STUDIES ON THE COBALT CARBONYL CATALYZED CARBON CHAIN EXTENSION REACTION AND REDUCTION USING HYDROSILANES

TOSHIAKI MURAI

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STUDIES ON THE COBALT CARBONYL CATALYZED CARBON CHAIN EXTENSION REACTION AND REDUCTION USING HYDROSILANES

(コバルトカルボニルを触媒とするヒドロシランを用いた炭素鎖延長反応および還元反応に関する研究)

TOSHIAKI MURAI

1985

Preface

The studies presented in this thesis have been carried out under the direction of Professor Noboru Sonoda at the Department of Applied Chemistry, Faculty of Engineering, Osaka University for five years, from 1979 to 1983, and at the Department of Chemistry, Faculty of Engineering, Gifu University for the following three years, from 1983 to 1985.

The thesis is concerned with the cobalt carbonyl catalyzed carbon chain extension reaction and reduction using hydrosilanes.

Yanagido, Gifu
December 1985

Toshiaki Murai

List of Publications

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

1 Cobalt Carbonyl Catalyzed Reaction of Tetrahydrofurans with a Hydrosilane and Carbon Monoxide at Atmospheric Pressure.
Murai, T.; Hatayama, Y.; Murai, S.; Sonoda, N.
Organometallics 1983, 2, 1883.

2 Oxymethylative Opening of Oxiranes Leading to 1,3-Diol Derivatives by Cobalt Carbonyl Catalyzed Reaction with a Hydrosilane and Carbon Monoxide.
Murai, T.; Kato, S.; Murai, S.; Toki, T.; Suzuki, S.; Sonoda, N.
J. Am. Chem. Soc. 1984, 106, 6093.

3 Cobalt Carbonyl Catalyzed Reaction of Tetrahydrofurans with a Hydrosilane and Carbon Monoxide. A New Reaction Pathway Leading to Enol Silyl Ethers.
Murai, T.; Kato, S.; Murai, S.; Hatayama, Y.; Sonoda, N.
Tetrahedron Lett. 1985, 26, 2683.

4 Cobalt Carbonyl Catalyzed Reduction of Aromatic Nitriles with a Hydrosilane Leading to N,N-Disilylamines.
Murai, T.; Sakane T.; Kato, S.
Tetrahedron Lett. 1985, 26, 5145.

5 Cobalt Carbonyl Catalyzed Reaction of Oxetanes with a Hydrosilane and Carbon Monoxide.
Murai, T.; Furuta, K.; Kato, S.; Murai, S.; Sonoda, N.
J. Organomet. Chem. in press.

List of Other Publications

1 Preparation of Haloselenium and Halotellurium Trithiocarbonates.
Kato, S.; Kaga, K.; Ishida, M.; Murai, T.
Z. Naturforsch. 1985, 40b, 273.

2 Preparation and Characterization of Bis(thioacyl)-Tri- and Tetrasulfides.
Kato, S.; Nishiwaki, M.; Inagaki, S.; Oshima, S.; Ohno. Y.; Mizuta, M.; Murai, T.
Chem. Ber. 1985, 118, 1684.

3 Preparation and Some Reactions of Selenium and Tellurium Bis(dithiocarboxylates).
Kato, S.; Itoh, Y.; Ohta, Y.; Goto, K.; Kimura, M.; Mizuta, M.; Murai, T.
Chem. Ber. 1985, 118, 1696.

4 A Convenient Synthesis of Se-Aryl Oxoarylmethanesulfenoselenoates and Te-aryl Oxoarylmethanesulfenotelluroates: Electrophilic Thiocarboxylation of diaryl Diselenides

and Ditellurides.

Kato, S.; Kabuto, H.; Kimura, M.; Ishihara, H.; Murai, T.

Synthesis 1985, 519.

5 A Convenient Preparation of Se-Aryl Selenocarboxylates via Se-Aryl Acylmethanesulfenoates.

Kato, S.; Kabuto, H.; Ishihara, H.; Murai, T.

Synthesis 1985, 520.

Contents

General Introduction

Development of new synthetic reactions using carbon monoxide has been one of the most important subjects in organic synthesis and in industry.[1,2] Numerous recent works using transition metal catalyst have been devoted to carbonylation reactions of olefins or acetylenes.[1,2,3] Most of these reactions require elevated temperatures and high pressures. Only a few examples have been reported as to carbonylation reactions at room temperature and atmospheric pressure with the aid of a catalytic amount of transition metal complex.[4]

Recently, a new catalytic carbonylation reactions of oxygen containing compounds using a hydrosilane and carbon monoxide, which proceed under the relatively mild reaction conditions, has been developed in this laboratory.[5] During the course of the systematic study on this reagent system, it has been found that incorporation of carbon monoxide into cyclic ethers proceeded at room temperatures and at atmospheric pressure. In addition, the ability of a hydrosilane to undergo reduction of aromatic nitriles in the presence of a catalytic amount of $Co_2(CO)_8$ has been found. The prime objective of the present research was to clarify the scope and limitation of these new reactions.

This thesis consists of two chapters. Chapter 1 deals with cobalt carbonyl catalyzed reaction of cyclic ethers with

a hydrosilane and carbon monoxide at ambient temperatures and pressures. Novel synthetic methods for the introduction of a siloxymethyl group and a siloxymethylene group will be described. The study on the regio- and stereoselectivity of these reactions will be also described. Chapter 2 deals with cobalt carbonyl catalyzed reduction of aromatic nitriles with a hydrosilane. The selective addition of a hydrosilane to the carbon-nitrogen triple bond will be described.

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(3) Pruett, R. L. Adv. Organomet. Chem. 1979, 17, 1. Siegel, H.; Himmele, W. Angew. Chem., Int. Ed. Engl. 1980, 19, 178.

(4) (a) Cassar, L.; Chiusoli, G. P.; Guerrieri, F. Synthesis 1973, 509. (b) Alper H.; Heveling, J. J. Chem. Soc., Chem. Commun. 1983, 365. (c) Larock, R. C.; Narayanan K. J. Org. Chem. 1984, 49, 3411. and references cited therein.

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Chapter 1. Cobalt Carbonyl Catalyzed Reaction of Cyclic Ethers with a Hydrosilane and Carbon Monoxide

1.1. Introduction

Although the ease with which the insertion of carbon monoxide into carbon-cobalt bond takes place under mild reaction conditions has been well recognized in the study of stoichiometric reactions,[1] only a few example of catalytic incorporation of carbon monoxide using cobalt complexes at room temperature under 1 atm of CO have been reported.[2] This may be due to the difficulty in regenerating the catalyst species such as $HCo(CO)_4$ under mild reaction conditions, especially in the case when a reactant is molecular hydrogen. To overcome these difficulty, silicon compounds like hydrosilanes was examined as a reactant intead of molecular hydrogen, since it has been well-known that a hydrosilane reacts with transition metal complexes much easier than molecular hydrogen.[1a,3]

In recent years organosilicon reagents have been extensively used in organic syntheses.[4] Although reactions using new silicon reagents have been widely developed, relatively small attention has been paid to the organic reactions using compounds having silicon-transition metal bonds. One such reagent is the silylcobalt tetracarbonyl(1)

Chalk, Harrod, and MacDiarmid has found that $\underset{\sim}{1}$ was easily formed by the reaction of $HSiR_3$ and $Co_2(CO)_8$ (eq 1, 2).

$$HSiR_3 + Co_2(CO)_8 \longrightarrow R_3SiCo(CO)_4 + HCo(CO)_4 \quad (1)$$

$$HSiR_3 + HCo(CO)_4 \longrightarrow R_3SiCo(CO)_4 + H_2 \quad (2)$$

For the purpose of organic synthesis, the high oxophilicity of silicon atom[4a,6] in $\underset{\sim}{1}$ is very attractive as the driving force for the cleavage of the carbon-oxygen bond in the oxygen containing compounds to form an intermediate having carbon-cobalt bond. If carbon-cobalt bond is formed under mild reaction conditions, catalytic process with $HSiR_3$ and carbon monoxide can be attained at room temperature under 1 atm of CO. Recently Gladysz has developed new methods for the formation of carbon-manganese bond by using the stoichiometric reaction of $Me_3SiMn(CO)_5$ with oxygen containing compounds.[7] Unfortunately, the manganese reaction can not be made catalytically because of the poor reactivity of $HSiR_3$ with manganese complexes. The reaction of R_3Si-X reagents (X = halogen, CN, N_3, SR, SeR, TeR etc) with oxygen containing compounds has also been widely reported.[4] In the case of cyclic ethers, these reagents undergo ring opening easily to give the products of the type $R_3SiO\{CH_2\}_nX$.[8]

In the hope to realize the catalytic reactions using carbon monoxide at room temperature under 1 atm of CO, the

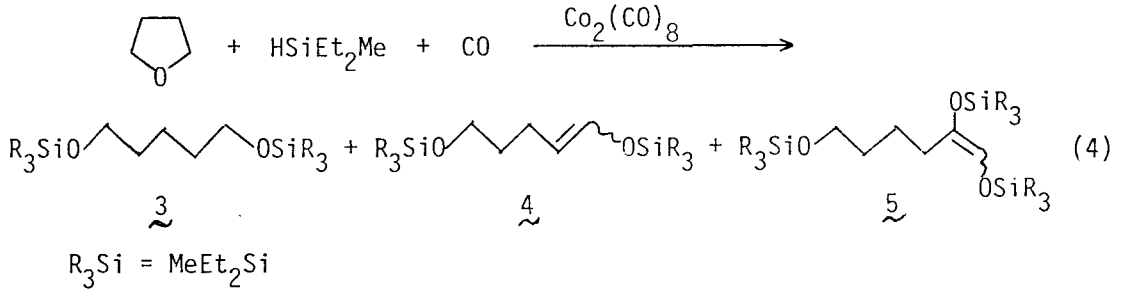
reaction of cyclic ethers with a hydrosilane and carbon monoxide in the presence of a catalytic amount of $Co_2(CO)_8$ has been studied. On the basis of the analysis described above, $R_3SiCo(CO)_4$, which would be easily generated in situ, was expected to react with cyclic ethers to form alkyl cobalt complexes of the formula $R_3SiO\{CH_2\}_nCo(CO)_4$ (eq 3).

$$\text{(cyclic ether)} + R_3SiCo(CO)_4 \longrightarrow R_3SiO\{CH_2\}_nCo(CO)_4 \qquad (3)$$

Cyclic ethers, especially oxiranes, are one of the most easily available classes of compounds[9] so that incorporation of carbon monoxide into them would lead to a new useful synthetic method.

1.2. Reaction of Unsubstituted Cyclic Ethers with a Hydrosilane and Carbon Monoxide

To begin with, the reactivity of unsubstituted tetrahydrofuran(2) was examined. The tetrahydrofuran(2) was reacted with three folds excess amounts of $HSiEt_2Me$ and CO in the presence of a catalytic amount of $Co_2(CO)_8$ in C_6H_6 at 25°C under 1 atm of CO. After 20 hrs GLC analysis showed the formation of 46 % yield of 1,5-disiloxypentane(3) and 29 % yield of 1,2,6-tris(siloxy)-hexene(5)[10] (eq 4). As



(4)

shown in Table I, the selectivity of the reaction was improved by elevating reaction temperature (at 40°C) or by changing the solvent. The reaction in CH_2Cl_2 yielded 3 exclusively (86 %). Interestingly when CH_3CN was employed as the solvent, 1,5-disiloxy-1-pentene (4) was obtained as the principal product. The results of the reaction in CH_3CN will be discussed in detail in Chapter 1.6. As the hydrosilane, $HSiMe_3$ and $HSiEt_3$ were also effective. As shown in eq 4, one

Table I. Cobalt Carbonyl Catalyzed Reaction of a Tetrahydrofuran with $HSiEt_2Me$ and CO [a]

solvent	temp, °C	yield, % [b] 3	4	5
C_6H_6	25	46	0	29
C_6H_6	40	87	0	15
C_6H_6	60	85	0	3
CH_2Cl_2	25	86	0	13
CH_2Cl_2	40	80	0	3
CH_2Cl_2	25	77	0	0 [c]
CH_2Cl_2	25	81	0	0 [d]
C_6H_{12}	25	39	3	16
Et_2O	25	56	1	11
Et_2O	40	39	1	6
DME	25	53	8	17
CH_3CN	25	2	40	2
C_6H_5CN	25	1	5	1
CCl_4, $CHCl_3$, CS_2		no reaction		

a) Reaction conditions: tetrahydrofuran(2.5 mmol), $HSiEt_2Me$(7.5 mmol), $Co_2(CO)_8$(0.2 mmol), solvent(2.5 mL), CO(1 atm). 20 h.
b) GLC yield. c) $HSiMe_3$ was used. d) $HSiEt_3$ was used.

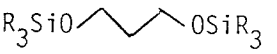
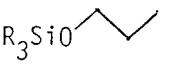
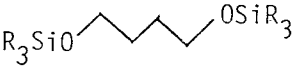
molecule of tetrahydrofuran, one molecule of carbon monoxide, and two molecules of the hydrosilane are cleanly incorporated into the product 3. The overall transformation leading to 3 is formally a nucleophilic introduction of an oxymethyl group which is not an easy task[12] from the view point of organic synthesis.

To establish the range of the applicability of this new

type of transformation, other type of cyclic ethers were also reacted with $HSiR_3$ and CO. The results are summarized in Table II.

The reaction of ethylene oxide proceeded smoothly to form 1,3-disiloxy-propane(6) in good yield. The use of n-hexane as a solvent fairly retarded the reaction rate.

Table II. Reaction of Cyclic Ethers with $HSiEt_2Me$ and CO. [a]

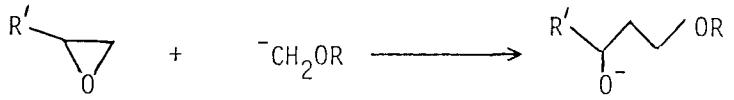
cyclic ether	solvent time	products [b] yield, %	
		 6	
	CH_2Cl_2, 5 h	91	
	C_6H_6, 20 h	90	
	n-C_6H_{14}, 48 h	39	
		 7	 8
	CH_2Cl_2, 2 h	83	16
	C_6H_6, 7 h	17	63
	DME, 7 h	17	66
	n-C_6H_{14}, 7 h	trace	96
	CH_2Cl_2, 72 h	no reaction	
	CH_2Cl_2, 72 h	no reaction	

a) Reaction conditions: cyclic ether(2.5 mmol), $HSiEt_2Me$(7.5 mmol), $Co_2(CO)_8$(0.1 mmol), solvent(5 mL), CO(1 atm), 25°C.
b) GLC yield. c) R_3Si = $MeEt_2Si$.

The reaction of oxetane in CH_2Cl_2 completed within 2 h as monitored by GLC. The products obtained, however, were 1-siloxy-propane(7) (83 % yield) and 1,4-disiloxybutane (8) (16 % yield), showing that the principal reaction of oxetane took place without incorporation of carbon monoxide. Interestingly the product distribution of this reaction was highly dependent on the solvent used. As shown in Table II, incorporation of carbon monoxdie to give 8 became exclusive reaction course when n-hexane was employed as the solvent.

The reaction of tetrahydropyran or oxepane with $HSiEt_2Me$ and CO in CH_2Cl_2 at 25°C under 1 atm of CO did not proceed and the starting material was quantitatively recovered even after 72 h.

According to these results the new reagent system of $HSiR_3$ and CO can be utilized as an oxymethylating agent of three-, four-, and five-membered cyclic ethers. The transformation is equivalent to the formal nucleophilic oxymethylation such that depicted in eq 5 for the case of 1,3-diol synthesis.

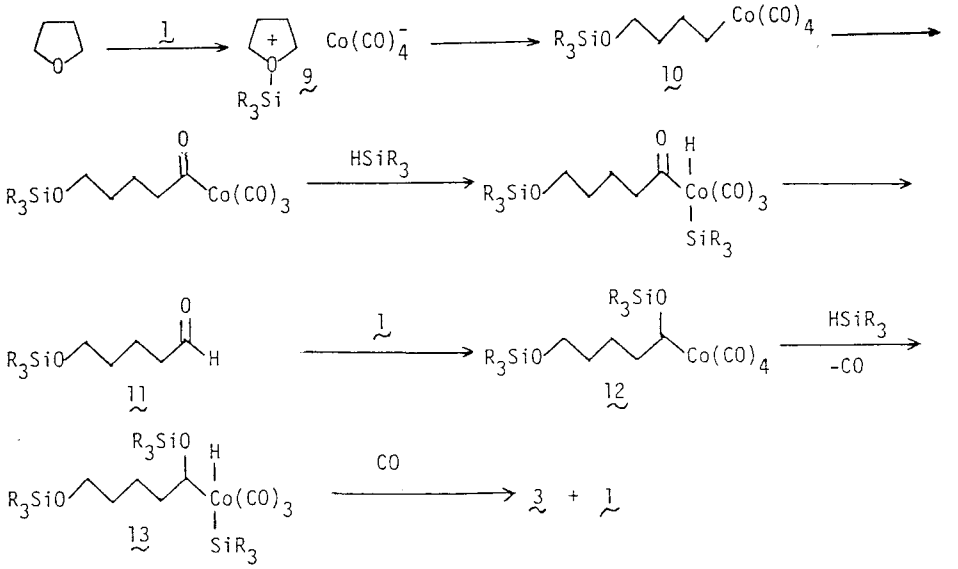


(5)

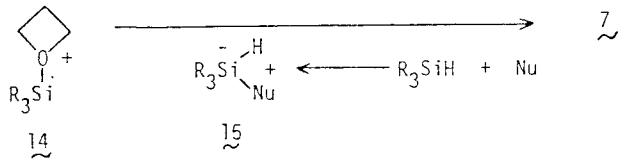
1.3. Mechanistic Aspects

Although the mechanistic details of the cobalt carbonyl catalyzed reaction of cyclic ethers with a hydrosilane and carbon monoxide has not well understood, reasonable speculations can be made on the basis of the knowledges about the accepted mechanisms of cobalt-catalyzed carbonylation[1] and cobalt carbonyl catalyzed reactions of olefins, aldehydes, and alkyl acetates with a hydrosilane and carbon monoxide.[11,13] The proposed mechanism for the formation of 3 is depicted in Scheme I. The key catalyst species in the present reaction (eq 4) would be a silylcobalt carbonyl 1. The catalytic cycle would begin with the reaction of 1 with the substrate 2 to form a silyloxonium ion intermediate 9 and $Co(CO)_4^-$, followed by nucleophilic attack of $Co(CO)_4^-$ on 9 to give an alkyl cobalt complex 10. These processes illustrate a new entry to alkyl-cobalt carbonyls. The complex 10 would undergo successive transformations, i.e. alkyl migration, oxidative addition, and reductive elimination to form siloxy aldehyde 11.[14] The aldehyde would react again with 1 to give 12 and finally afford the product 3 and regenerate silylcobalt 1 by the reductive elimination from 13. The similar reaction pathway would be depicted for the reactions of ethylene oxide and oxetane. According to the results listed in Table I and II, oxetane seems to be the most

Scheme I



Scheme II



reactive to 1 among cyclic ethers. It may be due to the higher basicity of oxygen of oxetane[15] and high strain energy of oxetane ring.[16] In the case of oxetane the product 7 may be obtained by the hydrogen transfer from $HSiR_3$[17] to 14 as depicted in Scheme II. The hydrogen transfer may require activation of $HSiR_3$ into a pentacoordinate form such as 15.[18]

The products obtainable from hydrogen transfer were not found in the reaction of ethylene oxide or tetrahydrofuran. Oxetane might play a role as the nucleophile to form the penta-coordinated intermediate 15. After transferring hydride, 15 may be converted to silyloxonium ion 14. These processes may be accelerated in a polar solvent.

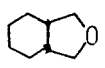
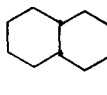
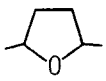
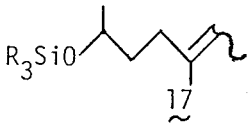
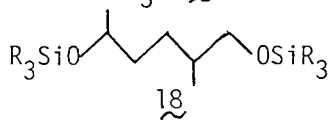
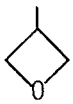
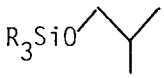
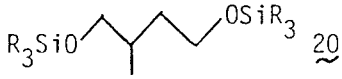
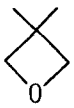
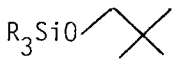
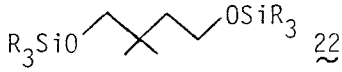
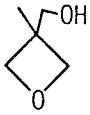
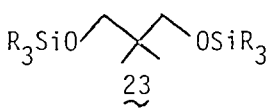
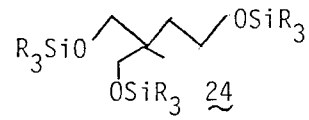
1.4. Reaction of Symmetrically Substituted Cyclic Ethers with a Hydrosilane and Carbon Monoxide

The cobalt carbonyl catalyzed reaction of cyclic ethers having substituents at various positions has been studied. Generally, incorporation of carbon monoxide took place at 25 °C under 1 atm of CO in CH_2Cl_2, C_6H_6 or n-hexane in a similar manner as has been shown for unsubstituted cyclic ethers (Table I, II) to form the corresponding diol disilyl ethers. The results obtained for symmetrically substituted cyclic ethers are given in Table III.

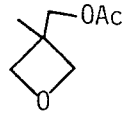
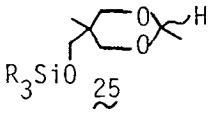
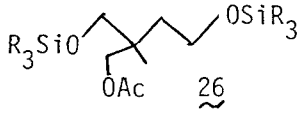
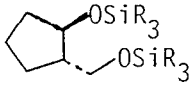
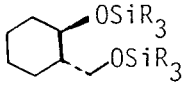
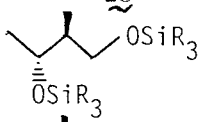
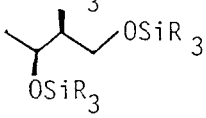
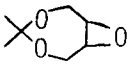
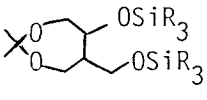
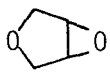
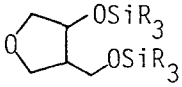
In the case of 2,5-dimethyltetrahydrofuran, the product having an unsaturated bond was detected. It may be ascribed to β-hydride elimination from the intermediate similar to 12. In such a case, the use of $HSiMe_3$ instead of $HSiEt_2Me$ was found to be effective in suppressing the byproduct formation. The less bulky $HSiMe_3$ would undergo oxidative addition (see 12 and 13 in Scheme I) more easily than $HSiEt_2Me$ to give the desired product exclusively.

Similarly to oxetane, product distribution of the reaction of substituted oxetanes was also dependent on the solvent used. Although the alkyl substituents seemed to retard the reaction rates, the reaction in n-hexane proceeded smoothly to give desired 1,4-disiloxy butanes. The reaction of oxetane having acetoxy group with $HSiEt_2Me$ and CO in n-hexane gave

Table III. Cobalt Carbonyl Catalyzed Reaction of Symmetrically Substituted Cyclic Ethers with $HSiR_3$ and CO [a]

cyclic ether	conditions	product [b], yield, % [c]	
	$HSiEt_2Me$, C_6H_6 25°C, 20 h	 56 %	
		 17	 18
	$HSiEt_2Me$, CH_2Cl_2 25°C, 20 h	38 %	56 %
	$HSiMe_3$, CH_2Cl_2 25°C, 20 h	0 %	71 %
		 19	 20
	$HSiEt_2Me$, CH_2Cl_2 0°C, 2 h	64 %	11 %
	$HSiEt_2Me$, n-C_6H_{14} 25°C, 20 h	1 %	95 %
		 21	 22
	$HSiEt_2Me$, CH_2Cl_2 0°C, 7 h	68 %	12 %
	$HSiMe_3$, n-C_6H_{14} 25°C, 20 h	trace	67 %
		 23	 24
	$HSiMe_3$, CH_2Cl_2 25°C, 20 h	61 %	0 %
	$HSiMe_3$, n-C_6H_{14} 25°C, 20 h	7 %	76 %

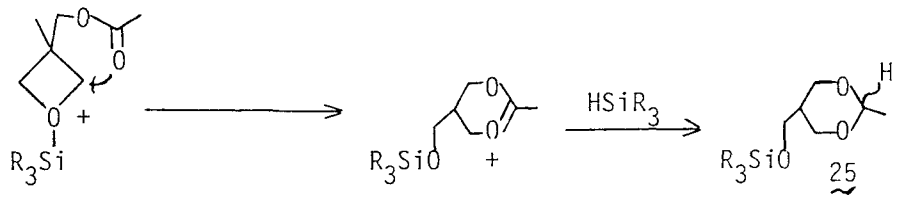
Continued

		 25	 26	
	$HSiEt_2Me$, CH_2Cl_2 25°C, 20 h	81 %	4 %	
	$HSiMe_3$, n-hexane 25°C, 20 h	0 %	87 %	
	$HSiEt_2Me$, n-hexane 25°C, 20 h	18 %	36 %	
	$HSiEt_2Me$, C_6H_6 25°C, 3 h	 27		88 %
	$HSiEt_2Me$, C_6H_6 25°C, 1 h	 28		65 %
	$HSiEt_2Me$, C_6H_6 25°C, 20 h	 29		60 %
	$HSiEt_2Me$, C_6H_6 25°C, 20 h	 30		73 %
	$HSiMe_3$, $CH_3C_6H_5$ 25°C, 20 h	 31		86 % [d]
	$HSiEt_2Me$, C_6H_6 25°C, 20 h	 32		100 % [d]

a) Reaction conditions: cyclic ether(2.5 mmol), $HSiEt_2Me$(7.5 mmol), or $HSiMe_3$(2.5 mmol), $Co_2(CO)_8$(0.1 mmol), solvent(5 mL), CO(1 atm). b) R_3Si stands for $MeEt_2Si$ or Me_3Si. c) GLC yield. d) The stereochemistry has not been established yet.

the product 26 and cyclic compounds 25, respectively, in low yield. The product 25 may be obtained by the intramolecular attack of acetoxy group on silyloxonium ion intermediate (Scheme III). The product 25 was selectively obtained by the

Scheme III



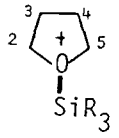
reaction in CH_2Cl_2. The desired reaction leading to 26 could be attained by the reaction with $HSiMe_3$ in n-hexane.

The stereochemistry of the reaction is of interest and importance. The results obtained for cyclopentene oxide indicates the stereochemical course of the ring opening to be trans. This is also the case with cyclohexene oxide (65 % yield of the corresponding disilyl ether).[19,20] The trans opening has been further demonstrated in the acyclic system, namely, the stereospecific synthesis of threo- and erythro-2-methyl-1,3-diol derivatives. These results imply that the carbon-oxygen bond cleavage with concomitant formation of the carbon-cobalt bond (9⟶10 in Scheme I) would proceed with inversion of configuration at the carbon atom.[21]

Chemo- and stereoselective ring opening was observed for the reaction of cyclic ether having both three- and five-membered ring.[22]

1.5. Reaction of Unsymmetrically Substituted Cyclic Ethers with a Hydrosilane and Carbon Monoxide

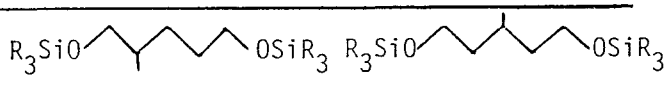
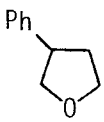
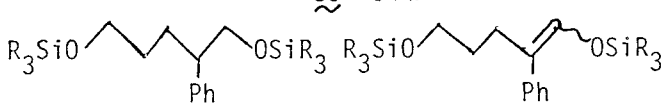
The regiochemistry of the reaction of unsymmetrically substituted cyclic ethers has been studied. As summarized



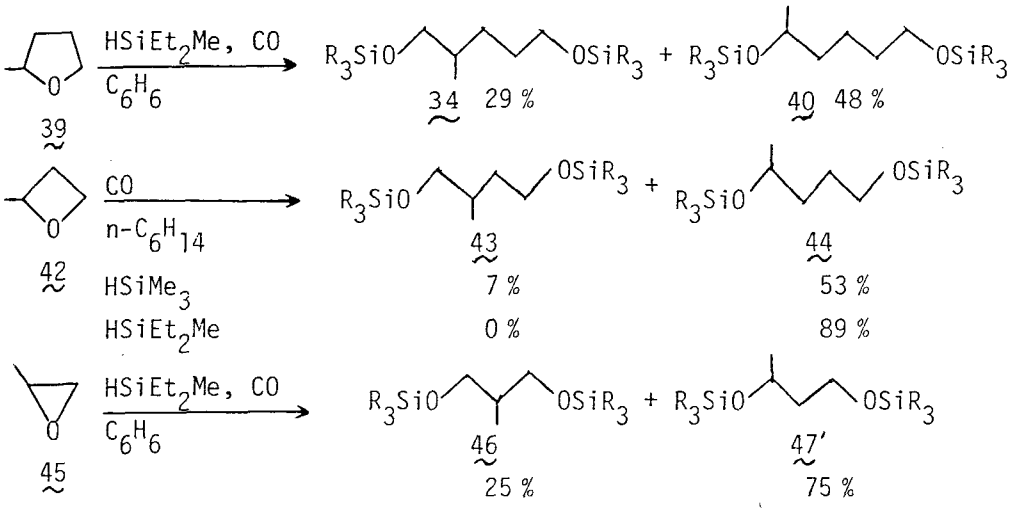
9

in Table IV, introduction of substituents at the C-3 position of tetrahydrofuran has resulted in the incorporation of carbon monoxide predominantly (run 1) or exclusively (run 2,3 4) at C-5, probably due to sterically unfavorable approach of $Co(CO)_4^-$ to C-2 in the silyloxonium ion corresponding to 9.

Table IV.

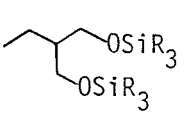
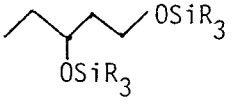
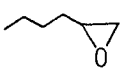
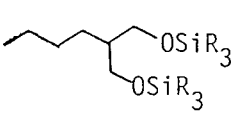
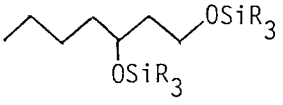
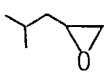
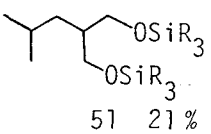
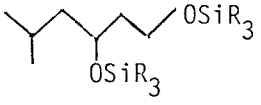
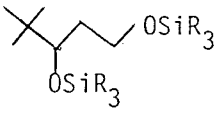
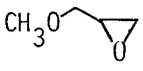
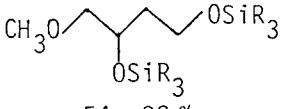
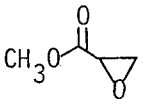
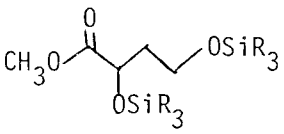
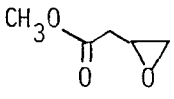
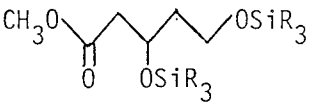
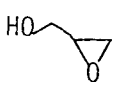
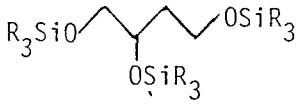
run	THF	conditions	product, yield
1		$HSiEt_2Me$, C_6H_6 25°C, 20 h	 34 70 % 35 8 %
2		$HSiEt_2Me$, C_6H_6 25°C, 20 h	 36 84 %
			 37 38
3		$HSiEt_2Me$, CH_2Cl_2 25°C, 20 h	59 % 18 %
4		$HSiMe_3$, CH_2Cl_2 25°C, 20 h	54 % 2 %

Although a byproduct having double bond was observed for 3-phenyltetrahydrofuran, the use of $HSiMe_3$ suppressed the formation of the byproduct.

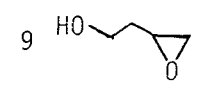
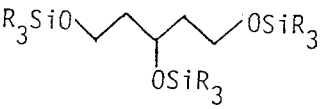
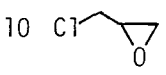
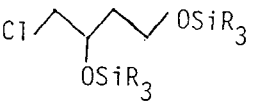
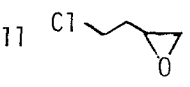
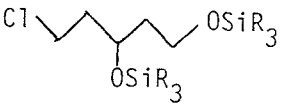
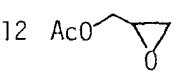
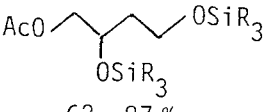
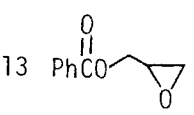
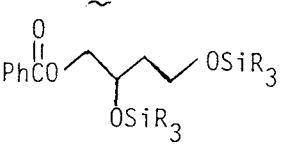


The ring opening of 2-methyltetrahydrofuran(39) took place both at C-5 and C-2 to give 2-methyl-1,5-disiloxypentane (40) and 3-methyl-1,5-disiloxypentane(34) in a ratio of 62 : 38 in 77 % combined yield. Similar tendency for regioselectivity was observed for the reaction of propene oxide (45). Interestingly ring opening of 2-methyloxetane(42) with $HSiMe_3$ and CO in n-hexane took place predominantly at less-substituted carbon center.[23] A complete regioselection was observed for the reaction of 42 with $HSiEt_2Me$ and CO in n-hexane, only 2-methyl-1,4-disiloxybutane(44) being obtained in 89 % yield. Comparing with the regioselectivity of ring opening of 39 or 45, the oxetane 42 seems to be the special case to exhibit the high regioselectivity. Although no clear

Table V.

run	oxirane	conditions	product, yield, %
1		$HSiEt_2Me$, 25°C C_6H_6, 9 h	 47 33 %  48 66 %
2		$HSiEt_2Me$, 25°C C_6H_6, 20 h	 49 18 %  50 40 %
3		$HSiMe_3$, 25°C CH_2Cl_2, 48 h	 51 21 %  52 60 %
4		$HSiMe_3$, 0°C CH_3-Ph, 10 h	 53 73 %
5		$HSiEt_2Me$, 25°C C_6H_6, 20 h	 54 82 %
6		$HSiEt_2Me$, 25°C C_6H_6, 48 h	 55 83 %
7		$HSiEt_2Me$, 25°C CH_2Cl_2, 24 h	 56 83 %
8		$HSiMe_3$, 0°C CH_3-Ph, 20 h	 57 92 %

continued

9		$HSiEt_2Me$, 25°C C_6H_6, 20 h	 58 81 %
10		$HSiMe_3$, 25°C C_6H_6, 48 h	 59 71 %
11		$HSiMe_3$, 25°C C_6H_6, 48 h	 60 63 %
12		$HSiMe_3$, 0°C C_6H_6, 72 h	 62 87 %
13		$HSiMe_3$, 25°C CH_2Cl_2, 20 h	 64 98 %

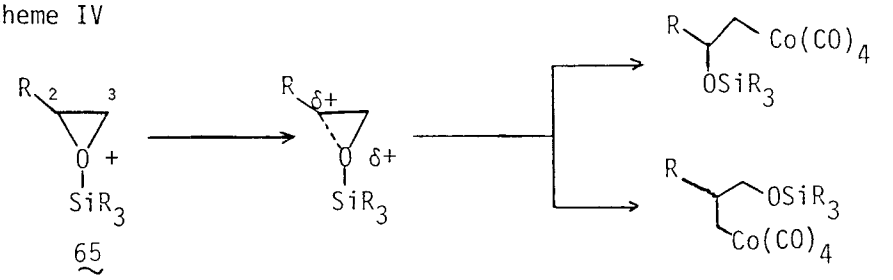
explanation for the high regioselectivity can be offered at the present time, similar high regioselectivity was observed by Weber et al., in the ring opening of 42 with Me_3SiCl.[24]

The regioselectivity of the reaction of various oxiranes were investigated, since functionalized oxiranes are readily accessible from substituted olefins[9], and the regioselective introduction of a siloxymethyl group to oxiranes would provide a useful method for the preparation of 1,3-diol derivatives.[25] The results were summarized in Table V. As in the

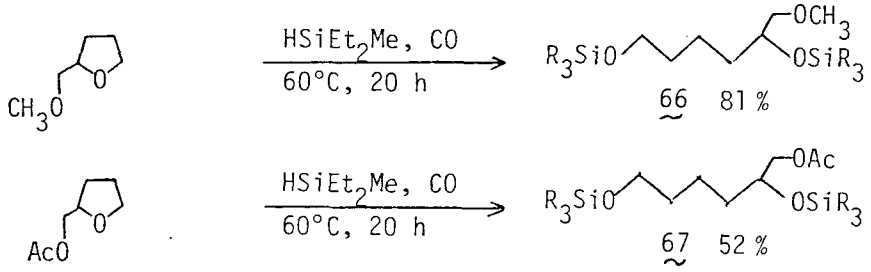
case of oxirane 45 described above, a mixture of regioisomers were obtained from alkyl substituted oxiranes (run 1, 2, and 3). Highly regioselective ring opening of the oxirane having t-butyl group (run 4) indicates importance of steric factor. High regioselectivity was observed in the reaction of oxiranes having oxygen or chlorine substituents. In these cases functional groups such as methoxy, methoxycarbonyl, chloro, acetyl, or benzoyl could tolerate the reaction conditions. The purity of the products was estimated as greater than 95 % on the basis of 100 M Hz NMR spectra (CCl_4) for runs 5 - 11. In the case of runs 12 and 13, addition of $Eu(thd)_3$ to NMR samples of the products causes separation of signals for the regioisomeric methylene protons. These spectra showed that the ring opening took place at C-2 to form 62 and 64 with ca. 90 % selectivity.

The regio-determing step of the reaction may be the attack of $Co(CO)_4^-$ on silyloxonium ion intermediate(65), as depicted in Scheme IV. The ring opening at C-3 (a primary center) is likely to involve S_N2-like attack of $Co(CO)_4^-$,

Scheme IV



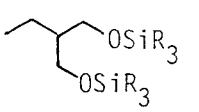
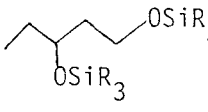
whereas cleavage at C-2(a secondary center) would be accounted for by assuming the development of partial positive charge at this carbon atom in the transition state and proceed by a borderline S_N2 mechanism in which S_N2 transition state possesses substantial S_N1 character. High regioselectivity observed for run 5 - 13 may be due to the suppression of the development of the partial positive charge at C-2 by an electron withdrawing group. The effect of electron withdrawing group has been further demonstrated by the reaction of tetrahydrofurfuryl alchol derivatives.



As listed in Table VI, various attempts to achieve highly regioselective ring opening of 1-butene oxide[26] has been made. Although the yield was rather low, the use of tetramethylurea resulted in the improvement of the regioselectivity.

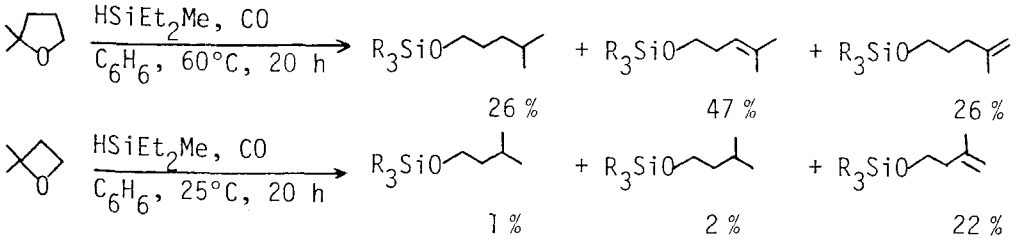
The ring opening of cyclic ethers having tertiary carbon center was expected to occur at a tertiary center, since the development of the partial positive charge would be highly enhanced at a tertiary center. As expected, the ring opening

Table VI

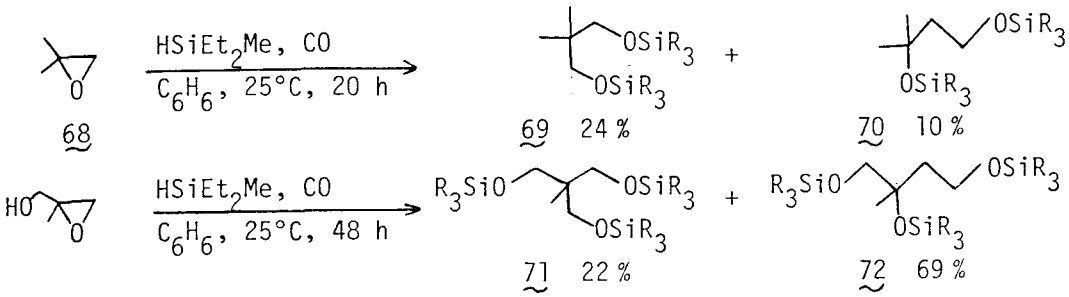
$HSiR_3$	solvent	additive	yield, % 		ratio
$HSiEt_2Me$	C_6H_6	-	33	66	1 : 2.0
		$Me_4N^+OAc^-$	23	45	1 : 1.9
		$Bu_4N^+F^-$	20	42	1 : 2.2
$HSiMe_3$	$CH_3C_6H_5$	-	15	31	1 : 2.0
		Bu_3P	12	33	1 : 2.8
		Et_3N	15	54	1 : 3.6
		$(Me_2N)_2C=O$	3	25	1 : 11.7

Reaction conditions: 1-butene oxide(2.5 mmol), $HSiEt_2Me$(7.5 mmol) or $HSiMe_3$(25 mmol), $Co_2(CO)_8$(0.1 mmol), additive(0.2 mmol), solvent (5 mL), CO(1 atm), 25°C, 20 h.

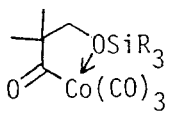
of 2,2-dimethyltetrahydrofuran and 2,2-dimethyloxetane took place exclusively at the tertiary centers, but without incorporation of carbon monoxide.



Interestingly the ring opening of 2-methylpropene oxide (68) took place at both sites to form 24 % yield of 2,2-



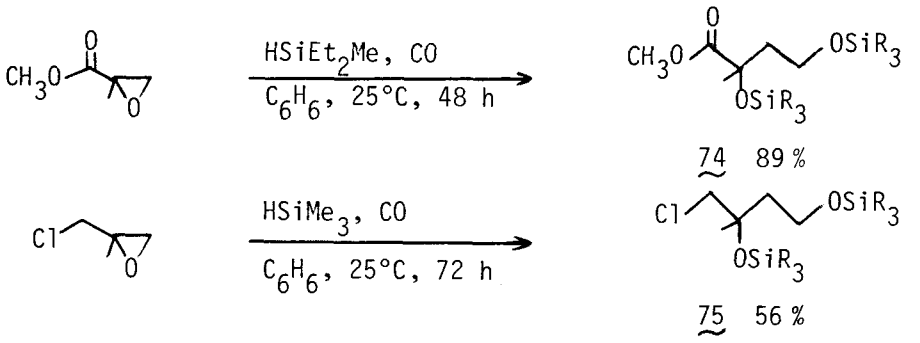
dimethyl-1,3-disiloxypropane(69) and 10 % yield of 2-methyl-1,3-disiloxybutane(70) with byproducts derived from ring opening at a tertiary center without incorporation of CO. The incorporation of carbon monoxide took place at the tertiary carbon center of 68. It should be noted that the precedents of CO insertion into a tertiary carbon transition metal bond were extremely limited even in the stoichiometric reactions.[27,28] In the case of 2-methyl-2,3-epoxypropanol, carbon monoxide was also incorporated into the product drived from ring opening at the tertiary center. Incorporation of CO into the tertiary center at oxiranes may be due to the stabilization of an acyl complex by a coordination of oxygen to cobalt like 73.



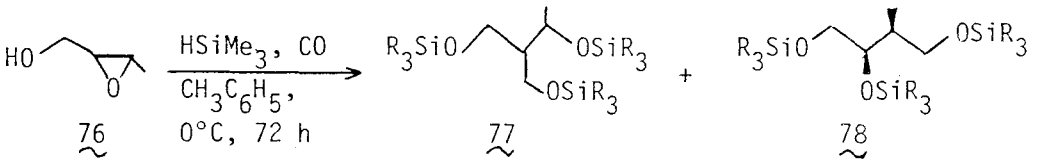
73

For the similar type of oxiranes but having an electron

withdrawing group, incorporation of CO at the tertiary center was not observed.



Finally the ring opening of trans-2,3-epoxybutane-1-ol (76) has been studied. The reaction of 76 with $HSiMe_3$ and CO in CH_2Cl_2 at 0°C proceeded slowly to form 77 and 78 in 34 and 56 % yield. The structure of the product 78 was



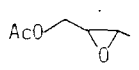
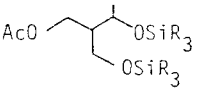
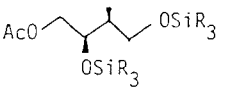
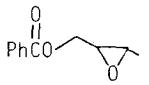
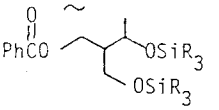
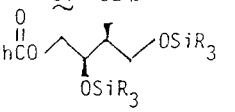
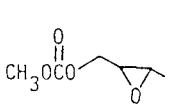
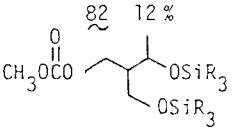
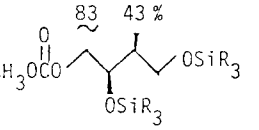
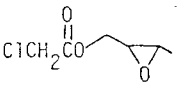
identified by the comparison of 270 MHz NMR data of the hydrolysis product of the mixture of 77 and 78 with the 1H NMR data of 2-methyl-1,2,4-butane-triol (79) in the literature.[29]

threo-79 erythro-79

As already observed for cis and trans 2-butene oxide, the

ring opening of 76 proceeded with inversion to give threo form of 78. Since preparation of optically pure epoxy alchol 76 has been reported by Sharpless et al.,[30] optically pure triol 79, which is often employed as a key intermediate in natural products syntheses,[31] will be obtained by the reaction of $HSiR_3$ and CO. In order to enhance the regioselectivity leading to 78, the reaction of some ester derivatives of 76 was investigated.[32] As shown in Table VII, the regioselectivity was moderately improved by the introduction of acetyl, benzoyl, or methoxycarbonyl group. High enhancement of regioselectivity was achieved by derivatization of the alchol 76 with chloroacetyl group.

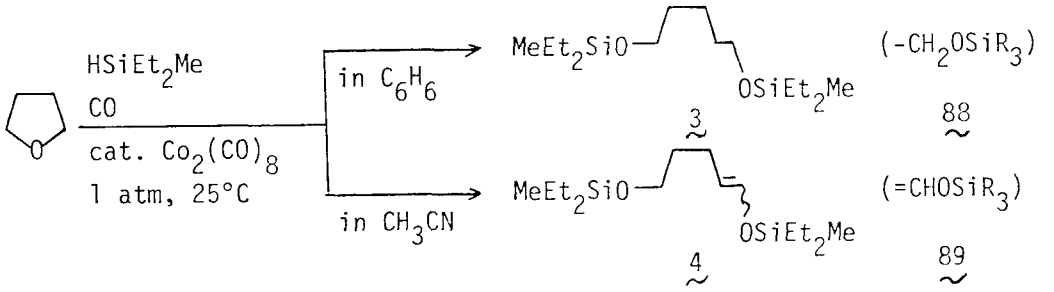
Table VII

oxirane	temp, time	product, yield	
	0°C, 72 h	 80 17 %	 81 62 %
	25°C, 48 h	 82 12 %	 83 43 %
	25°C, 48 h	 84 12 %	 85 60 %
	0°C, 72 h	86 3 %	87 67 %

Reaction conditions: oxirane(2.5 mmol), $HSiMe_3$(25 mmol), $Co_2(CO)_8$(0.1 mmol), solvent(5 mL), CO(1 atm).

1.6. Ring Opening of Tetrahydrofurans Leading to Enol Silyl Ethers

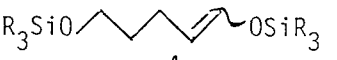
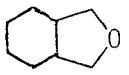
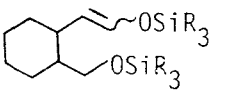
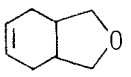
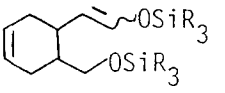
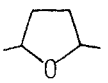
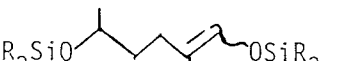
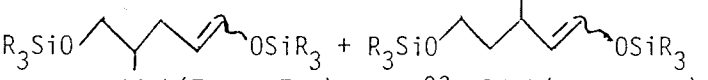
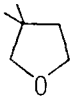
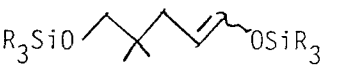
During the course of the study on the cobalt carbonyl catalyzed reactions of tetrahydrofuran (2) with a hydrosilane and carbon monoxide, a new type of reaction of 2 has been found. As already described in Chapter 1.2., the reaction of 2 with $HSiEt_2Me$ and CO in the presence of $Co_2(CO)_8$ at 1 atm and 25°C using C_6H_6 or CH_2Cl_2 as the reaction solvent gave 1,5-disiloxypentane (3), into which the reactant CO is incorporated as the oxymethyl group (88). The complete change in the product distribution has been brought about by simply changing the reaction solvent from C_6H_6 to CH_3CN. In the present reaction, carbon monoxide has ended up in the form of an oxymethylidene group (89) instead of the oxymethyl moiety (88)



The cobalt carbonyl catalyzed reaction of 2 with $HSiEt_2Me$ and CO in CH_3CN gave a stereoisomeric mixture (57 %

yield) of (Z)- and (E)-4 (3 : 1) and a small amount of 3 (3 % yield). The reaction also proceeded in a mixed solvent of CH_3CN-C_6H_6 (1 : 1) to give 4 (66 %, Z : E = 3 : 1) and 3 (0.3 %).

Table VIII. Cobalt Carbonyl Catalyzed Reaction of Tetrahydrofurans with $HSiEt_2Me$ and CO in CH_3CN

tetrahydrfuran	product(R_3Si = $MeEt_2Si$), yield, %
	 57 % (Z:E = 3:1)
	4
	 90 50 % (Z:E = 1:1)
	 91 41 % (Z:E = 1:1)[a]
	 16 % (Z:E = 1:1) (50 %)[b]
	17
	
	92 34 % (Z:E = 7:3) 93 16 % (Z:E = 7:3)
	 40 % (Z:E = 7:3)
	94

Reaction conditions: tetrahydrofuran(2.5 mmol), $HSiEt_2Me$(7.5 mmol), $Co_2(CO)_8$(0.2 mmol), CH_3CN(5 mL), CO(1 atm), 25°C, 20 h
a) $Co_2(CO)_8$(0.4 mmol). b) $Co_2(CO)_8$(1.25 mmol).

The results obtained for some substituted tetrahydrofurans in CH_3CN are given in Table VIII. Although the yields are only moderate, the selective formation of enol silyl ethers seems of general for tetrahydrofurans.[33] The function of CH_3CN is not understood yet. There exist many possibilites: acetonitrile may act as a ligand for a cobalt intermediate, as a base for proton abstraction from an intermediate, or as a solvent to stabilize a carbocationic intermediate. It has been reported that an enol silyl ether similar to 4 was found among the products when $Me_3SiCo(CO)_4$ was decomposed in tetrahydrofuran (2).[34]

1.7. Experiment

1.7.1 General Procedures

Infrared spectra were recorded with a Shimazu IR-400 or JASCO grating IR spectrophotometer IR-G; absorptions are reported in reciprocal centimeters. ^{1}H NMR were recorded on a Japan Electron Optics JNM-PS-100 spectrometer or Japan Electron Optics JNM-GX 270 FT-NMR spectrometer operating at 100 and 270 MHz respectively with Me_4Si or $CHCl_3$ as an internal standard. The position of Me_4Si was recognized by adding the standard after the spectrum recorded without it. Otherwise the signal of the standard may be confused with that of organosilicon compounds. 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 Japan Electron Optics JNM-FX-60s spectrometer and are reported in ppm from tetramethylsilane on the δ scale. Mass spectra were recorded on a model RMU-6E instrument operating at 70 eV. Elemental analyses were performed by Elemental Analyses Center of Osaka University. Analytical gas chromatography (GLC) were carried out on a Shimazu GC-3BF or a Hitachi Model 163 equipped with a flame ionization detector, using a 6 m $\times$ 3 mm stainless steel

column packed with 5% Silicone OV-1 supported on 60-80 mesh Chromosorb W(AW). Preparative GLC was carried out using Hitachi Model K 53 gas chromatograph using 2 m × 10 mm stainless steel column packed with 5% Silicone OV-1 supported on 60-80 mesh Chromosorb W.

Benzene, toluene, 1,2-dimethoxyethane (DME), and n-hexane were distilled from sodium-lead alloy. Dichloromethane was distilled from CaH_2. Acetonitrile was distilled from sodium carbonate after drying over phosphorus pentoxide. Carbon monoxide was purchased from Neriki gas Co. and used as received. $Co_2(CO)_8$ was purchased from Strem Chemical Co., recrystallized from n-hexane (25°C to -20°C) and stored under carbon monoxide atmosphere in a refrigerator. Hydrosilanes were prepared from Chlorosilanes following literature procedures.[35]

1.7.2 General procedure for Cobalt Carbonyl Catalyzed Reaction of Cyclic Ethers with a Hydrosilane and Carbon Monoxide

A 10 mL two-necked round-bottom flask equipped with a Teflon-coated magnetic stirrer bar was flame dried and then charged with 0.0342 g (0.1 mmol) of $Co_2(CO)_8$, fitted with a serum cap and CO balloon and flushed with carbon monoxide. To the flask was added 1.1 mL (7.5 mmol) of $HSiEt_2Me$ with a syringe. After five minutes, to this solution were added 5

mL of solvent and 2.5 mmol of cyclic ether. The solution was stirred for an appropriate period, a few drops of pyridine were added to it, and the air was bubbled for about fifteen minutes. The precipitate was separated by centrifugation. Solvent was evaporated in vacuo and distillation gave a pure sample of the product, when necessary, purification by preparative GLC was carried out. For GLC yields, appropriate hydrocarbons ($n\text{-}C_nH_{2n+2}$) calibrated against purified products were added before or immediately after the reaction.

1.7.3 Characterization of Products

Spectroscopic properties of the products are as follows. ^1H NMR data without indication were obtained at 100 MHz.

3,11-Diethyl-3,11-dimethyl-4,10-dioxa-3,11-disilatridecane(3): for a sample obtained by distillation, bp 99-101 °C/0.3 mmHg; IR (neat) 2950, 2910, 2875, 1460, 1255, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.01 (s, 6H, $Si\text{-}CH_3$), 0.36-0.66(m, 8H, $Si\text{-}CH_2$), 0.76-1.06(m, 12H, $Si\text{-}C\text{-}CH_3$), 1.14-1.68(m, 6H, CH_2), 3.52(t, 4H, J = 5.7 Hz, CH_2); Mass m/e 289 (0.4, M^+-Me), 275 (0.4, M^+-Et), 189(30), 161(19), 101(7), 89(21), 69(100); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.91. Found: C, 59.02; H, 12.13.

2,2,10,10-Tetramethyl-3,9-dioxa-2,10-disilaundecane: for a sample obtained by bulb to bulb distillation, bp 120 °C(oven)/22 mmHg; IR (neat) 2950, 2850, 1440, 1392, 1250, 1095, 840 cm^{-1}; ^1H NMR (CCl_4) δ 0.00(s, 18H, Si-CH_3), 1.34 (m, 6H, CH_2), 3.44(t, J = 8 Hz, CH_2-O); Mass m/e 233(M^+-CH_3, 4), 177(11), 158(15), 147(100), 103 (19); Anal. Calcd for $C_{17}H_{40}O_2Si_2$: C, 53.16; H, 11.36. Found: C, 53.01; H, 11.57.

3,3,11,11-Tetraethyl-4,10-dioxa-3,11-disilatridecane: for a sample obtained by bulb to bulb distillation, bp 120 °C(oven)/0.3 mmHg; IR (neat) 2850, 1455, 1415, 1385, 1230, 1090, 1000, 790, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.59(m, 12H, Si-CH_2), 0.97(m, 18H, Si-C-CH_3), 1.36(m, 2H, CH_2), 1.52(t, J = 7.11 Hz, 4H, CH_2), 3.60(t, J = 7.11 Hz, 4H, CH_2-O); Mass m/e 303(M^+-Et, 21), 274(5), 217(55), 189(45), 89(24), 69 (100); Anal. Calcd for $C_{17}H_{40}O_2Si_2$: C, 61.38; H, 12.12. Found: C, 61.24; H, 12.32.

3,9-Diethyl-3,9-dimethyl-4,8-dioxa-3,9-disilaundecane (6): for a sample obtained by distillation, bp 120°C/1 mmHg: IR (neat) 2952, 2911, 2877, 1460, 1418, 1252, 1090, 797, 750 cm^{-1}; ^1H NMR (CCl_4) δ 0.00(s, 6H, Si-CH_3), 0.4-0.88(m, 20H, Si-CH_2-C, Si-C-CH_3), 1.63(quintet, J = 6 Hz, 2H, C-CH_2-C), 3.62(t, J = 6 Hz, 4H, CH_2-OSi); Mass m/e 276(M^+, 1.2), 247 (68), 189(100), 161(56); Anal. Calcd for $C_{13}H_{32}O_2Si_2$: C,

56.46; H, 11.66. Found: C, 56.39; H. 11.72.

3,10-Diethyl-3,10-dimethyl-4,9-dioxa-3,10-disiladodecane: (8): for a sample obtained by bulb to bulb distillation; bp 100 °C(oven)/0.4 mmHg; IR (neat) 2950, 2880, 1460, 1420, 1390, 1260, 1100, 1010, 800, 760 cm^{-1}; ^1H NMR (CCl_4) δ 0.01(s, 6H, $Si-CH_3$), 0.6(m, 8H, $Si-CH_2$), 1.2(m, 12H, $Si-C-CH_3$), 1.33(m, 4H, CH_2), 3.64(m, 4H, CH_2-O); Mass m/e 261(M^+-Et, 26), 190(100), 161 (51); Anal. Calcd for $C_{14}H_{34}O_2Si_2$: C, 57.87; H, 11.79. Found: C, 57.72; H, 12.00.

(cis-2-Diethylmethylsiloxymethyl)cyclohexylethoxy-(diethylmethyl)silane(16): for a sample obtained by distillation bp 124-126 °C/ 0.35 mmHg; IR (neat) 2950, 2920, 2880, 1460, 1415, 1390, 1255, 1080, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.01(s, 6H, $Si-CH_3$), 0.37-0.69(m, 8H, $Si-CH_2$), 0.77-1.09(m, 12H, $Si-C-CH_3$), 1.09-1.97(c, 12H), 3.46 (d, 2H, J = 6.0 Hz, CH_2O), 3.56(t, 2H, J = 6.5 Hz, CH_2-O); Mass m/e 329(M^+-Et, 4.3), 211(41), 189(67), 161(26), 123(100), 81(81); Anal. Calcd for $C_{19}H_{42}O_2Si_2$: C, 63.62; H, 11.80. Found: C, 63.88; H, 11.96.

3,11-Diethyl-4,10-dioxa-3,11-disila-3,5,8,10-tetramethyltrideçane(18): for a sample obtained by bulb to bulb distillation; bp 100°C(oven)/0.35 mmHg; IR (neat) 2960, 2945,

2910, 2880, 1460, 1380, 1250, 1090, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 6H, Si-CH_3), 0.34-0.70(m, 8H, Si-CH_2), 0.81-1.01(m, 18H, Si-C-CH_3, CH_3), 1.19- 1.72(c, 5H, CH_2, CH), 3.35(dd, 2H, J = 5.5 Hz and 1.0 Hz, CH_2-O), 3.71(sextet, 1H, J = 5.7 Hz, CH-O); Mass m/e 303(M^+-Et, 2), 189(32), 101(18), 97(90), 89 (11), 73(19), 61(20), 55(100); Anal. Calcd for $C_{19}H_{42}O_2Si_2$: C, 61.38; H, 12.12. Found: C, 61.67; H, 12.32. No effort was made to determine the ratio of diastereoisomers at present time.

(2,5-Dimethyl-5-pent-1-enyl)bis(oxy)bis(diethylmethyl)-silane (17): for a mixture of (E) and (Z)-stereoisomers; bp 106-110°C/0.5 mmHg; IR (neat) 2955, 2945, 2910, 2880, 1680 (C=C), 1460, 1255, 1080, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 6H, Si-CH_3), 0.09(s, 6H, Si-CH_3), 0.37-0.74(m, 8H, Si-CH_2), 0.82-1.17(m, 15H, Si-C-CH_3, CH_3), 1.25-1.59(m, 5H, =C-CH, CH_2), 1.69-2.29(m, 2H, =C-CH_2), 3.71(sextet, 1H, J = 6.0 Hz, CH-O), 5.88-6.02(m, 1H, CH=); Mass m/e 330(M^+, 4.1), 315(M^+ -Me, 0.9), 301(8.4), 212(76), 189(14), 101(54), 89(100); Anal. Calcd for $C_{17}H_{38}O_2Si_2$: C, 61.75; H, 11.58. Found: C, 61.48; H, 11.84. It was difficult to determine the E/Z ratio from these spectra.

2,2,4,7,10,10-Hexamethyl-3,9-dioxa-2,10-disilaundecane (18): for a samplle obtained by bulb to bulb distillation;

bp 130°C(oven)/1 mmHg; IR (neat) 2950, 2900, 2860, 1460, 1390, 1250, 1090, 840 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 18H, Si-CH_3), 0.8(d, 3H, J = 6 Hz, CH_3), 1.04(d, 3H, J = 6 Hz, CH_3), 1.3(m, 5H, CH_2, CH), 3.27(dd, 2H, J = 2 Hz and 6 Hz, CH_2O), 3.65 (sextet, 1H, J = 6 Hz, CH-O); Mass m/e 186(M^+-CH_3, 6). 147 (5), 117(100), 97(4), 73(13); Anal. Calcd for $C_{17}H_{38}O_2Si_2$: C, 56.46; H, 11.66. Found: C, 56.26; H, 11.78. No effort was made to determine the ratio of diastereoisomers at present time.

3,10-Diethyl-3,6,10-trimethyl-4,9-dioxa-3,10-disiladodecane(20): for a sample obtained by bulb to bulb distillation; bp 120°C(oven)/ 3 mmHg; IR (neat) 2950, 2880, 1460, 1420, 1400, 1260, 1100, 800, 760 cm^{-1}; ^1H NMR (CCl_4) δ 0.04 (s, 6H, Si-CH_3), 0.6(m, 8H, Si-CH_2), 0.9(m, 15H, Si-C-CH_3 and CH_3), 1.3(m, 2H, CH_2), 1.6(m, 1H, $CH(C)_2$), 3.5(dd, J = 6 Hz and 2 Hz, CH_2-O), 3.7(t, J = 6 Hz, 2H, CH_2-O); Mass m/e 285 (M^+-Et, 10), 217(14), 187(100), 172(50); Anal Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.91. Found: C, 58.97; H, 12.13.

3,10-Diethyl-3,6,6,10-tetramethyl-4,9-dioxa-3,10-disiladodecane(22): for a sample obtained by bulb to bulb distillation: bp 97°C(oven)/ 1 mmHg: IR (neat) 2940, 2860, 1460, 1250, 1090, 1000, 830, 800, 780 cm^{-1}; ^1H NMR (CCl_4) δ 0.1(s, 6H, Si-CH_3), 0.8(m, 8H, Si-CH_2), 1.2(complex, 18H, Si-C-CH_3

and CH_3), 1.68(t, J = 6 Hz, 2H, CH_2), 3.42(s, 2H, CH_2-O), 3.84(t, J = 6 Hz, 2H, CH_2-O); Mass m/e 289(M^+-Et, 15), 287 (10), 201(5), 187(100); Anal. Calcd for $C_{16}H_{38}O_2Si_2$: C, 60.30; H, 12.02. Found: C, 60.05; H, 12.11.

2,2,5,5,9,9-Hexamethyl-3,8-dioxa-2,9-disiladecane(22): for a sample obtained by bulb to bulb distillation: bp 150°C (oven)/20 mmHg; IR (neat) 2950, 2800, 1475, 1395, 1365, 1250, 1080, 990, 870, 830, 750 cm^{-1}; ^1H NMR(CCl_4) δ 0.02(s, 18H, Si-CH_3), 0.9(s, 6H, CH_3), 1.46(t, J = 8 Hz, 2H, CH_2), 3.22(s, 2H, CH_2-O), 3.62(t, J = 8 Hz, 2H, CH_2-O); Mass m/e 262(M^+, 3), 177(17), 157(28), 147(100), 144(72); Anal. Calcd for $C_{12}H_{30}O_2Si_2$: C, 54.90; H, 11.52. Found: C, 54.96; H, 11.71.

2,2,5,5,8,8-Hexamethyl-3,7-dioxa-2,8-disilanonane(23): for a sample obtained by bulb to bulb distillation: bp 120°C (oven)/12 mmHg; IR (neat) 2910, 2856, 2821, 1475, 1398, 1359, 1258, 1087, 1000, 913, 874, 843, 748 cm^{-1}; ^1H NMR (CCl_4) δ 0.09(s, 18H, Si-CH_3), 0.80(s, 6H, CH_3), 3.25(s, 4H, CH_2-O); Mass m/e 233(M^+-CH_3,3), 191 (7), 168(22), 157(92), 153(89), 133(11), 103(27), 73(100); Anal. Calcd for $C_{11}H_{28}O_2Si_2$: C, 53.16; H, 11.35. Found: C, 52.96; H, 11.37.

((5-β,β-Dimethyl)-α-oxa-β-sila)butyl-2,2,5,9,9-pentamethyl-3,8-dioxa-2,9-disiladecane(24): for a sample obtained

by bulb to bulb distillation: bp 150°C(oven)/15 mmHg; IR (neat) 2910, 2856, 2821, 1475, 1401, 1259, 1245, 1077, 1038, 906, 871, 843, 759 cm^{-1}; ^1H NMR (CCl_4) δ 0.09(s, 27H, Si-CH_3), 0.80(s, 3H, CH_3), 1.42(t, 2H, J = 7.5 Hz, CH_2), 3.30(s, 4H, CH_2-O), 3.60(t, 2H, J = 7.0 Hz, CH_2-O). Mass m/e 335(M^+-CH_3, 2), 245(4), 217(5), 191(9), 170(10), 155(98), 147(44), 143 (17), 103(31), 73(100); Anal. Calcd for $C_{15}H_{38}O_2Si_2$: C, 51.36; H, 10.92. Found: C, 51.34; H, 10.87.

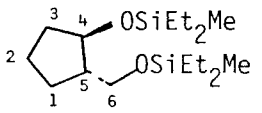
Acetic acid 2-(γ,γ-dimethyl-β-oxa-γ-sila)butyl-5-oxa-6-sila-2,6,6-trimethylheptyl ester(26): for a sample obtained by bulb to bulb distillation: bp 150°C(oven)/ 15 mmHg; IR (neat) 2910, 2856, 2821, 1737, 1377, 1248, 1087, 1035, 871, 839, 755 cm^{-1}; ^1H NMR (CCl_4) 0.08(s, 18H, Si-CH_3), 0.88(s, 3H, CH_3), 1.47(t, J = 7 Hz, 2H, CH_2), 1.98(s, 3H, CH_3C=O), 3.30(s, 2H, CH_2-O), 3.60(t, J=7 Hz, 2H, CH_2-O), 3.82(s, 2H, CH_2-O); Mass m/e 305(M^+-CH_3, 2), 245(3), 217(4), 205(8), 191(7), 171 (10), 155(34), 147(23), 143(13), 117(33), 103(58), 73(100); Anal. Calcd for $C_{14}H_{32}O_4Si_2$: C, 52.45; H, 10.06. Found: C, 52.54; H, 10.11.

Acetic acid 2-(γ-ethyl-γ-methyl-β-oxa-γ-sila)pentyl-2,6-dimethyl-6-ethyl-5-oxa-6-silaoctyl ester(26): for a sample obtained by bulb to bulb distillation: bp 180°C(oven)/ 15 mmHg; IR (neat) 2928, 2910, 2875, 1732, 1455, 1374, 1237,

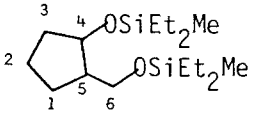
1092, 1039, 1010, 971, 953, 833, 801, 762, 684 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ 0.05(s, 3H, Si-CH_3), 0.08(s, 3H, Si-CH_3), 0.58(q, 4H, J = 6.3 Hz, Si-CH_2), 0.88-0.95(t, 12H, J = 3.2 Hz, Si-C-CH_3), 1.54(t, 2H, J = 6.8 Hz, CH_2-OSi), 2.03(s, 3H, C(O)CH_3), 3.44(s, 2H, CH_2-O), 3.65(t, 2H, J = 6.8 Hz, CH_2-O), 3.89 (s, 2H, CH_2-O); Mass m/e 347(M^+-Et, 7), 285(5), 243(15) 199(25), 161 (51), 157(56), 131(100), 103(57), 101(69); Anal. Calcd for $C_{18}H_{40}O_4Si_2$: C, 57.39; H, 10.70. Found: C, 57.17; H, 10.67.

(trans-(2-(Diethylmethylsiloxy)cyclopentyl)methoxy)-diethylmethylsilane(27): for a sample obtained by bulb to bulb distillation; bp 120°C(oven)/4 mmHg; IR (neat) 2960, 2880, 1470, 1420, 1390, 1260, 1110 cm^{-1}; ^1H NMR (CCl_4) δ 0.01(s, 6H, Si-CH_3), 0.59(m, 8H, Si-CH_2), 0.96(m, 12H, Si-C-CH_3), 1.6(m, 6H, CH_2), 1.8(m, 1H, C-CH), 3.34(d, J = 6 Hz, CH_2-O), 3.9(m, 1H, CH-OSi); ^{13}C NMR ($CDCl_3$) δ $MeEt_2Si$(O (q), 6.29(m), 6.78(m)), 22.2, 26.6, 35.1, 50.6, 64.2, 75.4; Mass m/e 287(M^+-Et, 33), 245(7), 189(100), 161(71); Anal. Calcd for $C_{16}H_{38}O_2Si_2$: C, 60.69; H, 11.46. Found: C, 60.52; H, 11.53. The trans stereochemistry was determined by comparison of the retension time in capillary gas chromatography (DEGS 20M 2.5 m, 120°C) and ^{13}C NMR spectrum with those of an authentic sample prepared as follows.

A mixture of cis and trans-2-hydroxycyclopentanemethanol was prepared by the reduction of 2-hydroxymethylcyclopentanone. The ^{13}C NMR spectrum indicated the ratio of trans to cis isomer to be 1.6 : 1 which agreed with the ^{13}C NMR data in the literature.[36] Thus obtained alchol was silylated to give (trans-2-diethylmethylsiloxy)cyclopentyl)methoxy)diethylmethylsilane ($HSiEt_2Me$/cat. $Co_2(CO)_8$, C_6H_6, 25°C, 20 h): ^{13}C NMR $MeEt_2Si$(6.29(m), 6.78(m), 6.83))



trans isomer



cis isomer

peak assingment of trans isomer: 22.2(rel. int. 1.60, C(2)), 26.6(1.70, C(1) or C(3)), 35.1(1.62, C(3) or C(1)), 50.6(1.61, C(5)), 64.2(1.60, C(4), 75.4(2.07, C(6)). peak assingment of cis isomer 21.7(rel. int. 0.96, C(2)), 26.2(1.13, C(1) or C(3)), 35.4(1.1, C(3) or C(1)), 48.4(0.95, C(5)), 62.7(0.82, C(4)), 73.9(0.78, C(6).

(trans-(2-(diethylmethylsiloxy)cyclohexyl)methoxy)diethylmethylsilane(28): for a sample obtained by distillation; bp 134-135°C/ 0.55 mmHg; IR (neat) 2955, 2935, 2880, 1265, 1112, 1087, 967, 807, 767 cm^{-1}; ^1H NMR (CCl_4) δ 0.01(s, 6H, $Si-CH_3$), 0.56(m, 8H, $Si-CH_2$), 1.0(m, 12H, $Si-C-CH_3$), 1.4(m,

8H, CH_2), 1.7(m, 1H, CH), 3.5(m, 2H, CH_2-O), 3.6(m, 1H, CH-OSi); Mass m/e 330(M^+, 0.7), 315(1.2), 301(54), 273(1.7), 212(35), 191(24), 189(100); Anal. Calcd for $C_{17}H_{38}O_2Si_2$: C, 61.73; H, 11.60. Found: C, 61.83; H. 11.82. The trans stereochemistry was determined by capillary gas chromatography (DEGS 20M 2.5 m, 120°C). The authentic sample was prepared as follows.

A mixture of cis and trans-((2-diethylmethylsiloxy)-cyclohexyl)methoxy)diethylmethylsilane was prepared by the silylation of cis and trans-2-hydroxycyclohexanemethanol and capillary gas chromatography (DEGS 20M 2.5 m, 120°C) indicated the ratio of trans to cis isomer to be 1.6 : 1: IR (neat) 2895, 2860, 1460, 1260, 1110, 1080, 1015 cm^{-1}; ^1H NMR (CCl_4) δ 0.01(s, 6H, Si-CH_3), 0.56(m, 8H, Si-CH_2), 1.0 (m, 12H, Si-C-CH_3), 1.4(m, 8H, CH_2), 1.7(m, 1H, CH), 3.5(m, 2H, CH_2-O), 3.6(m, 0.6H, trans-CH-OSi), 4.41(m, 0.4H, cis-CH-OSi).

threo-(3,9-Diethyl-3,5,6,9-tetramethyl)-4,8-dioxa-3,9-disilaundecane(29): for a sample obtained by bulb to bulb distillation; bp 120°C(oven)/0.1 mmHg; IR 2950, 2900, 2880, 1460, 1380, 1280, 1090 cm^{-1}; ^1H NMR (CCl_4) δ 0.01(s, 6H, Si-CH_3), 0.6(m, 8H, Si-CH_2), 1.0(m, 18H, CH_3 and Si-C-CH_3), 1.5(m, 1H, CH), 3.35(dd, J = 8 Hz and 5 Hz, 1H, CH_2-O), 3.50

(dd, J = 8 Hz and 5 Hz, 1H, CH_2-O), 3.70(quintet, J = 8 Hz, 1H, CH-O); Mass m/e 295(M^+-Et, 25), 189(100), 161(65), 145 (64); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.91. Found: C, 59.17; H, 12.06. for an authentic sample, see below.

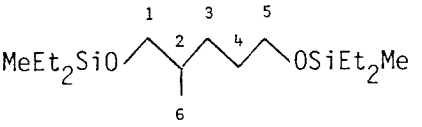
erythro-(3,9-Diethyl-3,5,6,9-tetramethyl)-4,8-dioxa-3,9-disilaundecane(30): for a sample obtained by bulb to bulb distillation: bp 120°C(oven)/0.1 mmHg; IR (neat) 2950, 2920, 2880, 1470, 1380, 1260, 1090 cm^{-1}; ^1H NMR (CCl_4) δ 0.04(s, 6H, Si-CH_3), 0.56(m, 8H, Si-CH_2), 0.9(m, 18H, Si-C-CH_3 and CH_3), 1.45(m, 1H, CH), 3.30(dd, J = 8 Hz and 10 Hz, 1H, CH-O), 3.48(dd, J = 8 Hz and 10 Hz, 1H, CH-O), 3.90(m, 1H, CH-O); Mass m/e 285(M^+-Et, 40), 189(100), 161(92), 145(65); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.91. Found: C, 59.23; H, 11.97.

threo-(3,9-Diethyl-3,5,6,9-tetramethyl)-4,8-dioxa-3,9-disilaundecane(29); An authentic sample of 29 was prepared by the silylation ($HSiEt_2Me$/cat. $Co_2(CO)_8$, C_6H_6, 25°C, 20 h) of 2-methyl-1,3-butanediol which was obtained by the reduction of butyl 3-hydroxy-2-methyl butanoate[39] with $LiAlH_4$.: ^1H NMR (CCl_4) δ 0.01(s, 6H, Si-CH_3), 0.58(m, 8H, Si-CH_2), 1.0(m, 18H, Si-C-CH_3 and CH_3), 1.6(m, 1H, CH), 3.32(dd, J = 8 Hz and 5 Hz, 1H, CH_2-O), 3.50(dd, J = 8 Hz and 5 Hz, 1H, CH_2-O), 3.70(quintet, J = 8 Hz, 1H, CH-O).

((2-Trimethylsiloxy)-5,5-dimethyl-4,6-dioxacycloheptyl-methoxy)trimethylsilane(31): for a sample obtained by bulb to bulb distillation: bp 120°C(oven)/1 mmHg: IR (neat) 2990, 1375, 1250, 1170, 1080, 1045, 1000, 860 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.04(s, 18H, Si-CH_3), 1.13(s, 3H, CH_3), 1.16(s, 3H, CH_3), 1.48(m, 1H, CH), 3.40(c, 7H, CH_2-OSi, CH_2-O and CH-O); ^{13}C NMR ($CDCl_3$) Me_4Si(0.32(m), 0.56(m)), 24.69, 24.85, 59.54, 60.75, 61.32, 65.22, 70.33, 101.03; Mass m/e 247(M^+-$SiMe_3$, 4), 231(100), 216(25), 191(25); Anal. Calc for $C_{14}H_{32}O_2Si_2$: C, 52.45; H, 10.06. Found: C, 52.31; H, 10.31.

4-(Diethylmethylsiloxy)-tetrahydrofuranmethanoldiethyl-methylether(32): for a sample obtained by bulb to bulb distillation; bp 150°C(oven)/0.3 mmHg; IR (neat) 2950, 2905, 2875, 1460, 1420, 1250, 1090, 1005, 800, 760 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.04(s, 6H, Si-CH_3), 0.52(m, 8H, Si-CH_2), 0.92(m, 12H, Si-C-CH_3), 2.12(m, 1H, CH), 3.42(m, 4H, CH_2-O), 3.72(t, J = 5.69 Hz, 1H, CH_2-O), 3.80(t, J = 5.69 Hz, 1H, CH_2-O), 4.12 (m, 1H, CH-O). Irradiation at δ 2.12 shows two doublets (J = 5.69 Hz) at δ 3.72 and δ 3.80 and a doublet-doublet (J = 4 Hz and 8 Hz) at δ 4.12; Mass m/e 289(M^+-Et, 64), 231 (10), 189(100), 171(41), 161(67), 131(82); Anal. Calcd for $C_{15}H_{34}O_2Si_2$: C, 56.55; H, 10.76. Found: C, 56.56; H, 10.92.

3,11-Diethyl-3,6,11-trimethyl-4,10-dioxa-3,11-disilatridecane(34):



for a sample of 34 containing 3,11-diethyl-3,7,11-trimethyl-4,10-dioxa-3,11-disilatridecane(35) (90 : 10 by ^{13}C NMR as described below) isolated from Co-catalyzed reaction, bp 104-106°C/0.6 mmHg; IR (neat) 2955, 2945, 2910, 2875, 1465, 1390, 1255, 1085, 800 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.00(s, 6H, Si-CH_3), 0.38-0.69(m, 8H, Si-CH_2), 0.8-1.08(m, 5H, Si-C-CH_3, CH_3), 1.20-1.72(m, 5H, CH_2, CH), 3.35 (dd, 2H, J = 5.8 Hz, J = 1.7 Hz, CH_2-O), 3.52(t, 2H, J = 6.0 Hz, CH_2-O). ^{1}H NMR does not allow to determine the ratio of 34 and 35; ^{13}C NMR ($CDCl_3$) $MeEt_2Si$(-4.949 (q), 6.363 (m), 6.802 (m)), C(6) 16.774 (q, rel. int. 1.000), C(3 or 4) 29.452(t, rel. int. 0.904), C(3 or 4) 30.476(t, rel. int. 0.905), C(2) 35.766(d, rel. int. 0.953) C(5) 63.268(t, rel. int. 1.12), C(1) 68.143(t, rel. int. 1.06) the spectrum ccntains signals due to the isomer 35(C(2) of 35 40.203(rel. int. 0.257) and C(1) of 35 61.002(rel. int. 0.224)). The ratio of 34 and 35 in this mixture is established as ca. 90 : 10 from the relative intensities of absorptions at 16.774 for 34 and those at 40.203 and 61.002 for 35; Mass m/e 289(M^+-Et, 12), 189(46), 101(10), 83(100); Anal. Calcd

for $C_{16}H_{38}O_2Si_2$: C, 60.31; H, 12.02. Found: C, 60.03; H, 12.22.

3,11-Diethyl-3,6,6,11-tetramethyl-4,10-dioxa-3,11-disilatridecane(36): for a sample obtained by distillation: bp 101°C/0.36 mmHg; IR (neat) 2960, 2920, 2880, 1440, 1420, 1395, 1365, 1255, 1100, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.015(s, 6H, Si-CH_3), 0.36-0.68(m, 8H, Si-CH_2), 0.78-1.04(m, 18H, Si-C-CH_3 and CH_3), 1.04-1.62(m, 4H, CH_2), 3.21(s, 2H, CH_2-O), 3.51(t, 2H, J = 6.3 Hz, CH_2-O); Mass m/e 303(M^+-Et, 4), 189(47), 161 (24), 101 (15), 97(100), 55(87); Anal. Calcd for $C_{17}H_{40}O_2Si_2$: C, 61.38; H, 12.12. Found: C, 61.41; H, 12.40.

(2-Phenyl-5-pent-1-enylbis(oxy)bis(diethylmethyl))silane (38): IR (neat) 2950, 2910, 2870, 1640(C=C), 1600, 1460, 1420, 1250, 1170, 1100, 1010 cm^{-1}; ^1H NMR (CCl_4) δ 0.00(s, 3H, Si-CH_3), 0.20(s, 3H, Si-CH_3), 0.4-0.8(m, 8H, Si-CH_2), 0.8-1.1(m, 12H, Si-C-CH_3), 1.54 (quintet, J = 6 Hz, 2H, CH_2), 2.52(t, J = 6 Hz, 2H, CH_2), 3.54(t, J = 6 Hz, 2H, CH_2-O), 6.48 (s, 1H, CH=), 7.18(brs, 5H, Ph); Mass m/e 378(M^+, 25), 269(8), 231(33), 189(25), 101(33), 89(100); Anal. Calcd for $C_{21}H_{38}O_2Si_2$: C, 66.60; H, 10.11. Found: C, 66.28; H, 10.30.

5-Phenyl-2,2,10,10-tetramethyl-3,9-dioxa-2,10-disilaundecane(37): IR(neat) 2900, 1640, 1490, 1455, 1385, 1250,

1090, 870, 840, 760, 700 cm^{-1}; ^1H NMR δ 0.00(s, 9H, Si-CH_3), 0.02(s, 9H, Si-CH_3), 1.41(m, 4H, CH_2), 2.63(m, 1H, CH), 3.43 (t, J = 6 Hz, 2H, CH_2-O), 3.48(d, J = 6 Hz, 2H, CH_2-O), 7.15 (c, 5H, Ph).

3,11-Diethyl-3,5,11-trimethyl-4,10-dioxa-3,11-disilatridecane (34) and 3,11-diethyl-3,6,11-trimethyl-4,10-dioxa-3,11-disilatridecane(40): for a mixture of compound 34 and 40 (62 : 38 ^1H NMR peak areas of δ 3.34 and 3.37) isolated from the Co catalyzed reaction of 2-methyltetrahydrofuran: bp 85-89°C/0.26 mmHg; IR (neat) 2950, 2940, 2900, 2875, 1255, 1035, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.02 (s, 6H, Si-CH_3), 0.39-0.67(m, 8H, Si-CH_2), 0.8-1.2(m, 15H, Si-C-CH_3 and CH_3), 1.2-1.7(m, 5H, CH_2 and CH), 3.34(dd, 1.92H, J = 6 Hz and 2 Hz, CH_2-O of 34), 3.52(t, 2H, J = 6 Hz, CH_2-O), 3.73(sextet, 0.68H, J = 6 Hz, CH-O of 40); Mass m/e 289(M^+-Et, 8), 189(69), 161(32), 101 (30), 83(100); Anal. Calcd for $C_{16}H_{38}O_2Si_2$: C, 60.31; H, 12.02. Found: C, 60.29; H, 12.22. The assingment described above has been done on comparison with a sample of 40 with 90 % purity obtained from Co catalyzed reaction of 3-methyltetrahydrofuran.

3,9-Diethyl-3,6,9-trimethyl-4,8-dioxa-3,9-disilaundecane (46) and 3,9-diethyl-3,5,9-trimethyl-4,8-dioxa-3,9-disilaundecane(47): for a mixture (25 : 75) obtained by distillation:

bp 87°C/25 mmHg; IR (neat) 3060, 3030, 2880, 1470, 1410, 1395, 1220, 1100, 1050, 1030, 995, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.00(s, 6H, Si-CH_3), 0.56(m, 8H, Si-CH_2), 0.96(m, 12H, Si-C-CH_3), 1.54(m, 1.75H, CH of 46, CH of 47), 3.56(c, 2.5H, CH_3), 3.96 (sextet, J = 6 Hz, 0.75H, CH of 47): Mass m/e 275(M^+-CH_2, 1), 261(31), 233(16), 191(28), 189(100), 161(54), 133(19), 101(23) 89(11); Anal. Calcd for $C_{14}H_{34}O_2Si_2$: C, 57.85; H, 11.81. Found: C, 57.67; H, 12.23.

3,10-Diethyl-3,5,10-trimethyl-4,9-dioxa-3,10-disiladodecane(44): for a sample obtained by bulb to bulb distillation: bp 150°C(oven)/1.2 mmHg; IR (neat) 2900, 2750, 1460, 1415, 1375, 1250, 1100, 1000, 790, 760 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ 0.02(s, 3H, Si-CH_3), 0.025(s, 3H, Si-CH_3), 0.54(q, J = 8 Hz, Si-CH_2), 0.92(t, J = 8 Hz, Si-C-CH_3), 1.14(d, J = 6 Hz, 3H, CH_2), 1.5(complex, 4H, CH_2), 3.55 (complex, 2H, CH_2-O), 3.767(sextet, J = 6 Hz, 1H, CH-O); Mass m/e 275(M^+-Et, 27), 233(33), 189(100), 161(53); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.92. Found: C, 59.25; H, 12.11.

3,10-Diethyl-3,5,10-trimethyl-4,9-dioxa-3,10-disiladodecane(44): for an authentic sample of 44 : bp 115°C/3 mmHg: IR (neat) 2950, 2860, 1460, 1410, 1390, 1260, 1100, 1050, 1000, 800, 750 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ 0.02(s, 3H, Si-CH_3), 0.025(s, 3H, Si-CH_3), 0.54(q, J = 7 Hz, 8H, Si-CH_2),

0.92(t, J = 7 Hz, 12H, Si-C-CH_3), 1.1(d, J = 6 Hz, 3H, CH_3-C), 1.5(complex, 4H, CH_2), 3.55(complex, 2H, CH_2-O), 3.767(sextet, J = 6 Hz, 1H, CH-O); Mass m/e 276(M^+-Et, 18), 232(29), 187 (100); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.92. Found: C, 58.88; H, 12.07.

3,10-Diethyl-3,6,10-trimethyl-4,9-dioxa-3,10-disiladodecane(43): for an authentic sample: IR (neat) 2950, 2880, 1470, 1260, 1100, 1010, 800, 760 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ 0.02(s, 3H, Si-CH_3), 0.025(s, 3H, Si-CH_3), 0.55(q, J = 7 Hz, 8H, Si-CH_2), 0.86(d, J = 6.5 Hz, CH_3), 0.92(t, J = 7 Hz, Si-C-CH_3), 1.28(m, 2H, CH_2), 1.68(m, 1H, CH), 3.34(dd, J = 4.6 Hz and 3 Hz, 1H, CH_2-O), 3.422(dd, J = 4.6 Hz and 3 Hz, 1H, CH_2-O), 3.616(m, 2H, CH_2-O); Mass m/e 276(M^+-Et, 18), 218 (11), 203 (3), 187(100); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.91. Found: C, 59.05; H, 12.20.

2,2,4,9,9-Pentamethyl-3,8-dioxa-2,9-disiladecane(44) and 2,2,5,9,9-pentamethyl-3,8-dioxa-2,9-disiladecane(43): for a mixture (88 : 12) obtained by bulb to bulb distillation: bp 160°C(oven)/20 mmHg; IR (neat) 2918, 1378, 1248, 1094, 842, 755 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ 0.016(s, 18H, Si-CH_3), 0.85(d, J = 6 Hz, 0.36H, CH of 43), 1.11(d, J = 6 Hz, 2.64H, CH_2 of 44), 1.5(complex, 3.88H, CH_2 of 44, CH, CH_2 of 43), 3.34(dd, J = 4.6 Hz and 3 Hz, 0.1H, CH_2-O of 43), 3.422(dd,

J = 4.6 Hz and 3 Hz, 0.1H, CH_2-O of 43), 3.55(complex, 2H, CH_2-O of 44, CH_2-O of 43), 3.76(sextet, J = 6 Hz, 1H, CH-O) of 44); Anal. Calcd for $C_{11}H_{28}O_2Si_2$: C, 53.16; H, 11.36. Found: C, 52.89; H, 11.56.

3,9-Dimethyl-3,6,9-triethyl-4,8-dioxa-3,9-disilaundecane (47) and 3,9-dimethyl-3,5,9-triethyl-4,8-dioxa-3,9-disilaundecane(48): for a mixture of compound 47 and 48 (34 : 66) obtained by bulb to bulb distillation, bp 100°C(oven)/0.5 mmHg, The isomer ratio was determined by GLC analysis (silicone OV-1 5% 6 m 180°C) comparing with authentic samples. IR (neat) 2955, 2910, 2875, 1474, 1253, 1089, 1054, 794, 759 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 6H, Si-CH_3), 0.32-0.66(m, 8H, Si-CH_2), 0.72-1.09(m, 21H, Si-C-CH_3 and CH_3-C), 1.09-1.62(m, 3.66H, CH and CH of compound 47, CH_2 of compound 48), 3.55(t, J = 6.4 Hz, 0.68H, CH_2-O) of compound 48 partially overlapping with a quintet centered at δ 3.69), 3.69(quintet, J = 6.4 Hz, 0.66H, CH-O of compound 48); Mass m/e 289(M^+-15, 0.5), 275(40), 247(20), 191(24), 189(100), 161(58); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.13; H, 11.93. Found: C, 58.82; H, 11.81.

An aunthentic sample of 47 was prepared by the silylation ($HSiEt_2Me$/cat. $Co_2(CO)_8$, Et_2O, 25°C, 20 h) of 2-ethyl-1,3-propane-diol which was obtained by the reduction of diethyl-2-ethylmalonate with $LiAlH_4$.[40] : IR (neat) 2950,

2880, 2850, 1460, 1420, 1380, 1253, 1089, 1054, 794, 754 cm^{-1}; ^1H NMR δ 0.01(s, 6H, Si-CH_3), 0.6(m, 8H, Si-CH_2), 1.0(m, 15H, Si-C-CH_3 and CH_3), 1.2(m, 3H, CH_2, CH), 3.50(d, J = 5 Hz, 4H, CH_2-O); Mass m/e 275(M^+-Et, 23), 189(100), 161(77), 157(25), 133(25), 101(14); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.13; H, 11.93. Found: C, 59.10; H, 12.10.

An authentic sample of 48 was prepared by the silylation ($HSiEt_2Me$/cat. $Co_2(CO)_8$, Et_2O, 25°C, 20h) of 1,3-pentanediol, which was obtained by the reduction of 4-hydroxypentanoic acid ethyl ester[40] with $LiAlH_4$.[38]: IR (neat) 2950, 2920, 2880, 1460, 1420, 1380, 1250, 1090, 1050, 1010, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.01 (s, 6H, Si-CH_3), 0.56(m, 8H, Si-CH_2), 0.9(m, 15H, Si-C-CH_3 and CH_3), 1.5(m, 4H, CH_2), 3.5(t, J = 6 Hz, 2H, CH_2-O partially overlapping with a quintet centered at δ 3.7), 3.7 (quintet, J = 6 Hz, 1H, CH-O); Mass m/e 275(M^+-Et, 34), 247 (33), 203(6), 189(100), 161(45); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.91. Found: C, 58.63; H, 11.96.

4-(α,α-Dimethyl)ethyl-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane(53): for a sample obtained by bulb to bulb distillation, bp 150°C(oven)/2 mmHg; IR (neat) 2990, 1490, 1400, 1370, 1250, 1100, 1030, 880, 840, 750 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 18H, Si-CH_3), 0.74(s, 9H, CH_3), 1.4(m, 2H, CH_2), 3.38(c, 3H, CH-O, CH_2-O); ^{13}C NMR ($CDCl_3$) δ $SiMe_3$ (0.324,

0.811), 26.314(51), 35.288(15), 35.532(21), 60.750(17), 77.682 (17); Mass m/e 261(M^+-CH_3, 5), 233(8), 219(83), 159(18), 147 (21), 103(100); Anal. Calcd for $C_{13}H_{32}O_2Si_2$: C, 56.46; H, 11.66. Found: C, 56.31; H, 11.77.

(5-(2-Oxapropyl))-3,9-diethyl-3,9-dimethyl-4,8-dioxa-3,9-disilaundecane(54): for a sample obtained by bulb to bulb distillation, bp 100°C(oven)/2 mmHg; IR (neat) 2955, 2920, 2880, 1470, 1420, 1260, 1100 cm^{-1}; ^1H NMR (CCl_4) δ 0.04(s, 6H, Si-CH_3), 0.56(m, J = 6 Hz, 8H, Si-CH_2), 0.92(t, J = 6 Hz, 12H, Si-C-CH_3), 1.52(m, 2H, CH_2), 3.16(d, J = 6 Hz, CH_2-O), 3.24(s, 3H, CH_3O), 3.6(t, J = 6 Hz, 2H, CH_2-O), 3.86(m, 1H, CH-O); Mass m/e 291(M^+-Et, 37), 275(19), 231 (26), 189(22), 171(26), 103(100); Anal. Calcd for $C_{15}H_{36}O_3Si_2$: C, 56.19; 11.32. Found: C, 55.87; H, 11.36.

2-(Diethylmethylsiloxy)-6-ethyl-6-methyl-5-oxa-6-sila-octanoic acid methyl ester(55): for a sample obtained by bulb to bulb distillation, bp 160°C(oven)/1.7 mmHg; IR (neat) 2910, 2870, 2835, 1730, 1225, 1110, 1070, 980 cm^{-1}; ^1H NMR (CCl_4) δ 0.04(s, 6H, Si-CH_3), 0.66(m, 8H, Si-CH_2), 1.00(m, 12H, Si-C-CH_3), 1.84(m, 2H, CH_2), 3.68(t, J = 5 Hz, 2H, CH_2-O), 3.70(s, 3H, CH_3O), 4.32(dd, J = 6.2 Hz, 5 Hz, 1H, CH-O). Irradiation at δ 1.84 gave two singlets for the methylene proton (δ 3.68) and methine proton (δ 4.32); Mass m/e 334(M^+,

0.6), 319(6), 305(100), 303(6), 277(15), 275(15), 273(9), 189 (38); Anal. Calcd for $C_{15}H_{34}O_2Si_2$: C, 53.84; H, 10.24. Found: C, 53.56; H, 10.24.

3-(Diethylmethylsiloxy)-7-ethyl-7-methyl-6-oxa-7-silanonaic acid methyl ester(56): for a sample obtained by bulb to bulb distillation, bp 120°C(oven)/0.25 mmHg; IR (neat) 2950, 2875, 1745, 1460, 1440, 1420, 1250, 1090, 1010, 800, 760 cm^{-1}; ^1H NMR (C_6H_6) δ 0.05(s, 3H, Si-CH_3), 0.13(s, 3H, Si-CH_3), 0.53(m, 8H, Si-CH_2), 0.99(m, 12H, Si-C-CH_3), 1.69(q, J = 6 Hz, 2H, CH_2), 2.39(dd, J = 14 Hz and 5.5 Hz, 1H, CH_2-CO), 2.47(dd, J = 14 Hz and 7 Hz, 1H, CH_2-CO), 3.34(s, 3H, CH_3O), 3.61(t, J = 6 Hz, 2H, CH_2-O), 4.38(quintet, J = 6 Hz, 1H, CH-O); Mass m/e 333(M^+-CH_3, 3), 319(100), 317(10), 201(42), 189(79), 161(42); Anal. Calcd for $C_{16}H_{36}O_4Si_2$: C, 55.12; H, 10.41. Found: C, 55.12; H, 10.57.

5-(Trimethylsiloxy)-2,2,9,9-tetramethyl-3,8-dioxa-2,9-disiladecane(57): for a sample obtained by bulb to bulb distillation, bp 150°C(oven)/0.8 mmHg; IR (neat) 2800, 1435, 1390, 1250, 1140, 1080, 1025, 955, 940, 825, 750 cm^{-1}; ^1H NMR (CCl_4) δ 0.04(s, 27H, Si-CH_3), 1.46(m, 2H, CH_2), 3.28(d, J = 6 Hz, 2H, CH_2-O), 3.44(t, J = 6 Hz, 1H, CH_2-O), 3.52(t, J = 6 Hz, 1H, CH_2-O), 3.66(m, 1H, CH-O); Mass m/e 306(M^+-CH_3, 0.3), 219(49), 147(26), 129(16), 103(100); Anal. Calcd for

$C_{13}H_{34}O_3Si_3$: C, 48.39; H, 10.62. Found: C, 48.13; H, 10.62.

7-(Diethylmethylsiloxy)-3,11,-diethyl-3,11-dimethyl-4,10-dioxa-3,11-disilatridecane(58): for a sample obtained by bulb to bulb distillation, bp 170°C(oven)/0.5 mmHg; IR (neat) 2980, 2950, 2900, 1465, 1415, 1380, 1255, 1090, 1045, 1005, 965, 800, 765 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 9H, Si-CH_3), 0.58(m, 12H, Si-CH_2), 0.94(m, 18H, Si-C-CH_3), 1.58(q, J = 6 Hz, 4H, CH_2), 3.58(t, J = 6 Hz, 4H, CH_2-O), 3.94(t, J = 6 Hz, 1H, CH-O). Irradiation at δ 1.58 gave two singlets for the methylene proton (δ 3.58) and methine proton (δ 3.94). Irradiation at δ 3.58 gave a doublet (J = 6 Hz) for the methylene proton (δ 1.58). Irradiation at δ 3.94 gave a triplet (J = 6 Hz) for the methine proton (δ 1.58); Mass m/e 391(M^+-Et, 31), 273(13), 189(38), 131(31), 103(100); Anal. Calcd for $C_{20}H_{48}O_3Si_3$: C, 57.08; H, 11.50. Found: C, 57.03; H, 11.56.

(4-Chloromethyl)2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane(59): for a sample obtained by bulb to bulb distillation, bp 107°C(oven)/11 mmHg; IR (neat) 2960, 2870, 1420, 1395, 1255, 1095, 842, 750 cm^{-1}; ^1H NMR (CCl_4) δ 0.08(s, 9H, Si-CH_3), 0.12(s, 9H, Si-CH_3), 1.40(m, 2H, CH_2), 3.26(d, J = 6 Hz, 2H, $ClCH_2$), 3.50(dd, J = 7 Hz and 5 Hz, 2H, CH-O), 3.84(m, 1H, CH-O). Irradiation at δ 1.40 gave a singlet and a broad triplet (J = 6 Hz) for the methylene proton (δ 3.50)

and methine proton (δ 3.84); Mass m/e 253(M^+-CH_3, 26), 219 (28), 147(82), 143(54), 103(37), 73(100); Anal. Calcd for $C_{10}H_{25}O_2Si_2Cl$: C, 44.66; H, 9.3.18. Found: C, 44.80; H, 9.58; Cl, 13.26.

(4-(2-Chloroethyl))-2,2,8,8-tetremethyl-3,7-dioxa-2,8-disilanonane(60): for a sample obtained by bulb to bulb distillation, bp 100°C(oven)/6 mmHg; IR (neat) 2955, 1445, 1250, 1090, 1035, 840, 745 cm^{-1}; ^1H NMR (CCl_4) δ 0.08(s, 9H, $Si-CH_3$), 0.11(s, 9H, $Si-CH_3$), 1.55(q, J = 6 Hz, 2H, CH_2), 1.78(q, J = 6 Hz, 2H, CH_2), 3.50(t, J = 6 Hz, 2H, $Cl-CH_2$ or CH_2-O), 3.56 (t, J = 6 Hz, 2H, CH_2-O or $Cl-CH_2$), 3.99(quintet, J = 6 Hz, 1H, CH-O). Irradiation at δ 3.99 gave two triplets (J = 6 Hz) for the methylene proton (δ 1.55 and 1.78). Irradiation at δ 1.67 gave a broad singlet for the methine proton (δ 3.99); Mass m/e 267(M^+-CH_3, 7), 239(7), 219(15), 165(36), 147(100), 103(52), 73(100); Anal. Calcd for $C_{11}H_{27}O_2Si_2Cl$: C, 46.69; H, 9.62; Cl, 12.53. Found: C, 46.40; H, 9.76; Cl, 12.66.

Acetic acid (2-(γ,γ-dimethyl-β-oxa-γ-sila)butyl)-5,5-dimethyl-4-oxa-5-silahexyl ester(61) and acetic acid (3-(β,β dimethyl)-α-oxa-βsila)propyl)-5,5-dimethyl-4-oxa-5-silahexyl ester(62): for a mixture (12 : 88) obtained by bulb to bulb distillation; bp 135°C (oven)/8 mmHg; IR (neat) 2950, 2900, 2870, 1750, 1425, 1370, 1240, 1090, 840, 750 cm^{-1}; ^1H NMR

(CCl_4 + Eu(thd)$_3$) δ 0.016(s, 9H, Si-CH_3), 0.036(s, 9H, Si-CH_3), 1.90(m, 1.88H, CH of 61, CH_2 of 62), 3.30(s, 2.64H, CH_3C=O of 62), 3.42(s, 0.36H, CH_3C=O of 61), 3.80(t, J = 6,38 Hz, 1.76H, CH_2-O of 62), 3.98(d, J = 4.25 Hz, 0.48H, CH_2-O of 61), 4.60(m, 0.88H, CH-O of 62), 5.38(dd, J = 8.51 Hz and 6.38 Hz, 1.76H, CH_2-O of 62), 6.44(dd, J = 12.77 Hz and 5.53 Hz, 0.24H, CH_2-O of 61); Mass m/e 277(M^+-CH_3, 6), 219(4), 189(11), 175(10), 117(43), 103(91), 73(100).

Benzoic acid (2-γ,γ-dimethyl-β -oxa-γ-sila)butyl)-5,5-dimethyl-4-oxa-5-silahexyl ester(63) and benzoic acid (3-β,β-dimethyl-α-oxa-β-sila)propyl) 5,5-dimethyl-4-oxa-5-silahexyl ester(64): for a mixture (11 : 89) obtained by bulb to bulb distillation; bp 160°C(oven)/6 mmHg; IR (neat) 2950, 2900, 2875, 1730, 1605, 1460, 1260, 1100, 850, 750, 710 cm^{-1}; ^1H NMR (CCl_4 + Eu(thd)$_3$) δ 0.12(s, 9H, Si-CH_3), 0.28(s, 9H, Si-CH_3), 1.89(c, 1.89H, CH_2 of 63, CH of 64), 3.77(t, J = 6.38 Hz, 1.78H, CH_2-O of 64), 4.00(d, J = 8.51 Hz, 0.44H, CH_2-O of 63), 4.62(m, 0.89H, CH-O of 64), 5.56(d, J = 5.96 Hz, 1.78H, CH_2-O of 64), 5.86(d, J= 6.38 Hz, 0.22H, CH_2-O of 63); Mass m/e 339(M^+-CH_3, 9), 219(57), 179(34), 105(100), 103(97), 73(74); Anal. Calcd for $C_{17}H_{30}O_4Si_s$: C, 57.38; H, 8.53. Found; c, 57.25: H, 8.46.

3,11-Diethyl-3,11-dimethyl-5-(β-oxapropyl)-4,10-dioxa-

3,11-disilatridecane(66): for a sample obtained by distillation; bp 116-117°C/0.6 mmHg; IR (neat) 2950, 2900, 2880, 1460, 1255, 1100, 1010, 800, 760 cm^{-1}; ^1H NMR (CCl_4) δ 0.01(s, 3H, Si-CH_3), 0.024(s, 3H, Si-CH_3), 0.37-0.75(m, 8H, Si-CH_2), 0.81-1.09(m, 12H, Si-C-CH_3), 1.19-1.65(c, 6H, CH_2), 3.16(d, J = 5.8 Hz, 2H, CH_2-O), 3.27(s, 3H, CH_3-O), 3.39-3.85(m, 3H, CH_2-O and CH-O); Mass m/e 319(M^+-Et, 11), 303(11), 157(44), 103(87), 101(100), 81(93); Anal. Calcd for $C_{17}H_{40}O_3Si_2$: C, 58.56; H, 11.56. Found: C, 58.70; H, 11.76.

Acetic acid 2-(β-ethyl-β-methyl-α-oxa-β-silabutyl)-8-ethyl-8-methyl-7-oxa-8-siladecyl ester(67): for a sample obtained by distillation; bp 115-120°C/0.28 mmHg; IR (neat) 2955, 2910, 2880, 1745, 1460, 1415, 1370, 1250, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 3H, Si-CH_3), 0.05(s, 3H, Si-CH_3), 0.76-1.16(m, 12H, Si-C-CH_3), 1.16-1.74(c, 6H, CH_2), 1.98(s, 3H, 3.56(t, J = 5.3 Hz, 2H, CH_2-O), 3.68-4.08(m, 3H, CH-O and CH_2-O); Mass m/e 361(M^+-CH_3, 0.2), 347911), 187(40), 131(100), 101(25), 81(43); Anal. Calcd for $C_{18}H_{40}O_2Si_2$: C, 57.40; H, 10.70. Found: C, 57.19; H, 10.76.

3,9-Diethyl-3,6,6,9-tetramethyl-4,8-dioxa-3,9-disilaundecane(69): for a sample obtained by bulb to bulb distillation and purified by preparative GLC; bp 115°C(oven)/3 mmHg; ^1H NMR (CCl_4) δ 0.04(s, 6H, Si-CH_3), 0.56(m, 8H, Si-CH_2),

1.00(m, 18H, Si-C-CH_3 and CH_3), 3.25(s, 4H, CH_2-O); Mass m/e 304(M^+, 1), 285(45), 189(100), 161(72), 133(21).

3,9-Diethyl-3,6,6,9-tetramethyl-4,8-dioxa-3,9-disilaundecane(69): for an authentic sample of 69 obtained by the silylation of the corresponding diol; bp 115°C(oven)/3 mmHg; IR (neat) 2950, 2900, 2880, 1465, 1255, 1090, 830 cm^{-1}; ^1H NMR (CCl_4) δ 0.04(s, 6H, Si-CH_3), 0.56(m, 8H, Si-CH_2), 1.00(m, 18H, Si-C-CH_3 and CH_3), 3.25(s, 4H, CH_2-O); Mass m/e 304(M^+, 1), 285(45), 189(100),161(72), 133(21); Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.91. Found: C, 58.92; H. 12.21.

3,9-Diethyl-3,5,5,9-tetramethyl-4,8-dioxa-3,9-disilaundecane(70): for an authentic sample of 70 obtained by the silylation of the corresponding diol; bp 115°C(oven)/3 mmHg; IR (neat) 2960, 2925, 2900, 1470, 1430, 1400, 1380, 1270 cm^{-1}; ^1H NMR (CCl_4) δ 0.01(s, 3H, Si-CH_3), 0.04(s, 3H, Si-CH_3), 0.50(t, J = 6 Hz, 8H, Si-CH_2), 0.90(t, J = 6 Hz, 12H, Si-C-CH_3), 1.10(s, 6H, CH_2), 1.58(t, J = 6 Hz, 2H, CH_2), 3.62(t, J = 6 Hz, CH_2-O); Mass m/e 299(M^+-CH_3, 9), 285(45), 286(33), 189 (100), 159(58).

6-((γ-Ethyl-γ-methyl-β-oxa-γ-sila)pentyl)-3,9-diethyl-3,6,9-trimethyl-4,8-dioxa-3,9-disilaundecane(71) and 5-((β-ethyl-β-methyl-α-oxa-β-sila)butyl)-3,9-diethyl-3,5,9-tri-

methyl-4,8-dioxa-3,9-dislaundecane(72): for a mixture (25 : 75) obtained by bulb to bulb distillation; bp 110°C(oven)/ 0.6 mmhg; IR (neat) 2950, 2920, 2880, 1465, 1420, 1260, 1095, 1005, 965, 800, 783 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 6.75H, Si-CH_3), 0.06(s, 2.25H, Si-CH_3), 0.40-0.84(m, 12H, Si-CH_2), 0.94(c, 18.75H, Si-C-CH_3 and CH_3 of 71), 1.16(s, 2.25H, CH_3), 1.64(t, J = 8.0 Hz, 1.5H, CH_2 of 72), 3.28(s, 1.5H, CH_2-O of 72), 3.38(s, 1.5H, CH_2-O of 71), 3.73(t, J = 8.0 Hz, 1.5H, CH_2-O of 72); Mass m/e 391(M^+-Et, 16), 289(100), 189(69), 185(49).

6-((γ-Ethyl-γ-methyl-β-oxa-γ-sila)pentyl0-3,9-diethyl-3,6,9-trimethyl-4,8-dioxa-3,9-disilaundecane(71); for an authentic sample obtained by bulb to bulb distillation; bp 110°C(oven)/0.6 mmHg; IR (neat) 2950, 2920, 2880, 1460, 1420, 1260, 1090, 1010 cm^{-1}; ^1H NMR (CCl_4) δ 0.01(s, 9H, Si-CH_3), 0.56(m, 12H, Si-CH_2), 0.90(m, 18H, Si-C-CH_3 and CH_3), 3.28(s, 3H, CH_3); Mass m/e 391(M^+-Et, 17), 283(34), 191(100), 186(3), 171(31); Anal. Calcd for $C_{20}H_{48}O_3Si_3$: C, 57.08; H, 11.50. Found: C, 57.22; H, 11.78.

1-((β-Ethyl-β-methyl-α-oxa-β-sila)butyl-5-ethyl-1,5-dimethyl-4-oxa-5-silaheptanoic acid methyl ester(74): for a sample obtained by bulb to bulb distillation; bp 150°C(oven)/ 1.7 mmHg; IR (neat) 2950, 2870, 1750, 1460, 1250, 1200, 1140,

1005, 795, 760 cm^{-1}; ^1H NMR (C_6D_6) δ 0.08(s, 3H, Si-CH_3), 0.23(s, 3H, Si-CH_3), 0.6(m, 8H, Si-CH_2), 1.0(m, 12H, Si-C-CH_3), 1.42(s, 3H, CH_3), 1.94(dd, J = 13 Hz and 7 Hz, 1H, CH_2), 2.19 (dd, J = 13 Hz and 7 Hz, 1H, CH_2), 3.32(s, 3H, CH_3O), 3.79(t, J = 7 Hz, 2H, CH_2-O); Mass m/e 333(M^+-CH_3, 6), 319(81), 317 (6), 189(55), 103(100); Anal. Calcd for $C_{16}H_{36}O_2Si_2$: C, 55.12; H, 10.41. Found: C, 55.21; H, 10.37.

5-(α-Chloro)methyl-3,9-diethyl-3,9-dimethyl-4,8-dioxa-3,9-disilaundecane(75): for a sample obtained by bulb to bulb distillation; bp 110°C(oven)/6 mmHg; IR (neat) 2955, 1380, 1250, 1150, 1090, 1055, 1010, 840 cm^{-1}; ^1H NMR (CCl_4) δ 0.08 (s, 9H, Si-CH_3), 0.12(s, 9H, Si-CH_3), 1.28(s, 3H, CH_3), 1.70 and 1.73(two overlapping triplets (J = 7 Hz) probably due to central two peaks of a AB quartet, 2H, CH_2), 3.33(d, J = 11 Hz, 1H, Cl-CH_2), 3.35(d, J = 11 Hz, 1H, Cl-CH_2), 3.62(t, J = 7 Hz, 2H, CH_2-O); Mass m/e 267(M^+-CH_3, 11), 239(7), 233(38), 165(2), 147(24), 103(40), 73(100); Anal. Calcd for $C_{11}H_{27}O_2Si_2$: C, 46.69; H, 9.62; Cl, 12.53. Found; c, 47.02; H, 9.91; Cl: 12.49.

5-((γ,γ-Dimethyl-β-oxa-γ-sila)butyl)-2,2,6,8,8-pentamethyl-3,7-dioxa-2,8-disilanonane(77) and threo-5-((β,β-dimethyl-α-oxa-β-sila)propyl)-2,2,6,9,9-pentamethyl-3,8-dioxa-2,9-disiladecane(78): for a mixture obtained by bulb

to bulb distillation; 100°C(oven)/0.5 mmHg; IR (neat) 2955, 1380, 1250, 1080, 840, 740 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ 0.120(s, 27H, Si-CH_3), 0.81(d, 2.2H, J = 7.04 Hz, CH_3 of 78), 1.14(d, 0.8H, J = 6.46 Hz, CH_3 of 77), 1.605(c, 0.4H, CH of 77), 1.79(m, 0.6H, CH of 78), 3.36(dd, J = 10.2 Hz and 6.96 Hz, CH_2-O of 78), 3.43-3.75(c, 2.8H, CH_2-O), 3.81(td, J = 6.0 Hz and 3.12 Hz, 0.6H, CH_2-O of 78), 3.975(quintet, J = 6.0 Hz, 0.4H, J = 6.0 Hz, CH-O of 77). Irradiation at δ 0.8082 shows a triplet doublet (J = 5.79 Hz and 2.89 Hz) at δ 1.798. Irradiation at δ 1.1350 shows a doublet (J = 5.68 Hz) at δ 3.975. Irradiation at δ 1.6001 shows a triplet (J = 5.92 Hz at δ 3.975. Irradiation at δ 1.769 shows a doublet (J = 10.5 Hz) at δ 3.37, a triplet (J = 5.66 Hz) at δ 3.821, and a singlet at δ 0.79. Irradiation at δ 3.3684 shows a doublet-triplet (J = 14.38 Hz and 3.36 Hz) at δ 1.771. Irradiation at δ 3.975 shows a singlet at δ 1.13; Mass m/e 336(M^+, 1), 321(M^+-CH_3, 1), 246(6), 233(45), 147(38), 143995), 117 (100), 103(93)

2-(α-Hydroxymethyl)-1,4-butanediol(96) and threo-2-methyl-1,2,4-butanetriol(79): for a mixture obtained by hydrolysis of a mixture of 77 and 78; 270 M Hz ^1H NMR (D_2O) δ 0.775(d, J = 7.00 Hz, 1.2H, CH_2 of 79), 1.090(d, J = 7.00 Hz, 0.8 Hz, CH_2 of 96), 1.551-1.730(m, 1H, CH), 3.355(dd, J = 10.8 Hz and 6.3 Hz, 1.2H, CH_2 of 79), 3.410-3.679(m, 3.4H,

CH_2 of 96, CH_2 and CH of 79), 3.840 (quintet, J = 6.3 Hz, 0.4H, CH of 96). Irradiation at δ 1.0984 shows a doublet (J = 5.68 Hz) at δ 3.835. Irradiation at δ 1.6056 shows a quartet (J = 6.5 Hz) at δ 3.835. Irradiation at δ 1.6869 shows a doublet(J = 10.6 Hz) at δ 3.342 and a singlet at δ 0.730. Irradiation at δ 3.6166 shows a broad singlet at δ 1.585 and a quartet (J = 5.87 Hz) at δ 1.673. Irradiation at δ 3.3839 shows a singlet at δ 1.195.

Acetic acid 2-(γ,γ-dimethyl-β-oxa-γsilabutyl)-3,5,5-trimethyl-4-oxa-5-silahexyl ester(80) and Acetic acid 2-(β,β-dimethyl-α-oxa-β-sila)-3,6,6-trimethyl-5-oxa-6-silaheptyl ester(81): for a mixture (22 : 78) obtained by bulb to bulb distillation; IR (neat) 2950, 2880, 1740, 1440, 1370, 1250, 1060, 960, 840, 750 cm^{-1}; ^1H NMR (CCl_4) δ 0.08(s, 18H, Si-CH_3), 0.70(d, J = 6 Hz, 2.34H, CH_3 of 81), 1.06(d, J = 6.0 Hz, 0.66H, CH_3 of 80), 1.32-1.72(m, 1H, CH), 1.90 (s, 3H, CH_3C=O), 3.28(d, J = 6 Hz, 1.56H, CH_2-O of 81), 3.44(d, J = 6 Hz, 0.44H, CH_2-O of 80), 3.68-4.12(c, 3H, CH_2-O and CH-O); Mass m/e 291(M^+-CH_3, 4), 261(1), 233(41), 175(29), 147(53), 117(62), 103(62), 103(88), 73(100); Anal. Calcd for $C_{13}H_{40}O_4Si_2$: C, 50.94; H, 9.86. Found: C, 51.21; H, 9.62.

Benzoic acid 2-(γ,γ-dimethyl-β-oxa-γ-silabutyl)-3,5,5-trimethyl-4-oxa-5-silahexyl ester(82) and benzoic acid 2-(β,β-di-

methyl-α-oxa-β-sila)-3,6,6-trimethyl-5-oxa-6-silaheptyl ester (83): for a mixture (22 : 78) obtained by bulb to bulb distillation; bp 200°C(oven)/0.5 mmHg; IR (neat) 3000, 2950, 1725, 1680, 1615, 1590, 1455, 1385, 1320, 1270, 1250, 1100, 965, 830, 755, 715, 690 cm^{-1}; 270 MHz ^1H NMR($CDCl_3$) δ 0.13(s, 18H, Si-CH_3), 0.88(d, J = 7.17 Hz, 2.34H, CH_3 of 83), 1.22(d, J = 5.97 Hz, 0.66H, CH_3 of 82), 1.76-1.99(m, 1H, CH), 3.415 (dd, J = 6 Hz and 10.4 Hz, 0.78H, CH of 83), 3.510(dd, J = 7.2 Hz and 10.4 Hz, 0.78H, CH_2 of 83), 3.64(dd, J = 5.4 Hz and 9.6 Hz, 0.22H, CH_2 of 82), 3.71(dd, J = 6 Hz and 9.6 Hz, 0.22H, CH_2 of 82), 4.115-4.21(m, 1H, CH of 83), 4.24-4.39(c, 2H, CH_2), 7.35-7.36(c, 3H, Ar), 7.95-8.11(c, 2H, Ar). Irradiation at δ 1.8552 shows a singlet at δ 0.88 and a doublet doublet (J = 4.41 Hz and 5.50 Hz) at δ 4.16; Mass m/e 353 (M^+-CH_3, 3), 233(40), 231(31), 189(29), 105(100), 103(71); Anal. Calcd for $C_{18}H_{32}O_4Si_2$; c, 58.65; H, 8.75. found: C, 58.41; H, 8.71.

Methyl 2-(γ,γ-dimethyl-β-oxa-γ-silabutyl0-3,5,5-trimethyl-4-oxa-5-silahexy carbonate(84) and methyl, 2-(β,β-dimethyl-α-oxa-β-sila)-3,6,6-trimethyl-5-oxa-6-silaheptyl carbonate(85): for a mixture (17 : 83) obtained by bulb to bulb distillation; bp 170°C(oven)/1 mmHg; IR (neat) 2990, 2950, 1750, 1445, 1250, 1090, 975, 840, 750, 700 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ 0.12(s, 18H, Si-CH_3), 0.81(d, J = 7.4

Hz, 2.49H, CH_3 of 85), 1.16(d, J = 6.6 Hz, 0.51H, CH_3 of 84), 1.66-1.89(c, 1H, CH), 3.372(dd, J = 6.13 Hz and 9.82 Hz, 0.83H, CH_2 of 85), 3.430(dd, J = 7.36 Hz and 9.82 Hz, 0.83H, CH_2 of 85), 3.535(dd, J = 6.55 Hz and 9.82 Hz, 0.17H, CH_2 of 84), 3.601(dd, J = 5.7 Hz, 0.17H, CH_2 of 84), 3.732-3.830(m, 1H, CH) overlapping with a singlet at δ 3.756, 3.756(s, 3H, CH_3O), 4.014(dd, J = 3.03 Hz and 5.32 Hz, 0.83H, CH_2 of 85), 4.055(dd, J = 4.91 Hz and 5.32 Hz, 0.83H, CH_2 of 85), 4.112 (d, J = 6.5 Hz, 0.17H, CH_2 of 84). Irradiation at δ 0.81 shows a triplet-doublet (J = 3.0 Hz and 6.75 Hz) at δ 1.711. Irradiation at δ 1.69 shows a singlet at δ 0.82 and two doublets (J = 10.87 Hz) at δ 3.379 and 3.442; Mass m/e 307 (M^+-CH_3, 10), 233(52), 231(54), 191(24), 133(32), 103(84), 73(100); Anal. Calcd for $C_{13}H_{30}O_5Si_2$: C, 48.41; H, 9.37. Found: C, 48.40; H, 9.45.

Chloroacetic acid 2-(γ,γ-dimethyl-β-oxa-γ-silabutyl)-3,5,5-trimethyl-4-oxa-5-silahexyl ester(86) and chloroacetic acid 2-(γ,γ-dimethyl-β-oxa-γ-sila)-3,6,6-trimethyl-5-oxa-6-silaheptyl ester (87): for a mixture (4 : 96) obtained by bulb to bulb distillation; 170°C(oven)/1 mmHg: IR (neat) 2975, 2910, 1750, 1400, 1280, 1245, 1170, 1080, 980, 830, 740, 675 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ 0.09 (s, 9H, Si-CH_3), 0.12(s, 9H, Si-CH_3), 0.84(d, J = 6.28 Hz, 1.92H, CH_2 of 87), 1.165(d, J = 6.28 Hz, 0.08H, CH_2 of 86), 1.69(m, 1H, CH),

3.385(dd, J = 4.97 Hz and 8.53 Hz, 1H, CH_2), 3.445(dd, J = 4.97 Hz and 9.95 Hz, 1H, CH_2), 4.020(m, 1H, CH) overlapping with a singlet at δ 4.045, 4.045(s, 2H, CH_2), 4.115(dd, J = 3.55 Hz and 7.82 Hz, 1H, CH_2), 4.180(dd, J = 3.55 Hz and 11.37 Hz, 1H, CH_2). Irradiation at δ 1.6735 shows a singlet at δ 0.805 and two doublets at δ 3.390(J = 9.49 Hz) and 3.445(J = 9.49 Hz). Irradiation at δ 3.4065 shows a quartet-doublet (J = 6.28 Hz and 3.84 Hz) at δ 1.701; Mass m/e 327 (M^+-CH_3, 1.7), 325(3.3), 297(1.3), 295(2.3), 233(0.8), 231 (13), 211(12), 209(25), 189(17), 103(100).

((6-Ethyl-6-methyl-5-oxa-6-silaoctylidene)methoxy) diethylmethylsilane(4): for a sample obtained by bulb to bulb distillation; bp 77°C(oven)/0.33 mmHg; IR (neat) 3030, 2955, 2950, 2910, 2880, 1655, 1255, 800 cm^{-1}; ^1H NMR (CCl_4) δ 0.00 (s, 3H, Si-CH_3), 0.10(s, 3H, Si-CH_3), 0.35-0.75(m, 8H, Si-CH_2), 0.82-1.10(m, 12H, Si-C-CH_3), 1.30-1.67(m, 2H, CH_2), 1.75-2.22 (m, 2H, CH_2), 3.51(t, J = 6.5 Hz, 2H, CH_2-O), 4.35(dt, J = 6.0 Hz and 7.3 Hz, 0.64H, CH=C of Z-isomer), 4.82(dt, J = 12.3 Hz and 7.6 Hz, 0.36H, CH=C of E-isomer), 6.05(dt, J = 6.0 Hz and 1.3 Hz, 0.64H, C=CH of Z-isomer), 6.09(dt, J = 12.3 Hz and 1.2 Hz, 0.36H, C=CH of E-isomer); Mass m/e 304(M^+, 6.70, 287(M^+-CH_3, 0.4), 275(0.4), 189(30), 161(19), 101(7), 89(21), 69(100); Anal. Calcd for $C_{15}H_{34}O_2Si_2$: C, 59.54; h, 11.33. Found; c, 59.21; H, 11.68.

((α-(Diethylmethylsiloxymethyl)cyclohexyl)methylidene-methoxy)-diethylmethylsilane(90): for a sample obtained by bulb to bulb distillation; bp 140°C(oven)/0.5 mmHg; IR (neat) 2950, 2900, 2870, 1650, 1430, 1410, 1225, 1120, 1080, 830, 800, 760 cm^{-1}; ^1H NMR (CCl_4) δ 0.00(s, 6H, Si-CH_3), 0.4-0.6(m, 8H, Si-CH_2), 0.95(m, 12H, Si-C-CH_3), 1.4(c, 9H, cyclohexane ring), 2.2(m, 1H, CH), 3.45(m, 2H, CH_2-O), 4.5(m, 0.54H, CH=C of Z-isomer), 5.1(m, 0.46H, CH=C of E-isomer), 6.1(m, 1H, C=CH); Mass m/e 327(M^+-Et, 44), 245(11), 23(10), 189(80), 161 (78), 121(100); Anal. calcd for $C_{19}H_{40}O_2Si_2$: C, 63.98; H, 11.30. Found: C, 63.66; H, 11.50.

((α-(Diethylmethylsiloxymethyl)cyclohexyl)methylidene-methoxy)-diethylmethylsilane(91): for a sample obtained by distillation: bp 113-115°C(oven)/0.65 mmHg; IR (neat) 3020, 2950, 2905, 2875, 2840, 1658, 1650, 1460, 1435, 1255, 800 cm^{-1}; ^1H NMR (CCl_4) -0.004, 0.014(s, 3H, Si-CH_3), 0.095, 0.119(s, 3H, Si-CH_3), 0.36-0.75(m, 8H, Si-CH_2), 0.83-1.11(m, 12H, Si-C-CH_3), 1.11-2.56(c, allyl methylene and methine), 2.82-3.15(c, 1H, allylmethylene), 3.12-3.72(m, 2H, CH_2-O), 4.42(dd, J = 9.9 Hz and 6.2 Hz, 0.54H, CH=C of Z-isomer), 4.89(dd, J = 11.7 Hz and 9.6 Hz, 0.46H, CH=C of E-isomer), 5.59(bs, 2H, CH=CH), 6.11(dd, J = 6.2 Hz and 1.3 Hz, 0.54H, C=CH-O of Z-isomer), 6.179d, j = 11.8 Hz, 0.46H, C=CH-O of E-isomer); Mass m/e 354(M^+, 6), 339(2), 325(52), 236(53),

189(85), 161(56), 119(60), 101(65), 89(65), 73(100); Anal. Calcd for $C_{19}H_{38}O_2Si_2$: C, 64.34; H, 10.80. Found: C, 64.23; H, 11.20.

((4,6-Dimethyl-6-ethyl-5-oxa-6-silaoctylidene)methoxy)-diethylmethylsilane(92) and ((3,6-dimethyl-6-ethyl-5-oxa-6-silaoctylidene)-methoxy)diethylmethylsilane(93): for a sample obtained by distillation; bp 93-101.5°C/0.6 mmHg; IR (neat) 3035, 2955, 2910, 2880, 1655, 1460, 1410, 1255, 1080, 800 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ 0.03(s, 3H, Si-CH_3), 0.1(s, 3H, Si-CH_3), 0.39-0.72(c, 8H, Si-CH_2), 0.76-1.06(c, 12H, Si-C-CH_3), 1.42-2.52(c, 3H, CH_2), 3.25-3.75(c, 2H, CH_2-O), 4.43(dt, J = 7.7 Hz and 7 Hz, 0.58H, CH=C of Z-isomer of 92), 4.63(dt, J = 9 Hz and 2.6 Hz, 0.05H, CH=C of Z-isomer of 93), 4.93(dt, J = 12 Hz and 8.4 Hz, 0.25H, CH=C of E-isomer of 92), 5.11(d, J = 1.9 Hz, 0.12H, CH=C of E-isomer of 93), 6.11-6.37 (c, 1H, =CH-O); Mass m/e 316(M^+, 1), 301(1), 289(3), 287(16), 198(71), 189(49), 161(36), 101(52), 89(100), 73(57); Anal. Calcd for $C_{16}H_{36}O_2Si_2$: C, 60.69; H, 11.46. Found: C, 60.34; H, 11.79.

((6-Ethyl-4,4,6-trimethyl-5-oxa-6-silaoctylidene)-methoxy)-diethylmethylsilane(94): for a sample obtained by distillation; IR (neat) 2950, 2870, 1630, 1460, 1418, 1260, 1100, 1010, 830, 800, 760 cm^{-1}; ^1H NMR (CCl_4) δ 0.00(s, 3H,

Si-CH_3), 0.10(s, 3H, Si-CH_3), 0.56(m, 8H, Si-CH_2), 0.89(c, 18H, Si-C-CH_3, CH_3), 1.72(d, J = 8 Hz, 0.58H, 0.58H, CH_2 of E-isomer), 1.90(d, J = 8 Hz, 1.42H, CH_2 of Z-isomer), 3.16(s, 2H, CH_2-O), 4.32(m, 0.71H, CH=C of Z-isomer), 4.86(m, 0.29H, CH=C of E-isomer), 6.14(m, 1H, C=CH-O); Mass m/e 301(M^+-Et, 33), 244(20), 212(40), 197(33), 189(67), 161(33), 157(73), 101(100); Anal. Calcd for $C_{17}H_{38}O_2Si_2$: C, 61.75; H. 11.58. Found: C, 61.52; H, 11.74.

1.8. References and Notes

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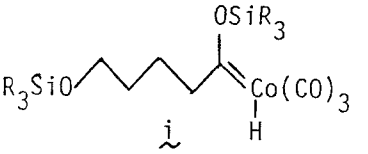

i

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(21) The subsequent alkyl migration is known to proceed with retention. Flood, T. C. Top. Stereochem. 1981, 12, 37.

(22) The use of $HSiMe_3$ resulted in the formation of low yield of the diol disilyl ether contaminated with mixtures of further reacted products.

(23) The reaction of 42 in CH_2Cl_2 proceeded in a manner similar to oxetane to give 2-methyl-1-siloxypropane and 2-methyl-1,4-disiloxybutane in 85 % and 13 % yields, respectively, both of which did not contain the regioisomers.

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ponding to 3 and 4 in a nonselective manner, whereas oxiranes afforded many products in low yields.

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(37) ^{13}C NMR spectrum and capillary gas chromatography (DEGS 20 M, 2.5 m, 120°C) indicated the ratio of trans and cis isomer to be 1.6 : 1.

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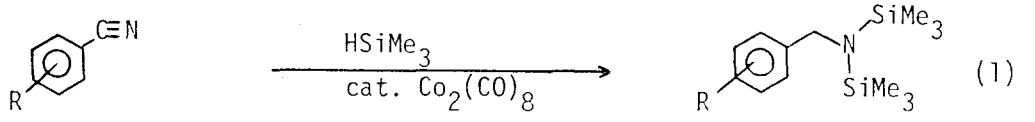
Chapter 2. Cobalt Carbonyl Catalyzed Reduction of Aromatic Nitriles with a hydrosilane

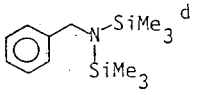
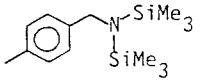
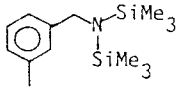
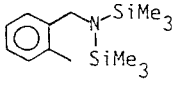
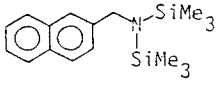
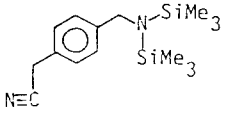
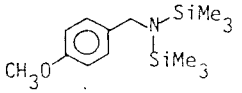
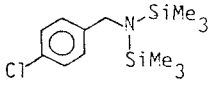
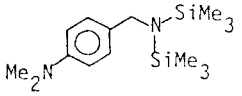
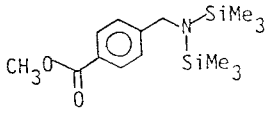
2.1. Introduction

The hydrosilylation of alkynes using transition metal catalyst has been an important and well-known process as a convenient route to silicon containing compounds.[1] On the other hand little attention has been paid to the addition of hydrosilanes to nitriles,[2,3] despite the potential utility of N-silylated compounds.[4] For example, the addition of $HSiMe_2Cl$ to methacrylonitrile has been reported, but the product yield was very low.[3] Nevertheless the selective reduction of aromatic nitriles having various functional groups is an important route to primary amines, although few studies has been carried out.[5] In this Chapter, a novel and effective method for the overall reduction of aromatic nitriles using cobalt carbonyl catalyzed addition of two molecules of $HSiMe_3$ (eq 1) will be described.



(1)

Table I. Cobalt Carbonyl Catalyzed Addition of $HSiMe_3$ to Aromatic Nitriles.[a] Products, Yields, and Boiling points.

entry	product	yield,%[b]	bp, °C/mmHg
1	 [d]	64	130/20
2		91	150/20
3		57(68)	150/19
4[e]		11(22)	150/10
5		64(67)	150/0.5
6[e]		(36)	150/0.5
7		(88)	160/10
8[e,f]		(53)	150/5
9		(73)	120/0.5
10[e,f]		(46)[g]	150/0.7

a) All reactions were carried out on a scale as described in the text unless otherwise noted. b) GLC yields in parentheses. c) Oven Temperature of bulb to bulb distillation apparatus. d) ref. 6 e) $Co_2(CO)_8$ (0.625 mmol) was used. f) For 40 hrs. g) Partially hydrolyzed product, i.e., a monosilylated amine , was also obtained in 19 % yield.

2.2. Cobalt Carbonyl Catalyzed Reaction of Aromatic Nitriles with a Hydrosilane

p-Tolunitrile was reacted with a hydrosilane in the presence of a catalytic amount of $Co_2(CO)_8$ in toluene at 25°C under CO atmosphere. After 20 h, GLC analysis showed that only 3 % yield of N,N-bis(trimethylsilyl)-p-methylbenzylamine (1) was obtained and starting material was almost quantitatively recovered. When elevating the reaction temperature to 60°C, the reaction proceeded smoothly to form 1 in 91 % yield. The reaction could also be effected by using a nitrogen atmosphere, although the yield was slightly decreased (71 % yield). The N,N-di(silyl)amine was quantitatively converted to p-methyl-benzylamine by treating with hot methanol.

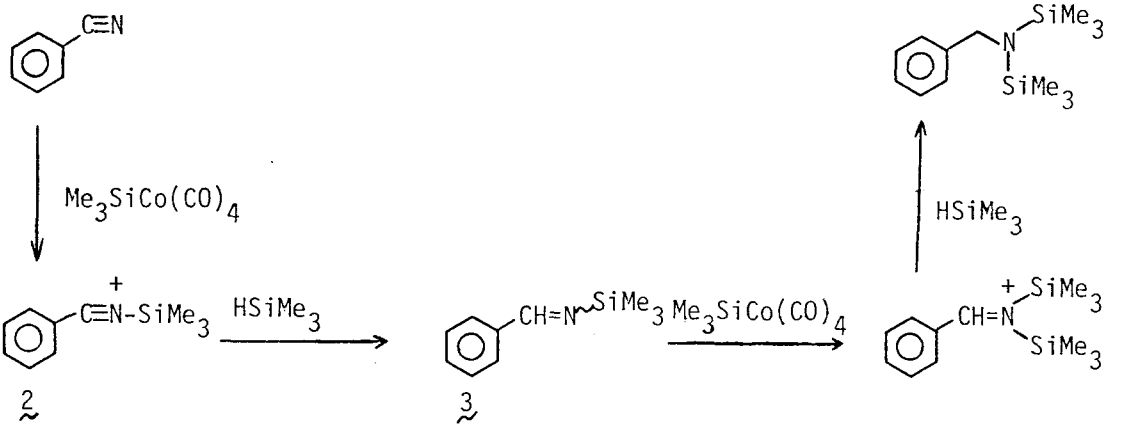
In a similar manner a number of N,N-disilylamines were prepared from the corresponding nitriles as shown in Table I. The reaction conditions could be torelant of various functional groups like methoxy, chloro, dimethylamino, or methoxycarbonyl (entry 7, 8, 9, 10). Since the aliphatic nitriles did not react with $HSiMe_3$, the cyano group ajacent to benzene ring selectively reacted with $HSiMe_3$ in the case of p-(cyano-methyl)benzonitrile (entry 6). The rate of conversion of aromatic nitriles having electron withdrawing group or sterically hindered nitriles seems to be rather low (entry 4, 8, 10).

The plausible reaction pathway is depicted in Scheme I. $R_3SiCo(CO)_4$,[7] generated by the reaction of $HSiR_3$ and $Co_2(CO)_8$,[8] may react with a nitrile to give N-silylnitrilium ion intermediate (2) and $Co(CO)_4^-$. Transfer of hydrogen from a hydrosilane to 2 might occur to form silylimine (3).[9] The addition of $HSiMe_3$ to 3 in a similar manner would result in the formation of N,N-disilylamine.[10]

Scheme I

$$HSiMe_3 + Co_2(CO)_8 \longrightarrow Me_3SiCo(CO)_4 + HCo(CO)_4$$

$$HSiMe_3 + HCo(CO)_4 \longrightarrow Me_3SiCo(CO)_4 + H_2$$



2.3. Experimental

2.3.1. General Procedure for Cobalt Carbonyl Catalyzed Reaction of Aromatic Nitriles with a Hydrosilane

The following procedure for the reaction of p-tolunitrile is representative. A 10 mL two-necked round-bottom flask equipped with a dry ice condenser and a Teflon-coated magnetic stirrer bar was flame dried and then charged with 0.0684 g (0.2 mmol) of $Co_2(CO)_8$, fitted with a serum cap and CO balloon and flushed with carbon monoxide. To the flask was added 2.83 mL (25 mmol) of $HSiMe_3$ with a pressurized syringe at -20°C. After about five minutes to this solution were added 10 mL of toluene and 0.3 mL (2.5 mmol) of p-tolunitrile at -20°C. The reaction mixture was stirred at 60°C for 20 h. Solvent was removed by rotary evaporator and the residue was distilled by bulb to bulb distillation (bp 150°C(oven)/20 mmHg) to give 0.606 g (91 % yield) of 1 as a colorless liquid.

2.3.2. Characterization of Products

N,N-Bis(trimethylsilyl)-p-methylbenzylamine(1): for a sample obtained by bulb to bulb distillation; bp 150°C/20 mmHg; IR (neat) 2955, 1510, 1460, 1409, 1353, 1304, 1287,

1253, 1194, 1174, 1069, 1034, 940, 873, 835, 763 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 18H, Si-CH_3), 2.18(s, 3H, CH_3), 3.96(s, 2H, CH_2), 6.93(m, 4H, Ar); Mass m/e 265 (M^+, 23), 250(100), 176(34), 174(20), 149(47), 73(44); Anal. Calcd. for $C_{14}H_{27}NSi_2$: C, 63.32; H, 10.25; N. 5.28. Found: C, 63.23; H, 10.41; N, 5.14.

N,N-Bis(trimethylsilyl)benzylamine: for a sample obtained by bulb to bulb distillation; bp 130°C(oven)/20 mmHg; 3085, 2975, 1600, 1492, 1353, 1248, 1194, 1085, 1061, 1028, 912, 866, 838, 753, 727 cm^{-1}; ^1H NMR δ 0.02(s, 18H, Si-CH_3), 3.97 (s, 2H, CH_2), 7.05(m, 5H, Ar); Mass m/e 251(M^+, 20), 236(100), 174(20), 162(46), 135(30), 73(43); Anal. Calcd for $C_{13}H_{25}NSi_2$: C, 62.08; H, 10.02; N, 5.57. Found: C, 61.83; H, 10.23; N, 5.55.

N,N-Bis(trimethylsilyl)-m-methylbenzylamine: for a sample obtained by bulb to bulb distillation; bp 150°C(oven) /19 mmHg; IR (neat) 3060, 2975, 1606, 1593, 1494, 1347, 1288, 1253, 1148, 1068, 1029, 908, 839, 861, 767, 755 cm^{-1}; ^1H NMR δ 0.02(s, 18H, Si-CH_3), 2.20(s, 3H, CH_3), 3.95(s, 2H, CH_2), 6.68-7.01(m, 4H, Ar); Mass m/e 265(M^+, 29), 250(100), 176(34), 174(20), 149(47), 73(44); Anal. Calcd for $C_{14}H_{27}NSi_2$: C, 63.32; H, 10.25; O, 5.28. Found: C, 63.06; H, 10.37; N, 4.97.

N,N-Bis(trimethylsilyl)-o-methylbenzylamine: for a sample obtained by bulb to bulb distillation; bp 150°C(oven) /10 mmHg; IR (neat) 2975, 1601, 1485, 1455, 1406, 1382, 1352, 1291, 1252, 1208, 1178, 1115, 1065, 1040, 1018, 945, 879, 839, 742 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 18H, Si-CH_3), 2.12(s, 3H, CH_3), 3.90(s, 2H, CH_2), 6.83-7.09(m, 4H, Ar); Mass m/e 265(M^+, 19), 250(34), 176(20), 174 (13), 149(19), 104(100), 73(26); Anal. Calcd for $C_{14}H_{27}NSi_2$: C, 63.32; H, 10.25; N, 5.28. Found: C, 62.55; H, 10.22; N, 5.23.

N,N-Bis(trimethylsilyl)-β-naphtylmethane: for a sample obtained by bulb to bulb distillation; bp 150°C(oven)/0.5 mmHg; IR (neat) 2970, 1627, 1505, 1449, 1366, 1249, 1154, 1119, 1070, 1028, 949, 896, 868, 837, 750 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 18H, Si-CH_3), 4.41(s, 2H, CH_2), 7.07-7.72(m, 7H, Ar); Mass m/e 301(M^+, 32), 286(100), 212(21), 198(14), 185 (28), 174(23), 141(22), 73(38); Anal. Calcd for $C_{17}H_{27}NSi_2$: C, 67.71; H, 9.02; N, 4.64. Found: C, 67.49; H, 9.07; N, 4.71.

N,N-Bis(trimethylsilyl)-p-cyanomethylbenzylamine: for a sample obtained by bulb to bulb distillation; bp 150°C(oven) /0.5 mmHg; IR (neat) 2970, 1507, 1455, 1414, 1353, 1293, 1248, 1173, 1073, 1031, 1020, 958, 876, 837, 764, 750 cm^{-1}; ^1H NMR (CCl_4) δ 0.06(s, 18H, Si-CH_3), 3.58(s, 2H, CH_2), 4.03 (s, 2H, CH_2), 6.83-7.30(m, 4H, Ar); Mass m/e 290(M^+, 17),

275(M^+-Me, 100), 201(37), 187(13), 174(34), 130(13), 73(59); Anal. Calcd for $C_{15}H_{26}N_2Si_2$: C, 62.01; H, 9.02; N, 9.64. Found: C, 61.67; H, 9.07; N, 9.11.

N,N-Bis(trimethylsilyl)-p-methoxybenzylamine: for a sample obtained by bulb to bulb distillation; bp 160°C(oven) /10 mmHg; IR (neat) 2975, 1608, 1583, 1508, 1459, 1440, 1409, 1354, 1299, 1247, 1181, 1167, 1108, 1068, 1042, 1011, 935, 875, 838, 757 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 18H, Si-CH_3), 3.72 (s, 3H, CH_3), 4.00(s, 2H, CH_2), 6.16-7.08(m, 4H, Ar); Mass m/e 281(M^+, 28), 266(100), 192(20), 174(18), 165(71), 121(45), 73(55); Anal. Calcd for $C_{14}H_{27}NOSi_2$: C, 59.73; H, 9.67; N, 4.97. Found: C, 59.30; H, 9.86; N, 4.83.

N,N-Bis(trimethylsilyl)-p-chlorobenzylamine: for a sample obtained by bulb to bulb distillation; bp 150°C(oven) /5 mmHg; IR (neat) 2970, 1593, 1576, 1486, 1454, 1403, 1343, 1280, 1249, 1187, 1094, 1069, 1025, 1012, 942, 871, 835, 751 cm^{-1}; ^1H NMR (CCl_4) δ 0.02(s, 18H, Si-CH_3), 3.96(s, 2H, CH_2), 7.09(m, 4H, Ar); Mass m/e 285(M^+, 10), 270(100), 196(45), 174(17), 169(21), 86(27), 73(83); Anal. Calcd for $C_{13}H_{24}ClNSi_2$: C, 54.60; H, 8.46; N, 4.90. Found: C, 54.39; H, 8.49; N, 4.80.

N, N-Bis(trimethylsilyl)-p-dimethylaminobenzylamine: for a sample obtained by bulb to bulb distillation; bp 120°C

(oven)/0.5 mmHg; IR (neat) 2975, 1610, 1564, 1512, 1476, 1440, 1341, 1247, 1179, 1161, 1064, 1029, 949, 930, 873, 837, 754 cm^{-1}; ^1H NMR (CCl_4) δ 0.04(s, 18H, Si-CH_3), 2.88(s, 6H, CH_3), 3.99(s, 2H, CH_2), 6.40-7.24(m, 4H, Ar); Mass m/e 294 (M^+, 41), 279(19), 178(33), 172(100), 73(21); Anal. Calcd for $C_{15}H_{30}N_2Si_2$: C, 61.16; H, 10.26; N, 9.51. Found: C, 60.79; H, 10.35; N, 9.43.

N,N-Bis(trimethylsilyl)-p-methoxycarbonylbenzylamine: for a sample obtained by bulb to bulb distillation; bp 150 °C(oven)/0.7 mmHg; IR (neat) 2970, 1716, 1607, 1572, 1432, 1412, 1350, 1278, 1266, 1252, 1191, 1170, 1110, 1074, 1028, 1019, 968, 886, 840, 750 cm^{-1}; ^1H NMR (CCl_4) δ 0.06(s, 18H, Si-CH_3), 3.85(s, 3H, CH_3), 4.12(s, 2H, CH_2), 7.17-8.16(m, 4H, Ar); Mass m/e 309(M^+, 15), 294(100), 220(34), 193(20), 190(29), 174(19), 73(52); Anal. Calcd for $C_{15}H_{27}NO_2Si_2$: C, 58.20; H, 8.79; N, 4.53. Found: C, 58.04; H, 8.85; N, 4.39.

2.4. References and Notes

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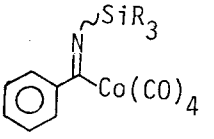

i

Conclusion

The objective of this rearch was to develop a cobalt carbonyl catalyzed carbon chain extension reactions and reduction using hydrosilanes. The important results mentioned in each chapter of this thesis are summarized as follows.

In Chapter 1, a new cobalt carbonyl catalyzed reaction of cyclic ethers with a hydrosilane and carbon monoxide has been described. Catalytic reaction of cyclic ethers like oxiranes, oxetanes, and tetrahydrofurans took place at 25°C and 1 atm to undergo incoproration of one molecule of carbon monoxide as an oxymethyl group. High stereoselectivity was observed for the ring opening of symmetrically substituted cyclic ethers. Ring opening of oxiranes having oxygen containing substituents took place highly regioselectively to form 1,3-diol derivatives. Especially regio- and stereoselective ring opening of trans-2,3-epoxybutanol with a hydrosilane and carbon monoxide was achieved by the protection of the hydroxy group with chloroacetyl group and the reaction gave a 2-methyl-1,3-butane diol derivative which is an important intermediates in organic synthesis. Furthermore, incorporation of carbon monoxide into a tertiary carbon center, which is a very rare reaction, was observed. Finally conversion of tetrahydrofurans to enol silyl ethers using cobalt carbonyl catalyzed reaction with a hydrosilane

and carbon monoxide in acetonitrile has been described.

Characteristic features of these reactions are summarized as follows.

(1) In the viewpoint of organometallic chemistry, the reactions described in Chapter 1 demonstrate a new method for the formation of carbon-transition metal bond by utilizing the high oxophilicity of silicon under mild reaction conditions (25°C, 1 atm).

(2) In the viewpoint of organic synthesis, these catalytic reactions provide a novel direct method for the nucleophilc oxymethylation, which is not an easy task using conventional methods.

In Chapter 2, selective reduction of aromatic nitriles with a hydrosilane in the presence of $Co_2(CO)_8$ has been described. This reaction provides a new route to N,N-disilylamines.

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