Journal of Organometallic Chemistry, 140 (1977) 361–378

TRANSITION METAL REACTIONS OF SILANES II.* THE REACTION OF CYCLOALKENES WITH VARIOUS HYDROSILANES AND CARBON MONOXIDE CATALYZED BY $Co_2(CO)_8$.

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(Received July 6th, 1977)

Summary

The reaction of cycloalkenes(cyclopentene, cyclohexene, cycloheptene, cyclooctene, 1-methylcyclohexene, and norbornene) with Et_2MeSiH and carbon monoxide in the presence of $Co_2(CO)_8$ gave the corresponding diethylmethylsiloxymethylenecycloalkanes. In such reactions of cyclohexene, the following hydrosilanes gave the corresponding siloxymethylenecyclohexanes: Me_3SiH, $EtMe_2SiH$, Et_2MeSiH, Et_3SiH, $PhMe_2SiH$, Ph_2MeSiH. Effects of the reaction conditions(the pressure of carbon monoxide, the temperature, and the molar ratio of cyclohexene to Et_2MeSiH) were examined. The yield of diethylmethylsiloxymethylenecyclohexane increased remarkably with increasing molar ratio of cyclohexene to Et_2MeSiH. At higher temperature, the yield of the isomerization product, 1-(diethylmethylsiloxymethyl)-cyclohex-1-ene, increased.

Introduction

It is well known that the metal-catalyzed reactions of a

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*For part 1, see ref. [1].

hydrosilane parallels those of hydrogen. For example, in the case of oxidative addition to an Ir(I) complex, both of a hydrosilane[2] and hydrogen[3a] react to give cis-adducts. Hydrosilylation[4], the catalyzed addition of R_3SiH to an olefin, is formally analogous to catalytic hydrogenation[3]. Moreover, mechanistically these reactions seem to be very closely related[2, 3, 5a].

The well-known hydroformylation involves addition of hydrogen and carbon monoxide to olefins[5]. The formal similarity between a hydrosilane and hydrogen in transition metal reactions has made us curious about the catalyzed reaction of olefins with a hydrosilane and carbon monoxide. However, no such reaction has been reported, to the best of our knowledge, except for an interesting reaction described by Chalk and Harrod in 1967[6]. They studied the dicobalt octacarbonyl-catalyzed reaction of olefins with triethylsilane and carbon monoxide. The reaction of pent-1-ene and cyclohexene was reported to be "very complex" and no details were given. In the case of ethylene, however, a complex mixture of the reaction products with boiling points ranging from 90°C to 300°C was fractionated into thirty three fractions and one of them was found to contain unsaturated alkoxy silane(s) of the formula $C_3H_5OSi(C_2H_5)_3$ which gave the 2,4-dinitrophenylhydrazone of propionaldehyde on treatment with the hydrazine.

Beside the above mentioned work, surprisingly few studies have been made and somewhat discouraging results have been reported on the reaction of carbon monoxide with organosilicon compounds in the presence of transition metals. The scattered examples seem to be mostly limited to studies dealing with the catalyzed reaction involving a hydrosilane and carbon monoxide or the reaction between the complexes containing silicon-metal bonds and carbon monoxide. Chalk and Harrod reported that no direct carbonylation of triethylsilane occurred at temperatures up to 300°C and carbon monoxide pressures up to 1700 psi in the presence of $Co_2(CO)_8$[6]. It has been reported that attempts to induce carbonyl insertion into the Si-Co[7], Si-Mn[8], and Si-Rh[9] bonds by direct reaction with carbon monoxide were unsuccessful. Hagen and co-workers carried out the reaction of $MeSiCl_2Co(CO)_4$ with 4000 atm of carbon monoxide at 90°C, but no insertion of carbon monoxide into the silicon-cobalt bond was observed[10]. It has been reported that the use of carbon monoxide, as well as of phosphines, inhibited dicobalt octacarbonyl-catalyzed addition of dimethylchlorosilane to acrylonitrile[11].

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

Results and discussion

Reaction of cycloalkenes with diethylmethylsilane and carbon monoxide

Contrary to the "very complex" results reported by Chalk and Harrod for the reaction of cyclohexene with

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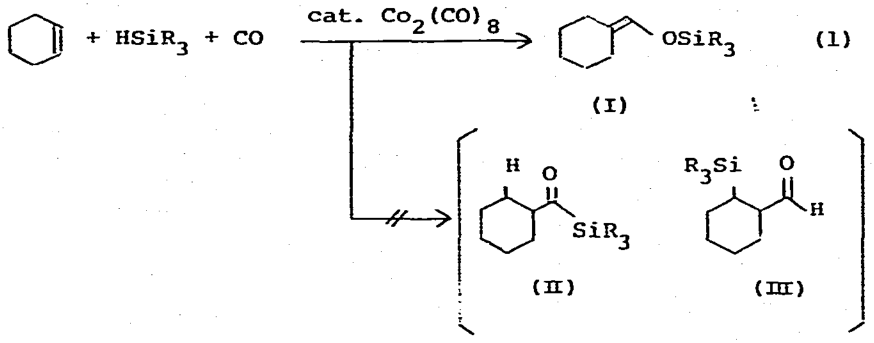
* A portion of this work has been published in preliminary form, see ref. [1].

triethylsilane and carbon monoxide in the presence of $Co_2(CO)_8$, as mentioned above, we have found that this reaction gave triethylsiloxymethylenecyclohexane(Id) as a sole product in a good yield.* For diethylmethylsilane, a similar result was found. If one assumes that the reaction proceeds in a formally similar way as



hydroformylation, two types of products, (II) and (III), may be expected. However, neither of these compounds was found. The stoichiometry of the reaction can be presented as shown in eq. 1, and all three reactants are incorporated into the product(I). While it is obvious that the carbon and oxygen atoms of carbon monoxide are found in the oxymethylene group of the product, it is not yet known which hydrogen in the product(I) has come from the hydrosilane used.**

The results obtained for the reaction using cycloalkenes (3 equivalents) and diethylmethylsilane(1 equivalent) are given in the Table 1. All the catalytic reactions were

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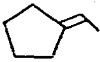
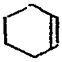
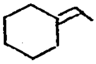
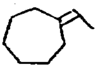
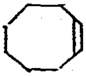
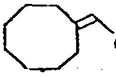
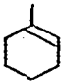
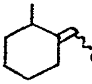
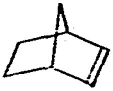
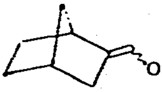
* Unfortunately, it is not possible to explain the difference in the results of Chalk and Harrod and ours, since no experimental details were given in their paper. See ref. [6].

** Deuterium labeling experiments are now in progress.

TABLE 1

REACTION OF VARIOUS OLEFINS WITH Et_2MeSiH AND $CO^{a)}$

Olefin	Catalyst	Product	Yield(%) (GLC)
	$Co_2(CO)_8$	 $OSiEt_2Me$(IV)	48
	$Co_2(CO)_8$	 $OSiEt_2Me$(Ic)	71
	$Ru_3(CO)_{12}$	-	1.4
	$RhCl(PPh_3)_3$		0.5
	$Co_2(CO)_8$	 $OSiEt_2Me$(V)	74
	$Co_2(CO)_8$	 $OSiEt_2Me$(VI)	69
	$Co_2(CO)_8$	 $OSiEt_2Me$(VII)	22
	$Co_2(CO)_8$	 $OSiEt_2Me$(VIII)	45

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

carried out using a 100 ml stainless steel autoclave. Generally, a solution of a cycloalkene(30 mmol), Et_2MeSiH (10 mmol), and $Co_2(CO)_8$(0.2 mmol) in benzene(20 ml) was heated under a pressure of carbon monoxide at 140°C for 20 h to give diethylmethylsiloxymethylenecycloalkanes(Ic and IV-VIII). The pressure of carbon monoxide was initialy 80 kg/cm^2 at 25°C, then reached 105-108 kg/cm^2 at 140°C, and it was finally 76-79 kg/cm^2 at 25°C after the reaction had been completed. While simple cyclic olefins(cyclohexene, cycloheptene, and cyclooctene), except for cyclopentene, gave the expected product in good yield, the reaction of 1-methylcyclohexene, a trisubstituted olefin, and norbornene, a bicyclic olefin, gave the expected product only in moderate yield. All the reactions were accompanied by the formation of the corresponding disiloxane in 5-15% yield.

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

Reaction of cyclohexene with various hydrosilanes

Cyclohexene reacted with various hydrosilanes and carbon monoxide in the presence of $Co_2(CO)_8$ to give the corresponding siloxymethylenecyclohexanes(I) as shown in eq. 1. The results were summarized in Table 2.

Trialkylsilanes, except for Me_3SiH, yielded the corresponding siloxymethylenecyclohexanes(Ib-Id) in good yield. In the case of hydrosilanes having a phenyl substituent, the yield of the products(Ie and If) decreased in the order $PhMe_2SiH > Ph_2MeSiH > Ph_3SiH$. The following hydrosilanes did not give the corresponding siloxymethylenecyclohexane: Ph_3SiH, Ph_2SiH_2, and $(MeO)_2MeSiH$. The reaction of $(MeO)_2MeSiH$ gave very complex results, without recovery of the hydrosilane. These results show that hydrosilanes with electron-donating substituents have good reactivity in the present reaction. The reason for the low yield in the case of Me_3SiH is not clear. It may be intrinsic or due to the different experimental procedure(see Experimental Part).

TABLE 2

REACTION OF CYCLOHEXENE WITH VARIOUS HYDROSILANES AND CO[a)]

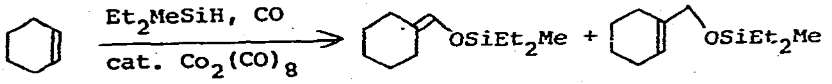
Hydrosilane	Yield of the product(I)	Recovered hydrosilane(%)	$(R_3Si)_2O$ [b)]
Me_3SiH	(Ia) 4	88	0
$EtMe_2SiH$	(Ib) 57	36	5
Et_2MeSiH	(Ic) 71	5	8
Et_3SiH	(Id) 74	0	23
$PhMe_2SiH$	(Ie) 51	29	18
Ph_2MeSiH	(If) 26	57	6
Ph_2SiH_2	0	39	18
Ph_3SiH	0	88	0
$(MeO)_2MeSiH$	0	0	0

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

b) Disiloxanes corresponding to hydrosilanes used.

Effects of the reaction conditions

When a three fold excess of cyclohexene was used, as in all the reactions described above, only a single product (I) was obtained. However, when these reactions were carried out using equimolar amounts of a cycloalkene and a hydrosilane at higher temperature, another product(IX) was obtained in addition to I (eq. 3). The product(IX) may be formed by catalyzed double-bond isomerization of the product(Ic). The yield and distribution of the products



(3)

(Ic) (IX)

were found to be affected by the reaction conditions such as molar ratio of reactants, temperature, and the pressure of carbon monoxide. The results obtained for the reaction of cyclohexene with diethylmethylsilane and carbon monoxide are shown in the Table 3.

TABLE 3

EFFECT OF THE REACTION CONDITIONS[a)]

Reaction conditions Cyclohexene mmol	 Et_2MeSiH mmol	 Temp. °C	 CO pressure[c)] kg/cm^2	Combined[b)] yield (Ic+IX) (%)	Product[b)] distribution Ic : IX(%)
10	10	140	30	12	99 : 1
10	10	140	60	36	97 : 3
10	10	140	80	37	98 : 2
20	10	140	80	51	98 : 2
30	10	140	80	71	100 : 0
30	10	200	80	84	80 : 20

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

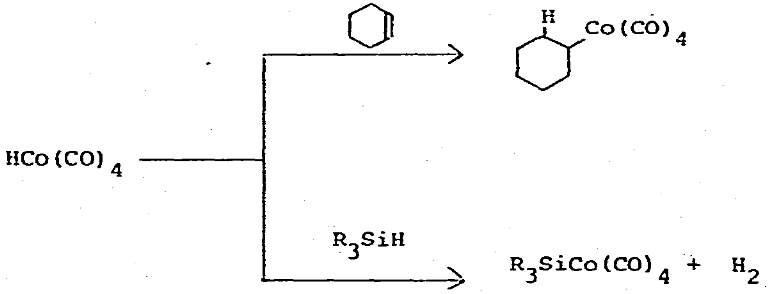
b) The yields and the product distribution were determined by GLC.

c) Initial pressure at room temperature.

The combined yield of Ic and IX increased with an increase in the pressure of carbon monoxide, but the difference was very small at 60-80 kg/cm^2. The combined yield increased remarkably with increasing molar ratio of cyclohexene to Et_2MeSiH. The combined product yield was best at 200°C, but the yield of the initial product(Ic) decreased and that of the isomerization product(IX) increased.

The fact that the use of a higher molar ratic of cyclohexene to the hydrosilane has resulted in a higher yield of the product suggested the importance of hydrocobalt-tetracarbonyl, $HCo(CO)_4$, as the active catalyst in the present reaction. The reaction of trialkylsilanes with $Co_2(CO)_8$ has been known to give $HCo(CO)_4$ and $R_3SiCo(CO)_4$ [6, 13] (eq. 4). The hydrocobaltcarbonyl may react with olefins to initiate a catalytic cycle(eq. 5) However, when a sufficient amount of the olefin is not present in the system, it reacts

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



(5)

(6)

with the hydrosilane to give $R_3SiCo(CO)_4$ and hydrogen[6, 13] (eq. 6). This reaction(eq. 6) would stop the catalytic cycle. The alkylcobalt complex formed in eq. 5 may give an acylcobalt complex which then reacts with a hydrosilane to give the product(I) with regeneration of hydrocobaltcarbonyl. In a preliminary report, we have stated that an aldehyde or an acylsilane may not be an intermediate in the present reaction. We are now reexamining all possibilities. More experiments are needed before we can understand the nature of the catalytic cycle of the present reactions.

The discovery of the present reaction has raised many interesting questions. How closely is the present reaction related to hydroformylation? What kind of metal complexes are effective in catalyzing the reaction? Are the effective metal complexes hydroformylation catalysts or hydrosilylation catalysts? What kind of olefins can be used? Is the present reaction appliciable only to olefins? All these questions will be dealt with in forthcoming papers.

It should be pointed out that enol silyl ethers are highly versatile intermediates for organic synthesis[14] and that the present reaction represents the first method for the synthesis of enol silyl ethers from olefins.

Experimental

General comments

All temperatures are uncorrected. IR spectra were recorded with a Shimazu IR-400. The ^{1}H-NMR spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer with Me_4Si as an internal standard. The position of Me_4Si was recognized by adding it after recording spectrum without the standard. Otherwise the signal of the standard may be confused with that of a organosilicon compound. Mass spectra were recorded on a Hitachi mass spectrometer Model RMU-6E. High resolution mass spectra were recorded on a Hitachi RMU-7M. Analytical gas chromatography(GLC) were carried out on a Shimazu GC-3BF and a Shimazu GC-6A equipped with flame ionization detecters. The GLC columns used were as follows: (A) 6m × 3mm stainless steel containing 5% Silicon OV-1 supported on 60-80 mesh Uniport KS; (B) 6m × 3mm stainless steel containing 15% DEGS supported on 60-80 mesh cromosorb W. Preparative GLC was carried out using a Varian Aerograph Model 90-P gas chromatograph. Olefins were commercially available and were purified by distillation. Benzene was dried over sodium-lead alloy and stored over 5A molecular sieves. $Co_2(CO)_8$ were prepared according to the literature[15]. $Ru_3(CO)_{12}$ and $RhCl(PPh_3)_3$ were commercially available. Hydrosilanes were prepared by standard methods [16]. Authentic samples of disiloxanes were prepared by $RhCl(PPh_3)_3$ catalyzed silylation of water with appropriate hydrosilanes(benzene as solvent, reflux 48 h, quantitative yields).

General procedure for the reaction of cycloalkenes with hydrosilanes and carbon monoxide in the presence of $Co_2(CO)_8$

A 100 ml stainless steel autoclave equipped with a 300 kg/cm^2 pressure gauge and a magnetic stirring bar was charged with 30 mmol of the cycloalkene, 10 mmol of the hydrosilane, 0.2 mmol of $Co_2(CO)_8$ and 20 ml of benzene. The autoclave was flushed with N_2(80 kg/cm^2) and CO (50 kg/cm^2), then charged with CO to 80 kg/cm^2. The reaction vessel was then heated with magnetic stirring in an oil bath. After 1 h, the pressure reached 105-108 kg/cm^2 at 140°C. The temperature was maintained at 140°C for 20 h. The vessel was then cooled to room temperature. The pressure decreased to 76-79 kg/cm^2. The gas pressure was slowly released and the autoclave was opened. Analysis of the reaction mixture by GLC(column A) with an internal standard (n-tridecane, n-tetradecane, n-pentadecane, or n-eicosane) showed it to contain the products (I and IV-IX) and $(R_3Si)_2O$. RRT(relative retention time) of the products to an internal standard is shown below for each case. RRT(relative retention time)=retention time of the compounds/retention time of the standard. The hydrosilane recovered was analyzed by GLC(column A and B) with an appropriate internal standard. Distillation of the reaction mixture and/or preparative GLC afforded the analytical samples.

Diethylmethylsiloxymethylenecyclohexane(Ic)

Analysis by GLC(column A, 130°C, n-tetradecane as an internal standard(RRT 1)); Ic(71%, RRT 0.79) and $(Et_2MeSi)_2O$ (8%, RRT 0.29). Ic; bp 130-138°C(28 mm); IR(neat) 2924, 1680, 1450, 1380, 1260, 1240, 1220, 1160, 1090, 1070, 1010, 970, 910, 820, 800, 760 cm^{-1}; NMR(CCl_4) $\underline{\delta}$ 0.08(s 3H), 0.58(m 4H), 0.96(m 6H), 1.36-1.60(c 6H), 1.88(m 2H), 2.10(m 2H), 5.88 (s 1H); mass spectrum m/e(rel. intensity) 212(33), 183(40), 101(9), 89(100).

Anal. Calcd for $C_{12}H_{24}OSi$: P^+, 212.1595; C, 67.85; H, 11.38. Found: P^+, 212.1561; C, 67.80; H, 11.40.

Diethylmethylsiloxymethylenecyclopentane(IV)

Analysis by GLC(column A, 120°C, *n*-tridecane as an internal standard(RRT 1)); IV(48%, RRT 0.80) and $(Et_2MeSi)_2O$ (8% RRT 0.46). IV; bp 98-100°C(15 mm); IR(neat) 2950, 2875, 1685, 1460, 1415, 1250, 1170, 1120, 1005, 960, 950, 840-820, 800, 760 cm^{-1}; NMR(CCl_4) $\underline{\delta}$ 0.08(s 3H), 0.60(m 4H), 0.96(m 6H), 1.58(m 4H), 2.12(m 4H), 6.04(s 1H); mass spectrum m/e(rel. intensity) 198(30), 169(39), 103(9), 89(100).

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

Diethylmethylsiloxymethylenecycloheptane(V)

Analysis by GLC(column A, 140°C, *n*-tetradecane as an internal standard(RRT 1)); V(74%, RRT 1.29) and $(Et_2MeSi)_2O$ (9%). V; bp 155-165°C(50 mm); IR(neat) 2950, 1660, 1450, 1260, 1190, 1160, 1130, 1000, 960, 870, 810, 760 cm^{-1}; NMR(CCl_4) $\underline{\delta}$ 0.08(s 3H), 0.58(m 4H), 0.96(m 6H), 1.40-1.70(c 8H), 1.99 (m 2H), 2.20(m 2H), 5.92(s 1H); mass spectrum m/e(rel. intensity) 226(13), 197(35), 101(11), 89(100).

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

Diethylmethylsiloxymethylenecyclooctane(VI)

Analysis by GLC(column A, 150°C, *n*-tetradecane as an internal standard(RRT 1)); VI(69%, RRT 1.96) and $(Et_2MeSi)_2O$

(11%). VI; bp 126-135°C(25 mm); IR(neat) 2920, 1660, 1480, 1250, 1235, 1200, 1160, 1090, 1060, 1000, 960, 860, 800, 770 cm^{-1}; NMR(CCl_4) δ 0.08(s 3H), 0.58(m 4H), 0.97(m 6H), 1.36-1.72(c 10H), 1.98(m 2H), 2.14(m 2H), 5.94(s 1H); mass spectrum m/e(rel. intensity) 240(13), 211(33), 121(21), 101(18), 89(100).

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

1-Diethylmethylsiloxymethylene-2-methylcyclohexane(VII)

Analysis by GLC(column A, 130°C, n-tridecane as an internal standard(RRT 1)); VII (22%, RRT 1.64), unidentified compound(5%, RRT 1.52), and $(Et_2MeSi)_2O$ (15%). The structure of the unidentified compound is not clear, but NMR spectrum of an 1:1 mixture(by GLC) of VII and it is not consistent with 2-diethylmethylsiloxyethenyl-1-cyclohexane. VII ; bp 120-125°C(17 mm); IR(neat) 2950, 2900, 1680, 1460, 1260, 1150, 1100, 1010, 960, 880, 820, 800, 770 cm^{-1}; NMR(CCl_4) δ 0.08 (s 3H), 0.60(m 4H), 0.88-1.20(m 6H)overlapped with 0.96(s 3H), 1.20-1.86(c 6H), 1.86-2.12(c 2H), 2.60-2.80(c 1H), 5.88(s 1H); mass spectrum m/e (rel. intensity) 226(11), 211(5), 197(11), 101(11), 89(100).

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

2-Diethylmethylsiloxymethylenenorbornene(VIII)

Analysis by GLC(column A, 150°C, n-tetradecane as an internal standard (RRT 1)); VIII(45%, RRT 1.71) and $(Et_2MeSi)_2O$ (7%). VIII; bp 130-140°C(10 mm); IR(neat) 2940, 2860, 1690, 1250, 1160, 1140, 1100, 1000, 850, 810, 760 cm^{-1}; NMR(CCl_4) δ 0.08(s 3H), 0.57(m 4H), 0.90(m 6H), 1.12-1.32(c 4H), 1.47(m 1H), 1.61(m 1H), 1.86(m 1H), 2.04(m 1H), 2.31(m 1H), 2.55(m 1H), 6.02(m 1H); In addition, small absorptions at 3.06 and 5.79 were also observed. The product may contain two stereo isomers. mass spectrum m/e (rel. intensity) 224(39), 195(100), 101 (44), 89(39).

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

Dimethylethylsiloxymethylenecyclohexane(Ib)

Analysis by GLC(column A, 110°C, n-tridecane as an internal standard(RRT 1)); Ib(57%, RRT 0.70) and $(EtMe_2Si)_2O$ (5%, RRT 0.13). Ib; bp 82-88°C(13 mm); IR(neat) 2910, 2850, 1680, 1450, 1380, 1250, 1150, 1080, 1060, 1000, 960, 900, 840, 780 cm^{-1}; NMR(CCl_4) δ 0.11(s 6H), 0.57(m 2H), 0.96 (m 3H), 1.35-1.59(c 6H), 1.88(m 2H), 2.10(m 2H), 5.84(s 1H); mass spectrum m/e (rel. intensity) 198(25), 169(22), 89(14), 75(100).

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

Triethylsiloxymethylenecyclohexane(Id)

Analysis by GLC(column A, 135°C, n-pentadecane as an internal standard (RRT 1)): Id(74%, RRT 0.77) and $(Et_3Si)_2O$ (23%, RRT 0.44). Id; bp 135-139°C(20 mm); IR(neat) 2920, 2895, 1675, 1445, 1260, 1240, 1220, 1150, 1090, 1010, 910, 820, 740 cm^{-1}; NMR(CCl_4) δ 0.70(m 6H), 1.09(m 9H), 1.44-1.74(c 6H), 2.01(m 2H), 2.22(m 2H), 6.02(s 1H); mass spectrum m/e (rel. intensity) 226(24), 197(41), 169(11), 103(100), 87(17), 75(55).

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

Dimethylphenylsiloxymethylenecyclohexane(Ie)

Analysis by GLC(column A, 160°C, n-pentadecane as an internal standard (RRT 1)); Ie(51%, RRT 1.97) and $(PhMe_2Si)_2O$ (18%, RRT 2.19). Ie; bp 150-151°C(16 mm); IR(neat) 3050, 2910, 2850, 1680, 1590, 1430, 1250, 1200, 1150, 1120, 970, 830, 780, 720, 700 cm^{-1}; NMR(CCl_4) δ 0.39(s 6H), 1.35-1.59(c 6H), 1.86(m 2H), 2.16(m 2H), 5.88(s 1H), 7.26 (m 3H), 7.44(m 2H); mass spectrum m/e (rel. intensity) 246 (42), 231(4), 168(10), 153(19), 137(78), 135(100).

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

Diphenylmethylsiloxymethylenecyclohexane(If)

Analysis by GLC(column A, 220°C, n-eicosane as an internal standard (RRT 1)); If(26%, RRT 1.65) and $(Ph_2MeSi)_2O$ (6%, RRT 6.31). If; bp 150-156°C(0.55 mm); IR(neat); 3050, 2910, 2850, 1680, 1590, 1430, 1250, 1140, 1120, 1080, 1060, 900, 830, 790, 720, 700 cm^{-1}; NMR(CCl_4) δ 0.63(s 3H), 1.53 (c 6H), 1.91(m 2H), 2.25(m 2H), 6.01(s 1H), 7.34(m 6H), 7.55 (m 4H); mass spectrum m/e (rel. intensity) 308(38), 215(33), 199(63), 197(100), 137(91).

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

Trimethylsiloxymethylenecyclohexane(Ia)

A solution of cyclohexene(30 mmol) and $Co_2(CO)_8$ (0.2 mmol) in 20 ml of benzene was placed in a 100 ml stainless steel autoclave. The autoclave was flushed with N_2(80 kg/cm^2) and CO(50 kg/cm^2) and cooled to -70°C. Trimethylsilane (10 mmol) was introduced to the autoclave by trap-to-trap distillation under vacume(10 mm) and then the autoclave was charged with CO to 80 kg/cm^2 at 25°C and heated at 140°C.

The GLC retention time of the product was identical to that of trimethylsiloxymethylenecyclohexane which was independently prepared from cyclohexanecarboxaldehyde and trimethylchlorosilane by House's method [17].

Analysis by GLC(column A, 100°C, _n_-dodecane as an internal standard (RRT 1)); Ia(4%, RRT 0.65). Ia; bp 91°C (23 mm); IR(neat) 2950, 2850, 1675,1445, 1250, 1210, 1150, 1080, 900, 840, 740 cm^{-1}; NMR(CCl_4) _δ_ 0.14(s 9H), 1.44(c 6H), 1.84(m 2H), 2.04(m 2H), 5.80(s 1H); mass spectrum m/e (rel. intensity) 184(44), 169(42), 155(21), 75(100) 73(98).

Anal. Calcd for $C_{10}H_{20}OSi$: P^+, 184.1282. Found: P^+, 184.1279.

1-(Diethylmethylsiloxymethyl)-cyclohex-1-ene(IX)

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

Analysis by GLC(column A, 100°C, _n_-tetradecane as an internal standard (RRT 1)); IX(17%, RRT 0.81), Ic(67%, RRT 0.79), and $(Et_2MeSi)_2O$ (15%, RRT 0.29). IX; IR(neat); 2920, 2870, 1675, 1460, 1420, 1255, 1160, 1090, 1070, 1010, 965, 840, 800, 760 cm^{-1}; NMR(CCl_4) _δ_ 0.01(s 3H), 0.53(m 4H), 0.93(m 6H), 1.60 (m 4H), 1.80-2.12(c 4H), 3.85(s 2H), 5.50(m 1H); mass spectrum m/e (rel. intensity) 212(14), 183(31), 103(7), 89(100).

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

Acknowledgments

This work was generously supported in part by a Grant-in-Aid for Scientific Research by the Ministry of Education of Japan. We thank Shin-Etsu Industry Co., Ltd. for the supply of organosilanes.

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