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**STUDIES ON THE COBALT-CATALYZED REACTION WITH
CARBON MONOXIDE AND HYDROSILANE**

〔一酸化炭素とヒドロシランを用いる〕
コバルト触媒反応に関する研究

NAOTO CHATANI

Preface

The studies presented in this thesis have been carried out under the direction of Professor Noboru Sonoda at the Department of Petroleum Chemistry, Faculty of Engineering, Osaka University. The thesis is concerned with the cobalt-catalyzed reaction with carbon monoxide and hydrosilane.

The author expresses his deep gratitude to Professor Noboru Sonoda for his kind guidance, helpful suggestions and hearty encouragement during this work. The author is also sincerely grateful to Associate Professor Shinji Murai for his useful suggestions and stimulating discussions. The author acknowledges the continuing encouragement of Dr. Noritaka Miyoshi, Dr. Ilhyong Ryu, Dr. Yoshio Seki, and Dr. Nobuaki Kambe.

Furthermore the author wishes to thank Mr. Toshikazu Kato, Mr. Hidenori Furukawa, Mr. Satoru Fujii, and Mr. Yasuhiro Yamasaki for their collaborations. His gratitude is expended to all the members of the research group of Professor Noboru Sonoda for their occasional discussions, helpful assistances, and profound interests.

Finally the author would like to express his thanks to his parents for their perpetual support.

Suita, Osaka

January 1984

Naoto Chatani

List of Publications

The contents of this thesis are composed of the following papers.

- 1 Conversion of Alkyl Acetates to (Siloxymethylene)alkanes by $\text{Co}_2(\text{CO})_8$ -Catalyzed Reaction with a Hydrosilane and Carbon Monoxide
Chatani, N.; Murai, S.; Sonoda, N.
J. Am. Chem. Soc. 1983, 105, 1370.
- 2 A New Entry to π -Allylcobalt Tricarbonyls Using $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$
Chatani, N.; Yamasaki, Y.; Murai, S.; Sonoda, N.
Tetrahedron Lett. 1983, 24, 5649.
- 3 Catalytic Incorporation of Carbon Monoxide into a Ketonic Carbon.
Conversion of Cyclobutanones to Disiloxycyclopentenones with Hydrosilane and Carbon Monoxide in the Presence of Cobalt Carbonyl
Chatani, N.; Furukawa, H.; Kato, T.; Murai, S.; Sonoda, N.
J. Am. Chem. Soc. 1984, 106, xxxx.
- 4 Cobalt Carbonyl-Catalyzed Reaction of Esters and Lactones with Hydrosilane and Carbon Monoxide. A Novel Synthetic Method for Introduction of Siloxymethylidene Group
Chatani, N.; Fujii, S.; Yamasaki, Y.; Murai, S.; Sonoda, N.
to be submitted for publication.

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General Introduction

Carbonylation reactions with the aid of various transition metal complexes have been the subject of numerous studies.^{1,2} Much attention has been focused on carbonylation reactions of olefins (e.g., hydroformylation and the related carbonylation reactions)³ because of their importance in organic synthesis and in industry. In contrast, carbonylation reactions of oxygen containing compounds, apart from synthesis of acetic acid from methanol and homologation of methanol to ethanol,² have received little attention. Carbonylation reactions of oxygen containing compounds have been known to proceed generally with low conversion, low yield, and low selectivity because of low efficiency of the known catalyst systems for the formation of a carbon-transition metal bond, which is required for incorporation of carbon monoxide. In addition, further reactions of initially formed products take place frequently.

The prime objective of the present research was to develop new catalytic carbonylation reactions of oxygen containing compounds with the aid of transition metal complexes through the examination of a new method for formation of carbon-transition metal bond.

This thesis consists of three chapters. Chapter 1 deals with cobalt carbonyl-catalyzed reaction of esters and lactones with carbon monoxide and hydrosilane. Novel synthetic methods for introduction of siloxymethylidene, 1,2-disiloxyvinyl, and siloxymethyl groups will be described. Chapter 2 deals with cobalt

carbonyl-catalyzed reaction of ketones with carbon monoxide and hydrosilane. The new method for construction of five-membered rings via ring expansion will be described. In chapter 3, a new entry to π -allylcobalt tricarbonyls using $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ will be described.

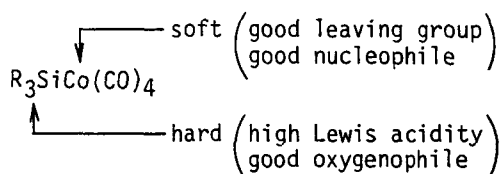
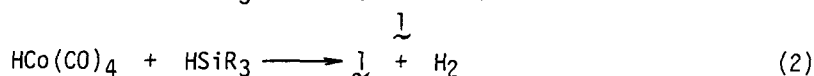
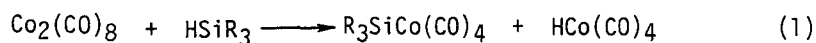
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- (2) Falbe, J. "New Syntheses with Carbon Monoxide"; Springer-Verlag: New York, 1980.
- (3) Pruett, R. L. Adv. Organomet. Chem. 1979, 17, 1. Siegel, H.; Himmele, W. Angew. Chem., Int. Ed. Engl. 1980, 19, 178.

Chapter 1 Cobalt Carbonyl-Catalyzed Reaction of Esters and Lactones with Carbon Monoxide and Hydrosilane

1-1 Introduction

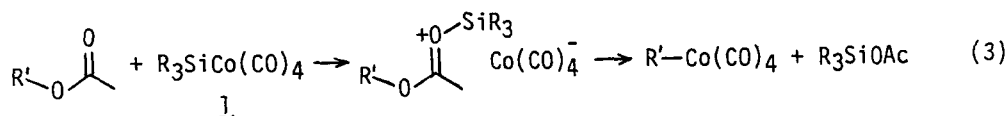
Silylcobalt tetracarbonyl, $R_3SiCo(CO)_4$ (1), is formed by the well established process of reactions 1 and 2, which have been found by Chalk, Harrod, and MacDiarmid.¹ Silylcobalt complex 1



is the combination of hard acid (oxygenophile)-soft base (nucleophile) so that high reactivity of 1 with oxygen containing compounds was expected. Much attention has been focused on the reactions of R_3SiX (X =halogen, CN , N_2 , SR , SeR , etc) with oxygen containing compounds on the basis of the hard-soft principle.² Furthermore, Gladysz has recently developed new efficient methods for the formation of carbon-manganese bonds by using the stoichiometric reaction of $Me_3SiMn(CO)_5$ with oxygen containing compounds.³

To test the applicability and the effectiveness of the methodology described above, the reaction of alkyl acetates with

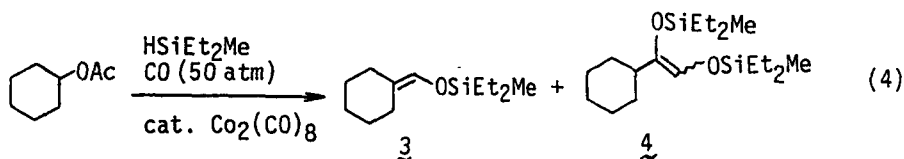
carbon monoxide and hydrosilane in the presence of $\text{Co}_2(\text{CO})_8$ have been studied. The analysis based on the above mentioned concepts suggested that activation of an acetoxy group into a better leaving group as shown in eq 3 was highly plausible to occur in a catalytic



process. As a consequence, development of a new entry to an alkylcobalt tetracarbonyl (eq 3) leading to a new catalytic reaction was expected. Moreover, alkyl acetates are one of the most easily available classes of oxygen containing compounds so that incorporation of carbon monoxide into them would lead to a new useful synthetic method.⁴

1-2 The Reaction of Cyclohexyl Acetate with Carbon Monoxide and Hydrosilane

Cyclohexyl acetate (2) was found to react with HSiEt_2Me and carbon monoxide in the presence of a catalytic amount of $\text{Co}_2(\text{CO})_8$ to give siloxymethylidenecyclohexane (3) and a byproduct, disiloxyvinylcyclohexane (4) (eq 4). In addition, R_3SiOAc was found as an another byproduct. Since the reaction to give 3 and 4



required two and three equivalent of hydrosilane, respectively, the reactant molar ratio of 3:1 with a hydrosilane to an alkyl acetate was generally employed in the experiments.

Selected results obtained for the catalytic reaction of **2** using HSiEt_2Me as a hydrosilane are shown in Table I. The best result with respects to the yield of **3** and ratio of **3**:**4** was obtained in the reaction run under 50 atm of carbon monoxide and at 200°C in benzene (or toluene) using $\text{Co}_2(\text{CO})_8$ as the catalyst (or the catalyst precursor) (runs 8 and 9). The reaction did not take place at below 100°C and increase in the reaction temperature resulted in increase in the yield of and the selectivity to **3** (runs 1,2,7, and 8). Some cobalt complexes, such as $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$ (run 5) and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (run 11), were also effective as the catalyst but less efficient than $\text{Co}_2(\text{CO})_8$ or $\text{Me}_3\text{SiCo}(\text{CO})_4$ ¹ (run 10). Under the conditions equivalent to run 2 or 8, various transition metal complexes, selected mainly from those known to be effective for carbonylation⁵ and/or hydrosilylation,⁶ were examined on their ability to catalyze the reaction 4. All of the complexes examined, however, showed little or no catalytic activity: these complexes were $\text{Fe}(\text{CO})_5$,^{7,8} $\text{Fe}(\text{CO})_5/\text{N-methylpiperidine}$,⁷ $[\text{CpFe}(\text{CO})_2]_2$,⁷ (cyclobutadiene) $\text{Fe}(\text{CO})_3$,⁷ FeCl_3 ,⁸ $\text{Ru}_3(\text{CO})_{12}$,^{7,8} $\text{RhCl}(\text{PPh}_3)_3$,⁷ $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$,⁷ [(norbornadiene) $\text{RhCl}]_2$,⁷ $[\text{RhCl}(\text{CO})_2]_2$,^{7,8} $\text{Rh}_2(\text{OAc})_4$,⁷ $\text{Rh}_6(\text{CO})_{16}$,^{7,8} $\text{PtCl}_2(\text{PPh}_3)_2$,⁷ $\text{NiCl}_2/\text{Et}_2\text{S}$,⁸ $\text{IrCl}(\text{CO})(\text{PPh}_3)$,^{7,8} PdCl_2 .^{7,8} The effective range of catalysts for this particular reaction 4 seems to be limited to those

Table I. The Catalytic Reaction of Cyclohexyl Acetate (2)
with CO and HSiEt₂Me^a

run	catalyst /additive	solvent, temp (°C)	yield (%) ^b	
			<u>3</u>	<u>4</u>
1	Co ₂ (CO) ₈	C ₆ H ₆ , 100	5	9
2	Co ₂ (CO) ₈	C ₆ H ₆ , 140	56	21
3	Co ₂ (CO) ₈ /pyridine ^c	C ₆ H ₆ , 140	58	12
4	Co ₂ (CO) ₈ /PPh ₃ ^d	C ₆ H ₆ , 140	12	0
5	Co ₂ (CO) ₆ (PPh ₃) ₂	C ₆ H ₆ , 140	28	3
6	Co ₂ (CO) ₈	CH ₂ Cl ₂ , 140	54	2
7	Co ₂ (CO) ₈	C ₆ H ₆ , 180	68	4
8	Co ₂ (CO) ₈	C ₆ H ₆ , 200	75	3
9	Co ₂ (CO) ₈	PhCH ₃ , 200	79	e
10	Me ₃ SiCo(CO) ₄	C ₆ H ₆ , 200	70	e
11	Co(OAc) ₂ ·4 H ₂ O	C ₆ H ₆ , 200	66	e

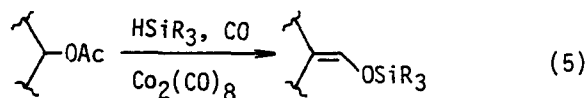
^a Reaction conditions: 2(10 mmol), HSiEt₂Me(30 mmol), CO (50 atm, initial pressure at 25°C), catalyst(0.4 mmol), solvent (20 mL) unless otherwise noted. Reaction time was 20 h for runs 1-6 and 6 h for runs 7-11. ^b GLC yield based on 2. ^c Pyridine(2 mmol) was added. ^d PPh₃(1 mmol) was added. ^e Not determined, but <5%. ^f The amount of HSiEt₂Me was 40 mmol.

containing cobalt (Table I). However, a cluster complex, $\text{C}_6\text{H}_5\text{CCo}_3(\text{CO})_9$,⁹ was not effective in the present reaction.

As a hydrosilane, HSiEt_2Me was used throughout the present work because of the ease in handling with a hypodimeric syringe due to its appropriate boiling point (bp 78°C) and advantage in NMR assignment of products due to their methyl singlets. Other trialkylhydrosilanes gave similar results in the reaction 4, i.e., 82, 72, and 58% yields of **3** were obtained from HSiMe_3 , HSiEt_3 , and HSiPh_2Me , respectively, under the conditions of run 8 in Table I.¹⁰ However, the catalytic reaction of **2** using H_2SiPh_2 gave a complex mixture (not identified). In the case of $\text{HSiMe}(\text{OEt})_2$, no reaction proceeded.

Alkyl esters such as cyclohexyl formate, benzoate, and pivalate can also be used in place of the acetate **2**. The relative reactivities of these esters were measured quantitatively. The half life times of cyclohexyl acetate, formate, benzoate, and pivalate under the conditions used for run 8 in Table I were 1.2, 1.2, 2.1. and 4.5 h, respectively. From the viewpoints of reactivity and availability, alkyl acetates are the satisfactory substrates especially for the synthetic purpose.

The transformation of an ester given in eq 5 finds no precedent. Carbon monoxide has been cleanly incorporated into the



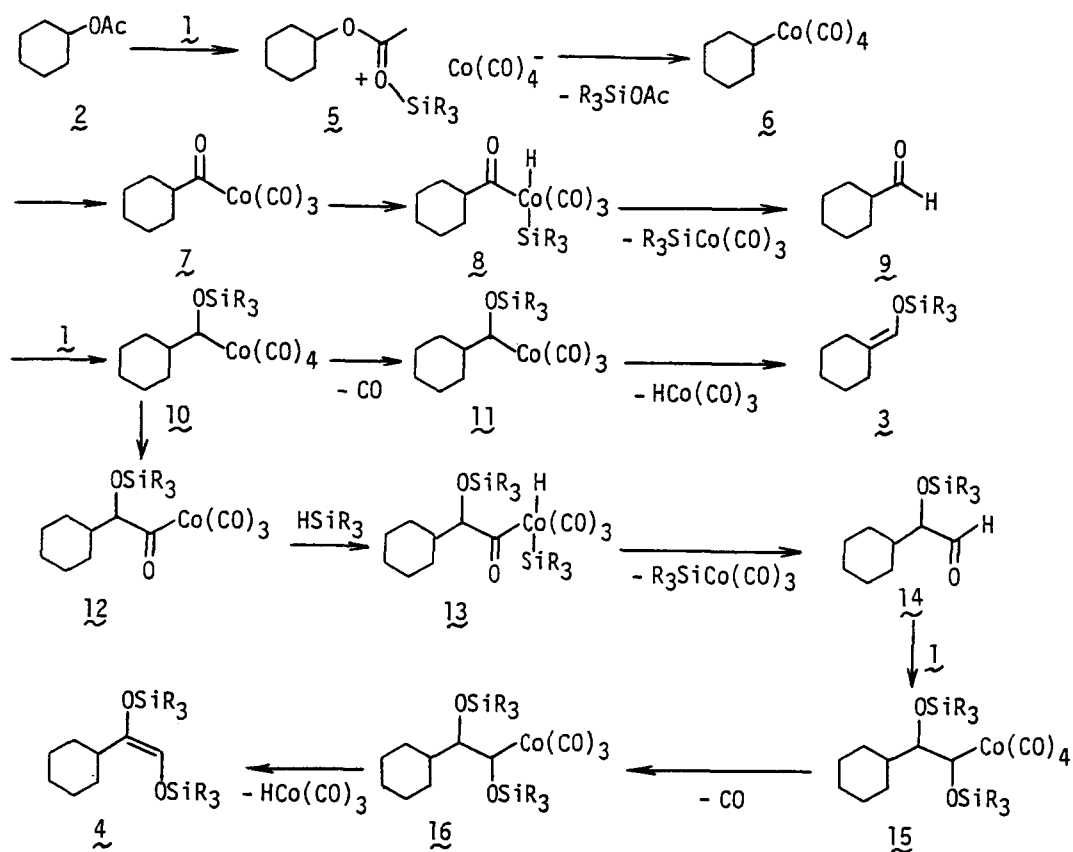
carbon atom bearing the acetoxy group as a part of the siloxy-methylidene group. New carbon-carbon bond has been formed as the result of carbon-oxygen bond cleavage.

1-3 Mechanism

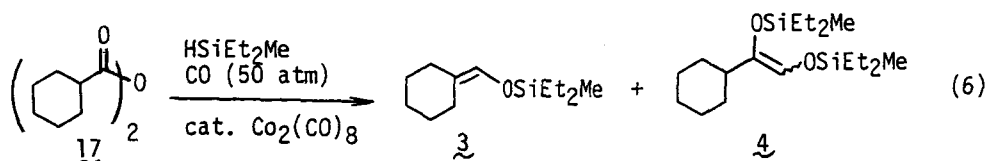
Although the mechanism of the cobalt carbonyl-catalyzed reaction of cyclohexyl acetate with carbon monoxide and hydrosilane (eq 4) is not fully understood yet, reasonable speculations can be made on the basis of the knowledges about the accepted mechanisms of cobalt-catalyzed carbonylation,⁵ olefin hydrosilylation,⁶ and the reaction of olefins with hydrosilane and carbon monoxide,¹¹ the latter being reinforced by the elegant studies by Gladysz on the stoichiometric reactions of $\text{Me}_3\text{SiMn}(\text{CO})_5$ with various oxygen containing compounds.³ As expected (eq 3), the key catalyst species in the present reaction (eq 4) would be a silylcobalt carbonyl 1, which would be generated in the catalytic cycle by reactions 1 and 2. The proposed mechanism for reaction 4 is depicted in Scheme I. The catalytic cycle would begin with the interaction of 1 with the substrate 2 to form an oxonium ion 5 followed by the nucleophilic displacement of the activated acetoxy group by $\text{Co}(\text{CO})_4^-$ to give an alkylcobalt complex 6. These processes illustrate a new entry to alkylcobalt carbonyls. It is interesting to note that the reaction of alkyl carboxylates with Me_3SiI , a reagent analogous to 1 with respect to hard acid (or oxygenophile)-soft base combination, is known to give alkyl iodides.¹² Alkyl

migration would convert 6 to an acyl complex 7 and oxidative addition of HSiR_3 leading to 8 and subsequent reductive elimination from 8 would afford an aldehyde 9 as an intermediate. The aldehyde 9 would react again with 1 to give 10 and finally afford the enol silyl ether 3 by β -hydride elimination from 11. Another product

Scheme I. Mechanism

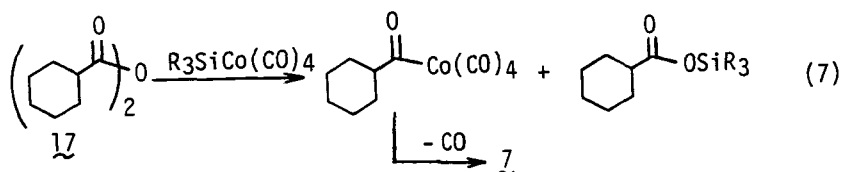


4 could arise from 10 via alkyl migration leading to 12 and successive steps shown in Scheme I. That the higher reaction temperature favored the selective formation of 3 (see runs 2, 7 and 8 in Table I) would imply that the process from 10 involving β -hydride elimination leading 3 would become relatively faster than alkyl migration in 10 to form 12 at the higher temperature. Although intermediacy of the aldehydes 9 and 14 has not been substantiated experimentally,¹³ they are suggested as the key intermediate in present reaction since the cobalt-catalyzed reaction of 9 with HSiEt_2Me and carbon monoxide has been already shown to afford 14 or 4 in addition to 3.¹⁴ Moreover, Gladysz has recently reported the reaction of aldehydes with $\text{Me}_3\text{SiMn}(\text{CO})_5$ to give acyl complexes analogous to 12.^{3c} As a control experiment, a different entry to the acyl complex 7 was studied. The reaction of cyclohexanecarboxylic acid anhydride (17) with HSiEt_2Me and carbon monoxide in the presence of $\text{Co}_2(\text{CO})_8$ under the same conditions used for runs 2 and 8 in Table I gave the results shown in eq 6 which were similar to those obtained from cyclohexyl



acetate (2) shown in Table I. A common intermediate 7 might have been formed also in the catalytic reaction of the anhydride 17 as

depicted in eq 7.



1-4 The Reaction of Secondary Alkyl Esters with Carbon Monoxide and Hydrosilane— A Novel Synthetic Method of Enol Silyl Ethers —

In the case of secondary alkyl acetates, cobalt carbonyl-catalyzed reaction proceeded in highly selective manner as has been shown for cyclohexyl acetate (Table I). The reaction provides a unique synthetic transformation, i.e., introduction of siloxymethylidene group into the carbon atom bearing an acetoxy group (eq 5). The reactions with primary and tertiary alkyl esters proceeded in somewhat different ways as will be described later. The results obtained for various secondary alkyl acetates are given in Table II. It should be emphasized that enol silyl ethers are known as extremely versatile synthetic intermediates.¹⁵ Among the various possible transformations envisaged, the desilylation of the enol silyl ethers was studied. As also shown below, desilylation of the enol silyl ethers with $\text{KF}/\text{CH}_3\text{OH}$ at 25°C

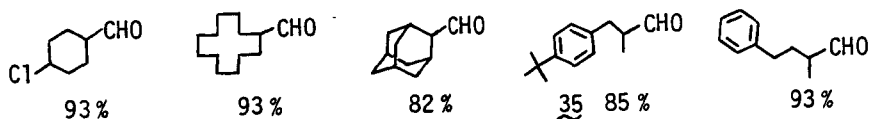
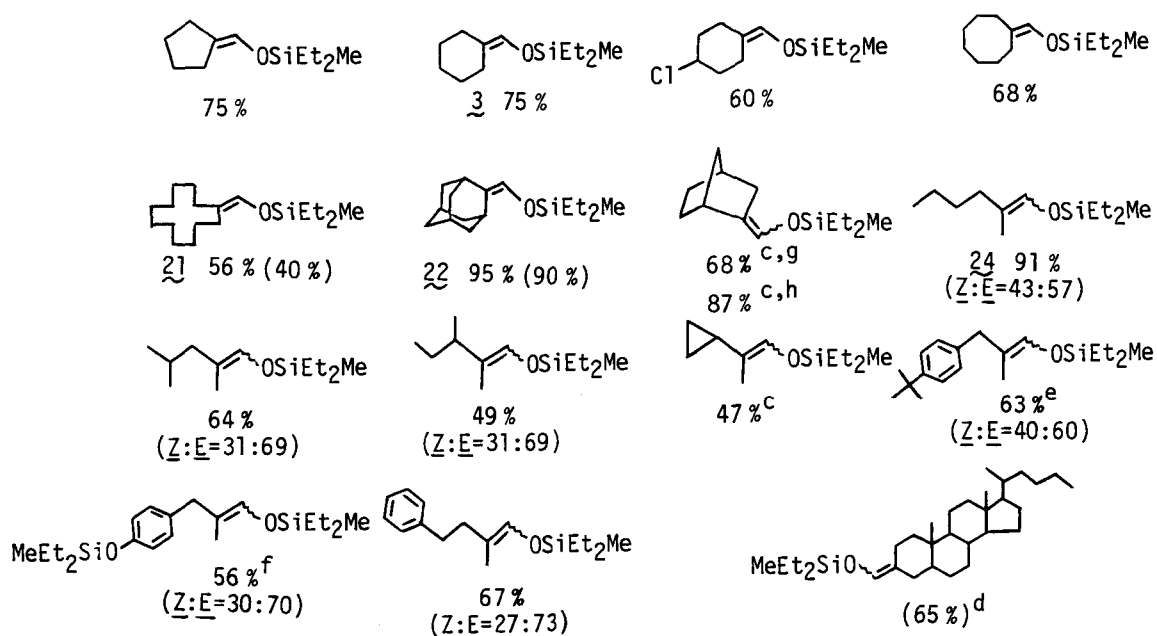
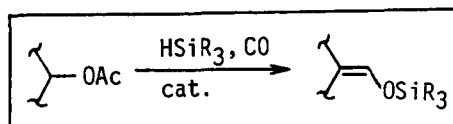
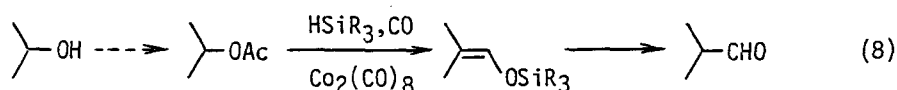


Table II. Synthesis of Enol Silyl Ethers by the Cobalt Carbonyl-Catalyzed Reaction of Secondary Alkyl Acetates^{a,b}



^a Reaction conditions: an acetate (10 mmol), HSiEt₂Me (30 mmol), CO (50 atm) CO₂(CO)₈ (0.4 mmol), C₆H₆ (20 mL), 200°C, 6 h unless otherwise noted. ^b Glc yields based on the acetates. Isolated yields are in parentheses. Ratio of Z:E was determined by Glc. ^c Ratio of Z:E could not be determined. ^d Yield are of isolated product purified by column chromatography (SiO₂). ^e HSiEt₂Me (50 mmol) and Co₂(CO)₈ (0.8 mmol) were used. ^f HSiEt₂Me (70 mmol) and Co₂(CO)₈ (0.8 mmol) were used. ^g From exo-acetate. ^h From endo-acetate.

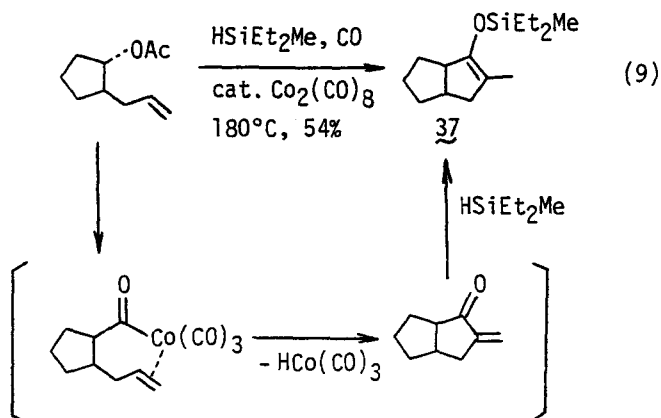
gave the corresponding aldehydes including Liliar¹⁶ (35) in quantitative yields. The overall transformation is formally the displacement of the acetoxy group with the formyl group and



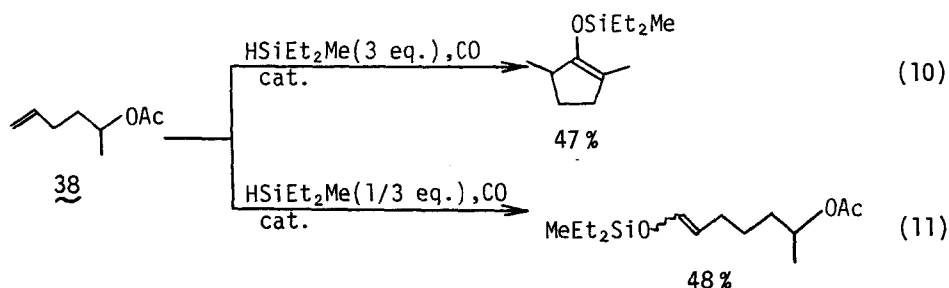
is important in relation to the current interests on homologation techniques.¹⁹ The desilylation to aldehydes is known to take place under both basic and acidic conditions. Indeed, the enol silyl ether 3 reacted with NaBH₄ in ethanol (25°C, 3 h) to give cyclohexanemethanol in 70% yield.

The principal byproducts in the catalytic reaction of secondary alkyl acetates were olefins obtained by formal elimination of acetic acid. For example, cyclododecene was formed from cyclododecyl acetate in 40% yield in addition to the desired enol silyl ether 21. The higher yield of 22 may be attributed to the difficulty of β-hydride elimination from the initially formed 2-adamantylcobalt tetracarbonyl similar to 6.

With an alkyl acetate having an olefinic function in the suitable position, intramolecular interception of an acylcobalt carbonyl intermediate by the olefin was expected to take place.²⁰ The cobalt-catalyzed reaction of trans-2-allylcyclopentanol acetate with HSiEt₂Me (3 equiv) and carbon monoxide (50 atm, 180°C, 20 h in C₆H₆) gave a bicyclic compound 37 in 54% yield (eq 9). The acylcobalt complex in eq 9 would be formed through SN 2 type



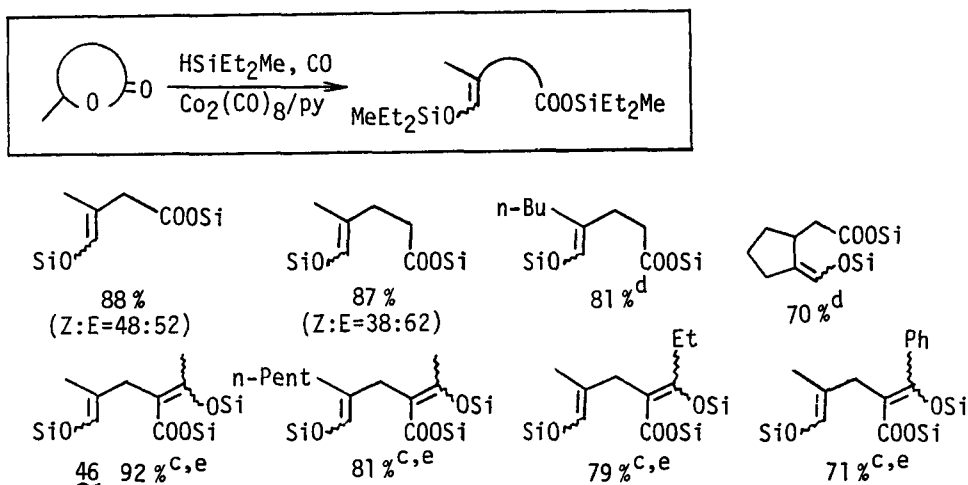
displacement of the activated acetoxy group with Co(CO)_4^- followed by successive migratory insertion of carbon monoxide. Since the same type of starting materials to that used in eq 9 can be readily prepared by the reaction of allyl anions with epoxides,²¹ the catalytic reaction suggests a new possibility in the preparation of five-membered ring compounds. Similarly 5-acetoxy-1-hexene (38) gave a cyclized product (eq 10). Interestingly, the reaction course can be controlled by changing the molar ratio of 38 to the hydrosilane. The use of an excess of 38, in turn, gave a product in which carbon monoxide was incorporated into only the olefinic



part of the starting olefinic acetate 38 (eq 11).

Similarly to the secondary alkyl acetates, lactones of the secondary alkyl ester-type underwent incorporation of carbon monoxide to give enol silyl ethers. The results obtained for the reactions using lactone (10 mmol), HSiEt_2Me (30 mmol), CO (50 atm), $\text{Co}_2(\text{CO})_8$ /pyridine (0.4 mmol/2 mmol), benzene (20 mL), at 140°C for 6 h are given in Table III. In these cases, the leaving groups

Table III. Synthesis of Enol Silyl Ethers from Lactones by the Cobalt Carbonyl-Catalyzed Reaction^{a,b}



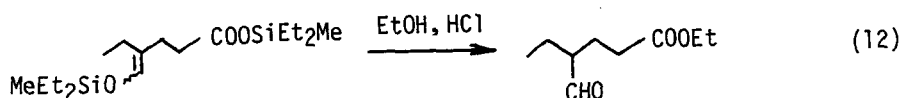
^a Reaction conditions: a lactone (10 mmol), HSiEt_2Me (30 mmol), CO (50 atm), $\text{Co}_2(\text{CO})_8$ (0.4 mmol), pyridine (2 mmol), C_6H_6 (20 mL), 140°C , 6 h.

^b Glc yields based on the lactones. Ratio of Z:E was determined by Glc.

^c Run at 110°C with HSiEt_2Me (50 mmol). ^d Ratio of Z:E could not be determined.

^e For ratio of stereoisomers, see experimental.

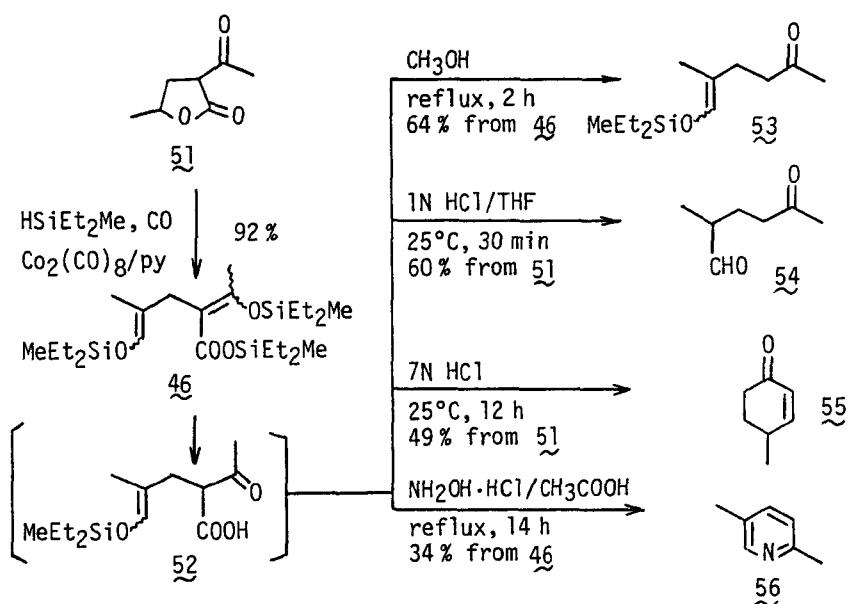
in the carbon-oxygen bond cleavage remained in the product as the silyl ester moieties. The introduced siloxymethylidene group can desilylated to give aldehyde as example being shown below. A new



method for the introduction of carbon-containing functional group to a five-membered ring is illustrated. The lactones having 2-acetyl, 2-propionyl, or 2-benzoyl group offer unique possibilities in organic synthesis. In the catalytic reaction of these lactones the siloxymethylidene group was introduced and at the same time the acyl groups at the 2-position of the lactones were protected in the form of enol silyl ether. As summarized in Scheme II, the controlled desilylation (CH_3OH) of the trisilylated compound 46 effected the removal of the silyl group of the protected ketone and that of the silyl ester while the silyl moiety of the siloxymethylidene group remained intact. Thus obtained β -keto acid 52 underwent spontaneous decarboxylation²² to give 5-siloxymethylidene-2-hexanone (53). On the other hand, the complete desilylation (1N HCl/THF) afforded 5-keto aldehyde 54. Such a 1,5-keto aldehyde as 54 has been known as the useful intermediate for the synthesis of cyclohexenones²³ or pyridines.²⁴ The reactions leading to cyclohexenone 55 and pyridine 56 via the 1,5-keto aldehyde 54 generated in situ (Scheme II) illustrates further the synthetic potential of the products derived from

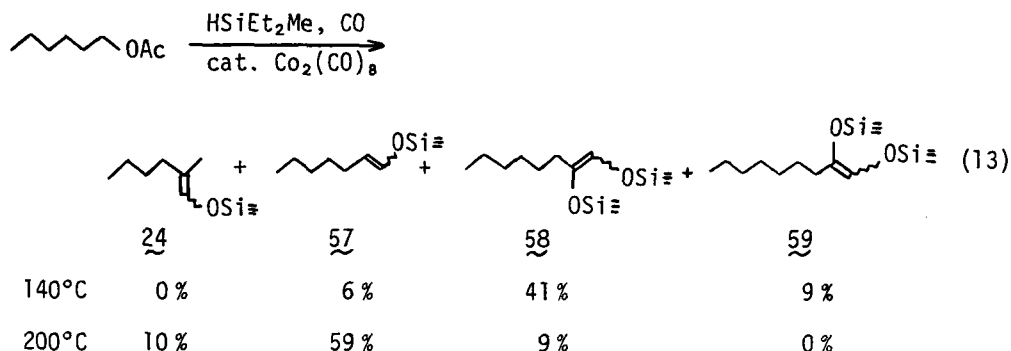
2-acyl- γ -lactones.

Scheme II. Synthetic Application by Desilylation of Trisilylated Product 46

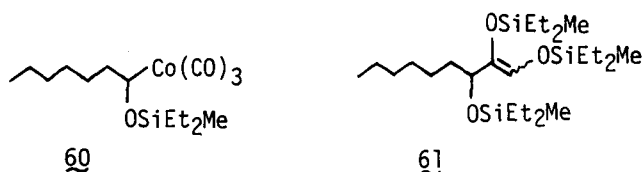


1-5 The Reaction of Primary Alkyl Esters with Carbon Monoxide and Hydrosilane

n-Hexyl acetate, a primary alkyl acetate, reacted with carbon monoxide and HSiEt_2Me in the presence of a catalytic amount of $\text{Co}_2(\text{CO})_8$ to give several products into which one, two, and even three molecules of carbon monoxide were incorporated (eq 13). Under the standard conditions (i.e., 200°C , 50 atm) the expected product 57 became a major one but considerable amounts of



by products 24 and 58 were formed. The formation of branched chain isomer 24 might imply the isomerization of primary alkylcobalt intermediate to the secondary one.²⁵ The product distribution of the reaction at the lower temperature (140°C) may be compared to that observed for cyclohexyl acetate in which incorporation of one molecule of carbon monoxide predominated even at 140°C (Table I). The predominant formation of the product 58 with incorporation of two molecules of carbon monoxide at 140°C can be attributed to the slower β -hydride elimination from 60 in which the β -hydrogen is a

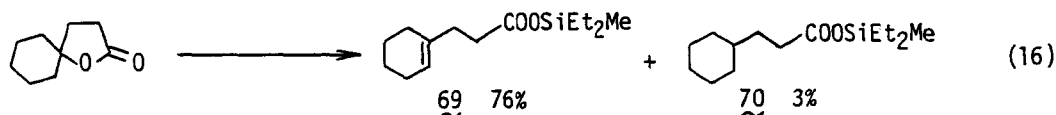
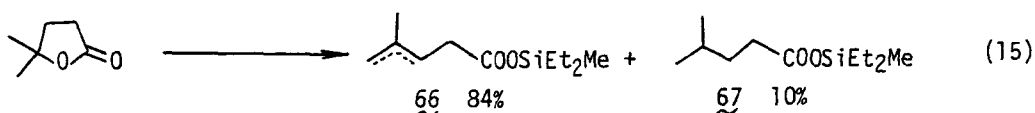
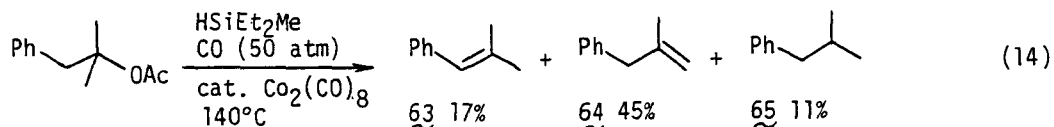


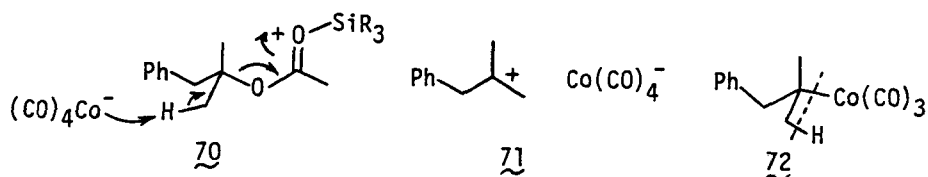
methylene type than that from 10 having β -hydrogen of methine type. Incorporation of three molecules of carbon monoxide indicated by the formation of 59 is remarkable. The catalyzed reduction of the allylic siloxy group in the presumed intermediate 61 with HSiEt_2Me could lead to 59. The formation of 59 indicates

a possibility and also limitation in realizing the proposal of co-polymerization of carbon monoxide and a hydrosilane.¹¹ The catalytic reaction of unsubstituted γ -butyrolactone, a lactone of the primary alkyl ester-type, proceeded in a similar way as n-hexyl acetate to give several products (by GLC) and no effort was made to characterize these products.

1-6 The Reaction of Tertiary Alkyl Esters with Carbon Monoxide and Hydrosilane

Carbon monoxide was not incorporated in the case of tertiary alkyl esters as shown in eq 14-16. Such results are not unexpected since only a few examples have been known of the incorporation of carbon monoxide into a tertiary carbon center with the aid of transition metals.²⁶ Many possibilities may be envisaged for the mechanism of the process leading to olefins from a tertiary alkyl





acetate: i.e., $\text{E}2$ process via 70, $\text{S}_\text{N}1$ process via 71, or β -hydride elimination via 72. Although the exact mechanism is not clear, the product distribution in reaction 14 is not likely to be controlled by a typical carbonium ion intermediate 71 since the yield of the 1-olefin 64 was higher than that of thermodynamically stable 2-olefin 63.²⁷ It seemed interesting to study the catalytic reaction of a tertiary alkyl acetate which could not easily undergo formal elimination of acetic acid to give an olefin according to Bredt's rule.²⁸ The results obtained for some bridgehead acetates²⁹ are given in Table IV. The observed incorporation of carbon monoxide represents the first efficient example of the transition metal-catalyzed incorporation of carbon monoxide into a tertiary carbon center.²⁶ The difficulty in β -hydride elimination process from 79³³ would be the key to the present success. The predominant formation of the product 74 (corresponding to 4 in Scheme I) with incorporation of two

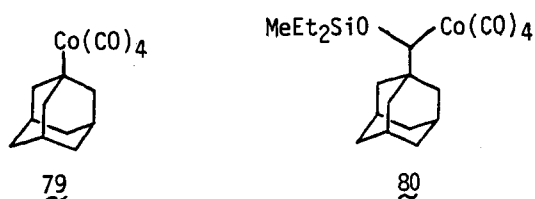
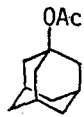
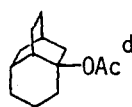


Table IV. Catalytic Reaction of Bridgehead Acetates with CO and HSiEt₂Me^a

substrate ROAc	product			
	R-OSiEt ₂ Me		R-  -OSiEt ₂ Me ^b	
	<u>73</u>	4 %	<u>74</u>	82 %
 ^d	<u>75</u>	17 %	<u>76</u>	78 %
 ^d	<u>77</u>	19 %	<u>78</u>	63 %

^a Reaction conditions: substrate (2.5 mmol), HSiEt₂Me (12.5 mmol), CO (50 atm), Co₂(CO)₈ (0.1 mmol), C₆H₆ (5 mL), 140°C, 6 h unless otherwise noted. ^b Glc yields based on substrate. Z-isomer only.

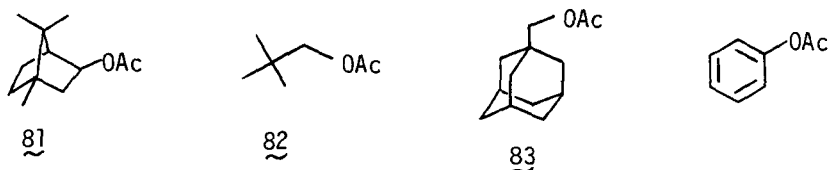
^d Pyridine (1 mmol) was added.

molecule of carbon monoxide may be attributed to unavailability of β-hydrogen atom in 80 (compare with 10 in Scheme I). That the reaction of 1-adamantyl acetate may involve the trapping of 1-adamantyl cation with Co(CO)₄⁻ to give 79 and may not involve Koch type carbonylation will be discussed in the next section (see chapter 1-8-1). It may be worth mentioning that extensive studies have been carried out for the development of preparative methods for various heterocyclic compounds containing

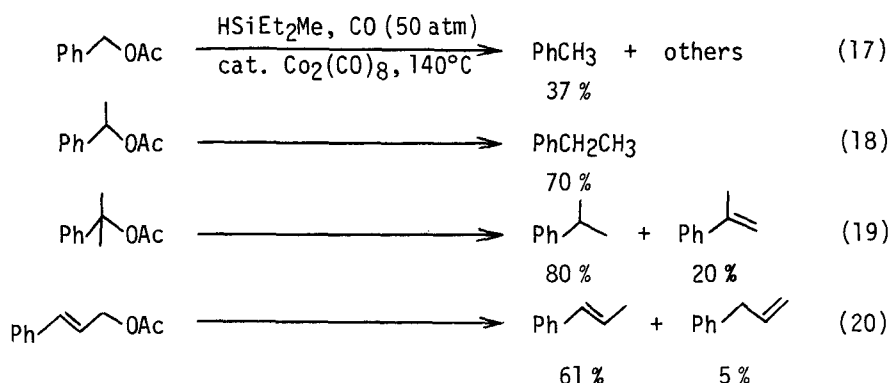
adamantyl substituents because of their promising properties of pharmaceutical importance.³⁰ The present reaction (Table IV) has open a new possibility in this field since the product 74 contains 1,2-disiloxyalkene moiety which have been known as an extremely useful synthon for the preparation of various hetroecycles.³¹

1-7 Limitation of Catalytic Incorporation of Carbon Monoxide.

The catalytic reaction of secondary alkyl acetates and lactones of secondary alkyl ester-type proceeded in highly selective manner. While norbornyl acetates reacted smoothly (see Table II), the reaction of bornyl acetate (81) proceeded only sluggishly to give several products in low yields (not identified). Neopentyl acetate (82) and 1-adamantanemethanol acetate (83) did not give



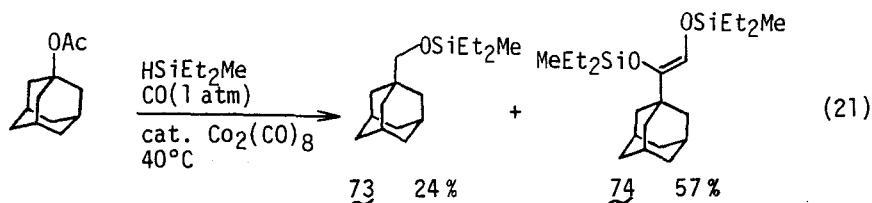
detectable amounts of products. These results indicate that the present catalytic reaction is somewhat sensitive to steric congestion at the reaction site. Neither did react phenyl acetate, an sp^2 -acetate. Benzyl or allylic acetates suffered from reduction in which probably $HSiEt_2Me$,³² or less likely $HCo(CO)_4$, would be the source of the hydrogen (eq 17-20).



1-8 The Catalytic Reaction with Carbon Monoxide and Hydrosilane under Atmospheric Pressure of Carbon Monoxide

1-8-1 The Catalytic Reaction of 1-Adamantyl Acetate

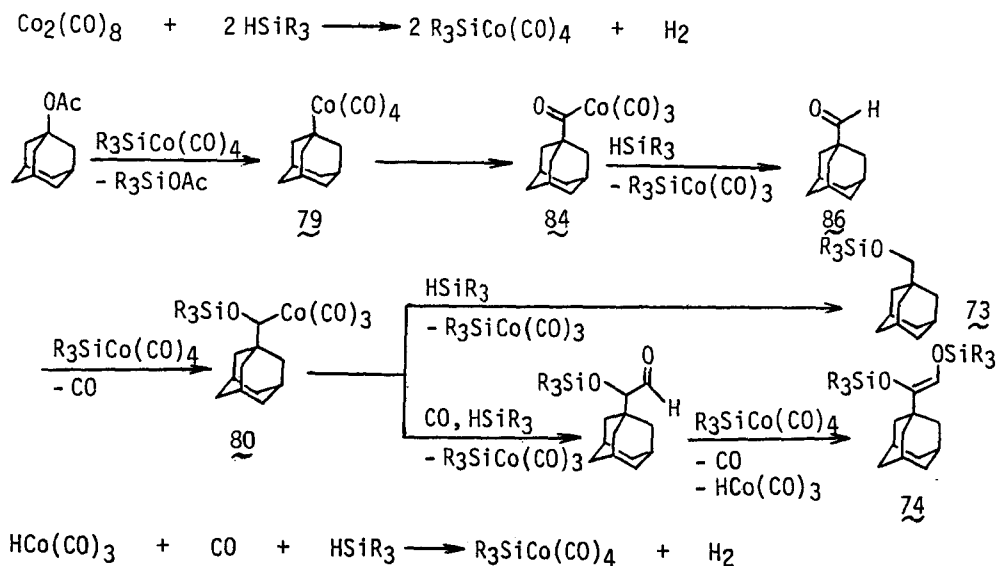
Catalytic reactions using carbon monoxide and hydrosilane described above required high reaction temperature ($>140^\circ\text{C}$) and high pressure (50 atm) of carbon monoxide. However, it is expected that incorporation of carbon monoxide proceeds even under milder reaction conditions (at room temperature and under atmospheric pressure of carbon monoxide) in the case of highly reactive alkyl acetates. Consequently, 1-adamantyl acetate was selected because of known high reactivity^{30a} and the expectation of incorporation of carbon monoxide (see chapter 1-6). The catalytic reaction of 1-adamantyl acetate under 1 atm of carbon monoxide at 40°C gave



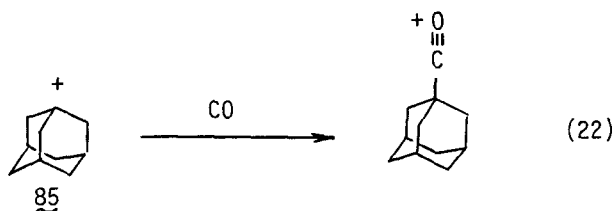
73 and 74 in 24% and 57% yield, respectively (eq 21). The results indicates that incorporation of carbon monoxide into a tertiary carbon center does take place.

Based on the mechanism described in chapter 1-3, the course of the reaction was suggested as shown in Scheme III. The initial interaction of the substrate with the catalyst species $R_3SiCo(CO)_4$ (1) would afford a tertiary alkylcobalt complex 79³³ and then an acyl complex 84. The known high reactivity of adamantane derivatives to afford an adamantyl cation (85) seems to be responsible for the ease of the present reaction. Hydrosilylation and siloxymethylidenation of the intermediary formed aldehyde 86 would give the observed products 73 and 74, respectively.

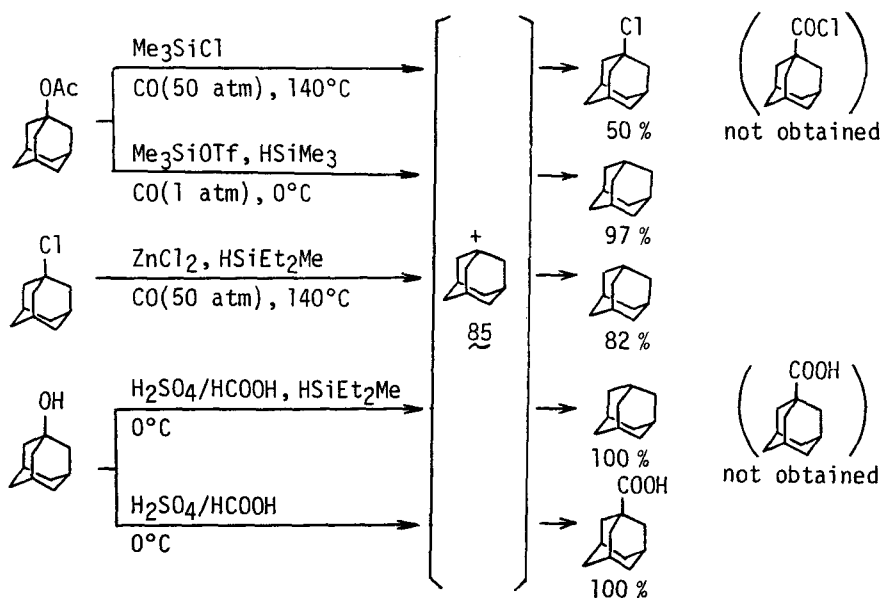
Scheme III.



An alternative pathway for the carbonylation process may be that involving Koch type carbonylation³⁴ of the cation 85 with uncoordinated carbon monoxide (eq 22). The results of the control experiments shown in Scheme IV may speak against the Koch type possibility in the reaction 21. All these reactions (Scheme IV)



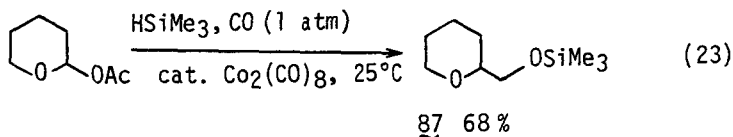
Scheme IV. Possibility of Koch-type Carbonylation



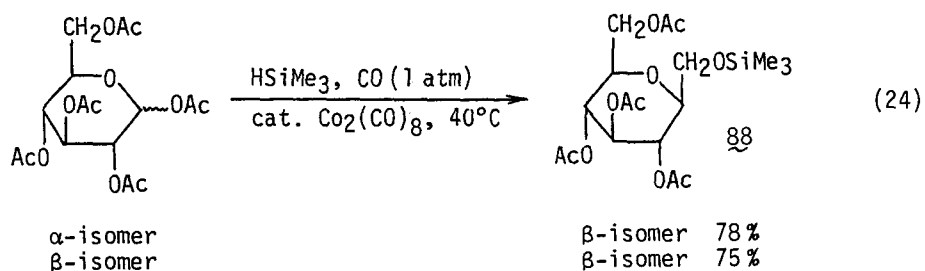
would proceed via adamantyl cation 85. In the presence of HSiR_3 , no carbonylation took place. When HSiR_3 was absent, the cation 85 could react with carbon monoxide (available from $\text{H}_2\text{SO}_4/\text{HCOOH}$) to afford the Koch product. In the catalytic reaction (eq 21), carbonylation has proceeded even in the presence of HSiR_3 . Therefore, the cation 85 is highly likely to have been trapped by the nucleophile $\text{Co}(\text{CO})_4^-$ to give 79 (Scheme III). The present experiments indicate that carbonylation can take place catalytically even at a tertiary carbon center when competitive pathways are unavailable or very slow ones.

1-8-2 The Catalytic Reaction of α -Oxygen Substituted Alkyl Acetates

Much efforts have been expended on the development of cobalt-catalyzed reaction using 1 atm of carbon monoxide, since the reaction of 1-adamantyl acetate was found (see chapter 1-8-2). Thus, substrates, having a carbon atom stabilized as a cation after liberation of acetoxy group, were selected. The reaction of 2-tetrahydropyranyl acetate with carbon monoxide (1 atm) and hydrosilane at 25°C underwent incorporation of carbon monoxide cleanly (eq 23).

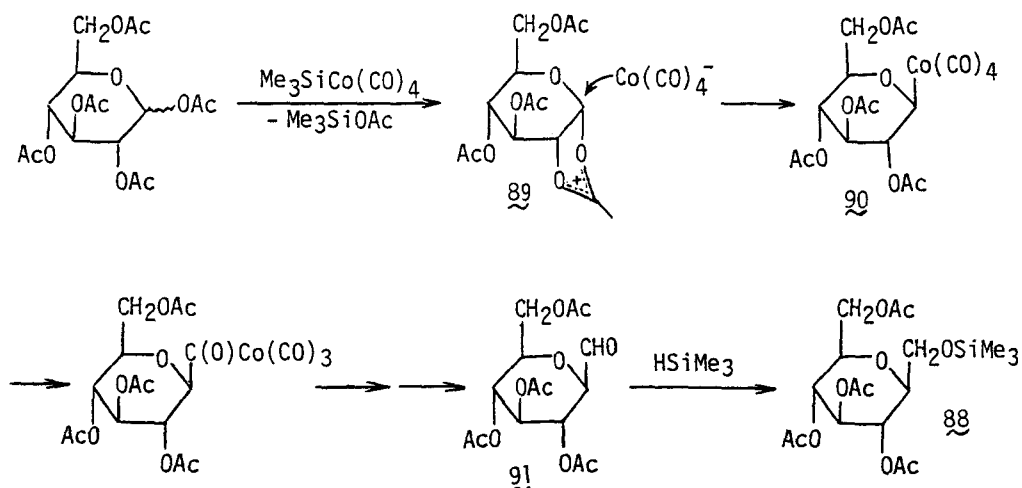


This new siloxymethylation was applicable to pentaacetyl α - and β -D-glucose. The results are expressed in eq 24.



Siloxymethylation at anomeric position of carbohydrates took place with complete stereoselectivity. Proposed reaction path is shown in Scheme V. Complete stereoselectivity shown above would be attributed to the β -attack of $\text{Co}(\text{CO})_4^-$ toward an acyloxonium ion 89 leading to an alkylcobalt complex 90.³⁵ Hydrosilylation of the intermediary formed aldehyde 91 afforded 88.

Scheme V.



Similarly, the catalytic reaction of pentaacetyl β -D-galactose took place stereoselective siloxymethylation in good yield. In contrast with pyranose acetates, the reaction of tetraacetyl β -D-ribose, a furanose acetate, gave a mixture of α - and β -siloxymethylanated products and other products.

In recent years a variety of synthetic methods for the construction of C-glycopyranosides have been developed because C-glycopyranosides represent subunits of many natural products.³⁶ In addition, a variety of C-analogues of saccharide phosphates are now highly demand for studies of sugar metabolism.³⁷ However, most of these methods reported so far have required multi-step procedures and have not given very high overall yields and high stereoselectivity. In view of the recent development of methods for synthesis of C-glycopyranosides, this reaction provides a general new tool for organic synthesis.

1-9 Experimental

1-9-1 General Procedures

Boiling points and melting points are uncorrected. Infrared spectra were recorded on a Shimadzu IR-400 spectrometer; absorptions are reported in reciprocal centimeters. ^1H NMR were recorded on a Japan Electron Optics JNM-PS-100 spectrometer and are reported in ppm from internal tetramethylsilane on the δ scale. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, c=complex, br=broad),

coupling constant (Hz), integration, and interpretation. ^{13}C NMR were recorded on a JEOL JNM-FX-60S spectrometer and are reported in ppm from trimethylsilane on the δ scale. Mass spectrometer were recorded on a Model RMU-6E. Elemental analyses were performed by Elemental Analyses Center of Osaka University. Analytical GLC was carried out on a Shimazu GC-3BF gas chromatograph, equipped with a flame ionization detector, using a 6 m x 3 mm stainless steel column packed with 5% Silicone OV-1 on 60-80 mesh Chromosorb W. Preparative GLC was performed on a Hitachi 164 gas chromatograph using a 2 m x 10 mm stainless steel column packed with 10% Silicone OV-1 on 60-80 mesh Chromosorb W and 15% DEGS on 60-80 mesh Chromosorb W.

1-9-2 General Procedure for the $\text{Co}_2(\text{CO})_8$ -Catalyzed Reaction of Esters with CO and HSiR_3

In a 100 mL stainless steel autoclave were placed 10 mmol of ester, 30 mmol of HSiR_3 , 0.4 mmol of $\text{Co}_2(\text{CO})_8$, 2 mmol of additive (if necessary), and 20 mL of benzene. The autoclave was charged with carbon monoxide to 50 atm at 25°C and then heated with stirring in an oil bath at 200°C or 140°C and for 6h or 20 h. After the reaction, the autoclave was cooled and depressurized. Solvent was evaporated in vacuo and distillation gave a pure sample of the products, but when necessary purification by preparative GLC was carried out. For Glc yields, appropriate hydrocarbons ($n\text{-C}_n\text{H}_{2n+2}$) calibrated against purified products were

added before or immediately after the catalytic reaction.

1-9-3 Characterization of Products

[(4-Chlorocyclohexylidene)methoxy]diethylmethylsilane (19). Bp 100-120°C (5 mmHg); IR (neat) 2930, 2910, 2870, 1680 (C=C), 1450, 1255, 1175, 1140, 1060, 1005, 965, 825, 800, 770 cm^{-1} ; NMR (CCl_4) δ 0.10 (s, 3H, Si-CH₃), 0.46-0.79 (m, 4H, Si-CH₂-), 0.79-1.15 (m, 6H, Si-C-CH₃), 1.42-2.80 (c, 8H, -CH₂-, =C-CH₂-), 4.08 (tt, J=6, 15 Hz, 1H, Cl-CH-), 6.01 (s, 1H, =CH); mass spectrum, m/e 248 (15, M⁺+2), 246 (38, M⁺), 217 (23, M⁺-Et), 109 (35), 107 (35), 101 (26), 93 (100), 73 (43); Anal. Calcd for C₁₂H₂₃OSiCl: C, 58.39; H, 9.39; Cl, 14.36. Found: C, 58.43; H, 9.67; Cl, 14.29.

[(Cyclododecylidene)methoxy]diethylmethylsilane (21). Bp 116-120°C (0.95 mmHg); IR (neat) 2920, 2870, 2850, 1660 (C=C), 1470, 1450, 1250, 1200, 1180, 1160, 1120, 1000, 960, 850, 830, 820, 800, 770 cm^{-1} ; NMR (CCl_4) δ 0.10 (s, 3H, Si-CH₃), 0.67 (m, 4H, Si-CH₂-), 0.97 (m, 6H, Si-C-CH₃), 1.90 (t, J=6 Hz, 2H, =C-CH₂-trans to OSi), 2.08 (t, J=6 Hz, 2H, =C-CH₂-cis to OSi), 6.01 (s, 1H, =CH); mass spectrum, m/e 296 (61, M⁺), 267 (21, M⁺-Et), 183 (11), 177 (11), 101 (32), 89 (100); Anal. Calcd for C₁₈H₃₆OSi: C, 72.90; H, 12.24. Found: C, 72.67; H, 12.40.

Diethylmethyl[(tricyclo[3.3.1.1^{3,7}]dodecylidene)methoxy]-silane (22). Bp 103-104.5°C (0.28 mmHg); IR (neat) 2950, 2900, 2850, 1685 (C=C), 1470, 1465, 1455, 1420, 1390, 1275, 1210, 1140,

1100, 1080, 1005, 860, 815 cm^{-1} ; NMR (CCl_4) δ 0.09 (s, 3H, Si- CH_3), 0.41-0.77 (m, 4H, Si- CH_2 -), 0.81-1.13 (m, 6H, Si-C- CH_3), 1.56-2.07 (c, 12H, $-\text{CH}_2$ -, $-\text{CH}$ -), 2.19 (m, 1H, $=\text{C}-\text{CH}$ - trans to OSi), 2.98 (m, 1H, $=\text{C}-\text{CH}$ - cis to OSi), 5.94 (s, 1H, $=\text{CH}$); mass spectrum, m/e 264 (100, M^+), 235 (58, M^+-Et), 101 (17), 89 (29); Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{OSi}$: C, 72.66; H, 10.68. Found: C, 73.00; H, 11.06.

Diethyl[(2.4-dimethyl-1-pentyl)oxy]methylsilane (25). Bp 92-95°C (27 mmHg); IR (neat) 2850-2950, 2825, 1670 ($\text{C}=\text{C}$), 1460, 1410, 1380, 1360, 1260, 1240, 1150-1180, 1080, 1000, 960, 940, 880, 820, 800, 760, 680 cm^{-1} ; NMR (CCl_4) δ 0.09 (s, 3H, Si- CH_3), 0.66 (m, 4H, Si- CH_2 -), 0.77- 1.17 (c, 12H, Si-C- CH_3 , $-\text{CH}_3$), 1.50 (s, 3H, $=\text{C}-\text{CH}_3$), 1.68 (m, 2H, $=\text{C}-\text{CH}_2$ -), 1.89 (m, 1H, $-\text{CH}$ -), 5.97 (m, 1H, $=\text{CH}$); mass spectrum, m/e 214 (11, M^+), 171 (91), 153 (8), 101 (100); Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$: C, 67.22; H, 12.22. Found: C, 66.95; H, 12.46.

Diethyl[(2.3-dimethyl-1-pentyl)oxy]methylsilane (26). Bp 70-87°C (23 mmHg); IR (neat) 2950, 2930, 2910, 2870, 1670 ($\text{C}=\text{C}$), 1460, 1415, 1380, 1255, 1250, 1175, 1130, 1015, 1005, 970, 860, 835, 800, 770, 760, 685 cm^{-1} ; NMR (CCl_4) δ 0.08 (s, 3H, Si- CH_3), 0.40-1.52 (c, 22H, including a $=\text{C}-\text{CH}_3$ singlet at 1.40 ppm, Si- CH_2CH_3 , $-\text{CH}_3$, $-\text{CH}_2$ -, $-\text{CH}$ -, $=\text{C}-\text{CH}_3$), 5.94 (s, 1H, $=\text{CH}$); mass spectrum, m/e 214 (17, M^+), 185 (100, M^+-Et), 157 (61), 101 (94), 73 (46); Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$: C, 67.22; H, 12.22. Found: C, 67.58; H, 12.48.

[(2-Cyclopropyl-1-propenyl)oxy]diethylmethylsilane (27). Bp 100-130°C (30 mmHg); IR (neat) 3000, 2950, 2900, 2875, 1670 (C=C), 1465, 1420, 1380, 1255, 1240, 1180, 1160, 1050, 1010, 1005, 960, 840, 795, 765, 755 cm^{-1} ; NMR (CCl_4) δ [0.09 (s, Si-CH₃), 0.10 (s, Si-CH₃), total 3H], 0.21-1.14 (c, 15H, Si-CH₂CH₃, CH₂-CH-CH₂), [1.13 (s, 1.35H, =C-CH₃ of Z-isomer), 1.44 (s, 1.65H, =C-CH₃ of E-isomer), total 3H], 1.56-2.01 (m, 1H, -CH-), 6.06 (s, 1H, =CH); mass spectrum, m/e 198 (19, M⁺), 185 (10, M⁺-Et), 183 (12), 169 (16), 101 (23), 89 (100), 73 (48); Anal. Calcd for C₁₁H₂₂OSi: C, 66.60; H, 11.18. Found: C, 66.28; H, 11.40.

Diethyl[[3-[4-(1,1-dimethylethyl)phenyl]-2-methyl-1-propenyl]oxy]methylsilane (28). Bp 116-120°C (0.55 mmHg); IR (neat) 2960, 2910, 2880, 1680 (C=C), 1520, 1465, 1420, 1370, 1260, 1240, 1185, 1155, 1100, 1051, 995, 970, 850, 835, 825, 800, 770, 690 cm^{-1} ; NMR (CCl_4) δ [0.12 (s, Si-CH₃), 0.14 (s, Si-CH₃), total 3H], 0.48-0.80 (m, 4H, Si-CH₂-), 0.84-1.12 (m, 6H, Si-C-CH₃), 1.28 (s, 9H, -C(CH₃)₃), 1.44 (c, 3H, =C-CH₃), [3.06 (s, 1.3H, Ph-CH₂-C= of E-isomer), 3.30 (s, 0.7H, Ph-CH₂-C= of Z-isomer), total 2H], 6.09 (m, 1H, =CH), 6.90-7.29 (m, 4H, aromatic H); mass spectrum, m/e 304 (100, M⁺), 289 (46, M⁺-Me), 275 (38, M⁺-Et), 247 (62), 145 (50), 101 (50), 89 (62), 73 (81); Anal. Calcd for C₁₉H₃₂OSi: C, 74.93; H, 10.59. Found: C, 74.44; H, 10.79.

Diethyl[[3-[4-[(diethylmethylsilyl)oxy]phenyl]-2-methyl-1-propenyl]oxy]methylsilane (29). Bp 150-180°C (3 mmHg) (bulb-to-bulb distillation); IR (neat) 2960, 2910, 2880, 1680 (C=C), 1610,

1510, 1465, 1420, 1260, 1190, 1055, 1110, 970, 915, 830, 800, 770, 690 cm^{-1} ; NMR (CCl_4) δ 0.12 (s, 3H, Si- CH_3), 0.18 (s, 3H, Si- CH_3), 0.45-0.81 (m, 8H, Si- CH_2 -), 0.81-1.17 (m, 12H, Si-C- CH_3), 1.44 (s, 3H, =C- CH_3), [3.06 (s, 1.4H, =C- CH_2 - of E-isomer), 3.27 (s, 0.6H, =C- CH_2 - of Z-isomer), total 2H], 6.12 (m, 1H, =CH), 6.57-7.07 (m, 4H, aromatic H); mass spectrum, m/e 364 (100, M^+), 349 (63, M^+ -Me), 335 (19, M^+ -Et), 265 (15), 247 (67), 237 (22), 207 (33), 101 (44), 73 (100); Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{O}_2\text{Si}_2$: C, 65.87; H, 9.95. Found: C, 65.78; H, 10.17.

Diethylmethyl[(2-methyl-4-phenyl-1-butenyl)oxy]silane (30). Bp 100-120°C (2 mmHg), (bulb-to-bulb distillation); IR (neat) 3030, 2950, 2940, 2910, 2880, 1160 (C=C), 1610, 1500, 1260, 1180, 1160, 1140, 1080, 1010, 970, 850, 835, 770, 750, 700 cm^{-1} ; NMR (CCl_4) δ [0.03 (s, Si- CH_3), 0.06 (s, Si- CH_3), total 3H], 0.24-0.78 (m, 4H, Si- CH_2 -), 0.78-1.11 (m, 6H, Si-C- CH_3), [1.50 (s, 0.75H, =C- CH_3 of Z-isomer), 1.56 (s, 2.25H, =C- CH_3 of E-isomer), total 3H], 1.71-2.46 (m, 2H, =C- CH_2 -), 2.64 (t, J=9 Hz, 2H, Ph- CH_2 -), 5.84-6.05 (m, 1H, =CH), 6.93-7.32 (m, 5H, aromatic H); mass spectrum, m/e 262 (4, M^+), 233 (5, M^+ -Et), 143 (9), 101 (80), 91 (17), 89 (14), 73 (46), 61 (100); Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{OSi}$: C, 73.22; H, 9.99. Found: C, 72.95; H, 10.05.

[(Cholestanylidene)methoxy]diethylmethyilsilane (31); Rf 0.16 (n-hexane); IR (neat) 2900, 2860, 2830, 1680 (C=C), 1465, 1455, 1450, 1380, 1250, 1160, 1110, 1005, 820, 800, 765 cm^{-1} ; NMR (CCl_4) δ 0.08 (s, 3H, Si- CH_3), 0.65 (m, 4H, Si- CH_2 -), 0.77-2.16 (c, 52H,

Si-C-CH, steroid framework), 590 (s, 1H, =CH); mass spectrum, m/e 500 (100, M^+), 485 (2, M^+ -Me), 471 (3, M^+ -Et), 171 (12), 101 (14), 73 (17); Anal. Calcd for $C_{33}H_{60}OSi$: C, 79.12; H, 12.07. Found: C, 78.94; H, 12.37.

Diethylmethyl[(3-methylbicyclo[3.3.0]octa-2-ene-1-yl)oxy]-silane (37). Bp 85-87°C (1 mmHg); IR (neat) 2940, 2910, 2875, 2830, 1690 (C=C), 1460, 1450, 1415, 1385, 1340, 1300, 1285, 1255, 1210, 1160, 1130, 1095, 1075, 1010, 970, 950, 880, 795, 770, 690 cm^{-1} ; NMR (CCl_4) δ 0.10 (s, 3H, Si-CH₃), 0.42-0.78 (m, 4H, Si-CH₂-), 0.78-1.10 (m, 6H, Si-C-CH₃), 1.10-1.94 (c, with a singlet superimposed at 1.45 (=C-CH₃), 10H, -CH₂-, -CH-, =C-CH-), 2.66-2.98 (c, 1H, =C-CH-); mass spectrum, m/e 238 (100, M^+), 223 (18, M^+ -Me), 209 (44, M^+ -Et), 197 (28), 101 (51), 89 (100); Anal. Calcd for $C_{10}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.67; H, 11.21.

[(6-Acetoxy-1-heptenyl)oxy]diethylmethylsilane (40). Bp 100-110°C (0.85 mmHg); IR (neat) 3040, 2960, 2930, 2870, 1740 (C=O), 1660 (C=C), 1460, 1410, 1370, 1235, 1160, 1140, 1080, 1015, 970, 950, 925, 805, 770, 690 cm^{-1} ; NMR (CCl_4) δ 0.10 (s, 3H, Si-CH₃), 0.38-0.74 (m, 4H, Si-CH₂-), 0.74-1.08 (m, 6H, Si-C-CH₃), 1.12 (d, J=7 Hz, -CH₃), 1.27-1.66 (c, 4H, -CH₂-), 1.66-2.17 (c, with a singlet superimposed at 1.93 (CO-CH₃), 5H, =C-CH₂-, CO-CH₃), [4.33 (pst, J=6 Hz, 0.4H, C=CH- of Z-isomer), 4.60-4.99 (m, with a doublet-triplet superimposed at 4.80 (J=6, 12 Hz, 0.6 H, C=CH- of E-isomer), 1.6 H, C=CH-, O-CH-), total 2H], [6.02 (d, J=6 Hz, =CH of Z-isomer), 6.05 (d, J=12 Hz, =CH of E-isomer), total 1H]; mass

spectrum, m/e 272 (2, M^+), 213 (14), 161 (100), 157 (25), 131 (97), 101 (76), 89 (54), 73 (46); Anal. Calcd for $C_{14}H_{28}O_3Si$: C, 61.72; H, 10.36. Found: C, 61.59; H, 10.21.

4-[(Diethylmethylsilyl)oxy]-3-methyl-3-butenic Acid
Diethylmethylsilyl Ester (41). Bp 123-125°C (3 mmHg); IR (neat) 2955, 2920, 2860, 1700 (C=O), 1680 (C=C), 1465, 1420, 1335, 1275, 1260, 1240, 1185, 1150, 1010, 965, 835, 800, 770 cm^{-1} ; NMR (CCl_4) δ 0.12 (s, 3H, Si-CH₃), 0.20 (s, 3H, Si-CH₃), 0.44-1.24 (m, 20H, Si-CH₂CH₃), 1.60 (m, 3H, =C-CH₃), [2.76 (s, 1H, =C-CH₂-CO of E-isomer), 3.00 (s, 1H, =C-CH₂-CO of Z-isomer), total 2H], 6.08 (m, 1H, =CH); mass spectrum, m/e 316 (7, M^+), 287 (25, M^+ -Et), 193 (100), 101 (90), 91 (83); Anal. Calcd for $C_{15}H_{32}O_3Si_2$: C, 56.91; H, 10.19. Found: C, 56.83; H, 10.35

5-[(Diethylmethylsilyl)oxy]-4-methyl-4-pentenic Acid
Diethylmethylsilyl Ester (42). Bp 117-118°C (0.35 mmHg); IR (neat) 2940, 2890, 2870, 1720 (C=O), 1160 (C=C), 1460, 1415, 1255, 1180, 1145, 1010, 965, 845, 830, 800, 765 cm^{-1} ; NMR (CCl_4) δ 0.10 (s, 3H, Si-CH₃), 0.20 (s, 3H, Si-CH₃), 0.64-1.24 (m, 20H, Si-CH₂CH₃), 1.57 (m, 3H, =C-CH₃), 2.03-2.47 (m, 4H, =C-CH₂-, CO-CH₂-), [5.98 (m, 0.3H, =CH), 6.04 (m, 0.7H, =CH), total 1H]; mass spectrum, m/e 330 (26, M^+), 301 (39, M^+ -Et), 189 (41), 171 (100), 101 (87); Anal. Calcd for $C_{16}H_{34}O_3Si_2$: C, 58.13; H, 10.34. Found: C, 57.87; H, 10.71.

5-[(Diethylmethylsilyl)oxy]-4-ethyl-4-pentenic Acid
Diethylmethylsilyl Ester (43). Bp 114°C (0.38 mmHg); IR (neat)

2940, 2900, 2860, 1710 (C=O), 1660 (C=C), 1460, 1410, 1360, 1250, 1170, 1140, 1060, 1000, 980, 790, 760 cm^{-1} ; NMR (CCl_4) δ 0.10 (s, 3H, Si-CH₃), 0.20 (s, 3H, Si-CH₃), 0.44-1.16 (c, 23H, Si-CH₂CH₃, -CH₃), 1.72-2.28 (c, 6H, =C-CH₂-, -CO-CH₂-), 6.00 (s, 1H, =CH); mass spectrum, m/e 344 (28, M⁺), 315 (43, M⁺-Et), 198 (43), 185 (100), 101 (76); Anal. Carcd for C₁₇H₃₆O₃Si₂: C, 59.24; H, 10.53. Found: C, 58.85; H, 10.71.

4-[[Diethylmethylsilyl]oxy]methylene]-nonanic Acid
Diethylmethylsilyl Ester (44). Bp 135-140°C (0.68 mmHg); IR (neat) 2960, 2930, 2880, 1725 (C=O), 1675 (C=C), 1465, 1420, 1385, 1370, 1260, 1150, 1010, 970, 805, 770, 695 cm^{-1} ; NMR (CCl_4) δ 0.10 (s, 3H, Si-CH₃), 0.19 (s, 3H, Si-CH₃), 0.52-1.20 (m, 23H, Si-CH₂CH₃, -CH₃), 1.20-1.62 (m, 6H, -CH₂-), 1.70-2.40 (m, 6H, =C-CH₂-, CO-CH₂-), [6.00 (m, 0.4H, =CH), 6.07 (m, 0.6H, =CH), total 1H]; mass spectrum, m/e 386 (3, M⁺), 249 (100), 131 (46), 89 (69); Anal. Carcd for C₁₉H₄₂O₃Si₂: C, 62.11; H, 10.95. Found: C, 61.87; H, 11.17.

2-[[Diethylmethylsilyl]oxy]methylene]-cyclopentaneacetic Acid Diethylmethylsilyl Ester (45). Bp 110-120°C (0.4 mmHg); IR (neat) 2950, 2910, 1875, 1715 (C=O), 1685 (C=C), 1465, 1415, 1360, 1280, 1255, 1180, 1140, 1005, 965, 800, 770, 690 cm^{-1} ; NMR (CCl_4) δ 0.09 (s, 3H, Si-CH₃), 0.20 (s, 3H, Si-CH₃), 0.45-1.14 (m, 20H, Si-CH₂CH₃), 1.17-3.15 (c, 9H, -CH₂-, =C-CH₂-, =C-CH-, CO-CH₂-), 6.12 (m, 1H, =CH); mass spectrum, m/e 356 (12, M⁺), 327 (12, M⁺-Et), 210 (50), 197 (100), 101 (62), 73 (87); Anal. Carcd for

$C_{18}H_{36}O_3Si_2$: C, 60.62; H, 10.17. Found: C, 60.83; H, 10.35.

5-[(Diethylmethylsilyl)oxy]-2-[1-[(diethylmethylsilyl)oxy]-ethylidene]-4-methyl-4-pentenoic Acid Diethylmethylsilyl Ester (46). Bp 160-170°C (1 mmHg); IR (neat) 2950, 2900, 2870, two strong absorptions with nearly equal intensities at 1680 and 1610 (the trisubstituted C=C at 1680 overlapping with C=C-C=O at 1680 and 1610), 1460, 1415, 1380, 1295, 1255, 1210, 1155, 1125, 1065, 1000, 965, 900, 820, 790, 690 cm^{-1} ; NMR (CCl_4) δ 0.07 (s, 3H, Si-CH₃), 0.21 (s, 6H, Si-CH₃), 0.31-1.15 (m, 30H, Si-CH₂CH₃), [1.35 (m, 0.6H, =C-CH₃ Z-configuration), 1.47 (m, 2.4H, =C-CH₃ E-configuration), total 3H], [2.11 (s, 0.3H, =C(OSi)CH₃ cis to COOSi), 2.25 (s, 2.7 H, =C(OSi)CH₃ trans to COOSi), total 3H], [2.79 (s, 1.6H, =C-CH₂-C= E-configuration), 3.07 (s, 0.4H, =C-CH₂-C= Z-configuration), total 2H], 5.93 (m, 1H, =CH); 90 % (100 x 2.7/3) of the above mixture could be accounted for by 5-[(diethylmethylsilyl)oxy]-2-(Z)-[1-[(diethylmethylsilyl)oxy]-ethylidene]-4-methyl-4-(E)-pentenoic acid diethylmethylsilyl ester, which will be referred as the (Z,E)-isomer (δ 1.47, 2.25, 2.79), and the (Z,Z)-isomer (δ 1.35, 2.25, 3.07) present in a ratio of 75:25 (or 2.4:0.6, or 1.6:0.4). These two isomers corresponding to two major peaks (79:21) in Glc. The absorption at 2.11 (CH₃ cis to COOSi) may indicate the presence of (E,E) and/or (E,Z)-isomers (total 10 %). mass spectrum, m/e 472 (3, M⁺), 443 (26, M⁺-Et), 354 (60), 325 (86), 101 (60), 73 (100); Anal. Calcd for $C_{23}H_{48}O_4Si_3$: C, 58.42, H, 10.23. Found: C, 58.22; H, 10.37.

2-[1-[(Diethylmethylsilyl)oxy]ethylidene]-4-[[[(diethylmethylsilyl)oxy]methylene]-6-methylheptanoic Acid Diethylmethylsilyl Ester (47). Bp 160-170°C (0.6 mmHg), (bulb-to-bulb distillation); IR (neat) 2950, 2910, 2875, 1685 (trisubstituted C=C, C=O), 1615 (tetrasubstituted C=C), 1460, 1420, 1380, 1255, 1210, 1150, 1125, 1060, 1020, 965, 840, 790, 690 cm^{-1} ; NMR (CCl_4) δ 0.06 (s, 3H, Si-CH₃), 0.20 (s, 6H, Si-CH₃), 0.39-1.19 (c, 36H, Si-CH₂CH₃, -CH₃), [1.53 (m, =C-CH₂- Z-configuration), 1.80 (m, =C-CH₂- E-configuration), total 2H, overlapping with 1H between 1.41-1.94 ppm (c, -CH-)], [2.10 (s, 0.15H, =C(OSi)CH₃ cis to COOSi), 2.22 (s, 2.85H, =C(OSi)CH₃ trans to COOSi), total 3H], [2.49 (s, 1.55H, =C-CH₂-C= E-configuration), 3.03 (s, 0.45H, =C-CH₂-C= Z-configuration) total 2H], 5.91 (m, 1H, =CH): 95% (100 x 2.85/3) of the above mixture could be accounted for by 2-(Z)-[1-[(diethylmethylene]-6-methylheptanoic acid diethylmethyl silyl ester, which will be referred as the (Z,E)-isomer (δ 1.80, 2.22, 2.49), and the referred as the (Z,E)- isomer (δ 1.80, 2.22 2.49), and the (Z,Z)-isomers (δ 1.53, 2.22, 3.03) present in a ratio of 78:22 (1.55:0.45). These two isomers corresponded to two major peaks (78:22) in Glc. The absorption at 2.10 (CH₃ cis to COOSi) may indicate the presence of (E,E) and/or (E,Z)-isomers (total 5%). mass spectrum, m/e 514 (17, M⁺), 485 (33, M⁺-Et), 396 (100), 369 (60), 367 (56), 101 (94); Anal. Calcd for C₂₆H₅₄O₄Si₃: C, 60.64; H, 10.57. Found: C, 60.63; H, 10.65.

2-[1-[(Diethylmethylsilyl)oxy]ethylidene]-4-[[[(diethylmethyl-

silyl)oxy]methylene]decanoic Acid Diethylmethylsilyl Ester (48).
 Bp 170-180°C (1.8 mmHg), (bulb-to-bulb distillation); IR (neat)
 2950, 2920, 2870, 1685 (trisubstituted C=C, C=O), 1620
 (tetrasubstituted C=C), 1465, 1420, 1385, 1300, 1260, 1215, 1155,
 1130, 1065, 1005, 985, 855, 800, 695 cm^{-1} ; NMR (CCl_4) δ 0.06 (s,
 3H, Si-CH₃), 0.21 (s, 6H, Si-CH₃), 0.39-1.10 (c, 33H, Si-CH₂CH₃,
 -CH₃), 1.26 (m, 8H, -CH₂-), [1.65 (m, =C-CH₂- Z-configuration),
 1.92 (m, =C-CH₂- E-configuration), total 2H], [2.10 (s, 0.2H,
 =C(OSi)CH₃ cis to COOSi), 2.22 (s, 2.8H, =C(OSi)CH₃ trans to
 COOSi), total 3H], [2.79 (s, 1.6H, =C-CH₂-C= E-configuration),
 3.03 (s, 0.4H, =C-CH₂-C= Z-configuration), total 2H], 5.91 (m, 1H,
 =CH): 93 % ($100 \times 2.8/3$) of the above mixture could be accounted
 for by (Z,E)-isomer (δ 1.92, 2.22, 2.79) and (Z,Z)-isomer (δ 1.65,
 2.22, 3.03) present in a ratio of 80:20 (1.6:0.4). These two
 isomers corresponded to two major peaks (81:19) in Glc. The
 absorption at 2.10 (CH₃ cis to COOSi) may indicate the presence of
 (E,E) and/or (E,Z)-isomers (total 7%). mass spectrum, m/e 542 (6,
 M^+), 513 (16, $\text{M}^+ - \text{Et}$), 424 (51), 397 (29), 395 (22), 227 (19), 101
 (19), 89 (100), 73 (92); Anal. Calcd for $\text{C}_{28}\text{H}_{58}\text{O}_4\text{Si}_3$: C, 61.93; H,
 10.77. Found: C, 61.74, H, 11.02.

5-[(Diethylmethylsilyloxy)-2-[1-[(diethylmethylsilyl)oxy]-
 propylidene]-4-methyl-4-pentenoic Acid Diethylmethylsilyl Ester
 (49). 140-160°C (0.4 mmHg), (bulb-to-bulb distillation); IR (neat)
 2950, 2910, 2870, 1715 (C=O), 1685 (trisubstituted C=C), 1610
 (tetrasubstituted C=C), 1465, 1420, 1330, 1280, 1255, 1240, 1210,

1155, 1130, 1080, 1060, 1040, 1005, 960, 865, 800, 690 cm^{-1} ;
 NMR(CCl_4) δ [0.06 (s, Si- CH_3), 0.21 (s, Si- CH_3), total 9H],
 0.38-1.26 (c, 33H, Si- CH_2CH_3 , - CH_3), [1.26 (s, =C- CH_3), 1.30 (s,
 =C- CH_3), 1.42 (s, =C- CH_3), 1.50 (s, =C- CH_3), total 3H], [2.02 (q,
 J=7.5 Hz, 0.6H, =C(OSi) CH_2 - cis to COOSi), 2.52 (q, J=7.5 Hz,
 1.4H, =C(OSi) CH_2 - trans to COOSi), total 2H], [2.72 (s, 1.5H,
 =C- CH_2 - E-configuration), 3.02 (s, 0.5H, =C- CH_2 - Z- configuration),
 total 2H], 5.86 (m, 1H, =CH): The absorptions at 1.26, 1.30, 1.42,
 1.50 may indicate that the above mixture contains four
 stereoisomers, ratio of which is (Z,E):(Z,Z):(E,E):(E,Z)=53:23:17:7
 determined by integration of =C- CH_3 singlet; mass spectrum, m/e
 486 (7, M^+), 457 (28, M^+ -Et), 368 (43), 339 (51), 171 (36), 131
 (40), 101 (60), 89 (61), 73 (100); Anal. Calcd for $\text{C}_{24}\text{H}_{50}\text{O}_4\text{Si}_3$: C,
 59.20, H, 10.35. Found: C, 59.18; H, 10.52.

5-[(Diethylmethylsilyl)oxy]-2-[1-[(diethylmethylsilyl)oxy]-
 1-phenylmethylene]-4-methyl-4-pentenoic Acid Diethylmethylsilyl
 Ester (50). Bp 170-180°C (0.9 mmHg); IR (neat) 2950, 2900, 2870,
 1710 (C=O), 1680 (trisubstituted C=C), 1625 (tetrasubstituted C=C),
 1600 (Ph), 1495, 1460, 1415, 1380, 1325, 1250, 1150, 1090, 1000,
 980, 850, 795, 770, 700 cm^{-1} ; NMR (CCl_4) δ [-0.14 (s, Si- CH_3),
 -0.12 (s, Si- CH_3), 0.10 (s, Si- CH_3), total 9H], 0.18-1.22 (c, 30H,
 Si- CH_2CH_3), [1.38 (s, =C- CH_3), 1.46 (s, =C- CH_3), 1.54 (s,
 =C- CH_3), total 3H], [2.70 (s, 0.6H, =C- CH_2 -C=), 3.14 (s, 1.1H,
 =C- CH_2 -C=), 3.42 (s, 0.3H, =C- CH_2 -C=), total 2H], 5.82-6.10 (m,
 1H, =CH), 6.94-7.50 (m, 5H, aromatic H); mass spectrum, m/e 534

(3, M^+), 505 (12, M^+-Et), 416 (53), 387 (25), 273 (47), 207 (21), 171 (35), 101 (83), 73 (100); Anal. Calcd for $C_{28}H_{50}O_3Si_4$: C, 62.86; H, 9.42. Found: C, 62.78; H, 9.71.

4-Methyl-4-pentenoic Acid Diethylmethylsilyl Ester and 4-Methyl-3-pentenoic Acid Diethylmethylsilyl Ester (66). Bp 104-108°C (40 mmHg); IR (neat) 2950, 2900, 2870, 1720 (C=O), 1650 (C=C), 1460, 1415, 1380, 1370, 1320, 1255, 1180, 1060, 1005, 960, 930, 885, 795, 760, 685 cm^{-1} ; NMR (CCl_4) δ 0.20 (s, 3H, Si-CH₃), 0.68 (m, 4H, Si-CH₂-), 0.92 (m, 6H, Si-C-CH₃), 1.68 (m, 3.6H, =C-CH₃), 2.12-2.56 (c, 3H, =C-CH₂-, CO-CH₂-), 2.92 (d, J=8 Hz, 0.4H, =C-CH₂-CO), 4.68 (m, 1.5H, =CH), 5.24 (m, 0.2H, =CH-); mass spectrum, m/e 214 (2, M^+), 199 (5, M^+-Me), 185 (100, M^+-Et), 101 (63), 89 (93); Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.35. Found: C, 61.55; H, 10.63.

3-(1-Cyclohexenyl)-propanoic Acid Diethylmethylsilyl Ester (68). Bp 98-102°C (0.7 mmHg); IR (neat) 2970, 2930, 2880, 1720 (C=O), 1470, 1450, 1420, 1370, 1350, 1290, 1180, 1010, 970, 800, 770 cm^{-1} ; NMR (CCl_4) δ 0.18 (s, 3H, Si-CH₃), 0.50-1.06 (m, 10H, Si-CH₂CH₃), 1.64 (m, 4H, -CH₂-), 1.90 (m, 4H, =C-CH₂-), 2.26 (m, 4H, =C-CH₂-, CO-CH₂-), 5.34 (m, 1H, =CH): NMR analysis showed the complete absence of the exo-methylene-isomer; mass spectrum, m/e 254 (7, M^+), 225 (100, M^+-Et), 101 (93), 89 (68); Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.08; H, 10.38. Found: C, 65.95; H, 10.43.

Diethylmethyl[[(tricyclo[3.3.1.1^{3,7}]dodecyl)methyl]oxy]silane (73). Spectral data of 73, which was obtained by preparative GLC,

was identified with those of an authentic sample, which was prepared by $\text{Co}_2(\text{CO})_8$ -catalyzed silylation of a corresponding alcohol. For an authentic sample obtained by distillation, bp $180\text{--}190^\circ\text{C}$ (2 mmHg) (bulb-to-bulb distillation); IR (neat) 2900, 2850, 1465, 1455, 1450, 1415, 1385, 1365, 1345, 1250, 1235, 1155, 1080, 1005, 840, 805, 765 cm^{-1} ; NMR (CCl_4) δ 0.00 (s, 3H, Si- CH_3), 0.33-0.69 (m, 4H, Si- CH_2 -), 0.77-1.08 (s, 6H, Si-C- CH_3), 1.36-1.57 (c, 6H, - CH_2 -), 1.57-1.80 (c, 6H, - CH_2 -), 1.80-2.05 (c, 3H, -CH-), 3.05 (s, 2H, O- CH_2 -); mass spectrum, m/e 266 (0, M^+), 237 (100, M^+ -Et), 149 (41), 135 (12), 89 (41), 73 (16), 61 (27); Anal. Calcd for $\text{C}_{16}\text{H}_{30}\text{OSi}$: C, 72.11; H, 11.35. Found: C, 71.95; H, 11.47.

Diethyl[[2-[(diethylmethoxysilyl)oxy]-2-(tricyclo[3.3.1.1^{3,7}]-dodecyl)ethenyl]oxy]methoxysilane (74). Bp $140\text{--}158^\circ\text{C}$ (0.9 mmHg) (bulb-to-bulb distillation); IR (neat) 2960, 2940, 2920, 2860, 1685 (C=C), 1460, 1420, 1360, 1260, 1245, 1195, 1150, 1100, 1075, 1050, 1020, 995, 960, 865, 805, 765, 695 cm^{-1} ; ^1H NMR (CCl_4) δ 0.08 (s, 3H, Si- CH_3), 0.12 (s, 3H, Si- CH_3), 0.39-0.81 (m, 8H, Si- CH_2 -), 0.81-1.07 (m, 12H, Si-C- CH_3), 1.41-1.81 (c, 12H, - CH_2 -), 1.81-2.05 (c, 3H, -CH-), 5.47 (s, 1H, =CH); ^{13}C NMR (CDCl_3) δ -4.89 (Si- CH_3), -3.52 (Si- CH_3), [6.36, 6.70, 7.09, 7.53 (Si- CH_2CH_3)], 28.57 (-CH-), 36.25 (-C-), [37.23, 38.70 (- CH_2 -)], 118.99 (=CH-OSi), 145.21 (=C-OSi); mass spectrum, m/e 394 (100, M^+), 365 (17, M^+ -Et), 189 (21), 161 (22), 135 (37), 101 (65), 73 (81); Anal. Calcd for $\text{C}_{22}\text{H}_{42}\text{O}_2\text{Si}_2$: C, 66.94; H, 10.73. Found: C, 67.10; H, 10.91.

Diethylmethyl[[(tricyclo[4.3.1.1^{2,5}]undecyl)methyl]oxy]silane (75). Mass spectrum and RRT of 75, which was obtained by preparative GLC, was identified with those of an authentic sample, which was prepared by Co₂(CO)₈-catalyzed silylation of a corresponding alcohol. For an authentic sample, bp 110-120°C (0.7 mmHg), (bulb-to-bulb distillation); IR (neat) 3040, 2930-2870, 2740, 1480, 1420, 1390, 1260, 1240, 1140, 1120, 1090, 1010, 970, 920, 830, 800, 770, 740, 690 cm⁻¹; NMR (CCl₄) δ 0.00 (s, 3H, Si-CH₃), 0.32-0.64 (m, 4H, Si-CH₂-), 0.80-2.52 (c, 23H, Si-C-CH₃, -CH₂-, -CH-), 3.08 (ABq, 2H, J=10, 27 Hz, O-CH₂-); mass spectrum, m/e 280 (1, M⁺), 251 (100, M⁺-Et), 161 (24), 149 (15), 89 (100); Anal. Calcd for C₁₇H₃₂OSi: C, 72.79; H, 11.50. Found: C, 72.44; H, 11.63.

Diethyl[[[2-[(diethylmethylsilyl)oxy]-2-tricyclo[4.3.1.1^{2,5}]undecyl]ethenyl]oxy]methylsilane (76). Bp 160-170°C (2 mmHg), (bulb-to-bulb distillation); IR (neat) 2940, 2925, 2880, 1680 (C=C), 1470, 1415, 1355, 1270, 1160, 1140, 1080, 1070, 1020, 970, 950, 890, 835, 800, 755, 690 cm⁻¹; ¹H NMR (CCl₄) δ 0.07 (s, 3H, Si-CH₃), 0.12 (s, 3H, Si-CH₃), 0.45-0.75 (m, 8H, Si-CH₂-), 1.15-2.25 (c, 29H, Si-C-CH₃, -CH₂-, -CH-), 5.40 (s, 1H, =CH); ¹³C NMR (CDCl₃) δ [-4.89, -3.47 (Si-CH₃)], [6.36, 6.70, 7.05, 7.63 (Si-CH₂CH₃)], [18.88, 25.98, 27.15, 27.64, 28.62, 32.63, 33.27 (-CH₂-)], [31.51, 40.80, 41.49 (-CH-)], 40.22 (-C-), 119.52 (=CH-OSi), 144.08 (=C-OSi); mass spectrum, m/e 408 (57, M⁺), 379 (10, M⁺-Et), 365 (10), 339 (50), 279 (33), 189 (10), 161 (20), 149

(10), 133 (10), 105 (15), 101 (37), 73 (100); Anal. Calcd for $C_{23}H_{44}O_2Si_2$: C, 67.58; H, 10.85. Found: C, 67.60; H, 11.01.

Diethylmethyl[[(tricyclo[3.3.2.^{3,9}1]undecyl)methyl]oxy]silane (77). Mass spectrum, IR, and RRT of 77, which was obtained by preparative GLC, was identified with those of an authentic sample, which was prepared by $Co_2(CO)_8$ -catalyzed silylation of a corresponding alcohol. For an authentic sample, bp 100-110°C (0.5 mmHg), (bulb-to-bulb distillation); IR (neat) 2900, 1470, 1420, 1380, 1250, 1120, 1110, 1080, 1010, 960, 840, 800, 760, 735, 685 cm^{-1} ; NMR (CCl_4) δ 0.03 (s, 3H, Si-CH₃), 0.36-0.66 (m, 4H, Si-CH₂-), 0.76-1.96 (c, 23H, Si-C-CH₃, -CH₂-, -CH-), 3.15 (ABq, J=9 Hz, 2H, O-CH₂-); mass spectrum, m/e 280 (3, M⁺), 251 (100, M⁺-Et), 161 (40), 149 (76), 89 (95), 67 (22); Anal. Calcd for $C_{17}H_{32}OSi$: C, 72.79; H, 11.50. Found: C, 72.75; H, 11.64.

Diethyl[[[2-[(diethylmethylsilyl)oxy]-2-tricyclo[3.3.2.^{3,9}1]-undecyl]ethenyl]oxy]methylsilane (78). Bp 170-180°C (1.5 mmHg), (bulb-to-bulb distillation); IR (neat) 2900, 2875, 1675 (C=C), 1465, 1410, 1360, 1255, 1135, 1100, 1085, 1075, 1010, 965, 840, 800, 760, 690 cm^{-1} ; ¹H NMR (CCl_4) δ 0.12 (s, 6H, Si-CH₃), 0.42-0.80 (m, 8H, Si-CH₂-), 0.80-2.00 (c, 29H, Si-C-CH₃, -CH₂-, -CH-), 5.75 (s, 1H, =CH); ¹³C NMR ($CDCl_3$) δ [-4.89, -3.33 (Si-CH₃)], [6.36, 6.65, 7.09, 7.73 (Si-CH₂CH₃)], [14.47, 23.39, 25.64, 31.07, 32.05, 34.30, 38.65 (-CH₂-)], [25.25, 31.95, 33.76 (-CH-)], 38.90 (-C-), 120.11 (=CH-OSi), 144.04 (=C-OSi); mass spectrum, m/e 408 (100, M⁺), 379 (13, M⁺-Et), 279 (43), 189 (11),

161 (20), 149 (20), 101 (17), 73 (33); Anal. Calcd for $C_{23}H_{44}O_2Si_2$: C, 67.58; H, 10.85. Found: C, 67.20; H, 11.14.

1-O-Diethylmethoxysilyl-3,4,5,7-tetra-O-acetyl-L-glycero-D-glucoheptitol (88). IR ($CDCl_3$) 2950, 2860, 1750 ($C=O$), 1365, 1215, 1150, 1100, 910, 855, 840, 725 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.10 (s, 9H, Si- CH_3), [(2.00, s), (2.00, s), (2.02, s), (2.03, s), (2.07, s), total 12 H, CO- CH_3], 3.54 (ddd, $J=9.76, 5.85, 2.93$ Hz, H_2), [3.66 (dd, $J=11.72, 5.85$ Hz, H_1), 3.70 (dd, $J=11.72, 2.93$ Hz, H_1), overlapping with a multiplet of H_6], [4.13 (dd, $J=12.69, 1.95$ Hz, H_7), 4.22 (dd, $J=12.69, 4.89$ Hz, H_7)], 5.03 (dd, $J=9.77, 8.79$ Hz, H_3), 5.06 (dd, $J=10.74, 9.77$ Hz, H_5), 5.20 (dd, $J=9.77, 8.79$ Hz, H_4); ^{13}C NMR ($CDCl_3$) δ -0.49 (Si- CH_3), [20.50, 20.65 (CO- CH_3)], 61.55 (SiO- CH_2 -), 62.53 (AcO- CH_2 -), [66.44, 67.61, 72.21, 73.92, 79.11 (-CH-)], [169.48, 170.07, 170.26 (CO)]; mass spectrum, m/e 434 (0, M^+), 419 (60, M^+-Me), 197 (36), 123 (38), 117 (100); Anal. Calcd for $C_{18}H_{30}O_{10}Si$: C, 49.75; H, 6.96. Found: C, 49.71; H 7.06.

1-10 References and Notes

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101, 6433. (b) Idem. Inorg. Chem. 1981, 20, 2508. (c) Marsi, M.; Gladysz, J. A. Organometallics 1982, 1, 1467. (d) Brinkmann, K. Gladysz, J. A. Organometallics in press.

(4) Only a little example have been known about the catalytic reaction of esters and lactones with carbon monoxide. See ref 5.

(5) For reviews, see: Pino, P.; Piacenti, F.; Bianchi, M. In "Organic Syntheses via Metal Carbonyls"; Wender, I; Pino, P., Eds.; Wiley: New York, 1977, Vol. II. Falbe, J. "New Syntheses with Carbon Monoxide"; Springer-Verlag: New York, 1980.

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(7) Under the conditions used for run 2 in Table I (at 140°C).

(8) Under the conditions used for run 8 in Table I (at 200°C).

(9) A cluster $C_6H_5CCO_3(CO)_9$ catalyzed hydroformylation of 1-pentene. Pittman, Jr., C. U.; Ryan, R. C. Chemtech, 1978, 8, 170.

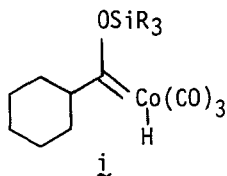
(10) $HSiMe_3$, $HSiEt_2Me$, and $HSiEt_3$ are commercially available (e.g., Petrach Systems. Co., Pennsylvania).

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(13) An alternative mechanism via a carbenoid complex i in

place of 11 may exist.



(14) The reaction of 9 (30 mmol) with HSiEt₂Me (10 mmol) and CO (50 atm) in C₆H₆ in the presence of Co₂(CO)₈/PPh₃ (0.4 mmol/0.4 mmol) for 20 h at 100°C gave 3 and 14 in 27% and 54% yields (based on HSiEt₂Me), respectively. The similar reaction but using 9 (10 mmol) and HSiEt₂Me (30 mmol) at 140°C gave 3 and 4 in 48% and 48% yields (based on 9), respectively.

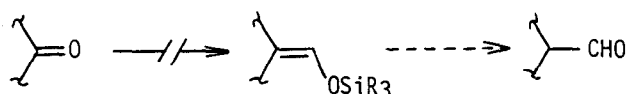
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(16) Liliar is important not only as a perfume component¹⁷ but also as an intermediate for pharmacological active amines.¹⁸

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(19) For a review of the current interest on this type of homologation, see: Martin, S. F. Synthesis 1979, 633. It should be noted that attempts for related conversion of ketonic oxygen to formyl group via enol silyl ethers have been unsuccessful.



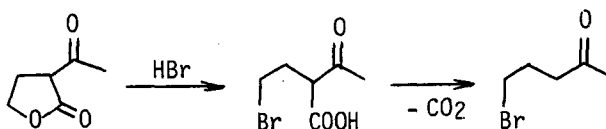
The attempted reactions and reagents used were as follows:

(a) $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{OSiMe}_2\text{-t-Bu/LiN(i-Pr)}_2$: Kluge, A. F.; Cloudsdale, I. S. J. Org. Chem. 1979, 44, 4847. (b) $(\text{EtO})_2\text{P}(\text{O})\text{CH(Ph)OSiMe}_3/\text{LiN(i-Pr)}_2$: Koenigkramer, R. E.; Zimmer, H. Tetrahedron Lett. 1980, 21, 1017. $\text{PPh}_3^+\text{CH}_2\text{OSiMe I}^-/\text{base}$: Martin, S. F.; Phillips, G. W.; Puckette, T. A.; Colapret, J. A. J. Am. Chem. Soc. 1980, 102, 5866.

(20) Cobalt carbonyl-mediated cyclization has been known. Fox, A. L. US Pat. 2995607; Chem. Abstr. 1962, 56, 1363. Heck, R. F. J. Am. Chem. Soc. 1963, 85, 3116.

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(25) In contrast, the reaction of 2-hexyl acetate (Table II) gave less than a few percent yield of straight chain product 57. The reason for this difference is not clear. The difference in the nature of the hydrogen atoms available from the β -hydride elimination in each alkyl acetate might be one of the reasons.

(26) Moreover, a few known examples of carbonylation at a tertiary carbon center were observed as a minor process or took place only sluggishly. (a) Hydroformylation of methyl methacrylate catalyzed by a rhodium complex: Pittman, Jr., C. U.; Honnick, W. D.; Yang, J. J. J. Org. Chem. 1980, 45, 684 and references cited therein. (b) Carbonylation at tertiary carbon of isobutylene (1% yield) under oxo reaction conditions: Wender, I.; Feldman, J.; Meltin, G.; Gwynn, B. H.; Orchin, M. J. Am. Chem. Soc. 1955, 77, 5760. (c) Stoichiometric reaction of HCo(CO)₄ with isobutylene: Heck, R. F.; Breslow, O. S. J. Am. Chem. Soc. 1961, 83, 4023. (d) Insertion of carbon monoxide into

tert-butyl lanthanoid complexes: Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. J. Chem. Soc., Chem. Commun. 1975, 706.

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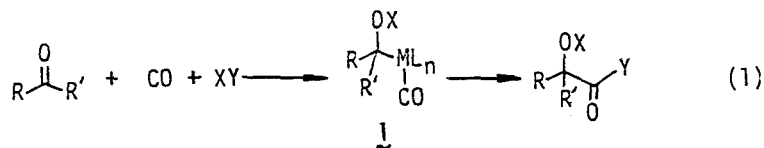
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Chapter 2 Cobalt Carbonyl-Catalyzed Reaction of Ketones with Carbon Monoxide and Hydrosilane

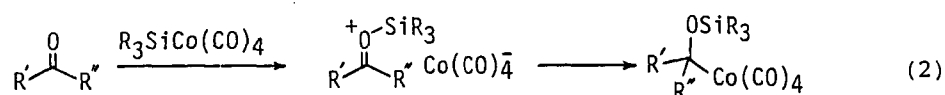
2-1 Introduction

Carbonylation of carbon-carbon double bonds with the aid of transition metal complexes is a popular catalytic reaction¹ which finds fruitful application in industry, hydroformylation of olefins being a representative example.^{1,2} In contrast, catalytic carbonylation of carbon-oxygen double bond (i.e., carbonyl group) with carbon monoxide remains almost unexplored. Of the two available reaction sites in a carbon-oxygen double bond, C-carbonylation (eq 1) is more important than O-carbonylation,³ since the former could bring about carbon chain extension.⁴ Investigations devoted to finding effective catalyst systems which would enable the conversion of formaldehyde to glycolaldehyde (eq 1, R, R', X, Y=H), or to ethylene glycol, via C-carbonylation has been made.⁵ Few example is known about the transition metal catalyst system which is effective for C-carbonylation of higher aldehydes^{6,7} (eq 1, R=alkyl, R'=H). To the best of our knowledge, no example of C-carbonylation of a ketone (eq 1, R, R'=alkyl) has been reported.⁸



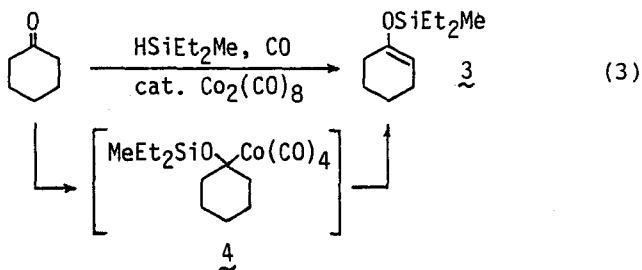
The difficulty in achieving reaction 1 lies mainly in the correct selection of a suitable catalyst which undergoes the

regioselective addition that affords an α -oxyalkyl transition metal intermediate 1.⁹ Intermediate 1 is required for the successive insertion of carbon monoxide and hence for C-carbonylation. The use of $R_3SiCo(CO)_4$ (2), which can be generated in situ in $HSiR_3/CO/Co_2(CO)_8$ system,¹⁰ seemed promising. The addition of 2 across the carbon-oxygen double bond was expected to take place in the desired direction because of the high oxygenophilicity of silicon (eq 2).¹¹

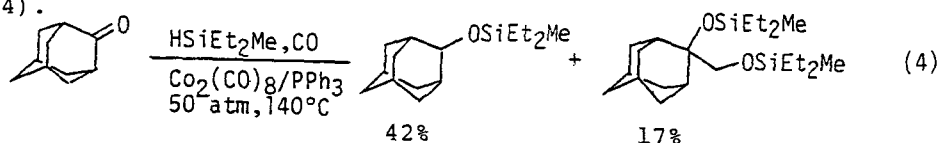


2-2 The Reaction of Ketones with Carbon Monoxide and Hydrosilane

In the reaction system $HSiR_3/CO/Co_2(CO)_8-PPh_3$, carbonylation at ketonic carbon of several ketones such as acetone, acetophenone, and cyclohexanone at 1-80 atm and 25-180°C failed resulting in the formation of enol silyl ethers, in which no carbon monoxide was incorporated. For example, the only product obtained from cyclohexanone was an enol silyl ether 3.¹² The result suggests that an α -oxyalkylmetal carbonyl 4, if it is formed from cyclo-



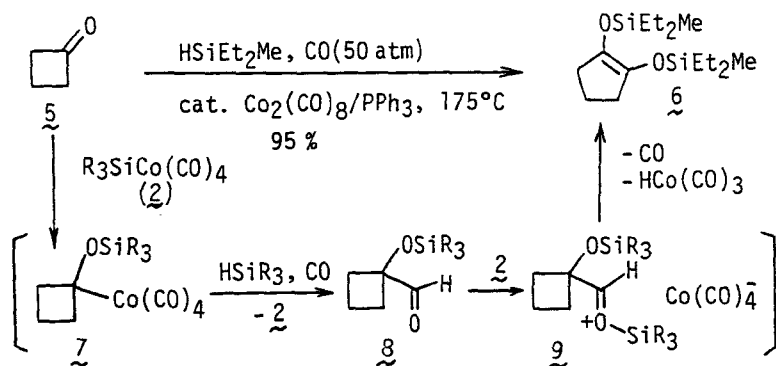
hexanone and 2, would undergo β -hydride elimination to give $\text{HCo}(\text{CO})_3$ and 3 rather than carbon monoxide insertion. Consequently, adamantanone, which might not give the corresponding enol silyl ether because of the ring strain, was reacted with HSiEt_2Me (3 equiv) and CO (50 atm) in the presence of $\text{Co}_2(\text{CO})_8/\text{PPh}_3$ in benzene at 140°C for 20 h. Although, simple hydrosilylation predominated, incorporation of carbon monoxide did take place (eq 4).



2-3 The Reaction of Cyclobutanones with Carbon Monoxide and Hydrosilane — A New Construction of Five-Membered Ring —

Encouraged by these observations described above, the reaction of cyclobutanone whose ring strain might also suppress the competitive enol ether formation was studied. The result of the experiment carried out under similar conditions as above

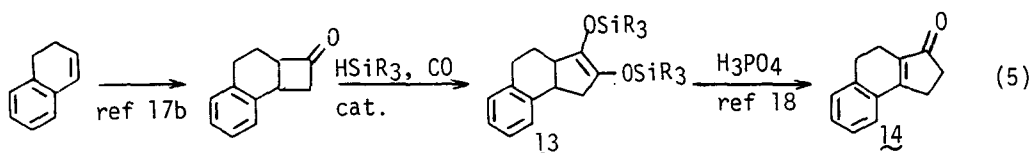
Scheme I



(175°C, 50 atm) was somewhat surprising. The product formed was disiloxycyclopentene **6** which showed the clean incorporation of carbon monoxide (Scheme I). The result would imply that C-formylation (5→7→8) and cationic ring enlargement (9→6)¹³ took place in the sequence, as outlined in Scheme I.¹⁴

Importantly, from the viewpoint of organic synthesis, the present catalytic reaction provides a novel method for the formation of five-membered rings containing a useful functional group (i.e., disiloxyalkene¹⁵). This new chemistry has been found applicable to the synthesis of polycyclopentanoids, an important class of compounds.¹⁶ The results are presented in Table I.

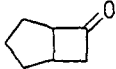
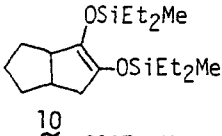
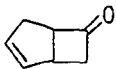
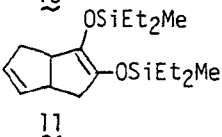
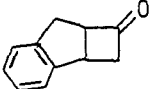
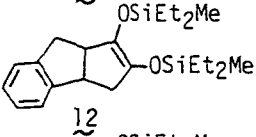
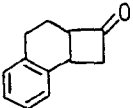
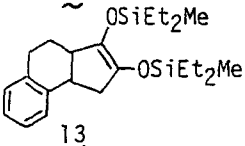
An example of the usefulness of these products is shown in eq 5. The overall transformation illustrated in eq 5 shows a new method of cyclopentenone annulation at an olefinic linkage.



In summary, present reaction (eq 4 and Table I) represents the first example for the catalytic incorporation of carbon monoxide into a ketonic carbon. Moreover, the transformation is potentially of high synthetic utility. The starting cyclobutanones are readily obtained from olefins and ketenes.¹⁷ The products are disiloxycyclopentenones, which contain the 1,2-disiloxyalkene moiety that is known to be a versatile synthon.¹⁵ Furthermore, the present methodology for C-carbonylation of a carbonyl compound

(i.e., the use of Lewis-acidic silicon to bind unshared electrons of the carbonyl oxygen) could be broader than mononuclear catalyst system. A cluster or a heterogenous surface, having a metal center and a Lewis acid center located in a suitable distance, might also be envisaged as a potentially effective catalyst.

Table I. Synthesis of Disiloxycyclopentenenes^a

cyclobutanone	reaction temp, °C	product ^b	yield, % ^c
	120		88
	100		73 ^d
	110		100(80)
	110		94(80)

^a Reaction conditions: cyclobutanone (2.5 mmol), HSiEt₂Me (7.5 mmol), CO (50 atm), Co₂(CO)₈ (0.1 mmol), PPh₃ (0.1 mmol), C₆H₆ (5 mL), 20 h. ^b For structural assignment, see experimental. ^c Glc yields based on cyclobutanones. Isolated yields are in parentheses. ^d Compound 11 was contaminated with a small amount (3% Glc yield) of 10.

2-4 Experimental

2-4-1 General Procedure for Conversion of Cyclobutanones to Disiloxycyclopentenenes.

The following procedure for the reaction of cyclobutanones is representative. To a 100 mL stainless steel autoclave were placed $\text{Co}_2(\text{CO})_8$ (0.1 mmol, 34 mg), PPh_3 (0.1 mmol, 27 mg), HSiEt_2Me (7.5 mmol, 1.1 mL), and benzene (2.5 mL) and then the mixture was stirred. Cyclobutanone (2.5 mmol, 0.19 mL) and benzene (2.5 mL) were added and the autoclave was charged with CO to 50 atm at 25°C. Then the reaction was performed at 175°C for 20 h. Analysis of the reaction mixture by GLC showed the presence of [1-cyclopentene-1,2-diylbis(oxy)]bis[(diethylmethyl)silane] (**6**) in 90% yield. Distillation (bulb-to-bulb distillation) gave pure **6**, bp 120°C (0.5 mmHg), in 80% yield.

2-4-2 Characterization of Products.

Diethylmethyl[(tricyclo 3.3.1.1^{3,7})dodecyl]oxysilane. Bp 94-120°C (0.5 mmHg); ^1H NMR (CCl_4) δ 0.02 (s, 3H, Si-CH₃), 0.34-0.70 (m, 4H, Si-CH₂-), 0.78-1.18 (m, 6H, Si-C-CH₃), 1.28-2.30 (c, 14H, -CH₂-, -CH-), 3.76 (c, 1H, O-CH-); IR (neat) 2980, 2845, 1450, 1035, 1005, 950, 850, 795, 760 cm^{-1} ; mass spectrum, m/e (rel intensity) 252 (2, M^+), 237 (2, $\text{M}^+ - \text{Me}$), 223 (100, $\text{M}^+ - \text{Et}$), 135 (4), 89 (75); Anal Calcd for $\text{C}_{15}\text{H}_{18}\text{OSi}$: C, 71.36; H, 11.18. Found; C, 71.09; H, 11.50.

Diethyl[2-[(diethylmethyl)silyl]oxy[(2-tricyclo 3.3.1.1^{3,7})-dodecylmethyl]oxy]]methylsilane. Bp 139-145°C (0.35 mmHg); ^1H NMR

(CCl₄) δ 0.04 (s, 3H, Si-CH₃), 0.07 (s, 3H, Si-CH₃), 0.38-0.78 (m, 8H, Si-CH₂-), 0.78-1.14 (m, 12H, Si-C-CH₃), 1.20-2.40 (c, 14H, -CH₂-, -CH-), 3.36 (s, 2H, O-CH₂-); IR (neat) 2950, 2900, 1455, 1415, 1380, 1360, 1250, 1160, 1115, 1085, 1065, 1045, 1000, 990, 845, 795, 680 cm⁻¹; mass spectrum, m/e (rel intensity) 353 (19, M⁺-Et), 251 (100), 73 (23); Anal Calcd for C₂₁H₄₂O₂Si₂; C, 65.90; H, 11.06. Found: C, 66.11; H, 11.39.

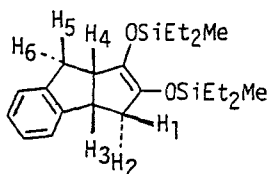
[1-Cyclopentene-1,2-diylbis(oxy)]bis[(diethylmethyl)silane] (6). Bp 120°C (0.5 mmHg), bulb-to-bulb distillation; ¹H NMR (CDCl₃) δ 0.24 (s, 6H, Si-CH₃), 0.56-0.92 (m, 8H, Si-CH₂-), 0.92-1.24 (m, 12H, Si-C-CH₃), 1.56-2.00 (c, 2H, -CH₂-), 2.32 (m, 4H, =C-CH₂-); IR (neat) 2960, 2930, 2880, 1710 (C=C), 1650, 1470, 1425, 1345, 1315, 1255, 1090, 1010, 970, 895, 840, 800, 770, 690 cm⁻¹; mass spectrum, m/e (rel intensity) 300 (100, M⁺), 271 (17, M⁺-Et), 189 (28), 169 (30), 101 (46), 73 (78); Anal Calcd for C₁₅H₃₂O₂Si₂; C, 59.94; H, 10.73. Found: C, 59.93; H, 10.91.

[Bicyclo[3.3.0]oct-2-ene-2,3-diylbis(oxy)][bis(diethylmethyl)silane] (10). Bp 123-127°C (1.2 mmHg); ¹H NMR (CCl₄) δ 0.09 (s, 6H, Si-CH₃), 0.38-0.78 (m, 8H, Si-CH₂-), 0.78-1.10 (m, 12H, Si-C-CH₃), 1.14-1.86 (c, 7H, -CH₂-, -CH-), 2.26-2.86 (c, 3H, =C-CH₂-, =C-CH-); ¹³C NMR (CDCl₃) δ -3.70 (Si-CH₃), 6.74, 7.22 (Si-CH₂CH₃), 24.97, 30.17, 35.90 (-CH₂-), 34.19 (-CH-), 38.01 (=C-CH₂-), 46.58 (=C-CH-), 129.30, 132.06 (C=C); IR (neat) 2950, 2870, 1705 (C=C), 1650, 1460, 1415, 1325, 1320, 1300, 1250, 1245, 1095, 1070, 1005, 965, 945, 930, 800, 765, 685 cm⁻¹; mass

spectrum, m/e (rel intensity) 340 (100, M^+), 311 (31, M^+-Et), 101 (15), 73 (34); Anal Calcd for $C_{18}H_{36}O_2Si_2$: C, 63.47; H, 10.65. Found: C, 63.48; H, 10.85.

[Bicyclo[3.3.0]octa-2,6-diene-2,3-diylbis(oxy)]bis[(diethylmethyl)silane] (11). Bp $143^\circ C$ (2.8 mmHg)- $150^\circ C$ (3.5 mmHg); 1H NMR (CCl_4) δ 0.07 (s, 3H, Si- CH_3), 0.09 (s, 3H, Si- CH_3), 0.40-0.80 (m, 8H, Si- CH_2 -), 0.80-1.16 (m, 12H, Si-C- CH_3), 1.86 (dt, $J=2.5$, 14 Hz, 1H, =C- CH_2 -), 2.24-2.40 (m, 2H, =C- CH_2 -), 2.60 (dd, $J=5$, 14 Hz, 1H, =C- CH_2 -), 2.96-3.20 (m, 2H, =C-CH-), 5.40-5.72 (c, 2H, -CH=CH-); IR (neat) 3045, 2950, 2900, 2870, 2840, 1705 (C=C), 1460, 1415, 1335, 1255, 1155, 1105, 1090, 1000, 970, 930, 870, 830, 800, 775, 760, 710, 685 cm^{-1} ; mass spectrum, m/e (rel intensity) 338 (100, M^+), 309 (6, M^+-Et), 101 (27), 73 (52); Anal Calcd for $C_{18}H_{34}O_2Si_2$: C, 63.87; H, 10.12. Found: C, 63.49; H, 10.28.

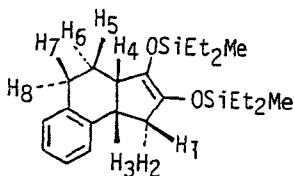
[3,3a,8,8a-Tetrahydrocyclopent[a]indene-1,2-diyl(oxy)]bis-(diethylmethyl)silane] (12). Bp $160-170^\circ C$ (0.4 mmHg),



bulb-to-bulb distillation; 1H NMR ($CDCl_3$) δ -0.02 (s, 3H, Si- CH_3), 0.09 (s, 3H, Si- CH_3), 0.30-1.16 (m, 20H, Si- CH_2CH_3), 2.18 (ddd, $J=1.5$, 3.5, 14 Hz, H_2), 2.86 (ddd, $J=2$, 7.5, 14 Hz, H_1), 2.98 (c, H_5 , H_6), 3.06-3.38 (c, H_4), 3.50 (brt, $J=7.5$ Hz, H_3); ^{13}C NMR

(CDCl₃) δ -3.67 (Si-CH₃), 6.56, 6.75, 7.24 (Si-CH₂CH₃), 35.18, 37.57 (=C-CH₂-, Ph-CH₂-), 41.68, 45.26 (=C-CH-), 129.41, 132.04, 142.52, 147.56 (Ph), 129.41, 132.04 (C=C), 142.52, 147.56 (Ph); IR (neat) 3015, 2945, 2900, 2865, 1700 (C=C), 1485, 1460, 1415, 1380, 1335, 1325, 1240, 1205, 1150, 1100, 1070, 1005, 985, 960, 860, 825, 800, 770, 740, 690 cm⁻¹; mass spectrum, m/e (rel intensity) 388 (100, M⁺), 257 (21), 171 (13), 101 (13), 73 (37); Anal. Calcd for C₂₂H₃₆O₂Si₂: C, 67.98; H, 9.34. Found: C, 67.71; H, 9.21.

[3a,4,5,9b-Tetrahydro-1H-benz[e]indene-2,3-diylbis(oxy)]bis-[(diethylmethyl)silane] (13). Bp 160-170°C (0.4 mmHg),



bulb-to-bulb distillation; ¹H NMR (CDCl₃) δ 0.10 (s, 3H, Si-CH₃), 0.18 (s, 3H, Si-CH₃), 0.42-0.86 (m, 8H, Si-CH₂-), 0.86-1.30 (m, 12H, Si-C-CH₃), 1.50-2.06 (c, H₅, H₆, Irradiation at δ 2.64 collapsed into a ABq, J=13.5 Hz), 2.22 (ddd, J=3, 8, 15 Hz, H₂, Irradiation at δ 3.46 (H₃) collapsed into a broad doublet, J=15 Hz), 2.54-3.06 (c, H₁, H₄, H₇, H₈), 3.46 (q, J=8 Hz, H₃, Irradiation at δ 2.22 (H₂) collapsed into a triplet, J=8 Hz), 7.14 (m, 4H, Ph); ¹³C NMR (CDCl₃) δ -3.67 (Si-CH₃), 6.65, 6.80, 7.19 (Si-CH₂CH₃), 25.64 (-CH₂-), 28.52, 39.43 (=C-CH₂-, Ph-CH₂-), 34.74, 41.73 (-CH-), 125.45, 126.13, 128.33, 128.43 (Ph), 129.70,

133.17 (C=C), 138.36, 140.80 (Ph); IR (neat) 3020, 2950, 2910, 2870, 1705 (C=C), 1495, 1460, 1415, 1360, 1325, 1300, 1255, 1240, 1085, 1010, 970, 915, 865, 830, 800, 690 cm^{-1} ; Anal Calcd for $\text{C}_{23}\text{H}_{38}\text{O}_2\text{Si}_2$: C, 68.60; H, 9.51. Found: C, 68.60; H, 9.39.

2-4-3 Hydrolysis of Disiloxycyclopentene to 2-Cyclopentenone.

1,2,4,5-Tetrahydro-3H-benz[e]indene-3-one (14). The reported procedure was modified.¹⁸ A mixture of 13 (0.5 mmol, 0.20 g) and 60% phosphoric acid (2.3 mL) was stirred at 90°C for 5 h under a nitrogen atmosphere. The mixture was diluted with benzene (20 mL) and the aqueous layer was extracted with benzene (3 x 20 mL). Combined organic layer was dried over CaSO_4 and evaporated in vacuo. The residue was purified by chromatography (silica gel, n-hexane/ether=8/2) to yield 14 (61 mg, 66% yield); mp 75-77°C (pale yellow solid); ^1H NMR (CCl_4) δ 2.30-3.10 (m, 8H, $-\text{CH}_2-$), 7.10-7.54 (m, 4H, Ph); ^{13}C NMR (CDCl_3) δ 18.13, 24.88, 27.87, 35.22 ($-\text{CH}_2-$), 124.16, 126.83, 128.19, 130.79 (Ph), 132.03, 137.75, 138.65 (Ph, $\text{C}=\text{C}-\text{C}=\text{O}$), 165.75 ($\text{C}=\text{C}-\text{C}=\text{O}$), 207.58 (C=O); IR (CDCl_3) 2920, 1680 (C=O), 1630 (C=C), 1570, 1445, 1395, 1300, 1280, 1190, 730 cm^{-1} ; mass spectrum, m/e (rel intensity) 184 (100, M^+), 155 (19), 142 (93), 128 (26).

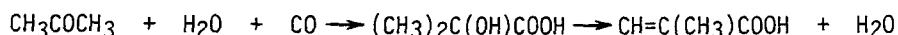
2-5 References and Notes

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presence of cobalt carbonyl to give 2-methyl-1-butanol and 1-pentanol in low yield. To the best of our knowledge, this reaction is only one example for carbonylation of ketones. However, this carbonylation reaction would proceed via reduction of substrate to 2-butanol. Ziesecke, K. H. Brennstoff Chem. 1952, 33, 385.

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(11) This has been suggested in the catalytic formylation of aldehydes.^{7, 10} For the stoichiometric reaction of $(\text{CH}_3)_3\text{SiMn}(\text{CO})_5$, with aldehydes, see: ref 9c.

(12) The $\text{Co}_2(\text{CO})_8$ -catalyzed conversion of ketones to enol silyl ethers with hydrosilane (without using CO) has been reported. Sakurai, H.; Miyoshi, K.; Nakadaira, Y. Tetrahedron Lett. 1977, 2671. See also ref 9c.

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R. Ibid. 1975, 97, 4749. Greene, A. E.; Depres, J.-P. Ibid. 1979, 101, 4003. Knapp, S.; Trope, A. F.; Ornaf, R. M. Tetrahedron Lett. 1980, 21, 4301. Ogura, K.; Yamashita, M.; Suzuki, M.; Tsuchihashi, G. Chem. Lett. 1982, 93. Yamashita, M.; Onozuka, J.; Ysuchihashi, G.; Ogura, K. Tetrahedron Lett. 1983, 24, 79.

(14) The reaction without PPh resulted in decreased yield of 6. Mechanistically, the role of PPh₃ is not clear at present time. For regeneration of 2 from HCo(CO)₃, CO, and HSiR₃ in the catalytic cycle. An alternative and less likely mechanism leading to 6 involves carbonylation by the reaction of uncoordinated carbon monoxide with 1-siloxy-cyclobut-1-yl cation formed from cyclobutanone and 2.

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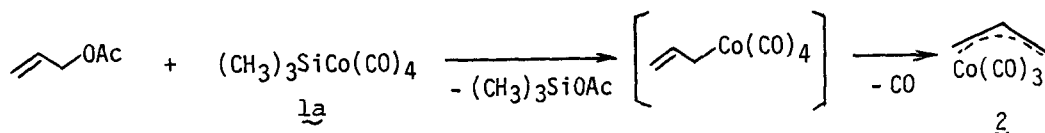
Chapter 3 Stoichiometric Reaction Using $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$

3-1 Introduction

As described in chapter 1 and 2, in the new cobalt carbonyl-catalyzed reactions of esters, lactones, and ketones with carbon monoxide and hydrosilane took place formation of new carbon-carbon bonds as a result of the carbon-oxygen bonds in the substrates. In these catalytic reactions, silylcobalt carbonyl, $\text{R}_3\text{SiCo}(\text{CO})_4$ (1), generated in situ has been suggested as the key catalyst species responsible for the formation of carbon-cobalt bond which is required for the incorporation of carbon monoxide. Although some silylcobalt carbonyl complexes 1 have long been known, their chemistry has not been well explored yet.¹ I have studied the stoichiometric reaction of 1 with some oxygen containing compounds with the expectation that the known oxygenophilicity of silicon in 1 would bring about cleavage of carbon-oxygen bond in the substrate with concomitant formation of carbon-cobalt bond. The reactions of $(\text{CH}_3)_3\text{SiMn}(\text{CO})_5$ with ethers and aldehydes have been recently reported by Gladysz.²

3-2 A New Entry to π -Allylcobalt Tricarbonyls Using $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$

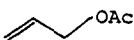
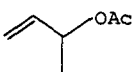
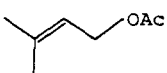
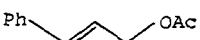
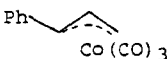
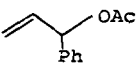
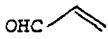
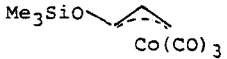
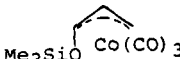
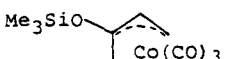
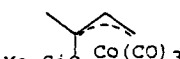
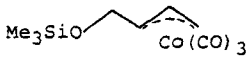
The reaction of allyl acetate with $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ (1a) gave π -allylcobalt tricarbonyl (2) in 80% yield (eq 1). Initially formed σ -allylcobalt carbonyl complex would be converted to stable π -form 2 by liberation of carbon monoxide. The reaction of the



silylcobalt carbonyl 1a can be conducted conveniently in a NMR tube using C_6D_6 as a solvent. Results obtained by the reaction of 1a with some allyl acetates were summarized in Table 1 (entry 1-5). In entry 4 and 5, only syn-isomer was obtained and anti-isomer was not detected by NMR analysis. The reaction of 1a with α,β -unsaturated compounds and diene monoepoxide afforded new type of π -allylcobalt complexes containing siloxy group (entry 6-8 in Table 1). In all cases, transient signals in NMR were observed before they collapsed to the final products. However, the assignment of these transient signals has not been established yet. Present reaction represents a new entry to π -allylcobalt tricarbonyls³ on the basis of high affinity of silicon in 1 toward oxygen.

Although synthetic application of π -allylcobalt carbonyls⁴ has been little studied so far as compared with that of π -allylpalladium and π -allylnickel complexes, π -allylcobalt complexes have been demonstrated recently by Hegedus to be promising discrete intermediates in organic synthesis.⁵ Present new method for the formation of π -allylcobalt complexes on the basis of high oxygenophilicity of silicon would be applicable to new synthetic method of various (new type of) organometallic complexes which are potentially of high utility.

Table 1. The Reaction of $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ with Allyl Acetates, Enones, and A Diene Monoepoxide^{a)}

entry	substrate	π -allylcobalt tricarbonyl ^{b)}	ref.
1		 80 %	c)
2		 52 %  28 %	d)
3		 44 %	d)
4		 63 %	e) f)
5		 56 %	e) f)
6		 44 %  20 %	
7		 12 %  46 %	g)
8		 50 %	f)

a) Reaction conditions: The reaction was conducted with substrate (0.5 mmol), $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ (0.7-0.9 mmol), and C_6D_6 (0.5 mL) under N_2 and at 50°C for 1-1.5 h in a NMR tube. b) NMR yields based on the substrates. Yields were calculated on the basis of known quantities of an added standard (C_6H_6 , C_6H_{12}) or $\text{CH}_3\text{COOSi}(\text{CH}_3)_3$ formed. c) Ref 8. d) J.A.Bertrand, H.B.Jonassen, and D.W.Moore, *Inorg. Chem.*, **2**, 601(1963). e) H.Alper, H.Des Abbayes, and D.Des Roches, *J. Organomet. Chem.*, **121**, C31(1976). f) NMR analysis of the reaction mixture showed the absence of the anti-isomer. g) The stereochemistry was tentatively assigned on the basis of NMR chemical shifts. See also Table 2.

3-3 Experimental

3-3-1 Preparation of $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ (1a)

The reported method for 1a⁶ was modified. To $\text{Co}_2(\text{CO})_8$ (0.68 g, 2 mmol) in a 10 mL flask equipped with dry ice condenser was added $\text{HSi}(\text{CH}_3)_3$ (3.5 mL, 30 mmol) at -78°C . The mixture was allowed to warm to 25°C with stirring over 1 h. The excess $\text{HSi}(\text{CH}_3)_3$ was removed in a stream of N_2 . The residual black solid was sublimed at $40\text{--}45^\circ\text{C}$ (0.5 mmHg) into a flask (-78°C) to give $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ (1a) (0.78–0.83 g, 80–85%, pale pink, ^1H NMR (C_6D_6 , TMS) δ 0.45 ppm, s). Good results were obtained in a cold room ($<15^\circ\text{C}$).

3-3-2 Synthesis of π -Allylcobalt Tricarbonyls

The following procedure for the reaction of allyl acetate is representative. To a solution of $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ (1.0 g, 4.2 mmol) in C_6H_6 (2.5 mL) was added allyl acetate (0.27 g, 2.5 mmol) at 50°C for 1.5 h under nitrogen. The formation of π -allylcobalt tricarbonyl (2) in the solution was evident from ^1H NMR (80% yield). Distillation (bulb-to-bulb, $\sim 30^\circ\text{C}/3$ mmHg)⁷ allowed the isolation (52% yield) of the pure cobalt complex as a pale yellow liquid. ^1H NMR spectral data of all products is shown in Table 2.

3-4 References and Notes

(1) Chalk, A. J.; Harrod, J. F. J. Am. Chem. Soc. 1965, 87, 1137; Ibid. 1967, 89, 1640. Baay, Y. L.; MacDiarmid, A. G. Inorg. Chem. 1969, 8, 986. Ang, H. G.; Lau, Organomet. Chem. Rev. 1972, A 8, 235. Cundy, C. S.; Kingston, B. M.; Lappert, M. F. Adv.

Organomet. Chem. 1973, 11, 235. Hofler, F. Topics Curr. Chem. 1974, 50. 129.

(2) Marsi, M.; Gladysz, J. A. Organometallics 1982, 1, 1467 and references cited therein. Brinkmann, K. C.; Gladysz, J. A. Organometallics in press.

(3) Known methods involve: $\text{CH}_2=\text{CH}-\text{CH}_2\text{X} + \text{NaCo}(\text{CO})_4$ (or $\text{KCo}(\text{CO})_4$), $\text{C}=\text{C}-\text{C}=\text{C} + \text{HCo}(\text{CO})_3$ and $\text{CH}_3\text{I} + \text{NaCo}(\text{CO})_4 + \text{C}=\text{C}-\text{C}=\text{C}$. For a review, see: Kemmitt, R. D. W.; Russell, D. R. "Comprehensive Organometallics Chemistry"; Wilkinson, G, Ed; Pergamon Press: Oxford, 1982, Vol 5, pp 211-222.

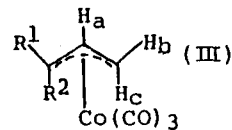
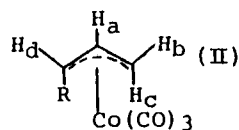
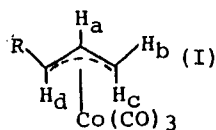
(4) (a) Heck reported that the treatment of $\text{NaCo}(\text{CO})_4$ with excess of allyl bromide in ether gave 1,5-hexadiene. Heck, R. F.; Breslow, D. S. J. Am. Chem. Soc. 1961, 83, 1097. (b) The reaction of 2 with benzaldehyde in methanol underwent allylation to afford allylbenzyl alcohol in 7% yield. Agnes, G.; Chiusoli, G. P.; Marraccin, A. J. Organomet. Chem. 1973, 49, 239. In both reactions, it is ambiguous that these reactions proceeded via σ -allylcobalt complexes or π -isomer.

(5) Hegedus, L. S.; Inoue, Y. J. Am. Chem. Soc. 1982, 104, 4917.

(6) Morrison, D. L.; Hagen, A. P. Inorg. Synth. 1972, 13, 65.

(7) Lit. 39°C (15 mmHg), McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L.; Howk, B. W. J. Am. Chem. Soc. 1961, 83, 1601.

Table 2. ^1H NMR Data for π -Allylcobalt Tricarbonyls (C_6D_6 , TMS)



R	H _a	H _b	H _c	H _d	R	J _{ab}	J _{ac}	J _{ad}	J _{dR}	J _{bc}	J _{bd}
H(I or II)	4.40 (tt)	2.68 (d)	1.85 (d)			6	11			~0	
CH ₃ (I)	4.26 (dt)	2.55 (d)	1.64 (d)	2.72 (dq)	1.23 (d)	6	10	10	6	~0	~0
CH ₃ (II)	4.48 (dt)	2.94 (d)	2.47 (d)	3.89 (quint)	0.83 (d)	6.5	12	6.5	6.5	~0	~0
Ph(I)	5.06 (dt)	2.69 (d)	1.84 (d)	3.67 (d)	7.04-7.12 (m)	6	10	10		~0	~0
OSi(CH ₃) ₃ (I)	4.59 (ddd)	2.38 (dd)	1.33 (dd)	5.01 (d)		6	10	7		1	~0
OSi(CH ₃) ₃ (II)	4.07 (ddd)	3.06 (dd)	3.18 (d)	6.17 (dd)		6	10.5	3.5		~0	1.5
CH ₂ OSi(CH ₃) ₃ (I)	4.52 (dt)	2.56 (d)	1.72 (d)	2.80 (ddd)	3.60 (ABqd) ^a	6	10	10	4, 5	~0	~0
R ¹ , R ²	H _a	H _b	H _c	R ¹	R ²	J _{ab}	J _{ac}	J _{bc}			
CH ₃ , CH ₃ (III)	4.28 (dd)	2.74 (d)	2.17 (d)	1.38 (s)	0.90 (s)	7	12	~0			
OSi(CH ₃) ₃ , CH ₃ (III) ^b	4.56 (dd)	2.60 (d)	ca. 1.7 ^c		1.29 (s)	6.5	10.5	2			
CH ₃ , OSi(CH ₃) ₃ (III) ^b	4.04 (dd)	2.94 (d)	2.86 (d)	1.70 (s)		6	10	~0			

a) $J_{AB}=12\text{ Hz}$. b) The assignment is a tentative one on the basis of NMR chemical shift; H_a syn to the siloxy group would be at lower field than H_a anti to the siloxy group. Compare the chemical shift with those H_a in $\text{R}=\text{OSi}(\text{CH}_3)_3(\text{I})$ and $\text{R}=\text{OSi}(\text{CH}_3)_3(\text{II})$. The assignment is also supported by CH_3 shift data. c) Overlapped with the $\text{CH}_3(\text{R}^1)$ group signal of another isomer ($\text{R}^1=\text{CH}_3$, $\text{R}^2=\text{OSi}(\text{CH}_3)_3$).

Conclusion

The objective of this research was to develop a new catalytic reaction of oxygen containing compounds using carbon monoxide with the aid of transition metal complexes. For this objection, a new method for formation of carbon-transition metal bond from carbon-oxygen bond in substrates has been studied. The important results mentioned in each chapter of this thesis are summarized as follows.

In chapter 1, a new cobalt carbonyl-catalyzed reaction of esters and lactones with carbon monoxide and hydrosilane has been described. Catalytic reaction of secondary alkyl acetates and lactones of secondary alkyl ester-type as well as that of bridgehead alkyl acetates underwent selective incorporation of one and two molecule of carbon monoxide. The results involve a very rare example of the transition metal-mediated incorporation of carbon monoxide into a tertiary carbon center. Furthermore, the catalytic reaction of highly reactive alkyl acetates resulted in incorporation of carbon monoxide under mild reaction conditions (at room temperature and under atomospheric pressure of carbon monoxide). A new method for the stereoselective carba-functionalization at anomeric position of carbohydrates has been described.

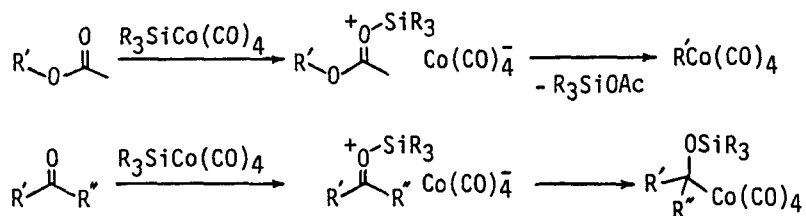
In chapter 2, a new cobalt carbonyl-catalyzed reaction of ketones with carbon monoxide and hydrosilane has been described. Catalytic reaction of cyclobutanones underwent clean incorporation of carbon monoxide with ring expansion to give disiloxycyclopentenenes.

This reaction represents the first example for the catalytic incorporation of carbon monoxide into a ketonic carbon.

In chapter 3, stoichiometric reaction of $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ with oxygen-containing compounds leading to π -allylcobalt tricarbonyls has been described. This reaction provides a new entry to π -allylcobalt tricarbonyls.

Important features of these cobalt-catalyzed reactions with carbon monoxide and hydrosilane are summarized as follows.

(1) In the viewpoint of organometallic chemistry, the reactions in this thesis demonstrate a new method for formation of carbon-transition metal bond by utilizing the high oxygenophilicity of silicon. This methodology for the formation of carbon-transition



metal bond may open up the possibility of development of both new catalytic and stoichiometric carbonylation reactions of oxygen containing compounds.

(2) In the viewpoint of organic synthesis, these catalytic reactions provide a novel synthetic method of (siloxymethylidene)-alkanes (enol silyl ethers) and disiloxyalkenes, which are known to be versatile synthetic intermediates, from esters, lactones, and cyclobutanones, which are among the most readily available

class of compounds. In these reactions, carbon monoxide was cleanly incorporated into oxygen containing compounds.