hz, 1H), 5.69 (dd, \(J = 9.3, 4.5\) Hz, 1H), 5.78 (ddd, \(J = 17.1, 10.2, 7.2\) Hz, 1H); \(^{13}\)C NMR (CDCl\textsubscript{3}) \(\delta\) -4.96, -4.20, 17.98, 25.74, 42.42, 63.42, 72.68, 115.94, 139.83. Found: C, 36.91; H, 6.21%. Calcd for C\textsubscript{11}H\textsubscript{22}Br\textsubscript{2}O\textsubscript{2}Si: C, 36.89; H, 6.19%.

**3-(tert-butyldimethylsiloxy)-1,1-dichlorobutane (17e):** Bp 110°C (8 Torr); IR (neat) 2954, 2928, 2888, 2856, 1472, 1363, 1257, 1139, 1050, 973, 836, 775, 754, 665 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\textsubscript{3}) \(\delta\) 0.08 (s, 3H), 0.09 (s, 3H), 0.89 (s, 9H), 1.18 (d, \(J = 6.0\) Hz, 3H), 2.21 (ddd, \(J = 14.0, 10.2, 3.9\) Hz, 1H).
9.6, 3.0 Hz, 1H), 2.32 (ddd, J = 14.0, 9.3, 3.6 Hz, 1H), 4.03 (ddq, J = 9.3, 3.0, 6.0 Hz, 1H), 5.81 (dd, J = 9.6, 3.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$) 8 = 5.09, -4.33, 17.82, 23.57, 25.69, 53.25, 65.61, 71.29. Found: C, 46.58; H, 8.84%. Calcd for C$_{10}$H$_{22}$Cl$_2$OSi: C, 46.69; H, 8.62%.

3-(tert-Butyldimethylsiloxy)-1,1-dichloropropane (17f): Bp 100 °C (9 Torr); IR (neat) 2952, 2928, 2880, 2856, 1472, 1387, 1257, 1108, 938, 835, 777, 756, 664 cm$^{-1}$; $^1$H NMR (CDCl$_3$) 8 0.06 (s, 6H), 0.89 (s, 9H), 2.38 (dt, J = 6.3, 5.4 Hz, 2H), 3.78 (t, J = 5.4 Hz, 2H), 5.92 (t, J = 6.3 Hz, 1H); $^{13}$C NMR (CDCl$_3$) 8 = 5.66, 18.13, 25.74, 46.40, 59.19, 71.07. Found: C, 44.53; H, 8.54%. Calcd for C$_9$H$_{20}$Cl$_2$OSi: C, 44.44; H, 8.29%.

1-(tert-Butyldimethylsiloxy)-3,3-dichloro-1-phenylpropane (17g): Bp 100 °C (1.0 Torr); IR (neat) 2952, 2928, 2886, 2854, 1464, 1363, 1254, 1093, 1005, 937, 836, 777, 745, 698, 671, 611 cm$^{-1}$; $^1$H NMR (CDCl$_3$) 8 0.22 (s, 3H), 0.05 (s, 3H), 0.88 (s, 9H), 2.37 (ddd, J = 14.1, 9.3, 3.3 Hz, 1H), 2.60 (ddd, J = 14.1, 9.6, 3.9 Hz, 1H), 4.84 (dd, J = 9.3, 3.3 Hz, 1H), 5.82 (dd, J = 9.6, 3.6 Hz, 1H), 7.20–7.40 (m, 5H); $^{13}$C NMR (CDCl$_3$) 8 = 5.29, -4.68, 17.67, 25.68, 54.41, 70.91, 72.33, 126.09, 127.91, 128.54, 143.46. Found: C, 56.19; H, 7.71%. Calcd for C$_{15}$H$_{24}$Cl$_2$OSi: C, 56.42; H, 7.57%.

2-(tert-Butyldimethylsiloxy)-1,4,4-trichlorobutane (17h): Bp 70 °C (0.5 Torr); IR (neat) 2952, 2928, 2886, 2854, 1465, 1390, 1363, 1257, 1153, 1092, 935, 836, 776, 665 cm$^{-1}$; $^1$H NMR (CDCl$_3$) 8 0.13 (s, 6H), 0.91 (s, 9H), 2.44 (dd, J = 14.4, 8.1, 4.2 Hz, 1H), 2.52 (ddd, J = 14.4, 9.3, 3.3 Hz, 1H), 3.44 (dd, J = 11.4, 6.3 Hz, 1H), 3.51 (dd, J = 11.4, 3.9 Hz, 1H), 4.10 (m, 1H), 5.81 (dd, J = 9.3, 4.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$) 8 = -4.97, -4.57, 17.87, 25.60, 47.72, 48.82, 69.36, 70.55. Found: C, 41.38; H, 7.39%. Calcd for C$_{10}$H$_{21}$Cl$_3$OSi: C, 41.17; H, 7.26%.

**General Procedure for One-pot synthesis of 19 (RCH(OSiMe$_2$-t-Bu)CH$_1$CX$_1$E') from 1.** A THF (2 ml) solution of tert-butyl(dichloromethyl)dimethylsilane (0.20 g, 1.0 mmol) was
added to a solution of lithium diisopropyl amide (1.2 mmol) in THF (3 ml) at -78 °C. After being stirred for 1 h at -78 °C, propylene oxide (0.07 g, 1.2 mmol) in THF (1 ml) was added and the mixture was warmed to -40 °C over 1 h. The resulting mixture was cooled to -78 °C and methyl iodide (0.21 g, 1.5 mmol) and HMPA (0.24 ml, 1.4 mmol) in THF (1 ml) were added successively. The whole mixture was allowed to warm to room temperature over 5 h. Extractive workup (1M HCl and hexane) followed by purification by silica-gel column chromatography gave 2-(tert-butyldimethylsiloxy)-4,4-dichloropentane (19b, 0.16 g) in 68% yield. When aldehydes were used as second electrophiles, the reaction mixture was allowed to warm to -20 °C and kept there for 1 h before workup. 19b: Bp 105 °C (9 Torr); IR (neat) 2954, 2928, 2894, 2856, 1464, 1377, 1257, 1138, 1037, 976, 938, 836, 775, 698, 655, 599 cm⁻¹; ¹H NMR (CDCl₃) δ 0.09 (s, 6H), 0.89 (s, 9H), 1.26 (d, J = 6.0 Hz, 3H), 2.20 (s, 3H), 2.38 (dd, J = 14.7, 3.9 Hz, 1H), 2.46 (dd, J = 14.7, 6.3 Hz, 1H), 4.25 (dq, J = 6.3, 3.9, 6.0 Hz 1H); ¹³C NMR (CDCl₃) δ -4.61, -4.05, 17.81, 25.05, 25.79, 38.05, 58.72, 66.66, 89.43. Found: C, 48.44; H, 9.10%. Calcd for C₁₁H₂₄Cl₂OSi: C, 48.70; H, 8.92%.

2,2-Dibromo-4-(tert-butyldimethylsiloxy)pentane (19a): Bp 95 °C (1 Torr); IR (neat) 2954, 2928, 2892, 2854, 1463, 1376, 1257, 1136, 1098, 1033, 972, 836, 774, 652 cm⁻¹; ¹H NMR (CDCl₃) δ 0.10 (s, 3H), 0.11 (s, 3H), 0.89 (s, 9H), 1.27 (d, J = 6.0 Hz, 3H), 2.59 (s, 3H), 2.62 (d, J = 5.1 Hz, 2H), 4.23 (dq, J = 5.1, 6.3 Hz, 1H); ¹³C NMR (CDCl₃) δ -4.43, -3.92, 17.80, 24.91, 25.82, 41.82, 61.78, 66.70, 68.50. Found: C, 36.85; H, 6.81%. Calcd for C₁₁H₂₄Br₂OSi: C, 36.68; H, 6.72%.

4-(tert-butyldimethylsiloxy)-2,2-dichloro-1-phenyl-1-pentanol (19c, 53:47 diastereomeric mixture): Bp 125 °C (0.3 Torr); IR (neat) 3424, 2952, 2926, 2892, 2854, 1456, 1377, 1256, 1128, 1052, 1004, 966, 833, 774, 700, 604 cm⁻¹; ¹H NMR (CDCl₃) δ 0.12 (s, 1.59H), 0.18 (s, 1.41H), 0.90 (s, 4.77H), 0.91 (s, 4.23H), 1.29 (d, J = 6.3 Hz, 1.59H), 1.31 (d, J = 6.3 Hz, 1.41H), 2.34 (dd, J = 15.3, 4.2 Hz, 0.53H), 2.43 (dd, J = 15.3, 6.6 Hz, 0.53H), 2.44 (dd, J = 15.3,
5.4 Hz, 0.47H), 2.86 (dd, \( J = 15.3, 8.4 \) Hz, 0.47H), 3.50 (d, \( J = 3.6 \) Hz, 0.53H), 4.07 (d, \( J = 4.5 \) Hz, 0.47H), 4.41 (m, 1H), 5.12 (d, \( J = 4.5 \) Hz, 0.47H), 5.14 (d, \( J = 3.6 \) Hz, 0.53H), 7.30–7.40 (m, 3H), 7.50–7.65 (m, 2H); \(^{13}\text{C NMR (CDCl}_3\)) \( \delta \) -4.49, -4.36, -4.30, -4.02, 17.92, 24.69, 24.90, 25.83, 52.28, 54.22, 66.91, 66.97, 79.28, 81.16, 94.55, 96.12, 143.91, 144.18, 144.90, 145.16, 145.64, 145.68, 153.43, 153.55. Found: C, 56.10; H, 7.82%. Calcd for C\(_{17}\)H\(_{28}\)Cl\(_2\)O\(_2\)Si: C, 56.19; H, 7.77%.

1-(tert-Butyldimethylsiloxy)-3,3-dichlorobutane (19d): Bp 110 °C (8 Torr); IR (neat) 2952, 2928, 2882, 2856, 1472, 1382, 1257, 1110, 902, 838, 776, 699 cm\(^{-1}\); \(^1\text{H NMR (CDCl}_3\)) \( \delta \) 0.08 (s, 6H), 0.90 (s, 9H), 2.20 (s, 3H), 2.49 (t, \( J = 6.6 \) Hz, 2H), 3.94 (t, \( J = 6.6 \) Hz, 2H); \(^{13}\text{C NMR (CDCl}_3\)) \( \delta \) -5.56, 18.07, 25.76, 37.98, 51.87, 60.05, 88.88. Found: C, 46.67; H, 8.57%. Calcd for C\(_{10}\)H\(_{22}\)Cl\(_2\)OSi: C, 46.69; H, 8.62%.

4-(tert-Butyldimethylsiloxy)-2,2-dichlorobutanal (19e): Bp 95 °C (4 Torr); IR (neat) 2952, 2928, 2882, 2856, 1751, 1472, 1390, 1363, 1257, 1105, 977, 837, 777, 663, 610 cm\(^{-1}\); \(^1\text{H NMR (CDCl}_3\)) \( \delta \) 0.03 (s, 6H), 0.86 (s, 9H), 2.64 (t, \( J = 5.7 \) Hz, 2H), 3.83 (t, \( J = 5.7 \) Hz, 2H), 9.15 (s, 1H); \(^{13}\text{C NMR (CDCl}_3\)) \( \delta \) -5.69, 18.20, 25.77, 46.18, 58.93, 87.65, 184.43. Found: C, 44.32; H, 7.73%. Calcd for C\(_{10}\)H\(_{20}\)Cl\(_2\)O\(_2\)Si: C, 44.28; H, 7.43%.
References and Notes


4. Tandem transformations initiated by the migration of a silyl group have been reviewed. Jankowski, P.; Raubo, P.; Wicha, J. Synlett. 1994, 985.


6. tert-Butyl(dibromomethyl)dimethylsilane (1a) was prepared in 89% yield by the addition of lithium diisopropylamide to a mixture of t-BuMe₂SiCl and CH₂Br₂ in THF at −78 °C. In similar fashion, t-BuMe₂SiCHCl₂ 1b was generated in 85% yield. Bacquet, C.; Masure, D.; Normant, J. F. Bull. Soc. Chim. Fr. 1975, 1797.


9. The yields are based on benzaldehyde employed.


11. Tetrahydrofuran was less effective than DME-THF for 1,3-migration of silicon (3 → 4).

12. Treatment of Ph$_3$SiClBr$_2$ with 2.4 eq. of benzaldehyde in THF gave the corresponding diol monosilylether PhCH(OSiPh$_3$)CBr$_2$CH(OH)Ph in 88% yield.


15. *tert*-Butyldimethylsilyldibromomethyllithium (2a) was stable at −40 °C but decomposed at −20 °C in ether or THF.


17. As shown in Scheme 6, the reaction of 2a with 1,2-epoxypropane in ether gave the unrearranged product 16b after quenching with methanol.

CHAPTER 2

Preparation of Alkyl Silyl Acetals from Carboxylic Esters with tert-Butyldimethylsilyldihalomethyllithium. 1,3-Rearrangement of Silyl Group from Carbon to Oxide

Treatment of ethyl benzoate or isopropyl formate with tert-butyldimethylsilyldibromomethyllithium gave an alkyl silyl mixed acetal via 1,3-rearrangement of silyl group from carbon to oxygen. One-pot synthesis of a three component coupling product R_1C(OR_2)(OSiMe_2-t-Bu)CX_2E' (X=Cl, Br) by successive addition of an ester (R_1CO_2R_2) and the second electrophile was achieved starting from tert-butyldimethylsilyldihalomethyllithium. The reaction of the mixed acetals with allylsilane in the presence of Lewis acid afforded allylated ethers.
Introduction

The tandem carbon-carbon bond formation reaction triggered by anionic rearrangement of silyl group from carbon to oxygen has increasingly attracted the attention of many chemists as a new methodology for the construction of complex organic molecules.\(^1\), \(^2\) Recently the author has reported that one-pot synthesis of \(R^1\text{CH(OSiMe}_2\text{-t-Bu)}\text{CX}_2\text{CH(OH)}R^2\) by successive addition of two different electrophiles has been achieved starting from \textit{tert-}butyldimethylsilyldihalomethylithium \(1\) (Scheme 1).\(^3\) The reaction proceeds via 1,3-rearrangement of silyl group from carbon to oxygen.\(^4\) Here the author wishes to describe further application of this type rearrangement to the synthesis of alkyl silyl acetals\(^5\) from carboxylic esters.

\begin{center}
\textbf{Scheme 1}
\end{center}

\[
\begin{align*}
\text{t-BuMe}_2\text{SiCX}_2 \quad &\xrightarrow{-78{}^\circ\text{C}} \quad \text{HMPA} \quad \xrightarrow{\text{R}^1\text{CHO}} \\
1 \quad &\xrightarrow{\text{R}^2\text{CHO}} \quad \text{t-BuMe}_2\text{SiO} \quad \text{OH} \\
\end{align*}
\]

Reaction of \textit{tert-}butyldimethylsilyldihalomethylithium with carboxylic esters

Ethyl benzoate 2 was added to a solution of \textit{tert-}butyldimethylsilyldibromomethylithium (1a) in THF, prepared from \textit{tert-}butyl(dibromomethyl)dimethylsilane and LDA, at \(-78{}^\circ\text{C}\) and the mixture was stirred for 20 min. Methanol was added to quench the reaction. Workup followed by silica gel column chromatography gave ethyl \textit{tert-}butyldimethylsilyl acetal 5 in 94\% yield. The use of acetic acid in place of methanol afforded hemiacetal 6 which decomposed to \(\alpha\)-silyl ketone 7 after standing for three days in NMR tube (CDCl\(_3\) solution). The formation of 5 is explained by 1,3-rearrangement of silyl group from carbon to oxygen in the intermediate \(\beta\)-oxido silane 3 (Scheme 2). An addition of methanol to 3 gave an equilibrium mixture of 3 and 6. The increased polarity of the solvent due to an addition of methanol promoted the rearrangement of silyl group (3 to 4). Protonolysis of 4 with methanol provided 5.

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In order to clarify the generality of this type of acetal formation, the reactions of tert-butyldimethylsilyldihalomethyllithium with various esters were investigated (Table 1). The facility of 1,3-rearrangement heavily depends on the structure of substrate. The use of methyl benzoate in place of ethyl benzoate also afforded the corresponding mixed acetal in good yield. Treatment of ethyl formate with 1a gave ethyl silyl acetal 8d in only 36% yield along with dibromo(tert-butyldimethylsilyl)-acetaldehyde (9d) (47%) which might be generated by elimination of ethoxide from β-oxido silane or rapid decomposition of hemiacetal after workup (entry 4). The use of isopropyl formate instead of ethyl formate improved the yield of mixed acetal 8e up to 80% and the formation of aldehyde was reduced (5%). tert-Butyl formate was not so effective for the acetal formation as isopropyl formate (entry 6). In the cases of α-halo substituted esters (entries 8, 9, and 10), the corresponding mixed acetals were provided and the use of ethyl trifluoroacetate gave the best result. Thus, treatment of ethyl trifluoroacetate with 1a gave ethyl silyl acetal 8j in 97% yield. Unfortunately alkanoate esters such as methyl octanoate (entry 11) gave no mixed silyl acetal but only bromo(tert-butyldimethylsilyl)methyl ketone 10k (38%) which might be produced by elimination of methoxide from β-oxido silane giving dibromo(tert-butyldimethylsilyl)methyl heptyl ketone (9k) followed by lithium-bromine exchange between 9k and 1a (Scheme 2). α-Bromo-α-silyl ketone 10l was also provided in the case of methyl cinnamate (44%).
Table 1. Reactions of tert-butyldimethylsilyldihalomethylithium with esters

\[
\begin{align*}
\text{RCO}_2\text{R'} & \xrightarrow{1) \text{SiCl LiX}_2} \text{1} \\
& \xrightarrow{2) \text{MeOH}} \text{2} \\
\text{Si} & = \text{t-BuMe}_2\text{Si}
\end{align*}
\]

<table>
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<th>Entry</th>
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<th>R’</th>
<th>X</th>
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<td>Br</td>
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Scheme 3

\[
\begin{align*}
\text{RCO}_2\text{Me} & \xrightarrow{1\text{a}} \text{MeO}_2\text{Li} \\
\text{R} & = \text{n-C}_7\text{H}_{15} \\
\end{align*}
\]

\[
\begin{align*}
\text{1a} & \xrightarrow{-\text{SiCBr}_3} \text{Li} \\
\text{Si} & = \text{t-BuMe}_2\text{Si}
\end{align*}
\]
It was anticipated that three-component coupling products would be obtained in a single operation, if the rearrangement of silyl group to form 12 could take place in the presence of second electrophiles. In fact, an addition of HMPA to the reaction mixture of tert-butyldimethylsilyldihalomethyllithium 1 and ethyl benzoate, isopropyl formate, or ethyl trifluoroacetate caused the rearrangement of silyl group providing a lithium carbenoid 12 which reacted with various second electrophiles effectively (Table 2).

Table 2. Tandem carbon-carbon bond formation reaction

<table>
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<th>R¹</th>
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<th>Electrophile</th>
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<tr>
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<td>Ph</td>
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<td>Br</td>
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<td>CH₂=CHCH₂</td>
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<td>CH₃</td>
</tr>
<tr>
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<td>i-Pr</td>
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<td>CH₃I</td>
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<tr>
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<td>H</td>
<td>i-Pr</td>
<td>Br</td>
<td>PhCH₂Br</td>
<td>PhCH₂</td>
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<td>CF₃</td>
<td>Et</td>
<td>Br</td>
<td>CH₂=CHCH₂Br</td>
<td>CH₂=CHCH₂</td>
</tr>
</tbody>
</table>

a) Dihalomethylsilane (1.0 mmol), ester (1.2 mmol), electrophile (1.5 mmol), and HMPA (1.4 mmol) were employed.

The use of benzaldehyde as a second electrophile in the above three-component coupling reaction starting from 1a and isopropyl formate of ethyl trifluoroacetate gave β-siloxy-α,α-dihaloaldehyde 13g and β-siloxy-α,α-dihaloalkyl trifluoromethylketone 13h in good yields. These products obviously resulted from double rearrangement of silyl group in the course of the reaction (Scheme 4).
Surprisingly, in the case of the reaction of 4 with benzaldehyde, monosilyl ether of diol 16 was provided in 53% yield and no desired β-siloxyketone was observed. The formation of the monosilyl ether of diol was rationalized as follows (Scheme 5). (1) The reaction of 4 with benzaldehyde afforded adduct 14. (2) In the adduct 14, second rearrangement of silyl group followed by cleavage of carbon-carbon bond with releasing of ethyl benzoate gave lithium carbenoid 15. (3) The reaction of lithium carbenoid 15 with benzaldehyde gave the mono silyl ether of diol 16.

Generally, the reaction of nucleophiles with esters provides substitution products through an addition intermediate which eliminates alkoxide as a leaving group. Thus, the construction of new asymmetric center is seldom performed in the nucleophilic addition to esters. In this reaction, however, new asymmetric center was produced without elimination of alkoxide, because the tetrahedral intermediate 11 was stable enough to form an addition products. It then occurred to us that, if the esters having chiral alkoxy group were employed, an asymmetric induction would be observed. In fact, our new reaction was successfully applied to the diastereoselective synthesis of
mixed acetals starting from benzoates, formates, or trifluoroacetates prepared from chiral secondary alcohols. For instance, treatment of 1-phenethyl benzoate with 1a gave 17a with high diastereoselectivity (>98/<2) in 66% yield. Typical examples are shown below (Figure 1). Higher degree of stereoselectivities were observed in the cases of benzoate and trifluoroacetate than in formates.

Reactions of Alkyl Silyl Mixed Acetals

Several reactions of mixed acetals were examined. Triethylborane-induced reduction of 17b with n-Bu₃SnH afforded HC(O-1-menthyl)(OSiMe₂-t-Bu)CH₃ (18b) quantitatively.¹⁰ Treatment of acetal 8e with allyltrimethylsilane in the presence of TiCl₄ in CH₂Cl₂ at -78 °C gave allylated silyl ether 19 in 98% yield.¹¹ In this case, isopropoxy group was substituted selectively. The nature of reagent affected which of alkoxy and silyloxy groups will be replaced. Treatment of 8e with Me₃Al¹² in toluene at 60 °C gave CH₃CH(O-i-Pr)CHBr₂ 20 (41%) as a single product along with starting material (Scheme 6).
Both diastereomers 21 and 22, which were obtained by the separation of 18b by silica gel column chromatography gave the same diastereomeric mixture 23 (68/32) in 89% yield upon treatment with allyltrimethylsilane in the presence of Me$_3$SiOTf at -78 °C. An addition of allyltrimethylsilane to acetal 24 (80/20) in the presence of Me$_3$SiOTf gave 1-phenethyl ether 25 (89/11) in 83% yield. These facts support that allylation reaction proceeds through cationic oxonium intermediate 26 (Scheme 7).
Experimental

Reaction of tert-Butyldimethylsilyldihalomethyllithium with Esters. The reaction of tert-butyldimethylsilyldihalomethyllithium with ethyl benzoate is representative. A THF solution (2 ml) of tert-butyl(dibromomethyl)dimethylsilane (0.29 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in THF (3 ml) at -78 °C under argon atmosphere. To the resulting yellow solution, ethyl benzoate (0.18 g, 1.2 mmol) was added and the mixture was stirred for 20 min. Methanol was added to quench the reaction and the whole was stirred for 5 min. Extractive workup (saturated aqueous ammonium chloride and hexane), followed by silica gel column chromatography gave 1,1-dibromo-2-ethoxy-2-phenylethane (50.41 g) in 94% yield: Bp 109–110 °C (bath temp, 0.5 Torr); IR (neat) 2928, 2854, 1472, 1448, 1391, 1257, 1157, 1062, 873, 837, 778, 701 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.16 (s, 3H), 0.35 (s, 3H), 1.03 (s, 9H), 1.20 (t, \(J = 7.0\) Hz, 3H), 3.39 (dq, \(J = 7.0, 9.0\) Hz, 1H), 3.58 (dq, \(J = 7.0, 9.0\) Hz, 1H), 5.83 (s, 1H), 7.35–7.45 (m, 3H), 7.55–7.65 (m, 2H); \(^13\)C NMR (CDCl\(_3\)) \(\delta\) –2.95, –2.11, 14.97, 19.14, 26.13, 53.22, 59.70, 100.80, 127.68, 128.21, 128.76, 138.60. Found: C, 44.10; H, 5.90%. Calcd for C\(_{16}\)H\(_{26}\)Br\(_2\)O\(_2\)Si: C, 43.85; H, 5.98%.

1-(tert-Butyldimethylsiloxo)-2,2-dichloro-1-ethoxy-1-phenylethane (8c): Bp 93 °C (bath temp. 0.5 Torr); IR (neat) 2928, 2854, 1449, 1390, 1258, 1211, 1169, 1091, 1062, 880, 837, 780, 700 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.20 (s, 3H), 0.32 (s, 3H), 1.00 (s, 9H), 1.18 (t, \(J = 7.0\) Hz, 2H), 3.33 (dq, \(J = 7.0, 9.1\) Hz, 1H), 3.52 (dq, \(J = 7.0, 9.1\) Hz, 1H), 5.81 (s, 1H), 7.30–7.40 (m, 3H), 7.50–7.65 (m, 2H); \(^13\)C NMR (CDCl\(_3\)) \(\delta\) –3.04, –3.25, 14.92, 19.12, 26.09, 59.20, 77.16, 101.95, 127.71, 128.25, 128.74, 138.22. Found: C, 55.01; H, 7.68%. Calcd for C\(_{16}\)H\(_{26}\)Cl\(_2\)O\(_2\)Si: C, 54.99; H, 7.50%.

1,1-Dibromo-2-(tert-butyldimethylsiloxo)-2-isopropoxyethane (8e): Bp 75 °C (0.5 Torr); IR (neat) 2956, 2928, 2892, 2854, 1464, 1382, 1254, 1138, 1059, 836, 777, 700 cm\(^{-1}\);
$^1$H NMR (CDCl$_3$) $\delta$ 0.16 (s, 3H), 0.17 (s, 3H), 0.92 (s, 9H), 1.20 (d, $J = 6.2$ Hz, 3H), 1.23 (d, $J = 6.2$ Hz, 3H), 3.89 (sep, $J = 6.2$ Hz, 1H), 4.84 (d, $J = 3.2$ Hz, 1H), 5.43 (d, $J = 3.2$ Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -4.22, -3.92, 18.09, 22.06, 23.08, 25.68, 48.72, 70.28, 96.27.

Found: C, 35.14; H, 6.27%. Calcd for C$_{11}$H$_{24}$Br$_2$O$_2$Si: C, 35.12; H, 6.43%.

1,1-(tert-Butyldimethylsiloxy)-2,2-dichloro-1-isopropoxyethane (8g): Bp 80 °C (1 Torr); IR (neat) 2930, 2888, 2856, 1465, 1383, 1364, 1328, 1256, 1132, 1063, 940, 835, 778 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.176 (s, 3H), 0.181 (s, 3H), 0.93 (s, 9H), 1.21 (d, $J = 6.2$ Hz, 3H), 1.25 (d, $J = 6.2$ Hz, 3H), 3.93 (sep, $J = 6.2$ Hz, 1H), 4.93 (d, $J = 4.2$ Hz, 1H), 5.47 (d, $J = 4.2$ Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -4.28, -4.10, 17.98, 21.90, 23.03, 25.58, 70.32, 73.61, 97.04. Found: C, 46.25; H, 8.45%. Calcd for C$_{11}$H$_{24}$Cl$_2$O$_2$Si: C, 45.99; H, 8.42%.

1,1-Dibromo-2-(tert-butyldimethylsiloxy)-2-ethoxy-3-fluoropropane (8i): Bp 70 °C (0.5 Torr); IR (neat) 2952, 2928, 2890, 2854, 1463, 1254, 1100, 1049, 989, 838, 779 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.19 (s, 3H), 0.23 (s, 3H), 0.93 (s, 9H), 1.23 (t, $J = 7.1$ Hz, 3H), 3.70 (dq, $J = 8.7$, 7.1 Hz, 1H), 3.78 (dq, $J = 8.7$, 7.1 Hz, 1H), 4.59 (dd, $J = 9.9$, 11.1 Hz, 1H), 4.74 (dd, $J = 9.9$, 11.1 Hz, 1H), 5.81 (d, $J = 1.8$ Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -3.50 (d, $J = 2.3$ Hz), -3.25 (d, $J = 1.7$ Hz), 15.21, 18.40, 25.65, 47.35, 58.58, 82.68 (d, $J = 181.5$ Hz), 97.54 (d, $J = 18.9$ Hz). Found: C, 33.34; H, 5.80%. Calcd for C$_{11}$H$_{23}$Br$_2$F$_2$O$_2$: C, 33.52; H, 5.88%.

1,1-Dibromo-2-(tert-butyldimethylsiloxy)-2-ethoxy-3,3,3-trifluoropropane (8j): Bp 80 °C (0.5 Torr); IR (neat) 2952, 2928, 2856, 1473, 1303, 1255, 1168, 996, 840, 784, 669 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.21 (s, 3H), 0.28 (s, 3H), 0.96 (s, 9H), 1.27 (t, $J = 7.1$ Hz, 3H), 3.71 (dq, $J = 7.1$, 7.1 Hz, 1H), 3.78 (dq, $J = 7.1$, 7.1 Hz, 1H), 5.86 (s, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -3.76, -2.94, 14.94, 18.42, 25.51, 42.61, 60.56, 96.73 (q, $J = 30.3$ Hz), 121.69 (q, $J = 296.1$ Hz). Found: C, 30.06; H, 4.87%. Calcd for C$_{11}$H$_{21}$Br$_2$F$_3$O$_2$: C, 30.56; H, 4.87%.
**Tandem Carbon-carbon Bond Formation Reaction in the Presence of HMPA.**

The reaction of tert-butyldimethylsilyldibromomethylthiilithium with ethyl benzoate and iodomethane is representative. A THF solution (2 ml) of tert-butyl(dibromomethyl)dimethylsilane (0.29 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in THF (3 ml) at -78 °C under argon atmosphere. To the resulting yellow solution, ethyl benzoate (0.18 g, 1.2 mmol) was added and the mixture was stirred for 20 min. Methyl iodide (1.5 mmol) in THF (1 ml) and HMPA (0.24 ml, 1.4 mmol) in THF (1 ml) were added successively to the reaction mixture and the resulting mixture was allowed to warm to room temperature over 5 h. Extractive workup (1M HCl and hexane) followed by purification by silica-gel column chromatography gave 2,2-dibromo-1-(tert-butyldimethylsiloxy)-1-ethoxy-1-phenylpropane (13a 0.37 g) in 81% yield. When aldehydes were used as second electrophiles, the reaction mixture was allowed to warm to -20 °C and kept there for 1 h before workup. **13a:** Bp 115 °C (0.5 Torr); IR (neat) 2952, 2926, 2852, 1448, 1258, 1211, 1094, 1063, 875, 836, 777, 706 cm⁻¹; ¹H NMR (CDCl₃) δ 0.24 (s, 3H), 0.38 (s, 3H), 1.03 (s, 9H), 1.26 (t, J = 6.9 Hz, 3H), 2.42 (s, 3H), 3.42 (dq, J = 8.4, 6.9 Hz, 1H), 3.58 (dq, J = 8.4, 6.9 Hz, 1H), 7.30-7.40 (m, 3H), 7.63-7.68 (m, 2H); ¹³C NMR (CDCl₃) δ -2.46, -2.11, 14.85, 19.64, 26.24, 36.70, 60.15, 104.24, 127.04, 128.76, 130.60, 136.10. Found: C, 45.08; H, 6.18%. Calcd for C₁₇H₂₈Br₂O₂Si: C, 45.14; H, 6.24%.

**4,4-Dibromo-5-(tert-butyldimethylsiloxy)-5-ethoxy-5-phenyl-1-pentene**

(13b): Bp 125 °C (0.5 Torr); IR (neat) 2950, 2926, 2852, 1643, 1258, 1209, 1142, 1063, 870, 836, 777, 704 cm⁻¹; ¹H NMR (CDCl₃) δ 0.25 (s, 3H), 0.38 (s, 3H), 1.04 (s, 9H), 1.27 (t, J = 7.2 Hz, 3H), 3.02 (m, 2H), 3.44 (dq, J = 9.0, 7.2 Hz, 1H), 3.59 (dq, J = 9.0, 7.2 Hz, 1H), 5.13 (dd, J = 1.0, 16.8 Hz, 1H), 5.23 (dd, J = 1.0, 10.5 Hz, 1H), 6.08 (ddt, J = 10.5, 16.8, 6.3 Hz, 1H), 7.30-7.40 (m, 3H), 7.60-7.70 (m, 2H); ¹³C NMR (CDCl₃) δ -2.41, -2.05, 14.82, 19.68, 26.24, 48.21, 60.18, 104.49, 118.92, 127.08, 128.83, 130.78, 135.04, 136.36. Found: C, 47.56;
1-(tert-Butyldimethylsiloxy)-2,2-dichloro-1-ethoxy-1-phenylpropane (13c): Bp 100 °C (0.5 Torr); IR (neat) 2928, 2898, 2854, 1448, 1255, 1125, 1063, 877, 836, 778, 701, 623 cm⁻¹; ¹H NMR (CDCl₃) δ 0.27 (s, 3H), 0.36 (s, 3H), 1.00 (s, 9H), 1.26 (t, J = 7.12 Hz, 3H), 2.03 (s, 3H), 3.40 (dq, J = 9.1, 7.1 Hz, 1H), 3.55 (dq, J = 9.1, 7.1 Hz, 1H), 7.32–7.39 (m, 3H), 7.60–7.65 (m, 2H); ¹³C NMR (CDCl₃) δ -2.72, -2.30, 14.81, 19.95, 26.21, 33.39, 59.65, 94.64, 104.70, 127.16, 128.70, 130.16, 137.19. Found: C, 56.04; H, 7.65%. Calcd for C₂₈H₂₈Cl₂O₂Si: C, 56.19; H, 7.77%.

2,2-Dibromo-1-(tert-butyldimethylsiloxy)-1-isopropoxypropane (13d): Bp 80 °C (0.5 Torr); IR (neat) 2956, 2926, 2892, 2854, 1465, 1373, 1255, 1127, 1068, 865, 835, 776, 678 cm⁻¹; ¹H NMR (CDCl₃) δ 0.20 (s, 3H), 0.22 (s, 3H), 0.93 (s, 9H), 1.216 (d, J = 6.0 Hz, 3H), 1.222 (d, J = 6.0 Hz, 3H), 2.38 (s, 3H), 3.97 (sep, J = 6.0 Hz, 1H), 4.89 (s, 1H); ¹³C NMR (CDCl₃) δ -3.99, -3.59, 18.28, 21.67, 23.17, 25.86, 33.66, 70.44, 70.69, 99.14. Found: C, 36.75; H, 6.91%. Calcd for C₁₂H₂₆Br₂O₂Si: C, 36.94; H, 6.71%.

2,2-Dibromo-1-(tert-butyldimethylsiloxy)-1-isopropoxy-3-phenylpropane (13e): Bp 110 °C (0.5 Torr); IR (neat) 2924, 2882, 2852, 1464, 1382, 1323, 1253, 1050, 940, 836, 777, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 0.25 (s, 3H), 0.26 (s, 3H), 0.98 (s, 9H), 1.26 (d, J = 6.3 Hz, 3H), 1.27 (d, J = 6.3 Hz, 3H), 3.56 (d, J = 14.4 Hz, 1H), 3.67 (d, J = 14.4 Hz, 1H), 4.05 (sep, J = 6.3 Hz, 1H), 5.09 (s, 1H), 7.30–7.36 (m, 3H), 7.44–7.50 (m, 2H); ¹³C NMR (CDCl₃) δ -3.79, -3.43, 18.38, 21.66, 23.21, 25.96, 46.95, 70.85, 77.87, 99.45, 127.33, 127.62, 131.91, 136.03. Found: C, 46.14; H, 6.26%. Calcd for C₁₈H₃₀Br₂O₂Si: C, 46.36; H, 6.48%.

4,4-Dibromo-5-(tert-butyldimethylsiloxy)-5-ethoxy-6,6,6-trifluoro-1-hexene (13f): Bp 95 °C (0.5 Torr); IR (neat) 2954, 2930, 2896, 2856, 1644, 1256, 1174, 924, 852, 758, 695, 654, 628 cm⁻¹; ¹H NMR (CDCl₃) δ 0.27 (s, 3H), 0.36 (s, 3H), 0.48 (s, 3H), 0.97 (s, 9H), 1.26 (t, J = 7.12 Hz, 3H), 2.03 (s, 3H), 3.40 (dq, J = 9.1, 7.1 Hz, 1H), 3.55 (dq, J = 9.1, 7.1 Hz, 1H), 4.01 (t, J = 6.3 Hz, 3H), 7.32–7.39 (m, 3H), 7.60–7.65 (m, 2H); ¹³C NMR (CDCl₃) δ -2.72, -2.30, 14.81, 19.95, 26.21, 33.39, 59.65, 94.64, 104.70, 127.16, 128.70, 130.16, 137.19. Found: C, 56.04; H, 7.65%. Calcd for C₂₈H₂₈Cl₂O₂Si: C, 56.19; H, 7.77%.
839, 783, 683 cm\(^{-1}\); ¹H NMR (CDCl\(_3\)) \(\delta\) 0.29 (s, 3H), 0.30 (s, 3H), 0.98 (s, 9H), 1.26 (t, \(J = 7.1\) Hz, 3H), 3.12 (dd, \(J = 6.6, 15.3\) Hz, 1H), 3.21 (dd, \(J = 6.6, 15.3\) Hz, 1H), 3.94 (dq, \(J = 7.1, 7.1\) Hz, 1H), 4.01 (dq, \(J = 7.1, 7.1\) Hz, 1H), 5.23 (dd, \(J = 1.8, 16.8\) Hz, 1H), 5.31 (dd, \(J = 1.8, 10.2\) Hz, 1H), 6.12 (ddt, \(J = 10.2, 16.8, 6.6\) Hz, 1H); ¹³C NMR (CDCl\(_3\)) \(\delta\) -3.532, -2.80, 15.13, 19.12, 25.76, 48.53, 62.18, 75.14, 98.45 (\(J = 29.2\) Hz), 119.72, 122.11 (\(J = 296.6\) Hz), 134.22. Found: C, 35.59; H, 5.42%. Calcd for C\(_{14}\)H\(_{25}\)Br\(_2\)F\(_3\)O\(_2\)Si: C, 35.76; H, 5.36%.

2,2-Dibromo-3-(tert-butyldimethylsiloxy)-3-phenylpropanal (13g): Bp 120 °C (0.5 Torr); IR (neat) 2952, 2926, 2888, 2854, 1736, 1255, 1100, 1074, 837, 778, 698 cm\(^{-1}\); ¹H NMR (CDCl\(_3\)) \(\delta\) -0.27 (s, 3H), 0.09 (s, 3H), 0.86 (s, 9H), 5.15 (s, 1H), 7.30–7.38 (m, 3H), 7.45–7.52 (m, 2H), 9.22 (s, 1H); ¹³C NMR (CDCl\(_3\)) \(\delta\) -5.42, -4.70, 17.97, 25.49, 75.41, 78.46, 127.75, 129.18, 129.30, 137.48, 185.50. Found: C, 42.56; H, 5.18%. Calcd for C\(_{15}\)H\(_{22}\)Br\(_2\)O\(_2\)Si: C, 42.67; H, 5.25%.

4-(tert-Butyldimethylsiloxy)-3,3-dichloro-1,1,1-trifluoro-4-phenyl-2-butane (13h): Bp 95 °C (0.5 Torr); IR (neat) 2954, 2930, 2858, 1768, 1262, 1219, 1173, 1077, 879, 840, 781, 700 cm\(^{-1}\); ¹H NMR (CDCl\(_3\)) \(\delta\) -0.28 (s, 3H), 0.05 (s, 3H), 0.84 (s, 9H), 5.45 (s, 1H), 7.34–7.42 (m, 3H), 7.50–7.56 (m, 2H); ¹³C NMR (CDCl\(_3\)) \(\delta\) -5.77, -4.58, 17.83, 25.38, 78.43, 85.20, 115.51 (q, \(J = 292.5\) Hz), 127.74, 129.50, 129.86, 135.58, 180.5 (q, \(J = 35.5\) Hz). Found: C, 47.75; H, 5.21%. Calcd for C\(_{16}\)H\(_{21}\)Cl\(_2\)F\(_3\)O\(_2\)Si: C, 47.89; H, 5.27%.

Diastereoselective Syntheses of Alkyl Silyl Mixed Acetals. The procedure is the same as that of the reaction of tert-butyldimethylsilyldihalomethylolithium with achiral esters: 1,1-Dibromo-2-(tert-butyldimethylsiloxy)-2-(1-phenylethoxy)-2-phenylethane (17a): Bp 150–153 °C (bath temp, 0.5 Torr); IR (neat) 3058, 3024, 2954, 2926, 2884, 2854, 1449, 1257, 1201, 1154, 1027, 873, 836, 778, 696 cm\(^{-1}\); ¹H NMR (CDCl\(_3\)) \(\delta\) 0.29 (s, 3H), 0.32 (s, 3H), 1.04 (s, 9H), 1.43 (d, \(J = 6.5\) Hz, 3H), 4.65 (q, \(J = 6.5\) Hz, 1H), 5.88 (s, 1H), 7.10–7.30 (m, 8H), 7.30–7.35
(m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ -2.05, -1.50, 19.11, 26.03, 26.20, 53.16, 73.95, 101.78, 125.86, 126.99, 127.41, 127.79, 128.08, 128.66, 137.96, 144.82. Found: C, 51.20; H, 5.89%. Calcd for C$_{22}$H$_{30}$Br$_2$O$_2$Si: C, 51.37; H, 5.88%.

1,1-Dibromo-2-(tert-butyldimethylsiloxy)-2-(l-methoxy)ethane (17b): Faster moving band; R$_f$ = 0.42 (Hexane); Bp 125 °C (0.5 Torr); IR (neat) 2950, 2924, 2856, 1463, 1364, 1254, 1137, 1055, 871, 836, 775, 712 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.16 (s, 3H), 0.17 (s, 3H), 0.79 (d, J = 6.9 Hz, 3H), 0.83-1.05 (m, 3H), 0.90 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H), 0.95 (s, 9H), 1.25-1.40 (m, 2H), 1.60-1.70 (m, 2H), 1.95-2.05 (m, 1H), 2.32 (ddq, J = 2.7, 6.9, 6.9 Hz, 1H), 3.41 (dd, J = 3.9, 10.5, 10.5 Hz, 1H), 4.92 (d, J = 1.5 Hz, 1H), 5.45 (d, J = 1.5 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -4.42, -4.26, 16.17, 17.99, 20.78, 22.27, 23.40, 25.26, 25.62, 31.36, 34.33, 39.46, 47.76, 49.12, 73.84, 92.62. Found: C, 45.61; H, 7.62%. Calcd for C$_{18}$H$_{36}$Br$_2$O$_2$Si: C, 45.77; H, 7.68%. slower moving band; R$_f$ = 0.35 (Hexane); Bp 125 °C (0.5 Torr); IR (neat) 2948, 2924, 2856, 1472, 1364, 1253, 1137, 1056, 870, 836, 776, 711 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.15 (s, 3H), 0.16 (s, 3H), 0.75 (d, J = 6.9 Hz, 3H), 0.80-1.15 (m, 3H), 0.88 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H), 0.93 (s, 9H), 1.20-1.40 (m, 2H), 1.55-1.70 (m, 2H), 2.03-2.13 (m, 1H), 2.38 (ddq, J = 2.4, 6.9, 6.9 Hz, 1H), 3.26 (ddd, J = 4.2, 10.5, 10.5 Hz, 1H), 4.85 (d, J = 1.5 Hz, 1H), 5.44 (d, J = 1.5 Hz, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ -4.25, -3.99, 15.92, 17.98, 21.09, 22.08, 22.79, 24.60, 25.61, 31.57, 34.10, 42.28, 48.30, 48.63, 78.34, 96.70. Found: C, 45.65; H, 7.63%. Calcd for C$_{18}$H$_{36}$Br$_2$O$_2$Si: C, 45.77; H, 7.68%.

1,1-Dibromo-2-(tert-butyldimethylsiloxy)-2-(1-phenylethoxy)ethane (17c, 80:20 isomeric mixture): Bp 110 °C (0.5 Torr); IR (neat) 2952, 2926, 2882, 2854, 1463, 1254, 1138, 1056, 837, 778, 699 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ -0.04 (s, 0.6H), -0.03 (s, 0.6H), 0.08 (s, 2.4H), 0.14 (s, 2.4H), 0.84 (s, 1.8H), 0.95 (s, 7.2H), 1.498 (d, J = 6.6 Hz, 2.4H), 1.503 (d, J = 6.6 Hz, 0.6H), 4.64 (d, J = 2.4 Hz, 0.8H), 4.74 (q, J = 6.6 Hz, 1H), 4.88 (d, J = 3.0 Hz, 0.2H), 5.23 (d, J = 2.4 Hz, 0.8H), 5.51 (d, J = 3.0 Hz, 0.2H), 7.24-7.40 (m, 5H); $^{13}$C
NMR (CDCl₃) δ -4.89, -4.53, -4.17, 17.90, 18.06, 23.12, 24.42, 25.50, 25.61, 48.32, 48.53, 75.28, 75.76, 95.33, 96.28, 126.49, 126.64, 127.76, 128.08, 128.44, 128.66, 142.49, 143.03. Found: C, 43.74%; H, 5.86%. Calcd for C₁₆H₂₆Br₂O₂Si: C, 43.85%; H, 5.98%.

1,1-Dibromo-2-(tert-butyldimethylsiloxy)-2-(1-(2,4,6-trimethylphenyl)ethoxy)ethane (17d, 89:11 isomeric mixture): Bp 125 °C (0.5 Torr); IR (neat) 2950, 2928, 2854, 1464, 1254, 1154, 1047, 837, 777, 708 cm⁻¹; ¹H NMR (CDCl₃) δ -0.06 (s, 0.33H), 0.02 (s, 0.33H), 0.20 (s, 2.67H), 0.22 (s, 2.67H), 0.85 (s, 0.99H), 0.97 (s, 8.01H), 1.51 (d, J = 6.6 Hz, 3.3H), 1.56 (d, J = 6.9 Hz, 2.67H), 2.34 (s, 0.33H), 2.25 (s, 2.67H), 2.41 (bs, 6H), 4.72 (d, J = 2.1 Hz, 0.89H), 4.92 (d, J = 3.3 Hz, 0.11H), 5.145 (d, J = 2.1 Hz, 0.89H), 5.151 (q, J = 6.9 Hz, 0.89H), 5.19 (q, J = 6.6 Hz, 0.11H), 5.43 (d, J = 3.3 Hz, 0.11H), 6.79 (s, 0.22H), 6.82 (s, 1.78H); ¹³C NMR (CDCl₃) δ -4.51, -3.95, 18.05, 20.51, 20.65, 20.84, 25.64, 48.61, 73.59, 98.29, 130.05, 134.96, 135.85, 136.91. Found: C, 47.45%; H, 6.65%. Calcd for C₁₉H₃₂Br₂O₂Si: C, 47.51%; H, 6.71%.

1,1-Dibromo-2-(tert-butyldimethylsiloxy)-3,3,3-trifluoro-2-(1-phenylethoxy)propane (17e, 95:5 isomeric mixture): Bp 100 °C (0.5 Torr); IR (neat) 2954, 2928, 2856, 1297, 1254, 1147, 1055, 866, 783, 698, 669 cm⁻¹; ¹H NMR (CDCl₃) δ 0.12 (s, 0.15H), 0.24 (s, 2.85H), 0.27 (s, 0.15H), 0.29 (s, 2.85H), 0.86 (s, 0.45H), 0.97 (s, 8.55H), 1.53 (d, J = 6.6 Hz, 0.15H), 1.55 (d, J = 6.6 Hz, 2.85H), 5.13 (q, J = 6.6 Hz, 1H), 5.54 (s, 0.95H), 5.74 (s, 0.05H), 7.24–7.38 (m, 5H); ¹³C NMR (CDCl₃) δ -3.41, -3.20, 18.70, 25.35, 25.67, 43.65, 72.71, 97.29 (q, 29.9 Hz), 121.69 (q, 296.1 Hz), 126.18, 127.76, 128.34, 142.89. Found: C, 40.53%; H, 5.02%. Calcd for C₁₉H₂₅Br₂F₃O₂Si: C, 40.33%; H, 4.98%.

1,1-(tert-Butyldimethylsiloxy)-1-(l-menthoxy)ethane (18): Faster moving band (21); Rf = 0.48 (Hexane/ACOEt = 40/1); Bp 85 °C (0.5 Torr); IR (neat) 2950, 2926, 2856, 1461, 1378, 1253, 1128, 1089, 965, 829, 774 cm⁻¹; ¹H NMR (CDCl₃) δ 0.07 (s, 3H), 0.08 (s,
3H), 0.76 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 7.2 Hz, 3H), 0.89 (s, 9H), 0.90 (d, J = 7.2 Hz, 3H), 0.91–1.40 (m, 5H), 1.27 (d, J = 5.1 Hz, 3H), 1.50–1.70 (m, 2H), 2.00 (m, 1H), 2.25 (ddq, J = 3.0, 7.2, 7.2 Hz, 1H), 3.37 (ddd, J = 3.9, 10.8, 10.8 Hz, 1H), 5.10 (q, J = 5.1 Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 4.67, 16.14, 17.95, 20.90, 22.33, 23.34, 24.84, 25.13, 25.70, 31.36, 34.51, 40.09, 47.80, 72.94, 90.25. Found: C, 68.92; H, 12.23%. Calcd for C\(_{18}\)H\(_{38}\)O\(_2\)Si: C, 68.73; H, 12.18%.

slower moving band (22); R\(_f\) = 0.45 (Hexane/AcOEt = 40/1); Bp 85 °C (0.5 Torr); IR (neat) 2950, 2926, 2856, 1460, 1379, 1253, 1128, 1087, 965, 829, 774 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.08 (5, 3H), 0.10 (5, 3H), 0.76 (d, J = 6.9 Hz, 3H), 0.80–1.40 (m, 5H), 0.87 (d, J = 6.9 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H), 0.90 (s, 9H), 1.29 (d, J = 5.1 Hz, 3H), 1.50–1.70 (m, 2H), 2.03–2.18 (m, 2H), 3.14 (ddd, J = 3.9, 10.5, 10.5 Hz, 1H), 4.96 (q, J = 5.1 Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 4.62, –4.29, 16.17, 17.85, 21.11, 22.11, 23.20, 24.57, 25.29, 25.67, 31.78, 34.32, 43.74, 48.07, 78.40, 96.48. Found: C, 68.85; H, 12.21%. Calcd for C\(_{18}\)H\(_{38}\)O\(_2\)Si: C, 68.73; H, 12.18%.

5,5-Dibromo-4-(tert-butyldimethylsiloxy)-1-pentene (19): Bp 80 °C (0.5 Torr); IR (neat) 2948, 2926, 2886, 2852, 1644, 1464, 1362, 1256, 1135, 1097, 912, 836, 775, 692 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.09 (s, 3H), 0.13 (s, 3H), 0.91 (s, 9H), 2.40–2.58 (m, 2H), 3.88 (ddd, J = 3.6, 5.4, 6.0 Hz, 1H), 5.13 (dd, J = 9.9, 1.5 Hz, 1H), 5.17 (dd, J = 16.8, 1.5 Hz, 1H), 5.59 (d, J = 3.6 Hz, 1H), 5.76 (ddt, J = 16.8, 9.9, 6.9 Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) –4.63, –4.38, 18.01, 25.66, 38.55, 51.00, 76.46, 118.86, 133.10. Found: C, 37.04; H, 6.14%. Calcd for C\(_{11}\)H\(_{22}\)Br\(_2\)OSi: C, 36.89; H, 6.19%.

4-(l-Menthoxy)-1-pentene (23, 68:32 isomeric mixture): Bp 85 °C (5 Torr); IR (neat) 2952, 2920, 2866, 1643, 1453, 1384, 1331, 1084, 1050, 910 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.74 (d, J = 6.9 Hz, 3H), 0.77–1.02 (m, 3H), 0.88 (d, J = 6.6 Hz, 3H), 0.89 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.0 Hz, 0.96H), 1.10–1.22 (m, 1H), 1.13 (d, J = 6.0 Hz, 2.04H), 1.23–1.42 (m, 1H), 1.54–1.66 (m, 2H), 1.97–2.36 (m, 3H), 3.06 (ddd, J = 4.5, 10.8, 10.8 Hz, 0.32H), 3.08
(ddd, \( J = 4.5 \), 10.8, 10.8 Hz, 0.68H), 3.52 (ddq, \( J = 6.0 \), 6.0, 6.0 Hz, 1H), 4.98-5.09 (m, 2H), 5.79 (ddd, \( J = 7.2 \), 10.2, 17.4 Hz, 0.68H), 5.81 (ddd, \( J = 6.6 \), 10.2, 17.1 Hz, 0.32H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 15.85, 19.62, 21.18, 21.27, 22.27, 22.89, 22.99, 24.73, 24.85, 31.54, 34.42, 41.19, 41.69, 42.07, 42.26, 48.48, 48.59, 72.57, 73.09, 76.58, 116.43, 116.81, 135.32, 135.69.

Found: C, 80.09%; H, 12.61%. Calcd for C\(_{15}\)H\(_{28}\)O: C, 80.29; H, 12.58%.

1-(tert-Butyldimethylsiloxy)-1-(1-phenylethoxy)ethane (24, 80:20 isomeric mixture): Bp 80°C (0.5 Torr); IR (neat) 2952, 2928, 2890, 2854, 1453, 1389, 1253, 1117, 1079, 974, 829, 775, 734, 699 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\(_3\)) \( \delta \) -0.01 (s, 0.6H), 0.00 (s, 2.4H), 0.01 (s, 0.6H), 0.03 (s, 2.4H), 0.82 (s, 1.8H), 0.90 (s, 7.2H), 1.28 (d, \( J = 5.4 \) Hz, 2.4H), 1.31 (d, \( J = 5.1 \) Hz, 0.6H), 1.40 (d, \( J = 6.3 \) Hz, 0.6H), 1.42 (d, \( J = 6.6 \) Hz, 2.4H), 4.69-4.80 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) -4.73, -4.60, -4.45, -4.35, 15.05, 17.92, 22.91, 24.27, 24.47, 24.78, 25.58, 25.68, 72.72, 73.17, 92.54, 93.30, 126.17, 126.30, 127.01, 127.36, 128.20, 128.47, 144.19, 144.82. Found: C, 68.39%; H, 9.98%. Calcd for C\(_{16}\)H\(_{28}\)O\(_2\)Si: C, 68.52; H, 10.06%.

4-(1-Phenylethoxy)-1-pentene (25, 89:11 isomeric mixture): Bp 45°C (0.5 Torr); IR (neat) 2970, 2924, 2872, 1643, 1452, 1374, 1092, 912, 759, 699 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\(_3\)) \( \delta \) 1.05 (d, \( J = 6.3 \) Hz, 0.33H), 1.14 (d, \( J = 6.3 \) Hz, 2.67H), 1.406 (d, \( J = 6.3 \) Hz, 0.33H), 1.412 (d, \( J = 6.3 \) Hz, 2.67H), 2.11 (dddt, \( J = 14.0 \), 7.2, 6.3, 1.2 Hz, 1H), 2.27 (dddt, \( J = 14.0 \), 7.2, 6.3, 1.2 Hz, 1H), 3.38 (ttq, \( J = 6.3 \), 6.3, 6.3 Hz, 1H), 4.54 (q, \( J = 6.3 \) Hz, 0.89H), 4.55 (q, \( J = 6.3 \) Hz, 0.11H), 4.94-5.03 (m, 2H), 5.71 (ddt, \( J = 17.1 \), 10.5, 7.2 Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 18.86, 24.59, 41.84, 71.80, 74.69, 116.57, 126.44, 127.35, 128.36, 135.45, 144.57. Found: C, 82.13%; H, 9.61%. Calcd for C\(_{13}\)H\(_{18}\)O: C, 82.06; H, 9.53%.
References and Notes


2. Tandem transformations initiated by the migration of a silyl group have been reviewed. Jankowski, P.; Raubo, P.; Wicha, J. Synlett. 1994, 985.


An addition of HMPA facilitated the rearrangement of silyl group. For instance, an addition of benzyl bromide and HMPA to a mixture derived from ethyl formate and 1a provided HC(OEt)(OSiMe2-t-Bu)CBr2CH2Ph in 70% yield.

Reaction of tert-butyldimethylsilyldibromomethyl lithium with ethyl trichloroacetate caused lithium-chlorine exchange reaction to form lithium enolate and no adduct could be observed in the reaction mixture. In the case of ethyl dichloroacetate, abstraction of α-proton of ester took place and gave a trace of adduct.


Diastereoselective formation of 1-menthyl trimethylsilyl acetal has been performed by the reduction of 1-menthyl carboxylate with i-Bu2AlH followed by stirring with trimethylsilyl triflate. See ref. 5 (b).

In contrast, treatment of 21 with allyltrimethylsilane in the presence of TiCl4 gave allylated silyl ether.

Diastereoselective formation of ether via silyl acetal intermediate from aldehyde, secondary alcohol silyl ether, and allyltrimethylsilane in the presence of a catalytic amount of Ph2BOTf has

CHAPTER 3

Facile Syntheses of $\alpha$-Bromo-$\alpha$-Silyl Ketones and $\alpha$-Bromoacylsilanes from tert-Butylidimethylsilyldibromomethane and Carbonyl Compounds

An addition of benzaldehyde to an ethereal solution of tert-butyldimethylsilyldibromomethyl lithium, derived from $t$-BuMe$_2$SiCHBr$_2$ and lithium diisopropylamide, provided $\alpha$-bromo-$\alpha$-silyl ketone. The use of ketone instead of aldehyde afforded $\alpha$-bromoacylsilane via a bromo silyl epoxide intermediate. Further treatment of the $\alpha$-bromo-$\alpha$-silyl ketone with butyllithium afforded lithium enolate which provided $\beta$-hydroxy-$\alpha$-silyl ketone upon treatment with aldehyde in ether. The enolate gave $\alpha,\beta$-unsaturated ketone or monosilyl ether of 2-acyl-1,3-diol in THF instead of ether. The use of isopropylmagnesium bromide in place of butyllithium also resulted in a formation of the corresponding magnesium enolate.
In the last two decades, both α-silyl ketone\(^1\) (β-ketosilane) and acylsilane\(^2\) have been extensively explored in organic synthesis. In many cases, they are prepared through a multistep operation involving oxidation of the corresponding hydroxysilane. The author discusses here a facile and non-oxidative method for formation of α-bromo-α-silyl ketones and α-bromoacylsilanes\(^3\) from tert-butylidemethylsilyldibromomethyl lithium and carbonyl compounds. The reductive formation of enolates from α-bromo-α-silyl ketones and their aldol-type reaction with aldehydes involving the 1,3-rearrangement of a silyl group (homo-Brook rearrangement) from carbon to oxygen is also described.\(^4\)

The author has reported\(^5\) that treatment of a THF solution of tert-butylidemethylsilyldihalomethyl lithium with aldehyde (R\(^1\)CHO) followed by an addition of a second aldehyde (R\(^2\)CHO) and HMPA gave a monosilyl ether of 1,3-diol (R\(^1\)CH(OSiMe\(_2\)-t-Bu)CX\(_2\)CH(OH)R\(^2\)) (Scheme 1). The use of ether instead of THF as a solvent has proved to change the reaction pathway dramatically and treatment of tert-butylidemethylsilyldibromomethyl lithium (1) with aldehyde (R\(^1\)CHO) gave α-bromo-α-silyl ketone (R\(^1\)COCBrSiMe\(_2\)-t-Bu). Furthermore, the reaction of 1 with ketone (R\(^2\)_2CO) under the same conditions afforded α-bromoacylsilane (R\(^2\)_2CBrCOSiMe\(_2\)-t-Bu).

![Scheme 1](image)

Treatment of tert-butylidemethylsilyldibromomethyl lithium (1), derived from t-BuMe\(_2\)SiCHBr\(_2\) and lithium diisopropylamide, with benzaldehyde in ether at -78 °C provided α-bromo-α-silyl ketone 3a in 76% yield upon warming the reaction mixture to room temperature. The representative results are shown in Scheme 2. Quenching the reaction mixture at -78 °C with dilute hydrochloric acid afforded a simple adduct (PhCH(OH)CBr\(_2\)SiMe\(_2\)-t-Bu) in 77% yield.\(^5\) Thus, the reaction obviously involves initial formation of adducts 2 followed by 1,2-migration of hydrogen\(^6\) giving α-bromo-α-silyl ketones. The tert-butylidemethylsilyl group played a critical role in the formation of α-bromo-α-silyl ketones. Thus, the reaction of
trimethylsilyldibromomethyllithium with benzaldehyde gave phenacyl bromide and 2,2-dibromo-1-phenyl-2-trimethylsilylethanol in 29% and 26% yield, respectively and no α,bromo-α-silyl ketone was detected in the reaction mixture. The formation of α-bromoacetophenone might result from desilylation of α-bromo-α-trimethylsilylacetophenone during aqueous workup. The use of tert-butyldimethylsilyldichloromethyllithium resulted in a formation of complex mixtures.

Scheme 2

The reaction of 1 with ketone such as cyclohexanone in place of aldehyde gave α-bromoacylsilane. The representative results are shown in Scheme 3. An addition of TMEDA increased the yield of the product, for example, from 54% to 72% in the case of 6a. Interestingly, the addition of TMEDA did not accelerate the 1,3-rearrangement of the silyl group from carbon to negatively charged oxygen. The effect of TMEDA is quite different from that of HMPA which does cause 1,3-rearrangement. The reaction would proceed via bromo silyl epoxide which is so unstable as to rearrange into acylsilane. This mechanism was supported by the following experiment (Scheme 4). Treatment of 1-bromo-1-trimethylsilyl-1-octene with m-chloroperoxybenzoic acid in dichloromethane afforded α-bromoacylsilane (n-C_6H_{13}CHBrCOSiMe_3) in 50% yield. In the case of aldehyde (vide supra), no corresponding α-bromoacylsilane could be observed. Thus, the 1,2-migration of hydrogen in the adduct 2 seems to be much faster than epoxide formation.
Then we turned our attention toward the reductive formation of enolate\(^7\) from \(\alpha\)-bromo-\(\alpha\)-silyl ketone. An addition of butyllithium to an ether solution of \(\alpha\)-bromo-\(\alpha\)-silyl ketone \(3\) at \(-78\, ^\circ\text{C}\) caused a lithium-bromine exchange to afford an enolate \(7^8\) which was quenched with dilute hydrochloric acid to give \(\alpha\)-silyl ketone \((R^1\text{COCH}_2\text{SiMe}_2\text{-t-Bu})\) quantitatively. The sequential treatment of the enolate \(7\) with aldehyde in ether followed by quenching with acetic acid yielded \(\beta\)-hydroxy-\(\alpha\)-silyl ketone \(9\). An addition of HMPA to the adduct \(8\) before quenching provided only \((E)-\alpha,\beta\)-unsaturated ketone \(10\) with high stereoselectivity in good yield. Six examples are shown below (Scheme 6).

**Scheme 5**

\[
\begin{align*}
\text{R}^1\text{COCH}_2\text{SiMe}_2\text{-t-Bu} \quad &\xrightarrow{\text{n-BuLi, } -78^\circ\text{C}} \quad \text{R}^1\text{CO} \overset{\text{OLi}}{\xrightarrow{\text{SiMe}_2\text{-t-Bu}}} \\
\text{8} \quad &\xrightarrow{\text{HMPA}} \quad \text{R}^1\text{CO} \overset{\text{OLi}}{\xrightarrow{\text{SiMe}_2\text{-t-Bu}}} \\
\end{align*}
\]

| \(9a\) | \(R^1 = R^2 = \text{Ph}\) | \(85\%\) |
| \(9b\) | \(R^1 = \text{Ph}, R^2 = n\text{-C}_6\text{H}_{13}\) | \(82\%\) |
| \(10a\) | \(R^1 = R^2 = \text{Ph}\) | \(85\%\) |
| \(10b\) | \(R^1 = \text{Ph}, R^2 = n\text{-C}_6\text{H}_{13}\) | \(80\%\) |
| \(10c\) | \(R^1 = \text{c.-C}_6\text{H}_{11}, R^2 = \text{Ph}\) | \(83\%\) |
| \(10d\) | \(R^1 = \text{c.-C}_6\text{H}_{11}, R^2 = n\text{-C}_6\text{H}_{13}\) | \(84\%\) |
Again, the reaction solvent played a critical role in the reaction of enolate 7 with aldehydes. In THF, the reaction of enolate 7 with aldehyde (1.1 equiv) provided (E)-α,β-unsaturated ketone 10 directly without an addition of HMPA (Scheme 6). For instance, the enolate 7a (R¹ = Ph) or 7b (R¹ = c-C₆H₁₁) gave α,β-unsaturated ketone 10a or 10d in 84% or 79% yield, respectively, upon treatment with benzaldehyde or heptanal. An addition of an excess of PhCHO⁹ to 7a gave monosilyl ether of 2-acyl-1,3-diol 12a (R¹ = R² = Ph), derived from two molecules of aldehyde, in addition to α,β-unsaturated ketone 10a. The yield of 12a increased with increase of the amount of benzaldehyde employed and the use of four molar equivalents of benzaldehyde per one mol of enolate gave a mixture of 10a and 12a in 23% and 73% yields, respectively. Thus, the 1,3-rearrangement¹⁰ of the silyl group (8→11) takes place readily in THF and an addition of 11 to the second molecule of aldehyde competes with elimination of t-BuMe₂SiOLi to give α,β-unsaturated ketone.

Scheme 6

In these reactions, α,β-unsaturated ketone does not arise from 1,2-elimination of silanoxide (Peterson elimination) from 8. This was confirmed by the following experiment (Scheme 7). The reaction of magnesium enolate 13 with heptanal (vide infra) gave a diastereomeric mixture (56/44) of β-hydroxy-α-silyl ketone 9d. It was anticipated that Peterson-type 1,2-elimination of silanoxide would proceed in syn fashion with high stereospecificity to afford a mixture of (E)- and (Z)-α,β-unsaturated ketone (E/Z = 56/44). However, treatment of the diastereomeric mixture 9d with lithium diisopropylamide provided only (E)-α,β-unsaturated ketone 10d.¹¹ Thus, stereoselective
formation of \((E)-\alpha,\beta\)-unsaturated ketone could be explained by the relative stabilities of the rotamer A of the intermediate enolate 11 (R1 = c-C6H11, R2 = n-C6H13), which is more stable than B (Figure 1).\(^{10}\)

Scheme 7

\[
\begin{array}{c}
\text{HO} \\
\text{SiMe}_2\text{-t-Bu} \\
\text{n-C}_6\text{H}_{13}
\end{array} \quad \xrightarrow{\text{LDA}} \quad
\begin{array}{c}
\text{O} \\
\text{n-C}_6\text{H}_{13}
\end{array}
\]

(\text{threo / erythro} = 56/44)

Figure 1

\[
\begin{array}{c}
\text{LiO} \\
\text{H} \\
\text{R}^1 \\
\text{H} \\
\text{H} \\
\text{OLi}
\end{array}
\]

\text{Favored A}

\[
\begin{array}{c}
\text{LiO} \\
\text{H} \\
\text{R}^1 \\
\text{H} \\
\text{H} \\
\text{OLi}
\end{array}
\]

\text{Disfavored B}

Treatment of \(\alpha\)-bromo-\(\alpha\)-silyl ketone 3 with isopropylmagnesium bromide in ether gave magnesium enolate 13 in good yields. The reaction of the magnesium enolate with aldehydes afforded \(\beta\)-hydroxy-\(\alpha\)-silyl ketone 9\(^{12}\) selectively in good yields (Scheme 8). No trace of \(\alpha,\beta\)-unsaturated ketone could be observed in the reaction mixture. 1,3-Rearrangement of the silyl group could not take place because of the lower nucleophilicity of magnesium alkoxide compared to lithium alkoxide.
Finally, one-pot synthesis of \( \alpha,\beta \)-unsaturated ketone starting from tert-butyldimethylsilyl(dibromomethyl)lithium (1) was conducted. An addition of aldehyde to an ethereal solution of 1 gave \( \alpha \)-bromo-\( \alpha \)-silyl ketone which was further converted into lithium enolate with sec-BuLi\(^{15} \) and then treated with second aldehyde and subsequently with HMPA to afford \( \alpha,\beta \)-unsaturated ketone 10a or 10b in 59% or 57% yield, respectively (Scheme 9).
Experimental

**General Procedure for the Preparation of α-Bromo-α-silyl Ketones.** An ethereal solution of tert-butyldimethyl(dibromomethyl)silane (0.29 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in ether (3 ml) at −78 °C under argon atmosphere. After the mixture was stirred for 1 h at −78 °C, benzaldehyde (0.13 g, 1.2 mmol) in Et$_2$O (1 ml) was added and the reaction mixture was allowed to warm to ambient temperature over 10 h with stirring. The mixture was poured into saturated aqueous ammonium chloride and extracted with hexane (20 ml × 3). The combined organic layer were dried over Na$_2$SO$_4$ and concentrated in vacuo. Purification by silica-gel column chromatography gave 1-bromo-1-(tert-butyldimethylsilyl)-2-phenyl-2-ethanone (3a, 0.24 g) in 76% yield: Mp 55–56 °C; IR (neat) 2952, 2926, 2856, 1676, 1465, 1448, 1261, 832, 732 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.01 (s, 3H), 0.24 (s, 3H), 0.95 (s, 9H), 4.90 (s, 1H), 7.40–7.65 (m, 3H), 7.90 (m, 2H); $^{13}$C NMR (CDCl$_3$) δ −6.11, 5.67, 17.96, 27.03, 35.73, 128.49, 128.77, 133.37, 136.61, 196.32. Found: C, 53.37; H, 6.79%. Calcd for C$_{14}$H$_{21}$BrOSi: C, 53.67; H, 6.76%.

1-Bromo-1-(tert-butyldimethylsilyl)-2-cyclohexyl-2-ethanone (3b): Bp 85 °C (0.5 Torr); IR (neat) 2926, 2852, 1703, 1685, 1450, 1251, 1000, 840, 824 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.10 (s, 3H), 0.23 (s, 3H), 0.96 (s, 9H), 1.15–1.95 (m, 10H), 2.65 (tt, J = 11.0, 3.1 Hz, 1H), 3.95 (s, 1H); $^{13}$C NMR (CDCl$_3$) δ −6.10, 17.78, 25.31, 25.69, 25.93, 26.99, 28.59, 29.71, 39.25, 50.05, 209.12. Found: C, 52.58; H, 8.67%. Calcd for C$_{14}$H$_{27}$BrOSi: C, 52.65; H, 8.52%.

1-Bromo-1-(tert-butyldimethylsilyl)-4-phenyl-3-buten-2-one (3c): Bp 100 °C (0.5 Torr); IR (neat) 2950, 2926, 2854, 1670, 1607, 1466, 1311, 1253, 1135, 1068, 980, 839, 823, 787 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.16 (s, 3H), 0.28 (s, 3H), 0.97 (s, 9H), 4.05 (s, 1H), 7.08 (d, J = 15.8 Hz, 1H), 7.35–7.60 (m, 5H), 7.66 (d, J = 15.8 Hz, 1H); $^{13}$C NMR (CDCl$_3$) δ −6.37, −5.97, 18.02, 26.85, 42.10, 122.95, 128.54, 128.95, 130.74, 134.29, 143.77, 194.70. Found: C, 56.46; H, 6.90%. Calcd for C$_{16}$H$_{23}$BrOSi: C, 56.63; H, 6.83%.
I-Bromo-1-(tert-butyldimethylsilyl)-3,3-dimethyl-2-butanone (3d): Bp 60 °C (0.5 Torr); IR (neat) 2958, 2856, 1698, 1366, 1251, 1209, 1053, 994, 842, 823, 779 cm⁻¹; ¹H NMR (CDCl₃) δ 0.03 (s, 3H), 0.32 (s, 3H), 0.97 (s, 9H), 1.22 (s, 9H), 4.18 (s, 1H); ¹³C NMR (CDCl₃) δ -5.95, -5.74, 17.60, 26.97, 27.05, 28.84, 46.00, 212.16. Found: C, 49.40; H, 8.60%. Calcd for C₁₂H₂₅BrOSi: C, 49.14; H, 8.59%.

I-Bromo-1-(tert-butyldimethylsilyl)-2-octanone (3e): Bp 82 °C (0.5 Torr); IR (neat) 2928, 2856, 1693, 1467, 1253, 838, 824, 775 cm⁻¹; ¹H NMR (CDCl₃) δ 0.11 (s, 3H), 0.24 (s, 3H), 0.87 (t, J = 7.5 Hz, 3H), 0.96 (s, 9H), 1.20–1.70 (br, 8H), 2.42 (ddd, J = 17.3, 8.2, 6.6 Hz, 1H), 2.78 (ddd, J = 17.3, 8.2, 6.6 Hz, 1H), 3.86 (s, 1H); ¹³C NMR (CDCl₃) δ -6.30, -5.95, 14.02, 17.83, 22.48, 24.15, 26.82, 28.81, 31.56, 41.28, 41.84, 206.66. Found: C, 52.43; H, 9.38%. Calcd for C₁₄H₂₉BrOSi: C, 52.32; H, 9.10%.

General Procedure for the Preparation of α-Bromoacylsilanes. An ethereal solution of tert-butyldimethyl(dibromomethyl)silane (0.29 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in ether (3 ml) at -78 °C under argon atmosphere. After being stirred for 1 h at -78 °C, cyclohexanone (0.12 g, 1.2 mmol) in Et₂O (1 ml) and TMEDA (0.14 g, 1.2 mmol) were added and the reaction mixture was allowed to warm to ambient temperature over 10 h with stirring. The mixture was poured into saturated aqueous ammonium chloride and extracted with hexane (20 ml × 3). The combined organic layer were dried over Na₂SO₄ and concentrated in vacuo. Purification by silica-gel column chromatography gave 1-bromocyclohexyl tert-butyldimethylsilyl ketone (6a, 0.22 g) in 72% yield: Bp 105 °C (1 Torr); IR (neat) 2928, 2854, 1633, 1464, 1448, 1249, 1112, 837, 774, 738, 674 cm⁻¹; ¹H NMR (CDCl₃) δ 0.34 (s, 6H), 0.97 (s, 9H), 1.20–1.36 (m, 1H), 1.60–1.70 (m, 3H), 1.70–1.85 (m, 4H), 2.11 (m, 2H); ¹³C NMR (CDCl₃) δ -3.45, 17.34, 22.73, 25.18, 26.95, 34.31, 79.81, 233.34. Found: C, 51.06; H, 8.44%. Calcd for
C\textsubscript{13}H\textsubscript{25}BrOSi: C, 51.14; H, 8.25%.

2-Bromo-1-(\textit{tert}-butyldimethylsilyl)-2-ethyl-1-butanone (6b): Bp 98 °C (1 Torr); IR (neat) 2930, 2882, 2856, 1635, 1463, 1249, 1097, 1015, 936, 821, 775, 676 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \( \delta \) 0.34 (s, 6H), 0.92 (t, \( J = 7.2 \) Hz, 6H), 0.97 (s, 9H), 2.00 (dq, \( J = 14.7, 7.2 \) Hz, 2H), 2.07 (dq, \( J = 14.7, 7.2 \) Hz, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \( \delta \) -3.42, 9.77, 17.45, 26.97, 28.72, 84.01, 235.53. Found: C, 49.37; H, 8.87%. Caled for C\textsubscript{12}H\textsubscript{25}BrOSi: C, 49.14; H, 8.59%.

2-Bromo-1-(\textit{tert}-butyldimethylsilyl)-2,2-diphenyl-1-ethanone (6c): Mp 148-149 °C; IR (neat) 1649, 1445, 1365, 1252, 1020, 834, 776, 701, 676 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \( \delta \) -0.03 (5, 6H), 0.99 (5, 9H), 7.20-7.30 (m, 4H), 7.30-7.40 (m, 6H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \( \delta \) -3.79, 17.70, 27.27, 81.02, 128.07, 128.44, 130.35, 137.70, 227.13. Found: C, 61.67; H, 6.42%. Caled for C\textsubscript{20}H\textsubscript{25}BrOSi: C, 61.69; H, 6.47%.

Preparation of Lithium Enolate and its Aldol-type Reaction in THF. Under argon atmosphere, to a solution of 1-bromo-1-(\textit{tert}-butyldimethylsilyl)-2-phenyl-2-ethanone 3a (0.16 g, 0.5 mmol) in THF (5 ml) was added butyllithium in hexane (1.60 M, 0.34 ml, 0.55 mmol) dropwise at -78 °C. After being stirred for 30 min, benzaldehyde (0.06 g, 0.55 mmol) in THF was added and the whole reaction mixture was stirred for another 1 h. Extractive workup (saturated aqueous ammonium chloride and ethyl acetate) followed by purification by silica-gel column chromatography gave phenyl 2-phenylethenyl ketone (10a, 0.18 g) in 85% yield. The use of large excess (4.0 equiv) of benzaldehyde afforded 2-(1-\textit{tert}-butyldimethylsiloxy)benzyl-3-hydroxy-1,3-diphenyl-1-propanone (12a, 0.16 g) in 73% yield. 12a: (mixture of two diastereomers) IR (neat) 3466, 3084, 3055, 2952, 2926, 2854, 1655, 1598, 1450, 1363, 1253, 1206, 1066, 937, 863, 836, 777, 699, 550 cm\textsuperscript{-1}; Major product: \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \( \delta \) -0.36 (s, 3H), -0.23 (s, 3H), 0.51 (s, 9H), 4.11 (dd, \( J = 2.7, 9.7 \) Hz, 1H), 4.43 (dd, \( J = 2.7, 10.4 \) Hz, 1H), 4.88 (d, \( J = 10.4 \) Hz, 1H), 5.37 (d, \( J = 9.7 \) Hz, 1H), 6.95-7.75 (m, 15H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \( \delta \) -5.74, -4.84, 17.69, 25.31, 60.00,
Preparation of Magnesium Enolate and its Aldol-type Reaction. Under argon atmosphere, to a solution of 1-bromo-1-(tert-butyldimethylsilyl)-2-phenyl-2-ethanone 3a (0.16 g, 0.5 mmol) in ether (5 ml) was added isopropylmagnesium bromide in ether (0.98 M, 0.61 ml, 0.6 mmol) dropwise at 0 °C. After being stirred for 1 h, the resulting purple solution was cooled to −78 °C and benzaldehyde (0.06 g, 0.6 mmol) in ether was added and the whole reaction mixture was stirred for another 1 h. Extractive workup (saturated aqueous ammonium chloride and ethyl acetate) followed by purification by silica-gel column chromatography gave 2-(tert-butyldimethylsilyl)-3-hydroxy-1,3-diphenyl-1-propanone (9a, 0.13 mg, 89:11 diastereomeric mixture) in 78% yield. 9a: IR (neat) 3430, 2952, 2926, 2854, 1636, 1597, 1449, 1339, 1251, 1202, 1051, 1002, 840, 823, 789, 697 cm⁻¹; ¹H NMR (CDCl₃) δ −0.14 (s, 0.33H), −0.05 (s, 2.67H), 0.22 (s, 0.33H), 0.32 (s, 2.67H), 0.89 (s, 8.01H), 0.91 (s, 0.99H), 2.35 (bs, 0.11H), 3.91 (d, J = 2.4 Hz, 0.89H), 4.02 (d, J = 9.3 Hz, 0.11H), 5.23 (dd, J = 2.4, 9.6 Hz, 0.89H), 5.36 (d, J = 9.6 Hz, 0.89H), 5.39 (d, J = 9.3 Hz, 0.11H), 7.13 (m, 1H), 7.20–7.35 (m, 6H), 7.46 (m, 1H), 7.54 (m, 2H); ¹³C NMR (CDCl₃, threo isomer) δ −5.81, −5.27, 17.81, 26.83, 46.66, 74.13, 124.96, 126.95, 128.09, 128.33, 128.51, 132.99, 139.33, 145.78, 207.39. Found: C, 73.83; H, 8.36%. Calcd for C₂₁H₂₈O₂Si: C, 74.07; H, 8.29%.

2-(tert-Butyldimethylsilyl)-3-hydroxy-1-phenyl-1-nonanone (9b, 88:12 diastereomeric mixture): IR (neat) 3464, 2928, 2854, 1637, 1467, 1414, 1345, 1251, 1199, 1002, 822, 725, 688 cm⁻¹; ¹H NMR (CDCl₃) δ −0.13 (s, 0.36H), −0.11 (s, 2.64H), 0.20 (s, 0.36H), 0.23 (s, 2.64H), 0.84 (t, J = 6.3 Hz, 3H), 0.86 (s, 7.92H), 0.88 (s, 1.08H), 1.20-1.40 (m, 6H), 1.40-1.64 (m, 4H),
2.08 (d, \(J = 4.5\) Hz, 0.12H), 3.640 (d, \(J = 2.4\) Hz, 0.88H), 3.641 (d, \(J = 7.8\) Hz, 0.12H), 3.99 (m, 0.88H), 4.30 (m, 0.12H), 4.32 (d, \(J = 10.5\) Hz, 0.88H), 7.47 (m, 2H), 7.58 (m, 1H), 7.87 (m, 2H); \(^{13}\)C NMR (CDCl\textsubscript{3}, threo isomer) \(\delta = -5.78, -5.15, 13.91, 17.81, 22.43, 26.56, 26.88, 29.02, 31.67, 38.98, 44.08, 73.01, 128.30, 128.76, 133.21, 139.51, 207.59\). Found: C, 72.46%; H, 10.40%. Calcd for C\textsubscript{21}H\textsubscript{36}O\textsubscript{2}Si: C, 72.36%; H, 10.41%.

2-(tert-Butyldimethylsilyl)-1-cyclohexyl-3-hydroxy-3-phenyl-1-propanone (9c, 72:28 diastereomeric mixture): IR (neat) 3422, 2924, 2854, 1662, 1452, 1337, 1251, 1114, 1048, 1003, 947, 839, 772, 698 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\textsubscript{3}) \(\delta = -0.05\) (s, 0.84H), 0.05 (s, 2.16H), 0.22 (s, 0.84H), 0.34 (s, 2.16H), 0.98 (s, 2.52H), 1.04 (s, 6.48H), 1.20-1.80 (m, 10H), 2.03 (tt, \(J = 11.4, 3.3\) Hz, 1H), 2.23 (d, \(J = 2.7\) Hz, 0.28H), 3.07 (d, \(J = 1.8\) Hz, 0.72H), 3.18 (d, \(J = 9.3\) Hz, 0.28H), 5.17 (dd, \(J = 9.3, 2.7\) Hz, 0.28H), 5.59 (d, \(J = 10.2\) Hz, 0.72H), 7.17-7.40 (m, 5H); \(^{13}\)C NMR (CDCl\textsubscript{3}, threo isomer) \(\delta = -5.68, -5.12, 17.86, 24.82, 25.48, 26.06, 26.11, 26.87, 27.38, 50.71, 52.76, 73.90, 125.09, 126.88, 128.14, 146.14, 219.83\). Found: C, 72.56%; H, 9.84%. Calcd for C\textsubscript{21}H\textsubscript{34}O\textsubscript{2}Si: C, 72.78%; H, 9.89%.

2-(tert-Butyldimethylsilyl)-1-cyclohexyl-3-hydroxy-1-nonanone (9d, 56:44 diastereomeric mixture): IR (neat) 3458, 2926, 2854, 1665, 1466, 1451, 1251, 1145, 1096, 1003, 839, 824cm\(^{-1}\); \(^{1}\)H NMR (CDCl\textsubscript{3}) \(\delta = -0.05\) (s, 1.32H), 0.01 (s, 1.68H), 0.21 (s, 1.32H), 0.22 (s, 1.68H), 0.86 (t, \(J = 6.6\) Hz, 3H), 0.97 (s, 9H), 1.10-2.00 (m, 20H), 2.26 (tt, \(J = 11.4, 3.3\) Hz, 1H), 2.34 (m, 0.44H), 2.82 (d, \(J = 2.1\) Hz, 0.56H), 2.85 (d, \(J = 6.9\) Hz, 0.44H), 3.76 (m, 0.56H), 4.04 (m, 0.44H), 4.42 (d, \(J = 10.2\) Hz, 0.56H); \(^{13}\)C NMR (CDCl\textsubscript{3}, threo isomer) \(\delta = -5.60, -5.01, 13.93, 17.81, 22.47, 24.96, 25.70, 26.30, 26.43, 26.62, 26.85, 29.09 29.62, 31.73, 39.32, 48.07, 52.76, 72.63, 220.84\). Found: C, 71.39%; H, 11.69%. Calcd for C\textsubscript{21}H\textsubscript{42}O\textsubscript{2}Si: C, 71.12%; H, 11.94%.

**General Procedure for One-pot Synthesis of \(\alpha,\beta\)-Unsaturated Ketones.** An ethereal solution of tert-butyldimethyl(dibromomethyl)silane (0.29 g, 1.0 mmol) was added to a solution of
lithium diisopropylamide (1.2 mmol) in ether (3 ml) at −78 °C under argon atmosphere. After being stirred for 1 h at −78 °C, benzaldehyde (0.13 g, 1.2 mmol) in Et₂O (1 ml) was added and the reaction mixture was allowed to warm to ambient temperature over 10 h to provide 3a. The reaction mixture was cooled to −78 °C and sec-butyllithium (2.5 mmol) was added. After the reaction mixture was stirred at −78 °C for 1 h, benzaldehyde (3.0 mmol) was added. The mixture was stirred for another 30 min and then HMPA (2.5 mmol) was added. The resulting mixture was stirred at −78 °C for 1 h, then at 0 °C for 10 min and poured into saturated ammonium chloride. Extractive workup followed by silica-gel column chromatography gave phenyl 2-phenylethenyl ketone (10a, 0.12 g) in 59% yield.
References and Notes


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9. The use of heptanal in place of benzaldehyde afforded a trace amount of the corresponding monosilyl ether of 2-acyl-1,3-diol.


11. Treatment of the diastereomeric mixture 9d with BF₃·OEt₂ also gave only (E)-10d in 90 % yield. The exclusive formation of (E)-isomer might be attributed to the isomerization of (Z)-isomer into (E)-isomer under the acidic reaction conditions.

12. Stereochemistry of products was determined based on the observed vicinal coupling constants for the Cα-Cβ protons. 14


15. Butyllithium was not so effective as sec-BuLi for the formation of enolate in one-pot procedure.
CHAPTER 4

Facile Preparation of Vicinal Allylsiloxy- and Vinylsiloxyhaloalkanes
and Their Radical Cyclization Reaction

Treatment of 2-(allyldimethylsiloxy)-1,1-dibromoalkane, which was easily prepared by an addition of aldehyde to an ethereal solution of (allyldimethylsilyl)dibromomethyl lithium, with tributyltin hydride in the presence of catalytic amount of triethylborane afforded 1-oxa-2-silacycloheptane derivative selectively in good yield. On the other hand, cyclization of vinyldimethylsiloxy derivative resulted in a formation of 3-methyl-1-oxa-2-silacyclopentane. An addition of allyldiphenylsilanol to ethyl vinyl ether in the presence of N-iodosuccinimide provided 1-(allyldiphenylsiloxy)-1-ethoxy-2-iodoethane, which was also converted into a seven-membered ring product upon treatment with tributyltin hydride.
Introduction

Radical cyclization reactions developed during the last decade represent a breakthrough for a synthetic radical chemistry. Among them, cyclizations of silylmethyl radicals bearing alkenyloxy group on the silicon atom are monumental and there are numerous works on the related system in which (bromomethyl)silyl group serves as a hydroxymethyl radical equivalent via oxidative cleavage of the Si–C bond (Scheme 1). In contrast, there are few reports on cyclizations of alkyl radicals possessing alkenysiloxy group (Scheme 2). The author wishes to disclose here two different methods of preparation of such radical cyclization precursors and their radical cyclizations to yield oxasilacycles which are synthetically useful intermediates.

Scheme 1

(1) Preparation of 2-Alkenylsiloxy-1,1-dibromoalkanes by Treatment of Carbonyl Compounds with Silyldibromomethyllithiums

The author has reported that the addition of silyldihalomethyllithium to carbonyl compounds, such as aldehydes or esters, provided the corresponding silyl ethers or alkyl silyl mixed acetals through the 1,3-rearrangement of silyl group from carbon to oxygen. It was anticipated that the use of allyl- or vinyl-substituted silyldibromomethyllithium (1 or 2) would give 2-allylsiloxy- or 2-vinylsiloxy-1,1-dibromoalkane via the 1,3-rearrangement of silyl group in the adducts 3 (Scheme 3). This was indeed the case and an addition of carbonyl compounds to a solution of...
(allyldimethylsilyl)dibromomethyl lithium (1) or (vinylidimethylsilyl)dibromomethyl lithium (2),
which were derived from (allyldimethylsilyl)dibromomethane or (vinylidimethylsilyl)dibromomethane
with lithium diisopropylamide at -78 °C, gave the corresponding silyl ethers or alkyl silyl mixed
acetals in good yields via the 1,3-rearrangement of allyldimethylsilyl group or vinylidimethylsilyl
group.

Scheme 3

\[
\begin{align*}
\text{Me}_2\text{Si} & \equiv \text{Br}_2\text{Li} \\
1: n = 1 & \quad 2: n = 0 \\
& \text{RCHO} \\
& \text{OLi} \\
& \text{R} \text{Si} \equiv \text{Li} \\
& \text{1,3-Rearrangement}
\end{align*}
\]

Some representative results are shown in Table 1. In method A, the reaction was quenched
with methanol to give 5 or 6 (E' = H). In method B, a three component coupled product 7 (E' =
CH₃) was prepared by a subsequent addition of methyl iodide and HMPA before quenching with
methanol. In these reactions, the increased polarity of solvent due to an addition of methanol or
HMPA facilitated the rearrangement of the silyl group. Cyclization of the products is discussed in
Section (3).

(2) Preparation of Halo Mixed Silyl Acetals by Treatment of Enol Ethers with
Silanols in the Presence of N-Halosuccinimide

The author has recently reported an iodonium ion induced intramolecular addition of silanol
moiety to the carbon-carbon double bond of alkenysilanols. However, no intermolecular addition
of silanol to electronically non-activated olefins, could not take place, presumably because the
nucleophilicity of silanol is lower than that of alcohol. Fortunately, t-butyldimethylsilanol proved to
add intermolecularly to electron rich olefins such as ethyl vinyl ether and to provide mixed alkyl silyl
acetals in good yields in the presence of N-iodosuccinimide (NIS) or N-bromosuccinimide (NBS)
Table 1. Preparation of 2-Alkenylsiloxy-1,1-dibromoalkanes with silyldibromomethyllithium.

![Chemical structure](image)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>Method</th>
<th>E'</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>1</td>
<td>Ph</td>
<td>H</td>
<td>A</td>
<td>H</td>
</tr>
<tr>
<td>5b</td>
<td>1</td>
<td>n-Hex</td>
<td>H</td>
<td>A</td>
<td>H</td>
</tr>
<tr>
<td>5c</td>
<td>1</td>
<td>Ph</td>
<td>OEt</td>
<td>A</td>
<td>H</td>
</tr>
<tr>
<td>6a</td>
<td>0</td>
<td>Ph</td>
<td>H</td>
<td>A</td>
<td>H</td>
</tr>
<tr>
<td>6b</td>
<td>0</td>
<td>n-Hex</td>
<td>H</td>
<td>A</td>
<td>H</td>
</tr>
<tr>
<td>7a</td>
<td>1</td>
<td>Ph</td>
<td>H</td>
<td>B</td>
<td>CH₃</td>
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<tr>
<td>7b</td>
<td>1</td>
<td>n-Hex</td>
<td>H</td>
<td>B</td>
<td>CH₃</td>
</tr>
</tbody>
</table>

Method A  The reaction mixture was quenched with methanol.
Method B  The reaction mixture was treated with iodomethane and HMPA.

(Scheme 4). The reactions took about one day to complete whereas the addition of alcohols to enol ethers generally completes within 1 h in the presence of NIS or NBS even at -78 °C.⁹ The use of N-chlorosuccinimide in place of NIS or NBS made the reaction much slower and gave the corresponding mixed silyl acetal in unacceptable yield (≤20%).
In a similar manner, treatment of allyl(diphenyl)silanol or (diphenyl)vinylsilanol with enol ethers in the presence of NIS or NBS afforded the corresponding allyl- or vinyl-substituted mixed silyl acetals in good yields (Table 2). Stereoselective addition of these silanols to 3,4-dihydro-2H-pyran was observed in the case of NIS. In contrast, the use of NBS in place of NIS resulted in a formation of a stereoisomeric mixture, however this is not a problem in the following radical cyclization reaction. In general, silanols are liable to dimerize to the corresponding disiloxanes; allyl(dimethyl)silanol, in fact, changed into 1,3-diallyl-1,1,3,3-tetramethyldisiloxane within five min along with concomitant formation of water. Allyl(diphenyl)silanol or (diphenyl)vinylsilanol, however, are stable on standing for a few months at room temperature under atmosphere and are easy to handle. The radical cyclization of iodo mixed alkenylsilyl acetals thus obtained is described in the next section.

(3) Cyclization of 3-Oxa-4-sila-5-alkenyl Radical and 3-Oxa-4-sila-6-alkenyl Radical

The radical cyclization of the precursors described in the previous two sections was performed by treatment with \( n\)-Bu\(_3\)SnH in the presence of a catalytic amount of triethylborane in benzene (0.017 M) (1 M = 1 mol dm\(^{-3}\)).\(^{11}\) The intramolecular cyclization of 1,1-dibromo-2-vinylsiloxyalkane 6 with two molar amounts of \( n\)-Bu\(_3\)SnH afforded only 1-oxa-2-silacyclopentanes selectively. These compounds were not stable enough to be purified by silica-gel column chromatography, and were converted into 1,3-diols in good yields as a diastereomeric mixture via direct oxidative cleavage of the Si–C bond (Scheme 5).
Table 2. Preparation of halo mixed silyl acetal from silanol\textsuperscript{a}

<table>
<thead>
<tr>
<th>Silanol</th>
<th>Enol ether</th>
<th>N-Halosuccinimide</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiPh}_2\text{OH} )</td>
<td>EtO( \equiv )</td>
<td>NIS</td>
<td><img src="image" alt="9a" /></td>
<td>78%</td>
</tr>
<tr>
<td>( \text{SiPh}_2\text{OH} )</td>
<td>Cyclopentene</td>
<td>NIS</td>
<td><img src="image" alt="9b" /></td>
<td>81%</td>
</tr>
<tr>
<td>( \text{SiPh}_2\text{OH} )</td>
<td>Cyclopentene</td>
<td>NBS</td>
<td><img src="image" alt="9c" /></td>
<td>75%</td>
</tr>
<tr>
<td>( \text{SiPh}_2\text{OH} )</td>
<td>EtO( \equiv )</td>
<td>NIS</td>
<td><img src="image" alt="10a" /></td>
<td>61%</td>
</tr>
<tr>
<td>( \text{SiPh}_2\text{OH} )</td>
<td>Cyclopentene</td>
<td>NIS</td>
<td><img src="image" alt="10b" /></td>
<td>50%</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Alkenylsilanol (1.0 mmol), enol ether (1.5 mmol), and N-halosuccinimide (1.1 mmol) were employed. The reaction was carried out in dichloromethane (3 ml) at room temperature with stirring for 24 h.
The cyclization of vinylsilyl mixed acetals 9 also gave five-membered acetals exclusively upon treatment with \( n\text{-Bu}_3\text{SnH-Et}_3\text{B} \). These findings obviously show that the cyclization of 3-oxa-4-sila-5-alkenyl system predominantly proceeded in 5-exo mode. These cyclic silyl acetals were not stable enough to be isolated, thus they were allylated with allyltrimethylsilane\(^\text{12}\) or reduced to ethers with triethylsilane\(^\text{13}\) in the presence of a catalytic amount of \( \text{Me}_3\text{SiOTf} \) (Scheme 6). In the reduction with triethylsilane, 12 was obtained as a mixture of trimethylsilyl ether and triethylsilyl ether.

In contrast to vinylsiloxy derivatives 6, treatment of 2-allylsiloxy-1,1-dibromoalkane 5 with two molar amounts of \( n\text{-Bu}_3\text{SnH} \) gave 1-oxa-2-silacycloheptanes exclusively (Table 3). Similarly, the cyclization of allylsilyl mixed acetals 10 also yielded only 7-alkoxy-1-oxa-2-silacycloheptanes 13 effectively. Thus, the cyclization of 3-oxa-4-sila-6-alkenyl system shows a distinct preference for 7-endo mode. Interestingly, the inclination for 7-endo mode cyclization in these cases is coincident with that observed in the case of 3-oxa-2-sila-6-alkenyl system.\(^\text{2e}\)
Table 3. The radical cyclization of allylsiloxy derivatives to 1-oxa-2-silacycloheptanes

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure 5a" /></td>
<td><img src="image" alt="Structure 13a" /></td>
<td>84%</td>
</tr>
<tr>
<td><img src="image" alt="Structure 5b" /></td>
<td><img src="image" alt="Structure 13b" /></td>
<td>87%</td>
</tr>
<tr>
<td><img src="image" alt="Structure 5c" /></td>
<td><img src="image" alt="Structure 13c" /></td>
<td>70%</td>
</tr>
<tr>
<td><img src="image" alt="Structure 10a" /></td>
<td><img src="image" alt="Structure 14a" /></td>
<td>89%</td>
</tr>
<tr>
<td><img src="image" alt="Structure 10b" /></td>
<td><img src="image" alt="Structure 14b" /></td>
<td>54%</td>
</tr>
</tbody>
</table>

a) Each substrate was treated with equimolar amount of n-Bu₃SnH and another amount after 6 h.
b) Each substrate was treated with equimolar amount of n-Bu₃SnH.

These seven-membered cyclic silyl ethers and acetals were stable and could be isolated by silica-gel column chromatography. The cyclic silyl acetals 14a and 14b were further converted into ethers upon treatment with silyl nucleophile such as allyltrimethylsilane and triethylsilane under the catalysis of Me₃SiOTf (Scheme 7).
An interesting stereochemical outcome was observed in the cyclization of 7a. Treatment of 7a with an equimolar amount of n-Bu3SnH in benzene (0.017 M) followed by the second reduction with another molar amount of tin hydride in hexane gave a stereoisomeric mixture of 17a (cis/trans = 87/13). Analysis of the reaction mixture, derived from 7a and equimolar amount of n-Bu3SnH, indicated that the products consisted of cyclic silyl ether 18a and acyclic silyl ether 19a (66/34) (Scheme 8). The silyl ether 19a was isolated and treatment with n-Bu3SnH-Et3B gave 17a nonstereoselectively (55/45). Hence it was anticipated that suppression of the formation of 19a in the first step would improve the stereoselectivity of 17a. In fact, the use of 1,1,1,3,3,3-hexamethyl-2-trimethylsilyltribrasilane in place of n-Bu3SnH in the first reduction step afforded 18a along with a trace amount of 19a and the second reduction with n-Bu3SnH at -78°C gave 17a in high stereoselectivity (cis/trans = 97/3). Unfortunately, the high selectivity was observed only in the case of phenyl derivative 7a. Radical cyclization of 7b afforded 17b with moderate stereoselectivity (cis/trans = 80/20) under the same reaction conditions presumably because of the flexibility of the seven-membered silyl ether ring.
The stereochemical assignment of 17a was performed as follows. The treatment of syn β-
siloxyster with i-Bu₂AlH gave β-siloxylaldehyde which was converted into syn unsaturated ester
by Horner-Emmons reaction. Reduction with i-Bu₂AlH to allylic alcohol, followed by
hydrogenation and deprotection provided syn diol which was identical with a major diol derived
from 17a by H₂O₂ oxidation (Scheme 9).

Finally, we performed an experiment to compare allylsilanol with allylic alcohol, since
allylsilanol can be regarded as a synthon of allyl alcohol through oxidative cleavage of Si–C bond
(Scheme 10). In the case of allylic alcohol, the cyclization of 20 with n-Bu₃SnH-Et₃B afforded
only five membered ether 21. Treatment of the cyclic ether 21 with allyltrimethylsilane in the presence of titanium tetrachloride gave only a branched alkenol 22 selectively. In contrast, in the case of allylsilanol, cyclization of 10a followed by subsequent treatment with allyltrimethylsilane and hydrogen peroxide provided a linear alkenol 23 exclusively. Therefore, two isomeric alkenol 22 and 23 could be prepared selectively by the choice of allyl alcohol or allylsilanol with alkyl vinyl ether.

**Scheme 10**

**Allyl alcohol**

\[
\begin{align*}
\text{BuO} & \quad \text{BuSnH} \quad \text{Et}_3\text{B} \quad \rightarrow \quad \text{BuO} \quad \text{Bu} \quad \text{SiMe}_3 \quad \rightarrow \quad \text{BuO} \quad \text{Bu} \quad \text{OH} \\
\text{Allylsilanol} & \quad \text{Ph}_2 \quad \text{OSi} \quad \text{n-BuSnH} \quad \text{Et}_3\text{B} \quad \rightarrow \quad \text{EtO} \quad \text{EtO} \quad \rightarrow \quad \text{EtO} \quad \text{EtO} \\
\text{Ph}_2 & \quad \text{SiMe}_3 \quad \text{Me}_3\text{SiOTf} \quad \rightarrow \quad \text{Ph}_2 \quad \text{Me}_3\text{SiOTf} \quad \rightarrow \quad \text{EtO} \quad \text{EtO} \\
\text{BuO} & \quad \text{Bu} \quad \text{SiMe}_3 \quad \rightarrow \quad \text{BuO} \quad \text{Bu} \quad \text{OH} \\
\text{10a} & \quad \text{14a} \quad \text{22} \quad \text{blanched} \quad \text{90\%} \\
\text{EtO} & \quad \text{EtO} \quad \rightarrow \quad \text{EtO} \quad \text{EtO} \\
\text{23} & \quad \text{linear} 
\end{align*}
\]
Experimental

General Procedure for the Reaction of Allylsilyl- or Vinylsilyldibromomethyl lithium with Carbonyl Compound (Method A). An ethereal solution of allyl(dibromomethyl)dimethylsilane (0.82 g, 3.0 mmol) was added to a solution of lithium diisopropylamide (3.6 mmol) in ether (9 ml) at -78 °C under argon atmosphere. After the mixture was stirred for 1 h at -78 °C, benzaldehyde (0.38 g, 3.6 mmol) in Et₂O (3 ml) was added and the reaction mixture was stirred for 20 min. The mixture was quenched with methanol and poured into saturated aqueous ammonium chloride and extracted with hexane (20 ml x 3). The organic layer was dried over Na₂SO₄ and concentrated in vacuo. Purification by silica-gel column chromatography gave 1-allyldimethylsiloxo-2,2-dibromo-1-phenylethane (5a, 0.91 g) in 80% yield: Bp 105 °C (0.5 Torr); IR (neat) 2956, 1454, 1255, 1135, 1092, 866, 837, 756, 700, 594 cm⁻¹; ¹H NMR (CDCl₃) δ 0.09 (s, 3H), 0.12 (s, 3H), 1.59 (d, J = 8.1 Hz, 2H), 4.82 (m, 2H), 4.97 (d, J = 5.1 Hz, 1H), 5.64 (d, J = 5.1 Hz, 1H), 5.69 (ddt, J = 9.6, 17.7, 8.1 Hz, 1H), 7.30–7.40 (m, 5H); ¹³C NMR (CDCl₃) δ -2.20, 24.58, 51.20, 79.87, 114.14, 127.36, 128.24, 128.74, 133.60, 139.66. Found: C, 41.23; H, 4.76%. Calcd for C₁₃H₁₈Br₂O₂Si: C, 41.29; H, 4.80%.

2-Allyldimethylsiloxo-1,1-dibromo-octane (5b): Bp 110 °C (1 Torr); IR (neat) 2952, 2922, 2854, 1632, 1255, 1153, 1103, 1051, 897, 839, 686 cm⁻¹; ¹H NMR (CDCl₃) δ 0.19 (s, 3H), 0.20 (s, 3H), 0.90 (t, J = 6.8 Hz, 3H), 1.20–1.50 (m, 8H), 1.55–1.85 (m, 2H), 1.70 (d, J = 8.1 Hz, 2H), 3.84 (ddd, J = 3.6, 3.6, 7.8 Hz), 4.92 (m, 2H), 5.61 (d, J = 3.6 Hz, 1H), 5.82 (ddt, J = 9.9, 16.8, 8.1 Hz, 1H); ¹³C NMR (CDCl₃) δ -1.86, -1.76, 13.94, 22.46, 24.96, 25.14, 29.01, 31.60, 33.59, 51.64, 77.31, 114.21, 133.74. Found: C, 40.31; H, 6.73%. Calcd for C₁₃H₂₆Br₂O₂Si: C, 40.43; H, 6.78%.

1-Allyldimethylsiloxo-2,2-dibromo-1-ethoxy-1-phenylethane (5c): Bp 115 °C (0.5 Torr); IR (neat) 3056, 2972, 2894, 1630, 1449, 1256, 1168, 1060, 895, 837, 701 cm⁻¹; ¹H
NMR (CDCl₃) δ 0.25 (s, 3H), 0.30 (s, 3H), 1.20 (t, J = 6.9 Hz, 3H), 1.72 (dd, J = 13.8, 8.1 Hz, 1H), 1.82 (dd, J = 13.8, 8.1 Hz, 1H), 3.38 (dq, J = 9.0, 6.9 Hz, 1H), 3.54 (dq, J = 9.0, 6.9 Hz, 1H), 4.89 (m, 1H), 4.93 (m, 1H), 5.83 (s, 1H), 5.85 (ddt, J = 16.5, 10.2, 8.1 Hz, 1H), 7.30–7.40 (m, 3H), 7.55–7.65 (m, 2H); ¹³C NMR (CDCl₃) δ -0.51, -0.05, 14.82, 26.00, 52.67, 59.24, 101.02, 114.11, 127.69, 128.39, 128.92, 134.12, 138.52. Found: C, 42.54; H, 5.23%. Calcd for C₁₅H₂₂Br₂O₂Si: C, 42.67; H, 5.25%.

1,1-Dibromo-2-dimethyl(vinyl)siloxy-2-phenylethane (6a): Bp 90 °C (0.5 Torr); IR (neat) 3048, 3030, 2956, 1495, 1407, 1254, 1134, 1090, 1073, 1007, 964, 862, 838, 786, 699 cm⁻¹; ¹H NMR (CDCl₃) δ 0.14 (s, 3H), 0.21 (s, 3H), 4.97 (d, J = 5.1 Hz, 1H), 5.66 (d, J = 5.1 Hz, 1H), 5.76 (dd, J = 5.7, 18.6 Hz, 1H), 5.99 (dd, J = 5.7, 14.7 Hz, 1H), 6.08 (dd, J = 14.7, 18.6 Hz, 1H), 7.30–7.45 (m, 5H); ¹³C NMR (CDCl₃) δ -1.83, -1.67, 51.19, 79.82, 127.42, 128.20, 128.68, 134.08, 136.76, 139.68. Found: C, 39.62; H, 4.46%. Calcd for C₁₂H₁₆Br₂O₂Si: C, 39.58; H, 4.43%.

1,1-Dibromo-2-dimethyl(vinyl)siloxyoctane (6b): Bp 75 °C (0.5 Torr); IR (neat) 2952, 2924, 2854, 1595, 1466, 1407, 1253, 1103, 1051, 1008, 959, 897, 837, 785, 703, 683 cm⁻¹; ¹H NMR (CDCl₃) δ 0.266 (5, 3H), 0.274 (5, 3H), 0.90 (t, J = 6.9 Hz, 3H), 1.20–1.50 (m, 8H), 1.58–1.84 (m, 2H), 3.83 (dd, J = 3.6, 3.6, 8.1 Hz, 1H), 5.61 (d, J = 3.6 Hz, 1H), 5.84 (dd, J = 19.5, 4.8 Hz, 1H), 6.07 (dd, J = 14.7, 4.8 Hz, 1H), 6.20 (dd, J = 19.5, 14.7 Hz, 1H); ¹³C NMR (CDCl₃) δ -1.55, -1.45, 13.96, 22.47, 25.17, 28.99, 31.61, 33.45, 51.69, 77.24, 134.06, 137.19. Found: C, 39.06; H, 6.50%. Calcd for C₁₂H₂₄Br₂OSi: C, 38.72; H, 6.50%.

**General Procedure for the Reaction of Allylsilyl- or Vinlysilyl-dibromomethylithium with Carbonyl Compound (Method B).** An ethereal solution of allyldibromomethyl)dimethylsilane (0.27 g, 1.0 mmol) was added to a solution of lithium
diisopropylamide (1.2 mmol) in ether (3 ml) at -78 °C under argon atmosphere. After the mixture was stirred for 1 h at -78 °C, benzaldehyde (0.13 g, 1.2 mmol) in Et₂O (1 ml) was added and the reaction mixture was stirred for 20 min. To the mixture was added iodomethane (0.21 g, 1.5 mmol) followed by HMPA (0.22 g, 1.2 mmol) and whole mixture was allowed to warm to ambient temperature for 5 h. Extractive workup and purification by silica-gel column chromatography gave 1-allyldimethylsiloxy-2,2-dibromo-1-phenylpropane (7a, 0.28 g) in 71% yield: BP 105 °C (0.5 Torr); IR (neat) 3062, 3028, 2956, 1630, 1453, 1255, 1153, 1098, 1071, 865, 754, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.04 (s, 3H), 0.10 (s, 3H), 1.57 (d, J = 8.1 Hz, 2H), 2.39 (s, 3H), 4.83 (m, 2H), 4.95 (s, 1H), 5.69 (ddt, J = 9.3, 17.4, 8.1 Hz, 1H), 7.30–7.36 (m, 3H), 7.48–7.53 (m, 2H); ¹³C NMR (CDCl₃) δ –2.32, –2.26, 24.56, 35.39, 72.52, 83.82, 114.02, 127.55, 128.63, 129.21, 133.70, 138.49. Found: C, 42.68; H, 5.13%. Calcd for C₁₄H₂₀Br₂OSi: C, 42.87; H, 5.14%.

3-Allyldimethylsiloxy-2,2-dibromononane (7b): BP 95 °C (0.5 Torr); IR (neat) 2954, 2924, 2854, 1632, 1442, 1375, 1255, 1103, 1061, 896, 840, 664 cm⁻¹; ¹H NMR (CDCl₃) δ 0.20 (s, 3H), 0.22 (s, 3H), 0.89 (t, J = 6.8 Hz, 3H), 1.20–1.40 (m, 6H), 1.20–1.60 (m, 3H), 1.72 (d, J = 8.1 Hz, 2H), 2.02 (m, 1H), 2.40 (s, 3H), 3.80 (dd, J = 8.7, 2.1 Hz, 1H), 4.84–4.95 (m, 2H), 5.80 (ddt, J = 17.1, 10.2, 8.1 Hz, 1H); ¹³C NMR (CDCl₃) δ –1.53, –1.33, 13.95, 22.50, 25.41, 26.78, 29.09, 31.62, 33.97, 35.97, 74.40, 82.91, 114.07, 134.05. Found: C, 41.81; H, 6.94%. Calcd for C₁₄H₂₈Br₂OSi: C, 42.01; H, 7.05%.

**General Procedure for the Reaction of Silanols with Enol Ethers.** The reaction of t-butyldimethylsilanol with ethyl vinyl ether is representative. To a stirred solution of t-butyldimethylsilanol (0.13 g, 1.0 mmol) and ethyl vinyl ether (0.11 g, 1.5 mmol) in dichloromethane (3 ml) was added N-iodosuccinimide (0.25 g, 1.1 mmol) at 0 °C. To the reaction mixture which had been stirred for 24 h, was added hexane (10 ml) and a white precipitate was formed. The whole mixture was filtered through a short alumina layer. The filtrate was concentrated in vacuo and purification of the residual oil by silica-gel column chromatography gave 1-(t-butyldimethylsiloxy)-
1-ethoxy-2-iodoethane (8a, 0.29 g) in 89% yield: Bp 90 °C (1 Torr); IR (neat) 2950, 2928, 2884, 2854, 1464, 1414, 1253, 1182, 1127, 1034, 867, 836, 777, 673 cm⁻¹; ¹H NMR (CDCl₃) δ 0.11 (s, 3H), 0.12 (s, 3H), 0.90 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H), 3.14 (dd, J = 10.2, 3.9 Hz, 1H), 3.21 (dd, J = 10.2, 5.7 Hz 1H), 3.47 (dq, J = 9.0, 7.1 Hz, 1H), 3.67 (dq, J = 9.0, 7.1 Hz, 1H), 4.80 (dq, J = 5.7, 3.9 Hz, 1H); ¹³C NMR (CDCl₃) δ –4.72, –4.43, 9.45, 14.91, 17.90, 25.58, 62.03, 96.46. Found: C, 36.10; H, 7.18%. Calcd for C₁₀H₂₃I₀₂Si: C, 36.37; H, 7.02%.

1-Bromo-2-(t-butyldimethylsiloxy)-2-ethoxyethane (8b): Bp 70 °C (1 Torr); IR (neat) 2952, 2928, 2886, 2856, 1464, 1254, 1123, 1035, 920, 837, 777, 681 cm⁻¹; ¹H NMR (CDCl₃) δ 0.12 (s, 3H), 0.13 (s, 3H), 0.90 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H), 3.27 (dd, J = 10.5, 4.2 Hz, 1H), 3.35 (dd, J = 10.5, 6.0 Hz 1H), 3.50 (dq, J = 9.0, 7.1 Hz, 1H), 3.69 (dq, J = 9.0, 7.1 Hz, 1H), 4.91 (dq, J = 6.0, 4.2 Hz, 1H); ¹³C NMR (CDCl₃) δ –4.69, –4.44, 14.97, 17.90, 25.55, 34.71, 62.18, 91.44, 96.53. Found: C, 42.36; H, 8.47%. Calcd for C₁₀H₂₃BrO₂Si: C, 42.40; H, 8.18%.

1-(Diphenyl)vinylsiloxy-1-ethoxy-2-iodoethane (9a): Bp 146 °C (0.5 Torr); IR (neat) 3066, 2972, 2880, 1592, 1429, 1405, 1374, 1348, 1332, 1182, 1113, 998, 853, 699 cm⁻¹; ¹H NMR (CDCl₃) δ 1.08 (t, J = 7.1 Hz, 3H), 3.19 (dd, J = 4.2, 10.2 Hz, 1H), 3.24 (dd, J = 6.2, 10.2 Hz, 1H), 3.36 (dq, J = 9.3, 7.1 Hz, 1H), 3.57 (dq, J = 9.3, 7.1 Hz, 1H), 4.90 (dq, J = 4.2, 6.0 Hz, 1H), 5.91 (dd, J = 3.6, 20.1 Hz, 1H), 6.31 (dd, J = 3.6, 14.7 Hz, 1H), 6.54 (dd, J = 14.7, 20.1, 1H), 7.35–7.50 (m, 6H), 7.60–7.70 (m, 4H); ¹³C NMR (CDCl₃) δ 9.26, 14.65, 63.22, 97.00, 127.95, 127.99, 130.31, 130.32, 133.40, 133.62, 135.20, 135.23, 137.93. Found: C, 50.84; H, 4.95%. Calcd for C₁₈H₂₁I₀₂Si: C, 50.95; H, 4.99%.

2-(Diphenyl)vinylsiloxy-3-iodo-1-oxacyclohexane (9b): Bp 150 °C (0.5 Torr); IR (neat) 3064, 3046, 2942, 2850, 1592, 1429, 1383, 1172, 1143, 1119, 1068, 1023, 993, 816, 713, 699 cm⁻¹; ¹H NMR (CDCl₃) δ 1.50–1.75 (m, 2H), 2.00 (ddt, J = 18.5, 8.4, 4.2 Hz, 1H), 2.43
(m, 1H), 3.47 (ddd, J = 11.4, 7.5, 3.6 Hz, 1H), 4.03 (m, 1H), 4.13 (ddd, J = 8.4, 5.4, 3.9 Hz 1H), 4.99 (d, J = 5.4 Hz, 1H), 5.93 (dd, J = 20.4, 3.9 Hz, 1H), 6.29 (dd, J = 14.7, 3.9 Hz, 1H), 6.52 (dd, J = 20.4, 14.7 Hz, 1H), 7.35–7.50 (m, 6H), 7.60–7.70 (m, 4H); 13C NMR (CDCl3) δ 25.61, 32.26, 32.63, 63.89, 98.00, 127.86, 127.89, 130.19, 130.23, 133.34, 133.42, 133.45, 135.32, 135.35, 137.66. Found: C, 52.58; H, 4.98%. Calcd for C19H21I02Si: C, 52.30; H, 4.85%.

3-Bromo-2-(diphenyl)vinylsiloxy-1-oxacyclohexane (9c, 56:44 diastereomeric mixture): Bp 140 °C (0.5 Torr); IR (neat) 3046, 2942, 2848, 1591, 1430, 1388, 1156, 1119, 1020, 990, 820, 712, 699 cm⁻¹; 1H NMR (CDCl3) δ 1.45–2.00 (m, 4H), 2.46 (ddd, J = 4.2, 8.7, 18.6 Hz, 0.56H), 3.47 (m, 1H), 3.99 (m, 1.44H), 4.97 (d, J = 5.6 Hz, 0.56H), 5.06 (dd, J = 3.0, 4.8 Hz 0.44H), 5.90 (m, 1H), 6.28 (m, 1H), 6.52 (m, 1H), 7.35–7.50 (m, 6H), 7.60–7.70 (m, 4H); 13C NMR (CDCl3) δ 19.28, 23.57, 25.23, 30.08, 32.85, 51.72, 62.72, 63.04, 94.34, 96.73, 127.80, 127.83, 127.88, 127.91, 129.98, 130.01, 130.21, 130.25, 133.25, 133.36, 133.41, 133.95, 134.18, 134.22, 135.14, 135.19, 135.22, 135.26, 137.05, 137.71. Found: C, 58.56; H, 5.41%. Calcd for C19H21BrO2Si: C, 58.61; H, 5.44%.

1-Allyldiphenylsiloxy-1-ethoxy-2-iodoethane (10a): Bp 150 °C (0.5 Torr); IR (neat) 3066, 2972, 2876, 1631, 1429, 1157, 1115, 1016, 997, 899, 769, 736, 699, 593 cm⁻¹; 1H NMR (CDCl3) δ 1.07 (d, J = 6.9 Hz, 3H), 2.25 (dd, J = 1.5, 8.1 Hz, 2H), 3.16 (dd, J = 4.2, 10.5 Hz, 1H), 3.21 (dd, J = 5.4, 10.5 Hz, 1H), 3.32 (dq, J = 9.3, 6.9 Hz, 1H), 3.52 (dq, J = 9.3, 6.9 Hz, 1H), 4.84 (dd, J = 4.2, 5.4 Hz, 1H), 4.94 (m, 2H), 5.82 (ddt, J = 9.9, 17.1, 8.1 Hz, 1H), 7.35–7.50 (m, 6H), 7.60–7.67 (m, 4H); 13C NMR (CDCl3) δ 9.27, 14.71, 22.27, 63.03, 96.89, 115.66, 127.96, 127.98, 130.33, 132.67, 133.71, 133.83, 135.03, 135.06. Found: C, 52.21; H, 5.23%. Calcd for C19H23I02Si: C, 52.06; H, 5.29%.

2-Allyldiphenylsiloxy-3-iodo-1-oxacyclohexane (10b): Bp 165 °C (0.5 Torr); IR
General Procedure for the Radical Cyclization of 1,1-Dibromo-2-(dimethyl)vinylsiloxalkanes and the Successive Oxidation. To a solution of 1,1-dibromo-2-(dimethyl)vinylsilox-2-phenylethane (6a, 0.18 g, 0.5 mmol) and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature under argon atmosphere. After this was stirred for 6 h, more tributyltin hydride (0.16 g, 0.55 mmol) and triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) were added and the mixture was stirred for another 3 h. The mixture was concentrated in vacuo and the residual oil was diluted with ethyl acetate (20 ml). Potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the whole mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. The residual oil was diluted with THF (2 ml) and MeOH (2 ml). Potassium fluoride (0.23 g, 4 mmol), KHCO₃ (1.0 g, 10 mmol), and H₂O₂ (30%, 1.1 g, 10 mmol) were added, and the mixture was stirred for 10 h at room temperature; then aqueous NaHSO₃ was added carefully. Extractive workup and purification by silica-gel column chromatography gave 1-phenyl-1,3-butanediol (57 mg, 69% yield).

General Procedure for the Radical Cyclization of 1-(Diphenyl)vinylsiloxy-2-iodoalkanes and the Successive Transformation into Ethers. To a solution of 1-(diphenyl)vinylsiloxy-1-ethoxy-2-iodoethane (9a, 0.21 g, 0.5 mmol) and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol)
at room temperature under argon atmosphere. After being stirred for 6 h, the mixture was concentrated in vacuo and CH$_2$Cl$_2$ (5 ml) and allyltrimethylsilane (0.11 g, 1.0 mmol) was added. This mixture was cooled to -78 °C and trimethylsilyl triflate (1.0 M, 0.1 ml, 0.1 mmol) was added; the whole mixture was stirred for 1 h. The mixture was poured into saturated aqueous NaHCO$_3$ and extracted with ethyl acetate (10 ml×5). The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated. The residual oil was diluted with ethyl acetate (20 ml); potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and this mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-gel column chromatography gave 4-ethoxy-6-(trimethylsiloxy)diphenylsilyle-1-heptene (11a, 0.14 g, 50:50 diastereomeric mixture) in 69% yield: Bp 130 °C (0.5 Torr); IR (neat) 3066, 2952, 2864, 1640, 1429, 1251, 1114, 1082, 840, 699 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.06 (s, 9H), 0.98 (d, $J$ = 7.1 Hz, 1.5H), 1.01 (d, $J$ = 7.1 Hz, 1.5H), 1.12 (t, $J$ = 6.9 Hz, 1.5H), 1.17 (t, $J$ = 6.9 Hz, 1.5H), 1.30-1.45 (m, 1H), 1.50-1.80 (m, 2H), 2.13 (ddd, $J$ = 6.9, 6.9, 13.5 Hz, 1H), 2.27 (ddd, $J$ = 6.9, 6.9, 13.5 Hz, 1H), 3.25-3.60 (m, 3H), 5.00 (m, 2H), 5.77 (m, 1H), 7.25-7.40 (m, 6H), 7.50-7.60 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 1.89, 1.92, 13.46, 14.20, 14.44, 15.48, 15.56, 15.92, 35.17, 35.58, 37.60, 39.13, 63.91, 64.12, 76.39, 78.19, 116.63, 116.68, 127.70, 127.74, 129.44, 129.47, 129.53, 129.56, 134.66, 134.69, 135.23, 135.44, 136.04, 136.27. Found: C, 69.76; H, 8.74%. Calcd for C$_{24}$H$_{36}$O$_2$Si$_2$: C, 69.85; H, 8.79%.

2-Allyl-3-{1-[(trimethylsiloxy)diphenylsilyl]ethyl}-1-oxacyclohexane (11b, 65:35 diastereomeric mixture): Bp 165 °C (0.5 Torr); IR (neat) 3068, 2950, 2846, 1639, 1429, 1253, 1109, 1027, 909, 840, 752, 702, 602 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.07 (s, 3.15H), 0.11 (s, 5.85H), 1.02 (d, $J$ = 7.8 Hz, 1.95H), 1.09 (d, $J$ = 7.8 Hz, 1.05H), 1.30-1.80 (m, 6H), 2.19 (m, 1H), 2.48 (m, 1H), 3.10-3.50 (m, 2H), 3.86 (m, 1H), 5.07 (m, 1H), 5.76 (ddd, $J$ = 6.0, 7.8, 10.5, 16.5 Hz 0.35H), 5.89 (ddd, $J$ = 6.3, 7.5, 9.9, 17.4 Hz, 0.65H), 7.28-7.42 (m, 6H), 7.47-7.62 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 1.96, 7.96, 14.63, 20.15, 20.89, 26.18, 26.62, 27.03, 27.89, 37.32, 37.78, 39.56, 46.41, 68.27, 68.46, 79.50, 79.72, 116.25, 116.38, 127.73, 127.75,
127.81, 127.88, 129.46, 129.56, 129.71, 134.32, 134.53, 134.81, 135.68, 135.75, 136.61, 136.89, 137.74. Found: C, 70.91; H, 8.74%. Calcd for C_{25}H_{36}O_{2}Si_{2}: C, 70.70; H, 8.54%.

**Synthesis of 1-(1-oxa-3-cyclohexyl)ethylidiphenylsilanol.** The use of triethylsilane in place of allyltrimethylsilane in the above reaction afforded 12 which was obtained as a mixture of trimethylsilyl ether and triethylsilyl ether. They were converted into 1-(1-oxa-3-cyclohexyl)ethylidiphenylsilanol (58:42 diastereomeric mixture) in 90% yield upon treatment with tetrabutylammonium fluoride in THF: Bp 160 °C (0.5 Torr); IR (neat) 3306, 3064, 2936, 2846, 1428, 1111, 1082, 908, 855, 738, 699 cm⁻¹; ¹H NMR (CDCl₃) δ 1.02 (d, J = 7.5 Hz, 1.26H), 1.03 (d, J = 7.5 Hz, 1.74H), 1.20–1.58 (m, 3.58H), 1.66–1.90 (m, 2.42H), 2.86 (bs, 0.42H), 2.97 (bs, 0.58H), 3.13 (t, J = 10.8 Hz, 0.42H), 3.18–3.27 (m, 1H), 3.32 (t, J = 9.9 Hz, 0.58H), 3.77 (m, 1.58H), 3.93 (ddd, J = 2.1, 3.9, 11.1 Hz, 0.42H), 7.30–7.45 (m, 6H), 7.55–7.65 (m, 4H); ¹³C NMR (CDCl₃) δ 10.77, 10.97, 21.21, 22.65, 25.84, 26.32, 27.33, 29.95, 37.00, 37.50, 68.15, 68.21, 72.16, 73.22, 127.93, 127.97, 127.99, 129.78, 129.83, 134.35, 134.37, 134.42, 134.46, 135.88, 136.02, 136.15, 136.28. Found: C, 72.95; H, 7.75%. Calcd for C_{19}H_{24}O_{2}Si: C, 73.03; H, 7.74%.

**General Procedure for the Radical Cyclization of 1-Allyldimethylsiloxy-2,2-dibromoalkanes.** To a solution of 1-allyldimethylsiloxy-2,2-dibromo-1-phenylethane (5a, 0.19 g, 0.5 mmol) and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature under argon atmosphere. After this had been stirred for 6 h, more tributyltin hydride (0.16 g, 0.55 mmol) and triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) were added and the mixture was stirred for another 3 h. This mixture was concentrated in vacuo and the residual oil was diluted with ethyl acetate (20 ml). Potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-
gel column chromatography gave 2,2-dimethyl-7-phenyl-1-oxa-2-silacycloheptane (13a, 93 mg) in 84% yield: Bp 100 °C (1 Torr); IR (neat) 2952, 2908, 2850, 1493, 1452, 1356, 1251, 1091, 1070, 999, 948, 895, 838, 822, 789, 741, 697 cm\(^{-1}\); \(\text{^1H NMR (CDCl}_3\) } \delta 0.15 (s, 3H), 0.21 (s, 3H), 0.74 (ddd, \(J = 3.0, 11.7, 15.0\) Hz, 1H), 0.86 (m, 1H), 1.40–1.65 (m, 2H), 1.75 (m, 1H), 1.84–2.10 (m, 3H), 4.81 (dd, \(J = 1.2, 9.0\) Hz, 1H), 7.18–7.38 (m, 5H); \(\text{^13C NMR (CDCl}_3\) } \delta –0.67, –0.60, 17.70, 23.26, 30.26, 40.99, 76.65, 125.44, 126.70, 128.15, 146.28. Found: C, 70.70; H, 9.36%. Calcd for C\(_{13}\)H\(_{20}\)O\(_2\)Si: C, 70.85; H, 9.15%.

7-Hexyl-2,2-dimethyl-1-oxa-2-silacycloheptane (13b): Bp 75 °C (1 Torr); IR (neat) 2908, 2852, 1457, 1250, 1087, 997, 836, 790, 692 cm\(^{-1}\); \(\text{^1H NMR (CDCl}_3\) } \delta 0.08 (s, 3H), 0.11 (s, 3H), 0.64 (ddd, \(J = 2.7, 12.0, 15.0\) Hz, 1H), 0.78 (m, 1H), 0.88 (t, \(J = 6.8\) Hz, 3H), 1.20–1.54 (m, 13H), 1.66–1.92 (m, 3H), 3.60 (m, 1H); \(\text{^13C NMR (CDCl}_3\) } \delta –0.86, 14.00, 17.63, 22.56, 23.15, 25.99, 29.18, 30.33, 31.85, 38.62, 38.89, 74.57. Found: C, 68.35; H, 12.62%. Calcd for C\(_{13}\)H\(_{28}\)O\(_2\)Si: C, 68.35; H, 12.35%.

7-Ethoxy-2,2-dimethyl-7-phenyl-1-oxa-2-silacycloheptane (13c): Bp 75 °C (0.5 Torr); IR (neat) 2928, 1447, 1253, 1173, 1140, 1044, 1014, 966, 835, 782, 753, 700 cm\(^{-1}\); \(\text{^1H NMR (CDCl}_3\) } \delta 0.22 (s, 3H), 0.31 (s, 3H), 0.73 (m, 2H), 1.10 (t, \(J = 7.1\) Hz, 3H), 1.10–1.30 (m, 1H), 1.50–1.72 (m, 3H), 2.06 (ddd, \(J = 2.4, 8.4, 15.3\) Hz, 1H), 2.17 (ddd, \(J = 2.4, 9.3, 15.3\) Hz, 1H), 3.00 (dq, \(J = 9.6, 7.1\) Hz, 1H), 3.45 (dq, \(J = 9.6, 7.1\) Hz, 1H), 7.20–7.37 (m, 3H), 7.43–7.49 (m, 2H); \(\text{^13C NMR (CDCl}_3\) } \delta –0.43, 0.08, 15.39, 16.45, 23.30, 23.40, 43.25, 56.82, 102.41, 126.80, 127.25, 127.84, 144.48. Found: C, 68.42; H, 9.43%. Calcd for C\(_{15}\)H\(_{24}\)O\(_2\)Si: C, 68.13; H, 9.15%.

**Radical Cyclization of 1-Allyldiphenylsiloxyl-1-ethoxy-2-iodoalkane.** To a solution of 1-allyldiphenylsiloxyl-1-ethoxy-2-iodoethane (10a, 0.22 g, 0.5 mmol) and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution,
0.1 ml, 0.1 mmol) at room temperature. After being stirred for 6 h, the mixture was concentrated in vacuo and the residual oil was diluted with ethyl acetate (20 ml). Potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-gel column chromatography gave 7-ethoxy-2,2-diphenyl-1-oxa-2-silacycloheptane (14a, 0.14 g) in 89% yield: Bp 145 °C (0.5 Torr); IR (neat) 2922, 2856, 1429, 1376, 1135, 1119, 1059, 1035, 978, 730, 701 cm⁻¹; ¹H NMR (CDCl₃) δ 1.12 (t, J = 7.1 Hz, 3H), 1.18–1.42 (m, 2H), 1.44–1.60 (m, 1H), 1.70–1.94 (m, 5H), 3.39 (dq, J = 9.6, 7.1 Hz, 1H), 3.79 (dq, J = 9.6, 7.1 Hz, 1H), 5.06 (dd, J = 5.7, 2.1 Hz, 1H), 7.30–7.45 (m, 6H), 7.55–7.65 (m, 4H); ¹³C NMR (CDCl₃) δ 14.73, 14.89, 23.22, 25.39, 37.99, 63.13, 99.61, 127.80, 127.90, 129.72, 134.34, 134.38, 136.55. Found: C, 73.03; H, 7.88%. Calcd for C₁₉H₂₄O₂Si: C, 73.03; H, 7.74%.

3,3-Diphenyl-2,11-dioxa-3-silabicyclo[5.4.0]undecane (14b): Bp 155 °C (0.5 Torr); IR (neat) 2924, 2856, 1429, 1118, 1085, 1068, 1045, 1009, 996, 981, 730, 701 cm⁻¹; ¹H NMR (CDCl₃) δ 1.29 (m, 2H), 1.40–1.95 (m, 9H), 3.63 (ddd, J = 11.4, 5.1, 5.1 Hz, 1H), 4.15 (ddd, J = 4.2, 9.0, 11.4 Hz, 1H), 5.28 (s, 1H), 7.30–7.43 (m, 6H), 7.60–7.67 (m, 4H); ¹³C NMR (CDCl₃) δ 15.43, 19.37, 24.38, 25.55, 32.84, 41.60, 62.04, 96.63, 127.80, 128.08, 129.72, 129.90, 134.12, 134.24, 135.89, 136.17. Found: C, 73.84; H, 7.61%. Calcd for C₂₀H₂₄O₂Si: C, 74.03; H, 7.45%.

Allylation of 7-Alkoxy-1-oxa-2-silacycloheptane. To a cooled solution of 7-ethoxy-2,2-diphenyl-1-oxa-2-silacycloheptane (14a, 0.16 g, 0.5 mmol) and allyltrimethylsilane (0.11 g, 1.0 mmol) in dichloromethane (5 ml) at −78 °C was added trimethylsilyl triflate (1.0 M, 0.1 ml, 0.1 mmol) and the whole mixture was stirred for 1 h. The mixture was poured into saturated aqueous NaHCO₃. Extractive workup followed by purification by silica-gel column chromatography gave 4-ethoxy-8-[diphenyl(trimethylsiloxy)silyl]-1-octene (15a, 0.20 g) in 92% yield: Bp 130 °C (0.5 Torr); IR (neat) 3066, 2928, 2858, 1620, 1429, 1253, 1116, 1062, 1027, 839, 754, 732, 699 cm⁻¹; ¹H...
NMR (CDCl₃) δ 0.09 (s, 9H), 1.07 (t, J = 7.8 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H), 1.25–1.50 (m, 6H), 2.21 (ddd, J = 1.2, 5.7, 6.9 Hz 2H), 3.22 (m, 1H), 3.40 (dq, J = 9.0, 7.2 Hz, 1H), 3.51 (dq, J = 9.0, 7.2 Hz, 1H), 5.03 (m, 2H), 5.80 (ddt, J = 17.1, 9.9, 7.2 Hz, 1H), 7.30–7.45 (m, 6H), 7.50–7.60 (m, 4H); ¹³C NMR (CDCl₃) δ 1.87, 15.45, 15.70, 23.14, 29.23, 33.59, 38.45, 46.21, 78.81, 116.64, 127.74, 129.49, 134.21, 135.31, 137.47. Found: C, 70.21; H, 9.20%. Calcd for C₂₅H₃₈O₂Si₂: C, 70.36; H, 8.98%.

2-Allyl-3-[3-diphenyl(trimethylsiloxy)silylpropyl]-1-oxacyclohexane (15b, 67:33 diastereomeric mixture): Bp 155 °C (0.5 Torr); IR (neat) 3066, 3046, 2930, 2846, 1429, 1253, 1113, 1066, 860, 840, 753, 732, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.09 (s, 9H), 1.02 (m, 2H), 1.20–1.85 (m, 9H), 2.06 (m, 1H), 2.31 (m, 1H), 3.00 (ddd, J = 2.7, 7.8, 10.5 Hz, 6H), 3.30 (ddd, J = 3.6, 11.4, 14.7 Hz, 0.67H), 3.42 (m, 0.66H), 5.03 (m, 2H), 5.69–5.93 (m, 1H), 7.30–7.43 (m, 6H), 7.50–7.56 (m, 4H); ¹³C NMR (CDCl₃) δ 1.89, 15.71, 15.86, 19.55, 20.78, 21.62, 26.26, 26.38, 28.96, 29.23, 35.45, 35.93, 36.20, 37.53, 39.25, 67.71, 68.21, 79.88, 81.69, 116.24, 116.35, 127.77, 129.56, 134.18, 135.73, 137.32, 137.38. Found: C, 71.20; H, 8.86%. Calcd for C₂₆H₃₈O₂Si₂: C, 71.18; H, 8.73%.

Reduction of 7-Alkoxy-1-oxa-2-silacycloheptane. The use of triethylsilane in place of allyltrimethylsilane in the above reaction afforded ether 15 which was obtained as a mixture of trimethylsilyl ether and triethylsilyl ether. They were converted into (5-ethoxypentyl)diphenylsilanol in 93% yield upon treatment with tetrabutylammonium fluoride in THF: Bp 160 °C (0.5 Torr); IR (neat) 3348, 3064, 2972, 2926, 1429, 1113, 852, 737, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 1.15 (t, J = 7.8 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H), 1.34–1.60 (m, 6H), 2.20–2.60 (bs, 1H), 3.36 (t, J = 6.5 Hz, 2H), 3.43 (q, J = 7.1 Hz, 2H), 7.30–7.45 (m, 6H), 7.55–7.64 (m, 4H); ¹³C NMR (CDCl₃) δ 14.79, 15.04, 22.61, 29.01, 29.54, 66.04, 70.54, 127.94, 129.84, 134.23, 136.60. Found: C, 72.31; H, 8.58%. Calcd for C₁₉H₂₈O₂Si: C, 72.10; H, 8.92%.
3-(1-Oxa-3-cyclohexyl)propyldiphenylsilanol: Bp 165 °C (0.5 Torr); IR (neat) 3336, 3064, 2920, 2846, 1429, 1117, 1082, 856, 731, 699 cm⁻¹; ¹H NMR (CDCl₃) δ 0.90–1.25 (m, 5H), 1.30–1.56 (m, 5H), 1.75 (m, 1H), 2.94 (t, J = 10.5 Hz, 1H), 3.03 (bs, 1H), 3.27 (m, 1H), 3.74 (ddd, J = 1.8, 3.9, 11.4 Hz, 1H), 3.80 (m, 1H), 7.30–7.45 (m, 6H), 7.55–7.60 (m, 4H); ¹³C NMR (CDCl₃) δ 15.18, 19.89, 25.66, 29.70, 35.45, 36.05, 68.37, 73.33, 127.93, 129.86, 134.21, 136.49. Found: C, 73.81; H, 8.23%. Calcd for C₂₀H₂₆O₂Si: C, 73.57; H, 8.03%.

Cyclization of 1-Allyldimethylsiloxyl-2,2-dibromoalkane into 2,2,6-trimethyl-1-oxa-2-silacycloheptane. To a solution of 1-allyldimethylsiloxyl-2,2-dibromo-1-phenylpropane (7a, 0.20 g, 0.5 mmol) and 1,1,1,3,3,3-hexamethyl-2-trimethylsilyltrisilane (0.14 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature under argon atmosphere. After being stirred for 6 h, the mixture was concentrated in vacuo and the residual oil was diluted with hexane (5 ml). Then tributyltin hydride (0.16 g, 0.55 mmol) and triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) were added successively at −78°C and the mixture was stirred for another 2 h. The mixture was concentrated and the residual oil was diluted with ethyl acetate (20 ml). Potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-gel column chromatography gave 2,2,6-trimethyl-7-phenyl-1-oxa-2-silacycloheptane (17a, 97:3 diastereomeric mixture) in 68% yield: Bp 60 °C (0.5 Torr); IR (neat) 2958, 2910, 2854, 1450, 1251, 1097, 1041, 911, 848, 835, 799 cm⁻¹; ¹H NMR (CDCl₃) δ 0.08 (s, 2.91H), 0.12 (s, 0.09H), 0.15 (s, 0.09H), 0.19 (s, 2.91H), 0.53 (d, J = 6.9 Hz, 0.09H), 0.65–0.76 (m, 1H), 0.73 (d, J = 6.9 Hz, 2.91H), 0.79–0.90 (m, 1H), 1.60–2.05 (m, 4H), 2.11 (m, 1H), 4.26 (d, J = 9.3 Hz, 0.03H), 4.93 (s, 0.97H), 7.16–7.40 (m, 5H); ¹³C NMR (CDCl₃) δ −1.55, −0.90, 10.95, 17.58, 17.81, 38.12, 40.24, 77.02, 125.80, 126.29, 127.68, 145.05. Found: C, 71.51; H, 9.43%. Calcd for C₁₄H₂₂O₂Si: C, 71.73; H, 9.46%.
7-Hexyl-2,2,6-trimethyl-1-oxa-2-silacycloheptane (17b, 80:20 diastereomeric mixture): Bp 80 °C (1 Torr); IR (neat) 2922, 2852, 1460, 1380, 1250, 1160, 1088, 1034, 906, 834, 797, 694 cm⁻¹; ¹H NMR (CDCl₃) δ 0.04 (s, 2.4H), 0.06 (s, 0.6H), 0.08 (s, 2.4H), 0.09 (s, 0.6H), 0.54–0.76 (m, 2H), 0.80–0.90 (m, 6H), 1.10–1.80 (m, 15H), 3.31 (ddd, J = 2.7, 8.1, 8.1 Hz, 0.2H), 3.65 (dd, J = 2.4, 9.3 Hz, 0.8H); ¹³C NMR (CDCl₃) δ −1.41, −0.94, −0.89, −0.49, 12.16, 14.00, 17.37, 17.55, 17.90, 18.66, 20.54, 22.57, 22.59, 25.99, 26.65, 29.24, 29.35, 31.90, 36.02, 38.05, 38.12, 40.93, 76.19, 78.21. Found: C, 69.38; H, 12.52%. Calcd for C₁₄H₃₀O₄Si: C, 69.35; H, 12.47%.

Synthesis of 4-Butoxy-2-methyl-6-hepten-1-ol (22). To a solution of 1-allyloxy-1-butoxy-2-iodoethane (20, 0.14 g, 0.5 mmol) and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature. After being stirred for 6 h, the mixture was concentrated and CH₂Cl₂ (5 ml) and allyltrimethylsilane (0.11 g, 1.0 mmol) was added. Then titanium tetrachloride (1.0 M, 1 ml, 1.0 mmol) was added at −78 °C and stirred for 1 h. The mixture was poured into saturated aqueous NaHCO₃ and extracted with ethyl acetate (10 ml×5). The organic layer was dried and concentrated. The residual oil was diluted with ethyl acetate (20 ml); then potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-gel column chromatography gave 4-butoxy-2-methyl-6-hepten-1-ol (22, 70:30 diastereomeric mixture) in 90% yield: Bp 110 °C (5 Torr); IR (neat) 3370, 3072, 2956, 2926, 1642, 1460, 1437, 1378, 1348, 1091, 1042, 994, 912 cm⁻¹; ¹H NMR (CDCl₃) δ 0.92 (m, 6H), 1.37 (m, 2H), 1.46–1.68 (m, 4H), 1.80 (m, 0.3H), 1.92 (m, 0.7H), 2.31 (m, 2H), 2.72 (s, 0.3H), 3.03 (s, 0.7H), 3.30–3.65 (m, 5H), 5.08 (m, 2H), 5.79 (ddt, J = 9.9, 17.1, 7.2 Hz, 1H); ¹³C NMR (CDCl₃) δ 13.75, 17.51, 17.79, 19.25, 31.99, 33.85, 37.75, 37.93, 38.30, 39.03, 68.02, 68.46, 68.64, 68.77, 77.05, 77.99, 117.10, 117.32, 134.52, 134.81. Found: C, 71.83; H, 12.23%. Calcd for C₁₂H₂₄O₂: C, 71.95; H, 12.08%.
References and Notes


7. (Allyldimethylsilyl)dibromomethane or (vinyldimethylsilyl)dibromomethane was easily prepared by an addition of lithium diisopropylamide to a mixture of dibromomethane and the corresponding allyl- or vinyl-substituted chlorosilane at -78°C. See ref. 5.

9. Treatment of allyl alcohol with butyl vinyl ether in the presence of NIS at -78°C for 1 h afforded 1-allyloxy-1-butoxy-2-iodoethane (20) in 96% yield.

10. Allyl(diphenyl)silanol was obtained in 85% yield by an addition of allylmagnesium chloride to a solution of dichlorodiphenylsilane in THF at -78°C followed by hydrolytic workup. Vinyl(diphenyl)silanol was easily prepared from commercially available chlorodiphenylvinylsilane by hydrolysis with 1 M aqueous sodium hydroxide in ether at 0 °C in 95% yield.


15. The β-siloxy ester was prepared by t-butyldimethylsilylation of syn β-hydroxy ester generated according to the reported procedure. Taniguchi, M.; Fujii, H.; Oshima, K.; Utimoto, K. *Tetrahedron* **1993**, *49*, 11169.

16. Physical data of 2-methyl-1-phenyl-1,5-pentanediol: Bp 120 °C (1 Torr); IR (neat) 3268, 2932, 2870, 1459, 1377, 1030, 762, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.93 (d, J = 6.9 Hz, 3H), 1.05–1.21 (m, 1H), 1.38–1.75 (m, 5H), 1.75–1.87 (m, 1H), 3.59 (t, J = 6.5 Hz 2H), 4.57 (d, J = 5.4 Hz, 1H), 7.20–7.38 (m, 5H); ¹³C NMR (CDCl₃) δ 14.28, 28.85, 30.08, 39.77, 62.81, 77.65, 126.39, 127.24, 128.17, 143.63. Found: C, 73.93; H, 9.24%. Calcd for C₁₂H₁₈O₂: C, 74.19; H, 9.34%.

APPENDIX

A Facile Preparation of Alkenyl- and Allenylmetallic Compounds
by Means of Iodine-Metal Exchange and Their Use
in Organic Synthesis

Stereospecific lithium-halogen exchange of alkenyl iodides was performed upon treatment with butyllithium in non-polar solvents such as hexane, benzene, and toluene at 25 °C to provide alkenyllithiums quantitatively with retention of configuration. Metal-iodine exchange of allenyl iodides with \( n\text{-BuLi} \), \( i\text{-PrMgBr} \) or \( \text{Et}_2\text{Zn} \) was also performed effectively to afford the corresponding allenylmetallic reagents. An addition of carbonyl compounds to the metallic reagents gave homopropargylic alcohols with high regioselectivity in good yields.
A room temperature preparation of alkenyllithiums by lithium-halogen exchange between alkenyl iodides and n-BuLi in hydrocarbon solvents.

Numerous methods for the preparation of organometallic compounds are known. Among them, the metal-halogen exchange reaction is extremely valuable for preparing organolithium compounds and particularly useful for preparing alkenyllithium compounds by reaction of alkyllithium with alkenyl halides. Alkenyllithiums are generally prepared by an addition of tert-butyllithium to 1-bromo-1-alkenes or 1-iodo-1-alkenes at low temperature such as -78 °C or -120 °C. The reactions are normally carried out in ether or tetrahydrofuran (THF). One feature of the exchange reaction that can cause complications is the presence of the alkyl halide product. When the desired organolithium reagent is warmed for subsequent reaction, it can couple with the alkyl halide, giving alkenyl-alkyl. This type of side reaction may be avoided by the use of two equivalents of tert-butyllithium. The second equivalent rapidly reacts with the tert-butyl halide formed to give the innocuous by-products lithium halide and isobutene. Here the author wishes to describe that the side reaction can be eliminated by an appropriate selection of the reaction conditions and treatment of alkenyl iodides with butyllithium at room temperature in hydrocarbons resulted in a quantitative formation of alkenyllithiums which react with various electrophiles to afford the corresponding adducts in good yields.

Butyllithium (1.5 mmol) was added to a hexane solution of (E)-1-iodo-1-dodecene (1.0 mmol) at 25 °C and the resulting solution was stirred at 25 °C for 15 min. An addition of pentanal (1.2 mmol) afforded the corresponding allylic alcohol, (E)-6-heptadecen-5-ol quantitatively. One and a half molar equivalent of butyllithium was used for the exchange reaction to obtain alkenyllithium quantitatively. The use of 1.2 molar equivalent or 1.0 molar equivalent of butyllithium decreased the yield of the adduct, (E)-6-heptadecen-5-ol to 78% or 72%, respectively. The other results are summarized in Table 1.
Table I. Preparation of alkenyllithiums and their reaction with electrophiles

![Diagram](https://via.placeholder.com/150)

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<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>R&lt;sup&gt;3&lt;/sup&gt;</th>
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a) Iodoalkene (1.0 mmol), butyllithium (1.5 mmol), and carbonyl compound (1.2 mmol) were employed.  
b) A solution of Me<sub>3</sub>SiCl (1.2 mmol) in THF (1.0 ml) was added to alkenyllithiums.  
c) CH<sub>3</sub>I (1.0 ml) was added to alkenyllithiums.  
d) Three molar equivalents of butyllithium were used.
Several features of the reaction are worth noting. (1) Conversion of alkenyl bromide to alkenyllithium was not so effective as alkenyl iodide. For instance, treatment of (E)-1-bromo-1-dodecene with butyllithium at 25 °C followed by an addition of pentanal to the resulting 1-dodecenyllithium gave (E)-6-heptadecen-5-ol in only 40% yield. (2) A choice of solvent is critical for the successful reaction. Hexane and benzene proved to be equally effective solvents for the metal-halogen exchange reaction. Treatment of (Z)-1-iodo-1-dodecene with butyllithium in hexane or benzene and successively with pentanal provided (Z)-6-heptadecen-5-ol quantitatively. In other solvents such as toluene, ether, and THF, (Z)-6-heptadecen-5-ol was obtained in 85%, 58%, and <5% yields, respectively. In the case of the reactions in ether and THF, starting 1-iodo-1-dodecene was consumed completely and unidentified complex mixture was obtained in addition to (Z)-6-heptadecen-5-ol. (3) Alkenyllithiums were stable in hydrocarbon solvents and potential side-reactions such as alkylation of, or elimination from the organic halide (iodobutane), which was produced in the metal-halogen exchange process, were not troublesome. Thus, butylated alkene could not be observed in the reaction mixture. (4) Stereochemistry of alkenyl iodides was completely conserved during the reaction. Whereas (E)-1-iodo-1-dodecene gave (E)-6-heptadecen-5-ol exclusively upon treatment with butyllithium and subsequent addition of pentanal, (Z)-1-iodo-1-dodecene afforded the corresponding (Z)-isomer selectively (Run 10). (5) Dialkyl substituted iodoalkene [(E)-6-iodo-6-dodecene, Run 15–18] provided the corresponding alkenyllithium effectively upon treatment with butyllithium as well as monoalkyl substituted iodoalkenes or iodoethene (Run 1 and 2). (6) An addition of three molar equivalents of butyllithium to 2-iodo-2-propen-1-ol gave alkenyllithium which afforded the corresponding allylic diol in moderate yield upon treatment with benzaldehyde (Run 19).

Alkenyllithiums were easily transformed into organometallics such as cuprates. For instance, an addition of CuCN to a solution of alkenyllithium, prepared from (E)-1-iodo-1-dodecene and butyllithium, provided alkenylcuprate which reacted with 2-cyclohexenone to give 1,4-adduct in 75% yield (Scheme 1).
Scheme 1

(2) Preparation of allenylmetallics by metal-iodine exchange between allenyl iodides and \( n\)-BuLi, \( i\)-PrMgBr, or \( Et_2Zn\).

The chemistry of acetylene and allene has attracted much attention during the past two decades. One of the most versatile preparative methods for these compounds is a use of propargyl and allenyl organometallics. Organometallics of allenic structure are usually prepared by the reactions of metals with propargylic or allenic halides, or by metalation with alkylolithiums of the corresponding hydrocarbons. Here the author wishes to discuss a facile alternative approach to allenic organometallics based on the exchange reaction between allenyl iodides and organometallics such as \( n\)-BuLi, \( i\)-PrMgBr or \( Et_2Zn\).

The preparative method for alkenyllithiums described in section (1) was applied to the generation of allenyl organometallic reagents. An addition of \( n\)-BuLi to a hexane or toluene solution of 1-iodo-1,2-octadiene at \(-78^\circ C\) gave the corresponding organolithium compound which provided the adducts upon treatment with carbonyl compounds such as PhCHO and PhCOCH\(_3\). Not only butyllithium but also \( i\)-PrMgBr and \( Et_2Zn\) were also effective for the preparation of organometallic reagents from 1-iodo-1,2-alkadienes via metal-halogen exchange. The results are summarized in Table 2.
Table 2. Preparation of allenylmetallic reagents and their reaction with carbonyl compounds

\[
\begin{align*}
\text{R'Mtl} & \quad \text{Solvent} & \quad \text{R}^1\text{COR}^2 & \quad \text{Yield} & \quad \text{Ratio} & \quad \text{erythro/threo} \\
\text{n-BuLi} & \quad \text{hexane} & \quad \text{PhCHO} & \quad 83\% & \quad >99 : <1 & \quad 55 / 45 \\
\text{n-BuLi} & \quad \text{toluene} & \quad n-C_4H_9CHO & \quad 87\% & \quad >99 : <1 & \quad 31 / 69 \\
\text{n-BuLi} & \quad \text{toluene} & \quad t-BuCHO & \quad 64\% & \quad >99 : <1 & \quad <1 / >99 \\
\text{n-BuLi} & \quad \text{toluene} & \quad \text{PhCOCH}_3 & \quad 96\% & \quad 92 : 8 & \quad 40 / 60 \\
\text{n-BuLi} & \quad \text{toluene} & \quad n-C_9H_{19}COCH}_3 & \quad 83\% & \quad 50 : 50 & \quad 50 / 50 \\
\text{n-BuLi} & \quad \text{toluene} & \quad \text{cyclohexanone} & \quad 67\% & \quad 65 : 35 & \quad — \\
\text{n-BuLi} & \quad \text{toluene} & \quad \text{Me}_3\text{SiCl}^a & \quad 63\%^b & \quad — & \quad — \\
\text{i-PrMgBr} & \quad \text{hexane} & \quad \text{PhCHO} & \quad 70\% & \quad >99 : <1 & \quad 46 / 54 \\
\text{i-PrMgBr} & \quad \text{Et}_2\text{O} & \quad \text{PhCHO} & \quad 80\% & \quad >99 : <1 & \quad 43 / 57 \\
\text{i-PrMgBr} & \quad \text{Et}_2\text{O} & \quad n-C_4H_9CHO & \quad 72\% & \quad >99 : <1 & \quad 11 / 89 \\
\text{i-PrMgBr} & \quad \text{Et}_2\text{O} & \quad t-BuCHO & \quad 58\% & \quad >99 : <1 & \quad <1 / >99 \\
\text{i-PrMgBr} & \quad \text{Et}_2\text{O} & \quad \text{PhCOCH}_3 & \quad 88\% & \quad 92 : 8 & \quad 25 / 75 \\
\text{i-PrMgBr} & \quad \text{Et}_2\text{O} & \quad n-C_9H_{19}COCH}_3 & \quad 67\% & \quad >99 : <1 & \quad 47 / 53 \\
\text{i-PrMgBr} & \quad \text{Et}_2\text{O} & \quad \text{cyclohexanone} & \quad 51\% & \quad 91 : 9 & \quad — \\
\text{Et}_2\text{Zn} & \quad \text{Et}_2\text{O} & \quad \text{PhCHO} & \quad 58\% & \quad >99 : <1 & \quad 37 / 63 \\
\text{Et}_2\text{Zn} & \quad \text{Et}_2\text{O} & \quad n-C_4H_9CHO & \quad 63\% & \quad >99 : <1 & \quad 13 / 87 \\
\text{Et}_2\text{Zn} & \quad \text{Et}_2\text{O} & \quad t-BuCHO & \quad 44\% & \quad >99 : <1 & \quad <1 / >99 \\
\text{Et}_2\text{Zn} & \quad \text{Et}_2\text{O} & \quad \text{PhCOCH}_3 & \quad 61\% & \quad >99 : <1 & \quad 14 / 86 \\
\text{Et}_2\text{Zn} & \quad \text{Et}_2\text{O} & \quad n-C_9H_{19}COCH}_3 & \quad 62\% & \quad >99 : <1 & \quad 48 / 52 \\
\text{Et}_2\text{Zn} & \quad \text{Et}_2\text{O} & \quad \text{cyclohexanone} & \quad 76\% & \quad >99 : <1 & \quad — \\
\end{align*}
\]

a) THF (1.0 ml) solution of Me$_3$SiCl (1.1 mmol) was added.

b) Product is Me$_3$SiCH=CH-CH-$_n$-C$_5$H$_{11}$. 

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Several comments are worth noting. (1) Lithium-iodine exchange between allenyl iodide and $n$-BuLi was performed in hexane or toluene at $-78 \, ^\circ C$. The reaction at $0 \, ^\circ C$ gave complex mixtures upon treatment with carbonyl compounds. Meantime, metal-halogen exchange with $i$-PrMgBr or $Et_2Zn$ proceeded efficiently at $0 \, ^\circ C$. Diethyl ether was a more suitable solvent than hexane or toluene in the case of $i$-PrMgBr or $Et_2Zn$. (2) The use of $i$-PrMgBr was essential for the successful metal-halogen exchange reaction. Treatment of 1-iodo-1,2-octadiene with MeMgI or $n$-BuMgBr followed by an addition of PhCHO gave the corresponding homopropargylic alcohols in only $<3\%$ or $8\%$ yield. The adduct between Grignard reagent and PhCHO ($PhCH(OH)Me$ or $PhCH(OH)-n-Bu$) was obtained in good yield and 1-iodo-1,2-octadiene was recovered ($95\%$ or $80\%$). (3) Whereas an addition of aldehyde to allenyllithium, derived from 1-iodo-1,2-octadiene and $n$-BuLi, provided homopropargylic alcohol almost exclusively, an addition of ketone such as acetophenone or 2-undecanone afforded a regioisomeric mixture of homopropargylic alcohol and allenyl alcohol. In contrast, allenylzinc reagent, generated from 1-iodo-1,2-octadiene and $Et_2Zn$, gave homopropargylic alcohols regioselectively upon treatment with not only aldehydes but also ketones. (4) Diastereoselectivities (ratio of *erythro/threo*) were not so high except with the reaction of $t$-BuCHO.

Diastereoselective synthesis of homopropargylic alcohols was achieved by the reaction of allenylzinc chloride derived from 1-lithio-1,2-octadiene and zinc chloride. Thus, lithiation of 1-iodo-1,2-octadiene in toluene with butyllithium at $-78 \, ^\circ C$ followed by transmetalation with zinc chloride produced the corresponding allenylzinc reagent. An addition of aldehydes afforded *threo*-homopropargylic alcohols diastereoselectively (Table 3).$^{12}$ The selectivities are higher than those of the reaction with allenylethylzinc in Table 2. The high selectivities of the reaction with allenylzinc chloride might be attributed to lower reaction temperature compared to the reaction with latter reagent ($-78 \, ^\circ C$ vs $0 \, ^\circ C$). Whereas the reaction with allenylzinc chloride proceeded at $-78 \, ^\circ C$, the reaction with allenylethylzinc did not proceed at that temperature.
Table 3. Preparation of allenylzinc chloride by transmetalation and its reaction with aldehydes

\[
\text{\textbf{\textit{RCHO}} \quad \textbf{Yield of Adduct (\%)} \quad \textbf{Ratio of \textit{erythro}:\textit{threo}}
\]

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<td>9 : 91</td>
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<td>\textit{c-C}_6\textit{H}_11\textit{CHO}</td>
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<tr>
<td>\textit{t-BuCHO}</td>
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<td>&lt;1 : &gt;99</td>
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Treatment of an ethereal solution of a mixture of 1-iodo-1,2-propadiene and 3-iodo-1-propyne (2:1)\textsuperscript{13} with \textit{n-BuLi} or \textit{Et}_2\textit{Zn} resulted in a formation of the corresponding organozinc reagent. An addition of various carbonyl compounds to the organometallic compound afforded the corresponding homopropargylic alcohols selectively (Table 4).\textsuperscript{14}

Table 4. Preparation and reaction of 1, 2-propadienyllithium and 1, 2-propadienylzinc

\[
\text{\textbf{\textit{Reaction Conditions}} \quad \textbf{\textit{R}{}^1\textit{COR}{}^2} \quad \textbf{Yield of Adduct} \quad \textbf{Ratio of 3 : 4}}
\]

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</table>
The formation of allenylmagnesium and allenylzinc reagents was examined by $^1$H NMR spectra. The addition of isopropylmagnesium bromide (1.1 equiv) to a solution of 1-iodo-1,2-octadiene (A) in C$_6$D$_6$ containing anisole as an internal standard produced new signals at $\delta$ 4.28 (dt) and 5.28 (dt), which have been assigned to olefinic protons of allenylmagnesium compound. The peak of isopropyl iodide was also observed. On the other hand, the olefinic signals of A at $\delta$ 4.73 and 5.45 disappeared completely (Fig 1). The addition of benzaldehyde to the resulting mixture provided the corresponding homopropargylic alcohol as a single product in 80% yield.

The addition of 1 equiv of diethylzinc to a solution of 1-iodo-1,2-octadiene (A) in C$_6$D$_6$ produced a signal of EtI and reduced the signals of olefinic protons of A at $\delta$ 4.73 and 5.45 to 60% of the original peaks. In contrast to the case of i-PrMgBr, no clear new peaks corresponding to allenylzinc or propargylzinc could be observed because of its polymeric nature. The olefinic signals of A (50~60% of original peaks) remained even after being stirred for 2h at 25 °C. However, an addition of PhCHO to the mixture resulted in disappearance of olefinic protons of A and provided the corresponding homopropargylic alcohol in good yield. Thus, we are tempted to assume that equilibration between allenylzinc (and/or propargylzinc) and starting allenyl iodide has been established by the addition of Et$_2$Zn to A (Scheme 2). Then, an addition of benzaldehyde, which reacts with allenylzinc but does not react with diethylzinc, shifted the equilibrium to right and eventually consumed the starting allenyl iodide to give the adduct in good yield.

\[ \text{Scheme 2} \]

\[ \text{R}^-\text{I} + \text{Et}_2\text{Zn} \leftrightarrow \text{R}^-\text{ZnEt} + \text{EtI} \]

\( (\text{R} = n\text-C_5\text{H}_{11}) \)
Figure 1

\[ \text{R} \quad \text{A} \quad \text{I} + \text{i-PrMgBr} \rightarrow \text{R} \quad \text{B} \quad \text{MgBr} + \text{i-PrI} \]

\[ \text{Et}_2\text{O} \quad \text{PhOCH}_3 \]

A + PhOCH₃

A + PhOCH₃ + i-PrMgBr
Transmetalation of optically active allenyl iodide was examined. Treatment of (R)-1-ido-1,2-octadiene\textsuperscript{16} (98\% ee) with \( n\text{-BuLi} \) at \(-78^\circ\text{C} \) and then with \( \text{PhCHO} \) or \( \text{Me}_3\text{SiCl} \) provided the corresponding homopropargylic alcohol \( \text{PhCH(OH)}\text{-CH}(n\text{-C}_5\text{H}_{11})\text{-C}=\text{CH} \) (\( \approx 0\% \) ee) or 1-trimethylsilyl-1,2-octadiene (\( \approx 0\% \) ee) in 80\% or 65\% yield, respectively (Scheme 3). The complete loss of optical purity could be attributed to fast equilibrium between allenyllithium and propargyllithium. In the latter form, optical purity might be lost because of its stereochemical instability. The use of \( i\text{-PrMgBr} \) or \( \text{Et}_2\text{Zn} \) in place of \( n\text{-BuLi} \) also resulted in a complete loss of optical purity. Thus, organometallics, prepared here via iodine-metal exchange, could exist as an equilibrium mixture of allenic and propargylic organometallic derivatives although only allenic magnesium species has been observed in NMR study.

\textbf{Scheme 3} 

\[ 
\begin{array}{c}
\text{H} \\
\text{n-C}_5\text{H}_{11} \\
\text{R} \\
\text{H}
\end{array} \xrightarrow{\text{RMtl}} \xrightarrow{\text{PhCHO}} 
\begin{array}{c}
\text{OH} \\
\text{Ph} \\
\text{H} \\
\text{n-C}_5\text{H}_{11}
\end{array} 
\] 

(\( \text{R} \) 98\% ee) 

0\% ee
Experimental

General Procedure for the Preparation of Alkenyllithium and Its Reaction with Carbonyl Compound. Butyllithium (1.57 M hexane solution, 0.95 ml, 1.5 mmol) was added to a hexane (5.0 ml) solution of (E)-1-iodo-1-dodecene (0.29 g, 1.0 mmol) at 25 °C. The resulting solution was stirred at 25 °C for 15 min. Pentanal (0.10 g, 1.2 mmol) was added at 0 °C and the whole mixture was stirred for 10 min at 0 °C, then 10 min at 25 °C. Extractive workup followed by silica gel column purification gave (E)-6-heptadecen-5-ol (0.26 g) quantitatively.

(E)-1-Phenyl-2-tridecen-1-ol: Bp 140 °C (0.5 Torr, bath temp); IR (neat) 3322, 2952, 2922, 2850, 1454, 1379, 1072, 1030, 1007, 967, 754, 720 cm⁻¹; ¹H NMR (CDCl₃) δ 0.88 (t, J = 6.6 Hz, 3H), 1.21–1.40 (m, 16H), 1.85–1.86 (m, 1H), 2.05 (dt, J = 6.6, 6.6 Hz, 2H), 5.17 (d, J = 6.9 Hz, 1H), 5.65 (dd, J = 6.9, 15.3 Hz, 1H), 5.77 (dt, J = 15.3, 6.6 Hz, 1H), 7.25–7.39 (m, 5H); ¹³C NMR (CDCl₃) δ 14.1, 22.7, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 32.2, 75.3, 126.1, 127.5, 128.4, 132.1, 133.0. Found: C, 83.21%; H, 11.03%. Calcd for C₁₉H₃₀O: C, 83.15%; H, 11.02%.

(E)-1-Cyclohexyl-2-tridecen-1-ol: Bp 140 °C (0.5 Torr, bath temp); IR (neat) 3342, 2920, 2850, 1461, 1451, 1083, 1003, 969, 891, 720 cm⁻¹; ¹H NMR (CDCl₃) δ 0.88 (t, J = 6.6 Hz, 3H), 0.92–1.43 (m, 23H), 1.61–1.88 (m, 5H), 2.03 (dt, J = 6.6, 6.6 Hz, 2H), 3.77 (dd, J = 6.9, 6.9 Hz, 1H), 5.44 (ddt, J = 15.3, 6.9, 1.17 Hz, 1H), 5.62 (dt, J = 15.3, 6.6 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.1, 22.7, 26.1, 26.5, 28.7, 28.8, 29.2, 29.3, 29.5, 29.6, 31.9, 32.3, 43.6, 77.8, 131.3, 133.2. Found: C, 81.20%; H, 13.24%. Calcd for C₁₉H₃₆O: C, 81.36%; H, 12.94%.

(E)-1-(1-Hydroxycyclohexyl)dodecene: Bp 126 °C (0.5 Torr, bath temp); IR (neat) 3352, 2922, 2850, 1449, 1378, 1174, 1136, 1056, 1036, 969 cm⁻¹; ¹H NMR (CDCl₃) δ 0.88 (t, J = 6.6 Hz, 3H), 1.26–1.38 (m, 18H), 1.46–1.65 (m, 9H), 2.02 (dt, J = 6.3, 6.3 Hz, 2H), 5.55 (d, J = 15.7 Hz, 1H), 5.66 (dt, J = 15.7, 6.3 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.1, 22.3, 22.7, 25.6, 29.1, 29.3, 29.5, 29.6, 31.9, 32.4, 38.1, 71.3, 128.3, 137.6. Found: C, 81.42%; H, 13.10%. Calcd for C₁₈H₃₄O: C, 81.14%; H, 12.86%. 114
(Z)-6-Heptadecen-5-ol: Bp 114 °C (0.5 Torr, bath temp); IR (neat) 3326, 2922, 2852, 1466, 1007, 721 cm⁻¹; ¹H NMR (CDCl₃) δ 0.86–0.93 (m, 6H), 1.22–1.62 (m, 23H), 2.04–2.10 (m, 2H), 4.43 (dt, J = 8.5, 6.5 Hz, 1H), 5.35 (ddt, J = 11.0, 8.5, 1.5 Hz, 1H), 5.49 (dt, J = 11.0, 7.4 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.0, 14.1, 22.7, 27.6, 27.7, 29.2, 29.3, 29.5, 29.6, 29.7, 31.9, 37.2, 67.7, 132.4, 132.5. Found: C, 80.00; H, 13.64%. Calcd for C₁₇H₃₄O: C, 80.24; H, 13.47%.

(Z)-1-Cyclohexyl-2-tridecen-1-ol: Bp 140 °C (0.5 Torr, bath temp); IR (neat) 3328, 3002, 2922, 2852, 1466, 1451, 1081, 1011, 744, 720 cm⁻¹; ¹H NMR (CDCl₃) δ 0.88 (t, J = 6.6 Hz, 3H), 0.94–1.38 (m, 23H), 1.63–1.74 (m, 4H), 1.90–2.09 (m, 3H), 4.14 (dd, J = 8.7, 7.5 Hz, 1H), 5.37 (ddt, J = 11.2, 8.5, 1.3 Hz, 1H), 5.54 (dt, J = 11.2, 7.3 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.1, 22.7, 26.0, 26.5, 27.8, 28.6, 28.8, 29.3, 29.5, 29.6, 29.7, 31.9, 43.9, 71.9, 130.9, 133.2. Found: C, 81.13; H, 13.18%. Calcd for C₁₉H₃₆O: C, 81.36; H, 12.94%.

(Z)-2-Methyl-3-tetradecen-2-ol: Bp 93 °C (0.5 Torr, bath temp); IR (neat) 3350, 2924, 2850, 1466, 1376, 1362, 1145, 954, 893, 721 cm⁻¹; ¹H NMR (CDCl₃) δ 0.88 (t, J = 6.6 Hz, 3H), 1.21–1.59 (m, 23H including δ 1.37 (s, 6H)), 2.31 (ddt, J = 7.0, 1.6, 7.0 Hz, 2H), 5.30 (dt, J = 11.8, 7.4 Hz, 1H), 5.48 (dt, J = 11.8, 1.6 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.1, 22.7, 28.1, 29.3, 29.4, 29.6, 30.1, 31.1, 31.9, 71.6, 131.5, 136.6. Found: C, 79.30; H, 13.36%. Calcd for C₁₅H₃₀O: C, 79.58; H, 13.36%.

(Z)-1-(1-Hydroxycyclohexyl)-dodecene: Bp 127 °C (0.5 Torr, bath temp); IR (neat) 3604, 3420, 2920, 2850, 1450, 1378, 1255, 1165, 1056, 961, 906, 720 cm⁻¹; ¹H NMR (CDCl₃) δ 0.88 (t, J = 6.6 Hz, 3H), 1.23–1.67 (m, 27H), 2.34 (dt, J = 6.9, 6.9 Hz, 2H), 5.38 (dt, J = 11.7, 6.9 Hz, 1H), 5.46 (dt, J = 11.7, 0.78 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.1, 22.4, 22.7, 25.4, 28.5, 29.3, 29.4, 29.6, 30.1, 31.9, 39.2, 132.7, 135.9. Found: C, 81.12; H, 13.10%. Calcd for C₁₈H₃₄O: C, 81.14;
(E)-6-Pentyl-6-dodecen-5-ol: Bp 112 °C (0.5 Torr, bath temp); IR (neat) 3318, 2952, 2924, 2856, 1466, 1379, 1303, 1274, 1115, 1032, 866, 727 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.87–0.92 (m, 9H), 1.22–1.57 (m, 19H), 1.96–2.06 (m, 4H), 4.00 (t, \(J = 6.6\) Hz, 1H), 5.6 (t, \(J = 7.5\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 14.1, 22.5, 22.6, 22.7, 27.5, 28.2, 29.5, 29.7, 31.6, 32.4, 35.4, 126.9, 142.0. Found: C, 79.98%; H, 13.60%. Calcd for C\(_{17}\)H\(_{34}\)O: C, 80.24%; H, 13.47%.

(E)-3-Pentyl-2-phenyl-3-nonen-2-ol: Bp 124 °C (0.1 Torr, bath temp); IR (neat) 3442, 2954, 2924, 2856, 1493, 1466, 1459, 1448, 1378, 1061, 1028, 920, 907, 762, 699 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.80 (t, \(J = 6.6\) Hz, 3H), 0.90 (t, \(J = 6.6\) Hz, 3H), 1.11–1.14 (m, 11H), 1.57 (bs, 1H), 1.66 (s, 3H), 1.71–1.94 (m, 3H), 2.06 (dt, \(J = 7.2, 7.2\) Hz, 2H), 5.62 (t, \(J = 7.2\) Hz, 1H), 7.19–7.43 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 14.0, 14.1, 22.3, 22.6, 27.9, 28.6, 29.4, 29.5, 29.8, 30.2, 31.7, 32.5, 77.9, 125.5, 125.8, 126.6, 127.9, 144.2, 146.9. Found: C, 83.54%; H, 11.34%. Calcd for C\(_{20}\)H\(_{32}\)O: C, 83.27%; H, 11.18%.

(E)-6-Trimethylsilyl-6-dodecene: Bp 103 °C (20 Torr, bath temp); IR (neat) 2954, 2924, 2856, 1612, 1467, 1247, 835, 750, 686 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.05 (s, 9H), 0.90 (t, \(J = 6.6\) Hz, 6H), 1.25–1.39 (m, 12H), 2.04–2.11 (m, 4H), 5.70 (t, \(J = 6.8\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) –1.1, 14.1, 22.56, 22.61, 28.4, 29.3, 29.7, 29.9, 31.7, 32.3, 140.3, 140.8. Found: C, 75.09%; H, 13.37%. Calcd for C\(_{15}\)H\(_{32}\)Si: C, 74.91%; H, 13.41%.

2-Methylene-1-phenyl-1,3-propanediol: Bp 140 °C (1.0 Torr, bath temp); IR (neat) 3308, 2922, 2870, 1493, 1453, 1020, 916, 760, 699 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.95 (bs, 1H), 2.70 (bs, 1H), 4.16 (d, \(J = 13.1\) Hz, 1H), 4.50 (d, \(J = 13.1\) Hz, 1H), 5.22 (d, \(J = 0.9\) Hz, 2H), 5.37 (s, 1H), 7.26–7.41 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 64.0, 76.3, 113.4, 126.2, 127.8, 128.5, 141.7, 149.2. Found: C, 72.92%; H, 7.66%. Calcd for C\(_{10}\)H\(_{12}\)O\(_2\): C, 73.15%; H, 7.36%.
Preparation of Alkenylcuprate and Its Reaction with 2-Cyclohexen-1-one. To a solution of CuCN (0.07 g, 0.75 mmol) in Et$_2$O (5 ml) was added alkenyllithium at -78 °C, prepared from (E)-1-iodo-1-dodecene (0.29 g, 2.0 mmol) and butyllithium (1.5 mmol) in hexane. The mixture was stirred for 30 min and warmed to -20 °C. A solution of 2-cyclohexen-1-one (0.12 g, 1.2 mmol) in Et$_2$O (2 ml) was added and the resulting mixture was allowed to warm to room temperature during 1 h. The mixture was poured into water and extracted with Et$_2$O (20 ml×3). Concentration and purification by silica-gel column chromatography gave (E)-1-(3-Oxocyclohexyl)-1-dodecene (0.40 g) in 75% yield: Bp 134 °C (0.5 Torr, bath temp); IR (neat) 2918, 2852, 1715, 1460, 1449, 1423, 1345, 1315, 1222, 966 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.88 (t, $J = 6.6$ Hz, 3H), 1.26–1.33 (m, 16H), 1.40–2.45 (m, 11H), 5.36 (dd, $J = 15.5$, 5.5 Hz, 1H), 5.43 (dd, $J = 15.5$, 5.7 Hz, 1H); $^{13}$C NMR (CDCl$_3$) δ 14.1, 22.7, 24.9, 29.1, 29.3, 29.4, 29.5, 29.6, 31.6, 31.9, 32.5, 41.3, 41.6, 47.7, 130.0, 132.9. Found: C, 81.67; H, 12.15%. Calcd for C$_{18}$H$_{32}$O: C, 81.75; H, 12.20%.

1-Iodo-1,2-octadiene. The title compound was prepared according to the procedure reported in the literature.$^{16}$

Standard Procedure for Preparation of Allenyllithium and Its Reaction with Electrophiles. Reaction with pentanal is representative. To a solution of 1-iodo-1,2-octadiene (0.24 g, 1.0 mmol) in toluene (5 ml) was added butyllithium (1.58 M hexane solution, 0.76 ml, 1.2 mmol) at -78 °C. After the mixture was stirred for 5 min, pentanal (0.09 g, 1.1 mmol) in toluene (3 ml) was added and the mixture was stirred for 10 min at -78 °C and another 10 min at room temperature. The mixture was poured into 1 M HCl and extracted with ethyl acetate (20 ml×3). The combined organic layer were dried over Na$_2$SO$_4$ and concentrated in vacuo. Purification by silica-gel column chromatography gave 3-pentyl-1-octyn-4-ol (0.17 g) in 87% yield.
Standard Procedure for Preparation of Allenylmagnesium Reagents and Their Reaction with Electrophiles. Reaction with pentanal is representative. To a solution of 1-iodo-1,2-octadiene (0.24 g, 1.0 mmol) in Et₂O (5 ml) was added t-PrMgBr (1.0 M hexane solution, 1.2 ml, 1.2 mmol) at 0 °C. After being stirred for 30 min, pentanal (0.09 g, 1.1 mmol) in Et₂O (2 ml) was added and the mixture was stirred for another 30 min. To the reaction mixture, 1 M HCl was added carefully and extracted with ethyl acetate (20 ml×3). The combined organic layer were dried over Na₂SO₄ and concentrated in vacuo. Purification by silica-gel column chromatography gave 3-pentyl-1-octyn-4-ol (0.14 g) in 72% yield.

Standard Procedure for Preparation of Allenylzinc Reagents and Their Reaction with Electrophiles. Reaction with pentanal is representative. To a solution of 1-iodo-1,2-octadiene (0.24 g, 1.0 mmol) in Et₂O (5 ml) was added Et₂Zn (1.0 M hexane solution, 1.2 ml, 1.2 mmol) at 0 °C. After being stirred for 30 min, pentanal (0.09 g, 1.1 mmol) in Et₂O (2 ml) was added and the mixture was stirred for another 30 min. To the reaction mixture, 1 M HCl was added carefully and extracted with ethyl acetate (20 ml×3). The combined organic layer were dried over Na₂SO₄ and concentrated in vacuo. Purification by silica-gel column chromatography gave 3-pentyl-1-octyn-4-ol (0.12 g) in 63% yield.

2-Pentyl-1-phenyl-3-butyn-1-ol (47:53 diastereomeric mixture): Bp 105 °C (0.5 Torr, bath temp); IR (neat) 3406, 3300, 3028, 2922, 2858, 2108, 1495, 1454, 1194, 1045, 714, 760, 701, 631 cm⁻¹; ¹H NMR (CDCl₃) δ 0.86 (t, J = 6.9 Hz, 3H), 1.10–1.70 (m, 8H), 2.11 (d, J = 2.4 Hz, 0.43H), 2.20 (s, 0.43H), 2.22 (d, J = 2.4 Hz, 0.57H), 2.51 (s, 0.57H), 2.71 (m, 0.57H), 2.80 (m, 0.43H), 4.58 (d, J = 6.6 Hz, 0.57H), 4.75 (d, J = 5.7 Hz, 0.57H); ¹³C NMR (CDCl₃) δ 13.86, 13.89, 22.36, 22.42, 26.81, 26.83, 29.46, 31.10, 31.37, 31.48, 39.97, 41.10, 71.88, 72.40, 75.66, 76.06, 84.21, 84.57, 126.61, 126.70, 127.87, 128.03, 128.19, 128.40, 141.61, 141.75. Found: C, 83.00; H, 9.42%. Calcd for C₁₅H₂₀O: C, 83.29; H, 9.32%.
3-Pentyl-1-octyn-4-ol (16:84 diastereomeric mixture): Bp 75 °C (0.5 Torr, bath temp); 
IR (neat) 3400, 3304, 2854, 2108, 1467, 1380, 1249, 1120, 901, 727, 626 cm⁻¹; ¹H NMR 
(CDCl₃) δ 0.90 (t, J = 6.9 Hz, 3H), 0.92 (t, J = 6.9 Hz, 3H), 1.20–1.60 (m, 8H), 1.67 (d, J = 7.5 
Hz, 0.84H), 2.12 (d, J = 2.4 Hz, 0.16H), 2.14 (d, J = 2.4 Hz, 0.84H), 2.41 (m, 0.84H), 2.51 (m, 
0.16H), 3.50 (m, 0.84H), 3.58 (m, 0.16H); ¹³C NMR (CDCl₃) δ 13.91, 22.43, 22.55, 27.08, 27.90, 
29.85, 31.52, 33.23, 35.18, 38.85, 71.80, 72.98, 84.14. Found: C, 79.68; H, 12.38%. Calcd for 
C₁₃H₂₄O: C, 79.53; H, 12.32%.

threo-2,2-Dimethyl-4-pentyl-5-hexyn-3-ol: Bp 70 °C (0.5 Torr, bath temp); IR (neat) 
3450, 3304, 2860, 2106, 1467, 1366, 1075, 1013, 752, 623 cm⁻¹; ¹H NMR (CDCl₃) δ 0.90 
(t, J = 6.9 Hz, 3H), 0.97 (s, 9H), 1.20–1.80 (m, 8H), 1.97 (d, J = 10.2 Hz, 1H), 2.21 (d, J = 2.4 
Hz, 1H), 2.65 (m, 1H), 3.08 (d, J = 10.2 Hz, 1H); ¹³C NMR (CDCl₃) δ 13.90, 22.43, 26.20, 26.90, 
31.42, 33.75, 34.99, 35.95, 73.79, 80.01, 84.13. Found: C, 79.51; H, 12.30%. Calcd for 
C₁₃H₂₄O: C, 79.53; H, 12.32%.

3-Pentyl-2-phenyl-4-pentyn-2-ol: Bp 110 °C (0.5 Torr, bath temp); IR (neat) 
3462, 1496, 1448, 1066, 851, 759, 699, 629 cm⁻¹; ¹H NMR (CDCl₃) δ 0.82 (t, 
J = 6.9 Hz, 3H), 1.0–1.64 (m, 8H), 1.70 (s, 3H), 2.15 (s, 1H), 2.22 (d, J = 2.4 Hz, 1H), 2.72 (ddd, 
J = 2.4, 3.0, 11.4 Hz, 1H), 7.10–7.50 (m, 5H); ¹³C NMR (CDCl₃) δ 13.86, 22.38, 27.37, 29.07, 
29.75, 31.30, 44.70, 72.40, 75.25, 84.69, 125.07, 126.77, 128.14, 145.36. Found: C, 83.20; H, 
9.83%. Calcd for C₁₆H₂₂O: C, 83.43; H, 9.63%.

4-Methyl-3-pentyl-1-tridecyn-4-ol (50:50 diastereomeric mixture): Bp 130 °C (0.5 Torr, 
bath temp); IR (neat) 3444, 3304, 2922, 2852, 2106, 1467, 1377, 1133, 930, 720, 623 cm⁻¹; ¹H 
NMR (CDCl₃) δ 0.88 (t, J = 6.9 Hz, 3H), 0.90 (t, J = 6.9 Hz, 3H), 1.21 (s, 1.5H), 1.23 (s, 1.5H), 
1.20–1.70 (m, 24.5H), 1.81 (s, 0.5H), 2.13 (d, J = 2.7 Hz, 0.5H), 2.15 (d, J = 2.4 Hz, 0.5H), 2.41 
(m, 1H); ¹³C NMR (CDCl₃) δ 13.92, 13.98, 22.47, 22.57, 23.25, 23.42, 27.80, 28.83, 29.19, 29.22,
29.47, 29.53, 30.08, 31.55, 31.58, 31.80, 39.16, 39.64, 43.32, 43.49, 71.57, 71.87, 73.43, 73.69, 85.04, 85.26. Found: C, 81.42; H, 13.19%. Calcd for C₁₆H₂₂O: C, 81.36; H, 12.94%.

1-(1-Pentyl-2-propynyl)cyclohexanol: Mp 49–50 °C; IR (neat, before crystalization) 3444, 3306, 2856, 2104, 1450, 1380, 1265, 1153, 968, 622 cm⁻¹; ¹H NMR (CDCl₃) δ 0.90 (t, J = 6.8 Hz, 3H), 1.10–1.70 (m, 19H), 2.15 (d, J = 2.4 Hz, 1H), 2.35 (ddd, J = 2.4, 2.4, 10.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 13.93, 21.73, 21.78, 22.46, 25.65, 27.73, 28.10, 31.57, 34.07, 35.05, 44.07, 71.89, 72.25, 85.06. Found: C, 80.48; H, 11.86%. Calcd for C₁₄H₂₄O: C, 80.71; H, 11.61%.

1-(Trimethylsilyl)-1,2-octadiene: Bp 70 °C (8 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1939, 1467, 1380, 1249, 841, 758, 696 cm⁻¹; ¹H NMR (CDCl₃) δ 0.09 (s, 9H), 0.89 (t, J = 6.9 Hz, 3H), 1.25–1.50 (m, 6H), 1.96 (ddt, J = 3.9, 6.9, 6.9 Hz, 2H), 4.77 (dt, J = 6.9, 6.9 Hz, 1H), 4.89 (dt, J = 6.9, 3.9 Hz, 1H); ¹³C NMR (CDCl₃) δ -1.06, 13.95, 22.41, 27.73, 29.29, 31.31, 82.43, 83.47, 210.28. Found: C, 72.28; H, 12.36%. Calcd for C₁₅H₂₂Si: C, 72.44; H, 12.16%.

Preparation of Allenylzinc Chloride and Its Reaction with aldehyde. To a toluene solution of allenyllithium, prepared from 1-iodo-1,2-octadiene (0.24 g, 1.0 mmol) and butyllithium (1.2 mmol) was added a suspension of zinc chloride (0.16 g, 1.2 mmol) in THF (3 ml). After stirring 10 min, pentanal (0.09 g, 1.1 mmol) in toluene (2 ml) was added and stirred for another 10 min. Extractive workup followed by silica gel column purification gave 3-pentyl-1-octyn-4-ol (0.14 g, 9:91 diastereomeric mixture) in 72% yield.

1-Phenyl-3-butyn-1-ol: Bp 95 °C (1.0 Torr, bath temp); IR (neat) 3288, 3028, 2910, 2114, 1420, 1189, 1050, 864, 755, 699, 631 cm⁻¹; ¹H NMR (CDCl₃) δ 2.08 (t, J = 2.6 Hz, 1H), 2.38 (bs, 1H), 2.65 (dd, J = 6.2, 2.6 Hz, 2H), 4.89 (t, J = 6.2 Hz, 1H), 7.25–7.45 (m, 5H); ¹³C NMR (CDCl₃) δ 29.37, 70.93, 72.27, 80.64, 125.70, 127.95, 128.43, 142.38. Found: C, 82.04; H, 7.11%. Calcd for C₁₀H₁₀O: C, 82.16; H, 6.89%.

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1-Octyn-4-ol: Bp 100 °C (18 Torr, bath temp); IR (neat) 3360, 3304, 2954, 2858, 2114, 1467, 1380, 1082, 1032, 844, 627 cm⁻¹; ¹H NMR (CDCl₃) δ 0.92 (t, J = 6.9 Hz, 3H), 1.30–1.50 (m, 4H), 1.50–1.60 (m, 2H), 1.93 (s, 1H), 2.06 (t, J = 2.6 Hz, 1H), 2.32 (ddd, J = 2.6, 6.9, 16.8 Hz, 1H), 2.44 (ddd, J = 2.6, 4.8, 16.8 Hz, 1H), 3.77 (m, 1H); ¹³C NMR (CDCl₃) δ 13.85, 22.46, 27.20, 27.62, 35.80, 69.84, 70.71, 80.93. Found: C, 75.95; H, 11.29%. Calcd for C₈H₁₄O: C, 76.14; H, 11.18%.

2-Phenyl-4-pentyn-2-ol: Bp 85 °C (1.0 Torr bath temp); IR (neat) 3288, 3026, 2976, 2930, 2114, 1495, 1447, 1376, 1273, 1098, 1069, 946, 852, 763, 698 cm⁻¹; ¹H NMR (CDCl₃) 1.65 (s, 3H), 2.06 (t, J = 2.7 Hz, 1H), 2.40 (s, 1H), 2.69 (dd, J = 16.8, 2.7 Hz, 1H), 2.78 (dd, J = 16.8, 2.7 Hz, 1H), 7.20–7.50 (m, 5H); ¹³C NMR (CDCl₃) δ 28.24, 33.59, 70.85, 72.31, 79.54, 123.90, 126.33, 127.45, 145.53. Found: C, 82.43; H, 7.67%. Calcd for C₁₁H₁₂O: C, 82.46; H, 7.55%.

1-(2-Propynyl)cyclohexanol: Bp 105 °C (20 Torr, bath temp); IR (neat) 3402, 3300, 2930, 2854, 2112, 1449, 1356, 1266, 1152, 1077, 976, 873, 734, 623 cm⁻¹; ¹H NMR (CDCl₃) δ 1.20–1.35 (m, 1H), 1.40–1.85 (m, 10H), 2.08 (t, J = 2.4 Hz, 1H), 2.37 (d, J = 2.4 Hz, 2H); ¹³C NMR (CDCl₃) δ 22.11, 25.53, 32.80, 36.71, 70.33, 71.40, 80.60. Found: C, 78.09; H, 10.48%. Calcd for C₉H₁₄O: C, 78.21; H, 10.21%.
References and Notes


3. A part of this work was published in a communication: Yokoo, T.; Shinokubo, H.; Oshima, K.; Utimoto, K. Synlett 1994, 645.


5. Metal-halogen exchange reaction of 1-iodo-1-dodecene with n-BuLi proceeded six times faster than that of 1-bromo-1-dodecene.

6. The examination of $^1$H NMR of the C$_6$D$_6$ solution derived from (E)-1-iodo-1-dodecene and n-BuLi showed a presence of alkenyllithium ($\delta$ 2.5 (bs, 2H), 6.8 (bs, 1H), 7.0 (bs, 1H)) and n-BuLi ($\delta$ 2.76 (t, 2H)) in a 1: 1 ratio.


10. Preparation of allenic lithium reagents upon treatment of 1-bromo-1,2-undecadiene with $n$-


13. Pure 1-iodo-1,2-propadiene could not be obtained. Treatment of propargyl bromide with sodium iodide in acetone followed by purification by distillation gave 2 : 1 mixture of 1-iodo-1,2-propadiene and propargyl iodide.


15. In hydrocarbon solvent, allenylzinc compound might be associated. An addition of Et2O to the C6D6 solution afforded clear new two olefinic peaks at δ 4.89 (dt) and 4.95 (m) which might be assigned to the corresponding allenylzinc compound.

Publication List

I. Parts of the present thesis have been published in the following journals.

Chapter 1
Hiroshi Shinokubo, Katsukiyo Miura, Koichiro Oshima, and Kiitiro Utimoto,
Hiroshi Shinokubo, Katsukiyo Miura, Koichiro Oshima, and Kiitiro Utimoto,

Chapter 2
Hiroshi Shinokubo, Koichiro Oshima, and Kiitiro Utimoto,

Chapter 3
Hiroshi Shinokubo, Koichiro Oshima, and Kiitiro Utimoto,
Hiroshi Shinokubo, Koichiro Oshima, and Kiitiro Utimoto,

Chapter 4
Hiroshi Shinokubo, Koichiro Oshima, and Kiitiro Utimoto,

Appendix
Toshiaki Yokoo, Hiroshi Shinokubo, Koichiro Oshima, and Kiitiro Utimoto,
*Synlett* **1994**, 645-646.
Hiroshi Shinokubo, Hiroaki Miki, Toshiaki Yokoo, Koichiro Oshima, and

II. Other publications not included in this thesis.

(1) Rearrangement of β-tert-Butyldimethylsiloxy Carbenoids. Regio- and Stereoselective
Synthesis of (Z)-1-Halo-2-tert-Butyldimethylsiloxy-1-alkenes. Hiroshi Shinokubo, Koichiro


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