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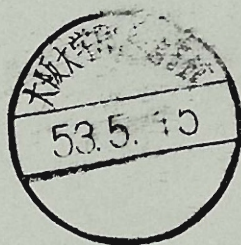
# YOSHIO SEKI

OSAKA UNIVERSITY
OSAKA JAPAN
JANUARY, 1978

# STUDIES ON NEW CATALYZED REACTIONS

## USING HYDROSILANES

## AND CARBON MONOXIDE

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# Preface

This thesis deals with the studies accomplished by the author under the guidance by Professor Noboru Sonoda at the Department of Petroleum Chemistry, Faculty of Engineering, Osaka University.

The author would like to express his sincere thanks to Professor Noboru Sonoda for his invaluable guidance and constant encouragement throughout this investigation since 1972.

The author is also deeply grateful to Associate Professor Shinji Murai for his helpful suggestion and discussions. Grateful acknowledgements are also due to the late Dr. Membo Ryang, Dr. Ilsong Rhee, Mr. Noritaka Miyoshi, and Dr. Kiyoshi Kondo for their valuable suggestions through stimulating discussions with the author.

The author expresses his gratitude to Mr. Iwao Yamamoto and Akihiko Hidaka for their collabolation in the course of experiment. The author's grateful thanks is also due to Shigeo Makino, Makoto Fukutani, and Toshikazu Kato for their assistance in the cource of experiment. The author wishes to thank all the members of Sonoda Laboratory.


Suita, Osaka

January, 1978


                                        Yoshio Seki


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# Contents

# Introduction

Carbon monoxide was discovered in 1776 by Lassone and already found technical application in 19th century. In the first half of the 20th century, many important reactions using carbon monoxide were discovered in Germany. Especially, hydroformylation(oxo reaction) discovered by O. Roelen in 1938[1] and Reppe reactions reported by W. Reppe in 1953[2] have still been employed for technical production of useful materials. A fundamental catalyzed reaction using carbon monoxide, however, has not been discovered since the discoveries of hydroformylation(oxo reaction) and Reppe reactions except for the rhodium(III)-catalyzed reaction which gives acetic acid from methanol and carbon monoxide.[3]

Recently, with a high price of oil and a shortage of natural gas, the countries without abundant indigeous oil resources must make good use of the coal resources again. This is resulting in the revival of carbon monoxide chemistry. Therefore, interest in a new catalytic process using carbon monoxide has increased again.

It is well known that the chemistries of hydrosilanes and of molecular hydrogen are very similar with respect to the various mechanisms of catalytic activation. For example, in the case of oxidative addition to Ir(I) complex, both of a hydrosilane[4] and hydrogen[5a] react to give cis-adducts. Hydrosilylation[6], the catalyzed addition of $R_3SiH$ to an olefin,

is formally analogous to catalytic hydrogenation[5] (Fig. 1).
Moreover, mechanistically, these reactions seem to be very
closely related.[5,6,7a]

The well-known hydroformylation (oxo reaction)[7] involves
addition of hydrogen and carbon monoxide to olefins. The
similarity between hydrogen and a hydrosilane has made us
curious about the catalyzed reaction of olefins with a
hydrosilane and carbon monoxide. However, no such reaction
has been reported so far except for very complex results
reported by Chalk and Harrod.[8] If the catalyzed reaction of

Fig. 1

| H-H | H-Si |
|---|---|
| hydrogenation | hydrosilylation |
| $C=C + H_2 \longrightarrow \underset{H}{C}-\underset{H}{C}$ | $C=C + HSi \longrightarrow \underset{H}{C}-\underset{Si}{C}$ |
| hydroformylation | Not known |
| $C=C + CO + H_2 \longrightarrow \underset{H}{C}-\underset{\underset{H}{C=O}}{C}$ | $C=C + CO + HSi$ |

an olefin with a hydrosilane and carbon monoxide is found,
it will be expected that the discovery opens an entirely
new field spanding over organosilicon chemistry, homogeneous
catalysis, and synthetic organic chemistry. From these
points of view, the author studied catalyzed reactions
using hydrosilanes and carbon monoxide.

This thesis consists of three chapters.

Chapter 1 deals with a catalyzed reaction of olefins with hydrosilanes and carbon monoxide. Futhermore, the mechanism is discussed on the bases of the reaction of cyclohexene with diethylmethyldeuteriosilane and carbon monoxide.

In chapter 2, a catalyzed reaction of cyclic ethers with a hydrosilane and carbon monoxide is described.

In chapter 3, a catalyzed reaction of aldehydes with a hydrosilane and carbon monoxide is described.

This thesis is composed of the following reports.

(1) The Reaction of Olefins with Silane and Carbon Monoxide Catalyzed by $Co_2(CO)_8$

Y. Seki, A. Hidaka, S. Murai, and N. Sonoda,

Angew. Chem., **89**, 196(1977); Angew. Chem. Int. Ed. Engl., **16**, 174(1977).

(2) Transition Metal Reactions of Silanes II. The Reaction of Cycloalkenes with Various Hydrosilanes and Carbon Monoxide Catalyzed by $Co_2(CO)_8$

Y. Seki, A. Hidaka, S. Makino, S. Murai, and N. Sonoda,

J. Organomet. Chem., **140**, 361(1977).

(3) The Reaction of Cyclic Ethers with a Hydrosilane and Carbon Monoxide Catalyzed By $Co_2(CO)_8$

Y. Seki, S. Murai, I. Yamamoto, and N. Sonoda,

Angew. Chem., **89**, 818(1977).

(4)    Catalyst-Dependent Product Distribution in the Reaction

of 1-Hexene with a Hydrosilane and Carbon Monoxide

Y. Seki, S. Murai, A. Hidaka, and N. Sonoda,

Angew. Chem., in press.


(5)    The Reaction of Aldehydes with a Silane and Carbon

Monoxide Catalyzed by $Co_2(CO)_8-Ph_3P$

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Chapter 1    A Catalyzed Reaction of Olefins with Hydrosilanes

and Carbon Monoxide

1-1    Introduction

There have been several studies dealing with the catalyzed

reaction involving a hydrosilane and carbon monoxide or the

reaction between the complexes containing silicon-metal bonds

and carbon monoxide.   Chalk and Harrod reported that no direct

carbonylation of triethylsilane occurred at temperatures up to

300 °C and carbon monoxide pressures up to 1700 psi in the

presence of $Co_2(CO)_8$.[1]   It has been reported that attempts

to induce carbonyl insertion into the $Si-Co$[2], $Si-Mn$[3], and

$Si-Rh$[4] bond by direct reaction with carbon monoxide were

unsuccessful.   Hagen and co-workers carried out the reaction

of $MeSiCl_2Co(CO)_4$ with 4000 atm of carbon monoxide at 90 °C,

but no insertion of carbon monoxide into the silicon-cobalt

bond was observed.[5]   Insertion of carbon monoxide into the

carbon-cobalt bonds is very easy[6].   This difference suggests

that silicon-cobalt bonds are similar to a hydrogen-cobalt

bond with respect to the insertion reaction of carbon

monoxide.   It has been reported that the use of carbon monoxide,

as well as of phosphines, inhibited dicobalt octacarbonyl-

catalyzed addition of dimethylchlorosilane to acrylonitrile[7].

Chalk and Harrod have reported an interesting reaction

in 1967[1].   They studied the dicobalt octacarbonyl-catalyzed

reaction of olefins with triethylsilane and carbon monoxide.

The reaction of 1-pentene and cyclohexene was reported to be

"very complex" and no detail were given.   In the case of

ethylene, however, a complex mixture of the reaction products

with boiling points ranging from 90°C to 300°C was fractionated into thirty three fractions and one of them was found to contain unsaturated alkoxy silane(s) of the formula $C_3H_5OSi(C_2H_5)_3$ which gave the 2,4-dinitrophenylhydrazone of propionaldehyde on treatment with the hydrazine.

In contrast to this previous work, the author has found that carbon monoxide reacts very smoothly with cycloalkenes and hydrosilanes in the presence of $Co_2(CO)_8$. The catalytic reaction gave remarkably clean results. From cycloalkenes, only one product, the trialkylsiloxymethylenecycloalkane, has been obtained in most cases studied. In this chapter, the results of the catalyzed reaction of olefins with hydrosilanes and carbon monoxide under various reaction conditions are described.

1-2    Results and Discussion

1-2-1    Reaction of Cycloalkenes with Diethylmethylsilane and
         Carbon Monoxide

Contrary to the "very complex" results reported by Chalk and Harrod for the reaction of cyclohexene with triethylsilane and carbon monoxide in the presence of $Co_2(CO)_8$, as mentioned above, we have found that this reaction gave triethylsiloxy-methylenecyclohexane(Id) as a sole product in a good yield.[*]

---

[*]    Unfortunately, it is not possible to explain the difference in the results of Chalk and Harrod and ours, since no experimental details were given in their paper.
See ref. (1).

For diethylmethylsilane, a similar result was found. If one

assumes that the reaction proceeds in a formally similar way

as hydroformylation, two types of products, (II) and (III), may

be expected. However, neither of these compounds was found.

The stoichiometry of the reaction can be presented as shown

in eq. 1, and all these reactants are incorporated into the

product(I). While it is obvious that the carbon and oxygen

atoms of carbon monoxide are found in the oxymethylene group

of the product, it will be discussed in this chapter which

hydrogen in the product(I) has come from the hydrosilane

used.

The results obtained for the reaction using cycloalkenes

(3 equivalents) and diethylmethylsilane(1 equivalent) are

given in the Table I. All the catalytic reactions were carried
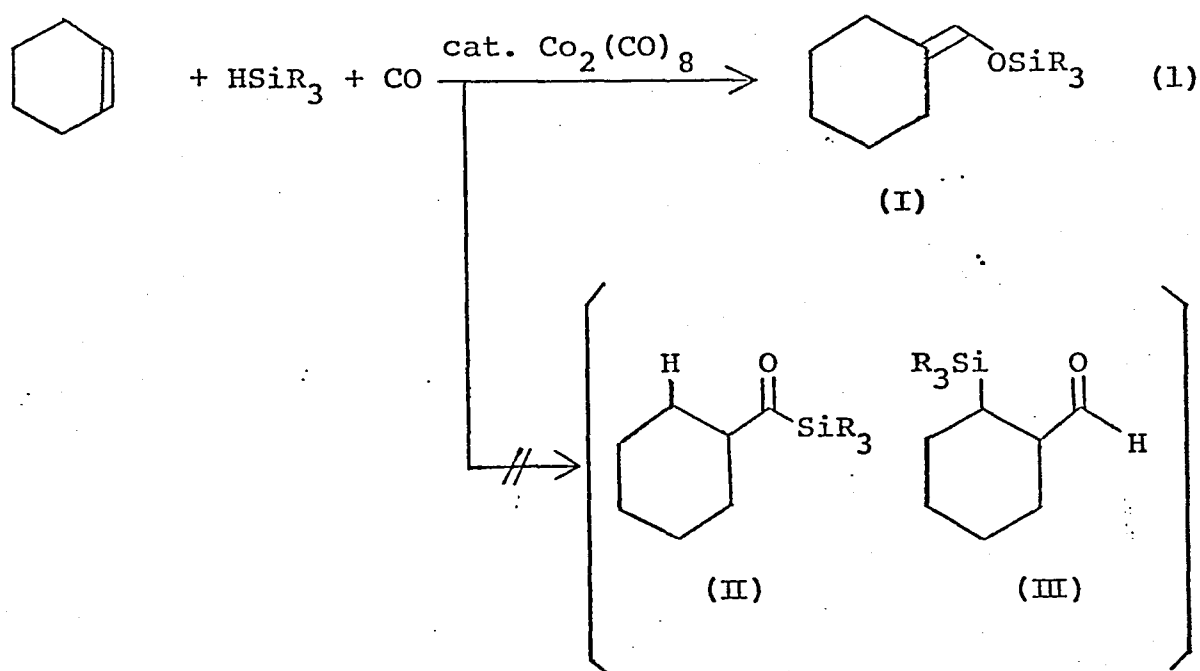
$$\text{(cyclohexene)} + \text{HSiR}_3 + \text{CO} \xrightarrow{\text{cat. Co}_2\text{(CO)}_8} \text{(cyclohexene-OSiR}_3\text{)} \quad (1)$$

(I)

$$\left[ \begin{array}{cc} \text{(II)} & \text{(III)} \end{array} \right]$$

(II)    (III)

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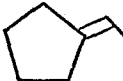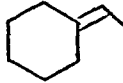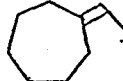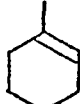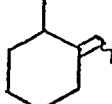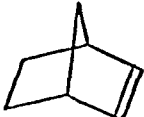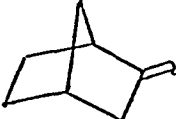
Table I  Reaction of Various Olefins with $Et_2MeSiH$ and $CO^a$

| Olefin | Catalysts | Product | Yield(%) (GLC) |
|---|---|---|---|
| (cyclopentene) | $Co_2(CO)_8$ | $\cdots OSiEt_2Me$ (IV) | 48 |
| (cyclohexene) | $Co_2(CO)_8$ | $OSiEt_2Me$ (Ic) | 71 |
| | $Ru_3(CO)_{12}$ | | 1.4 |
| | $RhCl(PPh_3)_3$ | | 0.5 |
| (cycloheptene) | $Co_2(CO)_8$ | $OSiEt_2Me$ (V) | 74 |
| (cyclooctene) | $Co_2(CO)_8$ | $OSiEt_2Me$ (VI) | 69 |
| (methylcyclohexene) | $Co_2(CO)_8$ | $OSiEt_2Me$ (VII) | 22 |
| (norbornene) | $Co_2(CO)_8$ | $OSiEt_2Me$ (VIII) | 45 |

a) Reaction conditions: cat. (0.2 mmol), olefin(30 mmol), $Et_2MeSiH$ (10 mmol), CO(80 kg/cm$^2$), 140°C, 20 h, in benzene(20 ml)

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out using a 100 ml stainless steel autoclave. Generally, a solution of a cycloalkene(30 mmol), $Et_2MeSiH$(10 mmol), and $Co_2(CO)_8$(0.2 mmol) in benzene(20 ml) was heated under a pressure of carbon monoxide at 140°C for 20 h to give diethylmethyl-siloxymethylenecycloalkane(Ic and IV-VIII). The pressure of carbon monoxide was initialy 80 $kg/cm^2$ at 25°C, then reached 105-108 $kg/cm^2$ at 140°C, and it was finally 76-79 $kg/cm^2$ at 25°C after the reaction had been completed. Simple cyclic olefins(cyclohexene, cycloheptene, and cyclooctene), except for cyclopentene, gave the expected product in good yield, while the reaction of 1-methylcyclohexene, a trisubstituted olefin, and norbornene, a bicyclic olefin, gave the expected product only in moderate yield. In the case of 1-methyl-cyclohexene, 2-diethylmethylsiloxyethenyl-1-cyclohexane was not obtained. All the reactions were accompanied by the formation of the corresponding disiloxane in 5-15% yield.

When $RhCl(PPh_3)_3$ and $Ru_3(CO)_{12}$ were used as a catalyst for the reaction of cyclohexene, only traces of the enol silyl ether(Ic) were obtained. This result is interesting, since hydroformylation of cyclohexene has been known to give good yields of cyclohexanecarboxaldehyde in the presence of $Ru_3(CO)_{12}$.[8]

1-2-2    Reaction of Terminal Olefins with Diethylmethylsilane
         and Carbon Monoxide

The reaction of terminal olefins with diethylmethylsilane and carbon monoxide gave four isomers(regio- and stereoisomers)

as shown in eq. 2. The results in the reaction of 1-hexene and methyl acrylate were summarized in Table II and III.

$$\text{R} \diagup\!\!=\!\!= \quad + \quad Et_2MeSiH \quad + \quad CO \quad \xrightarrow{\text{cat.}}$$

$$(R=n-C_4H_9, \; COOMe)$$

$$\begin{array}{c} \underset{Et_2MeSiO}{R}\diagdown\!\!\diagup\underset{H}{Me} \end{array} + \begin{array}{c} \underset{H}{R}\diagdown\!\!\diagup\underset{OSiEt_2Me}{Me} \end{array} + \begin{array}{c} \underset{Et_2MeSiO}{R}\diagdown\!\!\diagup\underset{H}{H} \end{array} + \begin{array}{c} \underset{H}{R}\diagdown\!\!\diagup\underset{OSiEt_2Me}{H} \end{array} \quad (2)$$

$$(Z)-(IX) \qquad (E)-(IX) \qquad (Z)-(X) \qquad (E)-(X)$$
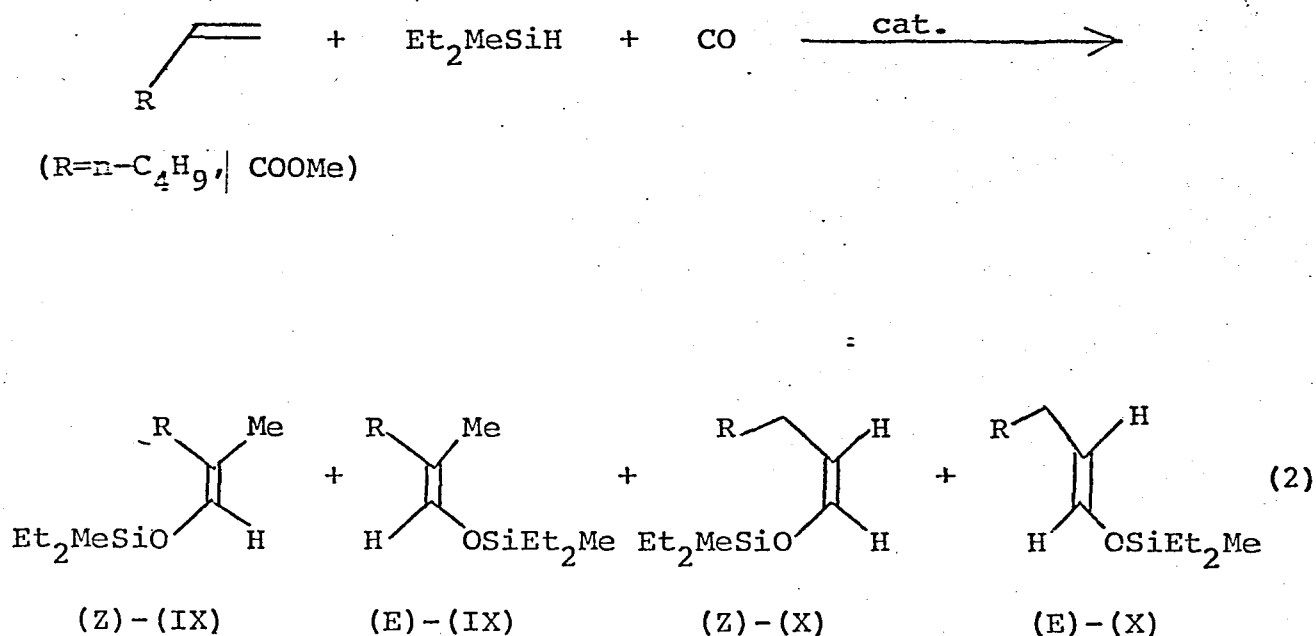
Table II    Catalyzed Reaction of 1-Hexene[a]

| Catalyst | Total yield(%) | Product distribution(%) | | | |
|---|---|---|---|---|---|
| | | (Z)-(IXa) | (E)-(IXa) | (Z)-(Xa) | (E)-(Xa) |
| $Co_2(CO)_8$ | 57 | 16 | 16 | 43 | 25 |
| $RhCl(PPh_3)_3$ | 41 | 9 | 9 | 58 | 24 |
| $Ru_3(CO)_{12}$ | 40 | 4 | 7 | 44 | 45 |

a) Reaction conditions; cat.(0.4 mmol), olefin(30 mmol), $Et_2MeSiH$ (10 mmol), CO(50 kg/cm$^2$), 140°C, 20 h , benzene(20 ml).

Table III  Catalyzed Reaction of Methyl Acrylate[a]

| Catalyst | MA (mmol) | HSi (mmol) | Total yield(%) | Product distribution | | | |
|---|---|---|---|---|---|---|---|
| | | | | (Z-IXb) | (E-IXb) | (Z-Xb) | (E-Xb) |
| $Co_2(CO)_8$ | 30 | 10 | 49 | 0 | 12 | 59 | 29 |
| | 10 | 30 | 6 | 0 | 5 | 72 | 23 |
| $RhCl(PPh_3)_3$ | 30 | 10 | 6 | 42 | 58 | 0 | 0 |
| | 10 | 30 | 18 | 11 | 89 | 0 | 0 |
| $Ru_3(CO)_{12}$ | 30 | 10 | 9 | 43 | 57 | 0 | 0 |
| | 10 | 30 | 22 | 36 | 64 | 0 | 0 |

a) Reaction conditions; $Co_2(CO)_8$ (0.2 mmol), $RhCl(PPh_3)_3$ (0.1 mmol), $Ru_3(CO)_{12}$ (0.05 mmol); methyl acrylate=MA; $CO(80 \text{ kg/cm}^2)$, 140°C, 20 h, benzene(20 ml).

In the reaction of cyclohexene, $RhCl(PPh_3)_3$ and $Ru_3(CO)_{12}$ were not effective catalysts, but the reaction of terminal olefins was catalyzed by these metal complexes.  In the reaction of methyl acrylate, straight chain isomers(X) were main products in the case of $RhCl(PPh_3)_3$ and $Ru_3(CO)_{12}$, while branched isomers(IX) were main products in the case of $Co_2(CO)_8$.  These results show that the rate—limiting step differs between the case of $RhCl(PPh_3)_3$ and $Ru_3(CO)_{12}$ and that of $Co_2(CO)_8$.  When a three fold excess of hydrosilane to methyl acrylate was used in the reaction catalyzed by $RhCl(PPh_3)_3$ or $Ru_3(CO)_{12}$, the yields increased to about 20%.

1-2-3    Reaction of Cyclohexene with Various Hydrosilanes

Cyclohexene reacted with various hydrosilanes and carbon monoxide in the presence of $Co_2(CO)_8$ to give the corresponding siloxymethylenecyclohexanes(I) as shown in eq. 1. The results were summarized in Table IV.

Table IV   Reaction of Cyclohexene with Various Hydrosilanes and Carbon Monoxide[a]

| Hydrosilane | Yield of the product(I) | | Recovered hydrosilane(%) | $(R_3Si)_2O$ [b] |
|---|---|---|---|---|
| $Me_3SiH$ | (Ia) | 4 | 88 | 0 |
| $EtMe_2SiH$ | (Ib) | 57 | 36 | 5 |
| $Et_2MeSiH$ | (Ic) | 71 | 5 | 8 |
| $Et_3SiH$ | (Id) | 74 | 0 | 23 |
| $PhMe_2SiH$ | (Ie) | 51 | 29 | 18 |
| $Ph_2MeSiH$ | (If) | 26 | 57 | 6 |
| $Ph_3SiH$ | | 0 | 88 | 0 |
| $Ph_2SiH_2$ | | 0 | 39 | 18 |
| $(MeO)_2MeSiH$ | | 0 | 0 | 0 |

a) Reaction conditions; $Co_2(CO)_8$(0.2 mmol), cyclohexene
   (30 mmol), hydrosilane(10 mmol), CO(80 $kg/cm^2$), 140°C,
   20 h, in benzene(20 ml).

b) Disiloxanes corresponding to hydrosilanes used.

Trialkylsilanes, except for Me$_3$SiH, yielded the corresponding siloxymethylenecyclohexanes(Ib-Id) in good yield. In the case of hydrosilanes having a phenyl substituent, the yield of the product(Ie and If) decreased in the order PhMe$_2$SiH $\rangle$ Ph$_2$MeSiH $\rangle$ Ph$_3$SiH. The following hydrosilanes did not give the corresponding siloxymethylenecyclohexane: Ph$_3$SiH, Ph$_2$SiH$_2$, and (MeO)$_2$MeSiH. The reaction of (MeO)$_2$MeSiH gave very complex results without recovery of the hydrosilane. These results show that hydrosilanes with electron-donating substituents have good reactivity in the present reaction. The reason for low yield in the case of Me$_3$SiH is not clear. It may be intrinsic or due to the different experimental procedure(see Experimental Part).

The reaction with dimethylchlorosilane was also examined. Two products were obtained in about 10% yields, respectively. One product was cyclohexanecarboxaldehyde and the other has not been identified yet. White solid precipitated from the liquid which was obtained by distillation(b.p. 83-95°C/15 torr) of the reaction mixture. The white solid was identified with 2,4,6-tricyclohexylparaldehyde. The expected product, dimethylchlorosiloxymethylenecyclohexane, may be very unstable to moisture and hydrolyzed during work-up.

1-2-4    Mechanism of the Reaction of Olefins with Hydrosilanes

and Carbon Monoxide

Effects of the reaction conditions such as the pressure of carbon monoxide, the temperature, and the ratio of methyl acrylate to $Et_2MeSiH$ on the total yield and the product distribution were examined in the reaction of methyl acrylate. The results are summarized in Table V

Table V   Reaction of Methyl Acrylate with $Et_2MeSiH$ and $CO^a$

| MA (mmol) | SiH (mmol) | $CO^c$ (kg/cm$^2$) | Temp. (°C) | Total yield(%) | Product distribution[b] (Z-IXb) | (E-IXb) | (Z-Xb) | (E-Xb) |
|-----------|------------|--------------------|------------|----------------|---------------------------------|---------|--------|--------|
| 30 | 10 | 80 | 140 | 49 | 0 | 12 | 59 | 29 |
| 30 | 10 | 50 | 140 | 50 | 0 | 16 | 58 | 26 |
| 30 | 10 | 30 | 140 | 49 | 0 | 12 | 61 | 27 |
| 30 | 10 | 30 | 70 | 29 | 8 | 55 | 30 | 7 |
| 10 | 10 | 80 | 140 | 44 | 0 | 9 | 68 | 23 |
| 10 | 30 | 80 | 140 | 6 | 0 | 5 | 72 | 23 |

a) All reactions were carried out in 20 ml of benzene for 20 h.

b) The yields and the product distribution were determined by GLC.

c) Initial pressure at room temperature.

When the other reaction conditions were fixed, the influence of the pressure of carbon monoxide on the total yields and the percentage of straight chain isomers may be neglected.

The total yield increased with increase in the ratio of methyl acrylate to diethylmethylsilane. Branched isomers(IXb) were main products at 70°C. It has already been reported that branched isomers increased at lower temperature in hydroformylation(oxo reaction) of ethyl acrylate catalyzed by $Co_2(CO)_8$.[9] The results suggest that the reaction path in the reaction of methyl acrylate with diethylmethylsilane and carbon monoxide is similar to that in hydroformylation(oxo reaction) of ethyl acrylate at the initial stage.

Similarly, effects of the reaction conditions on the total yield and the product distribution were examined in the reaction of cyclohexene. When the reaction were carried out at higher temperature or using equimolar amounts of cyclohexene and a hydrosilane, another product(XI) was obtained in addition to Ic (eq. 3). The product(XI) may be formed by catalyzed double-bond isomerization of the product(Ic).



$$\text{(Ic)} \xrightarrow{\quad O \quad} \text{(XI)} \qquad (3)$$

The yield and distribution of the products were found to be affected by the reaction conditions such as molar ratio of reactants, the temperature and the pressure of carbon monoxide. The results obtained for the reaction of cyclohexene with diethylmethylsilane and carbon monoxide are shown in the Table VI.

Table VI  Effects of the Reaction Conditions in the Reaction of Cyclohexene with $Et_2MeSiH$ and $CO^a$

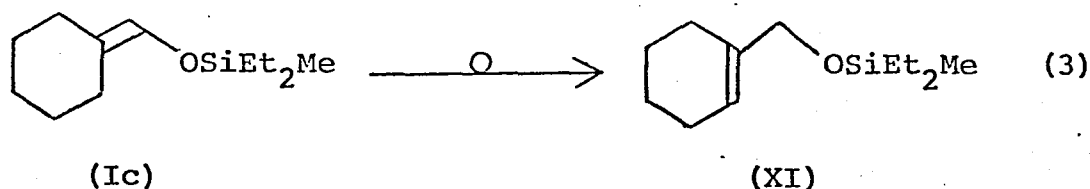| | Reaction conditions | | | Total[b] | Product[b] |
|---|---|---|---|---|---|
| Olefin | SiH | Temp. | CO pressure[c] | yield(%) | distribution |
| (mmol) | (mmol) | (°C) | (kg/cm$^2$) | (Ic + XI) | Ic : XI(%) |
| 10 | 10 | 140 | 30 | 12 | 99 : 1 |
| 10 | 10 | 140 | 60 | 36 | 97 : 3 |
| 10 | 10 | 140 | 80 | 37 | 98 : 2 |
| 20 | 10 | 140 | 80 | 51 | 98 : 2 |
| 30 | 10 | 140 | 80 | 71 | 100 : 0 |
| 30 | 10 | 200 | 80 | 84 | 80 : 20 |

a) All reactions were carried out in 20 ml of benzene for 20 h.

b) The yields and the product distribution were determined by GLC.

c) Initial pressure at room temperature.


The total yield of Ic and XI increased with an increase in the pressure of carbon monoxide, but the difference was very small at 60-80 kg/cm$^2$. The total yield increased remarkably with increasing molar ratio of cyclohexene to diethylmethylsilane. The total yield was best at 200°C, but the yield of the initial product(Ic) decreased and that of isomerization product(XI) increased.

The fact that the use of a higher molar ratio of cyclohexene to the hydrosilane has resulted in a higher yield of the product suggested the importance of hydrocobaltcarbonyl $HCo(CO)_4$, as the active catalyst in the present reaction. The reaction of trialkylsilane with $Co_2(CO)_8$ has been known to give $HCo(CO)_4$ and $R_3SiCo(CO)_4$[1,10] (eq. 4). The hydro-cobaltcarbonyl may react with olefins to initiate a catalytic cycle (eq. 5). However, when a sufficient amount of the olefin is not present in the system, it reacts with the hydrosilane to give $R_3SiCo(CO)_4$ and hydrogen [1,10] (eq. 6). This reaction (eq. 6) would stop the catalytic cycle. The alkylcobalt

$$R_3SiH \quad + \quad Co_2(CO)_8 \longrightarrow R_3SiCo(CO)_4 \quad + \quad HCo(CO)_4 \quad (4)$$

$$HCo(CO)_4 \begin{array}{l} \xrightarrow{RCH=CH_2} RCH_2CH_2Co(CO)_4 \qquad (5) \\[2em] \xrightarrow{R_3SiH} R_3SiCo(CO)_4 \quad + \quad H_2 \qquad (6) \end{array}$$
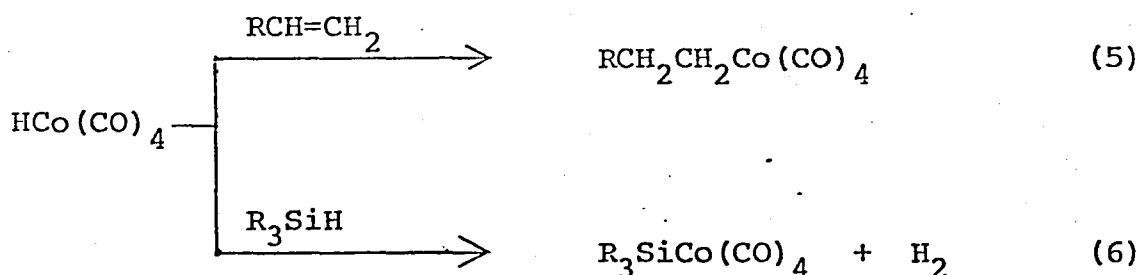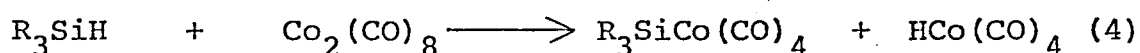
complex formed in eq. 5 may give an acylcobalt complex which then reacts with a hydrosilane to give the product with regeneration of hydrocobaltcarbonyl. The reaction path (eq. 5) is the same as the initial stage of hydroformylation.

As mentioned above, an acylcobalt complex is formed at the initial stage. Next, the reaction path from the acylcobalt complex to the products was investigated. To begin with, the deuterium position in the products was determined in the reaction of cyclohexene with diethylmethyl-deuteriosilane and carbon monoxide. The reaction gave the corresponding siloxymethylenecyclohexane in 87% yield as shown in eq. 7. The amount of deuterium incorporation at the vinyl position of the product was 91%.



(7)
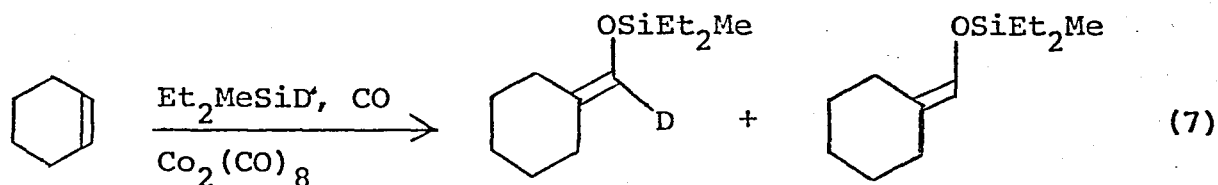
From these results, the following two reaction paths were proposed. The reaction path via an acylsilane or hydroformylation (oxo reaction) was completely excluded.

(1)

$$RCH_2CH_2\overset{\overset{O}{\|}}{C}Co(CO)_3 \xrightarrow{HSi} RCH_2CH_2\overset{\overset{O}{\|}}{C}\ \underset{\underset{H}{|}}{\overset{\overset{Si}{|}}{Co}}(CO)_3 \xrightarrow{CO}$$

(XII)

$$RCH_2CH_2CHO\ +\ SiCo(CO)_4 \longrightarrow \xrightarrow{-CO} RCH_2CH_2\underset{\underset{H}{|}}{\overset{\overset{OSi}{|}}{C}}Co(CO)_3$$

(XIII)

$$\xrightarrow{-HCo(CO)_3} RCH_2CH=CHOSi$$

-19-

(2)

$$(XII) \longrightarrow RCH_2CH_2\overset{\overset{\displaystyle OSi}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}=Co(CO)_3 \longrightarrow (XIII) \xrightarrow{-HCo(CO)_3}$$

(XIV)

$RCH_2CH=CHOSi$
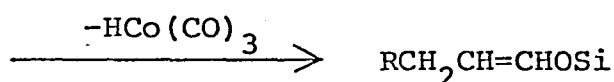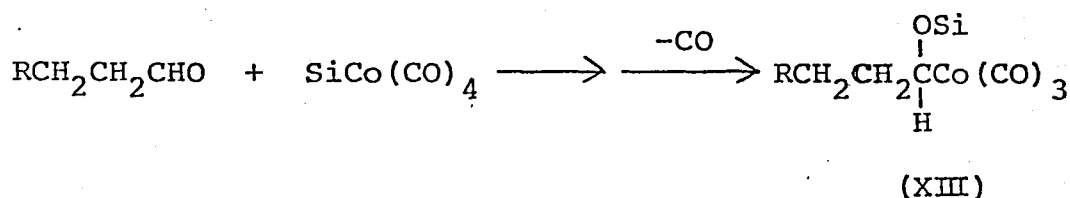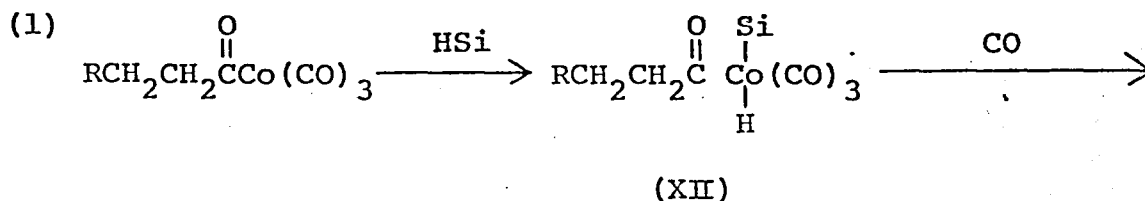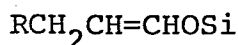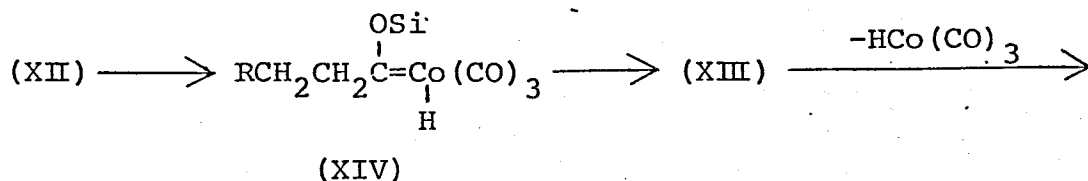
In the route(1), initially, a hydrosilane adds oxidatively to the acylcobalt complex to give the intermediate(XII) and then an aldehyde reductively eliminates. The aldehyde reacts with silylcobaltcarbonyl to give the intermediate(XIII). The last reaction probably involves the β-elimination of hydro-cobaltcarbonyl and the formation of the product.

In the route(2), the silyl group shifts to the oxygen of the acyl group in the intermediate(XII) produced to give the siloxycarbene complex(XIV) and then the carbene inserts to the cobalt-hydrogen bond to give intermediate(XIII). The subsequent path is the same as the route(1).

It is very difficult to determine which route is real. To begin with, the possibility of an aldehyde as an intermediate was investigated. Experimentally, a solution of n-heptanal (10 mmol), diethylmethylsilane(10 mmol), and $Co_2(CO)_8$(0.4 mmol) in benzene(20 ml) was heated at 140°C for 20 h under carbon monoxide(50 kg/cm$^2$) in 100 ml of autoclave. The results were shown in Table VII and eq. 8.

The reaction of the aldehyde(XV) with the hydrosilane (Run 1 and 2) gave almost alkoxysilane(XVI), while the reaction of olefins with the hydrosilane and carbon monoxide (Run 3)

$$\text{(XV)} \xrightarrow[\text{Co}_2\text{(CO)}_8]{\text{Et}_2\text{MeSiH}} \quad \text{(X) [(Z)+(E)]} + \text{(XVI)} \qquad (8)$$
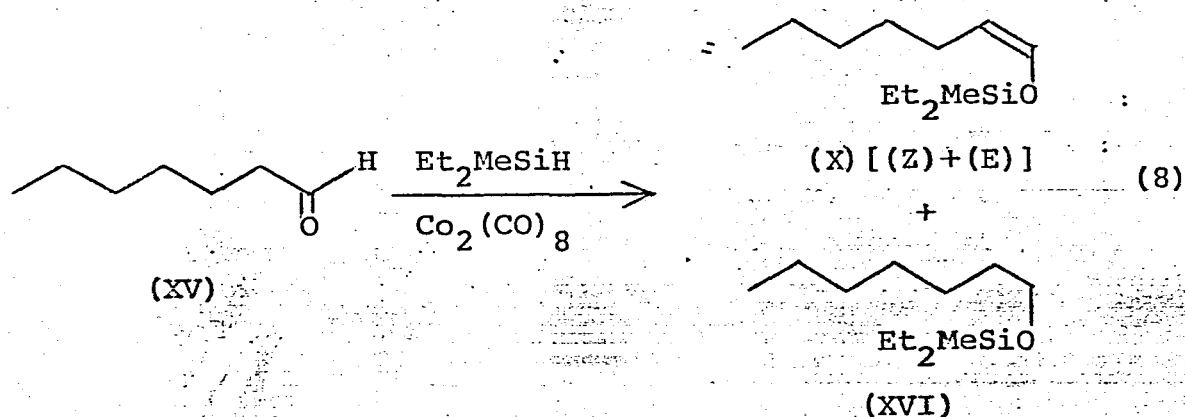
Table VII  Reaction of an Aldehyde and Reaction of an Olefin

| Run | Reactants | Yield of (X)+(XVI) | ( X : XVI ) |
|-----|-----------|--------------------|-------------|
| 1 | XV : HSi (1:1) | 40 | 18 : 82 |
| 2 | XV : HSi : 1-Octene (0.1:1:1) | 69 | 3 : 97 |
| 3 | HSi : 1-hexene(1:3) | 39 | 100 : 0 |

gave only the enol silyl ethers(X). These results suggest
that the aldehyde(XV) is not an intermediate. But it is
possible that hydrosilylation of the aldehyde(XV) occurres
for one hour, since it takes one hour that the temperature
rises from room temperature to 140°C. Therefore, the direct
reaction of the aldehyde(XV) with the hydrosilane at about
140°C was tried. Experimentally, a solution of an aldehyde
(2 mmol) in 2 ml of xylene was gradually added to the mixture
of diethylmethylsilane(4 mmol) and $Co_2(CO)_8$(0.04 mmol) in
4 ml of xylene at about 140°C. The enol silyl ethers(X) and
the alkoxysilane(XVI) were obtained in 79% and 21% yields,
respectively.

This result suggests that the enol silyl ethers(X) can be produced selectively under proper reaction conditions.[11] Therefore, it is reasonable that the reaction of an olefin with a hydrosilane and carbon monoxide proceeds via an aldehyde as an intermediate. The plausible mechanism was shown below.

$$HSi + Co_2(CO)_8 \longrightarrow HCo(CO)_4 + SiCo(CO)_4 \qquad (a)$$

$$HCo(CO)_4 \underset{\xleftarrow{\hspace{1cm}}}{\overset{-CO}{\xrightarrow{\hspace{1cm}}}} [HCo(CO)_3] \qquad (b)$$

$$RCH=CH_2 + [HCo(CO)_3] \rightleftharpoons RCH_2CH_2Co(CO)_3 \underset{\rightleftharpoons}{\overset{CO}{}} RCH_2CH_2Co(CO)_4 \qquad (c)$$

$$RCH_2CH_2Co(CO)_4 \rightleftharpoons RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(CO)_3 \underset{\rightleftharpoons}{\overset{CO}{}} RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(CO)_4 \qquad (d)$$

$$RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(CO)_3 + HSi \longrightarrow RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(HSi)(CO)_3 \qquad (e)$$

$$RCH_2CH_2\overset{O}{\overset{\|}{C}}Co(HSi)(CO)_3 \longrightarrow RCH_2CH_2CHO + SiCo(CO)_3 \qquad (f)$$

$$SiCo(CO)_3 \underset{\xleftarrow{\hspace{1cm}}}{\overset{CO}{\xrightarrow{\hspace{1cm}}}} SiCo(CO)_4 \qquad (g)$$

$$RCH_2CH_2CHO + SiCo(CO)_4 \longrightarrow RCH_2CH_2\underset{H}{\overset{OSi}{\underset{|}{\overset{|}{C}}}}Co(CO)_4 \qquad (h)$$

$$RCH_2CH_2\underset{H}{\overset{OSi}{\underset{|}{\overset{|}{C}}}}Co(CO)_4 \underset{\xleftarrow{\hspace{1cm}}}{\overset{-CO}{\xrightarrow{\hspace{1cm}}}} RCH_2CH_2\underset{H}{\overset{OSi}{\underset{|}{\overset{|}{C}}}}Co(CO)_3 \qquad (i)$$

$$RCH_2CH_2\underset{H}{\overset{OSi}{\underset{|}{\overset{|}{C}}}}Co(CO)_3 \longrightarrow RCH_2CH=CHOSi + HCo(CO)_3 \qquad (j)$$

Ojima and co-workers have already reported that hydrosilylation of acetophenone catalyzed by $RhCl(PPh_3)_3$ proceeded under more drastic conditions than that of acetone and the reactivity of triethylsilane and dimethylphenylsilane in hydrosilylation of benzaldehyde catalyzed by $RhCl(PPh_3)_3$ were almost similar.[12] From these results, the rate-limiting step in hydrosilylation of carbonyl compounds catalyzed by $RhCl(PPh_3)_3$ may be the stage of the addition of the silyl-rhodium complex to the carbonyl of the aldehyde or the ketones, since the steric hindrance of the carbonyl compounds effects on the reaction rate and that of hydrosilanes does not effect on the rate.

It was described in this chapter that the reaction of cyclohexene was catalyzed by $Co_2(CO)_8$ and not by $RhCl(PPh_3)_3$ and $Ru_3(CO)_{12}$. The hydroformylation reaction of cyclohexene catalyzed by $Ru_3(CO)_{12}$ has already been reported.[8] These results suggest that in the reaction of an olefin with a hydrosilane and carbon monoxide catalyzed by $RhCl(PPh_3)$ and $Ru_3(CO)_{12}$, the reaction of the aldehyde with silyl-metal complexes is the rate-limiting step. This is the reason why $RhCl(PPh_3)_3$ and $Ru_3(CO)_{12}$ are not effective catalysts in the reaction of cyclohexene. In the reaction catalyzed by $Co_2(CO)_8$, the oxidative addition of a hydrosilane to the acylcobalt complex(eq. e) may be the rate-limiting step from the results of the reaction with various hydrosilanes. In the case of 1-methylcyclohexene, 2-diethylmethylsiloxyethenyl-1-cyclohexane was not obtained. It has been reported that hydroformylation reaction of 1-methylcyclohexene gave

cyclohexaneacetaldehyde.[13] The result suggests that the oxidative addition of a hydrosilane to acylcobalt complexes is faster than that of hydrogen.

The relative reactivity of the cyclic olefins for hydroformylation has already been reported.[14] The order was shown below. The order is similar to hydroboration with
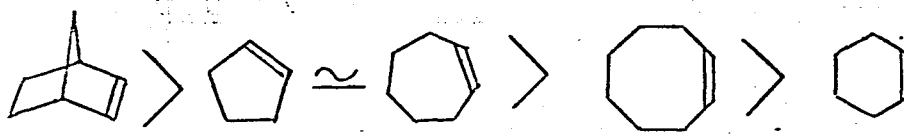


disiamylborane[15], the platinum(II)-catalyzed heterogeneous hydrogenation reaction[16], and the palladium(II)-catalyzed olefin carbonylation reaction[17]. The fact suggests that the formation of the π-complex will be important in determining the overall yield of product, because the order is the same as that of ring strain.[17] While the relative reactivity of cycloalkenes in the reaction of cycloalkenes with diethylmethyl-silane and carbon monoxide catalyzed by $Co_2(CO)_8$ showed the alternative order as shown below. Therefore, the rate-limiting |step is not the reaction of an olefin with $HCo(CO)_4$.
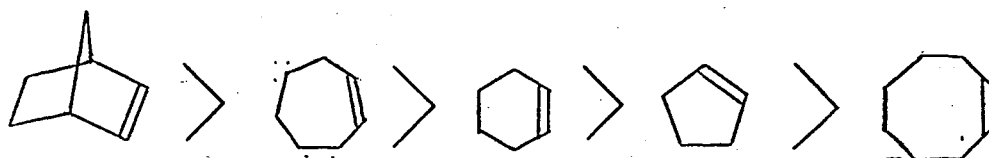
## 1-3 Experimental

### General comments

All temperature are uncorrected. IR spectra were recorded with a Shimazu IR-400. The $^1$H-NMR spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer with $Me_4Si$ as an internal standard. The position of $Me_4Si$ was recognized by adding it after recording spectrum without the standard. Otherwise the signal of the standard may be confused with that of a organosilicon compound. Mass spectra were recorded on a Hitachi mass spectrometer Model RMU-6E. High resolution mass spectra were recorded on a Hitachi RMU-7M. Analytical gas chromatography(GLC) were carried out on a Shimazu GC-3BF and a Shimazu GC-6A equipped with flame ionization detecters. The GLC columns used were as follows: (A) 6m✕3mm stainless steel containing 5% Silicon OV-1 supported on 60-80 mesh Uniport KS; (B) 6m✕3mm stainless steel containing 15% DEGS supported on 60-80 mesh cromosorb W. Preparative GLC was carried out using a Varian Aerograph Model 90-P gas chromatograph. Olefins were commercially available and were purified by distillation. Benzene was dried over sodium-lead alloy and stored over 5A molecular sieves. $Co_2(CO)_8$ were prepared according to the literature[18]. $Ru_3(CO)_{12}$ and $RhCl(PPh_3)_3$ were commercially available. Hydrosilanes were prepared by standard methods[19]. Authentic samples of disiloxanes were prepared by $RhCl(PPh_3)_3$ catalyzed silylation of water with appropriate hydrosilanes (benzene as solvent, reflux 48 h, quantitative yields).

General procedure for the reaction of cycloalkenes with

hydrosilanes and carbon monoxide in the presence of $Co_2(CO)_8$

A 100 ml stainless steel autoclave equipped with a

300 $kg/cm^2$ pressure gauge and a magnetic stirring bar was

charged with 30 mmol of cycloalkenes, 10 mmol of the hydrosilane,

0.2 mmol of $Co_2(CO)_8$ and 20 ml of benzene. The autoclave

was flushed $N_2$(80 $kg/cm^2$) and CO(50 $kg/cm^2$), then charged with

CO to 80 $kg/cm^2$. The reaction vessel was then heated with

magnetic stirring in an oil bath. After 1 h, the pressure

reached 105-108 $kg/cm^2$ at 140°C. The temperature was maintained

at 140°C for 20 h. The vessel was then cooled to room

temperature. The pressure decreased to 76-79 $kg/cm^2$. The gas

pressure was slowly released and the autoclave was opened.

Analysis of the reaction mixture by GLC(column A) with an

internal standard (n-tridecane, n-tetradecane, n-pentadecane,

or n-eicosane) showed it to contain the products (I and IV-VIII)

and $(R_3Si)_2O$. RRT(relative retention time) of the products

to an internal standard is shown below for each case. RRT

(relative retention time)=retention time of the compounds/

retention time of the standard. Distillation of the reaction

mixture and/or preparative GLC afforded the analytical samples.


Diethylmethylsiloxymethylenecyclohexane(Ic)

Analysis by GLC(column A, 130°C, n-tetradecane as an

internal standard(RRT 1)); Ic(71%, RRT 0.79) and $(Et_2MeSi)_2O$

(8%, RRT 0.29). Ic; bp 130-138°C/28 torr; IR(neat) 2924, 1680,

1450, 1380, 1260, 1240, 1220, 1160, 1090, 1070, 1010, 970, 910,

820, 800, 760 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.08(s 3H), 0.58(m 4H), 0.96(m 6H), 1.36-1.60(c 6H), 1.88(m 2H), 2.10(m 2H), 5.88 (s 1H); mass spectrum m/e(rel. intensity) 212(33), 183(40), 101(9), 89(100).

Anal. Calcd for C$_{12}$H$_{24}$OSi: P$^+$, 212.1595; C, 67.85; H, 1138. Found: P$^+$, 212.1561; C, 67.80; H, 11.40.


## Diethylmethylsiloxymethylenecyclopentane(IV)

Analysis by GLC(column A, 120°C, n-tridecane as an internal standard(RRT 1)); IV(48%, RRT 0.80) and (Et$_2$MeSi)$_2$O (8% RRT 0.46). IV; bp 98-100°C/15 torr; IR(neat) 2950, 2875, 1685, 1460, 1415, 1250, 1170, 1120, 1005, 960, 950, 840-820, 800, 760 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.08(s 3H), 0.60(m 4H), 0.96(m 6H), 1.58(m 4H), 2.12(m 4H), 6.04(s 1H); mass spectrum m/e(rel. intensity) 198(30), 169(39), 103(9), 89(100).

Anal. Calcd for C$_{11}$H$_{22}$OSi: P$^+$, 198.1438; C, 66.59; H, 11.18. Found: P$^+$, 198.1409; C, 66.35; H, 10.94.


## Diethylmethylsiloxymethylenecycloheptane(V)

Analysis by GLC(column A, 140°C, n-tetradecane as an internal standard(RRT 1)); V(74%, RRT 1.29) and (Et$_2$MeSi)$_2$O (9%). V; bp 155-165°C/50 torr; IR(neat) 2950, 1660, 1450, 1260, 1190, 1160, 1130, 1000, 960, 870, 810, 760 cm$^{-1}$; NMR (CCl$_4$) $\delta$ 0.08(s 3H), 0.58(m 4H), 0.96(m 6H), 1.40-1.70(c 8H), 1.99(m 2H), 2.20(m 2H), 5.92(s 1H); mass spectrum m/e(rel. intensity) 226(13), 197(35), 101(11), 89(100).

Anal. Calcd for C$_{13}$H$_{26}$OSi: P$^+$, 226.1750; C, 68.95; H, 11.57. Found: P$^+$, 226.1731; C, 68.97; H, 11.70.

## Diethylmethylsiloxymethylenecyclooctane(VI)

Analysis by GLC(column A, 150°C, n-tetradecane as an internal standard(RRT 1)); VI(69%, RRT 1.96) and $(Et_2MeSi)_2O$ (11%). VI; bp 126-135°C(25 mm); IR(neat) 2920, 1660, 1480, 1250, 1235, 1200, 1160, 1090, 1060, 1000, 960, 860, 800, 770 $cm^{-1}$; NMR(CCl$_4$) $\delta$ 0.03(s 3H), 0.58(m 4H), 0.97(m 6H), 1.36-1.72(c 10H), 1.98(m 2H), 2.14(m 2H), 5.94(s 1H); mass spectrum m/e(rel. intensity) 240(13), 211(33), 121(21), 101(18), 89(100).

Anal. Calcd for $C_{14}H_{28}OSi$: $P^+$, 240.1908; C, 69.92; H, 11.73. Found: $P^+$, 240.1914; C, 69.88; H, 11.64.

## 1-Diethylmethylsiloxymethylene-2-methylcyclohexane(VII)

Analysis by GLC(column A, 130°C, n-tridecane as an internal standard(RRT 1)); VII (22%, RRT 1.64), unidentified compound(5%, RRT 1.52), and $(Et_2MeSi)_2O$ (15%). The structure of the unidentified compound is not clear, but NMR spectrum of an 1:1 mixture(by GLC) of VII and it is not consistent with 2-diethylmethyl-siloxyethenyl-1-cyclohexane. VII; bp 120-125°C(17 mm); IR(neat) 2950, 2900, 1680, 1460, 1260, 1150, 1100, 1010, 960, 880, 820, 800, 770 $cm^{-1}$; NMR(CCl$_4$) $\delta$ 0.08 (s 3H), 0.60(m 4H), 0.88-1.20(m 6H)overlapped with 0.96(s 3H), 1.20-1.86(c 6H), 1.86-2.12(c 2H), 2.60-2.80(c 1H), 5.88(s 1H); mass spectrum m/e (rel. intensity) 226(11), 211(5), 197(11), 101(11), 89(100).

Anal. Calcd for $C_{13}H_{26}OSi$: $P^+$, 226.1751; C, 68.95; H, 11.57. Found: $P^+$, 226.1731; C, 68.59; H, 11.75.

## 2-Diethylmethylsiloxymethylenenorbornene (VIII)

Analysis by GLC(column A, 150°C, n-tetradecane as an internal standard (RRT 1)); VIII(45%, RRT 1.71) and $(Et_2MeSi)_2O$ (7%). VIII; bp 130-140°C(10 mm); IR(neat) 2940, 2860, 1690, 1250, 1160, 1140, 1100, 1000, 850, 810, 760 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.08(s 3H), 0.57(m 4H), 0.90(m 6H), 1.12-1.32(c 4H), 1.47(m 1H), 1.61(m 1H), 1.86(m 1H), 2.04(m 1H), 2.31(m 1H), 2.55(m 1H), 6.02(m 1H); In addition, small absorptions at 3.06 and 5.79 were also observed. The product may contain two stereo isomers. mass spectrum m/e (rel. intensity) 224(39), 195(100), 101 (44), 89(39).

Anal. Calcd for $C_{13}H_{24}OSi$: C, 69.57; H, 10.77. Found: C, 69.41; H, 10.91.

## Dimethylethylsiloxymethylenecyclohexane (Ib)

Analysis by GLC(column A, 110°C, n-tridecane as an internal standard(RRT 1)); Ib(57%, RRT 0.70) and $(EtMe_2Si)_2O$ (5%, RRT 0.13). Ib; bp 82-88°C(13 mm); IR(neat) 2910, 2850, 1680, 1450, 1380, 1250, 1150, 1080, 1060, 1000, 960, 900, 840, 780 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.11(s 6H), 0.57(m 2H), 0.96 (m 3H), 1.35-1.59(c 6H), 1.88(m 2H), 2.10(m 2H), 5.84(s 1H); mass spectrum m/e (rel. intensity) 198(25), 169(22), 89(14), 75(100).

Anal. Calcd for $C_{12}H_{22}OSi$: $P^+$, 198.1438; C, 66.59; H, 11.18. Found: $P^+$, 198.1428; C, 66.87; H, 11.18.

## Triethylsiloxymethylenecyclohexane (Id)

Analysis by GLC(column A, 135°C, n-pentadecane as an internal standard (RRT 1)); Id(74%, RRT 0.77) and $(Et_3Si)_2O$ (23%, RRT 0.44). Id; bp 135-139°C(20 mm); IR(neat) 2920, 2895, 1675, 1445, 1260, 1240, 1220, 1150, 1090, 1010, 910, 820, 740 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.70 (m 6H), 1.09 (m 9H), 1.44-1.74 (c 6H), 2.01 (m 2H), 2.22 (m 2H), 6.02 (s 1H); mass spectrum m/e (rel. intensity) 226(24), 197(41), 169(11), 103(100), 87(17), 75(55).

Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.95; H, 11.57. Found: C, 69.05; H, 11.62.

## Dimethylphenylsiloxymethylenecyclohexane (Ie)

Analysis by GLC(column A, 160°C, n-pentadecane as an internal standard (RRT 1)); Ie(51%, RRT 1.97) and $(PhMe_2Si)_2O$ (18%, RRT 2.19). Ie; bp 150-151°C(16 mm); IR(neat) 3050, 2910, 2850, 1680, 1590, 1430, 1250, 1200, 1150, 1120, 970, 830, 780, 720, 700 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.39 (s 6H), 1.35-1.59 (c 6H), 1.86 (m 2H), 2.16 (m 2H), 5.88 (s 1H), 7.26 (m 3H), 7.44 (m 2H); mass spectrum m/e (rel. intensity) 246 (42), 231(4), 168(10), 153(19), 137(78), 135(100).

Anal. Calcd for $C_{15}H_{22}OSi$: $P^+$, 246.1439. Found: $P^+$, 246.1462.

## Diphenylmethylsiloxymethylenecyclohexane (If)

Analysis by GLC(column A, 220°C, n-eicosane as an internal standard (RRT 1)); If(26%, RRT 1.65) and $(Ph_2MeSi)_2O$ (6%, RRT 6.31). If; bp 150-156°C(0.55 mm); IR(neat); 3050,

2910, 2850, 1680, 1590, 1430, 1250, 1140, 1120, 1080, 1060, 900, 830, 790, 720, 700 cm$^{-1}$; NMR(CCl$_4$) $\underline{\delta}$ 0.63(s 3H), 1.53 (c 6H), 1.91(m 2H), 2.25(m 2H), 6.01(s 1H), 7.34(m 6H), 7.55 (m 4H); mass spectrum m/e (rel. intensity) 308(38), 215(33), 199(63), 197(100), 137(91).

Anal. Calcd for C$_{20}$H$_{24}$OSi: C, 77.87; H, 7.84. Found: C, 77.58; H, 7.68.

## Trimethylsiloxymethylenecyclohexane(Ia)

A solution of cyclohexene(30 mmol) and Co$_2$(CO)$_8$ (0.2 mmol) in 20 ml of benzene was placed in a 100 ml stainless steel autoclave. The autoclave was flushed with N$_2$(80 kg/cm$^2$) and CO(50 kg/cm$^2$) and cooled to -70°C. Trimethylsilane (10 mmol) was introduced to the autoclave by trap-to-trap distillation under vacume(10 mm) and then the autoclave was charged with CO to 80 kg/cm$^2$ at 25°C and heated at 140°C. The GLC retention time of the product was identical to that of trimethylsiloxymethylenecyclohexane which was independently prepared from cyclohexanecarboxaldehyde and trimethylchlorosilane by House's method.[20]

Analysis by GLC(column A, 100°C, $\underline{n}$-dodecane as an internal standard (RRT 1)); Ia(4%, RRT 0.65). Ia; bp 91°C (23 mm); IR(neat) 2950, 2850, 1675,1445, 1250, 1210, 1150, 1080, 900, 840, 740 cm$^{-1}$; NMR(CCl$_4$) $\underline{\delta}$ 0.14(s 9H), 1.44(c 6H), 1.84(m 2H), 2.04(m 2H), 5.80(s 1H); mass spectrum m/e (rel. intensity) 184(44), 169(42), 155(21), 75(100) 73(98).

Anal. Calcd for C$_{10}$H$_{20}$OSi: P$^+$, 184.1282. Found: P$^+$, 184.1279.

## 1-(Diethylmethylsiloxymethyl)-cyclohex-1-ene(XI)

The experimental procedure was the same as the general procedure except that the reaction was carried out at 200°C.

Analysis by GLC(column A, 100°C, n-tetradecane as an internal standard (RRT 1)); XI(17%, RRT 0.81), Ic(67%, RRT 0.79), and $(Et_2MeSi)_2O$ (15%, RRT 0.29). XI; IR(neat); 2920, 2870, 1675, 1460, 1420, 1255, 1160, 1090, 1070, 1010, 965, 840, 800, 760 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.01(s 3H), 0.53(m 4H), 0.93 (m 6H), 1.60(m 4H), 1.80-2.12(c 4H), 3.85(s 2H), 5.50(m 1H); mass spectrum m/e (rel. intensity) 212(14), 183(31), 103(7), 89(100).

Anal. Calcd for $C_{12}H_{24}OSi$: P$^+$, 212.1594; C, 67.85; H, 11.38. Found: P$^+$, 212.1560; C, 67.83; H, 11.44.


General procedure for the reaction of 1-hexene with diethyl-methylsilane and carbon monoxide in the presence of a metal complex

A solution of 3.7 ml(30 mmol) of 1-hexene, 1.02g(10 mmol) of diethylmethylsilane, and 0.136g(0.4 mmol) of $Co_2(CO)_8$ in 20 ml of benzene was placed in a 100 ml stainless steel autoclave. The autoclave was flushed with $N_2$(50 kg/cm$^2$) and CO(50 kg/cm$^2$), then charged with CO to 50 kg/cm$^2$ and heated at 140°C with stirring. After 20 h, the autoclave was cooled and depressurized. Analysis of the reaction mixture by GLC(Silicon OV-1, 5%, on Uniport KS, 6m, 115°C) with an internal standard(n-tetradecane, RRT=1) showed it to contain enol silyl ethers((Z)-(IXa); RRT 0.36, (E)-(IXa); RRT 0.39, (Z)-(Xa); RRT 0.45, (E)-(Xa); RRT 0.60)) and $(Et_2MeSi)_2O$ in 57%(total) and 5% yields, respectively.

Analytical samples were obtained by fractional distillation

(bp 105-115°C/12 torr) followed by repeting preparative GLC.

The results under various reaction conditions were shown

in Table VIII and IX.

The spectral data are: (Z)-(IXa), IR(neat); 2950, 1670,

1460, 1260, 1170, 1090, 1010, 970, 750-800 $cm^{-1}$; NMR(CCl$_4$) $\underline{\delta}$

0.08(s 3H), 0.62(m 4H), 0.70-1.14(m 9H), 1.14-1.50(c 4H)

overlaped with 1.48(d 3H), 2.00(m 2H) 5.90( s 1H); mass

spectrum m/e (rel. intensity) 214(35), 199(6), 185(28),

171(50), 101(100); high resolution MS, parent ion m/e 214.1747

(calcd for C$_{12}$H$_{26}$OSi, 214.1751).

(E)-(IXa), IR(neat); 2920, 1670, 1460, 1260, 1170, 1100,

1010, 970, 740-800 $cm^{-1}$; NMR(CCl$_4$) $\underline{\delta}$ 0.08(s 3H), 0.60(m 4H),

0.84-1.12(m 9H), 1.12-1.50(m 4H) overlaped with 1.50(d 3H),

1.83(m 2H), 5.92(m 1H); mass spectrum m/e (rel. intensity)

(Z)-(Xa), IR(neat); 3050, 2950, 1660, 1460, 1400, 1260,

1170, 1140, 1090, 1010, 750-820 $cm^{-1}$; NMR(CCl$_4$) $\underline{\delta}$ 0.10(s 3H),

0.60(m 4H), 0.80-1.15(m 9H), 1.15-1.40(c 6H), 1.96(m 2H),

4.30(dt, J=6 Hz and 8 Hz), 1H), 6.02(d, J=6 Hz, 1H); mass

spectrum m/e (rel. intensity) 214(4), 185(76), 157(38), 101

(85), 89(100); high resolution MS, parent ion m/e 214.1728

C$_{12}$H$_{26}$OSi Calcd 214.1751.

(E)-(Xa), IR(neat); 2920, 1660, 1460, 1420, 1260, 1160, 1100,

1010, 960, 910 $cm^{-1}$; NMR(CCl$_4$) $\underline{\delta}$ 0.10(s 3H), 0.60(m 4H),

0.80-1.14(m 9H), 1.14-1.48(c 6H) 1.80(m 2H), 4.80(dt, J=12 Hz

and 6Hz, 1H), 6.08(d, J=12 Hz, 1H); mass spectrum m/e (rel.

intensity) 214(3), 185(54), 157(36), 101(66), 89(100); high

Table VIII Reaction of 1-Hexene with Et$_2$MeSiH and CO in the Presence of Co$_2$(CO)$_8$[a]

| Run | Olefin (mmol) | SiH (mmol) | Benzene (ml) | CO pressure init. | CO pressure fin. | Temp. (°C) | hr | Total yield(%) | Product distribution(%) (Z-IXa) | (E-IXa) | (Z-Xa) | (E-Xa) | Other isomer |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 30 | 10 | 20 | 50 | 49 | 140 | 20 | 57 | 16 | 16 | 43 | 25 | 0 |
| 2 | 60 | 20 | 40 | 80 | 70 | 140 | 20 | 52 | 15 | 17 | 44 | 24 | 3 |
| 3 | 20 | 20 | 40 | 80 | 79 | 140 | 44 | 38 | 15 | 17 | 43 | 25 | 2 |
| 4 | 20 | 20 | 40 | 80 | 80 | 140 | 20 | 21 | 13 | 16 | 48 | 23 | 2 |
| 5 | 20 | 30 | 40 | 80 | 78 | 200 | 20 | 22 | 27 | 27 | 32 | 14 | 8 |

a) Co$_2$(CO)$_8$ (0.4 mmol)

Table IX Reaction of 1-Hexene with Et$_2$MeSiH and CO in the Presence of Ru$_3$(CO)$_{12}$

| Run | Olefin (mmol) | SiH (mmol) | Ru$_3$(CO)$_{12}$ (mmol) | Benzene (ml) | CO (kg/cm$^2$) | Temp. (°C) | hr | Total yield(%) | Product distribution(%) (Z-IXa) | (E-IXa) | (Z-Xa) | (E-Xa) | Other isomer |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 30 | 10 | 0.4 | 20 | 50 | 140 | 20 | 40 | 4 | 7 | 44 | 45 | 0.0 |
| 2 | 30 | 10 | 0.05 | 20 | 80 | 140 | 20 | 16 | 7 | 7 | 35 | 51 | 0.4 |
| 3 | 20 | 20 | 0.1 | 40 | 80 | 140 | 20 | 30 | 8 | 7 | 31 | 54 | 2.0 |
| 4 | 20 | 30 | 0.4 | 40 | 80 | 200 | 20 | 22 | 10 | 9 | 48 | 33 | 4.0 |
| 5 | 20 | 20 | 0.1 | 40 | 80 | 140 | 20 | 33 | 9 | 9 | 37 | 45 | 3.0 |
| 6 | 10 | 15 | 0.1 | 20 | 30 | 140 | 44 | 29 | 6 | 8 | 28 | 58 | 1.0 |

resolution MS, parent ion -- Et m/e 185.1346 $C_{10}H_{21}OSi$ Calcd
185.1359.


Reaction of methyl acrylate with diethylmethylsilane and carbon
monoxide -

A solution of 2.7 ml(30 mmol) of methyl acrylate, 1.02g
(10 mmol) of $Et_2MeSiH$, and 0.068g(0.2 mmol) of $Co_2(CO)_8$ in 20
ml of benzene was placed in a 100 ml stainless steel autoclave.
The autoclave was flushed two times with CO(50 kg/cm$^2$), then
charged with CO to 80 kg/cm$^2$ and heated at 140°C with stirring.
After 20 h, the autoclave was cooled and depressurized. Analysis
of the reaction mixture by GLC(Silicon OV-1, 5%, on Uniport KS,
3m, 120°C) with an internal standard(n-tetradecane, RRT=1)
showed it to contain (Z)- and (E)-1-diethylmethylsiloxy-2-
carbomethoxyprop-1-ene(IXb) and (Z)- and (E)-1-diethylmethyl-
siloxy-3-carbomethoxyprop-1-ene(Xb) ((Z)-(IXb); RRT 0.633, (E)-
(IXb); RRT 0.744, (Z)-(Xb); RRT 0.625, (E)-(Xb); RRT 0.706)
and $(Et_2MeSi)_2O$ in 49%(total) and 7% yields, respectively.
Analytical samples were obtained by fractional distillation
(130-160°C/17 torr) followed by preparative GLC.  The results
under various reaction conditions were shown in Table III and
Table V.

The spectral data are described below.
(Z)-(IXb), IR(neat); 2950, 2860, 1725, 1700, 1640, 1300, 1260,
1190, 1130, 820, 770 cm$^{-1}$; NMR(CCl$_4$) $\underline{\delta}$ 0.17(s 3H), 0.68(m 4H),
1.00(m 6H), 1.69(s 3H), 3.65(s 3H), 6.53(s 1H); mass spectrum
(rel. intensity) 216(2), 201(6), 187(100), 159(23), 103(90),
91(35), 89(35), 75(52); high resolution MS parent ion - Et m/e
187.0804 $C_8H_{15}O_3Si$ calcd 187.0789.

(E)-(IXb), IR(neat); 2920, 1720, 1640, 1300, 1220, 1120, 820,

760 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.22(s 3H), 0.74(m 4H), 1.00(m 6H), 1.70

(d, J=2 Hz, 3H), 3.64(s 3H), 7.35(q, J=2 Hz, 1H); mass spectrum

(rel. intensity) 216(2), 201(7), 187(100), 103(95), 75(87);

high resolution MS parent - Et ion m/e 187.0821 C$_8$H$_{15}$O$_3$Si

calcd 187.0790.

(Z)-(Xb), IR(neat); 2950, 2870, 1740, 1660, 1330, 1260, 1160,

1120, 1040, 1010, 840, 750 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.15(s 3H), 0.66

(m 4H), 1.00(m 6H), 3.03(d, J=8 Hz, 2H), 3.60(s 3H), 4.59(dt,

J=8 Hz and 8 Hz, 1H), 6.15(d, J=8 Hz, 1H); mass spectrum (rel.

intensity) 216(3), 187(86), 157(20), 103(100), 101(43), 75(48),

73(41); high resolution MS parent -Et ion m/e 187.0802 C$_8$H$_{15}$O$_3$Si

calcd 187.0790.

(E)-(Xb), The NMR prectrum of (E)-(Xb) was determined from the

mixture of (E)-(Xb) and (E)-(IXb). NMR(CCl$_4$) $\delta$ 0.14(s), 0.51-

0.81(m), 0.90-1.11(m), 2.79(d, J=8 Hz), 3.58(s), 4.89(dt,

J=12 Hz and 8 Hz), 6.15(d, J=12 Hz).


Reaction of cyclohexene with diethylmethyldeuteriosilane and

carbon monoxide

A solution of 10.3 ml(100mmol) of cyclohexene, 1.03g

(10 mmol) of Et$_2$MeSiD, and 0.068g(0.2 mmol) of Co$_2$(CO)$_8$ in

20 ml of benzene was placed in a 100 ml stainless steel

autoclave. The autoclave was flushed with N$_2$(50 kg/cm$^2$) and

CO(50 kg/cm$^2$), then charged with CO to 50 kg/cm$^2$ and heated at

140°C with stirring. After 1 h, the pressure reached 105

kg/cm$^2$ at 140°C. The temperature was maintained at 140°C for

20 h. The vessel was then cooled to room temperature. The

pressure decreased to 77 kg/cm$^2$. The gas pressure was slowly

released and the autoclave was opened. Analysis of the

reaction mixture by GLC(Silicon OV-1, 3m, 130°C) with an

internal standard(n-tetradecane) showed it to contain

diethylmethylsiloxymethylenecyclohexane(Ic) and (Et$_2$MeSi)$_2$O

in 87% and 12% yields, respectively. Analytical samples were

obtained by fractional distillation(124-129°C/20 torr) followed

by preparative GLC.

The amount of deuterium incorporation was determined by

comparing the area in the vinyl and the methylene of

cyclohexane part with the methyl group of siloxy part. These

areas were measured five times at least with the largest

amptitude and averaged. The result was shown in Table X.

Table X   Comparison of Areas in NMR Spectrum

| | MeSi | $\mathrm{CH_2{-}}^{} C{=}C\overset{OSi}{\underset{}{}}$ | $\mathrm{CH_2{-}}^{} C{=}C\overset{OSi}{\underset{}{}}$ | $C{=}C\overset{OSi}{\underset{H}{}}$ | $\mathrm{CH_2{-}}\overset{CH_2}{\underset{CH_2}{}}$ |
|---|---|---|---|---|---|
| ratio of areas | 3 | 1.88 | 1.82 | 0.088 | 5.80 |
| deuterium content(%) | – | 7.5 | 7.5 | 91 | 3 |

From the Table X, the amount of deuterium incorporation was

determined to be 91% at the vinyl position, 15% at the adjacent

methylene group to carbon-carbon double bond, and 3% at the

another methylene group of the cyclohexane part.

Mass spectrometric analysis showed it to contain 12% $d_0$,

75% $d_1$, 11% $d_2$, 2% $d_3$.

The second trial was carried out under the same conditions described above except that 30 mmol of cyclohexene and 80 $kg/cm^2$ of carbon monoxide were used. The result was shown in Table XI.

Table XI   Comparison of Areas in NMR Spectrum

| | MeSi | $CH_2$ $C=C$ OSi | $CH_2$ $C=C$ OSi | $C=C$ OSi H | $CH_2$ ring $CH_2$ |
|---|---|---|---|---|---|
| ratio of areas | 3 | 1.93 | 1.73 | 0.18 | — |
| deuterium content(%) | — | 3.5 | 13.5 | 82 | — |

Mass spectrometric analysis showed it to contain 18% $d_0$, 61% $d_1$, 18% $d_2$, 4% $d_3$.

Reaction of n-heptanal with diethylmethylsilane in the presence of carbon monoxide and $Co_2(CO)_8$

A solution of n-heptanal(10 mmol), diethylmethylsilane (10 mmol), and $Co_2(CO)_8$(0.4 mmol) in benzene(20 ml) was placed in a 100 ml stainless steel autoclave. The autoclave was flushed two times with $N_2$(50 $kg/cm^2$), then charged with CO (50 $kg/cm^2$) and heated at 140°C with stirring. After 20 h, the autoclave was cooled and depressurized. Analysis of the reaction mixture by GLC(Silicon OV-1, 5%, 6m, 110°C) with an internal standard(n-tetradecane) showed it to contain X and XVI in 32.8% and 7.2% yields, respectively. The IR(neat) and NMR($CCl_4$) data of XVI are: IR, 2930, 1470, 1420, 1255, 1100, 1010, 800, 760; NMR δ 0.00(s 3H), 0.32(m 4H), 0.92(m 9H), 1.28(c 10H), 3.50(t, J=6 Hz, 2H).

Reaction of n-heptanal with diethylmethylsilane in the presence of $Co_2(CO)_8$

A solution of diethylmethylsilane(4 mmol) and $Co_2(CO)_8$ (0.04 mmol) in xylene(4 ml) was heated at 135°C. To the solution was added a solution of n-heptanal(2 mmol) in xylene. Gas evolution occurred immediately. Analysis of the reaction mixture by GLC(Silicon OV-1, 5%, 6m, 140°C) with an internal standard(n-tetradecane) showed it to contain (Z)-(Xa),(E)-(Xa), and XVI in 49%, 30%, and 21% yields, respectively. The results at various temperature were shown in Table XII .

Table XII  Yields and Distribution at Various temperature[a]

| Temp.(°C) | Yield(Xa + XVI) | Xa : XVI |
|-----------|-----------------|----------|
| 10 | 94 | 4: 96 |
| 28 | 100 | 6: 94 |
| 50 | 100 | 18: 82 |
| 80 | 76[c] | 53: 47 |
| 110 [b] | 93 | 64: 36 |
| 135 [b] | 100 | 79: 21 |

a) In benzene unless otherwise noted.
b) In xylene. c) Result after 1 h.

Reaction of styrene with diethylmethylsilane and carbon monoxide in the presence of $Co_2(CO)_8$

A solution of styrene(30 mmol), diethylmethylsilane(10 mmol), and $Co_2(CO)_8$(0.2 mmol) in benzene(20 ml) was placed in a 100 ml stainless steel autoclave. The autoclave was flushed with $N_2$ (80 kg/cm$^2$) and CO(50 kg/cm$^2$), then charged with CO(80 kg/cm$^2$) and heated at 140°C with stirring. After 20 h, the autoclave

was cooled and depressurized. Analysis of the reaction mixture by GLC(Silicon OV-1, 5%, 3m, 140°C) with 0.3 g of n-tridecane as an internal standard showed it to contain eight compounds (XVIIa ;RRT 1.86, XVIIb ;RRT 2.21, XVIIc ;RRT 2.54, XVIId ;RRT 3.00, XVIIe ;RRT 3.44, XVIIf ;RRT 5.00, XVIIg ;RRT 7.47, and $(Et_2MeSi)_2O$). Detector response calibrations are not determined except for XVIIa. The ratios of the peak areas of the compounds and the standard were obtained as follows: XVIIa ; 0.32(yield 6%), XVIIb ; 0.20, XVIIc ; 0.13, XVIId ; 0.17, XVIIe ; 0.45, XVIIf ; 0.10, XVIIg ; 0.27. Analytical samples were obtained by fractional distillation(110-120°C/17 torr) followed by preparative GLC. The product(XVIIa) was identified with (2-phenylethyl)diethylmethylsilane; NMR($CCl_4$) $\delta$ -0.04(s 3H), 0.51(m 4H), 1.04(m 8H), 2.55(m 2H), 7.05(s 5H). The product (XVIIb) was identified with β-diethylmethylsilylstyrene; IR (neat), 2940, 2860, 1600, 1570, 1490, 1250, 1000, 980, 790, 730 $cm^{-1}$; NMR($CCl_4$) $\delta$ 0.10(s 3H), 0.63(m 4H), 0.99(m 6H), 6.29 (d, J=20 Hz, 1H), 6.81(d, J=20 Hz, 1H), 7.05-7.35(c 5H). An exact mass determination gave m/e 204.1303(calcd for $C_{13}H_{20}Si$, 204.1333).

Reaction of styrene in the presence of $Ru_3(CO)_{12}$

The experimental procedure was the same as that described above except that styrene(10 mmol), diethylmethylsilane(20 mmol), $Ru_3(CO)_{12}$(0.05 mmol), and n-tridecane(0.2g) as an internal standard were used. The ratios of the peak areas of the compounds and the standard were obtained as follows: XVIIa ; 0.11 (1.4%), XVIIb ; 0.29, XVIIc ; 0.07, XVIId ; 0.02, XVIIe ;0.14, XVIIf ; 0.04, XVIIg ; 0.03.
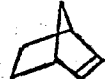
Reaction of acrylonitrile with diethylmethylsilane and carbon monoxide in the presence of $Ru_3(CO)_{12}$

A solution of acrylonitrile(10 mmol), diethylmethylsilane (30 mmol), and $Ru_3(CO)_{12}$(0.01 mmol) in benzene(20 ml) was placed in a 100 ml stainless steel autoclave. The autoclave was flushed with $N_2$(80 kg/cm$^2$) and CO(50 kg/cm$^2$), then charged with CO(80 kg/cm$^2$) and heated at 140°C with stirring. After 20 h, the autoclave was cooled and depressurized. Analysis of the reaction mixture by GLC(DEGS, 15%, on Cromosorb W, 6m, 130°C) with an internal standard(n-pentadecane) showed it to contain 1-cyanoethyl(diethylmethyl)silane in 56% yield. The IR(neat) and NMR(CCl$_4$) data are: 2950, 2860, 2220, 1460, 1260, 1010, 790, 750 cm$^{-1}$; $\delta$ 0.14(s 3H), 0.69(m 4H), 1.02(m 6H), 1.26(d, J=8 Hz, 3H), 1.65(q, J=8 Hz, 1H). An exact mass determination gave m/e 155.1125(calcd for $C_8H_{17}NSi$, 155.1128).

Competitive reaction of cycloalkenes

In a typical procedure, a solution of 0.62g(7.5 mmol) of cyclohexene, 0.83g(7.5 mmol) of cyclooctene, 0.75 ml(5 mmol) of diethylmethylsilane, and 0.1 mmol of $Co_2(CO)_8$ in 10 ml of benzene was placed in a 100 ml stainless steel autoclave. The autoclave was flushed two times with CO(50 kg/cm$^2$), then charged with CO(50 kg/cm$^2$) and heated at 140 °C with stirring. After 2 h, the autoclave was cooled and depressurized. Analysis of the reaction mixture by GLC(Silicon OV-1, 5% on Uniport KS, 6m, 150°C) showed it to contain (Ic) and (VI) in 5.5% and 4.3% yields, respectively. The results were shown in Table XIII.

Table XIII  Competitive Reaction of Cycloalkenes[a]

| Run | hr | Yield of enol silyl ether | | | | | Yield of $(Et_2MeSi)_2O$ |
|---|---|---|---|---|---|---|---|
| | | (pentene) | (hexene) | (heptene) | (octene) | (norbornene) | |
| 1 | 20 | 3.6 | 6.9 | | | | 99 |
| 2 | 20 | | 31 | 47 | | | 18 |
| 3 | 20 | | 31 | | 23 | | 22 |
| 4 | 20 | 6.1 | | | 3.6 | | 29 |
| 5[b] | 2 | | 6 | 12.4 | | | 8.2 |
| 6[b] | 2 | | 5.5 | | 4.3 | | 5 |
| 7[b] | 3 | 34 | | | 28 | | 9 |
| 8[b] | 2 | 4 | | | | 24 | 5 |

a) Reaction conditions; $Co_2(CO)_8$(0.2 mmol), olefin
(30 mmol 1:1), $Et_2MeSiH$(10 mmol), CO(50 kg/cm$^2$), 140°C,
20 h, benzene(20-ml) unless otherwise noted.

b) Reactions were carried out in a half scale and olefins
were weighted in gram unit.

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Experimentally, to a solution of LiAlD$_4$ (18 mmol) in 15 ml of diethyl ether was added dropwise a solution of Et$_2$MeSiCl (74 mmol) in 80 ml of diethyl ether for 20 min at room temperature and then the solution was heated to reflux for 1 hr. Diethylmethyldeuteriosilane was obtained in 59% yield.

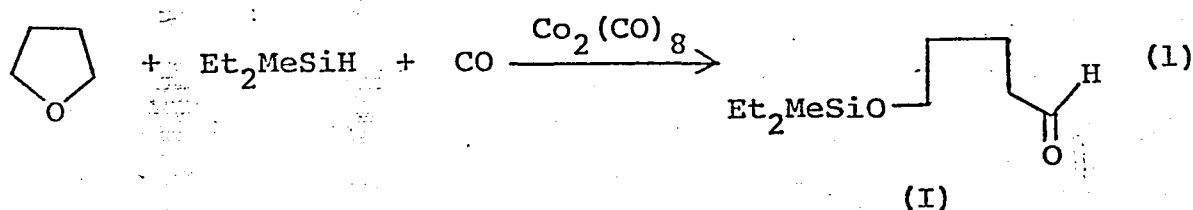20  H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, J. Org. Chem., 34, 2324(1969).

Chapter 2  A Catalyzed Reaction of Cyclic Ethers with a

Hydrosilane and Carbon Monoxide

## 2-1  Introduction

In chapter 1, the new catalyzed reaction of olefins with

hydrosilanes and carbon monoxide was described.  To know

the scope and limitation to the substrate is very important

in order to explore the utility of the reaction.  From this

point of view, the catalyzed reaction of cyclic ethers with

a hydrosilane and carbon monoxide was examined.  It was

found that when tetrahydrofuran (THF) was used as a solvent

in the reaction of olefins, the product obtained was not the

expected one, enol silyl ether, but a new compound.  This is

the reason why cyclic ethers were used as a substrate.


## 2-2  Results and discussion

The reaction of cyclic ethers( tetrahydrofuran , oxetane,

and cyclohexeneoxide) with diethylmethylsilane and carbon

monoxide was catalyzed by $Co_2(CO)_8$ to give diethylmethylsiloxy-

aldehyde (I), (II) , (III), respectively, in reasonable yields;

(I) 53%, (II) 40%, and (III) 51% as shown in eq. 1, 2, and 3.

$$\text{(THF)} \quad + \quad Et_2MeSiH \quad + \quad CO \xrightarrow{Co_2(CO)_8} \quad Et_2MeSiO-\!\!\!\diagup\!\!\!\searrow\!\!\!\diagdown_{\!O}^{\,H} \quad (1)$$

(I)

$$\text{(oxetane)} + Et_2MeSiH + CO \xrightarrow{Co_2(CO)_8} \underset{\textbf{(II)}}{Et_2MeSiO\text{-}CH_2CH_2CH_2\text{-}CHO} \quad \text{: (2)}$$

$$\text{(cyclohexene oxide)} + Et_2MeSiH + CO \xrightarrow{Co_2(CO)_8} \underset{\textbf{(III)}}{\text{2-(}OSiEt_2Me\text{)cyclohexyl-}CHO} \quad \text{(3)}$$
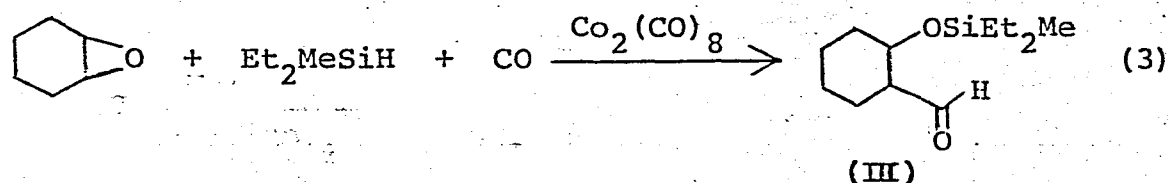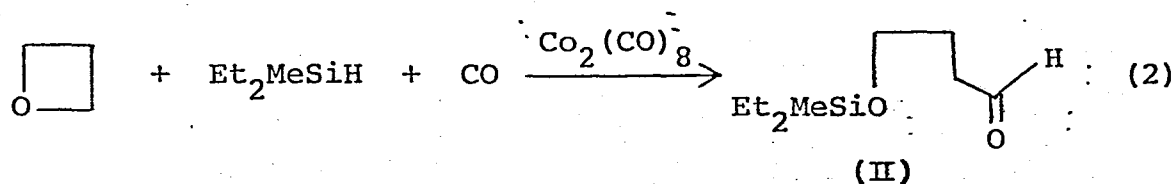
The reaction of cyclic ethers except for oxetane was carried out using 50 mmol of cyclic ethers, 10 mmol of diethylmethyl-silane, and 60 $kg/cm^2$ of carbon monoxide at 140°C for 20 h. The reaction conditions in the case of oxetane were the same as that described above except that 20 mmol of oxetane were used at 70°C.

Hydroformylation of cyclic ethers is known to give hydroxy aldehydes as the initial products[1]. The reaction, however, frequently suffers from undesirable side reactions or further reactions, since the hydroxy aldehydes are very labile compounds. For example, hydroformylation[2] of tetrahydrofuran did not afford the expected 4-hydroxybutanal but yielded various products arising from further carbonylation. as shown in eq. 4 and hydroformylation[3] of cyclohexeneoxide gave only condensation product of the expected 2-hydroxy-cyclohexanecarboxaldehyde as shown in eq. 5. While the reactions using a hydrosilane show a direct approach to the synthesis of pre-protected hydroxy aldehydes. Synthetically, functionalyzed aldehydes are very useful in elongation of carbon skeltone.

$$\text{tetrahydrofuran} \xrightarrow[\text{Co}_2(\text{CO})_8]{\text{H}_2, \text{CO}} \quad \delta\text{-valerolactone} \quad + \quad \text{(tetrahydropyranyl-CH}_2\text{OH)} \quad + \quad \text{HO}\!-\!\text{(CH}_2)_5\!-\!\text{OH} \tag{4}$$

$$\text{cyclohexene oxide} \xrightarrow[\text{Co}_2(\text{CO})_8]{\text{H}_2, \text{CO}} \tag{5}$$
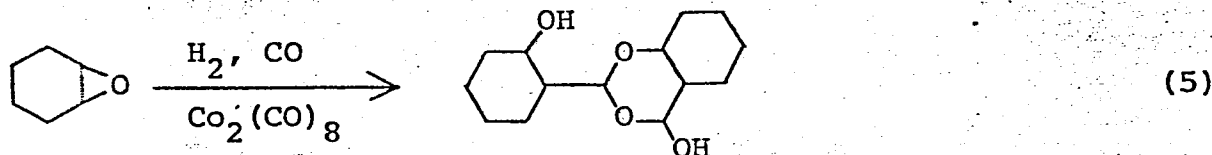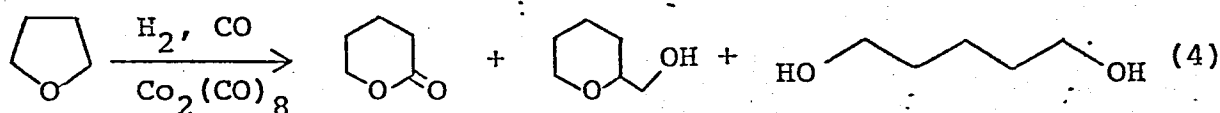
It is interesting to note that Chalk has reported the polimerization of tetrahydrofuran catalyzed by $\text{Co}_2(\text{CO})_8$ and triethylsilane(1:2) and proposed ring opening of tetrahydrofuran by a silylcobaltcarbonyl for the initiation step[4]. Corriu and co-workers have reported that a silylcobaltcarbonyl containing an optically active silicon reacted with methanol and triethylamine and the cleavage of the Si-Co bond took place with retention[5]. It is reasonable that the silicon group of the silylcobaltcarbonyl electrophilically attacked the oxygen of methanol. These results suggest that the ring opening of tetrahydrofuran by the silylcobaltcarbonyl is the initial step. This means that one can make a carbon cobalt bond utilyzing the high affinity of silicon to oxygen as a driving force. This is the new method to make bonds of carbon and transition metals. The reasonable reaction path was shown in scheme 1.

Scheme 1

$Et_2MeSiH$ + $Co_2(CO)_8$

$\longrightarrow$ $HCo(CO)_4$

$Et_2MeSiCo(CO)_4$

CO

(I)

$Et_2MeSiO$ $\overset{\displaystyle H}{\underset{\displaystyle SiEt_2Me}{\overset{|}{\underset{|}{Co(CO)_3}}}}$

$\overset{\|}{O}$

$Et_2MeSiH$

$Et_2MeSiO$ — $Co(CO)_4$

$Et_2MeSiO$ $Co(CO)_3$

$\overset{\|}{O}$

-49-
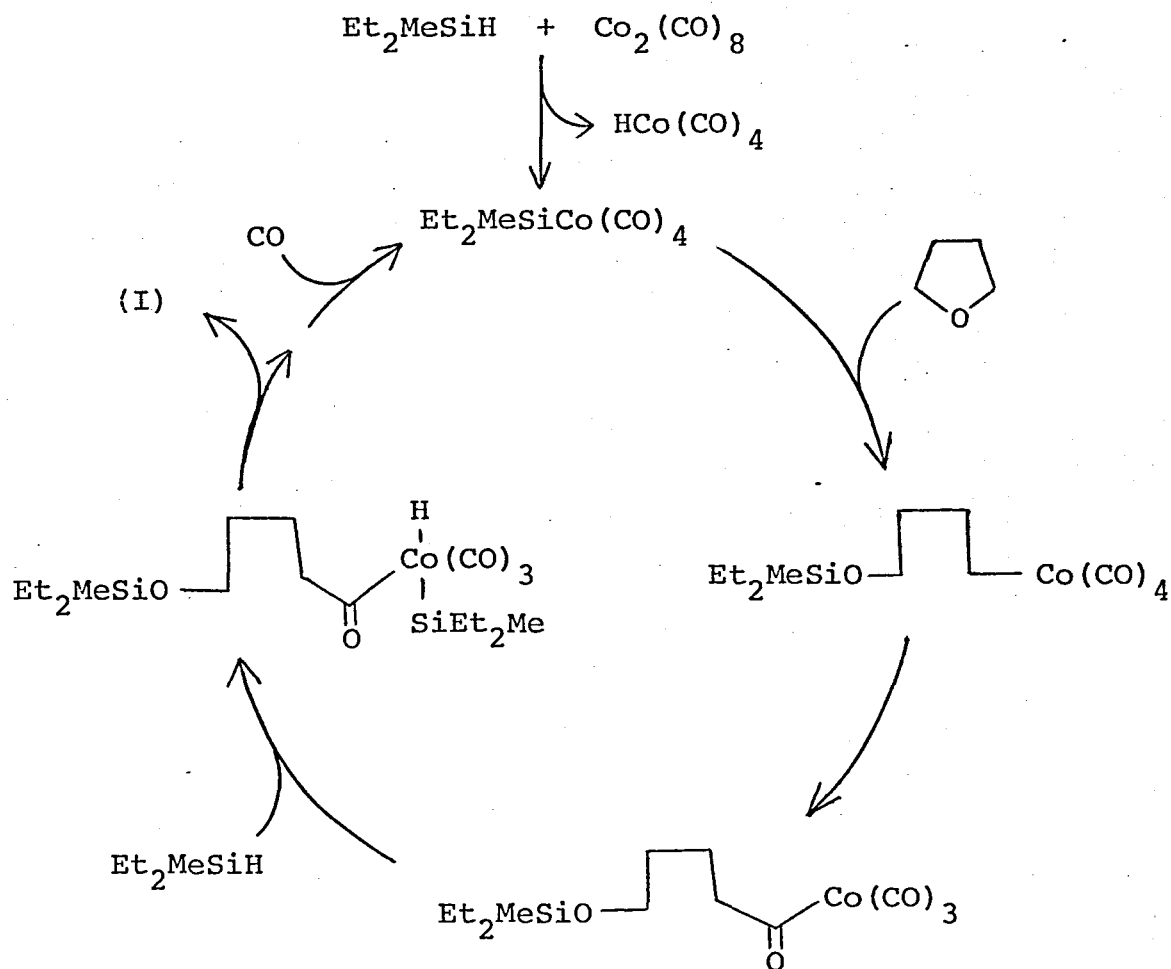
## 2-3 Experimental

Reaction of tetrahydrofuran with diethylmethylsilane and carbon monoxide in the presence of $Co_2(CO)_8$

A solution of 4 ml(50 mmol) of tetrahydrofuran, 1.02g (10 mmol) of diethylmethylsilane, and 0.068g(0.2 mmol) of $Co_2(CO)_8$ in 20 ml of benzene was placed in a 100 ml stainless steel autoclave. The autoclave was flushed with $N_2$ (60 $kg/cm^2$) and $CO$ (60 $kg/cm^2$), then charged with $CO$ (60 $kg/cm^2$) and heated at 140°C with stirring. After 20 h, the autoclave was cooled and depressurized. Analysis of the reaction mixture by GLC (Silicon OV-1, 5%, on Uniport KS, 3m, 135°C) with n-tetradecane as an internal standard showed it to contain 5-(diethylmethyl-siloxy)-n-pentanal (I) in 53% yield. An analytical sample of (I) was obtained by fractional distillation (bp 120-130°C/ 30 torr) followed by preparative GLC(Silicon OV-1, 5%, on Uniport KS, 3m X 8mm, 140°C). The spectral data are shown below. (I) , IR(neat), 2950, 2870, 1720, 1250, 1090, 1010, 800, 760 $cm^{-1}$; NMR($CCl_4$) δ 0.02 (s 3H), 0.56 (m 4H), 0.96 (m 6H), 1.58 (m 4H), 2.38 (m 2H), 3.56 (t, J=6 Hz, 2H), 9.60 (m 1H).

Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.34; H, 10.96. Found: C, 59.20; H, 11.10.

Reaction of oxetane with diethylmethylsilane and carbon monoxide

The reaction conditions were the same as that described above except that 20 mmol of oxetane were used and the temperature was 70°C. The spectral data are shown below.

Analysis of the reaction mixture by GLC(Silicon OV-1, 5%, on Uniport KS, 3m, 110°C) with n-tridecane as an internal standard showed it to contain 4-(diethylmethylsiloxy)-n-butanal(II) in 40% yield.

(II), IR(neat), 2920, 2860, 1725, 1480, 1460, 1250, 1080, 1000, 790, 750 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.03(s), 0.51(m), 0.93(m), 1.79(m), 2.43(m), 3.57(t, J=6), 9.64(m).

Anal. Calcd for C$_8$H$_{20}$O$_2$Si: C, 57.39; H, 10.70. Found: C, 57.35; H, 10.79.


Reaction of cyclohexeneoxide with diethylmethylsilane and carbon monoxide

The experimental procedure was the same as that in the case of tetrahydrofuran. Analysis of the reaction mixture by GLC(Silicon OV-1, 5%, on Uniport KS, 3m, 160°C) with n-tetradecane as an internal standard showed it to contain 2-(diethylmethylsiloxy)cyclohexanecarboxaldehyde(III) and an identified compound.

(III), RRT; 1.30, bp 165-166/30 torr, IR(neat), 2950, 2870, 1725, 1460, 1250, 1155, 1110-1060, 1010, 960, 800, 760 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.05(s 3H), 0.56(m 4H), 0.95(m 6H), 1.11-1.50 (c 4H), 1.50-2.04(c 4H), 2.04-2.40(c 1H), 3.76(td, J=10 Hz and 4 Hz, 1H), 9.66(d, J=2 Hz, 1H); mass spectrum(rel. intensity) 199(18), 110(24), 89(100), 81(31), 61(88).

Anal. Calcd for C$_{12}$H$_{24}$O$_2$Si: C, 63.10; H, 10.59. Found: C, 62.88; H, 10.75.

2-4    References and Footnotes

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# Chapter 3    A Catalyzed Reaction of Aldehydes with a Hydrosilane

and Carbon Monoxide

## 3-1    Introduction

It was shown that the new catalyzed reaction using
hydrosilane and carbon monoxide combination converts olefins
(C=C) to siloxy olefins in chapter 1 and cyclic ethers(C-O-C)
to siloxy aldehydes in chapter 2.   It is interesting question
whether aldehydes(C=O) can be used as a substrate in this new
reaction.   In chapter 2, the new method making a carbon cobalt
bond utilyzing the high affinity of silicon to oxygen as a
driving force was also described.   From these points of view,
the catalyzed reaction of aldehydes with a hydrosilane and carbon
monoxide was examined.

## 3-2    Results and discussion

The reaction of n-heptanal with diethylmethylsilane(three
fold excess to the aldehyde) and carbon monoxide in the presence
of $Co_2(CO)_8$ and $PPh_3$ gave a mixture of (Z)- and (E)-1,2-bis-
(diethylmethylsiloxy)-1-octene(Id) and unidentified compounds(II)
in 66% and 14% yields, respectively.
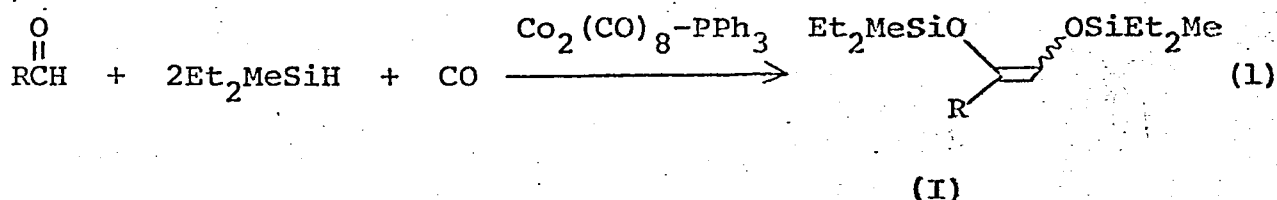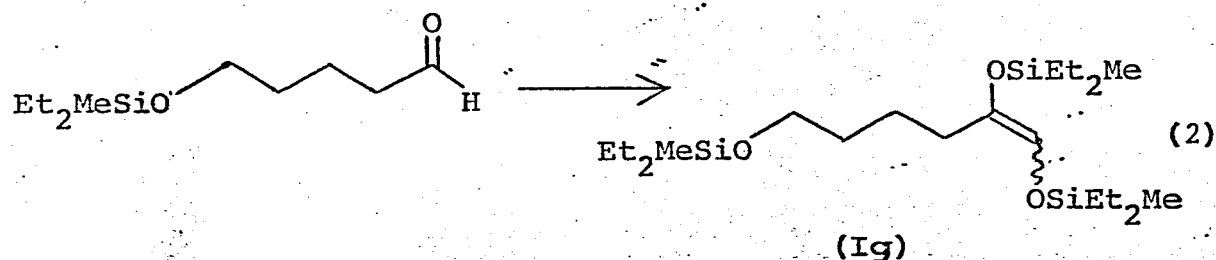
$$\underset{\text{(I)}}{\overset{\overset{\overset{O}{\parallel}}{RCH} + 2Et_2MeSiH + CO \xrightarrow{\quad Co_2(CO)_8-PPh_3 \quad}}{}}$$

$$\begin{array}{c} Et_2MeSiO \qquad OSiEt_2Me \\ \diagdown \quad / \\ C=C \\ / \\ R \end{array} \quad (1)$$

Table I   Reaction of Aldehydes with $Et_2MeSiH$ and $CO^a$

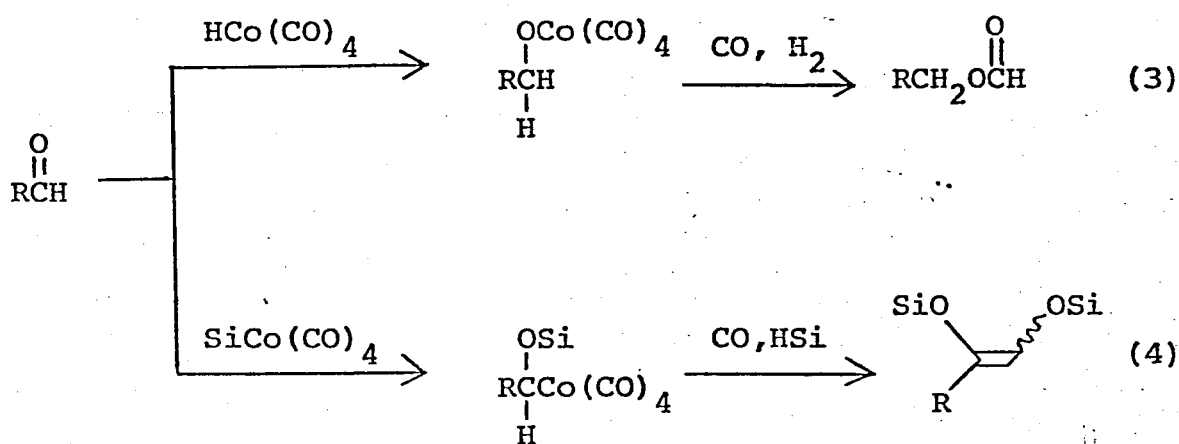| Aldehyde | Yield of (I) | Yield of (II) | $(Et_2MeSi)_2O$ |
|---|---|---|---|
| propanal (Ia) | 25 | 8 | 3 |
| isobutanal (Ib) | 21 | 1 | 2 |
| butanal (Ic) | 67 | 12 | – |
| n-heptanal (Id) | 66 | 14 | – |
| cyclohexane-carboxaldehyde (Ie) | 37 | 5 | 2 |
| n-hexanal (If) | 54 | 12 | – |

a) Reaction conditions; aldehyde(10 mmol), $Et_2MeSiH$(30 mmol)
$Co_2(CO)_8$(0.2 mmol), $PPh_3$(0.2 mmol), CO(50 kg/cm$^2$), 140°C,
20 h, benzene(20 ml).

The use of $PPh_3$ as a co-catalyst is necessary to prevent
undesired hydrosilylation of the aldehyde[1]. In the case of
cyclohexanecarboxaldehyde, the yield of (Ie) was low because
of the formation of diethylmethylsiloxymethylenecyclohexane(61%)
by dehydrogenative silylation.   Interestingly, the similar
reaction(i. e., using five fold excess of the hydrosilane, but
in this case without $PPh_3$) of tetrahydrofuran was found to
give the same type of compound(Ig) in 89% yield.   The
intermediate may be 5-(diethylmethylsiloxy)-n-pentanal which
was the product when the reaction was carried out using five
fold excess of tetrahydrofuran over the silane and without
$PPh_3$ as shown in eq. 2.

$$\text{Et}_2\text{MeSiO} \diagdown\diagup\diagdown\diagup\diagdown \overset{\overset{\displaystyle O}{\|}}{C}\diagup \text{H} \quad \xrightarrow{\hspace{2cm}} \quad \text{Et}_2\text{MeSiO}\diagdown\diagup\diagdown\diagup\diagup \overset{\text{OSiEt}_2\text{Me}}{\diagup}\diagdown_{\text{OSiEt}_2\text{Me}} \tag{2}$$

(Ig)

The fact that the reaction of tetrahydrofuran with five fold excess of the hydrosilane gave the corresponding 1,2-bissiloxyalkene in high yield suggests that $HCo(CO)_4$ is not the active catalyst in the reaction of cyclic ethers with a hydrosilane and carbon monoxide catalyzed by $Co_2(CO)_8$ in chapter 2.

Hydroformylation(oxo reaction) of aldehydes has been known to give formates as shown in eq. 3.[2] Thus the carbon atom of carbon monoxide is connected with the oxygen atom of aldehyde carbonyl. Contrastly, the carbon atom of carbon monoxide is linked with the carbon atom of aldehyde carbonyl in the reaction using a hydrosilane as shown in eq. 4.[3]



$$\underset{RCH}{\overset{\overset{\displaystyle O}{\|}}{}} \begin{array}{c} \xrightarrow{\;HCo(CO)_4\;} \quad \underset{\underset{H}{\overset{|}{\underset{\displaystyle}{RCH}}}}{\overset{OCo(CO)_4}{|}} \quad \xrightarrow{\;CO,\ H_2\;} \quad RCH_2O\overset{\overset{\displaystyle O}{\|}}{C}H \tag{3} \\[2em] \xrightarrow{\;SiCo(CO)_4\;} \quad \underset{\underset{H}{\overset{|}{\underset{\displaystyle}{RCCo(CO)_4}}}}{\overset{OSi}{|}} \quad \xrightarrow{\;CO,HSi\;} \quad \underset{R}{\overset{SiO}{}}\diagdown\diagup\diagdown^{OSi} \tag{4} \end{array}$$

The observed dramatic change may be attributed to the difference of reactivities of $HCo(CO)_4$ and $R_3SiCo(CO)_4$. Consequently, a carbon cobalt bond was formed utilyzing the high affinity of silicon to oxygen as a driving force.


3-3   Experimental


Reaction of n-heptanal with diethylmethylsilane and carbon monoxide in the presence of $Co_2(CO)_8$ and $PPh_3$

   A solution of 1.14 g(10 mmol) of n-heptanal, 4.4 ml (30 mmol) of diethylmethylsilane, 0.068 g(0.2 mmol) of $Co_2(CO)_8$, and 0.052 g(0.2 mmol) of $PPh_3$·in 20 ml of benzene was placed in a 100 ml stainless steel autoclave. The autoclave was flushed with $N_2$(50 kg/cm$^2$) and CO(50 kg/cm$^2$), then charged with CO(50 kg/cm$^2$) and heated at 140°C with stirring. After 20 h, the autoclave was cooled and depressurized. Analysis of the reaction mixture by GLC(Silicon OV-1, 5% on Uniport KS, 3m, 170°C) with n-cetane as an internal standard showed it to contain (Id) in 66% yield. In addition to Id there were at least two unidentified products(IId) (total ca. 14%) at longer retention time. An analytical sample of (Id) (a mixture of (Z) and (E) isomers) was obtained by fractional distillation(bp 120-123°C/0.5 torr) followed by preparative GLC(Silicon OV-1, 5%, on Uniport KS, 3m × 8mm, 190°C).

## 1,2-Bis(diethylmethylsiloxy)-1-octene (Id)

Analysis by GLC(Silicon OV-1, 170°C, n-cetane as an internal standard (RRT 1)); Id(RRT 2.04), bp 120-123°C/ 0.5 torr, IR(neat) 2950, 2870, 1685, 1460, 1250, 1160, 1090, 1000, 800, 760 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.08(s 3H), 0.10(s 3H), 0.63(m 8H), 0.80-1.11(m 15H), 1.29(c 8H), 1.80(m 2H), 5.44(s 0.83H), 5.90(s 0.17H).

Anal. Calcd for C$_{18}$H$_{40}$O$_2$Si$_2$: C, 62.72; H, 11.67. Found: C, 62.60; H, 11.71.

## 1,2-Bis(diethylmethylsiloxy)-1-pentene (Ic)

Analysis by GLC(Silicon OV-1, 140°C, n-tetradecane as an internal standard (RRT 1)); Ic(RRT 2.0), bp 130-150°C/25 torr, IR(neat) 2940, 2860, 1685, 1460, 1360, 1250, 1150, 1000, 850, 790, 750 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.08(s 3H), 0.10(s 3H), 0.32-0.80 (m 8H), 0.84-1.08(m 15H), 1.26-1.60(m 2H), 1.78(t, J=7 Hz, 2H), 5.44(s 0.92H), 5.92(s 0.08H); mass spectrum(rel. intensity) 302(43), 273(25), 189(43), 161(54), 101(100), 73(78), 45(29).

Anal. Calcd for C$_{15}$H$_{34}$O$_2$Si$_2$: C, 59.54; H, 11.32. Found: C, 59.21; H, 11.55.

## 1,2-Bis(diethylmethylsiloxy)-1-cyclohexylethylene (Ie)

Analysis by GLC(Silicon OV-1, 170°C, n-heptadecane as an internal standard (RRT 1)), Ie(RRT 1.9), bp 140-150°C/0.8 torr, IR(neat) 2920, 1685, 1250, 1210, 1160, 1120, 1010, 970, 860, 840, 760-800 cm$^{-1}$; NMR(CCl$_4$) $\delta$ 0.09(s 3H), 0.12(s 3H), 0.48-0.75(m 8H), 0.87-1.08(m 12H), 1.11-1.41(c 5H), 1.41-1.86(c 6H), 5.48(s 0.91H), 5.78(s 0.09H); mass spectrum(rel. intensity)

342(100), 313(38), 189(54), 161(73), 101(88), 73(87), 45(33).

Anal. Calcd for $C_{18}H_{38}O_2Si_2$: C, 63.09; H, 11.17. Found: C, 62.99; H, 11.21.

## 1,2-Bis(diethylmethylsiloxy)-1-heptene(If)

Analysis by GLC(Silicon OV-1, 6m, 180°C, n-pentadecane as an internal standard (RRT 1)); If, bp 117-119°C/1.0 torr, IR (neat) 2950, 1690, 1470, 1420, 1260, 1210, 1160, 1100, 1000, 840, 800, 770 $cm^{-1}$; NMR($CCl_4$) $\delta$ 0.08(s 3H), 0.09(s 3H), 0.62 (m 8H), 0.87-1.08(m 15H), 1.17-1.56(c 6H), 1.80(m 2H), 5.42 (s 0.87H), 5.88(s 0.13H); mass spectrum(rel. intensity) 330(50), 301(17), 189(40), 161(53), 101(100), 73(90), 45(30).

Anal. Calcd for $C_{17}H_{38}O_2Si_2$: C, 61.75; H, 11.58. Found: C, 61.48; H, 11.69.

## 1,2-Bis(diethylmethylsiloxy)-3-methyl-1-butene(Ib)

Ib, bp 150-160°C/30 torr, IR(neat) 2950, 2870, 1685, 1460, 1250, 1180, 1000, 970, 790, 760 $cm^{-1}$; NMR($CCl_4$) $\delta$ 0.08(s), 0.10(s), 0.60(m), 0.80-1.08(m), 1.98(m), 5.44(s), 5.70(s).

Anal. Calcd for $C_{15}H_{34}O_2Si_2$: C, 59.54; H, 11.32. Found: C, 59.59; H, 11.46.

## 1,2-Bis(diethylmethylsiloxy)-1-butene(Ia)

Ia, IR(neat) 2950, 2870, 1685, 1460, 1250, 1160, 1005, 795, 760 $cm^{-1}$; NMR($CCl_4$) $\delta$ 0.09(s 3H), 0.12(s 3H), 0.63(m 8.2H), 0.92(m 16H), 1.83(q, J=10 Hz, 1.5H), 5.42(s 0.75H); mass spectrum (rel. intensity) 288(41), 259(23), 189(35), 161(46), 101(100), 73(79), 45(26).

Anal. Calcd for $C_{14}H_{32}O_2Si_2$: C, 58.26; H, 11.17. Found: C, 58.27; H, 11.26.


## 1,2-Bis(diethylmethylsiloxy)-4-methyl-1-pentene(IIc)

(IIc), NMR(CCl$_4$) δ 0.08(s 3H), 0.10(s 3H), 0.66(m 8H), 0.93-1.14(m 18H), 1.65-1.74(m 2H), 1.74-2.07(c 1H), 5.48(s 1H); mass spectrum(rel. intensity) 316(31), 287(14), 273(28), 189(31), 161(44), 101(100), 89(38), 73(79), 61(32), 45(31).

Anal. Calcd for $C_{16}H_{36}O_2Si_2$: C, 60.69; H, 11.46. Found: C, 60.43; H, 11.55.


## 3-4 References and Footnotes

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3 When the reaction was carried out using excess aldehyde, 1,2-bissiloxyalkene was not obtained. The products have not been identified yet, but one of them may be α-siloxy aldehyde from IR and mass spectra. This result suggests that in the reaction of olefins described in chapter 1, the key intermediate is not a siloxycarbene complex but an aldehyde.

# Conclusion

The results obtained from the present work may be summarised as follows;
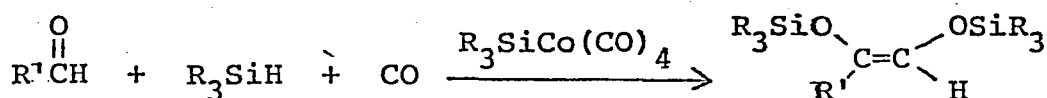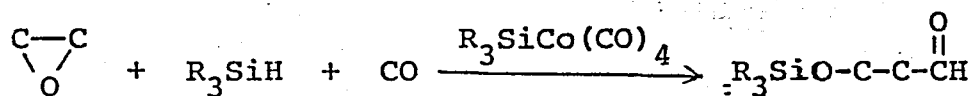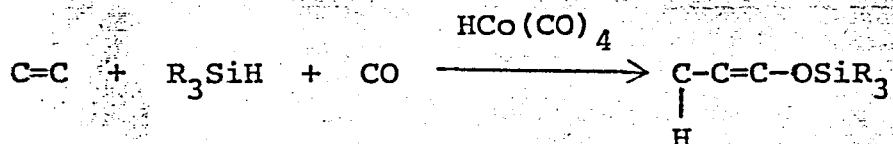
(1) Hydrogenation is related to hydrosilylation in a sence that hydrogen in the former is replaced by a hydrosilane in the latter. However, hydroformylation has no such a counterpart. In the present work, a new catalyzed reaction using hydrosilanes and carbon monoxide related to hydroformylation(oxo reaction) of an olefin has been found.

| H-H | H-Si |
|---|---|
| hydrogenation | hydrosilylation |
| $C=C + H_2 \longrightarrow \underset{\underset{H}{\vert}}{C}-\underset{\underset{H}{\vert}}{C}$ | $C=C + HSi \longrightarrow \underset{\underset{H}{\vert}}{C}-\underset{\underset{Si}{\vert}}{C}$ |
| hydroformylation | present work |
| $C=C + CO + H_2 \longrightarrow \underset{\underset{H}{\vert}}{C}-\underset{\overset{\vert}{\underset{\vert}{C=O}}}{C}$ | $C=C + CO + HSi \longrightarrow \underset{\underset{H}{\vert}}{C}-C=C-OSi$ |

(2) It is suggested that the initial stage of the new reaction is similar to that of hydroformylation(oxo reaction) and the key intermediate is an aldehyde.

(3) The range of the applicability of the new reaction has been extended to cyclic ethers and aldehydes, cyclic ethers give siloxyaldehydes and aldehydes yield bis-siloxyolefins. These reactions were a series of new catalyzed ones using hydrosilanes and carbon monoxide. In the case of olefins, $HCo(CO)_4$ may be the active catalyst, while in the cases of cyclic ethers and aldehydes, $R_3SiCo(CO)_4$ may play an important

role as the active catalyst. Interestingly, either of $HCo(CO)_4$ or $R_3SiCo(CO)_4$ formed by the reaction of $R_3SiH$ with $Co_2(CO)_8$ becomes the active catalyst according to the nature of the substrates.

$$C=C \ + \ R_3SiH \ + \ CO \ \xrightarrow{HCo(CO)_4} \ \underset{\underset{H}{|}}{C}-C=C-OSiR_3$$

$$\underset{\underset{O}{\diagup\diagdown}}{C-C} \ + \ R_3SiH \ + \ CO \ \xrightarrow{R_3SiCo(CO)_4} \ R_3SiO-C-\overset{\overset{O}{\|}}{C}-CH$$

$$R^1\overset{\overset{O}{\|}}{C}H \ + \ R_3SiH \ + \ CO \ \xrightarrow{R_3SiCo(CO)_4} \ \underset{R'}{\overset{R_3SiO}{>}}C=C\underset{H}{\overset{OSiR_3}{<}}$$

These products (siloxyalkenes, siloxyaldehydes, and 1,2-bissiloxyalkenes) are important intermediate of organic syntheses. It is to be hoped that a series of new catalyzed reactions comparable with hydroformylation (oxo reaction) will be established on the occasion when the scope and limitation of the new catalyzed reactions using hydrosilanes and carbon monoxide are completely revealed.