Exploitation of New Synthetic Reactions by Means of Cathodic Reduction

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Contents

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

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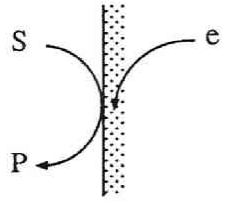
General Introduction

One of the main aims of the Electroorganic Chemistry is creation of novel organic synthesis through utilization of electrochemical reactions as key reactions.[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_{ox} or M_{red}) in the reaction system and M_{red} (or M_{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_{red} (or M_{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.[5]



S = Substrate
P = Product
M = Mediator

Fig. 1

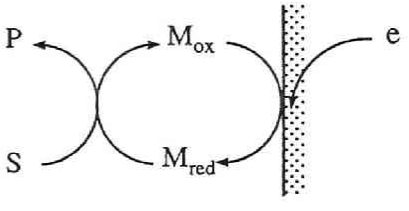


Fig. 2

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]

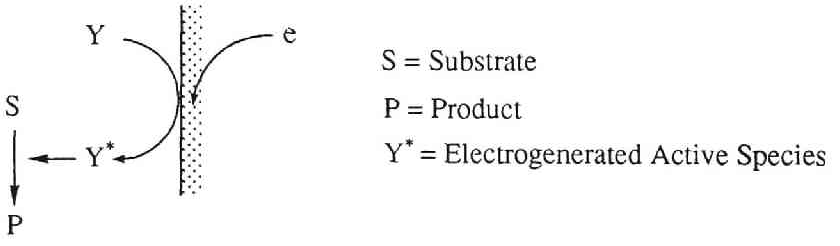


Fig. 3

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).[9]

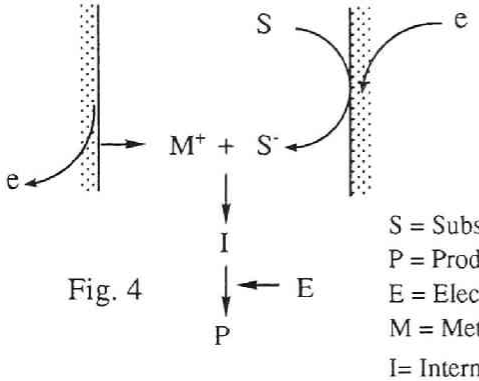


Fig. 4

S = Substrate
P = Product
E = Electrophile
M = Metal
I= Intermediate

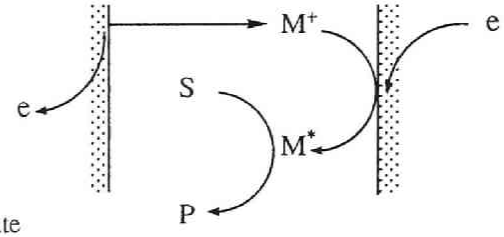


Fig. 5

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 nucleophiles) 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.

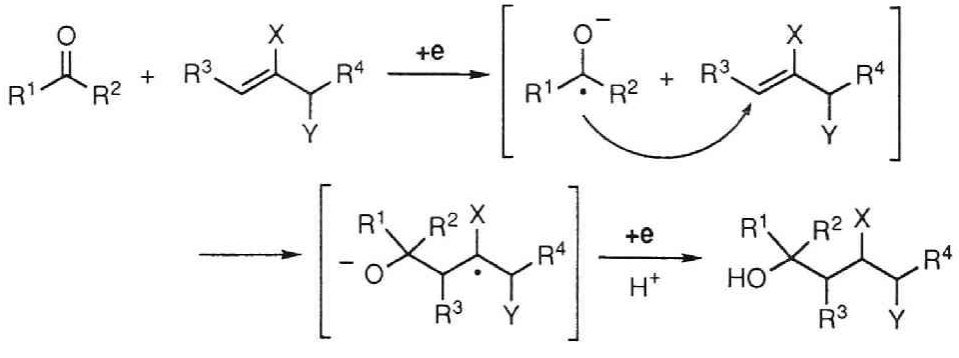
(6) Since the electron itself is used as a reagent, the reaction is non-polluting.

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 [13-15] 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



i) X = $SiMe_3$ or $Si(OEt)Me_3$ ii) Y = OH iii) X = $SiMe_3$ and Y = OH

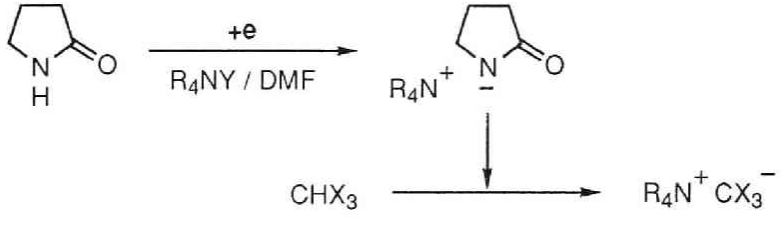
Chapter 1 deals with the regioselective intra- and inter-molecular cathodic couplings of ketones with vinylsilanes (X = $SiMe_3$ or $Si(OEt)Me_2$ in Scheme I) and some synthetic utilizations of the coupling products. A remarkable electronic effect of a trimethylsilyl group was found in the reactivity 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 = 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 = $SiMe_3$ and Y = 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.

Scheme II



R = alkyl groups ; Y = OTs, BF_4, or Br ; X = Cl or F

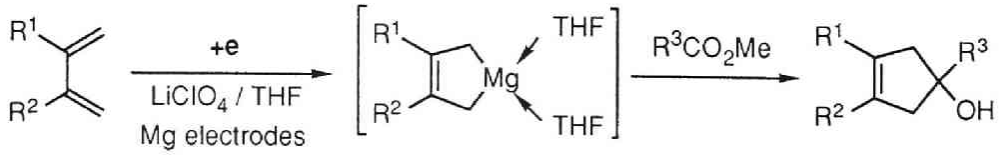
It is described in Chapter 4 that an electrogenerated base[16] prepared by the electroreduction of 2-pyrrolidone[17] is highly effective to the generation of trichloromethyl anion (X=Cl, Scheme II). Thus formed trichloromethyl anion possesses reasonable stability to react as a nucleophile, and 1,4-addition of the trichloromethyl anion to α,β-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.

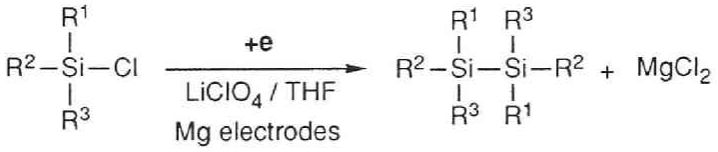
Chapter 6 deals with the cathodic coupling of 1,3-dienes with aliphatic esters promoted by Mg electrodes (Scheme III). In this reaction, Mg electrode is involved in the formation of magnesium complex of diene. The coupling of styrenes with aliphatic esters forming phenylcyclopropanol derivatives is also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

Scheme III



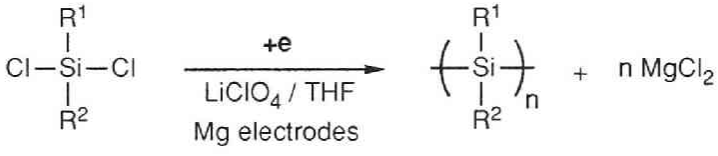
Chapter 7 deals with the electroreductive Si-Si bond formation using Mg electrodes. The electroreduction of chlorosilanes has been known to be difficult because of their highly negative reduction potential, whereas the strong reducing power of the Mg electrode system enabled the effective electroreductive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

Scheme IV



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

Scheme V



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Part I

Cathodic Coupling of Ketones with Olefinic Systems

Chapter 1

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

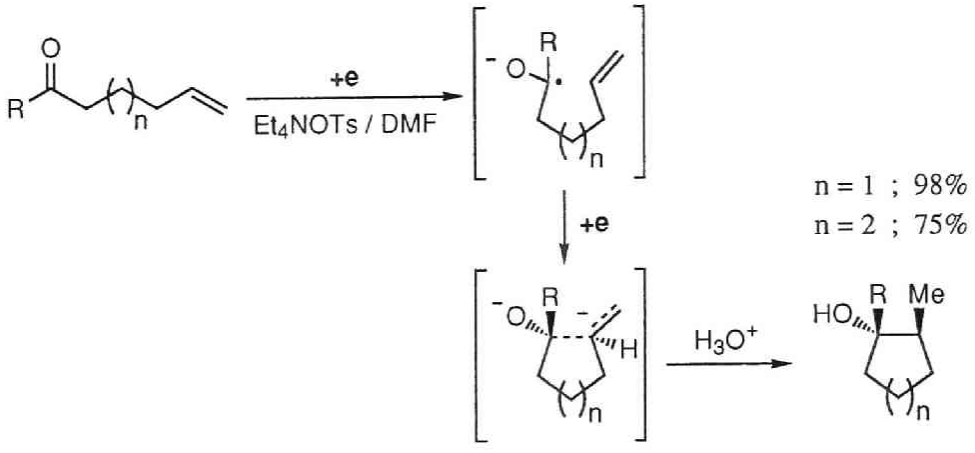
Abstract : Electroreductive intra- and inter-molecular coupling reactions of ketones with vinylsilanes have been found to take place regioselectively at the non-silylated side of the olefin. Namely, the intramolecular coupling reaction of 6-trimethylsilyl-6-hepten-2-one afforded *cis*-1-methyl-3-trimetylsilylcyclohexanol 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

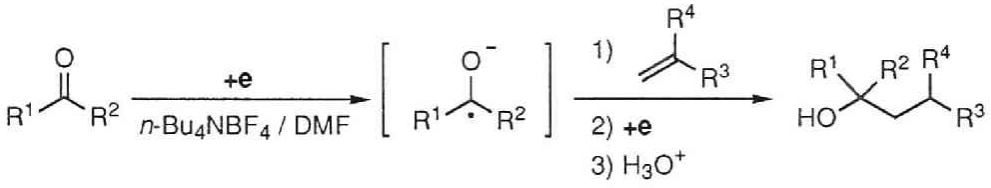


Recently it has also been reported that the intermolecular cathodic coupling of ketones with terminal olefins gave the corresponding tertiary alcohols with high regioselectivity (Scheme II).[8] The regioselectivity of the intermolecular coupling reaction is quite different from that of intramolecular 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 = an alkyl, R^4 = H) gave the corresponding tertiary alcohols in good yield, that with 2,2-disubstituted olefins (R^3, R^4 = 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 couping

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

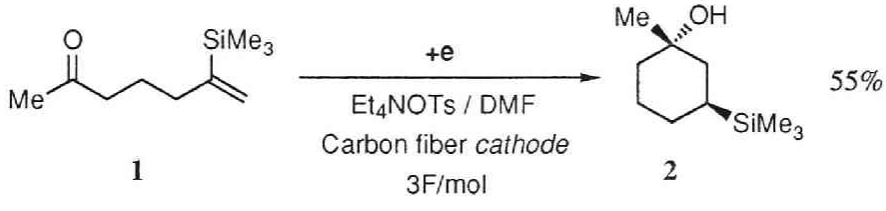


R^1 = Me, R^2 = Et, R^3 = *n*-C_6H_{13}, R^4 = H ; 77%
R^1 = Me, R^2 = Et, R^3 = *n*-Pr, R^4 = Me ; 21%

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 Et_4NOTs as a supporting electrolyte and carbon fiber as a cathode[9] 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

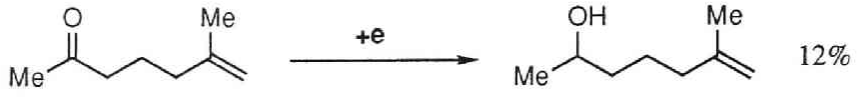


1 **2**

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

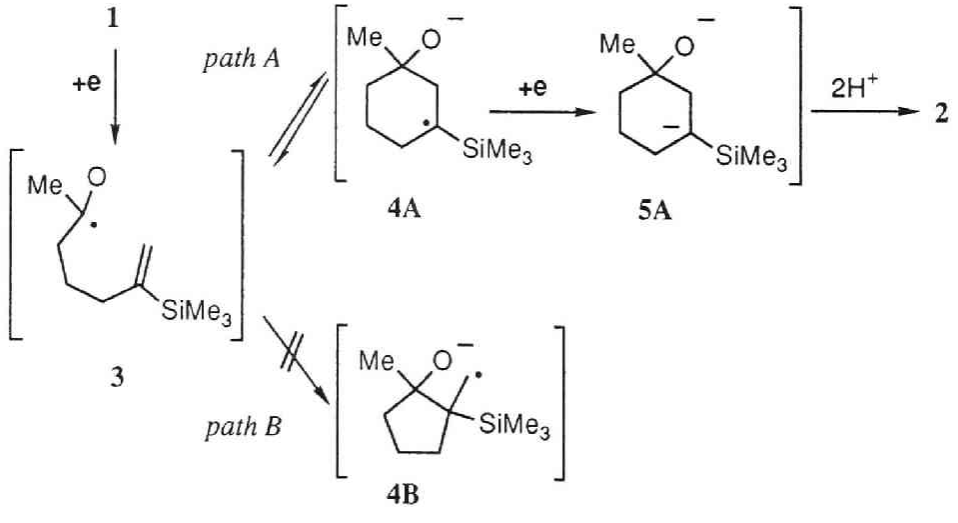
give the cyclized product but gave 6-methyl-6-hepten-2-ol in 12% yield (Scheme IV).[6]

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).

Scheme V



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.[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^3=H, **7b** ; R^3=Me, **7c** ; R^3=n-Pr) carried out in DMF using Et_4NOTs 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_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_2=C(R)R') instead of monosubstituted olefins (CH_2=CHR) resulted in the remarkable decrease of the yields of the coupling products.[8] 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[11-14] 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

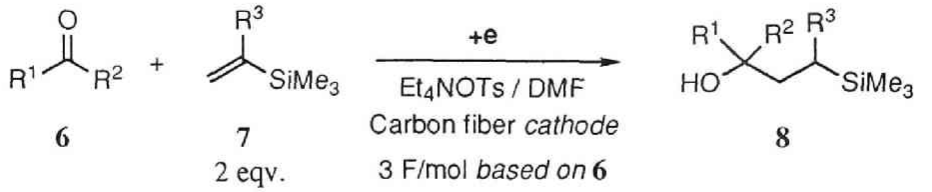
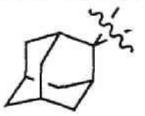
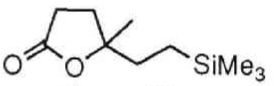
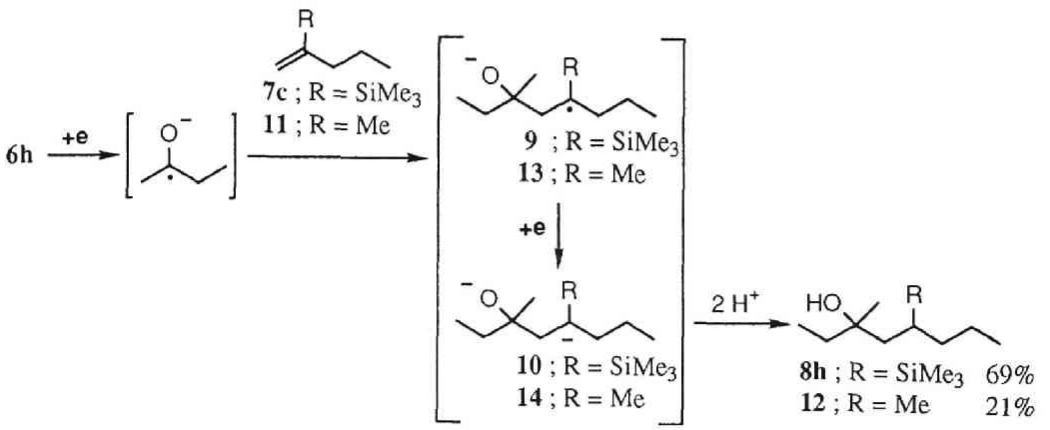


Table I. Cathodic Coupling of Ketones with Vinylsilanes

Run	Ketone **6**			Vinylsilane **7**		Product **8**	
	R^1	R^2		R^3		Yield / %[a]	
1			**6a**	H	**7a**	**8a**	74
2	-$(CH_2)_5$-		**6b**		**7a**	**8b**	74
3	*n*-C_5H_{11}	*n*-C_5H_{11}	**6c**		**7a**	**8c**	78
4	Me	*n*-C_6H_{13}	**6d**		**7a**	**8d**	72
5	Me	$CH_2CH_2CO_2Me$	**6e**		**7a**	 **8e**	31
6	Me	*n*-Pr	**6f**	Me	**7b**	**8f**	75
7	Me	*iso*-Pr	**6g**		**7b**	**8g**	68
8	Me	Et	**6h**	*n*-Pr	**7c**	**8h**	69

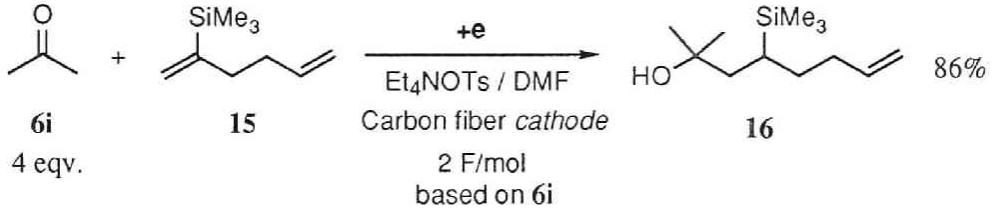
a) Isolated yields based on **6**.

Scheme VII



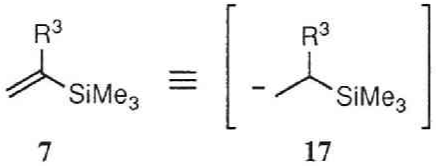
Thus, the intermolecular cathodic coupling of ketones with vinylsilanes is promoted by the electronic effect of trimethylsilyl group. It was also demonstrated by the reaction of acetone (**6i**) with 2-trimethylsilyl-1,5-hexadiene (**15**) (Scheme VIII). The anion radical formed by the electroreduction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

Scheme VIII



6i 4 eqv. **15** **16**

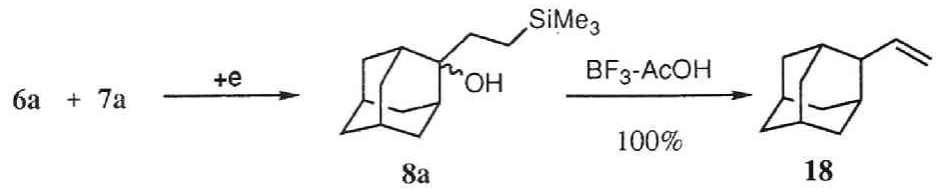
Not only from the mechanistic point of view mentioned above, the results summarized in Scheme VI and Table I seems to be also interesting from the synthetic view point. The formation of **8** by the cathodic coupling of ketones **6** and vinylsilanes **7** indicates that, under the conditions of electroreduction, **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]



7 **17**

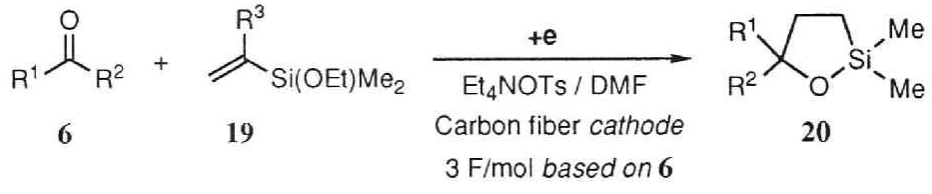
Some typical results shown in Table I indicated that this coupling reaction is widely applicable to the synthesis of a variety of β-trimethylsilyl alcohols **8**. Moreover, the compound **8** is the key intermediate for the reductive olefination of ketones (**6**, Scheme IX), for example, the treatment of **6a** (R^1, R^2 = 2-adamantyl) with BF_3-AcOH afforded **18** in quantitative yield.[16]

Scheme IX



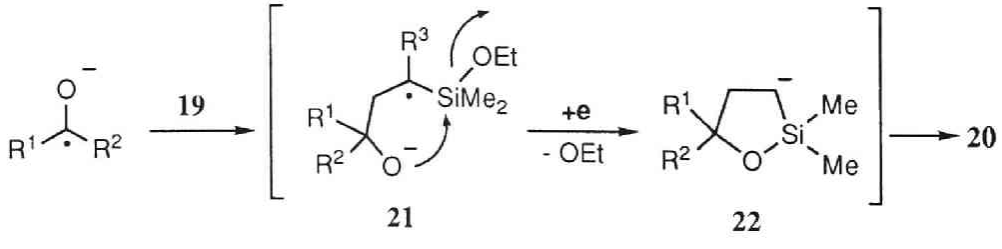
Intermolecular Cathodic Coupling Reaction of Ketones with Ethoxydimethylvinylsilanes. The cathodic intermolecular coupling reaction of **6** with ethoxydimethylvinylsilane (**19**) (Scheme X) was also found to take place at the non-silylated side of the double bond and formed oxasilacyclopetanes (**20**).

Scheme X



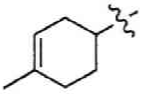
The driving force of this coupling reaction is not only the stabilization of the radical intermediate **21** by the silyl group but also the irreversible formation of thermodynamically stable siloxane ring **22** would be the important factor (Scheme XI).

Scheme XI



The typical results of this coupling reaction were shown in the 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.

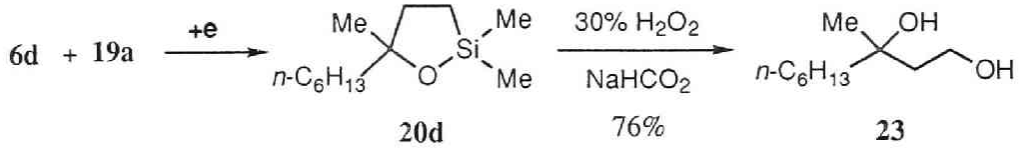
Table II. Cathodic Coupling of Ketones with Ethoxyvinylsilanes[a]

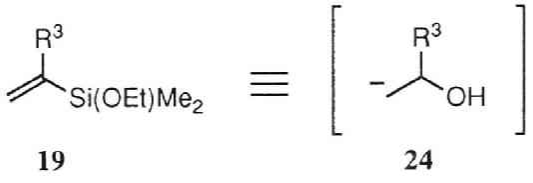
Run	Ketone **6**			Vinylsilane **19**		Product **20**	
	R^1	R^2		R^3		Yield / %[b]	
1	$-(CH_2)_5-$		**6b**	H	**19a**	70	**20b**
2	*n*-C_5H_{11}	*n*-C_5H_{11}	**6c**	**19a**		75	**20c**
3	Me	*n*-C_6H_{13}	**6d**	**19a**		75	**20d**
4	Me	*n*-Pr	**6e**	**19a**		79	**20e**
5	Me	Et	**6h**	*n*-Pr	**19b**	62	**20h**
6	Me		**6j**	**19a**		79	**20j**

a) 3F/mol of electricity based on **6** was passed.
b) Isolated yield based on **6**.

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% H_2O_2 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**).

Scheme XII





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. γ-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 atomosohere. 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 purred into aqueous saturated NH_4Cl (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 ($CDCl_3$) 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 $C_{10}H_{20}SiO$ 184.1284, found 184.1306.

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 Et_4NOTs (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 Et_4NOTs (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 ^{13}C-NMR and glc analyses. The *cis*-configuration of **2** was determined by the spectroscopic (^1H NMR, ^{13}C 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) δ -3.79 (CH_3), 20.26 (CH), 22.94 (CH_2), 26.00 (CH_2), 31.50 (CH_3), 38.67 (CH_2), 39.43 (CH_2), 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 $C_{10}H_{22}SiO$ 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[20] according to the known procedure.[22] The Wurtz coupling reaction[21] 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 $NaHCO_3$ (100 mL) and water (100 mL), and then dried over $MgSO_4$. 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 ($CDCl_3$) 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/e* (relative intensity) 142 (2, M^+), 127 (40), 99 (22), 73 (100), 59 (36) ; HRMS calcd for $C_8H_{18}Si$ 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 Et_4NOTs (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 Et_4NOTs (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 ($CDCl_3$) δ 0.00 (s, 9H), 0.40-0.50 (m, 2H), 1.43-1.88 (m, 16H); MS *m/e* (relative intensity) 237 (6, M^+-Me), 223 (79), 151 (100) ; Anal. Calcd for $C_{15}H_{28}SiO$: 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 ($CDCl_3$) 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 $C_{11}H_{24}SiO$: 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 ($CDCl_3$) 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 $C_{16}H_{36}SiO$: 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 ($CDCl_3$) δ -0.05 (s, 9H), 0.34-0.48 (m, 2H), 0.85 (t, J = 6.7 Hz, 3H), 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 $C_{13}H_{30}SiO$: 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 ($CDCl_3$) 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 $C_{10}H_{20}SiO_2$: 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 ($CDCl_3$) 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 $C_{11}H_{26}SiO$: 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 ($CDCl_3$) 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 $C_{11}H_{26}SiO$: 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 ($CDCl_3$) 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/e* (relative intensity) 201 (1, M^+-Me), 171 (3), 97 (30), 73 (100); Anal. Calcd for $C_{12}H_{28}SiO$: 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-dibromopropene[20] according to the known procedure.[22] The Wurtz coupling reaction[21] 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 ($CDCl_3$) 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/e* (relative intensity) 139 (17, M^+-Me), 111 (42), 80 (99), 73 (100), 59 (58); Anal. Calcd for $C_9H_{18}Si$: 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 ($CDCl_3$) 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/e* (relative intensity) 199 (1, M^+-Me), 183 (1), 109 (8), 82 (26), 73 (100), 55 (28); Anal. Calcd for $C_{12}H_{26}SiO$: 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.[16] 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}; ^1H NMR ($CDCl_3$) δ 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°C/760 mmHg, Yield 56%).

19b: IR (neat) 2970, 1250, 1105, 1080, 825, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 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 $C_9H_{20}SiO$: 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 ($CDCl_3$) 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 $C_{10}H_{20}SiO$ 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 ($CDCl_3$) δ 0.16 (s, 6H), 0.76 (t,J = 7.7 Hz, 2H), 0.86 (t, J = 6.3 Hz, 6H), 1.18-1.48 (m, 16H), 1.70 (t, J = 7.7 Hz, 2H); MS *m/e* (relative intensity) 256 (0.1, M^+), 213 (8), 185 (100), 75 (15); Anal. Calcd for $C_{15}H_{32}SiO$: C, 70.24; H, 12.57. Found: C, 69.96; H, 12.74.

5-Hexyl-2,2,5-trimetyl-1-oxa-2-silacyclopentane (20d): IR (neat) 2960, 2930, 2860, 1255, 955, 840 cm^{-1}; ^1H NMR ($CDCl_3$) 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 $C_{12}H_{26}SiO$: 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_9H_{20}SiO$ 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 ($CDCl_3$) 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 $C_{11}H_{24}SiO$: 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 ($CDCl_3$) 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 $C_{13}H_{24}SiO$ 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 $NaHCO_3$ using 30% H_2O_2 as a oxidizing agent.[17] The product **23** was isolated by a bulb to bulb distillation (Yield 76%).
23[23]**:** IR (neat) 3600, 2950, 1470, 1380, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) 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).

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Chapter 2

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

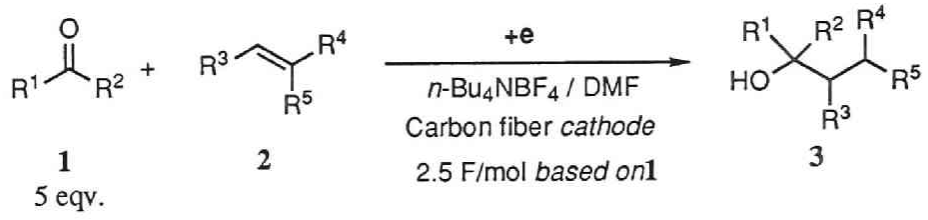
Abstract. : The intermolecular cathodic coupling of ketones with allylic alcohols was found to proceed regioselectively affording the corresponding 1,4-diols in high yields. This coupling reaction proceeded with excellent regioselectivity, and hence, the reaction of acetone with *trans*-(4R)-2-octen-4-ol 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 reported[4] 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**.

Scheme I

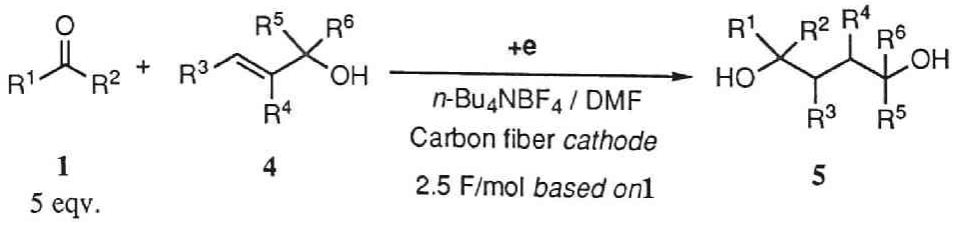


1 5 eqv. **2** **3**

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 γ-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.

Scheme II



1 5 eqv. **4** **5**

Results and Discussion

The electroreductive coupling of ketones (**1**) with olefinic alcohols was carried out in DMF using *n*-Bu_4NBF_4 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 crotyl (**4c**) types of alcohols gave the corresponding 1,4-diols in good yield (Run1-3).

From synthetic view point, 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).

Scheme III

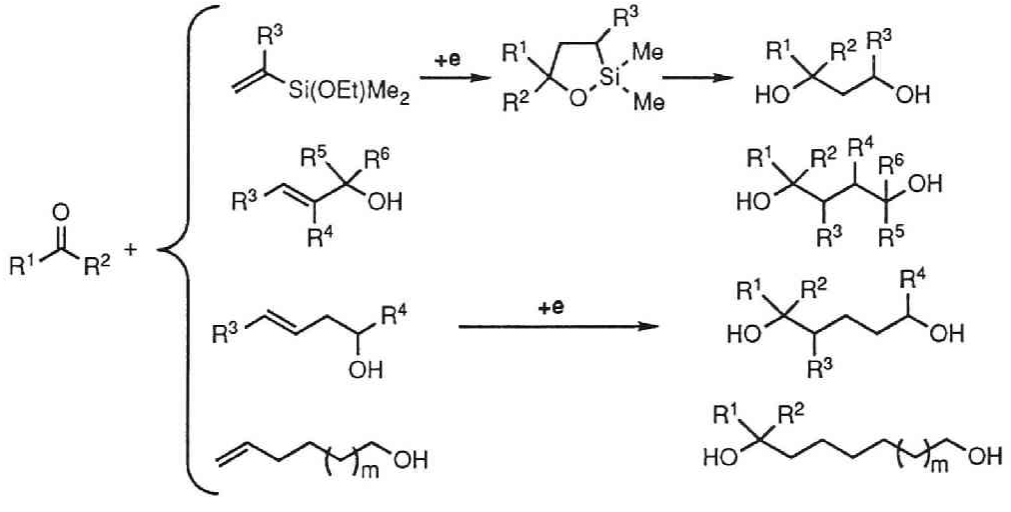
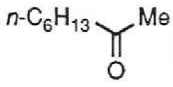
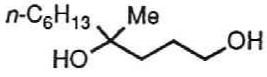
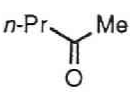
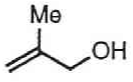
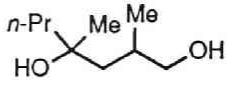
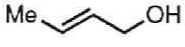
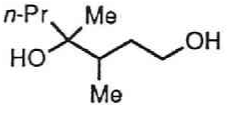
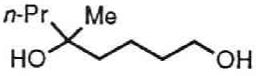
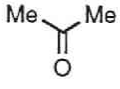
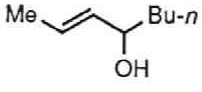
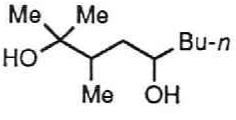
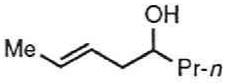
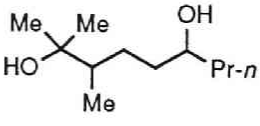
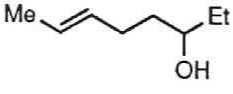
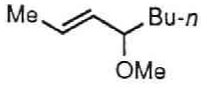


Table I. Intermolecular Cathodic Coupling of Ketones with Olefins

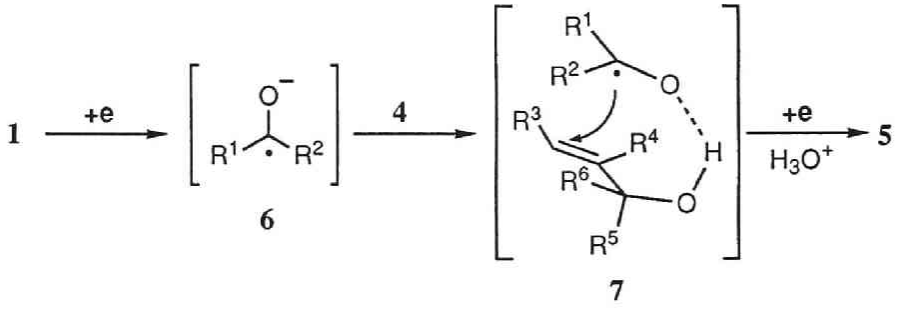
Run	Ketone (**1**)	Olefin	Product (**5**)	Yield / %[a]
1	 **1a**	 **4a**	 **5a**	89
2	 **1b**	 **4b**	 **5b**	71
3	**1b**	 **4c**	 **5c**	70
4	**1b**	 **4'a**	 **5'a**	75
5	 **1c**	 **4d**	 **5d**	78
6	**1c**	 **4'b**	 **5'b**	34
7	**1c**	 **4"a**		0
8	**1c**	 **2a**		0
9	**1c**	 **4d**-methylether		0

a) 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 *trans*-2-octen-4-ol (**4d**) gave **5d** in reasonable yield (Run 5), whereas the reaction with *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 *trans* 2-octen-6-ol (**4"a**) (Run 7) and *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).

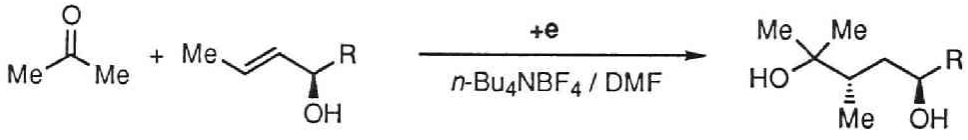
Although the role of the hydroxyl group at allylic position of double bond is not always clear, it would be reasonable to suppose that the allylic hydroxyl group interacts *via* hydrogen bonding with radical species **6** generated by the electroreduction of **1** and forms the intermediate **7** (Scheme 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,[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.

Scheme IV



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).[5] 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

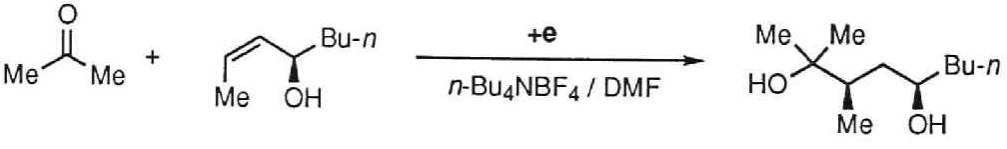


4d-*trans*-(R) ; *n*-Bu
$[\alpha]_D^{23}$ = +7.7 (c = 1.51, $CHCl_3$)
>96% *e.e.*

5d-(3S,5R)
$[\alpha]_D^{23}$ = +4.0 (c = 1.72, $CHCl_3$)
Yield 71%, >85% *d.e.*

4e-*trans*-(R) ; *iso*-Pr
$[\alpha]_D^{23}$ = -12.4 (c = 1.70, $CHCl_3$)
>96% *e.e.*

5e-(3S,5R)
$[\alpha]_D^{23}$ = -20.9 (c = 1.93, $CHCl_3$)
Yield 60%, >85% *d.e.*



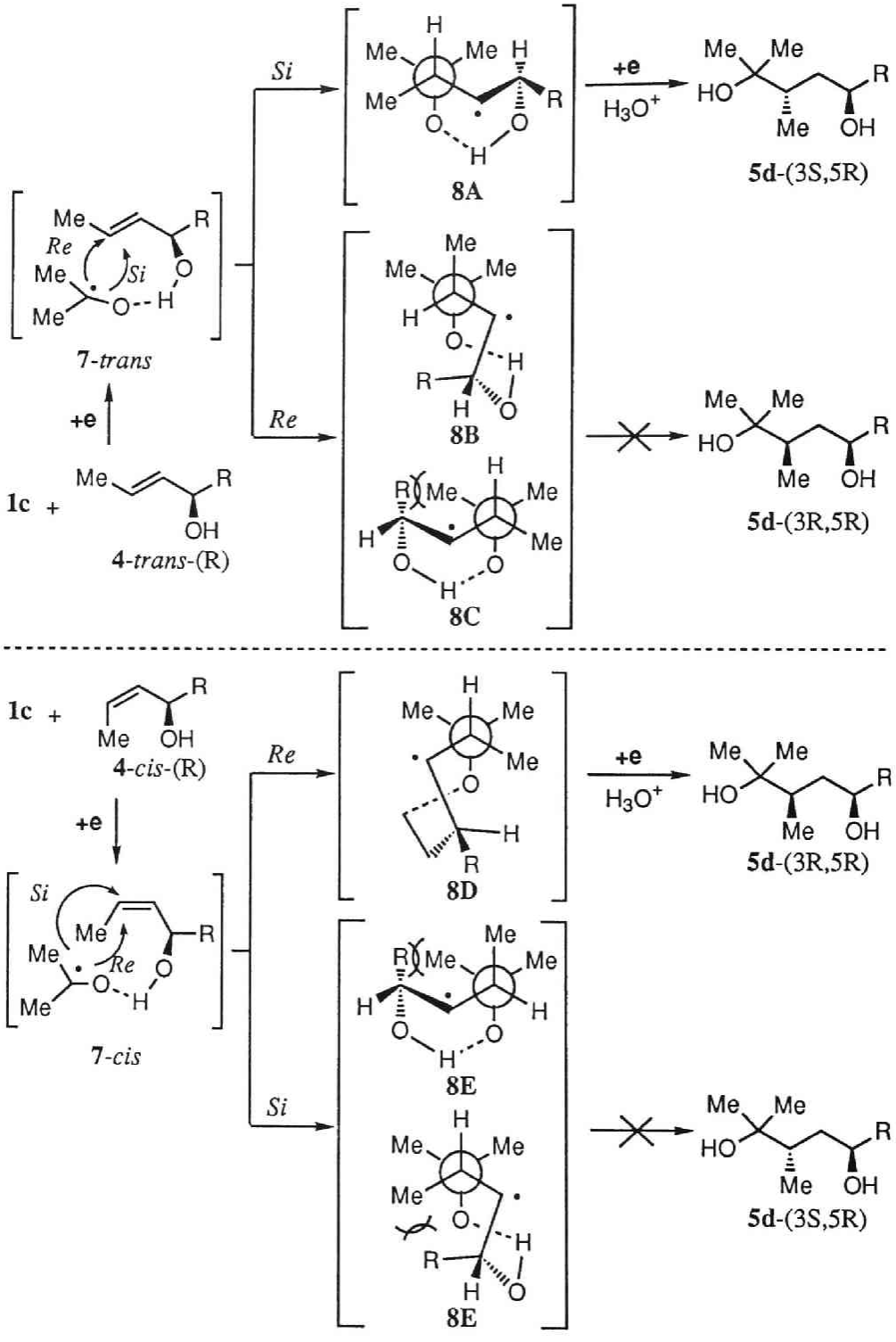
4d-*cis*-(R)
$[\alpha]_D^{23}$ = +21.9 (c = 1.94, $CHCl_3$)
>96% *e.e.*

5d-(3R,5R)
$[\alpha]_D^{23}$ = -16.0 (c =0.97, $CHCl_3$)
Yield 70%, >85% *d.e.*

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.

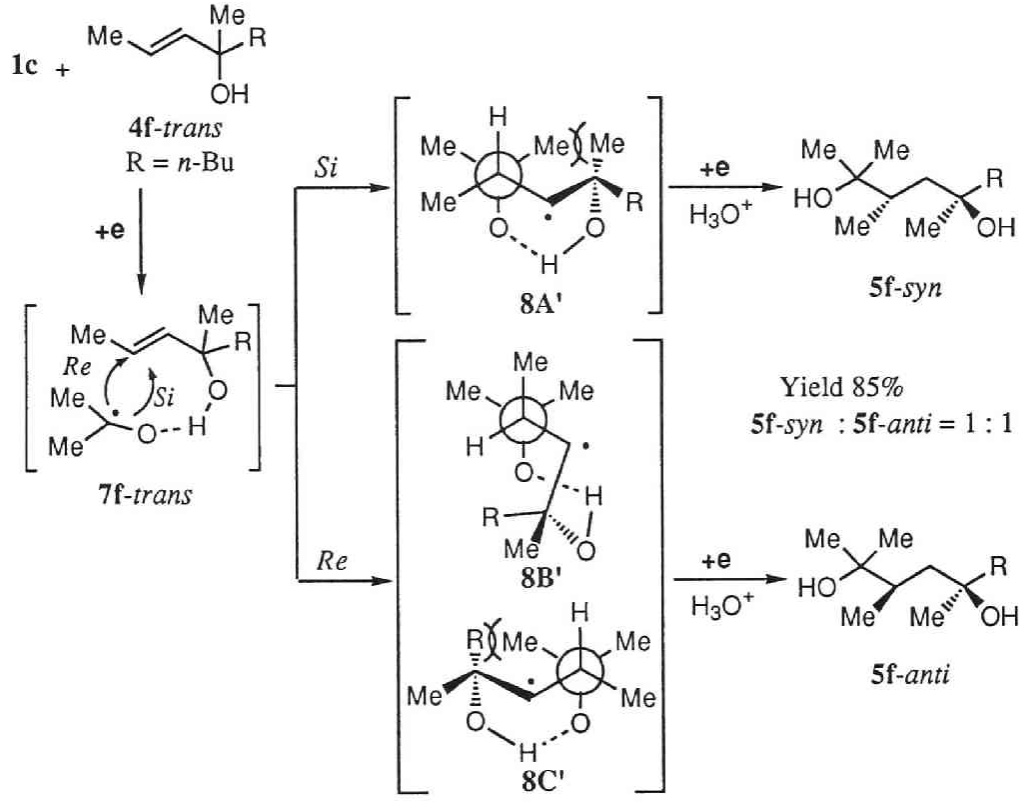
This diastereoselectivity was much influenced by the methyl group on the carbon bearing hydroxyl group. The cathodic coupling of **1c** with *trans*-4-methyl-2-octen-4-ol (**4f**) afforded 1:1 diastereomeric mixture of the corresponding diol **5f** (Scheme VII). The perturbation by the substitution of 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 hydroxyl group. Resultingly, the stability of **8A'** is comparable with those of **8B'** and **8C'**.

Scheme VI

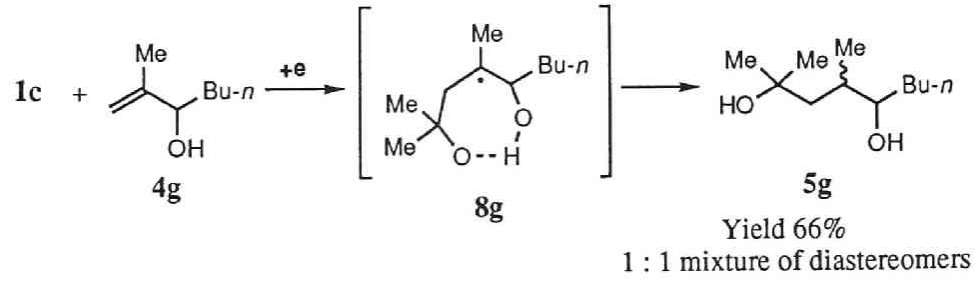

Si
Re
+e
H_3O^+
7-trans
1c +
4-trans-(R)
8A
8B
8C
5d-(3S,5R)
5d-(3R,5R)
4-cis-(R)
7-cis
8D
8E

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 dose not have the face selectivity.

Scheme VII

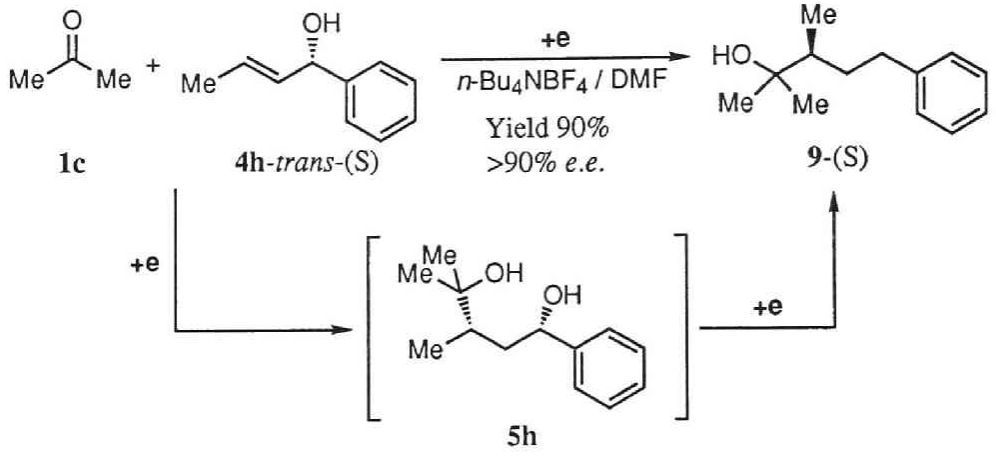


Scheme VIII



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 (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. 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.[7] Homoallyl alcohol **4'b** was prepared by $TiCl_4$ catalyzed coupling[8] of (1-methyl-2-propenyl)trimethylsilane[9] with butanal. The preparation of **4"a** was attained by the reaction of 3-pentenylmagunesium 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.[10,11] 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 polyacryronitrile (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 ($CDCl_3$) δ 0.90 (t, J = 6.0 Hz, 3H), 1.20-1.65 (m, 6H), 1.71 (d, J = 6.0 Hz,

3H), 4.04 (q, J = 6.0 Hz, 1H), 5.41-5.76 (m, 2H); $[\alpha]_D^{23}$ = +7.7° (c = 1.51, $CHCl_3$).

***cis*-(R)-2-Octen-4-ol [4d-*cis*-(R)]:** IR (neat) 3350, 2910, 2860, 1680, 1440, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 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° (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}; ^1H NMR ($CDCl_3$) δ 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 ($CDCl_3$) δ 17.56, 17.93, 18.03, 33.65, 78.31, 127.88, 132.58; $[\alpha]_D^{23}$ = -12.4° (c = 1.70, $CHCl_3$ [lit.[12] $[\alpha]_D^{25}$ = -12.9° (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}; ^1H NMR ($CDCl_3$) δ 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 ($CDCl_3$) δ 17.50, 75.16, 126.21, 127.62, 128.57, 133.67, 143.46;$[\alpha]_D^{23}$ = +46.5° (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_4NBF_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_4NBF_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}; ^1H NMR ($CDCl_3$) δ 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_2O), 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}; ^1H NMR ($CDCl_3$) δ 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, 7 H), 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 $C_9H_{20}O_2$: 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}; ^1H NMR ($CDCl_3$) δ 0.91, 0.95 (d, 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}; ^1H NMR ($CDCl_3$) δ 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_2O), 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}; ^1H NMR ($CDCl_3$) δ 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_2O-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}; ^1H NMR ($CDCl_3$) δ 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_2O-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}; ^1H NMR ($CDCl_3$) δ 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}; ^1H NMR ($CDCl_3$) δ 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 ($CDCl_3$) δ 13.98, 16.48, 22.68, 24.50, 27.92, 28.66, 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° (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.

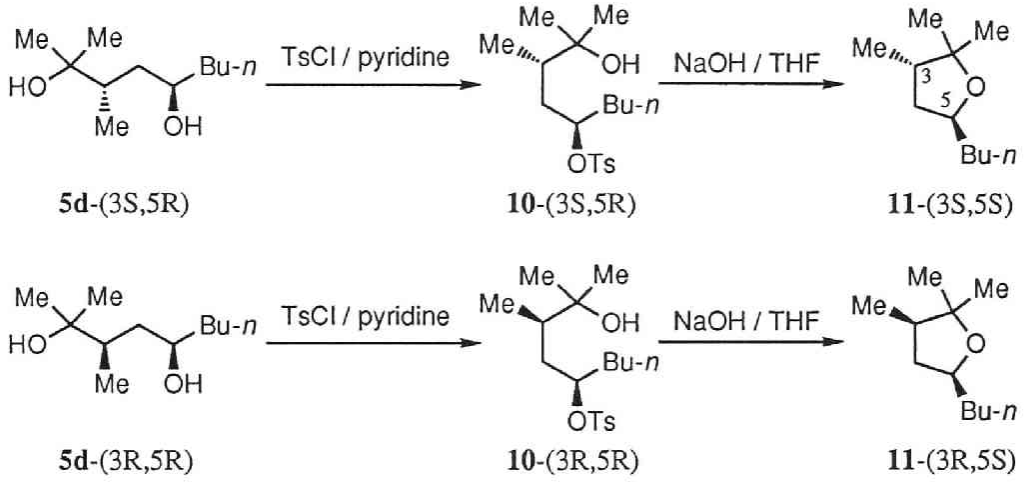
(3S,5S)-2,2,3-Trimethyl-5-butyl-1-oxacyclopentane [11-(3S,5S)]: IR (neat) 2920, 1450, 1360, 1150, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 0.92 (d, J = 7.0 Hz, 3H), 1.01 (s, 3H), 1.22 (s, 3H), 1.14-1.58 (m, 6H), 1.76 (m, 2H), 1.89 (m, 1H), 3.93 (m, 1H); MS *m/e* (relative intensity) 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 (δ 3.93) showed NOE at methyl group at 3-position (δ 0.92).

(3R,5R)-2,3-Dimethyl-2,5-nonanediol [5d-(3R,5R)]: IR (neat) 3350, 2930, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 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° (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}; ^1H NMR ($CDCl_3$) δ 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).

Scheme X



(3S,5R)-2,3,6-Trimethyl-2,5-heptanediol [5e-(3S,5R)]: IR (neat) 3300, 2920, 2880, 2360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 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° (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}; ^1H NMR ($CDCl_3$) δ 0.99 (d, J = 7.0 Hz, 3H), 1.14 (s, 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 ($CDCl_3$) δ 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°

(c = 1.95, $CHCl_3$); Anal.Calcd for $C_{13}H_{20}O$: C, 81.19; H, 10.49. Found: C, 81.08; H, 10.64.

References and Notes

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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)$_3$.
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Chapter 3

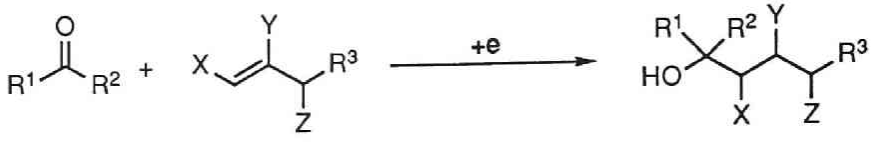
Cathodic Coupling of Ketones with Vinylsilanes Having a Hydroxy Group at the Allylic Position

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 = $SiMe_3$). The coupling of **1** with allylic alcohols (Scheme I, X = Me, Z = 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.

Scheme I



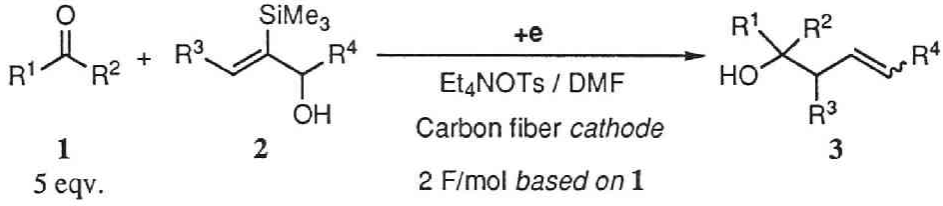
Thus, it would be attractive to examine the cathodic coupling of **1** with olefins having hydroxy and trimethylsilyl group in the same molecule (X or Y = $SiMe_3$, Z = OH). The coupling of **1** with such olefins was actually carried out and the results shown in this chapter seem to be interesting from 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, Et_4NOTs as a supporting electrolyte, and DMF as a solvent (Scheme II). Interestingly, the coupling product was not tirmethylsilyl substituted 1,4-diol (Scheme I, Y = $SiMe_3$, 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 R^3 seemed to disturb the coupling reaction,[1] and instead, base induced desilylation[2] 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,

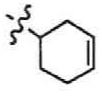
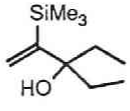
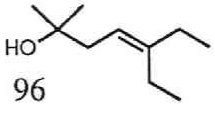
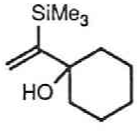
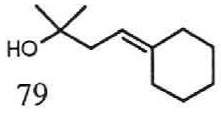
the fact that the formation of C-C bond takes place regioselectively at non-sililated side of the double bond is also interesting and deserves investigation.

Scheme II



1 5 eqv. **2** **3**

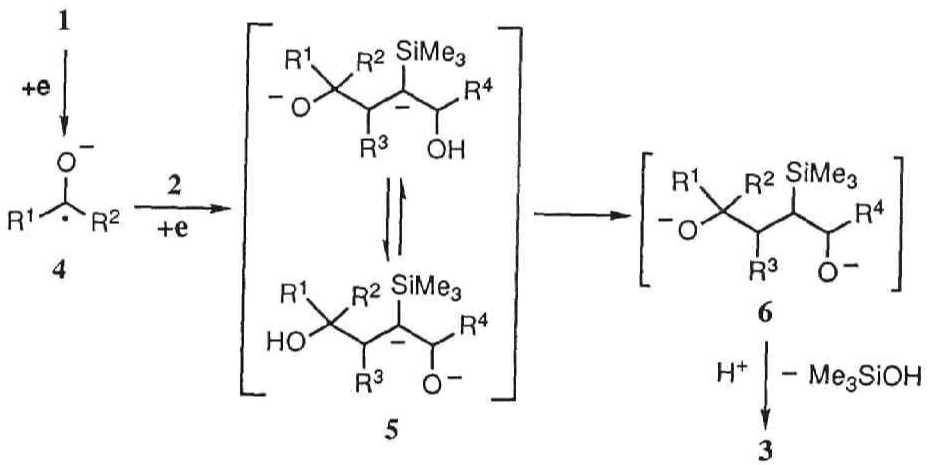
Table I. Cathodic Coupling of Ketones with Vinylsilanes 2.

Run	Ketone **1**			Vinylsilane **2**			Product **3**[a]		
	R^1	R^2		R^3	R^4		Yields (%)		*trans* / *cis*[b]
1	Me	Me	**1a**	H	*n*-Pr	**2a**	**3a**	70	4.7
2	-$(CH_2)_2$-		**1b**		**2a**		**3b**	67	4.0
3	**1a**			H	*iso*-Pr	**2b**	**3c**	87	4.0
4	Me	Et	**1c**		**2b**		**3d**	74	5.5
5	**1a**			H		**2c**	**3e**	88	4.6
6	**1a**					**2d**	**3f**	 96	
7	**1a**					**2e**	**3g**	 79	
8	**1a**			Me	*n*-Pr	**2f**	**3h**	35	6.9

a) Isolated yield. d) Determined by IR and ^{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.[3] 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,[4] the *cis-trans* ratio of the products listed in Table I may reflect the stereoselectivity of the protonation step of **5**.[5]

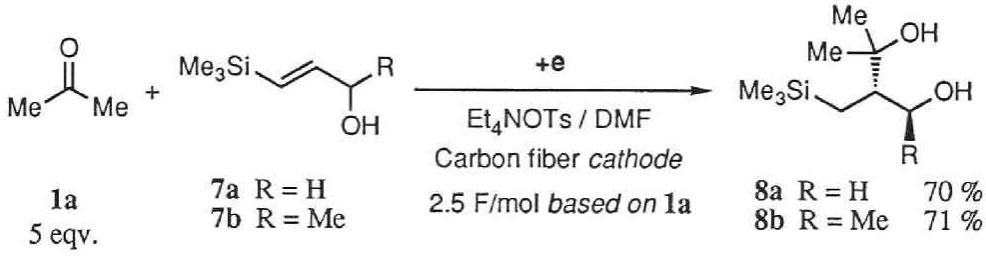
Scheme III



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



1a 5 eqv.

7a R = H
7b R = Me

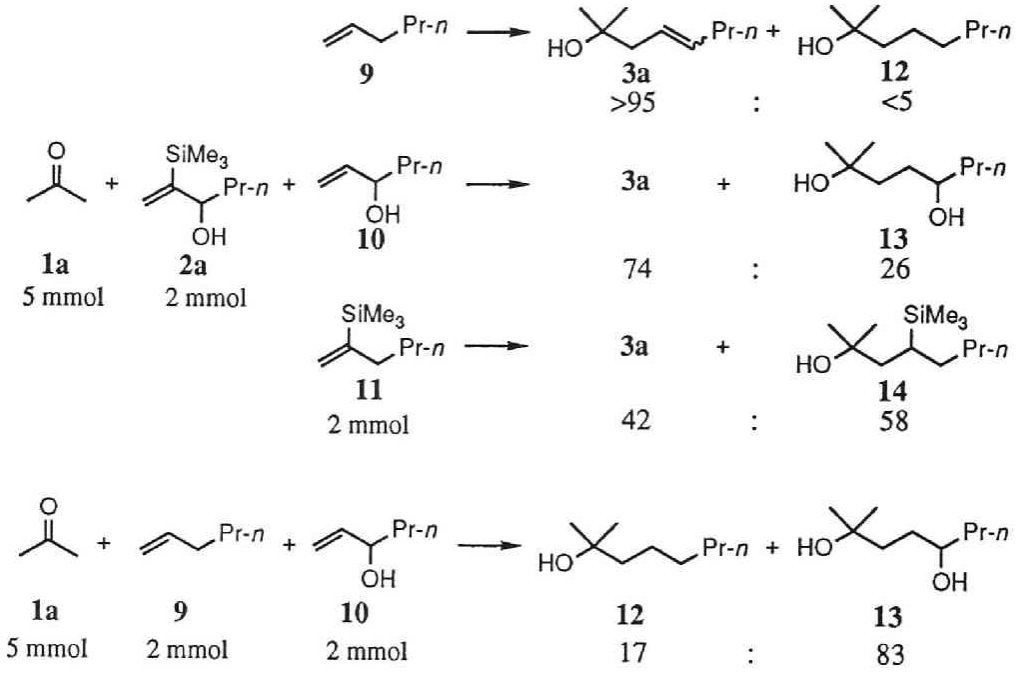
2.5 F/mol *based on* **1a**

8a R = H 70 %
8b R = Me 71 %

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[a,b]



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. α-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-cyclohexenecarboxyaldehyde, 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 ($CDCl_3$) δ 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 $C_9H_{20}OSi$: 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 ($CDCl_3$) δ 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-trimethlsilyl-1-propen-3-ol (2c): IR (neat) 3450, 3030, 2960, 2850, 1260, 840 cm^{-1}; ^1H NMR ($CDCl_3$) 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 $C_{12}H_{22}OSi$: 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 ($CDCl_3$) 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 $C_{10}H_{22}OSi$: 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 ($CDCl_3$) 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-iode-1-trimethylsilylpropene.[10] The resulting iodetrimethylsilane 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 ($CDCl_3$) 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 $C_{10}H_{22}OSi$: 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 Et_4NOTs (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 Et_4NOTs (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 NH_4Cl 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 ($CDCl_3$) 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); Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 75.79; H, 13.04.

1-(2-Hexenyl)-1-cyclohexanol (3b): IR (neat) 3360, 2925, 2860, 1450, 970 cm^{-1}; ^1H NMR ($CDCl_3$) 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 (*tans* 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 $C_{12}H_{22}O$: 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 ($CDCl_3$) 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 $C_9H_{18}O$: 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 ($CDCl_3$) 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 ($CDCl_3$) 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 ($CDCl_3$) 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 $C_{10}H_{20}O$: 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 ($CDCl_3$) 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 $C_{11}H_{20}O$: 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 ($CDCl_3$) 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[12] with $LiAlH_4$ in diglyme.[13] The oxidation of **7a** with active MnO_2 (prepared by the Attenburrow's method)[14] in pentane gave 3-trimethylsilyl-2-propenal, which was treated with MeMgI in ether to yield 4-trimethylsilyl-3-buten-2-ol (**7b**)[15].

7a[16]: IR (neat) 3320, 2960, 2870, 1620, 1250, 1080, 990, 860, 840 cm^{-1}; ^1H NMR ($CDCl_3$) 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[15]: IR (neat) 3320, 2960, 1620, 1250, 1125, 1060, 990, 865, 840 cm^{-1}; ^1H NMR ($CDCl_3$) 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 NH_4Cl 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**

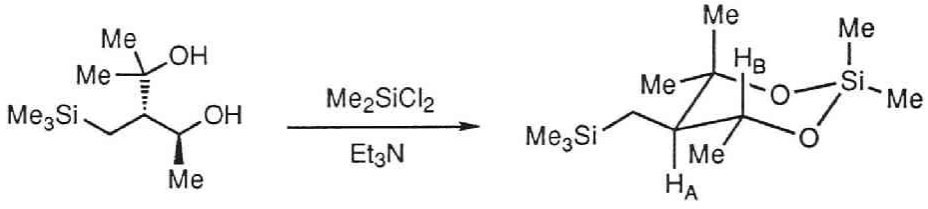
2-(Trimethylsilylmethyl)-1,3-butanediol (8a): IR (neat) 3320, 2950, 1250, 1170, 1025, 860, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 9H), 0.21 (dd, *J* = 15.0, 10.6 Hz, 1H), 0.42 (dd, *J* = 15.0, 2.3 Hz, 1H), 1.18 (s, 3H), 1.24 (s, 3H), 1.69-1.84 (m, 1H), 2.56 (OH), 3.62-3.68 (m, 2H); MS *m/e* (relative intensity) 157 (2, M^+-H_2O-Me), 131 (10), 115 (10), 73 (100), 55 (17); Anal. Calcd for $C_9H_{22}O_2Si$: 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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^+-H_2O-Me) 142 (4), 128 (9), 73 (100) ; Anal. Calcd for $C_{10}H_{24}O_2Si$: C, 58.77; H, 11.84. Found: C, 58.72; H, 12.04.

The stereochemistry of **8b** was deteermined as follows: As shown in Scheme VI, the reaction of **8b** with Me_2SiCl_2 / Et_3N gave the cyclic siloxane **15** [^1H NMR ($CDCl_3$) 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_A), 3.89 (qd, J = 6.2, 9.7 Hz, H_B) The stereochemical relation between H_A and H_B was determined to be *trans* since the couping constant of ^{1}H NMR between H_A and H_B was measured to be 9.7 Hz.[17]

Scheme VI



8b **15**

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[18] was prepared by the reaction of α-trimethylsilylvinyllithium[8] and butanal. 2-Methyl-2-octanol (**12**)[19] was identified by the comparison with the authentic sample prepared by the reaction of 2-octanone and methylmagnesium iodide.

2-Methyl-4-trimethylsilyl-2-octanol (14): IR (neat) 3400, 2950, 2870, 1460, 1380, 1250, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -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^+-Me), 185 (4), 126 (6), 111 (7), 84 (52), 73 (100), 69 (37), 56 (35); Anal. Calcd for $C_{12}H_{28}OSi$: 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.
2) Fristad, W. E.; Bailey, T. R.; Paquette, L. A. *J. Org. Chem.* **1980**, *45*, 3028.
3) The same stabilizing effect of trimethylsilyl group has been discussed in Chapter 3.
4) Colvin, E. W. In *Silicon Reagents in Organic Synthesis* Academic Press: London, **1988**.
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).
7) Ottolenghi, A.; Fridkin, M.; Zilkha, A. *Can. J. Chem.* **1963**, *41*, 2977.
8) Gröbel, B.-Th.; Seebach, D. *Chem. Ber.* **1977**, *110*, 867.
9) Chan,T.H. ; Mychajlowskij,W. ; Ong,B.S. ; Harpp,D.N. *J. Org. Chem.* **1978**, *43*, 1526.
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Part II

Generation of Trihalomethyl Anion by Electrogenerated Base

Chapter 4

Formation of a Reasonably Stabilized Trichloromethyl Anion by the Reaction of Chloroform with Electrogenerated Base, and its 1,4-Addition to α,β-Unsaturated Carbonyl Compounds

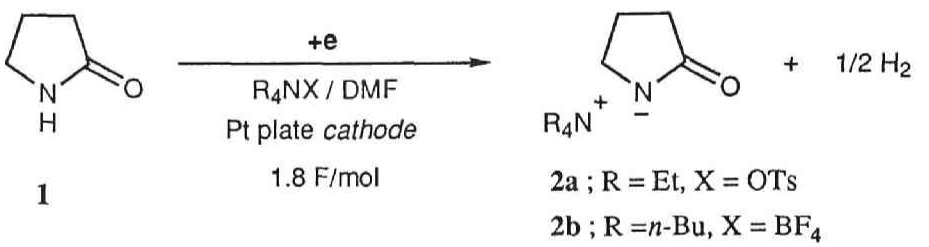
Abstract. : An electrogenerated base (EGB) prepared by the electroreduction of 2-pyrrolidone was used for the deprotonation of $CHCl_3$ forming trichloromethyl anion (CCl_3^-) effectively. Thus formed CCl_3^- was stable enough to react as a nucleophile, and its 1,4-addition to α,β-unsaturated esters and nitriles gave the corresponding β-trichloromethyl esters and nitriles in good yields, respectively. Moreover, this EGB was also applicable to the reaction of methyl dichloroacetate with α,β-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 nucleopiles 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,[3] that the electroreduction of 2-pyrrolidone (**1**) in DMF (Scheme I) using tetraalkylammonium salts (R_4NX) as supporting electrolytes yielded the corresponding anionic species **2** (**2a**; R=Et, **2b**; R= *n*-Bu) possessing interesting reactivities as bases.

Scheme I

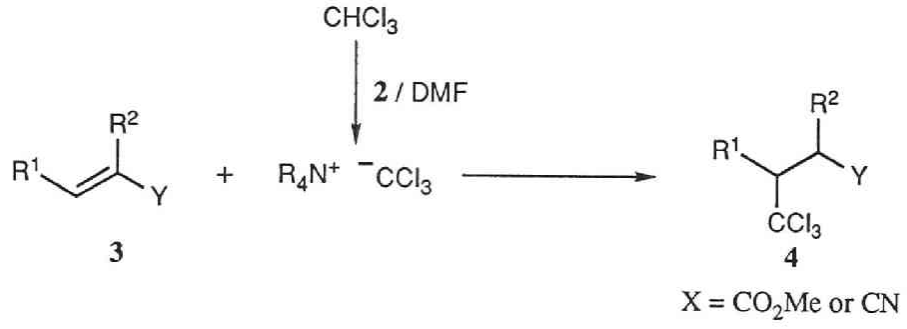


After this work, the formation of several EGBs which were prepared from other kinds of probasic compounds, such as molecular oxygen,[4-7] dicyano-(fluoren-9-ylidene)methane,[8] and carbontetrachloride,[9-12] have been reported. As compared with other EGBs mentioned above, **2** promotes a far wider variety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

In this chapter, it is described that a reasonably stabilized CCl_3^- was formed by the reaction of $CHCl_3$ with **2**, and the 1,4-addition of this CCl_3^- to α,β-unsaturated esters and nitriles **3** proceeded in excellent yields with affording β-trichloromethyl substituted compounds **4** (Scheme II). On the other hand, 1,4-addition of CCl_3^- to α,β-unsaturated carbonyl compounds is usually hardly applicable to the synthesis of β-trichloromethylcarbonyl compounds since CCl_3^- 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 CCl_3^-,[16,17] these CCl_3^- are not stable enough to be used for the 1,4-addition. For example, it has been reported that the addition of CCl_3^- to methyl acrylate (**3a** ; $R^1 = R^2 = H$, $Y = CO_2Me$) gave methyl β-trichloromethylpropionate (**4a** ; $R^1 = R^2 = H$, $Y = CO_2M$) in only 10-18% yield.[18-20] Although it was recently reported that rather stable CCl_3^- was formed

in liq.NH_3, the yield of **4a** formed through its addition to **3a** was still only 22%.[21]

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 β-trichloromethylpropionate (**4a**) in good yield.

Scheme III

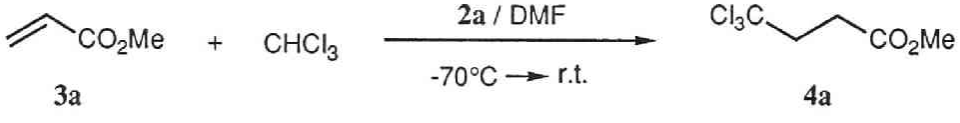


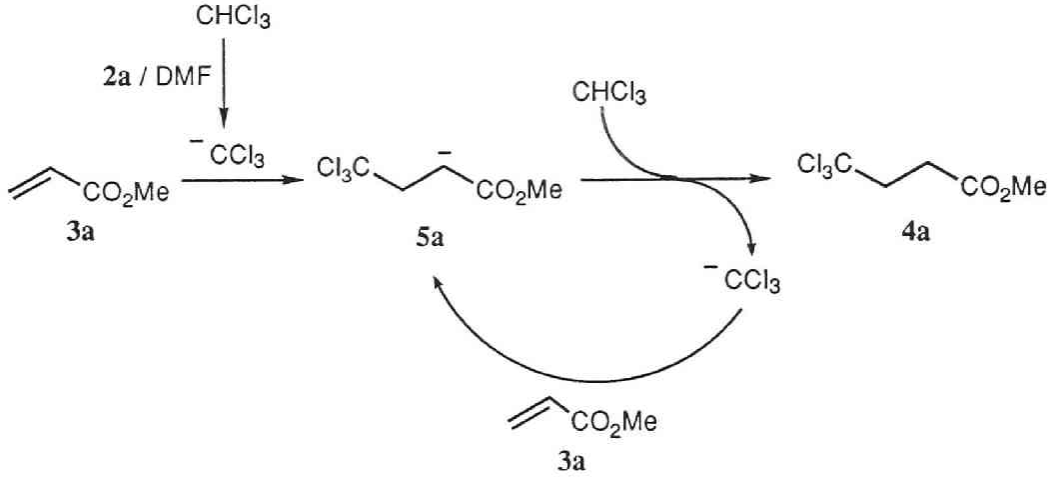
Table I. Trichloromethylation of Methyl Acrylate[a]

Run	Mol.ratio EGB **2a** / Methyl Acrylate (**3a**)	Yield of **4a** / %
1	1.5	87
2	0.3	87
3	0.2	52
4	0.1	3

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 $CHCl_3$ affords CCl_3^- and its addition to **3a** gives an anionic intermediate **5a**. The reaction of **5a** with $CHCl_3$ leads to the formation of the final product **4a** and CCl_3^-, and the addition of this reformed CCl_3^- to **3a** yields **5a**.[22]

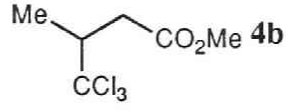
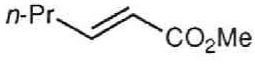
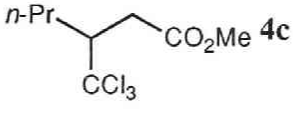
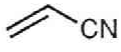
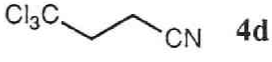
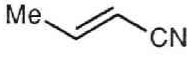
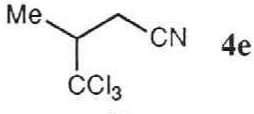
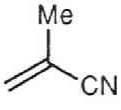
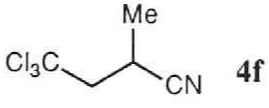
Scheme IV



The other examples are summarized in Table II. The use of **2a** as the base is effective to the 1,4-addition of CCl_3 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 study[15] that the activity of **2** as a base was largely influenced by the type of its counter cation (R_4N^+), the base **2b** (R = *n*-Bu) instead of **2a** (R = Et) was utilized for the reaction of **3c** with $CHCl_3$, and a reasonable increase in the yield of **4c** was observed (Run 3). Thus the bulkiness of R_4N^+ is one of the most important factors in this reaction. Since the reaction of **2** with $CHCl_3$ gives CCl_3^- having R_4N^+ as its counter cation, not only the basicity of **2** but also the nucleophilicity of CCl_3^- are much affected by R_4N^+. Namely, CCl_3^- bearing larger R_4N^+ (in the above case, R = *n*-Bu) is more nucleophilic than CCl_3^- bearing smaller R_4N^+ (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[a]

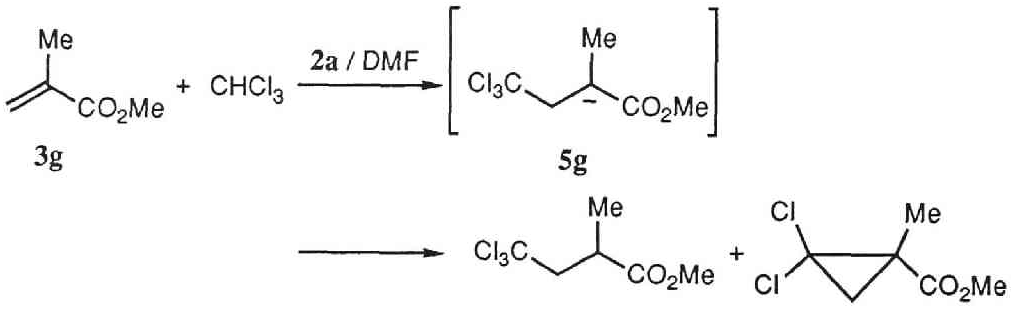
Run	α,β-Unsaturated ester and nitrile **3**	Product **4**	Yield of **4** / %[b]
1	 **3b**	 **4b**	78
2	 **3c**	 **4c**	18
3	**3c**	**4c**	35[c]
4	 **3d**	 **4d**	67
5	 **3e**	 **4e**	70
6	 **3f**	 **4f**	82

a) 0.3 eqv. of **2** and 3 eqv. of $CHCl_3$ were used. b) Isolated yields based on α,β-unsaturated esters and nitriles. c) **2b** was used as the base.

Interestingly, the reaction of $CHCl_3$ with methyl methacrylate (**3g**) carried out under the same typical reaction conditions (**2a** : $CHCl_3$ = 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** : $CHCl_3$ = 1.5 : 1) as the base, **6g** was obtained as the main product (70 % yield based on $CHCl_3$). Thus the amount of **2a** changed the aspect of the reaction of **3g** with $CHCl_3$. It can be explained as follows: Under

the typical reaction conditions, the anionic intermediate **5g** is easily protonated by the excess amount of $CHCl_3$ 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 $CHCl_3$. 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.

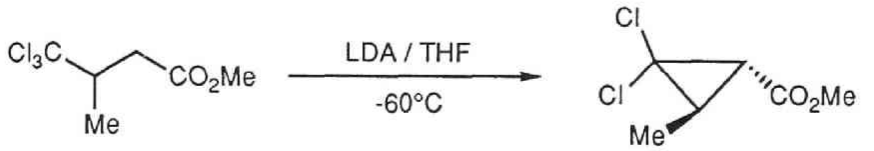
Scheme V



Conditions ;	4g	6g
2a (5 mmol), **3g** (15 mmol), $CHCl_3$ (45 mmol)	37%	10%
2a (15 mmol), **3g** (12 mmol), $CHCl_3$ (10 mmol)	10%	70%

On the other hand, the reaction of methyl acrylate (**3a**) or methyl crotonate (**3b**) with $CHCl_3$ 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.).

Scheme VI

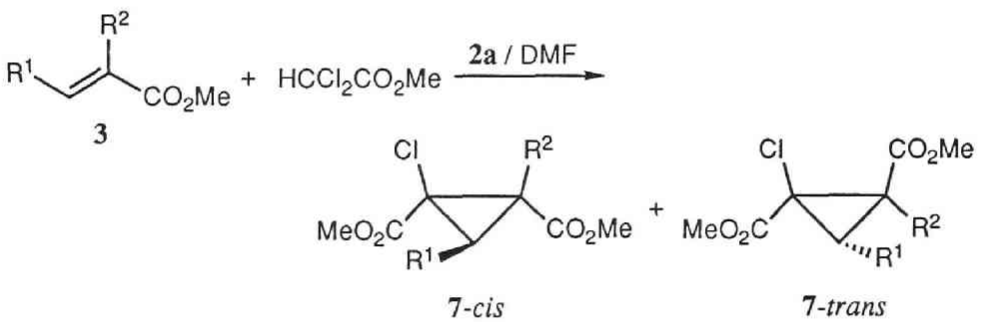


4b 78% **6b**

β-Trichloromethyl esters **4** are important materials to flame retardants of cotton,[23] and also **6b** and **6g** are key intermediates for the synthesis of insecticides.[24,25] 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).[26]

Scheme VII



7-cis *7-trans*

Table III. Reaction of 3 with Methyl Dichloroacetate[a]

Run	α,β-Unsaturated ester **3**			Product **7**	
	R^1	R^2		Total yield / %[b]	**7**-*cis* : **7**-*trans*
1	H	H	**3a**	**7a** 61	only **7a**-*trans*
2	Me	H	**3b**	**7b** 59	5 : 3
3	H	Me	**3g**	**7g** 97	1 : 1

a) Conditions ; **2a** (20 mmol), **3** (50 mmol), $HCCl_2CO_2Me$ (10 mmol).
b) Based on $HCCl_2CO_2Me$.

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 (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 GP-050-2 regulated DC power supply.

Material. Methyl 2-hexanoate was prepared by the known method.[27] Other α,β-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_4NOTs (5 mmol) as a supporting electrolyte was placed in a cathodic chamber of an electrolysis cell equipped with a platinum electrodes (2 x 2 cm^2) and a glass filter diaphragm. The anodic solution was 6 mL of DMF containing Et_4NOTs (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_4NBF_4 as a supporting electrolyte.

Trichloromethylation of α,β-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 NH_4Cl (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 $MgSO_4$, and concentrated. The residue was purified by a bulb to bulb distillation.

Methyl 4,4,4-Trichlorobutyrate (4a)[23]**:** IR (neat) 1742, 1440, 1310, 1208, 1180, 800, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) δ 17.01, 38.16, 51.65, 52.22, 104.91, 172.12; MS *m/e* (relative intensity) 187 (19, M^++4-^{35}Cl), 183 (12), 147 (24), 119 (52), 101 (90), 74 (100), 59 (59); Anal Calcd for $C_6H_9Cl_3O_2$: 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 ($CDCl_3$) 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 $C_8H_{13}Cl_3O_2$: C, 38.82; H, 5.29; Cl, 42.96. Found: C, 39.02; H, 5.26; Cl, 42.69.

4,4,4-Trichlorobutyronitrile (4d)[23]**:** IR (neat) 2250, 800, 780, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60-3.30 (m, 4H); MS *m/e* (relative intensity) 138 (65), 136 (100, M^+-Cl^{35}), 119 (32), 117 (34), 100 (31), 86 (37), 84 (53).

3-Methyl-4,4,4-trichlorobutyronitrile (4e): IR (neat) 2240, 1460, 765 cm^{-1}; ^1H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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

$C_5H_6Cl_3N$: 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 ($CDCl_3$) δ 1.53 (d, J = 7.0 Hz, 3H), 2.75-2.83 (m, 1H), 3.10-3.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.12, 23.34, 57.57, 96.65, 121.58; MS *m/e* (relative intensity) 187 (19, M^++4-^{35}Cl), 183 (12), 147 (24), 119 (52), 101 (90), 74 (100), 59 (59); Anal Calcd for $C_5H_6Cl_3N$: 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.

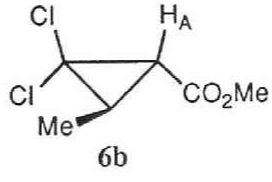
Trichloromethylation of Methyl Methacrylate (3g). Into a solution of methyl methacrylate (25 mmol) and chloroform (20 mmol) in DMF was added a solution of **2a** at -70°C under nitrogen atmosphere, and the mixture was stirred for 1 h at this temperature and for additional 4 h at room temperature. After 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_6H_9Cl_3O_2$: 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) δ 18.43, 31.00, 35.56, 52.97, 62.78, 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 $C_6H_8Cl_2O_2$ 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 st 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 $MgSO_4$, 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, 870, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (d, *J* =6.1 Hz, 3H), 2.09 (d, *J* =8.0 Hz, 1 H), 2.22 (qd, *J* = 6.2, 7.8 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$) 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 $C_6H_8Cl_2O_2$ 181.99024, found 181.99025. The stereochemistry of **6b** was determined by ^1H NMR using NOE between H_A and the methyl protons attached to cyclopropane ring (Figure I). That is, the irradiation of H_A (δ 2.09) showed strong NOE at methyl protons (δ 1.36), and this result indicated that the configuration between H_A and the methyl group is *cis*.

Figure I



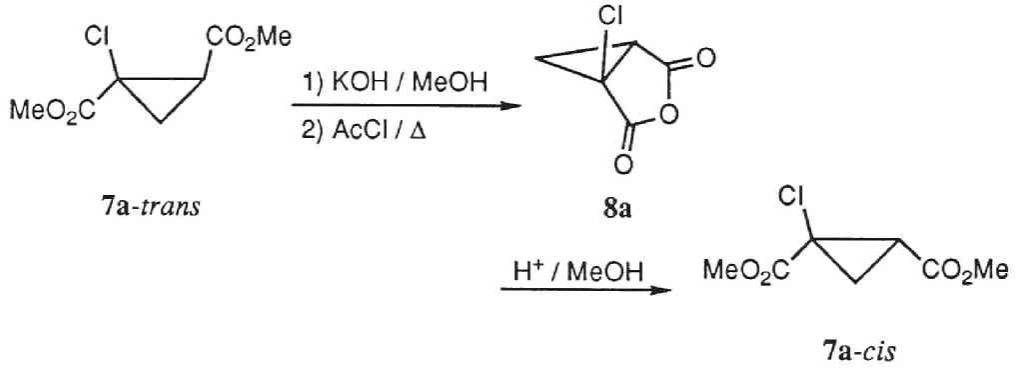
6b

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 NH_4Cl (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 $MgSO_4$. 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_7H_9ClO_4$ 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

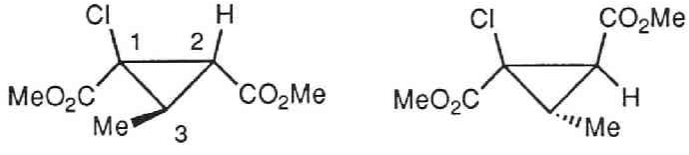


1-Chloro-1,2-cyclopropanedicarboxylic Anhydride (8a): IR (KBr disk) 1875, 1800, 1280, 1160, 995, 945, 930, 900, 870, 765, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.06 (dd, J = 8.8, 4.8 Hz, 1H), 2.02-2.23 (m, 2H).

Dimethyl 1-Chloro-1,2-*cis*-cyclopropanedicarboxylate (7a-*cis*): IR (neat) 1750, 1440, 1392, 1325, 1240, 1210, 1180, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) 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 ($CDCl_3$) 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}; ^1H NMR ($CDCl_3$) *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 $C_7H_9ClO_4$: C, 46.50; H, 5.37; Cl, 17.16 Found: C, 46.27; H, 5.33; Cl, 17.41. 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



7-cis *7-trans*

Dimethyl 1-Chloro-2-methyl-1,2-cyclopropanedicarboxylate (7c): IR (neat) 1740, 1440, 1305, 1280, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) *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 $C_8H_{11}ClO_4$ 206.03463, found 206.03481.

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Chapter 5

A Novel Trifluoromethylation of Aldehydes and Ketones Promoted by Electrogenerated Base

Absract : A base generated by the electroreduction of 2-pyrrrolidone deprotonated trifluoromethane to form a trifluoromethyl anion (CF_3^-). Thus formed CF_3^- bears tetraalkylammonium ion (R_4NX) 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_4NX. 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 analogoes 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 membrenes.

Concomitant with an increasing understanding of the behavior of organofluorine compounds,[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.[4] Although trifluoromethylation of aromatics has been achieved with a variety methods so far,[5] that of carbonyl compounds has been very limitted.

The trifluoromethyl anion, or its chemical equivalent, would obviously be valuable for trifluoromethylation of carbonyl compounds,[6] however, the generation of such a species is difficult, due to its low stability.[7,8] Its formation has so far been achieved by the reaction of dibromodifluoromethane[9,10] or iodotrifluoromethane[11-13] with Zn, under rather unusual reaction conditions. The recently reported[14,15] trifluoromethylation of carbonyl compounds involved the use of (trifluoromethyl)trimethylsilane[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)[17-20] was remarkably effective for the generation of trichloromethyl anion (CCl_3^-) by the deprotonation of chloroform ($CHCl_3$).[17] This CCl_3^- was found to react with α,β-unsaturated esters and nitriles yielding the corresponding β-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).

Scheme I

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 elecrogenerated 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 lager tetraalkylammonium ion (R_4N^+) seems to be more nucleophilic and has less tendency to decompose by elimination of fluoride ion.

Other electrogenerated bases bearing n-Bu_4N^+ 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 lather high basicity (pKa >14) is necessary to the deprotonation of CHF_3.[21]

Scheme III

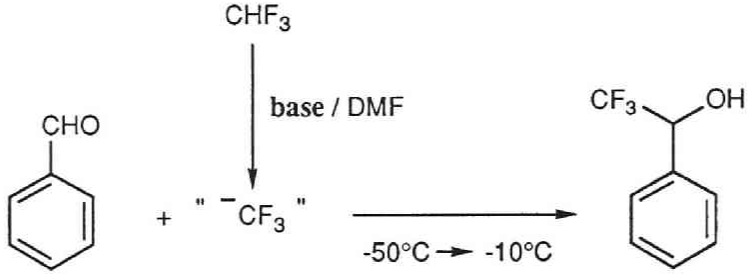
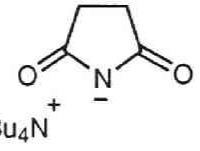
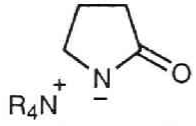
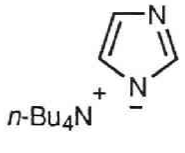


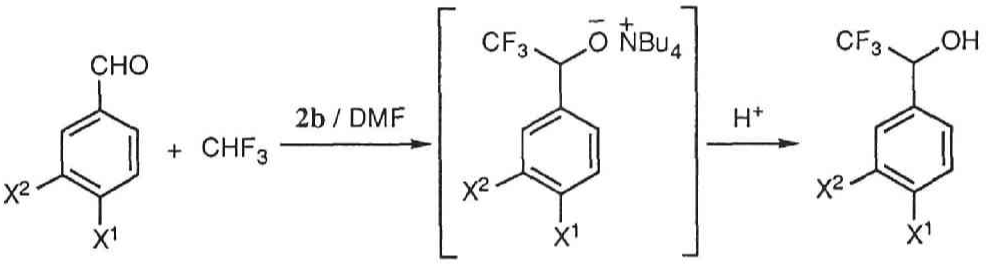
Table I. Trifluoromethylation of Benzaldehyde[a]

Run	Base	Yield of **4a** / %[b]	Run	Base	Yield of **4a** / %[b]
1	NaH	28			
2	LiH	0			
3	*tert.*-BuOK	40	8[c]		0
4	n-Bu_4NOH (40% aq.)	0			
5[c]	 **2a** (R = Et)	34	9[c]		21
6[c]	**2b** (R = n-Bu)	74			
7[c]	**2c** (R = n-Oct)	80			

a) Allreactions 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 $CF_3^{\cdot}$ reacts as a nucleophile. This results indicates that the rate of CF_3^- addtion step is not always important to this reaction but the stability of the intermediate **5** formed by the addition of CF_3^- to **3** (SchemeIV) 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_4N^+, and this tight interaction could promote the reaction.

Scheme IV



3 **5** **4**

Table II. Trifluoromethylation of Substituted Benzaldehydes using 2b

Run	Benzaldehydes **3**		Yield of **4** / %[a]
	X^1	X^2	
1	OMe	H	**4b** 92
2	*iso*-Pr	H	**4c** 56
3	Et	H	**4d** 60
4	OMe	OMe	**4e** 78
5	H	H	**4a** 74
6	Cl	H	**4f** 33

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 abve, 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_2O, Me_3SiCl, or H_2O 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.[24] 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

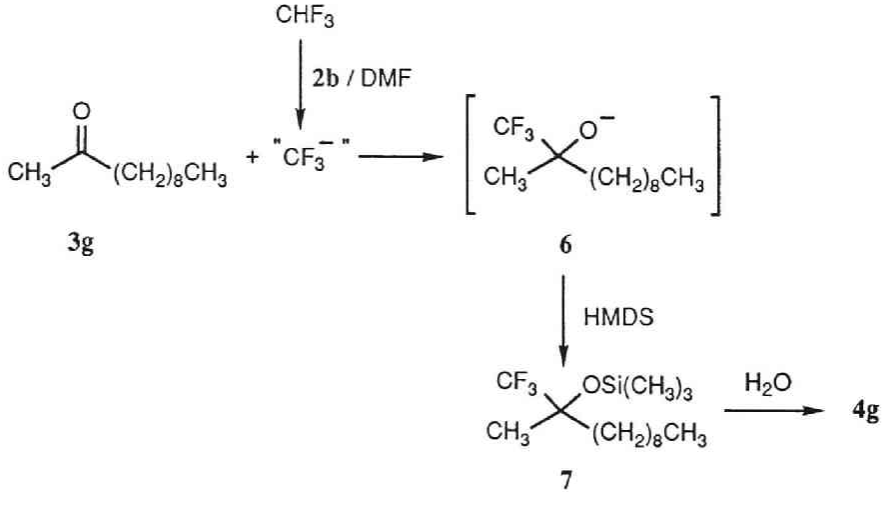
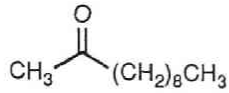
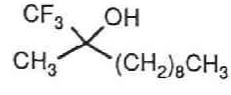
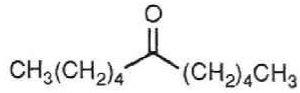
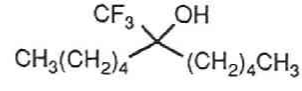
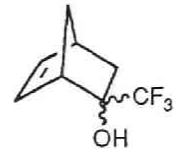
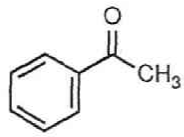
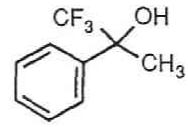
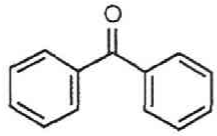
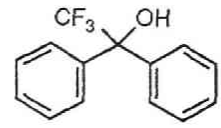
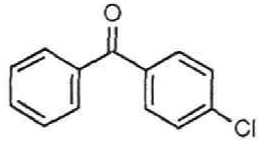
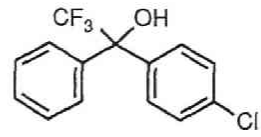
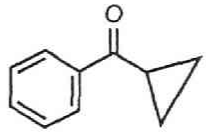
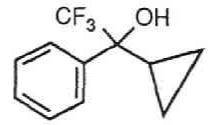
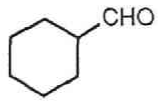
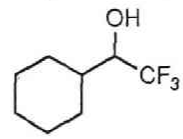


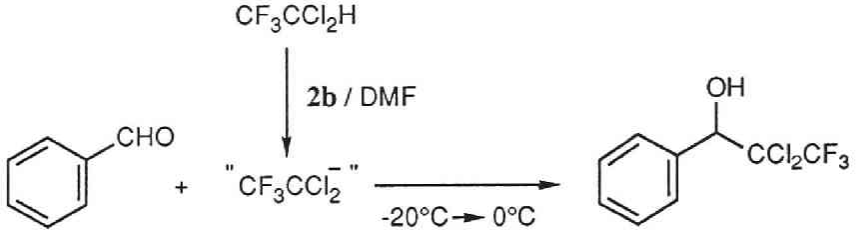
Table III. Trifluoromethylation of Carbonyl Compounds

Run	Carbonyl compound	Method[a]	Product		Yield / %[b]
1		A		**4g**	36
2		B			83
3		B		**4h**	71
4		B		**4i**	65
5		A		**4j**	trace
6		B			60
7		A		**4k**	64
8		B			84
9		A		**4l**	69
10		B		**4m**	73
11		B		**4n**	23

a) 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. b) 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_3CCl_2H) 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 ($CF_3CCl_2^-$) 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.

Scheme VI



3a **8**

45%
(25% of **3a** was recovered)

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}H NMR and ^{13}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 mesured 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 atomosphere. 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_4NX (**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_4NX (3 mmol). The preparation of a DMF solution **2** was accompished 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

trifluoromethane (*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 NH_4Cl, 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 $MgSO_4$. 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, 880, 845, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.83 (OH), 5.00 (q, J_{HCF} = 6.8 Hz, 1H), 7.30-7.53 (m, 5H); ^{13}C NMR ($CDCl_3$) 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 $C_8H_7F_3O$ 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 ($CDCl_3$) 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 $C_9H_9F_3O$ 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 ($CDCl_3$) 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 $C_{11}H_{13}F_3O$: 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{10}H_{11}F_3O$ 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 ($CDCl_3$) 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 $C_{10}H_{12}F_3O_3$: 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 ($CDCl_3$) 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 $C_8H_6ClF_3O$ 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 aqeous 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 ($CDCl_3$) δ 0.78-1.07 (m, 3H), 1.08-1.42 (m, 14H) 1.42-1.80 (m, 5H) 1.83 (OH); ^{13}C NMR ($CDCl_3$) 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^+-H_2O), 171 (14), 112 (42), 97 (27), 83 (61), 70 (100), 56 (73), 43 (54); Anal Calcd for $C_{12}H_{23}F_3O$: 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 ($CDCl_3$) δ 0.89 (t, J = 6.5 Hz, 6H), 1.20-1.46 (m, 12H) 1.51-1.75 (m, 4H) 1.80 (OH); ^{13}C NMR ($CDCl_3$) 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_2O), 171 (41), 151 (33), 131 (23), 71 (31), 56 (100), 43 (60); Anal Calcd for $C_{12}H_{23}F_3O$: 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}; ^1H NMR ($CDCl_3$) δ 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 $C_8H_9F_3O$ 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}; ^1H NMR ($CDCl_3$) δ 1.78(s, 3H), 2.53 (OH), 7.33-7.50 (m, 3H), 7.50-7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 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 $C_9H_9F_3O$ 190.06057, found 190.06125.

1,1-Diphenyl-2,2,2-trifluoroethanol (4k): IR (neat) 3450, 1510, 1480, 1280, 1170, 740, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 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 $C_{14}H_{11}F_3O$ 252.07623, found 252.07671.

1-(4-Chlorophenyl)-1-phenyl-2,2-trifluoroethanol (4l): IR (neat) 3450, 1505, 1280, 1170, 1070, 835, 772, 755, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 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 $C_{14}H_{10}ClF_3O$ 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}; ^1H NMR ($CDCl_3$) δ 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 $C_{11}H_{11}F_3O$ 216.07623, found 216.07672.

1-Cyclohexyl-2,2,2-trifluoroethanol (4n)[15]: IR (neat) 3420, 2940, 2860, 1460, 1280, 1165, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03-1.50 (m, 5H), 1.50-2.10 (m, 6H), 2.39 (OH), 3.72 (m, 1H); ^{19}F NMR ($CDCl_3$, in ppm upfield from internal standard $CFCl_3$) δ -76.14 (d, J_{HCF} = 7.3 Hz).

Preparation of 1-Phenyl-2,2-dichloro-3,3,3-trifluoropropanol (8).[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 addtion 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_4Cl (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 $MgSO_4$. 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^{-1}; ^1H NMR ($CDCl_3$) δ 4.83 (OH), 5.28 (s, 1H), 7.40-7.48 (m, 3H), 7.50-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 77.25, 122.50 (q, J_{CF} = 278.1 Hz), 128.21, 128.91, 129.78, 130.28, 135.68; MS *m/e* (relative intensity) 206 (2, M^+-Cl-OH), 107 (100), 79 (99).

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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^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H), 0.90 (t, J = 5.9 Hz, 3H), 1.24-1.35 (m, 16H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 1.88, 14.00, 20.92, 22.61, 22.72, 29.27, 29.50, 29.90, 31.86, 36.65, 76.24 (q, J_{CCF} = 23.0 Hz), 126.68 (q, J_{CF} = 287.2 Hz)

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Part III

Synthetic Reactions Utilizing Chemically Reactive Mg Electrode

Chapter 6

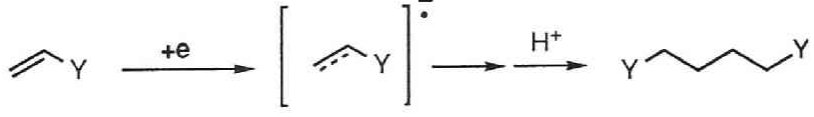
Electrochemically Promoted Cyclocoupling of 1,3-Dienes or Styrenes with Aliphatic Carboxylic Esters

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*-dehydroturmeron 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



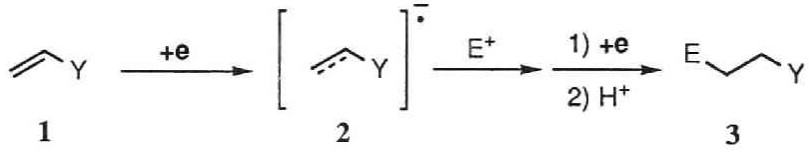
1 **2**

The fate of resulting species **2** depends on a number of experimental valuables such as solvent and electrolysis potential. For example, hydro-dimerization 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^+, Cr^{2+}, Mn^{2+}, and Zn^{2+} to the electrolysis solution inhibits the polymerization of **1** in aprotic media and enables some synthetically useful reactions such as hydrocylization.[3-5] The mixed reductive coupling of two different activated olefins can be attained by controlling the reduction potential.[6-8]

Moreover, the addition of electrophiles (E^+) in the electrolysis system provides another synthetic utility of this reaction. It has been shown in the previous studies of our laboratory[9,10] that the cathodic reduction of activated olefins **1** in the presence of electrophiles (E^+) 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^+since LUMO of **1** is sufficiently lowered by the strong electron withdrawing groups (Y), and anionic species **2** forms to react with E^+.

Scheme II



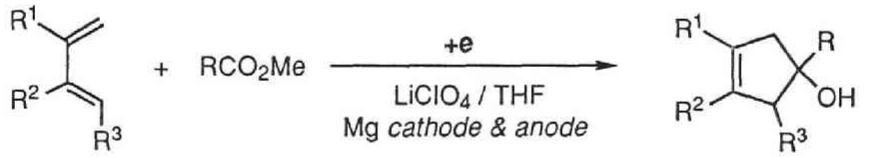
1 **2** **3**

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).[11] Accordingly, the cathodic coupling of 1,3-dienes with E^+ has never been actualized yet.

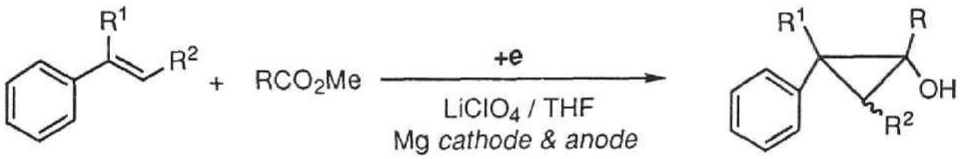
Recently, it has been found in our laboratory that the electroreduction with Mg electrodes possesses strong reducing power and promotes a variety of unique reactions such as the electroreduction of aliphatic esters.[12] Thus, it seems to be interesting to examine the electroreduction of 1,3-dienes with Mg electrodes in the presence of E^+ 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),[13] 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



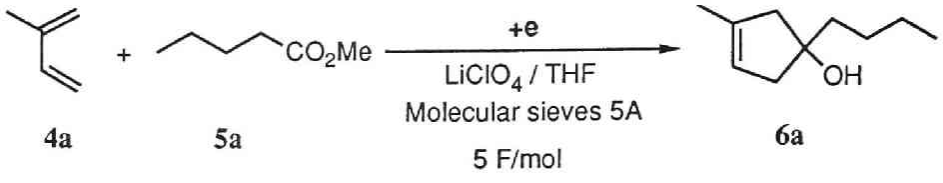
Scheme IV



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 oligamerization 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_2O 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



4a 5a 6a

Table I. Cathodic Coupling of Isoprene with Methyl Valerate

Run	Mol.ratio **4a** : **5a**	Additive	Yield of **6a** / %[a]
1	1 : 2	—	18
2	2 : 1	—	38
3	5 : 1	—	39
4	2 : 1	MS[b]	53
5	2 : 1[c]	—	70
6	2 : 1[c]	MS[b]	76

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

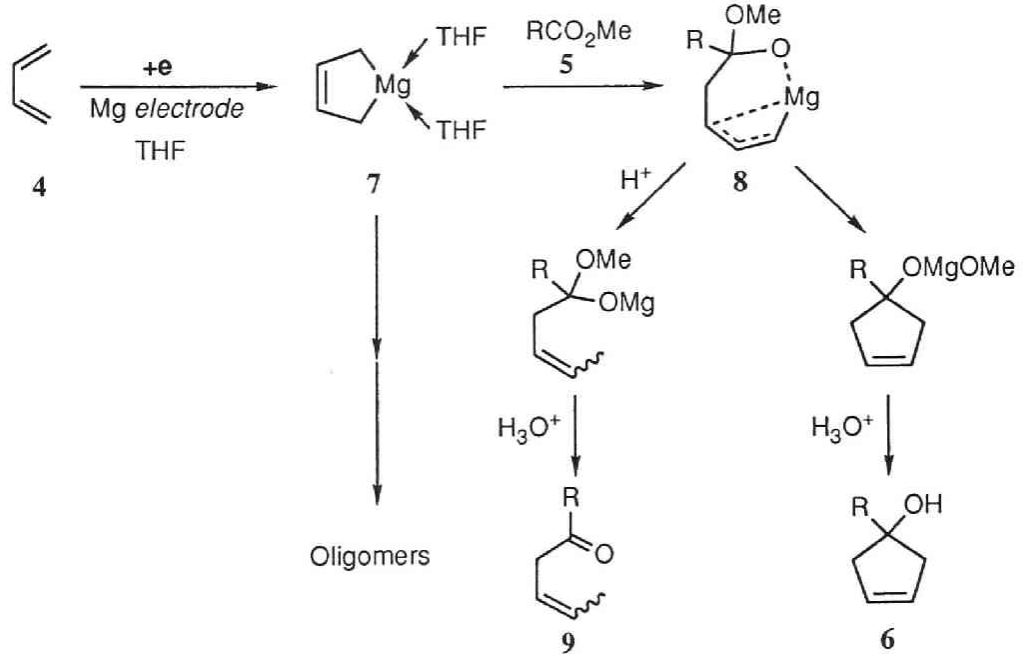
Table II. Effect of Electrode Materials[a]

Run	Materials of Electrodes		Yield of **6a** / %[b]
	Anode	Cathode	
1	Mg	Mg	76
2	Mg	Pt	75
3	Pt	Mg	0
4	Pt	Pt	0
5	Al	Al	trace[c]
6	Zn	Zn	0
7	Cu	Cu	0
8	Ni	Ni	0
9	Pb	Pb	0

a) The electroreduction was carried out under the optimized conditions (Table I, Run6). b) Isolated yield. c) The electrolysis solution bacame passivate after 1 F/mol of electricity was passed through the cell.

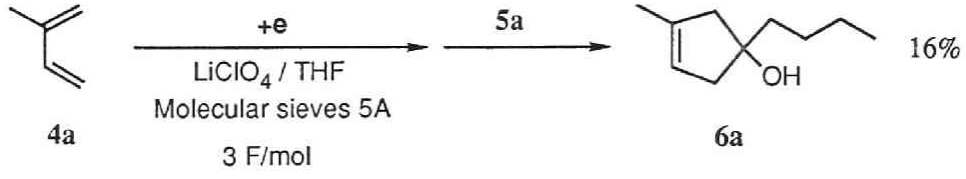
As shown in Table II, the use of Mg as the material of electrode was one of the most important factors in formation of **6a** since the electroreduction of a solution of **4a** and **5a** with other type electrode such as Pt, Al, Zn, Cu, Ni, or Pb did not afford **6a**. The use of Mg for anode and Pt 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



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 $LiClO_4$ 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 electrochchemical 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

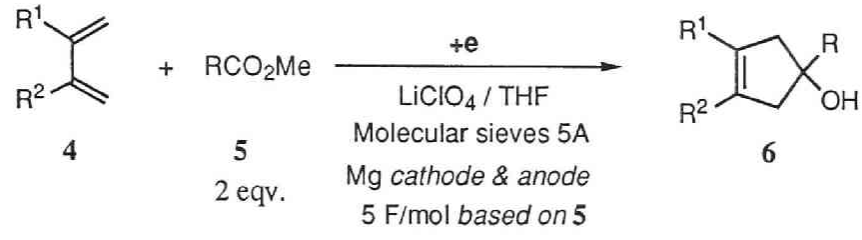
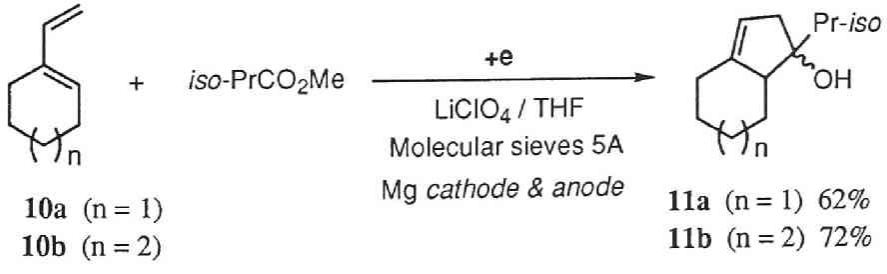


Table III. Cathodic Coupling of 1,3-Dienes with Aliphatic Esters

Run	1,3-Dienes **4**			Esters **5**		Yield of **6** / %[a]
	R^1	R^2		R		
1	Me	H	**4a**	*iso*-Pr	**5b**	**6b** 71
2	**4a**			$PhCH_2CH_2$	**5c**	**6c** 56
3	$CH_2CH_2CH{=}C(CH_3)_2$	H	**4b**	Et	**5d**	**6d** 63
4	H	H	**4c**	*n*-Bu	**5a**	**6e** 20
5	Me	Me	**4d**	*iso*-Pr	**5b**	**6f** 88

a) Isolated yield.

Scheme IX



10a (n = 1)
10b (n = 2)

11a (n = 1) 62%
11b (n = 2) 72%

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^2) groups were located on the same side of the cyclopropane ring (Scheme X). The stereochemistry of **13** was determined by ^1H 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.[26] Although formation of a Mg complex from **12** could not be detected,[27] it seems clear that the anionic intermediate formed by electroreduction of **12**[28] wit the Mg electrode has unique reactivity and the same intermediate is not formed by reduction of **12** with a Pt electrode.[30]

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

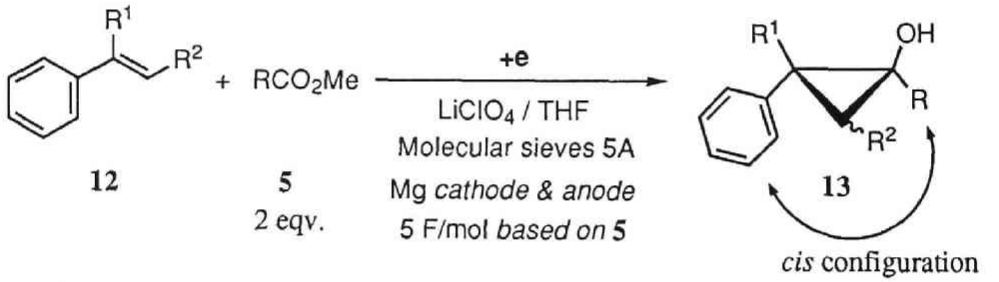


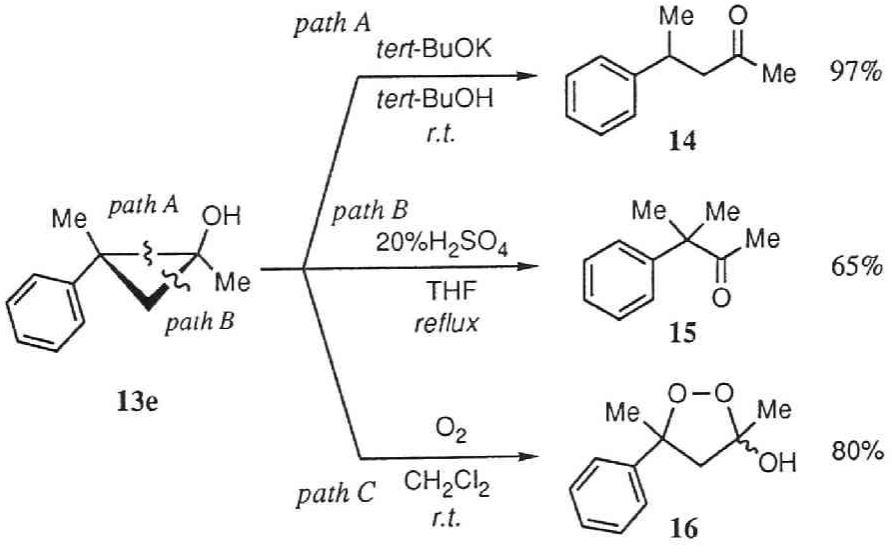
Table IV. Cathodic Coupling of Styrenes with Aliphatic Esters

Run	Styrenes **12**			Esters **5**		Yield of **13** / %[a]	
	R^1	R^2		R			
1	H	H	**12a**	Me	**5e**	**13a**	71
2		**12a**		*iso*-Pr	**5b**	**13b**	55
3		**12a**		Et	**5d**	**13c**	67
4		**12a**		*tert*-Bu	**5f**	**13d**	50
5	Me	H	**12b**		**5e**	**13e**	94
6	H	Me	**12c**		**5e**	**13f**	62

a) Isolated yield.

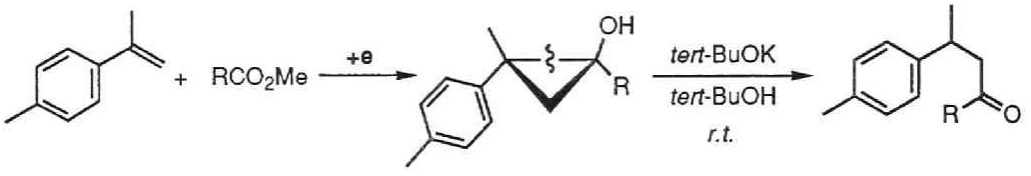
It has been reported that the treatment of **13a** with acid or base formed cyclopropane ring-opened products.[32,33] It was found in the present study that **13** yielded similar ring-opened products with much better selectivity under modified reaction conditions. Reaction of **13e** with a catalytic 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_2SO_4 (20 % aqueous H_2SO_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_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_2 did not take place without a catalyst such as AIBN.[34]

Scheme XI



The unique reactivity of **13** shown in the Scheme XI was successfully applied to the synthesis of *ar*-dihydroturmerone (R = CH_2CHMe_2) (**19**)[35] and curcumone (R = Me) (**20**).[36] Namely, the cathodic cyclocoupling of *p*-methyl-α-methylstyrene 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



17 R = $CH_2CH(CH_3)_2$; 82% **19** ; 90%

18 R = Me ; 96% **20** ; 88%

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, 860 cm^{-1}; ^1H 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 $C_9H_{16}O$: 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}; ^1H 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}; ^1H 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_2O, 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}; ^1H 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 *m/e* (relative intensity) 140 (M^+, 2), 85 (100), 57 (68); HRMS calcd for $C_9H_{16}O$ 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}; ^1H NMR ($CDCl_3$) δ 0.91 (d, J = 6.7 Hz, 6H), 1.47 (broad s, 1H), 1.60 (broad s, 6H), 1.71 (septet, J = 6.7 Hz, 1H), 2.08-2.18 (m, 2H), 2.40-2.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.70, 17.37, 36.84, 51.12, 82.16, 129.11; MS *m/e* (relative intensity) 154 (M^+, 34), 111 (100), 71 (98), 55 (48); HRMS calcd for $C_{10}H_{18}O$ 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}; ^1H NMR ($CDCl_3$) δ 0.94 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 1.05-1.50 (m, 4H), 1.69-2.08 (m,4H), 1.78 (septet, J = 6.8 Hz, 1H), 2.11-2.60 (m, 4H), 5.30 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 17.38 (CH_3), 17.77 (CH_3), 25.34 (CH_2), 26.14 (CH_2), 26.91 (CH_2), 29.06 (CH_2), 37.32 (CH), 44.93 (CH_2), 51.95 (CH), 84.12 (C), 117.72 (C), 144.19 (C); MS *m/e* (relative intensity) 180 (M^+, 30), 137 (26), 119 (9), 109 (29), 94 (26), 71 (100); HRMS calcd for $C_{12}H_{20}O$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}; ^1H NMR ($CDCl_3$) δ 0.91 (d, J = 6.9 Hz, 3H), 0.98 (d, J = 6.9 Hz, 3H), 1.30-1.95 (m, 9H), 2.03-2.67 (m,5H), 5.25-5.33 (m, 1H); MS *m/e* (relative intensity) 194 (M^+, 12), 167 (24), 149 (15), 124 (21), 108 (15), 95 (15), 81 (37), 71 (100); HRMS calcd for $C_{13}H_{22}O$194.16716, found 194.16957.

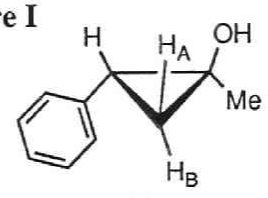
Electroreductive Coupling of Styrenes (12) with Esters (5). Electroreductive coupling of styrenes **12** with esters **5** was carried out under similar reaction conditions to those described above. The products **13** were isolated by a flash column chromatography (silica gel, EtOAc : hexane = 1 : 5). 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}; ^1H NMR ($CDCl_3$) δ 0.98 (dd, J = 7.0, 5.8 Hz, 1H), 1.19 (s, 3H), 1.25 (dd, J = 10.1, 5.8 Hz, 1H), 2.05 (broad s, 1H), 2.35 (dd, J = 10.1, 7.0 Hz, 1H), 7.10-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 18.73 (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



13a

***cis*-1-(1-Methylethyl)-2-phenyl-1-cyclopropanol (13b):** IR (neat) 3450, 2960, 1600, 1500, 1220, 1050, 895, 780, 700 cm^{-1}; ^1H 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}O$176.1208, found 176.11864.

***cis*-1-Ethyl-2-phenyl-1-cyclopropanol (13c):** IR (neat) 3300, 2960, 1600, 1500, 1460, 1205, 895, 700 cm^{-1}; ^1H 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}O$162.10452, found 162.10302.

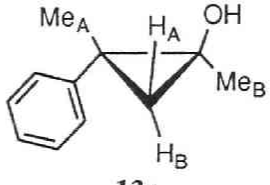
***cis*-1-(1,1-Dimethylethyl)-2-phenyl-1-cyclopropanol (13d):** IR (neat) 3400, 2950, 1600, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.17-1.30 (m, 2H), 2.23

(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 ($CDCl_3$) δ 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 ($CDCl_3$) δ 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, δ 1.13) showed NOE at the ring proton H_A (δ 1.05) and irradiation on the other methyl protons (Me_B, δ 1.52) showed NOE at the proton H_B (δ 0.84). These results supported the assigned structure.

Figure II



13e

1,3-Dimethyl-2-phenyl-1-cyclopropanol (13f): IR (neat) 3250, 1600, 1500, 1450, 1220, 1080, 805, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 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 ($CDCl_3$) δ 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}; ^1H NMR ($CDCl_3$) δ 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_2SO_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}; ^1H NMR ($CDCl_3$) δ 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-phenyl-cyclopropanol **13e** (1.2 mmol) was dissolved into CH_2Cl_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_2SO_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}; ^1H NMR ($CDCl_3$) δ 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), miner 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 ($CDCl_3$) δ 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),

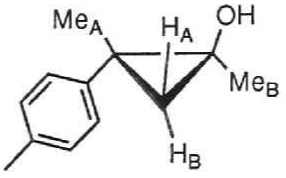
161 (100), 147 (19), 99 (19), 105 (64), 77 (19). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27; O, 24.71. Found: C, 68.13; H, 7.52; O, 24.72.

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}; ^1H NMR ($CDCl_3$) δ 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}; ^1H NMR ($CDCl_3$) δ 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); ^{13}C NMR ($CDCl_3$) δ 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 (Me_B, δ 1.50) showed NOE at the ring proton H_B (δ 0.81) (Figure III).

Figure III



18-*trans*

***cis*-1,2-Dimethyl-2-(4-methylphenyl)-1-cyclopropanol (18-*cis*):** IR (neat) 3200, 2940, 1430, 1220, 1065, 820 cm^{-1}; ^1H NMR ($CDCl_3$) 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)[35]: IR (neat) 2950, 2875, 1710, 810 cm^{-1}; ^1H NMR ($CDCl_3$) 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 $C_{15}H_{22}O$ 218.16716, found 218.16638.

4-(4-methylphenyl)-2-pentanone (Curcumone) (20)[36]: IR (neat) 2960, 2880, 1715, 820 cm^{-1}; ^1H NMR ($CDCl_3$) 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 $C_{12}H_{16}O$ 176.1202, found 176.11883.

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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.
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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]
29) Laitinen, H. A.; Wawzonek, S. *J. Am. Chem. Soc.* **1942**, *64*, 1765.
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~-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.

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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[1] and microlithography,[2] and also due to their potential utilities to the production of new class of materials having conducting,[3] photoconducting,[4] and nonlinear optical properties.[5] 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 organodichloro-monosilanes 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,[6] sonochemical reductive coupling of dichlorosilanes with alkali metals,[7] and ring opening polymerization of cyclic

organosilanes,[8] 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[9a] 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 alkylaryldichlorosialnes 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

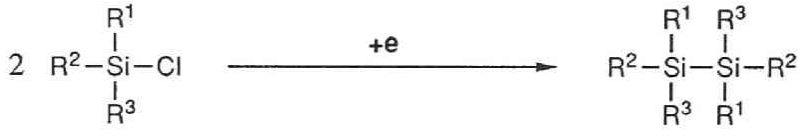
Preliminary Study on Electroreductive Formation of Si-Si bond. As mentioned above, Hengge and his co-workers reported in their frontier work that the electroreduction of organodichloromonosilanes **1** (Scheme I) carried out in a divided cell using Hg anode and Pt cathode afforded the corresponding disilanes **2**,[9] 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,[10] 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



1 (**1a** ; $R^1 = R^2 = Me, R^3 = Ph$)

2 (**2a** ; $R^1 = R^2 = Me, R^3 = Ph$)

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 $LiClO_4$ 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.[11] 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) Mg^{2+} formed in the anodic process traps Cl^-, forming $MgCl_2$.

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,[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)[a]

Run	Anode	Cathode	Alternation[b]	Yield / %
1	Mg	Mg	○	92
2	Pt	Pt	○	0
3	C	C	○	0
4	Zn	Zn	○	trace
5	Pt	Mg	×	0
6	Mg	Pt	×	93[c]

a) The electroreduction was carried out under the constant current condition (50 mA, supplied electricity = 2.0 F/mol).
b) The polarity of electrodes was alternated with the interval of 15 sec.
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 $LiClO_4$ as a supporting electrolyte gave the best result. The supporting electrolytes containing fluorine were not suitable for this reaction because fluoride ion released from electrolytes induced the halogen exchange of chlorosilane **1a** and the resulting fluorosilane was stable to the cathodic condition.[16]

Under the optimized reaction condition described above (Mg cathode and anode / the electrodes was alternated with the interval of 15 sec. / $LiClO_4$ 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%.[18]

Table II. Effect of Supporting Electrolytes and Solvents in the Electoreductive Formation of 2a[a]

Supporting electrolyte	Solvent		
	THF	DME	Dioxane
$LiClO_4$	92 %	70 %	0 %
$LiBF_4$	2	10	
n-Bu_4NClO_4	75	50	0
n-Bu_4NBF_4	12	2	

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

Scheme II

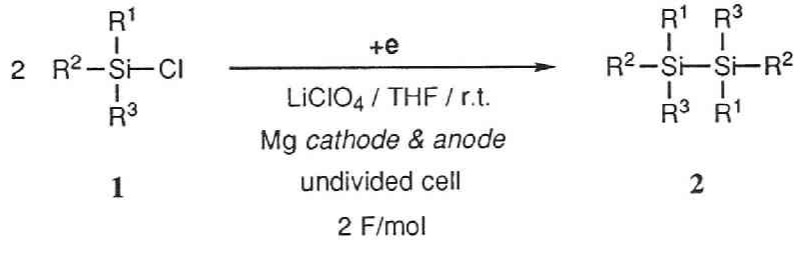


Table III. Electroreductive Formation of Disilanes (2)

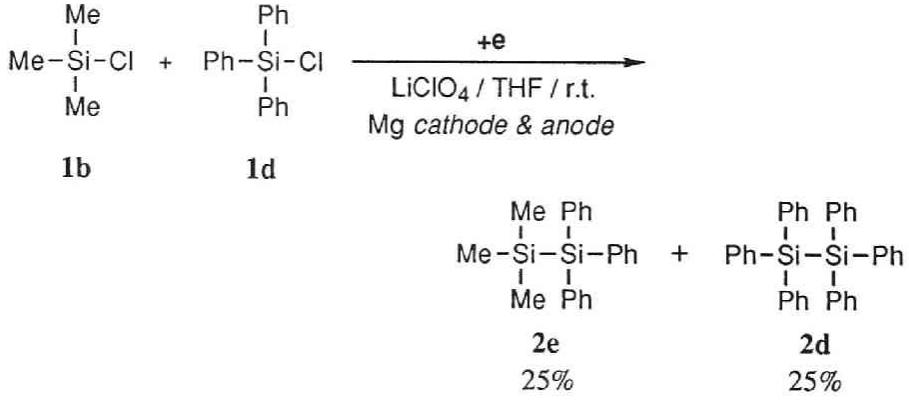
Run	Chlorosilanes **1**				Yield of **2** / %[a]	
	R^1	R^2	R^3			
1	Me	Me	Me	**1b**	**2b**	82
2	Me	Ph	Ph	**1c**	**2c**	77
3	Ph	Ph	Ph	**1d**	**2d**	85

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**[16,19]).

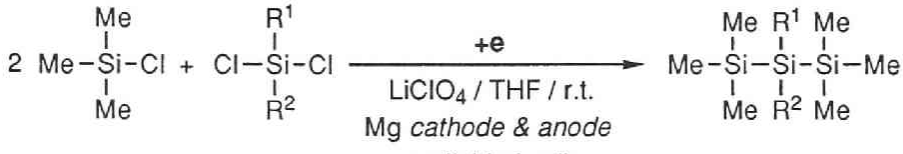
Scheme III



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.[20]

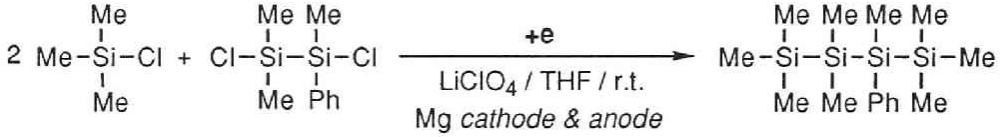
Scheme IV



1b 5eqv. **3** **4**

3a ; R^1 = Me, R^2 = Ph **4a** ; R^1 = Me, R^2 = Ph 59%
3b ; $R^1 = R^2$ = Ph **4b** ; $R^1 = R^2$ = Ph 73%
3c ; $R^1 = R^2$ = Mesityl **4c** ; $R^1 = R^2$ = Mesityl 92%

Scheme V



1b 5eqv. **5** **6** 55%

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 $MgCl_2$ 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

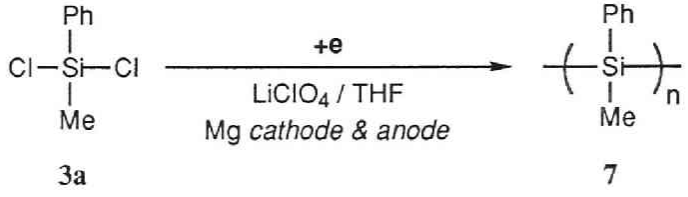


Table IV. Electroreductive Synthesis of Poly[methylphenylsilane] (7)[a,b]

Run	Alternation[c]	Sonication[d]	Mn	Mw/Mn	Yield of **7** / %[e]
1	○	○	5200	1.5	43
2	×	○	3900	1.4	17
3	○	×	4000	1.4	7

a) Concentration of monomer **3a** is 0.33 mol/L.
b) Supplied electricity is 4 F/mol.
c) The polarity of elactrodes 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 (Run4). After our work the similar result was reported[21] in the electroreductive polymerization of dichlorodimethylsilane using Al as electrodes, *n*-Bu_4NCl as supporting electrolyte, and DME as a solvent respectively, however, the

polysilanes having high molecular weight have never been obtained in this system.

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

Run	Material of Electrodes	Mn	Mw/Mn	Yield of 7 / %[b]
1	Mg	5200	1.5	43
2	Cu	700	1.1	—[c]
3	Ni	640	1.1	—[c]
4	Al	4700	1.5	15

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 elactrodes was alternated with the interval of 15 sec.
b) Purified by reprecipitation from benzene-EtOH.
c) No precipitate was obtained after usual repreciptation 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 resultingly 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

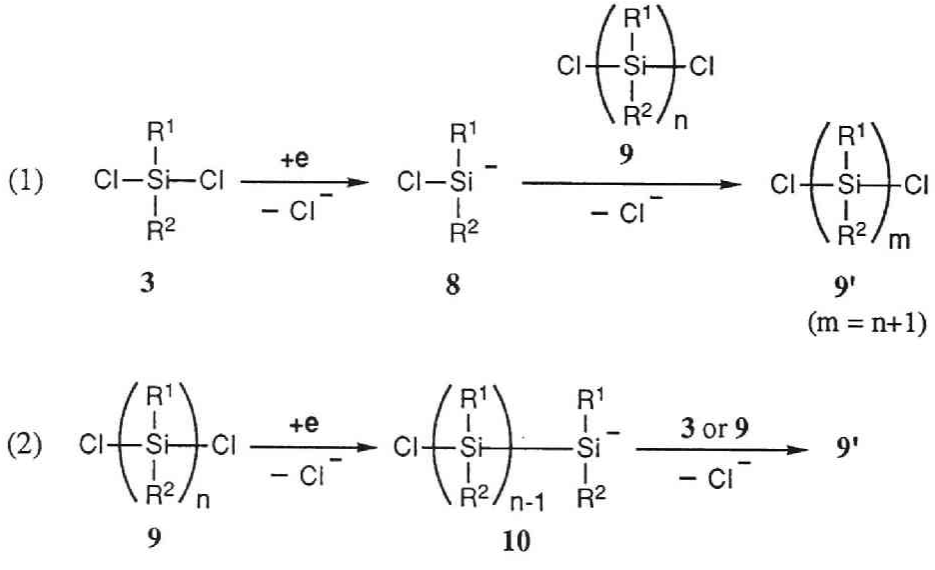
chlorosilanes (**9**). (2) The anionic species formed **10** by the electroreductive cleavage of Si-Cl bond of **9** attack monomer **3** or oligomer **9**.

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

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

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.[22]

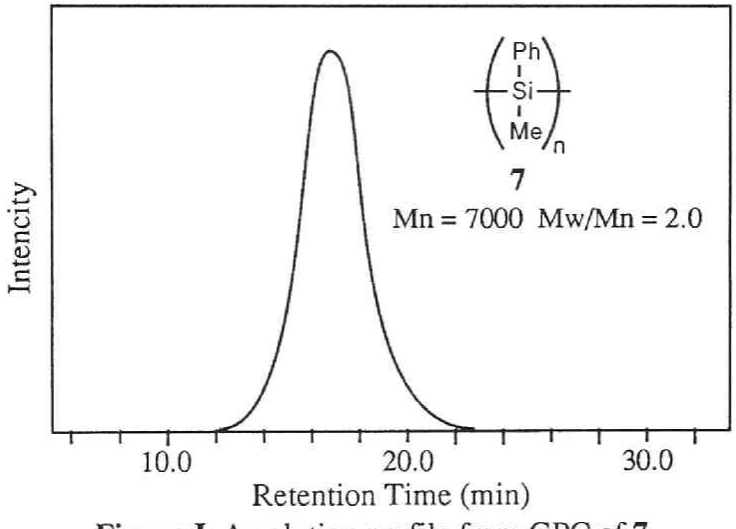
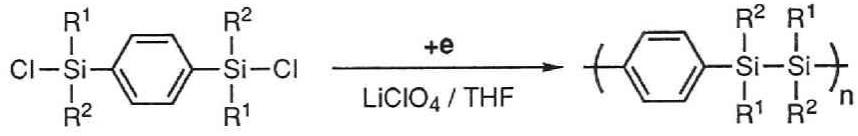


Figure I. An elution profile from GPC of **7**.

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.[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



11

11a ; R^1 = Et, R^2 = Me
11b ; R^1 = Ph, R^2 = Me

12

12a ; R^1 = Et, R^2 = Me
12b ; R^1 = Ph, R^2 = Me

The effect of electrode materials was investigated also in the electroreuctive 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[25], Zn, or Ni as a matrial of electrodes.

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

Run	Material of Electrodes	Mn	Mw/Mn	Yield of **12a** / %[b]
1	Mg	6700	1.6	61
2	Cu	1300	1.8	—[c]
3	Zn	1200	1.3	—[c]
4	Ni	2400	1.7	—[c]

a) Conditions : [Monomer **12a**] = 0.27 mol/L; [$LiClO_4$] = 0.47 mol/L; Supplied electricity = 4 F/mol; The electroreduction was carried out under sonication (47 kHz). The polarity of elactrodes was alternated with the interval of 15 sec.
b) Purified by reprecipitation from benzene-EtOH.
c) No precipitate was obtained after usual repreciptation 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).

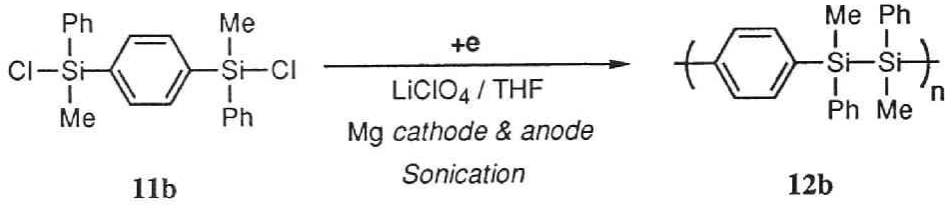
Table VIII. Effect of Concentration and Supplied Electricity in the Electroreductive Synthesis of 12a[a]

Run	[Monomer **3a**] mol/L	[$LiClO_4$] mol/L	Electricity F/mol	Mn	Mw/Mn	Yield of **12a**[b] %
1	0.24	0.47	2.5	4300	1.6	25
2	0.27	0.47	4.0	6700	1.6	61
3	0.27	0.47	5.0	5200	1.6	32
4	0.27	0.47	7.0	4200	1.6	27
5	0.27	0.94	4.0	7200	1.6	57
6	0.27	0.94	8.0	8600	1.6	50
7	0.27	1.41	12.0	10000	2.0	29
8	5.10	1.90	0.3	14900	1.9	3

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



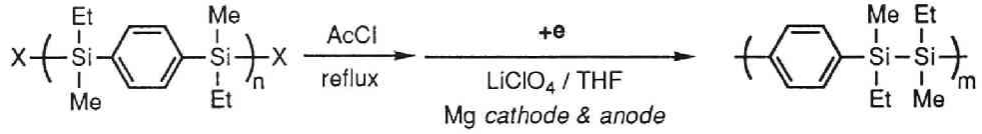
11b **12b**

[Monomer] = 0.27 mol/L
$[LiClO_4]$ = 0.94 mol/L
Supplied electricity = 8.0 F/mol

Yield = 73%
Mn = 9500
Mw/Mn = 1.9

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



12a X = OEt or H **12a'**

$\bar{n}$ = 21 (Mn = 4700, Mw/Mn = 1.5)
Electricity = 900 C (for 3 mmol of **12a**)

Yield 48%
Mn = 6400 Mw/Mn = 1.6

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 $CDCl_3$ 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 (Φ = 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

$LiClO_4$, 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 $MgSO_4$, 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 ($CDCl_3$) δ 0.35 (s, 12H), 7.20-7.65 (m, 10H); ^{13}C NMR ($CDCl_3$) 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, $PhMe_2Si^+$).

Hexamethyldisilane (2b)[31]**:** IR (neat) 2950, 2890, 1250, 835, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 6H); ^{13}C NMR ($CDCl_3$) δ -2.71; MS *m/e* (relative intensity) 146 (13, M^+), 131 (18, M^+-Me), 73 (100, Me_3Si^+).

1,2-Dimethyltetraphenyldisilane (2c)[13,30]**:** IR (KBr) 3020, 1480, 1420, 1250, 1100, 785, 730, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69 (s, 6H), 7.15-7.65 (m, 20H); ^{13}C NMR ($CDCl_3$) δ -4.25, 128.06, 129.16, 135.47, 136.84; MS *m/e* (relative intensity) 394 (1, M^+), 197 (100, Ph_2MeSi^+).

Hexaphenyldisilane (2d)[31]**:** IR (KBr) 3040, 1480, 1420, 1100, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20-7.70 (m, 30H); ^{13}C NMR ($CDCl_3$) δ 128.15, 130.38,

135.25, 136.75; MS *m/e* (relative intensity) 518 (2, M^+), 259 (100, Ph_3Si^+), 180 (49), 155 (10), 105 (22).

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%).
2e[32]**:** ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H), 7.30-7.50 (m, 15H); ^{13}C NMR ($CDCl_3$) δ -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 ($CDCl_3$) δ 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 ($CDCl_3$) δ 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_6D_6) δ 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 ($CDCl_3$) 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^+-$SiMe_3$), 193 (74), 174 (100), 116 (35); HRMS calcd for $C_{15}H_{32}Si_4$ 324.13810, found 324.15502.

Poly[methlphenylsilane] (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 $LiClO_4$, 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 atomosphere. 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 $MgSO_4$, 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 ($CDCl_3$) 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 (ε_{340} = 9000) is characteristic to polysilane.

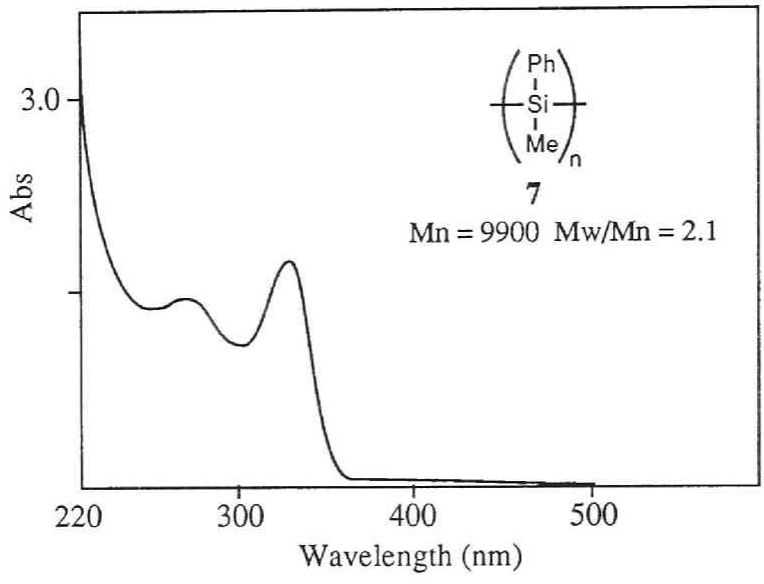


Figure II. UV spectrum of **7**.

Poly[*p*-(disilanylene)phenylene] (12). 1,4-Bis(chloroethylmethylsilyl)benzene (**11a**) and 1,4-bis(chloromethylphenysilyl)benzene (**11b**) were electrolyzed by using the same procedure for the polymerization of dichloromethylphenylsilane (**3a**) to give poly[*p*-(1,2-diethyldimethyldisilanylene)phenylene] (**12a**) and poly[*p*-(1,2-dimethyldiphenyldisilanylene)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}; ^1H NMR ($CDCl_3$) δ 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}; ^1H NMR ($CDCl_3$) δ 0.60 (broad s, 6H, SiMe), 7.26 and 7.30 (m, 14H, phenyl and phenylene ring protons).

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List of Publications

Chapter 1.

Shono, T.; Ishifune, M.; Morimoto, M.; Moriyoshi, N.; Kashimura, S. submitted to *J. Org. Chem.*

Chapter 2.

Shono, T.; Ishifune, M.; Morishima, Y.; Moriyoshi, N.; Kashimura, S. submitted to *J. Am. Chem. Soc.*

Chapter 3.

Shono, T.; Ishifune, M.; Morishima, Y.; Kashimura, S. to be published.

Chapter 4.

Shono, T.; Ishifune, M.; Ishige, O.; Uyama, H.; Kashimura, S. *Tetrahedron Lett.* **1990**, *31*, 7181.

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Chapter 6.

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Chapter 7.

Shono, T.; Kashimura, S.; Ishifune, M.; Nishida, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1160.

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"

Shono, T.; Ishifune, M.; Kashimura, S. *Chem. Lett.* **1990**, 449.

List of Oral Presentations

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

Shono, T.; Kashimura, S.; Ishifune, M.; Uyama, H. The 58th *Annual Meeting of Chemical Society of Japan* **1989**, April, Kyoto, 4 IIIE 26.

"Cathodic Coupling of Carbonyl Compounds with Vinylsilanes"

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"Trifluoromethylation of Carbonyl Compounds Using EGB"

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

Shono, T.; Kashimura, S.; Ishifune, M. The 61th *Annual Meeting of Chemical Society of Japan* **1991**, March, Yokohama, 1 A7 09.

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

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

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