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Kyoto University
Exploitation of New Synthetic Reactions
by Means of Cathodic Reduction

Manabu Ishifune
1992
Exploitation of New Synthetic Reactions by Means of Cathodic Reduction

Manabu Ishifune
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Preface

The studies presented in this thesis have been carried out under the direction of Professor Tatsuya Shono at the Department of Synthetic Chemistry of Kyoto University during 1988-1992. The thesis is concerned with new synthetic organic chemistry using the electroreductive methods.

The author wishes to express his sincerest gratitude to Professor Tatsuya Shono for his constant guidance, valuable suggestions, and hearty encouragement throughout the course of this work. The author also wishes to express his sincere thanks to Dr. Shigenori Kashimura for his continuous advice and helpful discussions during this work.

The author's grateful thanks are made to Assistant Professor Yoshihiro Matsumura, Dr. Naoki Kise, and Dr. Yoshihide Yamaguchi for their helpful suggestions.

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Finally, the author would express here his warmest acknowledgement to his parents, Mr. Noboru Ishifune and Mrs. Sachiko Ishifune for their constant encouragement throughout his work.

Manabu Ishifune

December 1992
General Introduction

One of the main aims of the Electroorganic Chemistry is creation of novel organic synthesis through utilization of electrochemical reactions as key reactions.\textsuperscript{1,4} Since formation of an active species is achieved by electron transfer between a substrate and a working electrode in the EOC, the EOC is classified into following four categories [(A)-(D)] based on the nature of the electron transfer process.

(A) Direct cathodic reduction (or anodic oxidation).
(B) Indirect cathodic reduction (or anodic oxidation).
(C) Reaction with the electrogenerated reagent.
(D) Reaction induced by chemically reactive electrode.

In the first category, the active species is generated by the direct electron transfer between the substrate (S) and the working electrode (Fig 1).

The second one, called indirect reaction, does not involve the direct electron transfer process between the substrate and the electrode, but it contains a third substance named a mediator (M\textsubscript{ox} or M\textsubscript{red}) in the reaction system and M\textsubscript{red} (or M\textsubscript{ox}) is activated by the direct electron transfer process prior to the reaction of the substrate (Fig. 2). The reduction (or oxidation) of the substrate by the activated mediator is the key point of the second category. The reaction of M\textsubscript{red} (or M\textsubscript{ox}) with S generally involves a chemical redox reaction. Therefore, the use of the mediator makes it possible to reduce (or oxidize) S which is hardly reduced (or oxidized) by the direct electron transfer system.\textsuperscript{5}

![Fig. 1](image1.png)

![Fig. 2](image2.png)
In the third type of reaction, electrochemical reaction is utilized as a method to generate active chemical reagents. In general, cathodic reduction (or anodic oxidation) of organic compounds (Y) forms active species (Y*) whose generation by non-electrochemical methods is not always easy. Such species (Y*) usually react immediately in situ with other substrates or solvent molecules (Fig. 3). Some of them, however, have rather long lifetime (several hours ~ several weeks) in the solution and can be used as chemical reagents which promote a variety of useful synthetic reactions. The electrogenerated base (EGB)⁶ formed by the cathodic reduction of Y, and electrogenerated acid (EGA) generated by the anodic oxidation of Y are typical such examples.⁷

![Diagram](image)

Fig. 3

In these three types (A)-(C) of reaction shown in Fig. 1-3, the role of electrode is just a donor (or acceptor) of electron and it is never involved into the reaction as a chemical reagent. On the other hand, some kinds of metallic electrode are able to promote the reaction not only as donors (or acceptors) of electron but also as chemical reagents. The last case (D) provides a new concept of such metallic electrodes called "chemically reactive electrodes."

Following two types of mechanism may be suggested for the chemically reactive electrodes," and they are illustrated in Fig. 4 and Fig. 5.

(1) The anode metal is dissolved into the electrolysis solution as a cationic species (M⁺), and M⁺ reacts with the cathodically generated anionic substrate (S⁻) to form the intermediate (I) (Fig. 4).⁸ The final product (P) is given by the reaction of (I) with electrophile (E).
(2) The cationic species (M\(^+\)) is reduced to active metal (M\(^*\)) at cathode. This M\(^*\) acts as a strong reductant and its reaction with S affords P (Fig. 5).

\[
\text{M}^+ + S \rightarrow \text{M}^* + \text{P}
\]

Fig. 4

\[
\text{S} \rightarrow \text{M}^+ \rightarrow \text{M}^* \rightarrow \text{P}
\]

Fig. 5

Thus, these four types of process [(A)-(D)] involve the electrochemical reaction as the key step with different manner. All cases, however, are blessed with the following unique advantages which are characteristic of the EOC and not always observed in the non-electrochemical reactions.\(^{10,11}\)

1. The electrode reaction enables the generation of highly active species which are difficult to be generated by normal chemical methods.
2. The umpolung of substrates is easily attained by the electrode reaction. Namely, the cathodic reduction (anodic oxidation) of an electrophile (a nucleophile) gives a new nucleophile (electrophile).\(^{12}\)
3. The fact that the reaction takes place within the electrical double layer on the electrode surface often brings about unique regio- and stereo-selectivities.\(^{13}\)
4. The reaction can be performed chemoselectively by control of the electrode potential.
5. The reaction can be controlled easily by the amount of supplied electricity.
(6) Since the electron itself is used as a reagent, the reaction is non-polluting.

These merits of EOC are useful in organic synthesis, and hence, the EOC has been developed remarkably in the past 25 years, and now it is regarded as one of the most important tools in organic synthesis.

The present thesis consists of three parts and they deal with the organic synthesis utilizing EOC, especially types (A), (C) and (D) as the key reactions.

A typical example of type (A) is presented in Part I (Chapter 1-3) which deals with the cathodic coupling of ketones with olefinic systems having a silyl group and/or a hydroxy group (Scheme I). The intra- and inter-molecular cathodic couplings of ketones with olefins have been well studied in our laboratory and these works are really frontiers of the EOC. The presence of the functional group on the olefinic system not only enlarged the synthetic utility of these coupling reaction but also induced high regio- and stereo-selectivities which were not observed in the cathodic coupling with unfunctionalized olefins.

Scheme I

![Scheme I](image)

i) $X = \text{SiMe}_3$ or $\text{Si(OEt)}\text{Me}_3$  
ii) $Y = \text{OH}$  
iii) $X = \text{SiMe}_3$ and $Y = \text{OH}$
Chapter 1 deals with the regioselective intra- and inter-molecular cathodic couplings of ketones with vinylsilanes ($X = \text{SiMe}_3$ or $\text{Si(OEt)}_2\text{Me}_2$ in Scheme I) and some synthetic utilizations of the coupling products. A remarkable electronic effect of a trimethylsilyl group was found in the reactivity of the olefin and the regioselectivity of the coupling reaction.

Chapter 2 deals with the diastereoselective intermolecular cathodic coupling of ketones with allylic alcohols ($Y = \text{OH}$ in Scheme I), which can be applied to the synthesis of chiral 1,4-diols. This diastereoselectivity was reasonably explained by the interaction between the electroreductively formed ketyl radical and the hydroxy group of allyl alcohol.

Chapter 3 deals with the intermolecular cathodic coupling of ketones with vinylsilanes having a hydroxy group at the allylic position ($X = \text{SiMe}_3$ and $Y = \text{OH}$ in Scheme I). In this reaction, homoallylic alcohols were obtained as the final products since the Peterson elimination easily took place in the first coupling products.

Part II, composed of two chapters (Chapters 4 and 5), contains utilization of the electrogenerated pyrrolidone anion as an electrogenerated base. The generation of trihalomethyl anions (Scheme II) promoted by the electrogenerated base provides some novel examples of type (C) reaction.
It is described in Chapter 4 that an electrogenerated base\textsuperscript{16} prepared by the electroreduction of 2-pyrrolidone\textsuperscript{17} is highly effective to the generation of trichloromethyl anion (X=Cl, Scheme II). Thus formed trichloromethyl anion possesses reasonable stability to react as a nucleophile, and 1,4-addition of the trichloromethyl anion to \(\alpha,\beta\)-unsaturated esters or nitriles was successfully achieved.

Chapter 5 deals with trifluoromethylation of carbonyl compounds promoted by the electrogenerated pyrrolidone anion and it provides the first example of the generation of trifluoromethyl anion from trifluoromethane (X=F, Scheme II).

Part III contains two chapters (Chapters 6 and 7) and they present some examples of an electroreduction system using chemically reactive Mg electrodes.

Chapter 6 deals with the cathodic coupling of 1,3-dienes with aliphatic esters promoted by Mg electrodes (Scheme III). In this reaction, Mg electrode is involved in the formation of magnesium complex of diene. The coupling of styrenes with aliphatic esters forming phenylcyclopropanol derivatives is also described and the utility of this reaction is demonstrated by the facile synthesis of \(ar\)-dihydroturmericone and curcumone.

**Scheme III**

![Scheme III](image)

Chapter 7 deals with the electroreductive Si-Si bond formation using Mg electrodes. The electroreduction of chlorosilanes has been known to be difficult because of their highly negative reduction potential, whereas the strong reducing power of the Mg electrode system enabled the effective electroreductive coupling of chlorosilanes to form disilanes (Scheme IV).
Scheme IV

\[
\begin{align*}
\text{R}^1 \text{R}^1 \text{Si-Cl} & \overset{+e}{\underset{\text{LiClO}_4 / \text{THF}, \text{Mg electrodes}}{\longrightarrow}} \text{R}^1 \text{Si-Si-R}^2 + \text{MgCl}_2 \\
\text{R}^2 \text{Si-Cl} & \overset{+e}{\underset{\text{LiClO}_4 / \text{THF}, \text{Mg electrodes}}{\longrightarrow}} \text{R}^1 \text{Si-Si-R}^2 + \text{MgCl}_2 \\
\text{R}^3 \text{Si-Cl} & \overset{+e}{\underset{\text{LiClO}_4 / \text{THF}, \text{Mg electrodes}}{\longrightarrow}} \text{R}^1 \text{Si-Si-R}^2 + \text{MgCl}_2 \\
\end{align*}
\]

This reaction was successfully applied to the preparation of polysilane high polymers (Scheme V).

Scheme V

\[
\begin{align*}
\text{Cl-Si-Cl} & \overset{+e}{\underset{\text{LiClO}_4 / \text{THF}, \text{Mg electrodes}}{\longrightarrow}} \left(\text{Si} \right)_n + n \text{MgCl}_2 \\
\text{R}^1 & \overset{+e}{\underset{\text{LiClO}_4 / \text{THF}, \text{Mg electrodes}}{\longrightarrow}} \left(\text{Si} \right)_n + n \text{MgCl}_2 \\
\text{R}^2 & \overset{+e}{\underset{\text{LiClO}_4 / \text{THF}, \text{Mg electrodes}}{\longrightarrow}} \left(\text{Si} \right)_n + n \text{MgCl}_2 \\
\end{align*}
\]
References and Notes


8
Part I

Cathodic Coupling of Ketones with Olefinic Systems
Chapter 1

Inter- and Intra-molecular Cathodic Coupling Reactions of Ketones with Vinylsilanes

Abstract: Electroreductive intra- and inter-molecular coupling reactions of ketones with vinylsilanes have been found to take place regioselectively at the non-silylated side of the olefin. Namely, the intramolecular coupling reaction of 6-trimethylsilyl-6-hepten-2-one afforded cis-1-methyl-3-trimethylsilylcyclohexanol in high regio- and stereo-selectivity, and the cathodic intermolecular coupling reaction of ketones with trimethylvinylsilanes gave γ-trimethylsilyl alcohols in excellent yield. Moreover, the cathodic coupling of ketones with ethoxydimethylvinylsilane gave 1-oxa-2-silacyclopentane derivatives in good yield, which was easily transformed to 1,3-diols by the oxidative desilylation.

Introduction

Since the first example of the cathodic coupling reaction of ketones with olefinic systems was reported by Shono and his co-workers in 1971, this type of cathodic reaction has attracted much attention from both synthetic and mechanistic point of views.1-3 The cathodic cyclization of non-conjugated olefinic ketones has been found to proceed with high regio- and stereo-selectivity affording cyclized tertiary alcohols (Scheme I).4-6 In this reaction, the anion radical formed by the cathodic reduction of the carbonyl group of non-conjugated olefinic ketones intramolecularly added to the inner site of double bond. The exclusive formation of the exo-cyclized product than endo-cyclized one can be explained in a similar way to the homolytic intramolecular coupling reaction between a radical and a double bond.7 And the repulsion between the anionic
center on the oxygen atom and the *exo*-methylene group which carries some negative charge during the cyclization brings about the formation of the *cis* isomer.$^5$

**Scheme I**

\[
\begin{align*}
\text{R} \quad \text{R} + e & \quad \xrightarrow{\text{El}_{4}\text{N}OTs / DMF} \quad \text{[cis-isomer]} \\
\text{R} \quad \text{R} + e & \quad \xrightarrow{\text{H}_3\text{O}^+} \quad \text{[trans-isomer]}
\end{align*}
\]

n = 1 ; 98%
n = 2 ; 75%

Recently it has also been reported that the intermolecular cathodic coupling of ketones with terminal olefins gave the corresponding tertiary alcohols with high regioselectivity (Scheme II).$^8$ The regioselectivity of the intermolecular coupling reaction is quite different from that of intramolecular one, that is, the radical intermediates formed by the cathodic reduction of ketones attack the terminal position of olefins. It is also noted that the structure of olefins much influences the yields of the coupling products. Although the cathodic coupling of ketones with monosubstituted terminal olefins ($R^3 = \text{an alkyl}, R^4 = \text{H}$) gave the corresponding tertiary alcohols in good yield, that with 2,2-disubstituted olefins ($R^3, R^4 = \text{alkyls}$) resulted in the remarkable decrease of the yields of the coupling products.

In this chapter, it is described that the cathodic intra- and inter-molecular coupling reactions of ketones with olefinic systems are highly effected by the substituents on olefins, and the use of vinylsilanes as the olefins leads to unprecedented types of unique cathodic coupling reactions. The introduction of the silyl groups to the olefinic systems alters the regioselectivity of the coupling...
reaction or increases the reactivity of olefins as the acceptors of the anion radicals. Moreover, the silyl functionality enabled some synthetic applications of the coupling products.

**Scheme II**

\[
\text{O} \quad \xrightarrow{\text{+e}} \quad \text{O}^{-} \quad \text{aryl} \quad \xrightarrow{\text{+e}} \quad \text{OH}^{+}
\]

\( R^1 = \text{Me}, R^2 = \text{Et}, R^3 = n\text{-C}_6\text{H}_{13}, R^4 = \text{H} ; 77% \)

\( R^1 = \text{Me}, R^2 = \text{Et}, R^3 = n\text{-Pr}, R^4 = \text{Me} ; 21% \)

**Results and Discussion**

**Cathodic Cyclization of 6-Trimethylsilyl-6-hepten-2-one.** The electroreduction of 6-trimethylsilyl-6-hepten-2-one (1) carried out in DMF using Et₄N OTs as a supporting electrolyte and carbon fiber as a cathode was found to afford the endo-cyclized product, cis-1-methyl-3-trimethylsilyl-1-cyclohexanol (2) as a single product (Scheme III).¹⁰

**Scheme III**

³F/mol

On the other hand, the cathodic cyclization of nonconjugated olefinic ketones having no functional groups give the exo-cyclized products exclusively as mentioned above. For example, 6-hepten-2-one was electrochemically reduced to form cis-1,2-dimethyl-1-cyclopentanol in 98% yield (Scheme I). In addition, the electroreduction of 6-methyl-6-hepten-2-one, the alkyl homologue of 1, did not
give the cyclized product but gave 6-methyl-6-hepten-2-ol in 12% yield (Scheme IV).  

**Scheme IV**

Thus the introduction of trimethylsilyl group into the olefinic system remarkably alters the regioselectivity of the cathodic cyclization. This difference seems to be explainable by the electronic effect of trimethylsilyl group. As shown in the scheme V, the cathodic reduction of 1 forms the radical species 3. The result shown in Scheme IV indicates that the exo-cyclization of 3 (Scheme V, path B) would be inhibited by the steric hindrance of trimethylsilyl group. Therefore, 3 may be only able to cyclize in endo manner (Scheme V, path A), which is usually unfavorable (Scheme I).
Although the cathodic cyclization of olefinic ketones in endo manner has never been observed so far, the electronic effect of trimethylsilyl group enables this cyclization. That is, the radical center of 3 attack the terminal position of the double bond forming the intermediates 4A, which would be rather easily reduced to the anionic intermediate 5A since it is stabilized by trimethylsilyl group.\textsuperscript{11,12} The formation of stable intermediate 5A promotes the endo-cyclization which is usually unfavored.

**Intermolecular Cathodic Coupling Reaction of Ketones and Vinylsilanes.** As shown in Scheme VI and Table I, the cathodic coupling of ketones 6 with trimethylvinylsilanes 7 (7a; R\textsuperscript{3}=H, 7b; R\textsuperscript{3}=Me, 7c; R\textsuperscript{3}=n-Pr) carried out in DMF using Et\textsubscript{4}N\textsuperscript{+}OTs as a supporting electrolyte was found to afford γ-trimethylsilyl alcohols 8 in satisfactory yields. In this intermolecular coupling, the remarkable influence of trimethylsilyl group was also observed. For example, the coupling of ketone (6) with 2,2-disubstituted terminal olefins (CH\textsubscript{2}=CH(R)R') such as isopropenyltrimethylsilane (7b, Run 6 and 7 in Table I) and 2-trimethylsilyl-1-pentene (7c, Run 8) afforded the corresponding coupling products in satisfactory yields. This is a highly attractive fact since the cathodic coupling of ketones with olefins shown in Scheme II is greatly influenced by the type of olefins, and the use of 2,2-dialkyl substituted terminal olefins (CH\textsubscript{2}=C(R)R') instead of monosubstituted olefins (CH\textsubscript{2}=CHR) resulted in the remarkable decrease of the yields of the coupling products. As shown in Scheme VII, the cathodic coupling of 2-butanone (6h) with 7c to form 8h seems to proceed by the intermediacy of radical species 9 and anionic species 10, and their stabilization by the neighboring trimethylsilyl group would be the crucial factor of the formation of 8h. On the other hand, in the case of the coupling of 6h with 2-methyl-1-pentene (11), the alkyl homologue of 7c, forming the tertiary alcohol 12, the intermediates 14 is not blessed with any stabilization, but is rather unstable because it has secondary anion structure.
Scheme VI

\[
\begin{align*}
\text{R}^1 \text{R}^2 + \text{R}^3 \text{SiMe}_3 & \xrightarrow{+e} \text{R}^1 \text{R}^2 \text{R}^3 \text{SiMe}_3 \\
& \text{Et}_4\text{NCl} / \text{DMF} \\
& \text{Carbon fiber cathode} \\
& \text{3 F/mol based on 6}
\end{align*}
\]

Table I. Cathodic Coupling of Ketones with Vinylsilanes

<table>
<thead>
<tr>
<th>Run</th>
<th>Ketone 6 ( R^1 \ R^2 )</th>
<th>Vinylsilane 7 ( \text{R}^3 )</th>
<th>Product 8</th>
<th>Yield / ( % )a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{R}^1 \text{R}^2 ) 6a</td>
<td>H 7a</td>
<td>8a</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>( n-C_5\text{H}_{11} ) 6b</td>
<td>7a</td>
<td>8b</td>
<td>74</td>
</tr>
<tr>
<td>3</td>
<td>( n-C_5\text{H}_{11} ) 6c</td>
<td>7a</td>
<td>8c</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>Me ( n-C_6\text{H}_{13} ) 6d</td>
<td>7a</td>
<td>8d</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>Me ( \text{CH}_2\text{CH}_2\text{CO}_2\text{Me} ) 6e</td>
<td>7a</td>
<td>8e</td>
<td>31</td>
</tr>
<tr>
<td>6</td>
<td>Me ( n-\text{Pr} ) 6f</td>
<td>Me 7b</td>
<td>8f</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>Me ( \text{iso-Pr} ) 6g</td>
<td>7b</td>
<td>8g</td>
<td>68</td>
</tr>
<tr>
<td>8</td>
<td>Me Et 6h</td>
<td>( n-\text{Pr} ) 7c</td>
<td>8h</td>
<td>69</td>
</tr>
</tbody>
</table>

a) Isolated yields based on 6.

Scheme VII

16
Thus, the intermolecular cathodic coupling of ketones with vinylsilanes is promoted by the electronic effect of trimethylsilyl group. It was also demonstrated by the reaction of acetone (6i) with 2-trimethylsilyl-1,5-hexadiene (15) (Scheme VIII). The anion radical formed by the electroreduction of 6i attacked the silylated double bond of 15 preferentially to afford 16 in 86% yield.

Scheme VIII

\[
\begin{align*}
\text{O} & \quad \text{SiMe}_3 \quad + \quad \text{SiMe}_3 \\
6i & \quad 15 \\
\text{Carbon fiber cathode} & \quad \text{Et}_4\text{N}^+\text{OTs} / \text{DMF} \quad 86\% \\
\text{4 eqv.} & \quad 2 \text{ F/mol} \quad \text{based on 6i}
\end{align*}
\]

Not only from the mechanistic point of view mentioned above, the results summarized in Scheme VI and Table I seems to be also interesting from the synthetic viewpoint. The formation of 8 by the cathodic coupling of ketones 6 and vinylsilanes 7 indicates that, under the conditions of electroreduction, 7 behave as the equivalent to the anion 17 which is usually unstable and the preparation of which is not always easy by the conventional non-electrochemical method.\(^{15}\)

\[
\begin{align*}
\text{R}^3 & \quad \text{SiMe}_3 \\
7 & \quad 17
\end{align*}
\]

Some typical results shown in Table I indicated that this coupling reaction is widely applicable to the synthesis of a variety of β-trimethylsilyl alcohols 8. Moreover, the compound 8 is the key intermediate for the reductive olefination of ketones (6, Scheme IX), for example, the treatment of 6a (R\(^1\), R\(^2\) = 2-adamantyl) with BF\(_3\)-AcOH afforded 18 in quantitative yield.\(^{16}\)
Intermolecular Cathodic Coupling Reaction of Ketones with Ethoxydimethylvinylsilanes. The cathodic intermolecular coupling reaction of 6 with ethoxydimethylvinylsilane (19) (Scheme X) was also found to take place at the non-silylated side of the double bond and formed oxasilacyclopentanes (20).

The driving force of this coupling reaction is not only the stabilization of the radical intermediate 21 by the silyl group but also the irreversible formation of thermodynamically stable siloxane ring 22 would be the important factor (Scheme XI).
The typical results of this coupling reaction were shown in Table II. It is noteworthy that the cathodic coupling of olefinic ketone 6j (Run 6 in the Table II) with 19a gave the coupling product (20j) in satisfactory yield and the unfunctionalized double bond of 6j remained intact.

<table>
<thead>
<tr>
<th>Run</th>
<th>Ketone 6</th>
<th>Vinylsilane 19</th>
<th>Product 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-(CH₂)₅-</td>
<td>H 19a</td>
<td>70 20b</td>
</tr>
<tr>
<td>2</td>
<td>n-C₅H₁₁</td>
<td>n-C₅H₁₁ 6c</td>
<td>75 20c</td>
</tr>
<tr>
<td>3</td>
<td>Me n-C₆H₁₃</td>
<td>6d 19a</td>
<td>75 20d</td>
</tr>
<tr>
<td>4</td>
<td>Me n-Pr</td>
<td>6e 19a</td>
<td>79 20e</td>
</tr>
<tr>
<td>5</td>
<td>Me Et</td>
<td>6h n-Pr 19b</td>
<td>62 20b</td>
</tr>
<tr>
<td>6</td>
<td>Me 6j</td>
<td>19a</td>
<td>79 20j</td>
</tr>
</tbody>
</table>

Table II. Cathodic Coupling of Ketones with Ethoxyvinylsilanes⁹

Moreover, from the synthetic viewpoint, the product 20 was the useful key intermediate for the transformation of 6 to 1,3-diol since, for example, the oxidative desilylation of 20d by 30% H₂O₂ afforded 1,3-diol 23 in 76% yield.¹⁷

In the cathodic coupling followed by the oxidative desilylation, ethoxyvinylsilanes (19) are formally used as an equivalent of β-hydroxyethyl-anion (24).
Conclusion. The cathodic coupling of a carbonyl group with the olefinic system has been much affected by the introduction of silyl functionality on the olefin. The effect of silyl functional group stabilizing the adjacent carbanion enlarged the feasibility of this coupling. Moreover, some chemical transformation of the coupling products were attained by using the desilylation procedure. \( \gamma \)-Trimethylsilylalcohols which are obtained by the cathodic coupling of ketones with trimethylvinylsilanes are the key intermediate of the reductive olefination of ketones, and oxa-2-silacyclopentanes which are obtained by the coupling of ketones with ethoxydimethylvinylsilanes can be easily transformed to 1,3-diols.
Experimental Section

General. $^1$H and $^{13}$C NMR spectra were recorded on Varian Gemini-200 spectrometer using TMS as an internal standard. IR spectra were obtained on Hitachi 260-10 spectrometer. High resolution mass spectra (HRMS) were measured by a JEOL JES-DX 300. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University. The cathodic reduction was performed by direct current power supply (GP-050-20, Takasagoseisakusho Co.LTD).

Materials Ketones (6a-6j), trimethylvinylsilane (7a,b), and ethoxydimethylsilane (19a) are commercially available and they were purified by distillation under reduced pressure. DMF was dried over fresh alumina (Alumina B, Act I, ICN Biochemicals) and stocked under nitrogen atmosphere. Carbon fiber as a cathode was Carbon Fiber 12000f (Asahi Nippon Carbon Fiber Co., LTD. Tokyo Japan).

Preparation of 6-Trimethylsilyl-6-hepten-2-one (1). The Grignard reagent of 2-(2-bromoethyl)-2-methyl-1,3-dioxolane (80 mmol) in THF (60 mL) was prepared by the known method.$^{18,19}$ Into this solution was added dropwise a solution of 2,3-dibromopropene (60 mol)$^{20}$ in dry THF (10 mL), and the reaction mixture was stirred for 1 hour at room temperature. The resulting solution was poured into aqueous saturated NH$_4$Cl (100 mL), and extracted with ether (50 mL x 3). The bulb to bulb distillation of crude product gave pure 2-(4-bromo-4-pentenyl)-2-methyl-1,3-dioxolane in 71 % yield. The Wurtz coupling reaction of 2-(4-bromo-4-pentenyl)-2-methyl-1,3-dioxolane (25 mmol) and chlorotrimethylsilane carried out according to the known procedure$^{21}$ afforded 2-(4-trimethylsilyl-4-pentenyl)-2-methyl-1,3-dioxolane. The crude product was dissolved in acetone (100 mL) containing a catalytic amount of p-toluenesulfonic acid (0.1 g) and the solution was stirred over night at room temperature. The reaction mixture was poured into saturated aqueous NaHCO$_3$ (100 mL), and the
aqueous solution was extracted with ether (50 mL x 3). The product 1 was obtained in 50 % overall yield after the purification through silica gel column (hexane-AcOEt = 5 : 1).

1: IR (neat) 3040, 2950, 1720, 1410, 1365, 1250, 915, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.07 (s, 9H), 1.60-1.80 (m, 2H), 2.12 (s, 3H), 2.12 (t, J = 7.5 Hz, 2H), 2.41 (t, 2H, J = 7.5 Hz), 5.33-5.35 (m, 1H), 5.53-5.58 (m, 1H); MS m/e (relative intensity) 184 (1, M⁺), 169 (16), 115 (10), 75 (100), 73 (42); HRMS calcd for C₁₀H₂₄SiO 186.1306, found 186.1306.

Electroreduction of 1 to cis-1-Methyl-3-trimethylsilylcyclohexanol (2). The electroreductive cyclization of 1 to 2 was carried out in a divided electrolysis cell (100 mL) equipped with a bundle of carbon fiber cathode (three thousand carbon fiber filament, 15 cm length), a platinum anode (2 x 2 cm), and a glass filter diaphragm (No.5). A solution of 1 (3 mmol) in dry DMF (20 mL) containing Et₄N OTs (10 mmol) as a supporting electrolyte was put into a cathodic chamber of the cell. The anodic solution was 15 mL of dry DMF containing Et₄N OTs (5 mmol). After 3F/mol of electricity based on 1 was passed through the cell under the constant current condition of 0.2A with cooling by ice cold water, the cathodic solution was poured into 100 mL of brine and extracted with ether (50 mL x 3). The evaporation of the solvent and the bulb to bulb distillation under reduced pressure gave 2. The formation of the stereo isomer of 2 was not detected by ¹³C-NMR and gc analyses. The cis-configuration of 2 was determined by the spectroscopic (¹H NMR, ¹³C NMR,IR) comparison of 2 with those of the reported values.¹⁰

2: IR (neat) 3300, 2920, 1440, 1250, 1140, 950, 865, 835 cm⁻¹; ¹H NMR (CDCl₃) δ -0.14 (s, 9H), 0.82-1.00 (m, 2H), 1.18 (s, 3H), 1.10-1.37 (m, 2H), 1.40 (OH), 1.40-1.70 (m, 5H); ¹³C NMR (CDCl₃) δ -3.79 (CH₃), 20.26 (CH), 22.94 (CH₂), 26.00 (CH₂), 31.50 (CH₃), 38.67 (CH₂), 39.43 (CH₂), 68.77 (C); MS m/e (relative intensity) 186 (2, M⁺), 171 (3), 168 (3), 143 (21), 94 (34), 81 (73), 73 (100); HRMS calcd for C₁₀H₂₂SiO 186.14406, found 186.14289.
Preparation of 2-Trimethylsilyl-1-pentene (7c). 2-Bromo-1-pentene was prepared by the reaction of EtMgBr with 2,3-dibromo-propene according to the known procedure. The Wurtz coupling reaction of 2-Bromo-1-pentene and chlorotrimethylsilane afforded 7c. A solution of 2-bromo-1-pentene (40 mmol) in dry ether (40 mL) was added dropwise into a mixture of chlorotrimethylsilane (60 mmol), sodium metal (100 mmol) in dry ether (120 mL). After the addition was completed, the solution was stirred for 24 h. The resulting sodium salts were filtered off, and the filtrate was washed with saturated aqueous NaHCO₃ (100 mL) and water (100 mL), and then dried over MgSO₄. The ether was distilled off by distillation and the middle fraction (70-80°C) was collected (Yield 47%).

7c: IR (neat) 2950, 1250, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.09 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H), 1.32-1.52 (m, 2H), 2.06-2.15 (m, 2H), 5.30 (m, 1H), 5.54 (m, 1H); MS m/z (relative intensity) 142 (2, M⁺), 127 (40), 99 (22), 73 (100), 59 (36); HRMS calcd for C₈H₁₈Si 142.11777, found 142.11806.

General Procedure for the Preparation of 8. The cathodic reduction was carried out in a divided electrolysis cell (100 mL) equipped with a cathode fiber, a platinum anode (2 x 2 cm), and a glass filter diaphragm (No.5). A solution of a ketone 6 (5 mmol) and a vinylsilane 7 (10 mmol) in dry DMF (20 mL) containing Et₄N OTs (10 mmol) as a supporting electrolyte was put into a cathodic chamber of the cell. The anodic solution was 15 mL of dry DMF containing Et₄N OTs (5 mmol). After 3F/mol of electricity based on 6 (constant current conditions of 0.2 A) was passed through the cell with cooling by ice cold water, the cathodic solution was poured into 100 mL of brine and extracted with ether (50 ml x 3). The residue obtained by evaporation of solvent was distilled under reduced pressure (bulb to bulb distillation) in order to give 8.

2-(2-Trimethylsilylethyl)-2-adamantanol (8a): IR (neat) 3400, 2960, 1255, 865, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.00 (s, 9H), 0.40-0.50 (m, 2H), 1.43-1.88 (m, 16H); MS m/z (relative intensity) 237 (6, M⁺-Me), 223 (79), 151 (100); Anal. Calcd for C₁₅H₂₈SiO : C, 71.36; H, 11.20. Found : C, 71.20; H, 11.47.
1-(2-Trimethylsilylethyl)-cyclohexanol (8b): IR (neat) 3370, 2920, 1245, 860, 835 cm⁻¹; ¹H NMR (CDCl₃) δ -0.02 (s, 9H), 0.40-0.52 (m, 2H), 1.10-1.65 (m, 12H); MS m/e (relative intensity) 185 (10, M⁺-Me), 171 (45), 99 (100), 73 (80); Anal. Calcd for C₁₁H₂₄SiO: C, 65.93; H, 12.07. Found: C, 65.87; H, 12.34.

6-(2-Trimethylsilylethyl)-6-undecanol (8c): IR (neat) 3460, 2940, 1255, 870, 845 cm⁻¹; ¹H NMR (CDCl₃) δ 0.00 (s, 9H), 0.30-0.48 (m, 2H), 0.80-0.97 (t, J = 6.0 Hz, 6H), 1.15-1.48 (m, 18H); MS m/e (relative intensity) 257 (2, M⁺-Me), 171 (100), 73 (42); Anal. Calcd for C₁₆H₃₆SiO: C, 70.51; H, 13.31. Found: C, 70.57; H, 13.58.

3-Methyl-1-trimethylsilyl-3-nonanol (8d): IR (neat) 3400, 2970, 1255, 865, 840 cm⁻¹; ¹H NMR (CDCl₃) δ -0.05 (s, 9H), 0.34-0.48 (m, 2H), 1.09 (s, 3H), 1.16-1.30 (m, 10H), 1.30-1.46 (m, 2H); MS m/e (relative intensity) 215 (3, M⁺-Me), 201 (39), 129 (100), 73 (87); Anal. Calcd for C₁₃H₃₀SiO: C, 67.75; H, 13.12. Found: C, 67.64; H, 13.39.

4-Methyl-4-(2-trimethylsilylethyl)-4-butenolide (8e): IR (neat) 2960, 1770, 1250, 1165, 860, 835 cm⁻¹; ¹H NMR (CDCl₃) δ 0.03 (s, 9H), 0.45-0.60 (m, 2H), 1.42 (s, 3H), 1.58-1.72 (m, 2H), 1.90-2.22 (m, 2H), 2.57-2.70 (m, 2H); MS m/e (relative intensity) 185 (14, M⁺-Me), 99 (60), 73 (100); Anal. Calcd for C₁₀H₂₀SiO₂: C, 59.95; H, 10.06. Found: C, 59.83; H, 10.02.

2-Trimethylsilyl-4-methyl-4-heptanol (8f): IR (neat) 3400, 2970, 1255, 860, 840 cm⁻¹; ¹H NMR (CDCl₃) δ -0.06 (s, 9H), 0.66-0.84 (m, 1H), 0.91 (t, J = 6.9 Hz, 3H), 1.03 (d, J = 7.7 Hz, 3H), 1.14 (s, 3H), 1.20-1.62 (m, 6H); MS m/e (relative intensity) 187 (1, M⁺-Me), 159 (10), 87 (48), 73 (100); Anal. Calcd for C₁₁H₂₆SiO: C, 65.27; H, 12.95. Found: C, 65.05; H, 13.19.

2,3-Dimethyl-5-trimethylsilyl-3-hexanol (8g): IR (neat) 3470, 2960, 1250, 860, 840 cm⁻¹; ¹H NMR (CDCl₃) δ -0.05 (s, 9H), 0.70-0.86 (m, 1H), 0.84, 0.88, 0.89, 0.93 (four doublets, J = 6.9 Hz, 6H), 1.05 (d, J = 7.7 Hz, 3H), 1.08 (OH), 1.12-1.28 (m, 1H), 1.52-1.82 (m, 2H); MS m/e (relative intensity) 187 (1, M⁺-Me), 159 (17), 143 (21), 87 (72), 73 (100); Anal. Calcd for C₁₁H₂₆SiO: C, 65.27; H, 12.95. Found: C, 65.04; H, 13.19.
3-Methyl-5-trimethylsilyl-3-octanol (8h): IR (neat) 3400, 1460, 1380, 1250, 855, 835 cm⁻¹; ¹H NMR (CDCl₃) δ -0.027, -0.031 (s, 9H), 0.71 (m, 1H), 0.86 (m, 3H), 0.88, 0.89 (t, J = 6.9 Hz, 3H), 1.11, 1.12 (s, 3H), 1.20-1.60 (m, 8H); MS m/z (relative intensity) 201 (1, M⁺-Me), 171 (3), 97 (30), 73 (100); Anal. Calcd for C₁₂H₂₈SiO: C, 66.59; H, 13.04. Found: C, 66.49; H, 13.32.

Preparation of 2-Trimethylsilyl-1,5-hexadiene (15). 2-Bromo-1,5-hexadiene was prepared by the reaction of allyl magnesium bromide with 2,3-dibromopropene²⁰ according to the known procedure.²² The Wurtz coupling reaction²¹ of 2-bromo-1,5-hexadiene (80 mmol) and chlorotrimethylsilane was carried out by the same procedure for the preparation of 7c. The product 15 was obtained in 48% yield after distillation (125-132°C).

15: IR (neat) 3050, 2950, 1640, 1420, 1250, 910, 830, 750 cm⁻¹; ¹H NMR (CDCl₃) δ 0.08 (s, 9H), 2.15-2.20 (m, 4H), 4.90-5.05 (m, 2H), 5.33 (d, J = 2.9 Hz, 1H), 5.56 (d, J = 2.9 Hz, 1H), 5.70-5.93 (m, 1H); MS m/z (relative intensity) 139 (17, M⁺-Me), 111 (42), 80 (99), 73 (100), 59 (58); Anal. Calcd for C₉H₁₈Si: C, 70.05; H, 11.76. Found: C, 69.60; H, 11.99.

Cathodic Coupling Reaction of Acetone (6i) with 15. The cathodic coupling of 6i (20 mmol) and 15 (5 mmol) was carried out under similar reaction conditions to those described above. After 2F/mol of electricity (based on 6i) was passed through the cell under a constant current conditions of 0.2 A, the cathodic solution was poured into 100 mL of brine and extracted with ether (50 mL x 3). The residue obtained by evaporation of solvent was distilled under reduced pressure (bulb to bulb distillation) in order to give 2-methyl-4-trimethylsilyl-7-octen-2-ol (16) in 86% yield.

16: IR (neat) 3400, 2950, 1370, 1250, 835 cm⁻¹; ¹H NMR (CDCl₃) δ 0.01 (s, 9H), 0.62-0.76 (m, 1H), 1.19 (s, 3H), 1.20 (s, 3H), 1.30-1.65 (m, 4H), 2.00-2.15 (m, 2H), 4.89-5.06 (m, 2H), 5.69-5.90 (m, 1H); MS m/z (relative intensity) 199 (1, M⁺-Me), 183 (1), 109 (8), 82 (26), 73 (100), 55 (28); Anal. Calcd for C₁₂H₂₆SiO: C, 67.21; H, 12.22. Found: C, 67.32; H, 12.48.
Transformation of 8a to 2-Vinyladamantane (18). The transformation of 8a to 18 was carried out by the reported procedure. The product 18 was the known compound, and its spectroscopic values were completely identical with those of reported one.

18: IR (neat) 3060, 1640, 1450, 910 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.45-2.00 (m, 15H), 4.98-5.22 (m, 2H), 5.94-6.14 (m, 1H); MS \(m/z\) (relative intensity) 162 (M\(^+\), 100), 92 (32), 79 (32).

Preparation of 19b. 2-Bromo-1-pentene was prepared by the reaction of EtMgBr with 2,3-dibromo-propene\(^{20}\) according to the known procedure.\(^{22}\) 2-Bromo-1-pentene (80 mmol) was added dropwise into a mixture of dimethyl diethoxysilane (85 mmol), magnesium turnings (80 mmol) in dry THF (80 mL). The reaction was initiated by the addition of a catalytic amount of I\(_2\). After the initiation, 2-bromo-1-propene was added at such a rate that the mixture gently refluxed. After the reaction mixture was reflux for 3 h, 100 mL of hexane was added into this solution, and precipitated magnesium salt was triturated. The resulting solution was filtered off, and the filtrate was concentrated. The product 19b was isolated by distillation under the reduced pressure (141-3\(^{\circ}\)C/760 mmHg, Yield 56%).

19b: IR (neat) 2970, 1250, 1105, 1080, 825, 780 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.17 (s, 6H), 0.89 (t, \(J = 7.3\) Hz, 3H), 1.17 (t, \(J = 7.0\) Hz, 3H), 1.35-1.54 (m, 2H), 2.06-2.17 (m, 2H), 3.62 (q, \(J = 7.0\) Hz, 2H), 5.40-5.43 (m, 1H), 5.60-5.63 (m, 1H); MS \(m/e\) (relative intensity) 157 (100, M\(^+\)-Me), 103 (65), 89 (18), 75 (41); Anal. Calcd for C\(_9\)H\(_{20}\)SiO: C, 62.72; H, 11.70. Found: C, 62.55; H, 11.90.

General Procedure for the Preparation of 20. The cathodic coupling of 6 and 19 was carried out under similar reaction conditions to those described above. After 3F/mol of electricity (based on 6) was passed through the cell under a constant current conditions of 0.2 A, the cathodic solution was poured into 100 mL of brine and extracted with ether (50 mL x 3). The residue obtained by
evaporation of solvent was distilled under reduced pressure (bulb to bulb distillation) in order to give 20.

Spiro[5,4]-7,7-dimethyl-6-oxa-7-siladecane (20b): IR (neat) 2940, 2870, 1455, 1255, 980, 900, 845 cm⁻¹; ¹H NMR (CDCl₃) δ 0.17 (s, 6H), 0.76 (t, J = 7.8 Hz, 2H), 1.28-1.60 (m, 10H), 1.71 (t, J = 7.8 Hz, 2H); MS m/e (relative intensity) 184 (27, M⁺), 155 (15), 141 (100), 128 (71), 75 (19); HRMS calcd for C₁₀H₂₀SiO 184.1284, found 184.12988.

2,2-Dimethyl-5,5-dipentyl-1-oxa-2-silacyclopentane (20c): IR (neat) 2950, 1255, 1010, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.16 (s, 6H), 0.76 (t, J = 7.7 Hz, 2H), 0.86 (t, J = 6.3 Hz, 6H), 1.14-1.48 (m, 16H), 1.70 (t, J = 7.7 Hz, 2H); MS m/e (relative intensity) 256 (0, M⁺), 213 (8), 185 (100), 75 (15); Anal. Calcd for C₁₅H₃₂SiO: C, 70.24; H, 12.57. Found: C, 69.96; H, 12.74.

5-Hexyl-2,2,5-trimethyl-1-oxa-2-silacyclopentane (20d): IR (neat) 2960, 2930, 2860, 1255, 955, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.15 (s, 3H), 0.18 (s,3H), 0.86 (t, J = 5.7 Hz, 3H), 1.14 (s,3H), 1.20-1.45 (m, 10H), 1.60-1.82 (m, 2H); MS m/e (relative intensity) 214 (1, M⁺), 199 (10), 157 (13), 129 (100), 75 (28); Anal. Calcd for C₁₂H₂₆SiO: C, 67.22; H, 12.22. Found: C, 67.32; H, 12.46.

2,2,5-Trimethyl-5-propyl-1-oxa-2-silacyclopentane (20e): IR (neat) 2970, 2880, 1255, 1090, 1010, 960, 935, 840, 780 cm⁻¹; ¹H NMR (CDCl₃) δ 0.14 (s, 3H), 0.17 (s, 3H), 0.79 (t, J = 7.9 Hz, 2H), 0.88 (t, J = 6.5 Hz, 3H), 1.13 (s, 3H), 1.20-1.50 (m, 4H), 1.56-1.84 (m, 2H); ¹³C NMR (CDCl₃) δ 0.12, 0.44, 10.34, 14.64, 17.54, 27.41, 35.49, 45.05, 81.82; MS m/e (relative intensity) 172 (4, M⁺), 157 (21), 129 (100), 75 (34); HRMS calcd for C₉H₂₀SiO 172.1284, found 172.1288.

5-Ethyl-2,2,5-trimethyl-3-propyl-1-oxa-2-silacyclopentane (20h): IR (neat) 2960, 2850, 1460, 1250, 1000, 945, 830, 780 cm⁻¹; ¹H NMR (CDCl₃) δ 0.04, 0.07 (s, 3H), 0.19, 0.21 (s, 3H), 0.70-0.95 (m, 6H), 1.11,1.20 (s, 3H), 1.15-1.60 (m, 8H), 1.89-1.90, 2.00-2.10 (m, 1H); MS m/e (relative intensity) 200 (1, M⁺), 185 (7), 171 (52), 149 (9), 131 (25), 83 (27), 75 (100); Anal. Calcd for C₁₁H₂₄SiO: C, 65.93; H, 12.07. Found: C, 65.89; H, 12.19.
2,2,5-Trimethyl-5-(4-methyl-3-cyclohexenyl)-1-oxa-2-silacyclopentane (20j): IR (neat) 2960, 1255, 940, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.14 (s, 3H), 0.20 (s, 3H), 0.78 (t, J = 7.5 Hz, 2H), 1.08, 1.10 (s, 3H), 1.63 (s, 3H), 1.50-2.05 (m, 9H), 5.39 (m, 1H); MS m/e (relative intensity) 224 (10, M⁺), 209 (6), 129 (100), 94 (10), 75 (21); HRMS calcd for C₁₃H₂₄SiO 224.15972, found 224.15767.

Oxidative Desilylation of 20d. According to the reported procedure, the transformation of 20d to 3-methyl-1,3-nonanediol (23) was carried out in MeOH-THF (1:1) containing NaHCO₃ using 30% H₂O₂ as a oxidizing agent. The product 23 was isolated by a bulb to bulb distillation (Yield 76%).

23: IR (neat) 3600, 2950, 1470, 1380, 1050 cm⁻¹; ¹H NMR (CDCl₃) δ 0.86 (t, J = 6.2 Hz, 3H), 1.21 (s, 3H), 1.20-1.57 (m, 8H), 1.55-1.82 (m, 2H), 2.24 (OH), 2.70 (OH), 3.70-3.92 (m, 2H).
References and Notes

7) For example, Julia, M. Acc. Chem. Res. 1971, 4, 386.
9) It has been reported in our laboratory that the use of carbon fiber cathode gave the best result in the cathodic coupling reaction of ketones with olefins.8
15) It has been reported that the reaction of 2-bromoethyltrimethylsilane with tert-BuLi or Mg metal gave the corresponding anion equivalents 17 (R3 = H), whereas this bromide is prepared by the hydrobromination of vinyltrimethylsilane and it is rather unstable.16


Chapter 2

Diastereoselective Cathodic Coupling of Ketones with Allylic Alcohols
Useful for the Synthesis of Optically Active 1,4-Diols

Abstract: The intermolecular cathodic coupling of ketones with allylic alcohols was found to proceed regioselectively affording the corresponding 1,4-diols in high yields. This coupling reaction proceeded with excellent regioselectivity, and hence, the reaction of acetone with trans-(4R)-2-octen-4-ol gave (3S,5R)-2,3-dimethyl-2,5-decanediol in >85% d.e, and that with cis-(4R)-2-octen-4-ol gave (3R,5R)-2,3-dimethyl-2,5-decanediol in >85% d.e. Thus, the reaction was successfully applied to the synthesis of optically active 1,4-diols, and 1,3-transcription of chirality.

Introduction

The study of our laboratory on the cathodic coupling of carbonyl groups with unsaturated systems was started in the early 1970s, when the intramolecular cathodic coupling of nonconjugated olefinic ketones was found to proceed in good yield and excellent regio- and stereo-selectivity affording the corresponding cyclized tertiary alcohols.1-3 In 1989 it has been also reported4 that the intermolecular cathodic coupling of ketones (1) with olefins (2) was attained by the use of carbon fiber as the material of cathode (Scheme I).

This intermolecular coupling was greatly influenced by the structure of 2. Namely, the coupling of 1 with monosubstituted terminal olefin (R^3 = R^4 = H, R^5 = an alkyl group) gave the coupling product (2) in excellent yield, that with disubstituted terminal olefin (R^3 = H, R^4, R^5 = alkyl groups) resulted in the remarkable decrease of the yield of 3, and that with disubstituted inner olefin (R^3, R^4 = alkyl groups, R^5 = H) did not afford 3.
On the other hand, it has been described in the preceding chapter that introduction of trimethylsilyl group on 2 (R^4 = SiMe\(_3\) in Scheme I) greatly affected the reactivity of 2. That is, not only the monosubstituted terminal olefin (R\(^3\), R\(^5\) = H, R\(^4\) = SiMe\(_3\)) but also the disubstituted terminal olefin (R\(^3\) = H, R\(^4\) = SiMe\(_3\), R\(^5\) = an alkyl group) reacted with 1 under the electroreductive conditions and formed the corresponding \(\gamma\)-trimethylsilylalcohols in good yield. These results shown in the preceding chapter seems to suggest that the appropriate selection of functional group on 2 may bring about the remarkable change of the reactivity of 2 toward cathodic coupling reaction.

In this chapter it is described that that allylic alcohol (4) shows quite unique reactivity in the cathodic coupling with 1. The hydroxyl group at allylic position is found to promote the cathodic coupling of 1 with 4, and the existence of alkyl groups (R\(^3\) and R\(^4\)) on the double bond of 4 dose not interfere the formation of the coupling product (5) (Scheme II). Moreover, this reaction was found to be highly diastereoselective, and hence, the cathodic coupling of 1 with optically active 4 gave chiral 1,4-diols (5) with excellent diasteromeric excesses.
Results and Discussion

The electroreductive coupling of ketones (1) with olefinic alcohols was carried out in DMF using n-Bu₄NB₄ as a supporting electrolyte and carbon fiber as the material of cathode.⁴ As the typical results are shown in the Table I, the coupling of 1 with allyl (4a), methallyl (4b), and crotol (4c) types of alcohols gave the corresponding 1,4-diols in good yield (Run1-3).

From synthetic viewpoint, cathodic coupling of ketone with olefinic systems is proved to be useful for the preparation of 1,n-diols. Namely, the coupling of 1 and 4 shown in this chapter afforded a variety of 1,4-diols, and the coupling of 1 with homoallyl alcohol having terminal olefin gave 1,5-diol in high yield (Run 4). In addition, it has already been described in the preceding chapter that the cathodic coupling of ketones with ethoxydimethylvinylsilanes followed by the oxidative desilylation yielded 1,3-diols in satisfactory yields. Moreover, it has been previously found in our laboratory that the cathodic coupling reaction between a ketone and an ω-hydroxy terminal olefin afforded the corresponding 1,ω-diol without protection of the hydroxyl group.⁴ Thus, 1,n-diols could be systematically prepared by using the intermolecular cathodic coupling of ketones with the olefins bearing a hydroxyl group (Scheme III).
Table I. Intermolecular Cathodic Coupling of Ketones with Olefins

<table>
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<tr>
<th>Run</th>
<th>Ketone (1)</th>
<th>Olefin</th>
<th>Product (5)</th>
<th>Yield / %&lt;sup&gt;a&lt;/sup&gt;</th>
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<tr>
<td>1</td>
<td>n-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;Me 1a</td>
<td>n-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;O-</td>
<td>4a</td>
<td>5a 89</td>
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<tr>
<td>5</td>
<td>MeMe</td>
<td>Me- Bu-n</td>
<td>Me- Bu-n</td>
<td>4d</td>
</tr>
<tr>
<td>6</td>
<td>1c</td>
<td>Me- Pr-n</td>
<td>Me- Pr-n</td>
<td>4'b</td>
</tr>
<tr>
<td>7</td>
<td>1c</td>
<td>Me- Et</td>
<td>Me-</td>
<td>4''a</td>
</tr>
<tr>
<td>8</td>
<td>1c</td>
<td>Me- Bu-n</td>
<td>2a</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>1c</td>
<td>Me- Bu-n</td>
<td>4d-methylether</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield.
Among these coupling reaction between 1 and olefinic systems, the coupling of 1 with 4 is especially interesting from mechanistic point of view. As the results summarized in Table I clearly show, the existence of a hydroxyl group at allylic position of double bond is important in this coupling reaction. That is, the reaction of acetone with \textit{trans}-2-octen-4-ol (4d) gave 5d in reasonable yield (Run 5), whereas the reaction with \textit{trans}-2-octen-5-ol (4'b) resulted in the remarkable decrease of the yield of the coupling product 5'b (Run 6), and that with \textit{trans} 2-octen-6-ol (4'a) (Run 7) and \textit{trans}-2-octene (2a) (Run 8) did not afford the coupling products. In addition, when the hydroxyl group on 4d was transformed to methoxyl group, the coupling reaction did not take place at all (Run 9).

Although the role of the hydroxyl group at allylic position of double bond is not always clear, it would be reasonable to suppose that the allylic hydroxyl group interacts \textit{via} hydrogen bonding with radical species 6 generated by the electroreduction of 1 and forms the intermediate 7 (Scheme IV). Since it has been previously reported that the cathodic intramolecular coupling reaction of olefinic ketones takes place more easily than that of intermolecular one,\textsuperscript{1,2,4} the formation of the cyclic intermediate such as 7 seems to promote the intermolecular coupling of 1 and 4. Moreover, when the radical intermediate 7 is actually formed, it would be supposed that the addition of the radical center of 7 to the double bond takes place at the same face as the hydroxyl group at allylic position.

\textbf{Scheme IV}

\begin{center}
\includegraphics[width=0.8\textwidth]{Scheme_IV.png}
\end{center}
In fact, it was found that the cathodic coupling of acetone (1c) with trans-2-octen-4-ol (4d-trans) proceeded stereoselectively to afford one diastereomer of 2,3-dimethyl-2,5-nonanediol (5d) in 85% d.e. In order to clarify the origin of the stereoselectivity and examine the availability of this coupling reaction for the asymmetric synthesis of 1,4-diols, the cathodic coupling of 1 with optically active allylic alcohols was performed. As shown in Scheme V, the cathodic coupling of 1c with (R)-trans-2-octen-4-ol [4d-trans-(R)] and (R)-trans-5-methyl-2-hexen-4-ol [trans-4e-trans-(R)] gave (3S,5R)-2,3-dimethyl-2,5-nonanediol [5d-(3S,5R)] and (3S,5R)-2,3,6-trimethyl-2,5-heptanediol [5e-(3S,5R)], respectively, while the reaction of acetone with cis-(R)-2-octen-4-ol [4d-cis-(R)] afforded (3R,5R)-2,3-dimethyl-2,5-nonanediol [5d-(3R,5R)] (Scheme V). The absolute configuration of 5d was determined by the transformation to the tetrahydrofuran derivatives whose stereochemistry could be determined by the NOE difference spectra (See Experimental Section).

**Scheme V**

```
\[ \begin{align*}
\text{Me} & \quad \text{Me} + \text{Me} & \quad \text{Me} & \quad \text{Me} \\
& \quad \text{OH} & \quad \text{R} \quad \rightarrow \quad +e \quad \text{n-Bu}_4\text{NBF}_4 / \text{DMF} \quad \text{Me} & \quad \text{Me} & \quad \text{OH} \\
4\text{d-trans-} & \quad \text{R} ; \quad \text{n-Bu} & \quad [\alpha]_D^{23} = +7.7 \quad (c = 1.51, \text{CHCl}_3) \\
\text{cis-} & \quad \text{Bu-n} & \quad \text{Me} & \quad \text{Me} & \quad \text{OH} & \quad \text{Me} & \quad \text{Me} & \quad \text{OH} & \quad \text{n-Bu}_4\text{NBF}_4 / \text{DMF} \\
4\text{d-cis-} & \quad \text{R} & \quad \text{Me} & \quad \text{OH} & \quad \text{Bu-n} & \quad \text{Me} & \quad \text{Me} & \quad \text{OH} \\
\text{[} \alpha \text{]}_D^{23} = +21.9 \quad (c = 1.94, \text{CHCl}_3) & \quad >96\% \text{ e.e.} & \quad >96\% \text{ e.e.} \\
\text{5d-(3R,5R)} & \quad \text{5d-(3S,5R)} & \quad [\alpha]_D^{23} = +4.0 \quad (c = 1.72, \text{CHCl}_3) \\
\text{Yield 71\%, >85\% d.e.} & \quad \text{Yield 60\%, >85\% d.e.} \\
\text{5e-(3S,5R)} & \quad [\alpha]_D^{23} = -20.9 \quad (c = 1.93, \text{CHCl}_3) \\
\text{Yield 60\%, >85\% d.e.} 
\end{align*} \]
```
These results clearly indicate that the diastereoselectivity is completely controlled by the hydroxyl group at allylic position and the structure of double bond. The seven-membered ring transition state model shown in Scheme VI seems to provides the reasonable explanation of this selectivity. The cathodic coupling of acetone (1c) with 4-trans-(R) gave the radical intermediate 7-trans. When the radical center of 7-trans attacks the Si-face of the double bond, the seven-membered ring structure 8A is formed, which has only one gauche interaction between Me groups at the newly formed C-C bond shown in the Newman projection. Ont he other hand, when the radical center attacks the Re-face of the double bond, two possible seven-membered ring structures 8B,C could be considered. Both of these structures, however, are more unstable than 8A because 8B has two gauche interactions between Me groups shown in the Newman projection, and 8C has one Me-Me gauche interaction and another steric hindrance between Me and R groups. Therefore, (3S,5R)-1,4-diol is preferentially formed via more favored structure 8A. The selective formation of (3R,5R)-1,4-diol by the coupling of 1c with 4-cis could be also explained in similar way. The attack of the radical center of 7-cis to the double bond from Re-face give 8D which has one Me-Me gauche interaction, while the Si-face attack gives more unfavored structures 8E,F (8E has two gauche interactions and one steric repulsion between Me and R groups, and 8F has one gauche interaction and one repulsion between Me and R groups). Then, the Re-face attack precedes the Si-face one.

This diastereoselectivity was much influenced by the methyl group on the carbon bearing hydroxy group. The cathodic coupling of 1c with trans-4-methyl-2-octen-4-ol (4f) afforded 1:1 diastereomeric mixture of the corresponding diol 5f (Scheme VII). The perturbation by the substitution of methyl group could be also reasonably explained by the transition state model described above. That is, the structure 8A' which is formed by the Si-face attack is destabilized by the additional steric hindrance between one methyl group of acetone and the methyl group jointed to the carbon bearing hydroxy group. Resultingly, the stability of 8A' is comparable with those of 8B' and 8C'.
Scheme VI

1c + Me\(\text{Me}_2\text{O-H}\)  

7-trans

Si

+e

Re

Me\(\text{Me}_2\text{O-H}\)  

4-trans-(R)

Me\(\text{Me}_2\text{O-H}\)  

7-cis

Si

+e

Re

Me\(\text{Me}_2\text{O-H}\)  

4-cis-(R)

Me\(\text{Me}_2\text{O-H}\)  

5d-(3S,5R)

5d-(3R,5R)

5d-(3S,5R)
The coupling of 1c with a methally type alcohol 4g showed no diastereoselectivity. The reason for non-selectivity is rather clear in this case. The newly formed stereogenic center is located at the radical center of the intermediately formed radical species 8g, and hence, the following protonation does not have the face selectivity.

Scheme VII

Scheme VIII

Yield 66%

1 : 1 mixture of diastereomers
Interestingly, another type of stereoselective cathodic coupling was observed when trans-(S)-1-phenyl-2-buten-1-ol [4h-trans-(S)] was used as olefin. That is, the cathodic coupling of acetone (1c) with 4h-trans-(S) afforded (S)-2,3-dimethyl-5-phenyl-2-pentanol [9-(S)] in 90% yield and >90% e.e. (Scheme IX).6 The product 9-(S) seems to be formed by the diastereoselective cathodic coupling of 1c and 4h-trans-(S) followed by the electroreduction of benzyl alcohol part of the intermediary formed chiral 1,4-diol 5h. In this case, 1,3-transcription of chirality occurred accompanied by the disappearance of the original chiral center.

Scheme IX

In conclusion, the introduction of hydroxyl group into the olefinic system at allylic position was found to enlarge the feasibility of the intermolecular cathodic coupling of ketones with olefins. Moreover, the coupling of acetone with crotyl type secondary alcohols proceeded in high diastereoselectivity, and this diastereoselective coupling was successfully applied to the asymmetric synthesis of 1,4-diols. This selectivity is completely controlled by the hydroxyl group at allylic position and geometry of double bond, and could be explained by the consideration of seven-membered ring transition state model which is constructed by the interaction between ketyl radical and hydroxyl group of allyl alcohols.
Experimental Section

General. IR spectra were obtained on a Hitachi 260-10 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were measured on a Varian Gemini-200 (200 MHz) spectrometer, and the chemical shift values ($\delta$) are expressed in ppm downfield from the internal TMS standard. GC analyses were carried out on a Shimadzu GC-4C or GC-12A instrument. High resolution mass spectra (HRMS) were determined on a JEOL JES-DX 300. Elemental analyses were performed by the Center for Instrumental Analysis of Kyoto University. The constant electrocurrent was supplied with Takasago GPO50-2 regulated DC power supply. Optical rotation was recorded by a Perkin-Elmer 243 polarimeter.

Material. Ketones (1a-1c), allyl alcohols (4a-4c), 3-butenyl alcohol (4'a), and 2-octene (2a) are commercially available. Racemic allyl alcohols 4d-trans, 4e-trans, and 4h-trans were prepared by the reaction of the corresponding Grignard reagents with crotonaldehyde. Allyl alcohols 4f and 4g were obtained by the reaction of n-butylmagnesium bromide with 3-penten-2-one and methacrolein respectively. Racemic 4d-cis was prepared by the controlled hydrogenation of 2-octyn-4-ol using Lindlar catalyst. Homoallyl alcohol 4'b was prepared by TiCl₄ catalyzed coupling of (1-methyl-2-propenyl)trimethylsilane with butanal. The preparation of 4''a was attained by the reaction of 3-pentenylmagnesium bromide with propanal. Chiral allyl alcohols 4d-trans-(R), 4d-cis-(R), 4e-trans-(R), and 4h-trans-(S) were prepared by the kinetic resolution of the corresponding racemic alcohols using Sharpless enantioselective epoxidation. DMF was dried over fresh alumina (Alumina B, Act I, ICN Biochemicals) and stocked under nitrogen atmosphere. Carbon fiber used as a cathode was carbonized polyacrylonitrile (Hi-Carbolon-3KS, diameter 7μm, Asahi Nippon Carbon Fiber Co., Ltd. Tokyo, Japan).

trans-(R)-2-Octen-4-ol [4d-trans-(R)]: IR (neat) 3350, 2900, 1430, 950 cm$^{-1}$; $^1$H NMR (CDCl₃) $\delta$ 0.90 (t, $J = 6.0$ Hz, 3H), 1.20-1.65 (m, 6H), 1.71 (d, $J = 6.0$ Hz,
cis-(R)-2-Octen-4-ol [4d-cis-(R)]: IR (neat) 3350, 2910, 2860, 1680, 1440, 1000 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta 0.91\) (t, \(J = 7.0\) Hz, 3H), 1.19-1.71 (m, 6H), 1.68 (d, \(J = 7.0\) Hz, 3H), 4.47 (q, \(J = 6.0\) Hz, 1H), 5.31-5.65 (m, 2H); \([\alpha]_D^{23} = +21.9^\circ\) (c = 1.94, CHCl\(_3\)).

trans-(R)-5-Methyl-2-hexen-4-ol [4e-trans-(R)]: IR (neat) 3350, 2930, 1370, 1000, 960 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta 0.88\) (d, \(J = 7.0\) Hz, 3H), 0.93 (d, \(J = 7.0\) Hz, 3H), 1.51 (OH), 1.68 (m, 1H), 1.72 (d, \(J = 6.0\) Hz, 3H), 3.77 (t, \(J = 7.0\) Hz, 1H), 5.75-5.41 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta 17.56, 17.93, 18.03, 33.65, 78.31, 127.88, 132.58\); \([\alpha]_D^{23} = -12.4^\circ\) (c = 1.70, CHCl\(_3\)) [lit.\(^{12}\) \([\alpha]_D = -12.9^\circ\) (c = 4.75, CHCl\(_3\))].

trans-(S)-1-Phenyl-2-buten-1-ol [4h-trans-(S)]: IR (neat) 3350, 3030, 2920, 2860, 1490, 1450, 1000, 960 750, 700 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta 1.72\) (d, \(J = 5.0\) Hz, 3H), 5.16 (d, \(J = 6.0\) Hz, 1H), 5.59-5.88 (m, 2H), 7.27-7.42 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta 17.50, 75.16, 126.21, 127.62, 128.57, 133.67, 143.46; [\alpha]_D^{23} = +46.5^\circ\) (c = 3.34, CHCl\(_3\)).

General Procedure of Cathodic Coupling of 1 with 4. The cathodic reduction was carried out in a divided cell equipped with a bundle of carbon fiber (twelve thousands carbon fiber filament, 15 cm length) as a cathode, a platinum anode (2 x 2 cm), and a glass filter diaphragm (No.5). A solution of 1 (10 mmol) and 4 (2 mmol) in dry DMF (20 mL) containing n-Bu\(_4\)NBF\(_4\) (5 mmol) as a supporting electrolyte was put into a cathodic chamber of the cell. The anodic solution was 15 mL of dry DMF containing n-Bu\(_4\)NBF\(_4\) (5 mmol). After 2.5 F/mol of electricity based on 1 was passed through the cell under the constant current of 0.2A, the cathodic solution was poured into 100 mL of brine and extracted with ether (50 mL x 3). The combined organic layer was washed with 1N HCl (50 mL), saturated aqueous NaHCO\(_3\) (50 mL), and brine (50 mL), and then dried over MgSO\(_4\). The residue obtained by evaporation of the solvent was column chromatographed (silica gel, hexane-AcOEt = 2 : 1) in order to obtain 4.
4-Methyl-1,4-decanediol (5a) \(^{13}\): IR (neat) 3350, 2950, 2860, 1460, 1380, 1060 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.87 (t, \(J = 6.7\) Hz, 3H), 1.17 (s, 3H), 1.20-1.38 (m, 6H), 1.40-1.75 (m, 8H), 3.66 (t, \(J = 6.5\) Hz, 2H); MS \(m/e\) (relative intensity) 170 (2, \(M^+\)-H\(_2\)O), 155 (7), 129 (26), 85 (100), 69 (34).

2,4-Dimethyl-1,4-heptanediol (5b): mixture of diastereomers: IR (neat) 3300, 2950, 2875, 1460, 1380, 1150, 1075, 1040 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.92 (d, \(J = 7.0\) Hz, 3H), 0.94 (t, \(J = 7.9\) Hz, 3H), 1.21 (s, 3H), 1.22-1.67 (m, 7H), 1.95 (OH), 2.85 (OH), 3.29-3.40 (m, 1H), 3.55-3.66 (m, 1H); MS \(m/e\) (relative intensity) 145 (1, \(M^+\)-Me), 99 (22), 87 (100), 69 (20); Anal.Calcd for C\(_9\)H\(_{20}\)O\(_2\): C, 67.45; H, 12.58. Found: C, 67.56; H, 12.46.

3,4-Dimethyl-1,4-heptanediol (5c): mixture of diastereomers: IR (neat) 3300, 2950, 2870, 1460, 1380, 1160, 1040 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.91, 0.95 (d, \(J = 6.4\) Hz, 3H), 0.94 (m, 3H), 1.15, 1.27 (s, 3H), 1.30-1.65 (m, 7H), 1.62 (OH), 3.55-3.88 (m, 2H); MS \(m/e\) (relative intensity) 145 (2, \(M^+\)-Me), 117 (15), 99 (28), 87 (100), 71 (20).

5-Methyl-1,5-octanediol (5'a)\(^{14}\): IR (neat) 3300, 2950, 2870, 1460, 1380, 1140, 1050 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.93 (t, \(J = 6.6\) Hz, 3H), 1.16 (s, 3H), 1.20-1.67 (m, 10H), 3.68 (t, \(J = 5.7\) Hz, 2H); MS \(m/e\) (relative intensity) 142 (5, \(M^+\)-H\(_2\)O), 127 (12), 109 (18), 99 (59), 87 (100), 69 (33).

2,3-Dimethyl-2,6-nonanediol (5'b), mixture of diastereomers: IR (neat) 3350, 2950, 2860, 1460, 1380, 1120, 1020 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.92 (d, \(J = 7.9\) Hz, 3H), 0.93 (t, \(J = 7.5\) Hz, 3H), 1.10, 1.23 (s, 3H), 1.16, 1.28 (s, 3H), 1.30-1.65 (m, 9H), 1.90 (OH), 3.50-3.90 (m, 1H); MS \(m/e\) (relative intensity) 155 (11, \(M^+\)-H\(_2\)O-Me), 127 (12), 109 (37), 84 (39), 70 (70), 59 (100); Anal.Calcd for C\(_{11}\)H\(_{24}\)O\(_2\): C, 70.16; H, 12.85. Found: C, 69.94; H, 12.61.

2,3,5-Trimethyl-2,5-nonanediol (5f), mixture of diastereomers: IR (neat) 3300, 2960, 2870, 1460, 1380, 1150 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.90 (t, \(J = 7.5\) Hz, 3H), 0.93 (d, \(J = 7.1\) Hz, 3H), 1.09, 1.10 (s, 3H), 1.16, 1.17 (s, 3H), 1.22, 1.23 (s, 3H), 1.20-1.55 (m, 7H), 1.72-1.95 (m, 2H), 2.58 (OH); MS \(m/e\) (relative intensity) 167 (17, \(M^+\)-H\(_2\)O-Me), 151 (5), 127 (77), 109 (29), 101 (36), 84 (100), 70 (82), 59 (43); Anal.Calcd for C\(_{12}\)H\(_{26}\)O\(_2\): C, 71.23; H, 12.95. Found: C, 71.00; H, 13.21.
2,4-Dimethyl-2,5-nonanediol (5g): mixture of diastereomers: IR (neat) 3350, 2920, 1450, 1370 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.91 (d, \(J = 6.0\) Hz, 3H), 0.91 (t, \(J = 6.0\) Hz, 3H), 1.24 (s, 3H), 1.25 (s, 3H), 1.28-2.05 (m, 9H), 3.33, 3.65 (m, 1H); MS \(m/e\) (relative intensity) 173 (1, M\(^+\)-Me), 155 (8), 113 (18), 95 (42), 84 (79), 69 (98), 59 (100); Anal. Calcd for C\(_{11}\)H\(_{24}\)O\(_2\): C, 70.16; H, 12.85. Found: C, 69.99; H, 12.88.

(3S,5R)-2,3-Dimethyl-2,5-nonanediol [5d-(3S,5R)]: IR (neat) 3300, 2930, 1460, 1380 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.91 (t, \(J = 6.0\) Hz, 3H), 0.93 (d, \(J = 7.0\) Hz, 3H), 1.14 (s, 3H), 1.22 (s, 3H), 1.09-1.80 (m, 9H), 3.64 (m, 1H); \(^13\)C NMR (CDCl\(_3\)) \(\delta\) 13.98, 16.48, 22.68, 24.50, 27.92, 38.66, 38.45, 39.97, 41.61, 70.81, 73.40; MS \(m/e\) (relative intensity) 173 (1, M\(^+\)-Me), 155 (12), 112 (41), 95 (39), 84 (53), 70 (78), 59 (100); \([\alpha]_D^23 = -16.0^\circ\) (c = 0.97, CHCl\(_3\)); Anal. Calcd for C\(_{11}\)H\(_{24}\)O\(_2\): C, 70.16; H, 12.85. Found: C, 69.99; H, 13.02.

The absolute configuration of 5d-(3S,5R) was determined as follows: As shown in Scheme X, the reaction of 5d-(3S,5R) with TsCl/pyridine gave the tosylate 10-(3S,5R) and the treatment of 10-(3S,5R) with NaOH gave the tetrahydrofuran 11-(3S,5S) through the intramolecular SN2 reaction.

(3S,5S)-2,2,3-Trtrimethyl-5-butyl-1-oxacyclopentane [11-(3S,5S)]: IR (neat) 2920, 1450, 1360, 1010 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.89 (t, \(J = 7.0\) Hz, 3H), 0.92 (d, \(J = 7.0\) Hz, 3H), 1.01 (s, 3H), 1.22 (s, 3H), 1.14-1.58 (m, 6H), 1.76 (m, 2H), 1.89 (m, 1H), 3.93 (m, 1H); MS \(m/e\) (relative intensity) 155 (24, M\(^+\)-Me), 113 (100), 95 (72). The stereochemical relation between a methyl group at 3-position and a butyl group at 5-position of 11-(3S,5S) was determined to be trans since the irradiation of proton at 5-position (\(\delta\) 3.93) showed NOE at methyl group at 3-position (\(\delta\) 0.92).

(3R,5R)-2,3-Dimethyl-2,5-nonanediol [5d-(3R,5R)]: IR (neat) 3350, 2930, 1360 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.91 (t, \(J = 6.0\) Hz, 3H), 0.96 (d, \(J = 7.0\) Hz, 3H), 1.17 (s, 3H), 1.24 (s, 3H), 1.17-1.52 (m, 7H), 1.60-1.75 (m, 2H), 3.77 (m, 1H); MS \(m/e\) (relative intensity) 173 (1, M\(^+\)-Me), 155 (5), 110 (15), 95 (15), 82 (100), 67 (39), 59 (49); \([\alpha]_D^23 = +4.0^\circ\) (c = 1.72, CHCl\(_3\)); Anal. Calcd for C\(_{11}\)H\(_{24}\)O\(_2\): C, 70.16; H, 12.85. Found: C, 69.97; H, 13.03.
The absolute configuration of 5d-(3R,5R) was also decided by the transformation to 11-(3R,5S) (Scheme X).

(3R,5S)-2,2,3-Trimethyl-5-butyl-1-oxacyclopentane [11-(3R,5S)]: IR (neat) 2920, 1450, 1360, 1140, 1010 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.89 (t, \(J = 7.0\) Hz, 3H), 0.94 (d, \(J = 7.0\) Hz, 3H), 1.01 (s, 3H), 1.21 (s, 3H), 1.23-1.42 (m, 6H), 1.59 (m, 1H), 1.98 (m, 1H), 2.06 (m, 1H), 3.86 (m, 1H); MS m/e (relative intensity) 155 (35, M\(^+\)-Me), 113 (100), 95 (70).

\[\text{Scheme X}\]

(3S,5R)-2,3,6-Trimethyl-2,5-heptanediol [5e-(3S,5R)]: IR (neat) 3300, 2920, 2880, 2360 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.93 (d, \(J = 7.0\) Hz, 9H), 1.14 (s, 3H), 1.23 (s, 3H), 1.55-1.79 (m, 4H), 3.40 (m, 1H); MS m/e (relative intensity) 155 (24, M\(^+\)-Me), 113 (100), 95 (72); \([\alpha]_D^{23} = -20.9^\circ\) (c = 1.93, CHCl\(_3\)); Anal. Calcd for C\(_{10}\)H\(_{22}\)O\(_2\): C, 68.90; H, 12.73. Found: C, 69.18; H, 12.90.

(S)-2,3-Dimethyl-5-phenyl-2-pentanol [5h-(S)]: IR (neat) 3350, 2970, 1460, 1380, 1140, 750, 700 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.99 (d, \(J = 7.0\) Hz, 3H), 1.16 (s, 3H), 1.20-1.52 (m, 2H), 1.86-2.04 (m, 1H), 2.41-2.58 (m, 1H), 2.71-2.87 (m, 1H), 7.15-7.34 (m, 5H); \(^13\)C NMR (CDCl\(_3\)) \(\delta\) 14.22, 25.97, 26.92, 33.48, 34.36, 43.71, 73.40, 125.85, 128.47, 142.92; MS m/e (relative intensity) 177 (6, M\(^+\)-Me), 174 (11), 159 (11), 134 (13) 104 (82), 92 (34), 59 (100); \([\alpha]_D^{23} = -32.2^\circ\)
(c = 1.95, CHCl₃); Anal. Calcd for C₁₃H₂₀O: C, 81.19; H, 10.49. Found: C, 81.08; H, 10.64.
References and Notes

5) The diastereomeric excesses of 5d-(3S,5R), 5e-(3S,5R), and 5d-(3R,5R) were determined by the transformation of the secondary hydroxyl groups of 5d-(3S,5R), 5e-(3S,5R), and 5d-(3R,5R) to the corresponding acetates followed by $^1$H-NMR analysis.
6) The enantiomeric excesses of 5h-(S) was determined by the transformation of the secondary hydroxyl groups of 5h-(S) to the corresponding acetates followed by $^1$H-NMR analysis in the presence of Eu(hfc)$_3$.
Chapter 3

Cathodic Coupling of Ketones with Vinylsilanes Having a Hydroxy Group at the Allylic Position

Abstract: Cathodic coupling of ketones (1) with vinyltrimethylsilanes having hydroxy group at allylic position has been found to be controlled by the position of trimethylsilyl group on the double bond. That is, the coupling of 1 with (1-trimethylsilylvinyl)alkyl carbinols gave homoallylic alcohols through the Peterson elimination of intermediately formed trimethylsilyl-1,4-diols, whereas that with (2-trimethylsilylvinyl)alkyl carbinols afforded trimethylsilyl substituted 1,3-diols. In both cases the regioselectivity of the coupling reaction was completely controlled by trimethylsilyl group and took place at the non-silylated side of the double bond. Moreover, in the latter case, the reaction was found to proceed diastereoselectively.

Introduction

It was shown in the preceding chapters that cathodic coupling reactions of ketone (1) with olefin were remarkably affected by the substituents on the olefinic systems. Namely, in the coupling of 1 with vinylsilanes shown in chapter 3, the electronic effect of trimethylsilyl group greatly enhanced the reactivity of the olefins. (Scheme I, $Y = \text{SiMe}_3$). The coupling of 1 with allylic alcohols (Scheme I, $X = \text{Me}$, $Z = \text{OH}$) was shown in chapter 4, and the hydroxy group at allylic position played an important role for determining the diastereoselectively and the chiral center at allylic position is transferred to newly formed stereocenter in 1,3-induction manner.
Thus, it would be attractive to examine the cathodic coupling of 1 with olefins having hydroxy and trimethylsilyl group in the same molecule (X or Y = SiMe₃, Z = OH). The coupling of 1 with such olefins was actually carried out and the results shown in this chapter seem to be interesting from synthetic and mechanistic view points.

Results and Discussion

The electroreductive coupling of ketones 1 with 2-trimethylsilyl-2-propen-1-ols (2) was performed in an divided cell using carbon fiber as a cathode, Et₄N·OTf as a supporting electrolyte, and DMF as a solvent (Scheme II). Interestingly, the coupling product was not trimethylsilyl substituted 1,4-diol (Scheme I, Y = SiMe₃, Z = OH) but the homoallylic alcohol 3. As the results are summarized in Table I, the cathodic coupling of 1 with vinylsilanes 2a-e which have terminal olefin structure afforded the corresponding homoallylic alcohols in good yield (Run 1-7), while that with trisubstituted olefin 2f afforded 3h in lower yield (Run 8). In the latter case, steric hindrance of R³ seemed to disturb the coupling reaction,¹ and instead, base induced desilylation² of 2 predominantly took place. When 2e which has trisubstituted olefin structure was used as an olefin, the exomethylene compound 3g was obtained (Run 7). Since the coupling of 1 and 2 provides a new route for the regioselective preparation of homoallylic alcohols from 1, the reaction seems to be useful for organic synthesis. Moreover,
the fact that the formation of C-C bond takes place regioselectively at non-sililated side of the double bond is also interesting and deserves investigation.

Scheme II

Scheme II

Table I. Cathodic Coupling of Ketones with Vinylsilanes 2.

<table>
<thead>
<tr>
<th>Run</th>
<th>Ketone 1</th>
<th>Vinylsilane 2</th>
<th>Product 3\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{R}^1 )</td>
<td>( \text{R}^2 )</td>
<td>( \text{R}^3 )</td>
</tr>
<tr>
<td>1</td>
<td>\text{Me}</td>
<td>\text{Me}</td>
<td>\text{i-Pr}</td>
</tr>
<tr>
<td>2</td>
<td>\text{Me}</td>
<td>\text{Me}</td>
<td>\text{i-Pr}</td>
</tr>
<tr>
<td>3</td>
<td>\text{i-Pr}</td>
<td>\text{Et}</td>
<td>\text{i-Pr}</td>
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<tr>
<td>4</td>
<td>\text{Me}</td>
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<tr>
<td>5</td>
<td>\text{i-Pr}</td>
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<tr>
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<td>\text{i-Pr}</td>
<td>\text{Et}</td>
<td>\text{i-Pr}</td>
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<tr>
<td>7</td>
<td>\text{i-Pr}</td>
<td>\text{Et}</td>
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<tr>
<td>8</td>
<td>\text{i-Pr}</td>
<td>\text{Me}</td>
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\( \text{a)} \) Isolated yield. \( \text{d)} \) Determined by IR and \textsuperscript{1}H NMR.
Scheme III shows a plausible mechanism of this coupling. The anion radical 4 generated by the electroreduction of ketone 1 attacks regioselectively to vinylsilane 2. The successive electroreduction of the resulting radical species forms the dianion 5 in which the anion center on carbon atom is stabilized by trimethylsilyl group. The protonation of C-anion center of 5 produces 6, and the Peterson elimination of 6 affords the product 3. Since the base induced Peterson elimination is known to demand a syn conformation, the cis-trans ratio of the products listed in Table I may reflect the stereoselectivity of the protonation step of 5.

Scheme III

The regioselectivity of the coupling is completely controlled by the position of trimethylsilyl group on the double bond. As shown in Scheme IV, the cathodic coupling of acetone (1a) with 3-trimethylsilyl-2-propen-1-ols (7) performed under the same reaction conditions as the coupling with 2 gave the trimethylsilyl substituted 1,3-diols 8 in good yield. In this case, the coupling was also occurred at the non-silylated side of the double bond. 1-Trimethylsilyl-1-alkene without hydroxy group, however, was not effective to this coupling reaction. This result indicates that not only trimethylsilyl group but also hydroxy group at allylic position plays an important roll in the reaction. In Chapter 2, it has been demonstrated that the interaction of hydroxy group and ketyl radical by a
hydrogen bonding resulted in the diastereoselective coupling. It is reasonable that
the similar type interaction promotes the coupling of 1a with 7. Actually, the
reaction of 1a with 7b was found to proceed diastereoselectively affording single
isomer of 8b.6

Scheme IV

In order to estimate the effects of trimethylsilyl group and hydroxy group
on the reactivity of olefins, the competitive reactions were carried out (Scheme
V). When the mixture of 2-trimethylsilyl-1-hexen-3-ol (2a) (2 mmol) and 1-
hexene (9) (2 mmol) was electroreduced in the presence of acetone (1a) (5 mmol)
supplied electricity = 1.5 F/mol based on 1a), 3a, the coupling product with 2a,
was formed predominantly. Similarly, 2a was found to be more reactive than 1-
hexen-3-ol (10) in the coupling reaction. On the other hand, the reactivity of 2a
and 2-trimethylsilyl-1-hexene (11) was found to be comparable. These results
indicated that the cathodic coupling of 1 with 2 is promoted mainly by the effect
of trimethylsilyl group. The cathodic coupling of 1 with olefins was also
promoted by the introduction of hydroxy group on the olefins. That is, the
cathodic coupling of 1a with the mixture of 9 and 10 gave the mixture of 12 and
13 in the ratio of 17 : 83. As concerns the regioselectivity, the effect of hydroxy
group seems to be weaker than that of trimethylsilyl group. A normal allylic
alcohol such as 10 reacted with 1a at γ-position to hydroxy group, whereas 7
reacted at β-position. In conclusion, it is clarified in the present study that the
introduction of trimethylsilyl group enhances the reactivity of the olefin by the
electronic effect and the coupling reaction takes place at the non-silylated side of
double bond, whereas the hydroxy group at allylic position promotes the reaction
through the interaction between hydroxy group and ketyl radical by a hydrogen bonding (the detail has already shown in chapter 4).

**Scheme V**

![Scheme V](image)

a) 1.5 F/mol (based on 1a) of electricity was passed. Total yield of the coupling products resulted in about 50%.

b) The ratios of the products were determined by GLC and $^1$H NMR.
Experimental Section

General. $^1$H and $^{13}$C NMR spectra were recorded on Varian Gemini-200 spectrometer using TMS as an internal standard. IR spectra were obtained on Hitachi 260-10 spectrometer. GC analyses were carried out on a Shimadzu GC-4C or GC-12A gas chromatograph. High resolution mass spectra (HRMS) were measured by a JEOL JES-DX 300. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University. The cathodic reduction was performed by direct current power supply (GP-050-20, Takasagoseisakusho Co.LTD).

Materials. Ketones (1a-1c) are commercially available and they were purified by distillation. DMF was dried over fresh alumina (Alumina B, Act I, ICN Biochemicals) and stocked under nitrogen atmosphere. Carbon fiber as a cathode was Carbon Fiber 12000f (Asahi Nippon Carbon Fiber Co., LTD. Tokyo Japan).

Preparation of 2a-e. $\alpha$-Bromovinyltrimethylsilane prepared by a known procedure$^{7}$ was lithiated by the reaction with tert-BuLi in dry THF at -78°C.$^{8}$ The resulting vinyllithium was treated by butanal, 2-methylpropanal, 3-cyclohexene-carboxyaldehyde, 3-pentanone, and cyclohexanone to give 2a-e respectively.

2-Trimethylsilyl-1-hexen-3-ol (2a): IR (neat) 3380, 2960, 2870, 1250, 1020, 840 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.12 (s, 9H), 0.91 (t, $J = 7.4$ Hz, 3H), 1.30-1.60 (m, 4H), 1.62 (OH), 4.22-4.33 (m, 1H), 5.39 (dd, $J = 2.6$, 1.0 Hz, 1H), 5.76 (dd, $J = 2.6$, 1.4 Hz, 1H); Anal. Calcd for C$_9$H$_{20}$OSi: C, 62.72; H, 11.70. Found: C, 62.64; H, 11.89.

2-Trimethylsilyl-4-methyl-1-propen-3-ol (2b)$^9$: IR (neat) 3400, 2950, 1460, 1245, 1020, 990, 830, 755 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.11 (s, 9H), 0.88 (d, $J = 6.6$ Hz, 3H), 1.40 (OH), 0.89 (d, $J = 6.6$ Hz, 3H), 1.79 (sept. $J = 6.6$ Hz, 1H), 3.94-4.01 (m, 1H), 5.46-5.49 (m, 1H), 5.73-5.77 (m, 1H).
1-(3-Cyclohexenyl)-2-trimethylsilyl-1-propan-3-ol (2c): IR (neat) 3450, 3030, 2960, 2850, 1260, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.12 (s, 9H), 1.15-1.40 (m, 2H), 1.50 (OH), 1.55-2.20 (m, 5H), 4.00-4.10 (m, 1H), 5.47-5.50 (m, 2H), 5.62-5.70 (m, 2H), 5.71-5.75 (m, 1H); Anal. Calcd for C₁₂H₂₂OSi: C, 68.51; H, 10.54. Found: C, 68.33; H, 10.73.

3-Ethyl-2-trimethylsilyl-1-penten-3-ol (2d): IR (neat) 3470, 2950, 1460, 1250, 1130, 925, 835 cm⁻¹; ¹H NMR (CDCl₃) δ 0.12 (s, 9H), 0.80 (t, J = 7.4 Hz, 6H), 1.40 (OH), 1.50-1.65 (m, 4H), 5.48 (d, J = 2.1 Hz, 1H), 5.55 (d, J = 2.1 Hz, 1H); Anal. Calcd for C₁₀H₂₂OSi: C, 64.45; H, 11.90. Found: C, 64.24; H, 12.11.

1-(1-Trimethylsilylethenyl)cyclohexanol (2e)⁸: IR (neat) 3400, 2920, 2850, 1250, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.14 (s, 9H), 1.39 (OH), 1.50-1.65 (m, 10H), 5.37 (d, J = 2.0 Hz, 1H), 5.69 (d, J = 2.0 Hz, 1H).

Preparation of 3-Trimethylsilyl-2-hepten-4-ol (2f). A solution of propyne (generated by the dehydrobromination of 1,2-dibromopropane) in dry ether was treated successively by n-BuLi and chlorotrimethylsilane to yield 1-trimethylsilylpropyne.¹⁰ Hydroalumination of 1-trimethylsilylpropyne with DIBAL-H followed by treatment with iodine gave 1-iodo-1-trimethylsilylpropene.¹⁰ The resulting iodotrimethylsilane was lithiated by n-BuLi in ether and then quenched with butanal to yield 2f.

2f: IR (neat) 3350, 2960, 2870, 1620, 1460, 1250, 1020, 840, 780 cm⁻¹; ¹H NMR (CDCl₃) δ 0.19 (s, 9H), 0.90 (t, J = 7.4 Hz, 3H), 1.25 (OH), 1.30-1.50 (m, 4H), 1.78 (d, J = 7.0 Hz, 3H), 4.09-4.19 (m, 1H), 6.30 (qd, J = 7.0, 1.1 Hz, 1H); Anal. Calcd for C₁₀H₂₂OSi: C, 64.45; H, 11.90. Found: C, 64.67; H, 11.97.

General Procedure for the Cathodic Coupling of 1 with 2. The cathodic reduction was carried out in a divided electrolysis cell (100 mL) equipped with a cathode fiber, a platinum anode (2 x 2 cm), and a glass filter diaphragm (No.5). A solution of a ketone 1 (10 mmol) and a vinylsilane 2 (2 mmol) in dry DMF (20 mL) containing Et₄N·OTs (10 mmol) as a supporting electrolyte was put into a cathodic chamber of the cell. The anodic solution was 15 mL of dry DMF.
containing Et₄N OTs (5 mmol). After 2 F/mol of electricity based on 1 (constant
current conditions of 0.2 A) was passed through the cell with cooling by ice cold
water, the cathodic solution was poured into 100 mL of saturated aqueous NH₄Cl
and extracted with ether (50 mL x 3). The residue obtained by evaporation of
solvent was distilled under reduced pressure (bulb to bulb distillation) in order to
give 3.

2-Methyl-4-octen-2-ol (3a): IR (neat) 3350, 2970, 2890, 1460, 1380, 1150, 975
cm⁻¹; ¹H NMR (CDCl₃) δ 0.90 (t, J = 7.4 Hz, 3H), 1.20 (trans isomer), 1.23 (cis
isomer) (s, 6H), 1.30-1.50 (m, 2H), 1.54 (OH), 1.96-2.10 (m, 2H), 2.15-2.18
(trans isomer), 2.22-2.28 (cis isomer) (m, 2H), 5.45-5.56 (m, 2H); MS m/e
(relative intensity) 127 (28, M⁺-Me), 109 (26), 84 (100), 69 (72), 59 (99), 56 (69);

1-(2-Hexenyl)-1-cyclohexanol (3b): IR (neat) 3360, 2925, 2860, 1450, 970 cm⁻¹;
¹H NMR (CDCl₃) δ 0.90 (trans isomer), 0.91 (cis isomer) (t, J = 7.3 Hz, 3H),
1.20-1.70 (m, 12H), 1.96-2.10 (m, 2H), 2.10-2.16 (trans isomer) 2.19-2.25 (cis
isomer) (m, 2H) 5.45-5.60 (m,2H); MS m/e (relative intensity) 167 (2, M⁺-Me),
99 (100), 81 (37); Anal. Calcd for C₁₂H₂₂O: C, 79.06; H, 12.16. Found: C, 79.07;
H, 12.04.

2,6-Dimethyl-4-hepten-2-ol (3c): IR (neat) 3370, 2975, 2890, 1470, 1380, 1150,
980 cm⁻¹; ¹H NMR (CDCl₃) δ 0.99 (trans isomer), 0.95 (cis isomer) (d, J = 6.7
Hz, 6H), 1.20 (trans isomer), 1.23 (cis isomer) (s, 6H), 1.65 (OH), 2.10-2.40 (m,
3H), 5.35-5.60 (m, 2H); MS m/e (relative intensity) 127 (1, M⁺-Me), 109 (8), 84
(40), 69 (41), 59 (100); Anal. Calcd for C₉H₁₈O: C, 76.00; H, 12.76. Found: C,
75.60; H, 13.03.

3,7-Dimethyl-5-octen-2-ol (3d)¹¹: IR (neat) 3400, 2970, 2890, 1460, 1380, 1140,
980 cm⁻¹; ¹H NMR (CDCl₃) δ 0.91 (trans isomer), 0.95 (cis isomer) (t, J = 7.6
Hz, 6H), 0.99 (d, J = 6.7 Hz, 6H), 1.13 (trans isomer), 1.16 (cis isomer) (s, 3H),
1.40-1.55 (m, 2H), 1.65 (OH), 2.14 (trans isomer), 2.22 (cis isomer) (d, J = 5.9
Hz, 2H), 2.20-2.40 (m, 1H), 5.30-5.60 (m, 2H); MS m/e (relative intensity) 141
(1, M⁺-Me), 109 (10), 84 (27), 73 (100), 69 (25), 55 (19).
5-(3-Cyclohexenyl)-2-methyl-4-penten-2-ol (3e): IR (neat) 3350, 3025, 2980, 2910, 2850, 1650, 1380, 1150, 980, 910 cm⁻¹; ¹H NMR (CDCl₃) δ 1.20 (trans isomer), 1.24 (cis isomer) (s, 6H), 1.30-1.50 (m, 1H), 1.57 (OH), 1.70-1.95 (m, 2H), 2.00-2.10 (m, 3H), 2.15-2.30 (m, 3H), 5.45-5.55 (m, 2H), 5.66-5.70 (m, 2H); MS m/e (relative intensity) 165 (1, M⁺-Me), 122 (60), 107 (20), 93 (30), 80 (40), 68 (99), 59 (100).

5-Ethyl-2-methyl-4-hepten-2-ol (3f): IR (neat) 3350, 2975, 2880, 1460, 1380, 1150, 910 cm⁻¹; ¹H NMR (CDCl₃) δ 0.96 (t, J = 7.6 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H), 1.22 (s, 6H), 1.70 (OH), 2.00-2.15 (m, 4H), 2.21 (d, J = 7.7 Hz, 2H), 5.19 (t, J = 7.7 Hz, 1H); MS m/e (relative intensity) 141 (3, M⁺-Me), 123 (5), 98 (56), 83 (14), 69 (48), 5 (100); Anal. Calcd for C₁₀H₂O₀: C, 76.86; H, 12.90. Found: C, 76.63; H, 13.15.

4-Cyclohexylidene-2-methyl-2-butanol (3g): IR (neat) 3360, 2920, 2850, 1440, 1150, 900 cm⁻¹; ¹H NMR (CDCl₃) δ 1.21 (s, 6H), 1.45-1.60 (m, 6H), 1.50 (OH), 2.10-2.22 (m, 6H), 5.15-5.25 (m, 1H); MS m/e (relative intensity) 153 (4, M⁺-Me), 150 (8), 135 (26), 110 (68), 81 (99); Anal. Calcd for C₁₁H₂O₀: C, 78.51; H, 11.98. Found: C, 78.31; H, 12.18.

2,3-Dimethyl-4-octen-2-ol (3h): IR (neat) 3400, 2970, 2880, 1460, 1380, 1140, 970 cm⁻¹; ¹H NMR (CDCl₃) δ 0.89 (t, J = 7.3 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H), 1.13 (trans isomer), 1.15 (cis isomer) (s, 3H), 1.18 (trans isomer), 1.19 (cis isomer) (s, 3H), 1.30-1.50 (m, 2H), 1.60 (OH), 1.95-2.22 (m, 3H), 5.29-5.60 (m, 2H); MS m/e (relative intensity) 141 (7, M⁺-Me), 123 (4), 98 (54), 69 (55), 59 (100).

Preparation of 7a-b. 3-Trimethylsilyl-2-propen-1-ol (7a) was prepared by the hydride reduction of 3-trimethylsilyl-2-propyn-1-ol with LiAlH₄ in diglyme. The oxidation of 7a with active MnO₂ (prepared by the Attenburrow's method) in pentane gave 3-trimethylsilyl-2-propenal, which was treated with MeMgI in ether to yield 4-trimethylsilyl-3-buten-2-ol (7b).
7a: IR (neat) 3320, 2960, 2870, 1250, 1080, 990, 860, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.06 (s, 9H), 1.54 (OH), 4.17 (dd, J = 4.2, 1.6 Hz, 2H), 5.90 (td, J = 1.6, 18.8 Hz, 1H), 6.17 (td, J = 4.2, 18.8 Hz, 1H)

7b: IR (neat) 3320, 2960, 1620, 1250, 1125, 1060, 990, 865, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.05 (s, 3H), 1.24 (d, J = 6.4 Hz, 3H), 1.61 (OH), 4.19-4.32 (m, 1H), 5.81 (dd, J = 20.4, 1.2 Hz, 1H), 6.07 (dd, J = 18.8, 4.8 Hz, 1H).

**General Procedure for the Cathodic Coupling of acetone (1a) with 7.** The cathodic coupling of 1a and 7 was carried out under similar reaction conditions to those described above. After 2 F/mol of electricity (based on 1a) was passed through the cell under a constant current conditions of 0.2 A, the cathodic solution was poured into 100 mL of saturated aqueous NH₄Cl and extracted with ether (50 mL x 3). The residue obtained by evaporation of solvent was distilled under reduced pressure (bulb to bulb distillation) in order to give 8

2-(Trimethylsilylmethyl)-1,3-butanediol (8a): IR (neat) 3320, 2950, 1250, 1170, 1025, 860, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.02 (s, 9H), 0.21 (dd, J = 15.0, 10.6 Hz, 1H), 0.42 (dd, J = 15.0, 2.3 Hz, 1H), 1.18 (s, 3H), 1.24 (s, 3H), 1.69-1.84 (m, 1H), 2.56 (OH), 3.62-3.68 (m, 2H); MS m/e (relative intensity) 157 (2, M⁺-H₂O-Me), 131 (10), 115 (10), 73 (100), 55 (17); Anal. Calcd for C₉H₂₂O₂Si: C, 56.79; H, 11.65. Found: C, 56.51; H, 11.91.

2-(Trimethylsilylmethyl)-1,3-pentanediol (8b): IR (neat) 3300, 2960, 1250, 1080, 860, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.02 (s, 9H), 0.10-0.37 (m, 2H), 1.18 (d, J = 6.2 Hz, 3H), 1.18 (s, 3H), 1.22 (s, 3H), 1.49-1.60 (m, 1H), 3.25 (OH), 3.70-3.86 (m, 1H); ¹³C NMR (CDCl₃) δ -0.37, 16.12, 23.09, 23.18, 30.57, 49.86, 72.60, 76.21; MS m/e (relative intensity) 171 (2, M⁺-H₂O-Me) 142 (4), 128 (9), 73 (100); Anal. Calcd for C₁₀H₂₄O₂Si: C, 58.77; H, 11.84. Found: C, 58.72; H, 12.04.

The stereochemistry of 8b was determined as follows: As shown in Scheme VI, the reaction of 8b with Me₂SiCl₂ / Et₃N gave the cyclic siloxane 15 [¹H NMR (CDCl₃) δ 0.03 (s, 9H), 0.13 (s, 3H), 0.15 (s, 3H), 0.18 (dd, J = 16.3, 3.8 Hz, 1H), 0.36 (dd, J = 16.3, 3.8 Hz, 1H), 1.17 (s, 3H), 1.19 (d, J = 6.0 Hz, 3H), 1.27 (s,
3H), 1.55-1.70 (m, H\textsubscript{A}), 3.89 (qd, J = 6.2, 9.7 Hz, H\textsubscript{B}) The stereochemical relation between H\textsubscript{A} and H\textsubscript{B} was determined to be \textit{trans} since the coupling constant of \textsuperscript{1}H NMR between H\textsubscript{A} and H\textsubscript{B} was measured to be 9.7 Hz.\textsuperscript{17}

\textbf{Scheme VI}

\begin{center}
\begin{tikzpicture}
  \node (8b) at (0,0) {\includegraphics{8b.png}};
  \node (15) at (2,0) {\includegraphics{15.png}};
  \node[align=center] at (1,0) {8b \quad Me\textsubscript{2}SiCl\textsubscript{2} \quad Et\textsubscript{3}N \quad MeOH};
  \draw[->] (8b) -- (15);
\end{tikzpicture}
\end{center}

\textbf{Competitive Coupling of Acetone (1a) with Olefins.} The competitive cathodic coupling of 1a (5 mmol) with the mixture of olefins (2 mmol each) was performed under similar reaction conditions to those described above. The reaction was quenched after 1.5 F/mol of electricity based on 1a was passed through the cell. At this point, total yield of the coupling products resulted in about 50%.

1-Hexene (9) is commercially available. 1-Hexen-3-ol (10) was prepared by the reaction of vinylmagnesium bromide and butanal. 2-Trimethylsilyl-1-hexene\textsuperscript{18} was prepared by the reaction of \alpha-trimethylsilylvinyllithium\textsuperscript{8} and butanal. 2-Methyl-2-octanol (12)\textsuperscript{19} was identified by the comparison with the authentic sample prepared by the reaction of 2-octanone and methylmagnesium iodide.

\textbf{2-Methyl-4-trimethylsilyl-2-octanol (14):} IR (neat) 3400, 2950, 2870, 1460, 1380, 1250, 840 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta -0.03 (s, 9H), 0.58-0.70 (m, 1H), 0.82-0.92 (m, 3H), 1.19 (s, 6H), 1.23-1.60 (m, 8H); MS m/e (relative intensity) 201 (1, M\textsuperscript{+}-Me), 185 (4), 126 (6), 111 (7), 84 (52), 73 (100), 69 (37), 56 (35); Anal. Calcd for C\textsubscript{12}H\textsubscript{28}OSi: C, 66.59; H, 13.04. Found: C, 66.52; H, 13.27.
References and Notes

1) The cathodic coupling of ketones with usual allylalcohols or vinylsilane which has the trisubstituted olefin structure has not given the coupling product at all.


3) The same stabilizing effect of trimethylsilyl group has been discussed in Chapter 3.


5) In Chapter 4 it has been described that the cathodic coupling of acetone with 2-methyl-1-hepten-3-ol is no diastereoselective but affords 1:1 diastereomixture of 2,4-dimethyl-2,5-nonanediol.

6) GLC, TLC, $^1$H NMR, and $^{13}$C NMR analyses clearly shows the exclusive formation of anti-isomer of 8b, and its stereochemistry was determined by $^1$H NMR of the cyclic siloxane derived from 8b (See Experimental Section).


Part II

Generation of Trihalomethyl Anion by Electrogenerated Base
Chapter 4

Formation of a Reasonably Stabilized Trichloromethyl Anion
by the Reaction of Chloroform with Electrognerated Base,
and its 1,4-Addition to \( \alpha,\beta \)-Unsaturated Carbonyl Compounds

Abstract. : An electrogenerated base (EGB) prepared by the electroreduction of 2-pyrrolidone was used for the deprotonation of \( \text{CHCl}_3 \) forming trichloromethyl anion (\( \text{CCl}_3^- \)) effectively. Thus formed \( \text{CCl}_3^- \) was stable enough to react as a nucleophile, and its 1,4-addition to \( \alpha,\beta \)-unsaturated esters and nitriles gave the corresponding \( \beta \)-trichloromethyl esters and nitriles in good yields, respectively. Moreover, this EGB was also applicable to the reaction of methyl dichloroacetate with \( \alpha,\beta \)-unsaturated esters yielding 1-chloro-1,2-cyclopropanedicarboxylic acid derivatives.

Introduction

The anionic species generated under the condition of electroreduction could act as not only nucleophiles but also bases, however, a few examples are known in the latter case. In 1968, it has been reported in our laboratory that phosphonium ylids were formed by the electroreduction of phosphonium salts.\(^1\) In this reaction, some kind of anionic species formed under the electroreductive condition acted as the base, whereas the actual structure of these species was not always clear. After our study, Iversen reported in 1969 that the electroreduction of azobenzene gave the corresponding anion radical species and it induced the Wittig reaction as the electrogenerated base (EGB).\(^2\) In this study, the structure of EGB is clarified and the role of azobenzene is also proved to be the probasic compound (PB), whereas the other kinds of EGBs had not been exploited until recently.
In 1983, it has been found in our laboratory,\textsuperscript{3} that the electroreduction of 2-pyrrolidone (1) in DMF (Scheme I) using tetraalkylammonium salts (R\textsubscript{4}NX) as supporting electrolytes yielded the corresponding anionic species 2 (2a; R=Et, 2b; R= n-Bu) possessing interesting reactivities as bases.

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

\begin{center}
\begin{align*}
\text{N} & \quad \text{H} \\
\text{R}_4\text{NX} \quad \text{DMF} \quad \text{Pt plate cathode} & \quad \text{1.8 F/mol} \\
1 & \quad \text{+e} + \frac{1}{2} \text{H}_2 \\
2a \quad R = \text{Et}, X = \text{OTs} & \\
2b \quad R = \text{n-Bu}, X = \text{BF}_4
\end{align*}
\end{center}

After this work, the formation of several EGBs which were prepared from other kinds of probasic compounds, such as molecular oxygen,\textsuperscript{4-7} dicyano-(fluoren-9-ylidene)methane,\textsuperscript{8} and carbon tetrachloride,\textsuperscript{9-12} have been reported. As compared with other EGBs mentioned above, 2 promotes a far wider variety of useful reactions which are not always achievable by using the bases prepared by the usual chemical methods.\textsuperscript{3,13-15}

In this chapter, it is described that a reasonably stabilized \textit{CCl\textsubscript{3}}\textsuperscript{-} was formed by the reaction of \textit{CHCl\textsubscript{3}} with 2, and the 1,4-addition of this \textit{CCl\textsubscript{3}}\textsuperscript{-} to \textit{\alpha,\beta-}unsaturated esters and nitriles 3 proceeded in excellent yields with affording \textit{\beta-trichloromethyl} substituted compounds 4 (Scheme II). On the other hand, 1,4-addition of \textit{CCl\textsubscript{3}}\textsuperscript{-} to \textit{\alpha,\beta-}unsaturated carbonyl compounds is usually hardly applicable to the synthesis of \textit{\beta-trichloromethyl}carbonyl compounds since \textit{CCl\textsubscript{3}}\textsuperscript{-} is unstable and shows a strong tendency toward formation of dichlorocarbene through the elimination of chloride ion. Although a number of methods have already been exploited for the formation of \textit{CCl\textsubscript{3}}\textsuperscript{-},\textsuperscript{16,17} these \textit{CCl\textsubscript{3}}\textsuperscript{-} are not stable enough to be used for the 1,4-addition. For example, it has been reported that the addition of \textit{CCl\textsubscript{3}}\textsuperscript{-} to methyl acrylate (3a ; R\textsubscript{1} = R\textsubscript{2} = H, Y = \text{CO}_2\text{Me}) gave methyl \textit{\beta-trichloromethylpropionate} (4a ; R\textsubscript{1} = R\textsubscript{2} = H, Y = \text{CO}_2\text{M}) in only 10-18\% yield.\textsuperscript{18-20} Although it was recently reported that rather stable \textit{CCl\textsubscript{3}}\textsuperscript{-} was formed
in liq.NH$_3$, the yield of 4a formed through its addition to 3a was still only 22%.$^{21}$

![Scheme II](image)

**Scheme II**

**Results and Discussion**

As shown in Scheme III and Table I, it was found that the addition of a solution of 2a into DMF solution of methyl acrylate (3a) and CHCl$_3$ gave methyl ß-trichloromethylpropionate (4a) in good yield.

![Scheme III](image)

**Scheme III**

**Table I. Trichloromethylation of Methyl Acrylate**

<table>
<thead>
<tr>
<th>Run</th>
<th>Mol.ratio EGB 2a / Methyl Acrylate (3a)</th>
<th>Yield of 4a / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>3</td>
</tr>
</tbody>
</table>

a) Excess amount (3 eqv. based on 3a) of chloroform was used.
Moreover, this reaction was found to be promoted by a catalytic amount (0.3 equivalent) of 2a based on 3a (Table I, Run 2). The catalytic cycle of this reaction seems to be completed by the following mechanism shown in Scheme IV. That is, the reaction of 2a with CHCl₃ affords CCl₃⁻ and its addition to 3a gives an anionic intermediate 5a. The reaction of 5a with CHCl₃ leads to the formation of the final product 4a and CCl₃⁻, and the addition of this reformed CCl₃⁻ to 3a yields 5a.²²

The other examples are summarized in Table II. The use of 2a as the base is effective to the 1,4-addition of CCl₃ to methyl crotonate (3b, Run 1) and nitriles (Runs 4-6), whereas it is not effective to the reaction of methyl hexenoate (3c, Run 2). Since it has already been found in our previous study¹⁵ that the activity of 2 as a base was largely influenced by the type of its counter cation (R₄N⁺), the base 2b (R = n-Bu) instead of 2a (R = Et) was utilized for the reaction of 3c with CHCl₃, and a reasonable increase in the yield of 4c was observed (Run 3). Thus the bulkiness of R₄N⁺ is one of the most important factors in this reaction. Since the reaction of 2 with CHCl₃ gives CCl₃⁻ having R₄N⁺ as its counter cation, not only the basicity of 2 but also the nucleophilicity of CCl₃⁻ are much affected by R₄N⁺. Namely, CCl₃⁻ bearing larger R₄N⁺ (in the above case, R = n-Bu) is more nucleophilic than CCl₃⁻ bearing smaller R₄N⁺ (in
the above case, R = Et). It is a reasonable result because the anion having large counter cation is known to be "naked", and have a strong nucleophilicity. From the synthetic point of view, it is noteworthy that the reactivity of EGB can be easily controlled by the selection of the cation part of the supporting electrolyte.

Table II. 1,4-Addition of Trichloromethyl Anion

<table>
<thead>
<tr>
<th>Run</th>
<th>α,β-Unsaturated ester and nitrile 3</th>
<th>Product 4</th>
<th>Yield of 4 / %b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me=C=CO₂Me 3b</td>
<td>Me=CCl₃=CO₂Me 4b</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>n-Pr=C=CO₂Me 3c</td>
<td>n-Pr=CCl₃=CO₂Me 4c</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>3c</td>
<td>4c</td>
<td>35c</td>
</tr>
<tr>
<td>4</td>
<td>CN=C≡CN 3d</td>
<td>Cl₃C≡C≡CN 4d</td>
<td>67</td>
</tr>
<tr>
<td>5</td>
<td>Me=C=CN 3e</td>
<td>Me=CCl₃=CN 4e</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>Me=C≡CN 3f</td>
<td>Cl₃C≡C≡CN 4f</td>
<td>82</td>
</tr>
</tbody>
</table>

a) 0.3 eqv. of 2 and 3 eqv. of CHCl₃ were used. b) Isolated yields based on α,β-unsaturated esters and nitriles. c) 2b was used as the base.

Interestingly, the reaction of CHCl₃ with methyl methacrylate (3g) carried out under the same typical reaction conditions (2a : CHCl₃ = 1 : 9) gave considerably different results from the other α,β-unsaturated esters (3a and 3b). Namely, the reaction gave a mixture of β-trichloromethyl ester 4g and dichlorocyclopropane type compound 6g (Scheme V). Furthermore, when excess amount of 2a was used (2a : CHCl₃ = 1.5 : 1) as the base, 6g was obtained as the main product (70 % yield based on CHCl₃). Thus the amount of 2a changed the aspect of the reaction of 3g with CHCl₃. It can be explained as follows: Under
the typical reaction conditions, the anionic intermediate 5g is easily protonated by the excess amount of CHCl₃ affording 4g, while using 2a in excess retards the protonation of 5g since pyrrolidone, which is formed from 2a by proton abstraction, is a much poor proton donor than CHCl₃. Without suffering the protonation, the anionic center of 5g intramolecularly attacks the trichloromethylated carbon, forming the cyclization product 6g. The presence of a methyl group at the carbon atom bearing the negative charge seems to be an additional essential factor to favor the formation of 6g since the methyl group will increase the reactivity of the anion.

![Scheme V](image)

On the other hand, the reaction of methyl acrylate (3a) or methyl crotonate (3b) with CHCl₃ by using excess 2a (1.5 eqv. based on 3) did not give the corresponding dichlorocyclopropane type product but yielded β-trichloromethyl ester 4a (Scheme III and Table I) or 4 (Table II, Run 1). The transformation of 4b to the corresponding cyclopropane derivative 6b was found to be attainable by the treatment of 4b with LDA (Scheme VI). In this reaction, it was also found that the product 6b was formed as the single stereoisomer of dichlorocyclopropanecarboxylic acid derivative. The configuration between methyl group and methoxycarbonyl group of 6b was trans, and it was determined by ¹H NMR using NOE (See Experimental Section.).
β-Trichloromethyl esters 4 are important materials to flame retardants of cotton, and also 6b and 6g are key intermediates for the synthesis of insecticides. The new method shown in this chapter certainly provides a convenient tool to the synthesis of these important compounds.

Methyl dichloroacetate also showed a similar reactivity to chloroform in the reaction with unsaturated esters (3a, 3b, and 3g) in the presence of 2a (Scheme VII). The reaction carried out in DMF gave the addition products 7 (7a, 7b, and 7g) with yields remarkably higher than those obtained in the similar type of reactions using usual bases (Table III).

Table III. Reaction of 3 with Methyl Dichloroacetate

<table>
<thead>
<tr>
<th>Run</th>
<th>α,β-Unsaturated ester 3</th>
<th>Product 7</th>
<th>Total yield / %</th>
<th>7-cis : 7-trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H H 3a</td>
<td>7a</td>
<td>61</td>
<td>only 7a-trans</td>
</tr>
<tr>
<td>2</td>
<td>Me H 3b</td>
<td>7b</td>
<td>59</td>
<td>5 : 3</td>
</tr>
<tr>
<td>3</td>
<td>H Me 3g</td>
<td>7g</td>
<td>97</td>
<td>1 : 1</td>
</tr>
</tbody>
</table>

a) Conditions; 2a (20 mmol), 3 (50 mmol), HCCl₂CO₂Me (10 mmol).
b) Based on HCCl₂CO₂Me.
Experimental Section

General. IR spectra were obtained on a Hitachi 260-10 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were measured on a Varian Gemini-200 (200 MHz) spectrometer, and the chemical shift values ($\delta$) are expressed in ppm downfield from the internal TMS standard. GC analyses were carried out on a Shimadzu GC-4C or GC-12A instrument. High resolution mass spectra (HRMS) were determined on a JEOL JES-DX 300. Melting points were measured by a Yanaco Micro melting point apparatus. Elemental analyses were performed by the Center for Instrumental Analysis of Kyoto University. The constant electrocurrent was supplied with Takasago GP-050-2 regulated DC power supply.

Material. Methyl 2-hexanoate was prepared by the known method. Other $\alpha,\beta$-unsaturated esters and nitriles are commercially available. They were freshly distilled before using. DMF was run slowly down a column of fresh alumina (ICN Alumina B, Act I) and stocked under nitrogen atmosphere. 2-Pyrrolidone was commercially available and used without further purification.

Preparation of a DMF Solution of 2a,b. A solution of 2-pyrrolidone 1 (5 mmol) in 10 mL of DMF containing Et$_4$N OTs (5 mmol) as a supporting electrolyte was placed in a cathodic chamber of an electrolysis cell equipped with a platinum electrodes ($2 \times 2$ cm$^2$) and a glass filter diaphragm. The anodic solution was 6 mL of DMF containing Et$_4$N OTs (3 mmol). The preparation of a DMF solution of 2a was accomplished by passing 1.8 F/mol of electricity through the cell at room temperature under the condition of constant current (0.2 A). A solution of 2b was prepared by the same procedure as above using $n$-Bu$_4$NBF$_4$ as a supporting electrolyte.

Trichloromethylation of $\alpha,\beta$-Unsaturated Esters 3a-c and Nitriles 3d-f. Into a mixture of 3 (15 mmol) and chloroform (45 mmol) in 5 mL of DMF was added a solution of 2a (5 mmol) at -70°C, and the solution was stirred for 1 h at this
temperature and then allowed to warm to room temperature. After stirring for additional 4 h, the reaction mixture was poured into an ice-cold saturated aqueous NH₄Cl (50 mL) and the aqueous solution was extracted with ether (50 mL x 3). The combined organic layer was then washed twice with 50 mL of brine, dried over MgSO₄, and concentrated. The residue was purified by a bulb to bulb distillation.

Methyl 4,4,4-Trichlorobutyrate (4a): IR (neat) 1742, 1440, 1310, 1208, 1180, 800, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 2.57-3.27 (m, 4H), 3.73 (s, 3H); MS m/e (relative intensity) 177 (17, M⁺+4-OMe), 175 (52), 173 (59), 171 (42), 169 (63), 137 (35), 109 (78), 105 (100), 59 (59).

Methyl 3-Methyl-4,4,4-trichlorobutyrate (4b): IR (neat) 1740, 1440, 1285, 1200, 1180, 800, 775 cm⁻¹; ¹H NMR (CDCl₃) δ 1.38 (d, J = 7.3 Hz, 3H), 2.42 (dd, J = 16.5, 10.3 Hz, 1H), 3.10 (dd, J = 16.5, 3.3 Hz, 1H), 3.07-3.23 (m, 1H), 3.74 (s, 3H); ¹³C NMR (CDCl₃) δ 17.01, 38.16, 51.65, 52.22, 104.91, 172.12; MS m/e (relative intensity) 187 (19, M⁺+4-35Cl), 183 (12), 147 (24), 119 (52), 101 (90), 74 (100), 59 (59); Anal Calcd for C₆H₉Cl₃O₂: C, 32.83; H, 4.13; Cl, 48.46. Found: C, 33.07; H, 4.16; Cl, 48.43.

Methyl 3-Trichloromethylhexanoate (4c): IR (neat) 1750, 1440, 1180, 800, 770 cm⁻¹; ¹H NMR (CDCl₃) δ 0.97 (t, J = 5.0 Hz, 3H), 1.13-2.07 (m, 4H), 2.37 (dd, J = 17.0, 9.0 Hz, 1H), 2.67-3.23 (m, 2H), 3.67 (s, 3H); MS m/e (relative intensity) 216 (5), 214 (5), 211 (5), 129 (78), 97 (75), 74 (100), 69 (61), 59 (22); Anal Calcd for C₈H₁₅Cl₃O₂: C, 38.82; H, 5.29; Cl, 42.96. Found: C, 39.02; H, 5.26; Cl, 42.69.

4,4,4-Trichlorobutynitrile (4d): IR (neat) 2250, 800, 780, 765 cm⁻¹; ¹H NMR (CDCl₃) δ 2.60-3.30 (m, 4H); MS m/e (relative intensity) 138 (65), 136 (100, M⁺-Cl), 119 (32), 117 (34), 100 (31), 86 (37), 84 (53).

3-Methyl-4,4,4-trichlorobutynitrile (4e): IR (neat) 2240, 1460, 765 cm⁻¹; ¹H NMR (CDCl₃) δ 1.57 (d, J = 7.2 Hz, 3H), 2.58 (dd, J = 16.2, 9.4 Hz, 1H), 2.90-3.02 (m, 1H), 3.02-3.15 (m, 1H); ¹³C NMR (CDCl₃) δ 16.36, 21.67, 51.51, 102.76, 117.32; MS m/e (relative intensity) 172 (5), 170 (5, M⁺-Me), 152 (64), 150 (100), 119 (71), 117 (71), 114 (74), 84 (31), 68 (59); Anal Calcd for
C₅H₆Cl₃N: C, 32.21; H, 3.24; Cl, 57.04; N, 7.51. Found: C, 32.18; H, 3.14; Cl, 56.91; N, 7.56.

2-Methyl-4,4,4-trichlorobutyronitrile (4f): IR (neat) 2250, 1460, 1080, 765, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 1.53 (d, J = 7.0 Hz, 3H), 2.75-2.83 (m, 1H), 3.10-3.30 (m, 2H); ¹³C NMR (CDCl₃) δ 19.12, 23.34, 57.57, 96.65, 121.58; MS m/e (relative intensity) 187 (19, M⁺+4 Cl), 183 (12), 147 (24), 111 (52), 101 (90), 74 (100), 59 (69); Anal Calcd for C₅H₆Cl₃N: C, 32.21; H, 3.24; Cl, 57.04; N, 7.51. Found: C, 32.09; H, 3.18; Cl, 56.80; N, 7.49.

Trichloromethylation of Methyl Methacrylate (3g). Into a solution of methyl methacrylate (25 mmol) and chloroform (20 mmol) in DMF was added a solution of 2a at -70°C under nitrogen atmosphere, and the mixture was stirred for 1 h at this temperature and for additional 4 h at room temperature. After usual aqueous workup, methyl 2,2-dichloro-3-methylcyclopropanecarboxylate (6g) was isolated by a bulb to bulb distillation (120-130°C/20 mmHg, 70% based on chloroform), and the distillation residue contained methyl 2-methyl-4,4,4-trichlorobutyrate (4g, 150°C/20 mmHg, 10%).

Methyl 2-Methyl-4,4,4-trichlorobutyrate (4g): IR (neat) 1745, 1440, 1180, 795, 712 cm⁻¹; ¹H NMR (CDCl₃) δ 1.34 (d, J = 7.2 Hz, 3H), 2.66 (dd, J = 14.9, 2.9 Hz, 1H), 2.99 (qdd, J = 7.2, 8.1, 2.9 Hz, 1H), 3.47 (dd, J = 14.9, 8.1 Hz, 1H), 3.73 (s, 3H); ¹³C NMR (CDCl₃) δ 19.03, 38.07, 52.40, 57.76, 98.61, 176.12; MS m/e (relative intensity) 191 (9, M⁺+4-OMe), 189 (28), 187 (29), 185 (8), 183 (13), 147 (31), 123 (52), 119 (51), 89 (45), 63 (53), 59 (100); Anal Calcd for C₆H₉Cl₂O₂: C, 32.83; H, 4.13; Cl, 48.46. Found: C, 32.90; H, 4.09; Cl, 48.28.

Methyl 2,2-Dichloro-1-methylcyclopropanecarboxylate (6g): IR (neat) 1742, 1420, 1288, 1205, 1170, 1100, 1055, 792, 755 cm⁻¹; ¹H NMR (CDCl₃) δ 1.43 (d, J = 7.6 Hz, 1H), 1.59 (s, 3H), 2.29 (d, J = 7.6 Hz, 1H), 3.78 (s, 3H); ¹³C NMR (CDCl₃) δ 18.43, 31.00, 35.56, 52.97, 52.78, 170.19; MS m/e (relative intensity) 184 (16, M⁺+2), 182 (24, M⁺), 151 (39), 147 (43), 125 (53), 123 (83), 119 (64), 103 (30), 87 (70), 69 (90), 59 (100); HRMS calcd for C₆H₈Cl₂O₂ 181.99024, found 181.99040.
Preparation of Methyl 2,2-Dichloro-3-methylcyclopropanecarboxylate (6b). Into a solution of lithium diisopropylamide prepared from 6 mmol of diisopropylamine in 10 mL of dry THF and 4 mL of n-buthyllitium (1.5 M solution in hexane) was added dropwise 4b (1.20 g, 5.5 mmol) in 5 mL of dry THF at -60°C under nitrogen atmosphere. The solution was stirred for 30 min at this temperature, allowed to warm to room temperature, and then treated with 20 mL of aqueous 1N HCl. After extraction with ether (20 mL x 3), the combined extracts were washed successively with 20 mL of 1N HCl and 20 mL of brine, dried over MgSO₄, and concentrated. The residue was purified by a bulb to bulb distillation (120°C/20 mmHg) to give 6b in 68% yield. IR (neat) 1745, 1440, 1325, 1225, 1172, 745 cm⁻¹; ¹H NMR (CDCl₃) δ 1.36 (d, J =6.1 Hz, 3H), 2.09 (d, J =8.0 Hz, 1H), 2.22 (qd, J = 6.2, 7.8 Hz, 1H), 3.87 (s, 3H); ¹³C NMR (CDCl₃) δ 13.72, 31.18, 38.83, 52.74, 63.47, 168.22; MS (m/e, relative intensity) 184 (10, M⁺+2), 182 (15, M⁺), 151 (22), 147 (27), 125 (50), 123 (78), 87 (37), 69 (39), 59 (100); HRMS calcd for C₆H₈Cl₂O₂ 181.99024, found 181.99025. The stereochemistry of 6b was determined by ¹H NMR using NOE between Hₐ and the methyl protons attached to cyclopropane ring (Figure I). That is, the irradiation of Hₐ (δ 2.09) showed strong NOE at methyl protons (δ 1.36), and this result indicated that the configuration between Hₐ and the methyl group is cis.

![Figure I](image)

Reaction between α,β-Unsaturated Esters and Methyl Dichloroacetate. Into a solution of α,β-unsaturated ester (25 mmol) and methyl dichloroacetate (5 mmol) in 10 mL of DMF was added a solution of 2a in DMF at -70°C. The solution was stirred for 1 h at this temperature, and then warmed to room temperature. After additional stirring for 3 h, the mixture was poured into
saturated aqueous NH₄Cl (70 mL) and the aqueous solution was extracted with ether (50 mL x 3). The combined ethereal solution was washed twice with brine (50 mL), and dried over MgSO₄. The residue obtained after evaporation was purified by silica gel column (hexane : AcOEt = 10 : 1) for 7a, or a bulb to bulb distillation for 7b-c.

Dimethyl 1-Chloro-1,2-trans-cyclopropanedicarboxylate (7a-trans): IR (neat) 1750, 1445, 1392, 1292, 1240, 1210, 1185, 1142 cm⁻¹; ¹H NMR (CDCl₃) δ 1.97 (d, J = 8.4 Hz, 2H), 2.71 (t, J = 8.5 Hz, 1H), 3.97 (s, 3H), 3.82 (s, 3H); ¹³C NMR (CDCl₃) δ 23.10, 30.82, 42.53, 52.80, 54.03, 167.93, 169.46; MS m/e (relative intensity) 192 (2, M⁺), 161 (50), 160 (42), 157 (85), 156 (99), 132 (83), 105 (48), 59 (100), 54 (58); HRMS calcd for C₇H₉C₁O₄ 192.01897, found 192.01799. The configuration between two methoxycarbonyl groups of 6a was determined to be trans by the comparison of the spectroscopic data of the cis-isomer. The procedure for the preparation of the cis-isomer is as follows: The saponification of 7a-trans gave the isomeric mixture of 1-chloro-1,2-cyclopropanedicarboxylic acid. This mixture was heated with acetylchloride to give the cyclic anhydride 8a (Scheme VIII), as the major product. The esterification of 8a in the acidic condition afforded dimethyl 1-chloro-1,2-cis-cyclopropanedicarboxylate (7a-cis).

Scheme VIII

1-Chloro-1,2-cyclopropanedicarboxylic Anhydride (8a): IR (KBr disk) 1875, 1800, 1280, 1160, 995, 945, 930, 900, 870, 765, 755 cm⁻¹; ¹H NMR (CDCl₃) δ 3.06 (dd, J = 8.8, 4.8 Hz, 1H), 2.02-2.23 (m, 2H).
Dimethyl 1-Chloro-1,2-cis-cyclopropanedicarboxylate (7a-cis): IR (neat) 1750, 1440, 1392, 1240, 1210, 1180, 1125 cm⁻¹; \(^1\)H NMR (CDCl₃) δ 1.71 (dd, \(J = 9.9, 6.5\) Hz, 1H), 2.18 (dd, \(J = 7.8, 6.5\) Hz, 1H), 2.47 (dd, \(J = 9.9, 7.8\) Hz, 1H), 3.72 (s, 3H), 3.79 (s, 3H); \(^13\)C NMR (CDCl₃) δ 22.40, 31.75, 43.05, 52.71, 53.64, 167.34, 169.03.

Dimethyl 1-Chloro-3-methyl-1,2-cyclopropanedicarboxylate (7b): IR (neat) 1740, 1440, 1260, 1185, 1120 cm⁻¹; \(^1\)H NMR (CDCl₃) cis-isomer δ 1.36 (d, \(J = 6.3\) Hz, 3H), 2.04 (d, \(J = 7.9\) Hz, 1H), 2.31 (m, 1H), 3.70 (s, 3H), 3.78 (s, 3H), trans-isomer δ 1.24 (d, \(J = 6.4\) Hz, 3H), 2.31 (m, 1H), 2.71 (d, \(J = 8.3\) Hz, 1H), 3.77 (s, 3H), 3.84 (s, 3H); MS m/e (relative intensity) 191 (2, M⁺-Me), 174 (49), 149 (95), 147 (99), 139 (52), 115 (72), 59 (100); Anal Calcd for C₇H₉ClO₄: C, 46.50; H, 5.37; Cl, 17.16. In each isomer, the stereochemical relation between methyl group at 3-position and methoxycarbonyl group at 2-position was determined to be trans since the irradiation of methyl group (δ 1.24 or 1.36) showed NOE on proton at 2-position (δ 2.71 or 2.04) (Figure II).

![Figure II](image.png)

Dimethyl 1-Chloro-2-methyl-1,2-cyclopropanedicarboxylate (7c): IR (neat) 1740, 1440, 1305, 1280, 1170 cm⁻¹; \(^1\)H NMR (CDCl₃) cis-isomer δ 1.28 (d, \(J = 6.5\) Hz, 3H), 1.59 (s, 3H), 2.32 (d, \(J = 6.5\) Hz, 1H), 3.69 (s, 3H), 3.76 (s, 3H), trans-isomer δ 1.43 (s, 3H), 1.88 (d, \(J = 6.7\) Hz, 3H), 2.08 (d, \(J = 6.6\) Hz, 1H), 3.79 (s, 3H), 3.84 (s, 3H); MS m/e (relative intensity) 206 (5, M⁺), 175 (53), 174 (53), 171 (28), 170 (32), 146 (100), 131 (39), 59 (36); HRMS calcd for C₈H₁₁ClO₄ 206.03463, found 206.03481.
References and Notes


(22) The similar catalytic cycle has been reported by Baizer.20 In this study the initial CCl$_3^-$ was formed by the cathodic reduction of CCl$_4$.


Chapter 5

A Novel Trifluoromethylation of Aldehydes and Ketones Promoted by Electrogenerated Base

Abstract: A base generated by the electroreduction of 2-pyrrolidone deprotonated trifluoromethane to form a trifluoromethyl anion (CF$_3^-$). Thus formed CF$_3^-$ bears tetraalkylammonium ion (R$_4$NX) as a counter ion and the nucleophilicity of CF$_3^-$ was found to be much influenced by the size of alkyl group (R) of R$_4$NX. Moreover, in the presence of hexamethyldisilazane, this CF$_3$ reacted with a variety of aldehydes and ketones to afford trifluoromethylcarbinols in high yield.

Introduction

Organofluorine compounds have recently found increasing use in the fields of agrochemicals and pharmaceuticals. A number of antiviral, antitumor, and antifungal agents have been developed, which showed new biological activity induced by fluorine substitution.$^1$ And organofluorine compounds are often used as probes for studying biochemical processes. These applications stem from the special properties conferred on a molecule by the presence of fluorine.$^2$ The influence of fluorine on a molecule can be summarized as follows:

1. Fluorine and hydrogen are comparable in size. Thus, a molecule and its fluoro analogues are, for example, almost indistinguishable to an enzyme-receptor site.
2. The high C-F bond energy leads to enhanced thermal stability.
3. The high electronegativity of fluorine frequently alters chemical properties.
4. Fluorine substitution usually increases lipid solubility and this increases the rate of transport of biologically active compounds across lipid membranes.

Concomitant with an increasing understanding of the behavior of organofluorine compounds,\textsuperscript{1-3} much effort has been put into developing new methods for the preparation of fluorinated and perfluoroalkylated compounds. Among them, the development of trifluoromethylating reagent has attracted special attention because of their potential use for the synthesis of biologically active drugs and agrochemicals.\textsuperscript{4} Although trifluoromethylation of aromatics has been achieved with a variety methods so far,\textsuperscript{5} that of carbonyl compounds has been very limited.

The trifluoromethyl anion, or its chemical equivalent, would obviously be valuable for trifluoromethylation of carbonyl compounds,\textsuperscript{6} however, the generation of such a species is difficult, due to its low stability.\textsuperscript{7,8} Its formation has so far been achieved by the reaction of dibromodifluoromethane\textsuperscript{9,10} or iodotrifluoromethane\textsuperscript{11-13} with Zn, under rather unusual reaction conditions. The recently reported\textsuperscript{14,15} trifluoromethylation of carbonyl compounds involved the use of ( trifluoromethyl)trimethylsilane\textsuperscript{16} as the source of the trifluoromethyl anion.

In the preceding chapter, it was described that pyrrolidone anion 2 prepared by the electroreduction of 2-pyrrolidone (1) (Scheme I)\textsuperscript{17-20} was remarkably effective for the generation of trichloromethyl anion (CCl$_3^-$) by the deprotonation of chloroform (CHCl$_3$).\textsuperscript{17} This CCl$_3^-$ was found to react with $\alpha,\beta$-unsaturated esters and nitriles yielding the corresponding $\beta$-trichloromethylated products in high yields though CCl$_3^-$ is usually known to be too unstable to react as a nucleophile.

In this chapter, it is described that trifluoromethyl anion (CF$_3^-$), which is far more unstable than CCl$_3^-$, could be efficiently formed by deprotonation of trifluoromethane (CHF$_3$) with the base 2 (Scheme II).
Results and Discussion

Because the formation of CF$_3^-$ by deprotonation of CHF$_3$ has never been reported, the effect of a variety of bases was studied. The species generated was then allowed to react with benzaldehyde (3a) (Scheme III).

Although CF$_3^-$ could be formed by treatment of CHF$_3$ with some common bases (Table I, Runs 1 and 3), the yield of phenyl(trifluoromethyl)carbinol (4a) from the subsequent reaction was low. The use of NaH or tert-BuOK as the base led to the formation of a mixture of benzyl alcohol and benzoic acid as the main products. They arose from the Cannizzaro reaction of 3a.

On the other hand, the use of electrogenerated 2b or 2c as the base led to a remarkable increase in the yield of 4a (Table I, Runs 6 and 7). Furthermore, the results shown in Table I clearly indicated that the structure of the counter ion of the electrogendrated pyrrolidone anion had great influence on both stability and reactivity of CF$_3^-$ (Table I, Runs 5, 6, and 7). That is, CF$_3^-$ bearing larger tetraalkylammonium ion (R$_4$N$^+$) seems to be more nucleophilic and has less tendency to decompose by elimination of fluoride ion.
Other electrogernated bases bearing \( n\)-Bu\(_4\)N\(^+\) were also tested for the generation of CF\(_3^-\) from CHF\(_3\) (Table I, Runs 8 and 9), however, they did not have the activity similar to 2. It indicates that rather high basicity (pKa >14) is necessary to the deprotonation of CHF\(_3\).\(^{21}\)

**Scheme III**

![Scheme III](image)

**Table I. Trifluoromethylation of Benzaldehyde\(^a\)**

<table>
<thead>
<tr>
<th>Run</th>
<th>Base</th>
<th>Yield of 4a / %(^b)</th>
<th>Run</th>
<th>Base</th>
<th>Yield of 4a / %(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaH</td>
<td>28</td>
<td>8</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>LiH</td>
<td>0</td>
<td>9</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>tert.-BuOK</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( n)-Bu(_4))NOH (40% aq.)</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5(^c)</td>
<td>[R(_2)N]^+]</td>
<td>34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6(^c)</td>
<td>2b (R = n-Bu)</td>
<td>74</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7(^c)</td>
<td>2c (R = n-Oct)</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) All reactions were performed in DMF using 1.5 eqv. of base based on 3a.  
\(^b\) Isolated yield.  
\(^c\) Generated by the electroreduction of the corresponding probasic compounds in DMF using tetraalkylammonium salts as supporting electrolytes.
The trifluoromethylation of aromatic aldehydes promoted by electro-generated 2b gave good yields of trifluoromethyl carbinols (Scheme IV, Table II). Interestingly, benzaldehydes (3) having electron donating groups were found to be favorable for the formation of 4. This substituent effect seems to be abnormal since CF$_3^-$ reacts as a nucleophile. This results indicates that the rate of CF$_3^-$ addition step is not always important to this reaction but the stability of the intermediate 5 formed by the addition of CF$_3^-$ to 3 (Scheme IV) or the product 4 is the dominant factor. The anionic center (O') of 5 which has electron donating group, such as methoxy group, could more tightly interact with R$_4$N$^+$, and this tight interaction could promote the reaction.

**Scheme IV**

![Scheme IV](image)

**Table II. Trifluoromethylation of Substituted Benzaldehydes using 2b**

<table>
<thead>
<tr>
<th>Run</th>
<th>Benzaldehydes 3</th>
<th>Yield of 4 / %$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OMe H</td>
<td>4b 92</td>
</tr>
<tr>
<td>2</td>
<td>iso-Pr H</td>
<td>4c 56</td>
</tr>
<tr>
<td>3</td>
<td>Et H</td>
<td>4d 60</td>
</tr>
<tr>
<td>4</td>
<td>OMe OMe</td>
<td>4e 78</td>
</tr>
<tr>
<td>5</td>
<td>H H</td>
<td>4a 74</td>
</tr>
<tr>
<td>6</td>
<td>Cl H</td>
<td>4f 33</td>
</tr>
</tbody>
</table>

$^a$ Isolated yield.
The trifluoromethylation of aliphatic ketones, however, did not give satisfactory results under the same reaction conditions (Table III, Runs 1 and 5). As mentioned above, the trapping of anion center (O') of the intermediate formed by the addition of CF$_3^-$ to a ketone is very important to this reaction. Then, various kinds of trapping reagents of O-anion were examined. Finally, it was found that the presence of hexamethyldisilazane (HMDS) in the reaction mixture brought about a remarkable increase in the yield of product (Table III, Runs 2 and 6). The presence of Ac$_2$O, Me$_3$SiCl, or H$_2$O in the reaction mixture, instead of HMDS, did not increase the yield of 4g. The presence of HMDS was also effective in promoting the trifluoromethylation of other ketones (Table III, Runs 3-10).

It seems reasonable to assume that HMDS promoted the reaction by silylating the intermediate 6, formed by the reaction of 2-undecanone (3g) with CF$_3^-$ (Scheme V). Silyl ether 7 was, in fact, detected in the reaction mixture. Another roll of HMDS could be the inhibitor of the aldol condensation of ketones since the effect of HMDS was remarkable in the trifluoromethylation of acetophenone which is labile to the aldol condensation (Table III, Run 5 and 6).

Scheme V
### Table III. Trifluoromethylation of Carbonyl Compounds

<table>
<thead>
<tr>
<th>Run</th>
<th>Carbonyl compound</th>
<th>Method&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Product</th>
<th>Yield / %&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$C(=O)(CH$_2$)$_6$CH$_3$</td>
<td>A</td>
<td>CF$_3$OH</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$C(=O)(CH$_2$)$_8$CH$_3$</td>
<td>B</td>
<td>CH$_3$C(=O)(CH$_2$)$_6$CH$_3$</td>
<td>4g</td>
</tr>
<tr>
<td>3</td>
<td>CH$_3$(CH$_2$)$_4$C(=O)(CH$_2$)$_4$CH$_3$</td>
<td>B</td>
<td>CF$_3$OH</td>
<td>4h</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>B</td>
<td></td>
<td>4i</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>A</td>
<td></td>
<td>4j</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>B</td>
<td></td>
<td>4k</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>A</td>
<td></td>
<td>4l</td>
</tr>
<tr>
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<td></td>
<td>B</td>
<td></td>
<td>4m</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>A</td>
<td></td>
<td>4l</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>B</td>
<td></td>
<td>4m</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>B</td>
<td></td>
<td>4n</td>
</tr>
</tbody>
</table>

<sup>a</sup> All reactions were performed in DMF, using 3 eqv. (based on carbonyl compound) of 2b. Method A: no HMDS present. Method B: 6 eqv. of HMDS present in the reaction mixture.<br>
<sup>b</sup> Isolated yield of pure compound.
It was also found that the addition of 2b into a mixture of benzaldehyde (3a) and 1,1,1-trifluoro-2,2-dichloroethane (CF$_3$CCl$_2$H) in DMF led to the formation of alcohol 8 in fair yield (Scheme VI). This result was interesting because the formation of 8$^{25}$ indicated the involvement of trifluorodichloroethyl anion (CF$_3$CCl$_2^-$) in which the negative charge is localized on the carbon atom α to the trifluoromethyl group. An anion of this type is highly unstable,$^{26,27}$ and hence reports of its nucleophilic addition to carbonyl compounds are rare.

Why the electrogenerated base was so effective in promoting the formation and subsequent reaction of the trifluoromethyl anion equivalent is not clear. However, it seems reasonable to assume that two factors, the use of a tetraalkylammonium counter ion and the use of a highly aprotic reaction medium, were, at least in part, responsible for the observed stability of CF$_3^-$.
**Experimental Section**

**General.** IR spectra were obtained on a Hitachi 260-10 spectrometer. \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR spectra were measured on a Varian Gemini-200 (200 MHz) spectrometer, and the chemical shift values (δ) are expressed in ppm downfield from the internal TMS standard. GC analyses were carried out on a Shimadzu GC-4C or GC-12A instrument. High resolution mass spectra (HRMS) were determined on a JEOL JES-DX 300. Melting points were measured by a Yanaco Micro melting point apparatus. Elemental analyses were performed by the Center for Instrumental Analysis of Kyoto University. The constant electrocurrent was supplied with Takasago GPO50-2 regulated DC power supply.

**Material.** 5-Norbornen-2-one was prepared by the known method.\(^{28}\) Other carbonyl compounds were commercially available and used after purification by distillation. Tetraoctylammonium bromide was prepared by the reaction of octyl bromide with trioctylamine. DMF was run down a column of fresh alumina (ICN Alumina B, Act I) and stocked under nitrogen atmosphere. 2-Pyrrolidone was commercially available and used without further purification.

**Preparation of a DMF Solution of 2a-c.** A solution of 2-pyrrolidone (1) (5 mmol) in 10 mL of DMF containing R\(_4\)NX (2a, R = Et; 2b, R = Bu; 2c, R = Oct; X = OTs, BF\(_4\), or Br) (5 mmol) as a supporting electrolyte was placed in a cathodic chamber of an electrolysis cell equipped with a platinum electrode (2 x 2 cm) and a glass filter diaphragm. Into the anodic chamber of the cell placed with platinum electrode (2 x 2 cm) was added 6 mL of DMF containing R\(_4\)NX (3 mmol). The preparation of a DMF solution 2 was accomplished by passing 1.8 F/mol of electricity through the cell at room temperature under the condition on constant current (0.2 A).

**Trifluoromethylation of Benzaldehydes 3a-f.** Into a cold solution (-50 °C) of a benzaldehyde 3 (3 mmol) in DMF (5 mL) was dissolved gaseous
trifluromethane (c.a. 1 g). A solution of 2b (5 mmol) in DMF (10 mL) was then added dropwise at such a rate as to maintain the temperature below -50 °C. The reaction mixture was allowed to warm to -10°C. After the stirring at this temperature for 5 h, the reaction solution was poured into 50 mL of saturated aqueous NH₄Cl, and extracted with ether (50 mL x 3). The combined organic extracts were washed successively with 1N HCl (50 mL) and brine (50 mL), and then dried over MgSO₄. After evaporation of solvent, the product was isolated by a silica gel column (Hexane : AcOEt = 10 : 1).

**1-Phenyl-2,2,2-trifluoroethanol (4a):** IR (neat) 3425, 1280, 1180, 845, 775 cm⁻¹; ¹H NMR (CDCl₃) δ 2.83 (OH), 5.00 (q, J_HCF = 6.8 Hz, 1H), 7.30-7.53 (m, 5H); ¹³C NMR (CDCl₃) δ 72.81 (q, J_CCF = 32.4 Hz), 124.42 (q, J_CF = 284.8 Hz), 128.61, 129.76, 130.74, 135.05; MS m/e (relative intensity) 176 (35, M⁺), 107 (100), 79 (43), 77 (15); HRMS calcd for C₈H₇F₃O 176.04491, found 176.04382.

**1-(4-Methoxyphenyl)-2,2,2-trifluoroethanol (4b):** IR (neat) 3450, 1620, 1520, 1260, 1180, 1135, 1040, 825, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 2.67 (OH), 3.75 (s, 3H), 4.93 (q, J_HCF = 6.8 Hz, 1H), 6.75-7.42 (m, 4H); MS m/e (relative intensity) 206 (43, M⁺), 137 (100), 109 (17), 77 (3); HRMS calcd for C₉H₉F₃O 206.05547, found 206.05436.

**1-[4-(1-Methylethyl)phenyl]-2,2,2-trifluoroethanol (4c):** IR (neat) 3400, 1620, 1520, 1270, 1175, 1130, 820, 695 cm⁻¹; ¹H NMR (CDCl₃) δ 1.27 (d, J = 7.2 Hz, 6H), 2.53 (OH), 2.94 (sept, J = 7.2 Hz, 1H), 4.97 (q, J_HCF = 6.9 Hz, 1H), 7.20-7.55 (m, 4H); MS m/e (relative intensity) 218 (55, M⁺), 203 (58), 185 (9), 149 (100), 119 (27), 105 (21); Anal Calcd for C₁₁H₁₃F₃O: C, 60.55; H, 6.00; F, 26.12. Found: C, 60.42; H, 5.98; F, 26.18.

**1-(4-Ethylphenyl)-2,2,2-trifluoroethanol (4d):** IR (neat) 3400, 1280, 1180, 1135, 825, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 1.25 (t, J = 7.8 Hz, 3H), 2.28 (OH), 2.70 (q, J = 7.8 Hz, 2H), 5.00 (q, J_HCF = 6.6 Hz, 1H), 7.20-7.52 (m, 4H); ¹³C NMR (CDCl₃) δ 15.46, 28.71, 73.01 (q, J_CCF = 31.9 Hz), 124.71 (q, J_CF = 284.0 Hz), 127.82, 128.59, 131.66, 146.32; MS m/e (relative intensity) 204 (84, M⁺), 189 (4), 135 (98), 120 (8), 105 (18), 79 (100); HRMS calcd for C₁₀H₁₁F₃O 204.07623, found 204.07798.
1-(3,4-Dimethoxyphenyl)-2,2,2-trifluoroethanol (4e): mp 111.0-111.5 °C (benzene); IR (KBr disk) 3460, 1615, 1600, 1520, 1292, 1260, 1235, 1150, 1120, 880, 860, 820, 750, 715 cm⁻¹; ¹H NMR (CDCl₃) δ 2.65 (OH), 3.90 (s, 6H), 4.95 (q, J_HCF = 6.0 Hz, 1H), 6.87-7.12 (m, 3H); MS m/e (relative intensity) 236 (91, M⁺), 167 (100), 139 (54), 124 (10), 108 (6); Anal Calcd for C₁₀H₁₂F₃O₃: C, 50.85; H, 4.69; F, 24.13. Found: C, 51.09; H, 4.65; F, 24.02.

1-(4-Chlorophenyl)-2,2,2-trifluoroethanol (4f): IR (neat) 3400, 1610, 1505, 1280, 1180, 1140, 820, 740, 690 cm⁻¹; ¹H NMR (CDCl₃) δ 2.92 (OH), 5.00 (m, 1H), 7.32 (m, 4H); MS m/e (relative intensity) 212 (9, M⁺+2), 210 (29, M⁺), 143 (33), 141 (100), 113 (14), 77 (32); HRMS calcd for C₈H₆ClF₃O 210.00598, found 210.00402.

Trifluoromethylation of Other Carbonyl Compounds. Into a cold solution (-50 °C) of a carbonyl compound 3 (3 mmol) and hexamethyldisilazane (18 mmol) in DMF (5 mL) was dissolved gaseous trifluoromethane (c.a. 1.5 g). A solution of 2b (5 mmol) in DMF (10 mL) was then added dropwise at such a rate as to maintain the temperature below -50 °C. The reaction mixture was allowed to warm to -10°C, and stirred for 5 h at this temperature and additional 8 h at room temperature. After the usual aqueous workup, the product was isolated by silica gel column (Hexane : AcOEt = 10 : 1).

1,1,1-Trifluoro-2-methylundecan-2-ol (4g): IR (neat) 3410, 2975, 2950, 2870, 1480, 1165 cm⁻¹; ¹H NMR (CDCl₃) δ 0.78-1.07 (m, 3H), 1.08-1.42 (m, 14H), 1.42-1.80 (m, 5H) 1.83 (OH); ¹³C NMR (CDCl₃) δ 14.16, 20.60, 22.78, 29.41, 29.63, 30.06, 32.02, 35.29, 73.99 (q, J_CCF = 29.8 Hz), 127.00 (q, J_CF = 288.8 Hz); MS m/e (relative intensity) 222 (8, M⁺-H₂O), 171 (14), 112 (42), 97 (27), 83 (61), 70 (100), 56 (73), 43 (54); Anal Calcd for C₁₂H₂₃F₃O: C, 59.98; H, 9.65; F, 23.72. Found: C, 60.10; H, 9.88; F, 23.85.

6-Trifluoromethylundecan-6-ol (4h): IR (neat) 3420, 2970, 2940, 2880, 1475, 1160 cm⁻¹; ¹H NMR (CDCl₃) δ 0.89 (t, J = 6.5 Hz, 6H), 1.20-1.46 (m, 12H) 1.51-1.75 (m, 4H) 1.80 (OH); ¹³C NMR (CDCl₃) δ 13.74, 22.17, 22.26, 32.07, 33.32, 75.55 (q, J_CCF = 26.5 Hz), 126.89 (q, J_CF = 287.9 Hz); MS m/e (relative intensity)
222 (1, M\(^{+}\)-H\(_2\)O), 171 (41), 151 (33), 131 (23), 71 (31), 56 (100), 43 (60); Anal Calcd for C\(_{12}\)H\(_{23}\)F\(_3\)O: C, 59.98; H, 9.65; F, 23.72. Found: C, 60.10; H, 9.83; F, 23.76.

2-Trifluoromethyl-5-norbornen-2-ol (4i): IR (neat) 3440, 1740, 1340, 1260, 1165, 1140, 1080, 1020, 730 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.20 (dd, \(J = 13.0, 3.6\) Hz, 1H), 1.50-2.00 (m, 3H), 2.22 (dd, \(J = 13.0, 3.6\) Hz, 1H), 3.00 (OH), 3.10-3.14 (m, 1H), 6.23 (dd, \(J = 5.8, 3.2\) Hz, 1H), 6.54 (dd, \(J = 5.8, 3.1\) Hz, 1H); MS m/e (relative intensity) 178 (4, \(M^{+}\)), 109 (26), 108 (24), 79 (43), 67 (100), 66 (98); HRMS calcd for C\(_8\)H\(_9\)F\(_3\)O 178.06057, found 178.06178.

1,1,1-Trifluoro-2-phenylpropan-2-ol (4j): IR (neat) 3450, 1510, 1460, 1175, 1100, 1080, 770, 740, 705 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.78 (s, 3H), 2.53 (OH), 7.33-7.50 (m, 3H), 7.50-7.70 (m, 2H); \(^13\)C NMR (CDCl\(_3\)) \(\delta\) 23.95, 75.08 (q, \(J_{CCF} = 29.1\) Hz), 126.00 (q, \(J_{CF} = 289.2\) Hz), 126.42, 128.74, 129.01138.87; MS m/e (relative intensity) 190 (18, \(M^{+}\)), 121 (100), 105 (18), 84 (8), 77 (5), 43 (96); HRMS calcd for C\(_9\)H\(_9\)F\(_3\)O 190.06057, found 190.06125.

1,1-Diphenyl-2,2,2-trifluoroethanol (4k): IR (neat) 3450, 1510, 1480, 1280, 1170, 740, 705 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 2.73 (OH), 7.17-7.60 (m, 10H); MS m/e (relative intensity) 252 (9, \(M^{+}\)), 183 (100), 105 (73), 77 (16); HRMS calcd for C\(_{14}\)H\(_{11}\)F\(_3\)O 252.07623, found 252.07671.

1-(4-Chlorophenyl)-1-phenyl-2,2,2-trifluoroethanol (4l): IR (neat) 3450, 1505, 1280, 1170, 1070, 835, 772, 755, 720 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.03 (OH), 7.10-7.47 (m, 9H); MS m/e (relative intensity) 288 (5, \(M^{+}+2\)), 286 (15, \(M^{+}\)), 219 (36), 217 (100), 141 (9), 139 (26), 105 (15), 77 (2); HRMS calcd for C\(_{14}\)H\(_{10}\)ClF\(_3\)O 286.03730, found 286.03716.

1-Cyclopropyl-1-phenyl-2,2,2-trifluoroethanol (4m): IR (neat) 3500, 1500, 1455, 1280, 1160, 1032, 1005, 890, 760, 700, 665 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.23-0.90 (m, 4H), 1.38-1.83 (m, 1H) 2.18 (OH), 7.27-7.82 (m, 2H); MS m/e (relative intensity) 216 (1, \(M^{+}\)), 188 (100), 147 (27), 119 (13), 118 (12), 105 (32), 104 (26), 91 (19), 77 (2); HRMS calcd for C\(_{11}\)H\(_{11}\)F\(_3\)O 216.07623, found 216.07672.
1-Cyclohexyl-2,2,2-trifluoroethanol (4n)\textsuperscript{15}: IR (neat) 3420, 2940, 2860, 1460, 1280, 1165, 1125 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 1.03-1.50 (m, 5H), 1.50-2.10 (m, 6H), 2.39 (OH), 3.72 (m, 1H); \textsuperscript{19}F NMR (CDCl\textsubscript{3}, in ppm upfield from internal standard CFCl\textsubscript{3}) \delta -76.14 (d, J\textsubscript{HCF} = 7.3 Hz).

Preparation of 1-Phenyl-2,2-dichloro-3,3,3-trifluoropropanol (8).\textsuperscript{29} Into a cold solution (-20°C) of 1,1-dichloro-2,2,2-trifluoroethane (10 mmol) and benzaldehyde (3 mmol) in 5 mL of DMF was added dropwise a solution of 2b. After the addition was complete, the solution was stirred for 5 h at -10°C and additional 1 h at room temperature. The reaction mixture was, then, piured into saturated aqueous NH\textsubscript{4}Cl (50 mL) and extracted with ether (50 mL x 3). The combined organic extracts were washed successively with 1N HCl (50 mL) and brine (50 mL), and then dried over MgSO\textsubscript{4}. After evaporation of solvent, the product 8 was separated by silica gel column (Hexane : AcOEt = 5 : 1) to give 5 in 45% yield (25% of benzaldehyde was recovered unchanged).

8: IR (neat) 3450, 1505, 1468, 1260, 1200, 1072, 882, 775, 708 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 4.83 (OH), 5.28 (s, 1H), 7.40-7.48 (m, 3H), 7.50-7.60 (m, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \delta 77.25, 122.50 (q, J\textsubscript{CF} = 278.1 Hz), 128.21, 128.91, 129.78, 130.28, 135.68; MS m/e (relative intensity) 206 (2, M\textsuperscript{+}-Cl-OH), 107 (100), 79 (99).
References and Notes


4) Organofluorine Compounds and Their Industrial Applications; Banks, R. E.; ed.; Ellis Horwood Ltd. Chichester, 1979.


21) The reported pKa values of succinimide anion, imidazole anion, and pyrrolidone anion are 9.6<sup>22</sup>, 13.9<sup>23</sup>, and ~16, respectively.


24) Although the compound 7 was easily hydrolyzed to form 4g during usual acidic work-up, the careful working-up of the reaction mixture under neutral conditions gave 7 and it was isolated by GLC. 7: IR (neat) 2950, 2860, 1250, 1170, 845 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 6 0.12 (s, 9H), 0.90 (t, <i>J</i> = 5.9 Hz, 3H), 1.24-1.35 (m, 16H), 1.32 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 6 1.88, 14.00, 20.92, 22.61, 22.72, 29.27, 29.50, 29.90, 31.86, 36.65, 76.24 (q, <i>J</i><sub>CCF</sub> = 23.0 Hz), 126.68 (q, <i>J</i><sub>CF</sub> = 287.2 Hz)


Part III

Synthetic Reactions Utilizing Chemically Reactive Mg Electrode
Abstract: The electroreductive cyclocoupling reaction of 1,3-dienes with aliphatic esters was promoted by using magnesium as the material of electrode and gave 3-cyclopentenol type products with 56-88% yields. Under similar reaction conditions, coupling of styrenes with aliphatic esters also took place yielding 2-phenylcyclopropanol type compounds with high stereoselectivity (yield; 55-94%). The latter type coupling has been successfully applied to the synthesis of ar-dehidroturmeron and curcumone.

Introduction

The cathodic reduction of activated olefins 1 (Y = CN, COR, CO_2R, C_6H_5 etc.) is generally initiated by injection of an electron into the lowest unoccupied molecular orbital (LUMO) of 1. Since the existence of an electron withdrawing substituent (Y) on 1 lowers the energy of LUMO, the cathodic reduction of 1 to form the corresponding anionic species 2 becomes feasible (Scheme I).

Scheme I

\[
\text{+e} \quad \text{1} \quad \rightarrow \quad \text{2} \quad \rightarrow \quad \text{Y} \quad \text{Y}
\]

The fate of resulting species 2 depends on a number of experimental valuables such as solvent and electrolysis potential. For example, hydrodimerization or saturation of double bond of 1 usually occurs in protic media\(^1,2\),
while oligomerization or polymerization mainly takes place in aprotic media. It is also well known that the addition of a proton donor or metal ion such as Li\textsuperscript{+}, Cr\textsuperscript{2+}, Mn\textsuperscript{2+}, and Zn\textsuperscript{2+} to the electrolysis solution inhibits the polymerization of 1 in aprotic media and enables some synthetically useful reactions such as hydrocyclization.\textsuperscript{3-5} The mixed reductive coupling of two different activated olefins can be attained by controlling the reduction potential.\textsuperscript{6-8}

Moreover, the addition of electrophiles (E\textsuperscript{+}) in the electrolysis system provides another synthetic utility of this reaction. It has been shown in the previous studies of our laboratory\textsuperscript{9,10} that the cathodic reduction of activated olefins 1 in the presence of electrophiles (E\textsuperscript{+}) such as aldehydes, ketones, and acid anhydrides gave the coupling products 3 (Scheme II) in reasonable yields. In these reactions, electroreduction of 1 takes place prior to that of E\textsuperscript{+} since LUMO of 1 is sufficiently lowered by the strong electron withdrawing groups (Y), and anionic species 2 forms to react with E\textsuperscript{+}.

Scheme II

\[
\begin{align*}
1 & \overset{+e}{\rightarrow} 2 \\
\text{E} & \rightarrow 1) +e \\
& 2) \text{H}^+ \rightarrow 3
\end{align*}
\]

Although the LUMO of 1,3-dienes is lowered in some extent by conjugation with double bond and they seem to be attractive candidates as activated olefins, their reduction potentials are not enough positive (-2.8 V vs. SCE).\textsuperscript{11} Accordingly, the cathodic coupling of 1,3-dienes with E\textsuperscript{+} has never been actualized yet.

Recently, it has been found in our laboratory that the electroreduction with Mg electrodes possesses strong reducing power and promotes a variety of unique reactions such as the electroreduction of aliphatic esters.\textsuperscript{12} Thus, it seems to be interesting to examine the electroreduction of 1,3-dienes with Mg electrodes in the presence of E\textsuperscript{+} having more negative reduction potential than 1,3-dienes.
In this chapter, it is described that the electroreduction of 1,3-dienes in the presence of aliphatic esters (reduction potential of them are reported to be < -3 V vs SCE), as $E^+$ with magnesium electrodes gave 3-cyclopentenol type compounds in one step (Scheme III). In addition, it was also found that the electroreduction of styrenes in the presence of aliphatic esters under the similar reaction conditions affords 1:1 coupling products, 2-phenylcyclopropanol type compounds, in high stereoselectivity (Scheme IV).

**Scheme III**

![Scheme III](image)

**Scheme IV**

![Scheme IV](image)

**Results and Discussion**

The reaction condition was optimized in the cathodic coupling of isoprene (4a) with methyl valerate (5a) (Scheme V and Table I). Excess use of 5a gave better results (Runs 1-3) because the high concentration of 4a caused oligomerization of 4a. This oligomerization was almost completely suppressed when the mixture of 4a and 5a was added dropwise into the electrolysis cell during the course of the reaction (Runs 4 and 6). The proton donor such as H$_2$O also inhibits this coupling reaction, especially the second cyclization step (vide infra). In the absence of molecular sieves 5A (a drying reagent) the non-cyclized product, nonconjugated eneone, was formed as a by-product (Runs 2, 4-6).
Scheme V

\[
\begin{align*}
\text{4a} & \quad + \quad \text{5a} & \quad \xrightarrow{+\text{e}} & \quad \text{6a} \\
& \quad \text{LiClO}_4 / \text{THF} & \quad \text{Molecular sieves 5A} & \quad \text{5 F/mol}
\end{align*}
\]

Table I. Cathodic Coupling of Isoprene with Methyl Valerate

<table>
<thead>
<tr>
<th>Run</th>
<th>Mol.ratio</th>
<th>Additive</th>
<th>Yield of 6a / %\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 : 2</td>
<td>—</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>2 : 1</td>
<td>—</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>5 : 1</td>
<td>—</td>
<td>39</td>
</tr>
<tr>
<td>4</td>
<td>2 : 1</td>
<td>MS\textsuperscript{b}</td>
<td>53</td>
</tr>
<tr>
<td>5</td>
<td>2 : 1\textsuperscript{c}</td>
<td>—</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>2 : 1\textsuperscript{c}</td>
<td>MS\textsuperscript{b}</td>
<td>76</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Isolated yield. \textsuperscript{b} Molecular sieves 5A (dried in vacuo at 180°C for 4hr). \textsuperscript{c} The mixture of 4a and 5a was added into the electrolysis cell during the course of the reaction.

Table II. Effect of Electrode Materials\textsuperscript{a}

<table>
<thead>
<tr>
<th>Run</th>
<th>Materials of Electrodes</th>
<th>Yield of 6a / %\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anode</td>
<td>Cathode</td>
</tr>
<tr>
<td>1</td>
<td>Mg</td>
<td>Mg</td>
</tr>
<tr>
<td>2</td>
<td>Mg</td>
<td>Pt</td>
</tr>
<tr>
<td>3</td>
<td>Pt</td>
<td>Mg</td>
</tr>
<tr>
<td>4</td>
<td>Pt</td>
<td>Pt</td>
</tr>
<tr>
<td>5</td>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td>6</td>
<td>Zn</td>
<td>Zn</td>
</tr>
<tr>
<td>7</td>
<td>Cu</td>
<td>Cu</td>
</tr>
<tr>
<td>8</td>
<td>Ni</td>
<td>Ni</td>
</tr>
<tr>
<td>9</td>
<td>Pb</td>
<td>Pb</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The electroreduction was carried out under the optimized conditions (Table I, Run6). \textsuperscript{b} Isolated yield. \textsuperscript{c} The electrolysis solution became passivate after 1 F/mol of electricity was passed through the cell.
As shown in Table II, the use of Mg as the material of electrode was one of the most important factors in formation of 6a since the electroreduction of a solution of 4a and 5a with other type electrode such as Pt, Al, Zn, Cu, Ni, or Pb did not afford 6a. The use of Mg for anode and Pt for cathode gave the similar result to the use of Mg for both anode and cathode, while the use of Pt for anode and Mg cathode was not effective. These results indicate that the role of Mg electrode is not necessarily just a donor of electron, but Mg is dissolved as ionic species into the electrolysis solution from anode, and involved in the reaction as a certain chemical reagent. Thus, it would seem reasonable for the mechanism of this cyclocoupling that a diene-magnesium complex 7 is formed from 1,3-diene 4 in the first step and it reacts with aliphatic ester (5) to afford the corresponding cyclopentenol 6 via the anionic intermediate 8 (Scheme VI). The high concentration of 4 promotes the oligomerization by the reaction of 7 with 4. The proton donor inhibits the second cyclization step, that is, 8 is protonated to form non-conjugated enone 9.

Scheme VI
The formation of the diene-magnesium complex was supported by the following results. That is, the coupling product 6a was formed in 16% yield when a solution of isoprene was electrochemically reduced with Mg electrode in the first step and the ester was added to the solution after the current was terminated (Scheme VII).

Scheme VII

![Scheme VII](image)

The same type of magnesium complex of 4 has been reported to be formed by the reaction of chemically activated Mg with 4,14,15 whereas the reaction of the Mg complex with 5 yielded 6 in poor yields (~20%).16-18 In the present system, however, the fact that the black slurry, which was obtained by the electroreduction of a solution of LiClO₄ in THF, did not reduced isoprene (4a) suggests that this reaction is not induced by the highly active Mg(0) generated under the electrochemical conditions or that the active Mg(0) actually forms electrochemically but its life time is very short.20 The yield of the product 6 also reflects the differences between the normal chemical method and the electroreductively promoted cyclocoupling. The present electrochemical method gave 6 in reasonable yields as some typical results are shown in the Table III (Runs 1-4). It should be also noted that 2,3-dimethyl-1,3-butadiene gave the cyclized product (6f) in high yield (Table III, Run 5), despite the fact that formation of the Mg complex from 2,3-dimethyl-1,3-butadiene is known to be difficult, as compared to isoprene.22,23 The reduction of 4 in the presence of aromatic ester, however, did not give the coupling product.24

The cathodic cyclocoupling reaction of 1-vinylcyclohexene (10a) or 1-vinylcycloheptene (10b) with methyl isovalerate (5b) also took place under the
same reaction conditions and gave the product containing a skeleton of hydroindenol 11a or hydroazulenol 11b in satisfactory yield (Scheme IX).

**Scheme VIII**

```
R1               + eR1 R
R2               + RCO2Me ----------^-
                LiClO4 / THF
                Molecular sieves 5A
                Mg cathode & anode
2 eqv. Mg cathode & anode
5 F/mol based on 5
```

**Table III. Cathodic Coupling of 1,3-Dienes with Aliphatic Esters**

<table>
<thead>
<tr>
<th>Run</th>
<th>1,3-Dienes 4</th>
<th>Esters 5</th>
<th>Yield of 6 / %a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>H</td>
<td>iso-Pr 5b</td>
</tr>
<tr>
<td>2</td>
<td>4a</td>
<td>PhCH2CH2</td>
<td>5c 56</td>
</tr>
<tr>
<td>3</td>
<td>CH2CH2CH=C(CH3)2</td>
<td>H</td>
<td>4b Et</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>H</td>
<td>n-Bu 5a</td>
</tr>
<tr>
<td>5</td>
<td>Me</td>
<td>Me</td>
<td>iso-Pr 5b</td>
</tr>
</tbody>
</table>

a) Isolated yield.

**Scheme IX**

```
10a (n = 1)     + iso-PrCO2Me ----------^-
R1               + e
R2               R
                LiClO4 / THF
                Molecular sieves 5A
                Mg cathode & anode
10a (n = 1) 62%
10b (n = 2) 72%```

105
Interestingly, cathodic reduction of a solution of styrene 12 and ester 5 with Mg electrodes afforded exclusively a 2-phenylcyclopropanol type compound 13 in which phenyl and alkyl (R<sup>2</sup>) groups were located on the same side of the cyclopropane ring (Scheme X). The stereochemistry of 13 was determined by <sup>1</sup>H NMR spectra using the NOE difference (See Experimental Section). In this reaction, the use of Mg electrode was essential since the cathodic reduction of a solution of 12 and 5 did not afford 13 when Pt, Cu, Ni, or Pb was used as electrode. Although formation of a Mg complex from 12 could not be detected, it seems clear that the anionic intermediate formed by electroreduction of 12 with the Mg electrode has unique reactivity and the same intermediate is not formed by reduction of 12 with a Pt electrode.

Although the reason for the stereoselectivity in formation of 13 is unclear, some typical results shown in Table IV indicate that this electroreductive method is effective for stereoselective synthesis of a variety of phenylcyclopropanols 13.

Scheme X

Table IV. Cathodic Coupling of Styrenes with Aliphatic Esters

<table>
<thead>
<tr>
<th>Run</th>
<th>Styrenes 12</th>
<th>Esters 5</th>
<th>Yield of 13 / %&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H H 12a</td>
<td>Me 5e</td>
<td>13a 71</td>
</tr>
<tr>
<td>2</td>
<td>12a</td>
<td>iso-Pr 5b</td>
<td>13b 55</td>
</tr>
<tr>
<td>3</td>
<td>12a</td>
<td>Et 5d</td>
<td>13c 67</td>
</tr>
<tr>
<td>4</td>
<td>12a</td>
<td>tert-Bu 5f</td>
<td>13d 50</td>
</tr>
<tr>
<td>5</td>
<td>Me H 12b</td>
<td>5e</td>
<td>13e 94</td>
</tr>
<tr>
<td>6</td>
<td>H Me 12c</td>
<td>5e</td>
<td>13f 62</td>
</tr>
</tbody>
</table>

a) Isolated yield.
It has been reported that the treatment of 13a with acid or base formed cyclopropane ring-opened products.\textsuperscript{32,33} It was found in the present study that 13 yielded similar ring-opened products with much better selectivity under modified reaction conditions. Reaction of 13e with a catalytic amount of tert-BuOK (0.1 equiv. based on 13e) in tert-BuOH, for example, resulted in cleavage of cyclopropane ring yielding 4-phenyl-2-pentanone (14) with high yield (Scheme XI, path A), whereas reaction of 13e with H\textsubscript{2}SO\textsubscript{4} (20 % aqueous H\textsubscript{2}SO\textsubscript{4} : THF = 1 : 1 ) led to formation of 3-phenyl-3-methyl-2-butanone (15) through the ring opening which took place at the different bond from the former ring opening (Scheme XI, path B). Moreover, it has also been found that the reactivity of phenylcyclopropane ring was greatly influenced by the hydroxy group located on the cyclopropane ring. Namely, reaction of 13e with O\textsubscript{2} afforded the corresponding 1,2-dioxolane 16 without catalyst (Scheme XI, path C), whereas it has recently been reported that reaction of phenylcyclopropane with O\textsubscript{2} did not take place without a catalyst such as AIBN.\textsuperscript{34}

Scheme XI
The unique reactivity of 13 shown in the Scheme XI was successfully applied to the synthesis of ar-dihydroturmerone (R = CH2CHMe2) (19)\(^{35}\) and curcumone (R = Me) (20).\(^{36}\) Namely, the cathodic cyclocoupling of p-methyl-α-methylstylene with methyl isovalerate and methyl acetate gave phenylcyclopropanol derivatives 17 and 18, respectively. Addition of tert-BuOK into a solution of 17 and 18 in tert-BuOH gave 19 and 20, respectively (Scheme XII).

Scheme XII

\[
\begin{align*}
\text{OH} & \rightarrow \text{etenBuOK} + \text{RCO}_2\text{Me} \rightarrow \text{R} \\
\text{tert-BuOH} & \rightarrow \text{r.t.} \\
17 \ R = \text{CH}_2\text{CH(CH}_3)_2 & ; 82\% \\
18 \ R = \text{Me} & ; 96\% \\
19 & ; 90\% \\
20 & ; 88\%
\end{align*}
\]

It has well been known that a six-membered ring is easily formed by the [2+4] cycloaddition of 1,3-diene 4 with a suitable dienophile, whereas formation of a five-membered ring is not always facile when 1,3-diene is used as one of the components.\(^{37,38}\) On the other hand, it has been found in the present study that electroreduction of a solution of 4 and aliphatic carboxylic ester 5 with magnesium electrode gave a 3-cyclopentenol type compound 6 in one step. This novel electroreductive cyclocoupling is seemingly corresponding to [4+1] cycloaddition of a one-carbon unit 5 with 4 and undoubtedly one of the simplest methods of formation of a five-membered ring system from 4. Moreover, the stereoselective formation of a three-membered ring system has been also attained by the electroreductive coupling of styrene 12 with 5, and this reaction could be formally regarded as [2+1] cycloaddition.
Experimental Section

General. IR spectra were obtained on a Hitachi 260-10 spectrometer. $^1$H-NMR and $^{13}$C-NMR spectra were measured on a Varian Gemini-200 (200MHz) spectrometer, and the chemical shift values (δ) were expressed in ppm downfield from the internal TMS standard. High resolution mass spectra (HRMS) were determined on a JEOL JES-DX 300. GC analyses were performed on a Shimadzu GC-4C or GC-12A instrument. The constant electrocurrent was supplied with Takasago GP-050-2 regulated DC power supply.

Material. All dienes 4 and esters 5 shown in the Table III, and styrenes 12a-c were commercially available and they were used as received. The dienes 10a,b in the Scheme IX, and p-methyl-α-methylstyrene in the Scheme XII were prepared by the known methods.39

Electroreductive Coupling of 1,3-Dienes (4) with Esters (5). Into a single compartment cell equipped with Mg rod electrodes (cathode and anode) (Φ = 7 mm, length = 5 cm) and dropping funnel were put a solution of anhydrous LiClO$_4$ (1 g) in dry THF (15 mL). Into this solution was added molecular sieves 5A (1 g) in order to remove residual water. Under nitrogen atmosphere, a solution of 1,3-diene 1 (5 mmol) and ester 2 (10 mmol) in dry THF (5 mL) was added dropwise (1 mL/hr) into the solution during the electroreduction performed under the conditions of constant current (0.05 A) with alternation of the polarity of electrodes at the interval of 15 sec. using a commutator. After 4 F/mol of electricity based on 1 was passed, the resulting solution was poured into brine (100 mL) and the aqueous solution was extracted with ether (50 mL x 3). The combined organic layer was washed with brine (50 mL x 2), dried over anhydrous MgSO$_4$, and concentrated under reduced pressure. The residue was purified by silica gel column (EtOAc : hexane = 1 : 10) to yield 3-cyclopenten-1-ols 3.

1-Butyl-3-methyl-3-cyclopenten-1-ol (6a): IR (neat) 3450, 2930, 1440, 1010, 900 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.90 (t, J = 7.3 Hz, 3H), 1.25-1.45 (m, 4H), 1.56-
1.69 (m, 2H), 1.70 (broad s, 3H), 1.94 (broad s, 1H), 2.14-2.52 (m, 4H), 5.23-5.28 (m, 1H); $^{13}$C NMR (CDCl$_3$) δ 14.03 (CH$_3$), 16.80 (CH$_3$), 23.17 (CH$_2$), 26.78 (CH$_2$), 41.01 (CH$_2$), 47.34 (CH$_2$), 51.12 (CH$_2$), 82.21 (C), 122.24 (CH), 138.58 (C); MS m/e (relative intensity) 154 (M$^+$, 6), 97 (25), 85 (100), 57 (85); HRMS calcd for C$_{10}$H$_{18}$O 154.14034, found 154.13570.

1-(1-Methylethyl)-3-methyl-3-cyclopenten-1-ol (6b): IR (neat) 3400, 2960, 1030, 900 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.92 (d, $J = 6.8$ Hz, 3H), 0.93 (d, $J = 6.8$ Hz, 3H), 1.53 (broad s, 1H), 1.72 (broad s, 3H), 1.74 (septet, $J = 6.8$ Hz, 1H), 2.08-2.30 (m, 2H), 2.37-2.55 (m, 2H), 5.27 (m, 1H); $^{13}$C NMR (CDCl$_3$) δ 16.79 (CH$_3$), 17.37 (CH$_3$), 17.51 (CH$_3$), 36.88 (CH), 45.90 (CH$_2$), 49.80 (CH$_2$), 84.78 (C), 122.34 (CH), 138.62 (C); MS m/e (relative intensity) 140 (M$^+$, 14), 97 (64), 83 (28), 71 (100). Anal. Calcd for C$_9$H$_{16}$O: C, 77.09; H, 11.50. Found: C, 76.95; H, 11.76.

1-(2-Phenylethyl)-3-methyl-3-cyclopenten-1-ol (6c): IR (neat) 3400, 1500, 1060, 900 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 1.65 (broad s, 1H), 1.75 (broad s, 3H), 1.92-2.00 (m, 2H), 2.24-2.62 (m, 4H), 2.71-2.80 (m, 2H), 5.31 (m, 1H), 7.15-7.35 (m, 5H); $^{13}$C NMR (CDCl$_3$) δ 16.79, 31.09, 43.25, 47.47, 51.29, 82.02, 122.20, 125.99, 128.63, 138.58, 142.87; MS m/e (relative intensity) 202 (M$^+$, 9), 184 (8), 133 (48), 105 (100), 91 (62), 80 (34); HRMS calcd for C$_{14}$H$_{18}$O 202.13584, found 202.13558.

1-Ethyl-3-(4-methyl-3-pentenyl)-3-cyclopenten-1-ol (6d)$^{17}$: IR (neat) 3360, 2960, 990, 880 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.95 (t, $J = 7.5$ Hz, 3H), 1.59 (broad s, 3H), 1.65 (q, $J = 7.5$ Hz, 2H), 1.67 (broad s, 3H), 2.00-2.14 (m, 4H), 2.15-2.51 (m, 4H), 5.09 (m, 1H), 5.29 (m, 1H); $^{13}$C NMR (CDCl$_3$) δ 8.74, 17.61, 25.60, 26.18, 31.12, 33.61, 46.56, 48.96, 82.12, 121.25, 124.45, 131.87, 142.91; MS m/e (relative intensity) 176 (M$^+$-H$_2$O, 6), 165 (13), 122 (20), 107 (19), 69 (100), 57 (90).

1-Butyl-3-cyclopenten-1-ol (6e): IR (neat) 3370, 3050, 2920, 900 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.93 (t, $J = 6.9$ Hz, 3H), 1.28-1.50 (m, 4H), 1.59-1.72 (m, 2H), 1.65 (broad s, 1H), 2.30-2.54 (m, 4H), 5.71 (m, 1H); $^{13}$C NMR (CDCl$_3$) δ 14.13,
23.29, 27.01, 40.95, 47.17, 81.67, 129.10; MS \textit{m/e} (relative intensity) 140 (M⁺, 2), 85 (100), 57 (68); HRMS calcd for C₉H₁₆O 140.12018, found 140.11870.

1-(1-Methylethyl)-3,4-dimethyl-3-cyclopenten-1-ol (6f): IR (neat) 3400, 2960, 1440, 1380, 1220, 1040, 965, 860 cm⁻¹; \[^{1}\text{H} \text{NMR (CDCl}_{3}\) \(\delta 0.91 \text{ (d, } J = 6.7 \text{ Hz, } 6\text{H}), 1.47 \text{ (broad s, } 1\text{H}), 1.60 \text{ (broad s, } 6\text{H}), 1.71 \text{ (septet, } J = 6.7 \text{ Hz, } 1\text{H}), 2.08-2.18 \text{ (m, } 2\text{H}), 2.40-2.55 \text{ (m, } 2\text{H}); \[^{13}\text{C NMR (CDCl}_{3}\) \(\delta 13.70, 17.37, 36.84, 51.12, 82.16, 129.11; MS \textit{m/e} (relative intensity) 154 (M⁺, 34), 111 (100), 71 (98), 55 (48); HRMS calcd for C₁₀H₁₈O 154.1358, found 154.1366.

7-(1-Methylethyl)bicyclo[4,3,0]non-9-en-7-ol (11a): IR (neat) 3460, 2930, 1650, 1440, 1380, 1000 cm⁻¹; \[^{1}\text{H} \text{NMR (CDCl}_{3}\) \(\delta 0.94 \text{ (d, } J = 6.8 \text{ Hz, } 3\text{H}), 0.96 \text{ (d, } J = 6.8 \text{ Hz, } 3\text{H}), 1.05-1.50 \text{ (m, } 4\text{H}), 1.69-2.08 \text{ (m, } 4\text{H}), 1.78 \text{ (septet, } J = 6.8 \text{ Hz, } 1\text{H}), 2.11-2.60 \text{ (m, } 4\text{H}), 5.30 \text{ (m, } 1\text{H}); \[^{13}\text{C NMR (CDCl}_{3}\) \(\delta 17.38 \text{ (CH}_{3}\), 17.77 \text{ (CH}_{3}\), 25.34 \text{ (CH}_{2}\), 26.14 \text{ (CH}_{2}\), 26.91 \text{ (CH}_{2}\), 29.06 \text{ (CH}_{2}\), 37.32 \text{ (CH}_{2}\), 44.93 \text{ (CH}_{2}\), 51.95 \text{ (CH}_{2}\), 84.12 \text{ (C), } 117.72 \text{ (C), } 144.19 \text{ (C); MS \textit{m/e} (relative intensity) 180 (M⁺, 30), 137 (26), 119 (9), 109 (29), 94 (26), 71 (100); HRMS calcd for C₁₂H₂₀O 180.1515, found 180.15295.

8-(1-Methylethyl)bicyclo[5,3,0]dec-10-en-8-ol (11b): IR (neat) 3450, 2910, 2850, 1440, 1000 cm⁻¹; \[^{1}\text{H} \text{NMR (CDCl}_{3}\) \(\delta 0.98 \text{ (d, } J = 6.9 \text{ Hz, } 3\text{H}), 1.30-1.95 \text{ (m, } 9\text{H}), 2.03-2.67 \text{ (m, } 5\text{H}), 5.25-5.33 \text{ (m, } 1\text{H); MS \textit{m/e} (relative intensity) 194 (M⁺, 12), 167 (24), 149 (15), 124 (21), 108 (15), 95 (15), 81 (37), 71 (100); HRMS calcd for C₁₃H₂₂O 194.16716, found 194.16957.

Electroreductive Coupling of Styrenes (12) with Esters (5). Electroreductive coupling of styrenes 12 with esters 5 was carried out under similar reaction conditions to those described above. The products 13 were isolated by a flash column chromatography (silica gel, EtOAc : hexane = 1 : 5). The analytically pure samples were obtained by recrystallization from pentane.

cis-1-Methyl-2-phenyl-1-cyclopropanol (13a): IR (neat) 3150, 1600, 1490, 1220, 1080, 945, 855, 780, 730, 690 cm⁻¹; \[^{1}\text{H} \text{NMR (CDCl}_{3}\) \(\delta 0.98 \text{ (dd, } J = 7.0, 5.8 \text{ Hz, } 1\text{H}), 1.19 \text{ (s, } 3\text{H}), 1.25 \text{ (dd, } J = 10.1, 5.8 \text{ Hz, } 1\text{H}), 2.05 \text{ (broad s, } 1\text{H}), 2.35 \text{ (dd, } J = 10.1, 7.0 \text{ Hz, } 1\text{H}, 7.10-7.32 \text{ (m, } 5\text{H); \[^{13}\text{C NMR (CDCl}_{3}\) \(\delta 18.73 \text{ (CH}_{2}\),...
20.57 (CH$_3$), 30.59 (CH), 57.51 (C), 126.18 (CH), 128.38 (CH), 128.61 (CH), 138.80 (C); MS m/e (relative intensity) 148 (M$^+$, 57), 133 (27), 105 (100), 91 (45); HRMS calcd for C$_{10}$H$_{12}$O 148.08886, found 148.08952.

The stereochemistry of 13a was determined by NOE difference spectra (Figure I). Irradiation on the benzyl proton (δ 2.35) showed NOE at the proton H$_A$ (δ 1.25), and irradiation on the proton H$_B$ (δ 0.98) showed NOE at the methyl protons (δ 1.19) and H$_A$ (δ 1.25). These results indicated that phenyl and methyl groups were located on the same side. The stereochemistry of 13b and 13c was also determined by NOE.

![Figure I](image)

**cis-1-(1-Methylethyl)-2-phenyl-1-cyclopropanol (13b):** IR (neat) 3450, 2960, 1600, 1500, 1220, 1050, 895, 780, 700 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.77 (d, J = 6.3 Hz, 3H), 1.05 (s, 3H), 1.00-1.25 (m, 3H), 2.05 (broad s, 1H), 2.42 (dd, J = 7.0, 9.9 Hz, 1H), 7.12-7.32 (m, 5H); $^{13}$C NMR (CDCl$_3$) δ 16.68 (CH$_3$), 17.51 (CH$_2$), 18.47 (CH$_3$), 30.07 (CH), 31.90 (CH), 64.94 (C), 126.06 (CH), 128.21 (CH), 128.57 (CH), 138.28 (C); MS m/e (relative intensity) 176 (M$^+$, 16), 133 (100), 105 (86), 91 (57); HRMS calcd for C$_{12}$H$_{16}$O176.1208, found 176.11864.

**cis-1-Ethyl-2-phenyl-1-cyclopropanol (13c):** IR (neat) 3300, 2960, 1600, 1500, 1460, 1205, 895, 700 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.90 (t, J = 7.3 Hz, 3H), 0.98-1.50 (m, 4H), 2.05 (broad s, 1H), 2.39 (dd, J = 10.0, 7.8 Hz, 1H), 7.10-7.35 (m, 5H); $^{13}$C NMR (CDCl$_3$) δ 9.33, 17.66, 26.63, 31.06, 61.85, 126.13, 128.31, 128.56; MS m/e (relative intensity) 162 (M$^+$, 29), 146 (29), 133 (60), 117 (39), 105 (78), 91 (100), 83 (40), 57 (67); HRMS calcd for C$_{11}$H$_{14}$O162.10452, found 162.10302.

**cis-1-(1,1-Dimethylethyl)-2-phenyl-1-cyclopropanol (13d):** IR (neat) 3400, 2950, 1600, 700 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 1.02 (s, 9H), 1.17-1.30 (m, 2H), 2.23
(dd, $J = 10.0, 7.8$ Hz, 1H), 7.18-7.37 (m, 5H); MS $m/e$ (relative intensity) 190 ($M^+$, 5), 133 (100), 105 (83), 91 (60), 57 (78); HRMS calcd for $C_{13}H_{18}O$ 190.13584, found 190.13493.

**trans-1,2-Dimethyl-2-phenyl-1-cyclopropanol (13e):** IR (neat) 3250, 1600, 1220, 765, 700 cm$^{-1}$; $^1H$ NMR (CDCl$_3$) $\delta$ 0.84 (d, $J = 5.6$ Hz, 1H), 1.05 (d, $J = 5.6$ Hz, 1H), 1.13 (s, 3H), 1.52 (s, 3H), 1.98 (broad s, 1H), 7.15-7.35 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ 22.00, 23.34, 25.05, 31.87, 59.67, 126.18, 128.49, 128.66, 144.88; MS $m/e$ (relative intensity) 162 ($M^+$, 17), 147 (100), 119 (47), 105 (62), 91 (40); HRMS calcd for $C_{11}H_{14}O$ 162.10452, found 162.10585.

The configuration of 13e was determined by NOE (Figure II). Irradiation on methyl protons (Me$_A$, $\delta$ 1.13) showed NOE at the ring proton H$_A$ ($\delta$ 1.05) and irradiation on the other methyl protons (Me$_B$, $\delta$ 1.52) showed NOE at the proton H$_B$ ($\delta$ 0.84). These results supported the assigned structure.

![Figure II](image)

1,3-Dimethyl-2-phenyl-1-cyclopropanol (13f): IR (neat) 3250, 1600, 1500, 1450, 1220, 1080, 805, 740, 700 cm$^{-1}$; $^1H$ NMR (CDCl$_3$) $\delta$ 0.70-0.90 (m, 1H), 1.19 (s, 3H), 1.32 (d, $J = 5.7$ Hz, 3H), 1.84 (broad s, 1H), 1.86 (d, $J = 6.5$ Hz, 1H), 7.10-7.40 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ 11.94, 21.39, 23.68, 37.02, 60.50, 126.00, 128.34, 128.48, 139.25; MS $m/e$ (relative intensity) 162 ($M^+$, 53), 147 (99), 129 (27), 119 (87), 107 (36), 91 (100), 78 (27); HRMS calcd for $C_{11}H_{14}O$ 162.10452, found 162.10377.

**Transformation of 13e to 14.** Into a solution of 2-phenyl-1-cyclopropanol 13e (1.3 mmol) in tert-BuOH (3 mL) was added tert-BuOK (0.1 mmol) at room temperature. After stirring for 30 min., the color of the solution turned to reddish brown and 13e was completely consumed (the reaction was monitored by TLC).
After usual work-up, the product **14** was purified by silica gel column (EtOAc : hexane = 1 : 5).

**4-Phenyl-2-pentanone (14)**: IR (neat) 2950, 1710, 1350, 1160, 760, 700 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 1.27 (d, $J = 7.0$ Hz, 3H), 2.09 (s, 3H), 2.71 (t, $J = 7.7$ Hz, 2H), 3.20-3.40 (m, 1H), 7.15-7.38 (m, 5H); MS m/e (relative intensity) 162 (M$^+$, 50), 147 (69), 119 (23), 105 (100), 91 (34).

**Transformation of 13e to 15.** A solution of 13e (1 mmol) in 20% H$_2$SO$_4$ (2.5 mL) and THF (2.5 mL) was refluxed for 3 hr. and consumption of 13e was monitored by TLC. After usual work-up, the product **15** was purified by silica gel column (EtOAc : hexane = 1 : 5).

**3-Methyl-3-phenyl-2-butanone (15):** IR (neat) 2975, 1710, 1440, 1350, 1115, 760, 700 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 1.49 (s, 6H), 1.92 (s, 3H), 7.20-7.43 (m, 5H); MS m/e (relative intensity) 162 (M$^+$, 2), 147 (3), 119 (100), 91 (41).

**Formation of 16 by the Autooxidation of 13e.** 1,2-Dimethyl-2-phenylcyclopropanol 13e (1.2 mmol) was dissolved into CH$_2$Cl$_2$ (2 mL) and the solution was stirred over night at room temperature under an atmosphere of oxygen. The reaction mixture was poured into brine (10 mL) and the aqueous solution was extracted with ether (10 mL x 3). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated. The residue was purified by silica gel column (EtOAc : hexane = 1 : 5).

**1,5-Dimethyl-5-phenyl-2,3-dioxacyclopentan-1-ol (16),** the mixture of two stereoisomers: IR (neat) 3450, 3000, 1455, 1380, 1235, 770, 705 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ major isomer 1.38 (s, 3H), 1.65 (s, 3H), 2.89 (d, $J = 12.9$ Hz, 1H), 3.05 (d, $J = 12.9$ Hz, 1H), 3.00 (OH), 7.20-7.50 (m,5H), minor isomer 1.63 (s, 3H), 1.70 (s, 3H), 2.76 (d, $J = 12.9$ Hz,1H), 2.99 (d, $J = 12.9$ Hz, 1H), 3.00 (OH), 7.20-7.50 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ major isomer 23.05, 26.95, 59.52, 87.66, 106.51, 124.74, 127.11, 128.49, 146.22, minor isomer 23.37, 27.53, 59.68, 87.15, 106.36, 125.43, 127.87, 128.75, 142.91; MS m/e (relative intensity) 194 (M$^+$, 2).
Anal. Calcd for C_{11}H_{14}O_{3}: C, 68.02; H, 7.27; O, 24.71. Found: C, 68.13; H, 7.52; O, 24.72.

Synthesis of ar-dihydroturmeron (19) and curcumone (20). The electroreductive coupling of p-methyl-α-methylstyrene (5 mmol) with methyl isovalerate (7.5 mmol) was carried out under the same conditions as described above. Since the product 17 was very sensitive to air, transformation of 17 to 19 was performed without any purification of 17 (crude yield 82%). Into a solution of crude 17 in tert-BuOH (5 mL) was added tert-BuOK (0.4 mmol). The solution was stirred for 15 min. at room temperature and then poured into brine. After usual work-up, the product 19 was isolated by silica gel column (EtOAc : hexane = 1 : 5). The reaction of p-methyl-α-methylstyrene (5 mmol) with methyl acetate (7.5 mmol) gave 18 (crude yield 96%, 85 : 15 trans-cis isomeric mixture) which was then transformed to 20 by the same procedure as described above.

2-Methyl-2-(4-methylphenyl)-1-(2-methylpropyl)-1-cyclopropanol (17): IR (neat) 3400, 2960, 1460, 1065, 820 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.83 (d, \(J = 6.8\) Hz, 3H), 0.84 (d, \(J = 5.8\) Hz, 1H), 0.90 (d, \(J = 6.8\) Hz, 3H), 1.12 (d, \(J = 5.8\) Hz, 1H), 1.49 (s, 3H), 1.55-1.80 (m, 2H), 2.80-2.05 (m, 1H), 7.10 (m, 4H).

trans-1,2-Dimethyl-2-(4-methylphenyl)-1-cyclopropanol (18-trans): IR (neat) 3200, 2940, 1430, 1220, 1065, 820 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.81 (d, \(J = 5.5\) Hz, 1H), 1.02 (d, \(J = 5.5\) Hz, 1H), 1.13 (s, 3H), 1.50 (s, 3H), 1.83 (OH), 2.32 (s, 3H), 7.11 (m, 4H); \(^1^3\)C NMR (CDCl\(_3\)) \(\delta\) 20.94, 22.07, 23.33, 25.05, 31.46, 59.70, 128.50, 129.22, 135.70, 141.85; MS m/e (relative intensity) 176 (M\(^+\), 47), 161 (42), 119(100), 105 (12); HRMS calcd for C\(_{12}\)H\(_{16}\)O 176.1202, found 176.12057.

The configuration of 18-trans was determined by NOE. Irradiation on methyl protons (MeB, \(\delta\) 1.50) showed NOE at the ring proton H\(_{B}\) (\(\delta\) 0.81) (Figure III).
Figure III

**cis-1,2-Dimethyl-2-(4-methylphenyl)-1-cyclopropanol (18-cis):** IR (neat) 3200, 2940, 1430, 1220, 1065, 820 cm⁻¹; \(^1\)H NMR (CDCl₃) δ 0.65 (d, \(J\) = 5.6 Hz, 1H), 1.01 (d, \(J\) = 5.6 Hz, 1H), 1.38 (s, 3H), 1.59 (s, 3H), 1.83 (OH), 2.32 (s, 3H), 7.11 (m, 4H).

**2-Methyl-6-(4-methylphenyl)-4-heptanone (ar-Dehydroturmerone) (19):** IR (neat) 2950, 2875, 1710, 810 cm⁻¹; \(^1\)H NMR (CDCl₃) δ 0.84 (d, \(J\) = 6.4 Hz, 3H), 0.85 (d, \(J\) = 6.4 Hz, 3H), 1.23 (d, \(J\) = 6.9 Hz, 3H), 2.00-2.22 (m, 3H), 2.31 (s, 3H), 2.64 (t, \(J\) = 7.1 Hz, 2H), 3.27 (septet, \(J\) = 6.4 Hz, 1H), 7.10 (m, 4H); MS m/e (relative intensity) 218 (M⁺, 30), 203 (23), 161 (20), 119(100); HRMS calcd for C₁₅H₂₂O 218.16716, found 218.16638.

**4-(4-methylphenyl)-2-pentanone (Curcumone) (20):** IR (neat) 2960, 2880, 1715, 820 cm⁻¹; \(^1\)H NMR (CDCl₃) δ 1.25 (d, \(J\) = 6.9 Hz, 3H), 2.06 (s, 3H), 2.31 (s, 3H), 2.69 (m, 2H), 3.26 (septet, \(J\) = 6.9 Hz, 1H), 7.11 (m, 4H); MS m/e (relative intensity) 176 (M⁺, 52), 161 (48), 119(100); HRMS calcd for C₁₂H₁₆O 176.1202, found 176.11883.
References and Notes

18) Rieke et al. reported recently that the highly activated Mg prepared by the reduction of MgCl2 was effective for the coupling of 1,2-bis(methylene)cycloalkanes with esters.19
20) Perichon et al. have recently reported\(^{21}\) that the electrochemical scouring of magnesium induces a chemical reduction of DMF when this metal is used as a sacrificial anode for electrocarboxylation of organic halides.


23) Recently Rieke et al. have reported\(^{14}\) that reaction of highly activated Mg with 2,3-dimethyl-1,3-butadiene formed the corresponding magnesium complex.

24) The fact that aromatic esters are generally reduced at more positive potential (methyl benzoate, \(-2.29\) V vs SCE in DMF)\(^{25}\) than dienes is the reason why the coupling did not take place.


26) The use of aluminum and zinc as electrode material in the cathodic coupling of \(12a\) with \(5e\) gave \(13a\) in 30% and 8% yields respectively.

27) The procedure that \(12a\) was reduced in the absence of \(5\) and \(5\) was added to the solution after the electricity was terminated did not give the coupling product, but the product was the oligomer of \(12a\).

28) The reduction potential of \(12a\) (\(-2.34\) V vs SCE in DME)\(^{29}\) is more positive than that of \(5\) (<\(-3.0\) V vs SCE)\(^{13}\).


30) It has been also found that the electroreduction of \(12a\) with Mg electrode in the presence of chlorotrimethylsilane (no reduction wave at the cathodic range of \(0\text{--}3\) V vs SCE)\(^{31}\) gave 1-phenyl-1,2-bis(trimethylsilyl)ethane in 81% yield, whereas the same reduction achieved with Pt electrode gave no bistrimethylsilylated product but the product was oligomer of \(12a\). These results suggest that the electroreduction of \(12a\) with Mg electrode forms an anionic intermediate which is not generated by the reduction of \(12a\) with Pt electrode.
Chapter 7

Electroreductive Formation of Polysilanes Using Chemically Reactive Mg Electrode

Abstract: The preparation of polysilane high polymers is attained by the electroreduction of dichlorosilanes with Mg electrodes in a single compartment cell. For example, the electroreduction of alkylaryldichlorosilanes with Mg cathode and anode gave poly[alkylarylsilane]s (Mn = 5200-31000, Mw/Mn = 1.4-1.8) in 79% yield. The effects of electrode materials, monomer concentration, supplied electricity, and sonication were found to be important for the formation of polymers having high molecular weight. Moreover, this method was applied to the synthesis of poly[p-(disilanylene)phenylene]s from bis(chloroethyl-methylsilyl)benzene or bis[chloromethyl-phenylsilyl]benzene.

Introduction

Silicon backbone polymers have recently attracted considerable attention due to their application as the materials for thermal ceramic precursors and microlithography, and also due to their potential utilities to the production of new class of materials having conducting, photoconducting, and nonlinear optical properties. In contrast to the growing interest of polysilanes, their preparative methods are very limited. The almost only practical method developed so far is Kipping's one, that is, the condensation of organodichloromonomosilanes with alkali metals. This method, however, requires drastic reaction conditions and has much limitation of the variety of substituents on the monomer units. Although several alternative or modified methods such as transition metal catalyzed reaction of hydrosilanes, sonochemical reductive coupling of dichlorosilanes with alkali metals, and ring opening polymerization of cyclic...
organosilanes, have been investigated, they also have some demerits, which make their industrialization difficult.

Another alternative is the electrochemical method. In 1976, Hengge and his co-workers demonstrated that the electroreductive coupling of dichlorosilanes by using mercury electrodes gave the corresponding disilanes. This was the frontier work in this area and apparently showed the electroreductive formation of Si-Si bond, however, this method was not applicable for the preparation of polysilanes.

On the other hand, it has been found in this study that the electroreduction of alkylaryl dichlorosilanes with magnesium electrodes afforded high molecular weight polysilanes having monomodal narrow distribution. This method could be performed in a single compartment cell under very mild conditions, and these merits may enlarge the possibility of industrialization.

Results and Discussion

Preliminary Study on Electroreductive Formation of Si-Si bond. As mentioned above, Hengge and his co-workers reported in their frontier work that the electroreduction of organodichloromonosilanes 1 (Scheme I) carried out in a divided cell using Hg anode and Pt cathode afforded the corresponding disilanes 2, however, the yields of 2 were very low (10-15%).

Exploiting effective method for the formation of Si-Si bond, the electroreduction of chlorodimethylphenylsilane (1a) was chosen as the model reaction, and it was carried out under a variety of conditions. Since Si-Si bond is electrochemically oxidized rather readily in the potential range 0.7-1.6V vs. SCE, the cathodic reduction was performed in a divided cell in our preliminary study. As a result, however, the low conductivity of the electrolytic system prevented completion of the reaction and the coupling product, 1,1,2,2-tetramethyl-1,2-diphenyldisilane (2a), was produced only in low yield.

It was shown in the preceding chapter that the electroreductive coupling of 1,3-dienes with aliphatic esters was achieved in an undivided cell by using Mg
sacrificial electrodes, and in this system the anodic oxidation of 1,3-dienes was prevented by the ionization of Mg from anode. These results seems to indicate that the same electroreduction system using Mg electrodes may be applicable for the formation of Si-Si bond in an undivided cell. As expected, the electroreduction of 1a with Mg electrodes was actually effective for the formation of Si-Si bond in an undivided cell, and 2a was obtained in excellent yield.

Scheme I

\[
\begin{align*}
\text{I} & \quad \text{R}^1 \quad \text{R}^2 - \text{Si} - \text{Cl} \quad \quad \text{+ e} \quad \quad \text{R}^2 - \text{Si} - \text{Si} - \text{R}^2 \\
\text{1a ; R}^1 = \text{R}^2 = \text{Me}, & \quad \text{R}^3 = \text{Ph} \quad \quad \text{2a ; R}^1 = \text{R}^2 = \text{Me}, & \quad \text{R}^3 = \text{Ph}
\end{align*}
\]

As shown in Table I, the material of electrodes is one of the most important factors in this homocoupling. When a solution of 1a in dry THF containing LiClO₄ as a supporting electrolyte was electrochemically reduced using Mg cathode and anode under the constant current condition (50 mA, supplied electricity = 2.0 F/mol), the coupling product 2a was obtained in 92% isolated yield (Run 1). The use of Pt, carbon, nor Zn was not effective to the electroreductive Si-Si bond formation (Run 2-4). These results indicates that Mg electrodes provide not only the place of electron transfer but are involved in the reaction as certain chemical reagent. Moreover, the fact that the electroreduction using Mg anode and Pt cathode (Run 6) gave almost same result as shown in Run 1 indicates that the ionization of Mg in the anodic oxidation process plays important rolls described as follows.

1. The anodic oxidation of Mg prevents the oxidative cleavage of Si-Si bond.
2. Mg²⁺ formed in the anodic process traps Cl⁻, forming MgCl₂.

The roll of Mg cathode or Mg deposited on cathode is not always clear at present, however, Mg cathode in the present system actually shows unprecedented strong reducing power, which has been also demonstrated in our
recent study of electroreduction of aliphatic esters,\textsuperscript{15} that is, the electroreduction of aliphatic esters was achieved only when Mg was used as the material of cathode.

Table I. Effect of Electrode Materials in the Electroreductive Formation of 1,1,2,2-tetramethyl-1,2-diphenyldisilane (2a)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Run</th>
<th>Anode</th>
<th>Cathode</th>
<th>Alternation\textsuperscript{b}</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg</td>
<td>Mg</td>
<td>○</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>Pt</td>
<td>Pt</td>
<td>○</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>C</td>
<td>○</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Zn</td>
<td>Zn</td>
<td>○</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Pt</td>
<td>Mg</td>
<td>×</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Mg</td>
<td>Pt</td>
<td>×</td>
<td>93\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The electroreduction was carried out under the constant current condition (50 mA, supplied electricity = 2.0 F/mol).
\textsuperscript{b} The polarity of electrodes was alternated with the interval of 15 sec.
\textsuperscript{c} The reaction was carried out under sonication.

The effect of supporting electrolytes and solvents was also investigated. As summarized in Table II, the use of THF as a solvent and LiClO\textsubscript{4} as a supporting electrolyte gave the best result. The supporting electrolytes containing fluoride were not suitable for this reaction because fluoride ion released from electrolytes induced the halogen exchange of chlorosilane 1\textsubscript{a} and the resulting fluorosilane was stable to the cathodic condition.\textsuperscript{16}

Under the optimized reaction condition described above (Mg cathode and anode / the electrodes was alternated with the interval of 15 sec. / LiClO\textsubscript{4} supporting electrolyte / THF solvent / 2.0 F/mol) the cathodic coupling of other organochlorosilanes was carried out (Scheme II). The results summarized in Table III shows the large feasibility of this method. Moreover, the contamination of siloxane (Si-O-Si) which was often a serious problem in the hitherto known methods was found to be less than 2\%.\textsuperscript{18}
Table II. Effect of Supporting Electrolytes and Solvents in the Electoreductive Formation of 2aa

<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>Solvent</th>
<th>THF</th>
<th>DME</th>
<th>Dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiClO₄</td>
<td></td>
<td>92%</td>
<td>70%</td>
<td>0%</td>
</tr>
<tr>
<td>LiBF₄</td>
<td></td>
<td>2</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>n-Bu₄NCIO₄</td>
<td></td>
<td>75</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>n-Bu₄NBF₄</td>
<td></td>
<td>12</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

a) The electroreduction was carried out under the constant current condition using Mg alternating electrodes.

Scheme II

\[
\begin{align*}
2 & \quad R^1 \quad R^2 - Si - Cl \quad \quad +e \quad \quad \quad R^1 \quad R^3 \\
& \quad \quad \quad LiClO₄ / THF / r.t. \quad Mg \quad cathode & anode \quad undivided \quad cell \\
& \quad \quad \quad 2 \quad F/mol
\end{align*}
\]

Table III. Electoreductive Formation of Disilanes (2)

<table>
<thead>
<tr>
<th>Run</th>
<th>Chlorosilanes 1</th>
<th>Yield of 2 / %a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R¹</td>
<td>R²</td>
</tr>
<tr>
<td>1</td>
<td>Me</td>
<td>Me</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>Ph</td>
</tr>
<tr>
<td>3</td>
<td>Ph</td>
<td>Ph</td>
</tr>
</tbody>
</table>

a) Isolated yield.
As concerns the reaction pathway of this Si-Si bond formation, two possibilities could be considered, that is, (1) homolytic coupling of silyl radicals and (2) formation of silyl anions and their nucleophilic attack to chlorosilanes. In order to clarify this point, the product study was performed in the electroreduction of the mixed system of chlorotrimethylsilane (1b) and chlorotriphenylsilane (1d) (1b : 1d = 1 : 1). As the result is shown in Scheme III, the mixed coupling product 2e and hexaphenyldisilane (2d), the homocoupling product of 1d were formed in the ratio of 1 : 1, while the formation of hexamethyldisilane (2b), the homocoupling product of 1b was not observed at all. This result clearly indicates that the active species of this reaction is the silyl anion (in the above case, triphenylsilyl anion) and that 1b was not reduced under the present condition.

The mechanism of the reductive cleavage of Si-Cl bond still has some ambiguity, however, the fact that the reduction of 1d preceded that of 1b denies the possibility of the reduction by the solvated electrons or Mg metal but strongly supported that Si-Cl bond is cleaved electrochemically under the control of the reduction potential difference between chlorosilanes (the reductive potential of 1d is more positive than that of 1b\textsuperscript{16,19}).

Scheme III

```
Me                                      +e
Me-Si-Cl + Ph-Si-Cl \xrightarrow{\text{LiClO}_4 / \text{THF} / \text{r.t.}} \text{Mg cathode & anode}
Me Ph                                      Ph
Me-Si-Si-Ph + Ph-Si-Si-Ph
Me Ph                                       Ph
2e                                         2d
25\%                                       25\%
```

Not only to the synthesis of disilanes this method is also applicable to the synthesis of trisilanes and tetrasilanes. For example, the electroreductive cross-coupling of organodichlorosilanes (3) and chlorotrimethylsilanes (1b) (5 equivalent to 3) gave the corresponding trisilanes 4 in good to moderate yield.
(Scheme IV) and that of 1,2-dichloro-1,1,2-trimethyl-2-phenyldisilane (5) and 1b (5 equivalent to 5) gave tetrasilane 6 in 55% yield (Scheme V). Trisilane 3a is an key intermediate for the photochemical synthesis of tetramesityldisilane which is known as an isolable disilene.\textsuperscript{20}

**Scheme IV**

\[
\text{MeR}_1\text{Me} + \text{ClSiCl}\text{Me} \xrightarrow{e} \text{MeSiSiSiMe}
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a; R\textsuperscript{1} = Me, R\textsuperscript{2} = Ph</td>
<td>59%</td>
</tr>
<tr>
<td>3b; R\textsuperscript{1} = R\textsuperscript{2} = Ph</td>
<td>73%</td>
</tr>
<tr>
<td>3c; R\textsuperscript{1} = R\textsuperscript{2} = Mesityl</td>
<td>92%</td>
</tr>
</tbody>
</table>

**Scheme V**

\[
\text{MeMeMeMe} + \text{ClSiSiSiMe} \xrightarrow{e} \text{MeSiSiSiSiMe}
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>5eqv.5F/mol based on 1b</td>
<td>55%</td>
</tr>
</tbody>
</table>

**Electroreductive Polymerization of Dichloromethylphenylsilane (3a).** When the optimized conditions established above was applied to the electroreductive polymerization of dichloromethylphenylsilane (3a) (Scheme VI), an undesirable result was observed. The terminal voltage increased gradually in the course of electrolysis due to the deposition of the forming polymer and MgCl\textsubscript{2} and it reached a practically undesirable value at a final stage (maximum voltage, ca. 50 V). The high voltage may induces the anodic cleavage of Si-Si bond and decrease the reproducibility of the reaction. This problem was finally overcome
by using two techniques, that is, alternation of electrode polarity and sonication of ultrasound (47 kHz). As shown in Table IV, these techniques are effective to the formation of poly[methylphenylsilane] (7), especially to the increase of the yield of 7.

**Scheme VI**

![Scheme VI](attachment:image.png)

**Table IV. Electroreductive Synthesis of Poly[methylphenylsilane] (7)\(^{a,b}\)**

<table>
<thead>
<tr>
<th>Run</th>
<th>Alternation(^c)</th>
<th>Sonication(^d)</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Yield of 7 / %(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>5200</td>
<td>1.5</td>
<td>43</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>3900</td>
<td>1.4</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>4000</td>
<td>1.4</td>
<td>7</td>
</tr>
</tbody>
</table>

\(^{a}\) Concentration of monomer 3a is 0.33 mol/L.
\(^{b}\) Supplied electricity is 4 F/mol.
\(^{c}\) The polarity of electrodes was alternated with the interval of 15 sec.
\(^{d}\) The ultrasound (47 kHz) was sonicated during the electroreduction.
\(^{e}\) Purified by reprecipitation from benzene-EtOH.

The effect of electrode materials was shown in Table V. The effectiveness of Mg as electrode material was confirmed again (Run 1). Although the Si-Si bond formation actually occurred by using Cu or Ni as electrodes, these materials were not effective to the electroreductive polymerization (Run 2,3). In the case of Al electrodes, the polymer was obtained after the usual reprecipitation procedure (Run 4). After our work the similar result was reported\(^{21}\) in the electroreductive polymerization of dichlorodimethylsilane using Al as electrodes, \(n\)-Bu\(_4\)NCl as supporting electrolyte, and DME as a solvent respectively, however, the
polysilanes having high molecular weight have never been obtained in this system.

<table>
<thead>
<tr>
<th>Run</th>
<th>Material of Electrodes</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Yield of 7 / %b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg</td>
<td>5200</td>
<td>1.5</td>
<td>43</td>
</tr>
<tr>
<td>2</td>
<td>Cu</td>
<td>700</td>
<td>1.1</td>
<td>—c</td>
</tr>
<tr>
<td>3</td>
<td>Ni</td>
<td>640</td>
<td>1.1</td>
<td>—c</td>
</tr>
<tr>
<td>4</td>
<td>Al</td>
<td>4700</td>
<td>1.5</td>
<td>15</td>
</tr>
</tbody>
</table>

Table V. Effect of Electrode Materials in the Electroreductive Synthesis of Poly[methylphenylsilane] (7)a

a) Conditions: [Monomer 3a] = 0.33 mol/L; Supplied electricity = 4 F/mol; The electroreduction was carried out under sonication (47 kHz). The polarity of electrodes was alternated with the interval of 15 sec.
b) Purified by reprecipitation from benzene-EtOH.
c) No precipitate was obtained after usual reprecipitation procedure.

In order to obtain high molecular weight polysilane, the effect of monomer concentration was next investigated. As shown in Table VI, higher concentration condition resulted in higher molecular weight. When the monomer concentration was 1.2 mol/L, poly[methylphenylsilane] (7) having 31000 of molecular weight (Mn) was obtained after 0.5 F/mol of electricity was passed. Enough amount of electricity under high concentration condition did not always give good results because the high concentration resulted in the high resistance of the electrolysis solution at a final stage and resulting the anodic cleavage of Si-Si bond coincided.

The plausible polymerization pathways were shown in Scheme VII. Since the active species in the present Si-Si bond formation are found to be anionic as mentioned above, the initiation step of the polymerization seems to include the electroreductive generation of an organomonochlorosilyl anion (8). As concerns the propagation step, two possibilities could be considered: (1) The anions 8 attack repeatedly the terminal silicon atom of the intermediary formed oligomeric
chlorosilanes (9). (2) The anionic species formed 10 by the electroreductive cleavage of Si-Cl bond of 9 attack monomer 3 or oligomer 9.

Table VI. Effect of Monomer Concentration in the Electroreductive Synthesis of 7

<table>
<thead>
<tr>
<th>Run</th>
<th>[Monomer 3a] mol/L</th>
<th>Electricity F/mol</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Yield of 7 / %b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.33</td>
<td>4.0</td>
<td>5200</td>
<td>1.5</td>
<td>43</td>
</tr>
<tr>
<td>2</td>
<td>0.67</td>
<td>4.0</td>
<td>9900</td>
<td>2.1</td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>2.2</td>
<td>18000</td>
<td>2.1</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>6.3</td>
<td>0.8</td>
<td>19000</td>
<td>2.8</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>0.5</td>
<td>31000</td>
<td>1.8</td>
<td>8</td>
</tr>
</tbody>
</table>

a) The electroreduction was carried out by using Mg electrodes under sonication (47 kHz) and the polarity of electrodes was alternated with the interval of 15 sec.
b) Purified by reprecipitation from benzene-EtOH.

Scheme VII
Above them the former pathway seems to be more reasonable because 3 is more reducible electrochemically than 9. Under high monomer concentration conditions, however, the latter pathway may coincide, which results in the remarkable increase of molecular weight.

An elution profile of a gel permeation chromatograph for a polymer sample is shown in Figure I. It should be noted that the resulting polysilane high polymer has relatively narrow (Mw/Mn = 1.4-2.8) monomodal distribution, whereas, the polysilanes prepared by the alkali metal condensation method often have broad bimodal distribution. In addition this result supports the anionic mechanism of the present polymerization.\textsuperscript{22}

![Figure I. An elution profile from GPC of 7.](image)

**Electroreductive Synthesis of Poly[p-(disilanylene)phenylene].** Nate and Ishikawa have studied the photochemical behavior of poly[p-(disilanylene)phenylene] 12 to find that 12 shows very high etching resistance against the oxygen plasma and can be used as the top imaging layer in the double-layer resist system.\textsuperscript{24} The electroreductive polymerization method established above was next applied to the synthesis of 12 (Scheme VIII) since 12 had ever been prepared only by using Kipping's method.
Scheme VIII

The effect of electrode materials was investigated also in the electroreductive polymerization of 1,4-bis(chloroethylmethylsilyl)benzene (11a) as a model compound. As shown in Table VII, the use of Mg electrodes gave the best result again. On the other hand, oligomeric 12a was obtained when 11a was electroreduced by using Cu, Zn, or Ni as a material of electrodes.

Table VII. Effect of Electrode Materials in the Electroreductive Synthesis of Poly[p-(disilanylene)phenylene] 12a

<table>
<thead>
<tr>
<th>Run</th>
<th>Material of Electrodes</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Yield of 12a / %b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg</td>
<td>6700</td>
<td>1.6</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>Cu</td>
<td>1300</td>
<td>1.8</td>
<td>—c</td>
</tr>
<tr>
<td>3</td>
<td>Zn</td>
<td>1200</td>
<td>1.3</td>
<td>—c</td>
</tr>
<tr>
<td>4</td>
<td>Ni</td>
<td>2400</td>
<td>1.7</td>
<td>—c</td>
</tr>
</tbody>
</table>

a) Conditions: [Monomer 12a] = 0.27 mol/L; [LiClO₄] = 0.47 mol/L; Supplied electricity = 4 F/mol; The electroreduction was carried out under sonication (47 kHz). The polarity of electrodes was alternated with the interval of 15 sec.
b) Purified by reprecipitation from benzene-EtOH.
c) No precipitate was obtained after usual reprecipitation procedure.
The influences of other factors to molecular weight and yield of 12a were summarized in Table VIII. The survey of the supplied electricity under the constant monomer concentration ([11a] = 0.27 mol/L) showed the maximum of molecular weight and yield at c.a. 4 F/mol (Run 1-4). In addition, the resistance of the electrolysis solution was observed to increase rapidly about after 4 F/mol of electricity was passed. These results indicate that the high voltage may induce the anodic cleavage of Si-Si bond. In order to lower the terminal voltage the concentration of supporting electrolyte was raised. As a result, the optimum values of supplied electricity was shifted and molecular weight of the resulting polymers was increased (Run 2, 5-7). Moreover, high monomer concentration condition resulted in the increase of molecular weight (Run 8).

Table VIII. Effect of Concentration and Supplied Electricity in the Electroreductive Synthesis of 12a

<table>
<thead>
<tr>
<th>Run</th>
<th>[Monomer 3a] mol/L</th>
<th>[LiClO₄] mol/L</th>
<th>Electricity F/mol</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Yield of 12a%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.24</td>
<td>0.47</td>
<td>2.5</td>
<td>4300</td>
<td>1.6</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>0.27</td>
<td>0.47</td>
<td>4.0</td>
<td>6700</td>
<td>1.6</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>0.27</td>
<td>0.47</td>
<td>5.0</td>
<td>5200</td>
<td>1.6</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>0.27</td>
<td>0.47</td>
<td>7.0</td>
<td>4200</td>
<td>1.6</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>0.27</td>
<td>0.94</td>
<td>4.0</td>
<td>7200</td>
<td>1.6</td>
<td>57</td>
</tr>
<tr>
<td>6</td>
<td>0.27</td>
<td>0.94</td>
<td>8.0</td>
<td>8600</td>
<td>1.6</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>0.27</td>
<td>1.41</td>
<td>12.0</td>
<td>10000</td>
<td>2.0</td>
<td>29</td>
</tr>
<tr>
<td>8</td>
<td>5.10</td>
<td>1.90</td>
<td>0.3</td>
<td>14900</td>
<td>1.9</td>
<td>3</td>
</tr>
</tbody>
</table>

a) The electroreduction was carried out by using Mg anode and cathode under sonication (47 kHz) and the polarity of electrodes was alternated with the interval of 15 sec.
b) Purified by reprecipitation from benzene-EtOH.
An aryl substituted monomer 11b was also polymerized in the same electroreductive condition (Scheme IX).

Scheme IX

\[
\begin{align*}
\text{Ph} & \quad \text{Me} & \quad \text{Me} & \quad \text{Ph} \\
\text{Cl} & \quad \text{Si} & \quad \text{Si} & \quad \text{Cl} & \quad \text{Ph} \\
11b & \quad +\text{e} & \quad \text{LiClO}_4 / \text{THF} & \quad \text{Mg cathode & anode} & \quad \text{Sonication} \\
& \quad \text{[Monomer]} = 0.27 \text{ mol/L} & \quad \text{Yield} = 73\% \\
& \quad [\text{LiClO}_4] = 0.94 \text{ mol/L} & \quad \text{Mn} = 9500 \\
& \quad \text{Supplied electricity} = 8.0 \text{ F/mol} & \quad \text{Mw/Mn} = 1.9
\end{align*}
\]

Since the reaction was quenched with EtOH, a part of the resulting poly[p-(disilanylene)phenylene] 12 has Si-OEt functionality at its terminal position. This Si-OEt terminal was transformed to Si-Cl group by treating 12 with acetyl chloride, then the polymer was further electrolyzed. As the result is shown in Scheme X, the molecular weight increased by 1.4 times while the distribution of molecular weight did not change. This result indicates that the polymer was actually activated and further propagated in the above procedure.

Scheme X

\[
\begin{align*}
\text{Et} & \quad \text{Me} & \quad \text{Me} & \quad \text{Et} \\
\text{X} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{X} \\
12a & \quad +\text{e} & \quad \text{LiClO}_4 / \text{THF} & \quad \text{Mg cathode & anode} & \quad \text{Sonication} \\
& \quad \text{n} = 21 \ (\text{Mn} = 4700, \text{Mw/Mn} = 1.5) & \quad \text{Yield} = 48\% \\
& \quad \text{Electricity} = 900 \text{ C (for 3 mmol of 12a)} & \quad \text{Mn} = 6400 \quad \text{Mw/Mn} = 1.6
\end{align*}
\]

Conclusion. The novel Si-Si bond formation was achieved by the electroreduction of organochlorosilanes using the Mg sacrificial electrode. Disilanes, trisilanes, and tetrasilanes were readily obtained in good yield. The use
of Mg electrodes was essential for this coupling reaction. And the result of the mixed coupling of chlorotrimethylsilane and chlorotriphenylsilane suggests that the Si-Si bond formation may not proceed by the radical coupling of silyl radicals, but by the nucleophilic attack of the electrochemically generated silyl anion to the chlorosilane. Moreover, the same reaction system was also applied to the synthesis of the silicon backbone polymer. The molecular weight and yield of the resulting polymer were controlled by the concentration of the monomer, the supplied electricity, the alternation of electrode polarity, and the sonication of the ultrasound. High molecular weight polysilanes (Mn = 31000) having relatively narrow distribution (Mw/Mn = 1.8) was finally obtained under high monomer concentration conditions. Using the same procedure, Poly[p-(disilanylene)-phenylene] (Mn = 10000, Mw/Mn = 1.5-1.9) could also synthesized from 1,4-bis(dialkylchlorosilyl)benzene or 1,4-bis(alkylarylchlorosilyl)benzene. Since the present electroreductive polymerization could be carried out in a single compartment cell under moderate conditions, it is undoubtedly one of the simplest and most powerful tools for synthesizing polysilanes.
Experimental Section

General. IR spectra were obtained on a Hitachi 260-10 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were measured on a Varian Gemini-200 (200 MHz) spectrometer, and the chemical shifts were referenced to CDC$_3$ peaks. UV spectra were recorded on a Shimadzu Double-Beam Spectrophotometer UV-190. GC analyses were carried out on a Shimadzu GC-4C or GC-12A instrument. High resolution mass spectra (HRMS) were determined on a JEOL JES-DX 300. Elemental analyses were performed by the Center for Instrumental Analysis of Kyoto University. Gel permeation chromatography (GPC) system consists of a Shimadzu LC-6A liquid chromatograph, Shimadzu SPD-6AV UV-Vis spectrophotomeric detector, and Shodex® GPC A-803 column. Molecular weight values are relative to the polystyrene standards [Shodex® STANDARD (SL-105) polystyrene]. The constant electrocurrent was supplied with Takasago GPO 50-2 regulated DC power supply. The supplied electricity was counted by a Hokuto Denko Coulomb Amperehour Meter HF-201. The sonication of ultrasound (47 kHz) was performed by using a Yamato Branson 2200.

Material. Organomonochlorosilanes 1a-e and organodichlorosilanes 3a,b are commercially available from Shin-Etsu Chemical Co. Ltd. and they were used after distillation. Dichlorodimesitylsilane (3c)$^{27}$, 1,2-dichloro-1,1,2-trimethyl-2-phenyldisilane (5)$^{28}$, 1,4-bis(chloroethylmethylsilyl)benzene (11a)$^{29}$, and 1,4-bis-(chloromethylphenylsilyl)benzene (11b)$^{29}$ were prepared by reported method. Tetrahydrofran (THF) was distilled from Na-benzophenoneketyl under a nitrogen atomosphere. Magnesium ingot is commercially available from Rare Metallic Co. Ltd. and it was cut into rods ($\Phi = 9$ mm, length = 4 cm) for electrodes. Mg electrodes were treated with conc. HCl, and then washed with water and acetone.

Disilane. The electrolysis of organomonochlorosilanes was carried out in a 30-mL three-necked flask equipped with Mg cathode and anode, and a three-way stopcock jointed to a balloon of nitrogen. Into this cell was placed 0.7 g of
LiClO₄, and the content of the cell was dried at 50°C in vacuo for 3 hr. Chlorotrimethylsilane (0.1 mL) and 15 mL of dry THF were then added under a nitrogen atmosphere. After the solution was magnetically stirred for 3 hr, the pre-electrolysis was carried out to remove traces of water and residual chlorotrimethylsilane from the electrolysis system. That is, 600 C of electricity was passed through the cell under the constant current condition (50 mA) with external cooling of ice-water bath. During the electroreduction the polarity of the electrodes was alternated with the interval of 15 sec using a comutator. The substrate chlorosilane (6 mmol) was then syringed into the cell in a stream of nitrogen, and the solution was further electrolyzed. The progress of the reaction was monitored by GLC or TLC. After the starting material was consumed (Supplied electricity = c.a. 2 F/mol based on the substrate chlorosilane), the reaction mixture was poured into an ice cold 1N HCl (100 mL) and the aqueous solution was extracted with ether (50 mL x 3). The combined organic layer was washed twice with 50 mL of brine, dried over MgSO₄, and concentrated. The residue was purified by a silica gel column, eluting with hexane.

**1,2-Diphenyltetramethyldisilane (2a)¹³,³⁰:** IR (neat) 3050, 2960, 1430, 1250, 1110, 835, 795, 765, 730, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.35 (s, 12H), 7.20-7.65 (m, 10H); ¹³C NMR (CDCl₃) δ -3.82, 127.71, 128.41, 133.88, 138.98; MS m/e (relative intensity) 270 (5, M⁺), 255 (30, M⁺-Me), 193 (62, M⁺-Ph), 135 (100, PhMe₂Si⁺).

**Hexamethyldisilane (2b)³¹:** IR (neat) 2950, 2890, 1250, 835, 820 cm⁻¹; ¹H NMR (CDCl₃) δ 0.02 (s, 6H); ¹³C NMR (CDCl₃) δ -2.71; MS m/e (relative intensity) 146 (13, M⁺), 131 (18, M⁺-Me), 73 (100, Me₃Si⁺).

**1,2-Dimethyltetraphenyldisilane (2c)¹³,³⁰:** IR (KBr) 3020, 1480, 1420, 1250, 1100, 785, 730, 695 cm⁻¹; ¹H NMR (CDCl₃) δ 0.69 (s, 6H), 7.15-7.65 (m, 20H); ¹³C NMR (CDCl₃) δ -4.25, 128.06, 129.16, 135.47, 136.84; MS m/e (relative intensity) 394 (1, M⁺), 197 (100, Ph₂MeSi⁺).

**Hexaphenyldisilane (2d)³¹:** IR (KBr) 3040, 1480, 1420, 1100, 730, 690 cm⁻¹; ¹H NMR (CDCl₃) δ 7.20-7.70 (m, 30H); ¹³C NMR (CDCl₃) δ 128.15, 130.38,
Cross Coupling of Chlorotrimethylsilane (1b) and Chlorotriphenylsilane (1d). A solution of chlorotrimethylsilane (1b) (3 mmol) and chlorotriphenylsilane (1d) (3 mmol) in 15 mL of dry THF was electrolyzed by using the same procedure described above to give 2d (GLC yield; 25%) and 1,1,1-trimethyl-2,2,2-triphenyldisilane (2e) (GLC yield 25%).

2e32: $^1$H NMR (CDCl$_3$) $\delta$ 0.20 (s, 9H), 7.30-7.50 (m, 15H); $^{13}$C NMR (CDCl$_3$) $\delta$ -1.04, 127.95, 128.17, 129.22, 136.17.

Trisilane. A solution of chlorosilane 1 (15 mmol) and dichlorosilane 3 (3 mmol) in dry THF was electrolyzed by using the same procedure for the preparation of disilane to afford trisilane (Supplied electricity = c.a. 4F/mol based on 3).

2-Phenylheptamethyltrisilane (4a)$^{13}$: IR (neat) 3050, 2940, 2890, 1425, 1245, 1095, 830, 775, 690 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.11 (s, 18H), 0.37 (s, 3H), 7.25-7.34 (m, 3H), 7.36-7.42 (s, 2H); MS m/e (relative intensity) 266 (23, M$^+$), 193 (100, M$^+$-SiMe$_3$), 135 (75), 116 (43), 73 (61).

2,2-Diphenylhexamethyltrisilane (4b): IR (neat) 2950, 2875, 1430, 1250, 1100, 835, 700 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.15 (s, 18H), 7.26-7.37 (m, 6H), 7.40-7.50 (m, 4H); MS m/e (relative intensity) 328 (28, M$^+$), 255 (67, M$^+$-SiMe$_3$), 178 (100, M$^+$-SiMe$_3$-Ph), 163 (55), 135 (48); HRMS calcd for C$_{18}$H$_{28}$Si$_3$ 328.1499, found 328.1493.

2,2-Dimesitylhexamethyltrisilane (4c): IR (KBr) 2950, 1600, 1440, 1240 1100, 830 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$) $\delta$ 0.25 (s, 18H), 2.12 (s, 6H), 2.29 (broad s, 12H), 6.75 (s, 4H); MS m/e (relative intensity) 412 (10, M$^+$), 397 (4, M$^+$-Me), 339 (100, M$^+$-SiMe$_3$), 220 (39), 205 (38), 177 (22); HRMS calcd for C$_{24}$H$_{40}$Si$_3$ 412.24377, found 412.24542.

2-Phenylnonamethyltetrasilane (6). A solution of chlorotrimethylsilane (1b) (15 mmol) and 1,2-dichloro-1,1,2-trimethyl-2-phenyldisilane (5) in dry THF was electrolyzed by using the same procedure described above to give 6 in 55% yield.
6: IR (neat) 2950, 2890, 1250, 835, 770, 700 cm⁻¹; ^1H NMR (CDCl₃) δ -0.06 (s, 9H), 0.12 (s, 9H), 0.17 (s, 6H), 0.42 (s, 3H), 7.25-7.31 (m, 3H), 7.35-7.42 (m, 2H); MS m/e (relative intensity) 324 (39, M⁺), 251 (60, M⁺-SiMe₃), 193 (74), 174 (100), 116 (35); HRMS calcd for C₁₅H₃₂Si₄ 324.13810, found 324.15502.

Poly[methylnaphthylsilane] (7). Into the electrolysis cell (30-mL three-necked flask equipped with one pair of Mg electrodes and a three-way stopcock jointed to a balloon of nitrogen), was placed 1 g of LiClO₄, and the cell was dried at 50°C in vacuo for 3 hr. Chlorotrimethylsilane (0.1 mL) and 15 mL of dry THF were then added under a nitrogen atmosphere. After pre-electrolysis was carried out by using the same procedure for disilane, dichloromethylphenylsilane (3a), the monomer, was syringed into the cell in a stream of nitrogen. The electroreduction was performed under the constant current condition (50 mA), and the polarity of the electrodes was alternated with the interval of 15 sec using a comutator. During the electrolysis the ultrasound (47 kHz) was sonicated under cooling with water. The supplied electricity was counted by a comutator. After the electricity listed Table VI was passed through the cell, the reaction was quenched by EtOH (10 mL). The mixture was then poured into an ice cold 1N HCl (100 mL) and the aqueous solution was extracted with ether (50 mL x 3). The combined organic layer was washed twice with 50 mL of brine, dried over MgSO₄, and concentrated. The resulting crude polymer was dissolved in 4 mL of benzene and reprecipitated from EtOH (100 mL). The molecular weight of the polymer was determined by GPC with THF as the eluent.

7: IR (KBr) 3050, 2960, 1430, 1250, 1100, 1025, 780, 760, 740, 700 cm⁻¹; ^1H NMR (CDCl₃) δ -1.00-0.70 (m, 3H, SiMe), 6.30-7.70 (m, 5H, ring protons). The UV spectrum of 7 was shown in Figure II. The absorption at 340 nm (ε₃₄₀ = 9000) is characteristic to polysilane.
Poly[p-(disilanylene)phenylene] (12). 1,4-Bis(chloroethylmethylsilyl)benzene (11a) and 1,4-bis(chloromethylphenylsilyl)benzene (11b) were electrolyzed by using the same procedure for the polymerization of dichloromethylphenylsilane (3a) to give poly[p-(1,2-diethyldimethylsilanylene)phenylene] (12a) and poly[p-(1,2-dimethylphényldisilanylene)phenylene] (12b) respectively. The applied reaction conditions were listed in Table VIII and Scheme IX.

12a$^{29}$ (Run 6 in Table VIII): Mn = 8600; IR (KBr) 3050, 2960, 2875, 1460, 1380, 1250, 1125, 1005, 785, 765, 715 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.34 (broad s, 6H, SiMe), 0.91 (broad s, 10H, SiEt), 7.27 (broad s, 4H, ring protons).

12b$^{29}$ (Scheme IX): Mn = 9500; IR (KBr) 3050, 1425, 1250, 1115, 1005, 780, 735, 695 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.60 (broad s, 6H, SiMe), 7.26 and 7.30 (m, 14H, phenyl and phenylene ring protons).
References and Notes


11) The same type of electroreductive Si-Si bond formation was reported independently by using aluminum sacrificial anode, and after the present study the use of silver and copper electrodes were reported to be effective to the electroreductive coupling of organochlorosilanes.


16) The reductive potential of fluorosilane is generally more negative than the corresponding chlorosilane.17


18) The contamination of siloxanes was apparently caused by residual H2O in the electrolysis solution. In order to attain highly dry condition the electrolysis system was pre-electrolyzed in the presence of catalytic amount of chlorotrimethylsilane (See Experimental Section).


22) Recently Sakurai and his co-workers reported23 that the anionic polymerization of masked disilenes initiated by alkyl lithium gave high molecular weight polysilanes whose Mw/Mn was 1.5-1.6.


25) Ishikawa and his co-workers have reported the similar result in the electroreductive polymerization of 1,4-bis(chloromethylphenyl silyl)benzene (11b) by using the similar electroreduction system which consisted of Cu anode, n-Bu4NBPh4 as a supporting electrolyte, DME as a solvent.26


31) The structures of 2b and 2d are confirmed by the comparison of the spectroscopic data of the commercially available authentic samples.

List of Publications

Chapter 1.

Chapter 2.

Chapter 3.

Chapter 4.

Chapter 5.

Chapter 6.

Chapter 7.

The following paper, which is not included in this thesis, has been published by the author et al.

"A New Method of the Zinc Promoted Transformation of Carbonyl Compounds to Homoallylic Alcohols"
List of Oral Presentations

"Synthesis of β-Trichloromethylesters Utilizing the Active Anionic Species Formed by the Electroreduction of 2-Pyrroldone"

"Cathodic Coupling of Carbonyl Compounds with Vinylsilanes"

"Trifluoromethylation of Carbonyl Compounds Using EGB"

"Allylation of Carbonyl Compounds Using Zn-DMF System"

"Cathodic Coupling of 1,3-Dienes with Esters"

"Synthesis of Poly[p-disilanylenephenylene]s Using Magnesium Electrodes"

"Synthesis of 1,3- and 1,4-Diols Using the Cathodic Coupling of Ketones with Olefins as a Key Reaction"
"Electroreductive Coupling of 1,3-Dienes with Esters Using Magnesium Electrodes"

"Cathodic Coupling of Ketones with Vinylsilanes"

"Asymmetric Cathodic Coupling of Ketones with Allylic Alcohols"

"Synthesis of Homoallylic Alcohols by the Cathodic Coupling of Ketones with β-Trimethylsilylallyl Alcohol"

"Cathodic Coupling of Styrenes with Esters Using Magnesium Chemically Reactive Electrode"

"Cathodic Coupling of Ketones with the Olefinic Systems Bearing the Silicon Functionalities"