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A regiodefined synthesis of α-trimethylsilyl ketones catalyzed by rhodium(I) hydride complex

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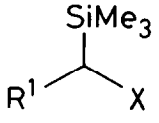
Abstract

Regiodefined synthesis of α-trimethylsilyl ketones is attained by one of three different routes: isomerization of β-trimethylsilyl allyl alcohols (route A), isomerization of β′-trimethylsilyl allyl alcohols (route B), and dehydrogenation of β-trimethylsilyl alcohols via transfer hydrogenation to α,β-enones (route C). All of these procedures are catalyzed efficiently by $HRh(PPh_3)_4$ at about 100 °C. Route A inevitably requires the presence of 2-trimethylsilyl-1-phenyl-2-propen-1-one as a cocatalyst for smooth isomerization. This strongly suggests that a kind of intermolecular transfer hydrogenation plays an important role in the catalytic cycle.

Introduction

During the past two decades, organosilicon compounds have attracted much attention as an indispensable tool in organic synthesis [2]. For example, β-functionalized silicon compounds such as, α-trialkylsilylcarboxylic esters (**1**) [3], nitriles (**2**) [4], aldehydes (**3**) [5], and ketones (**4**) [6] have been used to provide the highly reactive and selective homologation units.



1 X = C(=O)OR²

2 X = CN

3 X = C(=O)H

4 X = C(=O)R²

α-Trimethylsilyl ketones (**4**) are especially useful in the stereodefined synthesis of disubstituted and trisubstituted olefins [7] and in regiodefined cross aldol reactions of ketones [8]. Direct replacement of the trimethylsilyl group in **4** with an electro-

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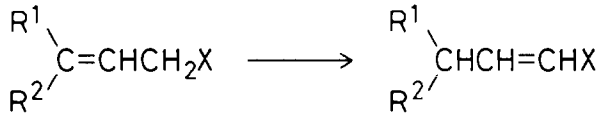
phile makes it possible to clearly distinguish the two α-positions of the unsymmetrically substituted ketones [9]. Thus, several types of indirect method have been reported for the selective synthesis of **4**, since direct silylation of the corresponding ketone gives only silyl enol ethers [10,11]. These are categorized as follows: (i) chromic acid oxidation of β-trimethylsilyl alcohols [7a,12], (ii) reaction of carboxylic acid derivatives with trimethylsilylmethyl anion [13], (iii) reaction of α-silyl carboxylic esters with Grignard reagents [14], and (iv) rearrangement of substrates such as 1,2-epoxysilanes [15], α,β-dihydroxysilanes [16], 2-chloro-1-trimethylsilyl alkoxide anions derived from an α-chloroacylsilane and methylmagnesium iodide [17], and the carbanions derived from silyl enol ethers [18]. All of these methods suffer from the lack of generality and require rather tedious procedures in order to retain the relatively labile silicon–carbon bond.

On the other hand, it is widely accepted that transition metal complexes accelerate the isomerization of an allylic double bond to a vinylic one in compound **5** as shown in eq. 1 [19].

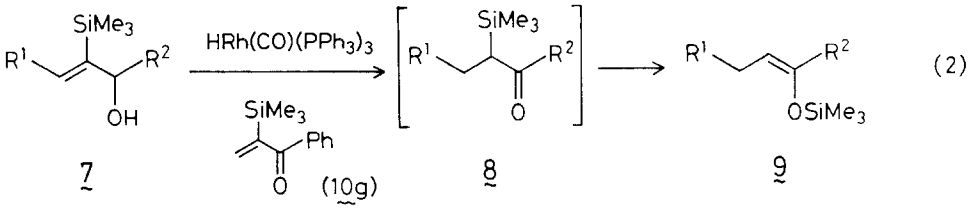


(1)

X = OH, OR, or NHR

5 **6**

This catalytic isomerization promises non-aqueous work-up under almost neutral conditions. Recently we reported the regiospecific formation of trimethylsilyl enol ethers (**9**) by the isomerization of β-trimethylsilyl allyl alcohols (**7**) in the presence of a catalytic amount of $HRh(CO)(PPh_3)_3$ and an α,β-enone (**10g**) (eq. 2) [20].



(2)

7 **8** **9**

This transformation involves consecutive migrations of double bond and trimethylsilyl group. Since both steps are non-discriminative under the reaction conditions, **9** was the ultimate product isolated. The probable formation of α-trimethylsilyl ketone (**8**) in the above course favored the selective migration of the double bond in **7**. Herein we report on a successful regio-defined synthesis of α-trimethylsilyl ketones from three different silyl alcohols, **7**, **12**, and **18**.

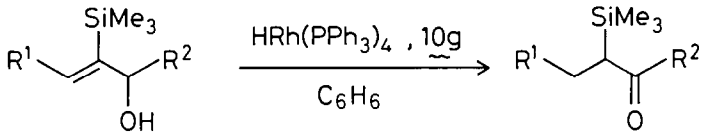
Results and discussion

Isomerization of β-trimethylsilyl allyl alcohols (7)

Double bond migration caused by an addition-elimination process of H–M was impossible in the isomerization of **7** because of the bulkiness of the trimethylsilyl

group. However, this hindrance was overcome by the introduction of α,β-enone, **10g** into the catalytic cycle [20]. This fact resembles the catalytic behavior of rhodium complex under transfer hydrogenation [21]. Selective acceleration of the first step in eq. 2 is expected if $HRh(CO)(PPh_3)_3$ is replaced by $HRh(PPh_3)_4$ which is an extremely active catalyst in transfer hydrogenation.

Thus, a benzene solution of trimethylsilyl allyl alcohol (**7d**) (1.0 mmol) was heated in a sealed tube containing a catalytic amount of **10g** (0.05 mmol) and $HRh(PPh_3)_4$ (0.05 mmol) at 105°C for 30 min. Subsequent evaporation of the solvent and bulb-to-bulb distillation of the residual oil gave the corresponding α-trimethylsilyl ketone **8d** in 90% yield (eq. 3).

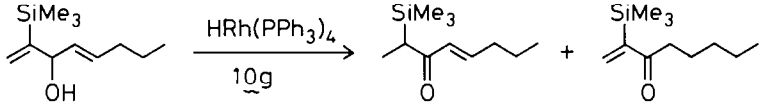


7 8 (3)

The presence of a catalytic amount of **10g** was also crucial in the case of $HRh(PPh_3)_4$, for smooth isomerization. The structure of **8d** was confirmed by the presence of a ν(C=O) (1692 cm^{-1}) absorption band in the IR spectrum, the presence of a sharp singlet (δ 0.05, Me_3Si), doublet (δ 1.06, CH_3–CH–Si) and quartet (δ 2.28, CH_3–C*H*–Si) in the ^1H NMR spectrum, and by elemental analysis. By contrast, trimethylsilyl enol ether **9d** was not detected in the ^1H NMR spectrum. Successful isomerization of **7d** to **8d** is thus an efficient preparative route to **8**. Thus, **7** isomerized readily to give **8** under analogous conditions, except for **7m**, and **7n** (vide infra). The results are listed in Table 1.

Although pure **8g** could not be isolated by distillation because of its subsequent isomerization to **9g**, the selective formation of **8g** was confirmed from the ^1H NMR spectrum of the crude product.

A remarkable example is **7j** in that it has two isomerizable olefinic moieties in the same molecule (eq. 4).



7j 8j 10j (4)

Two α,β-enones, **8j** and **10j**, were expected and were isolated as the products, but predominant formation of **8j** (**8j**/**10j** = 92/8) shows that the present catalytic system is able to discriminate between the two double bonds in **7j**. This fact suggests that the catalytic cycle which incorporates **10g** proceeds more rapidly than the isomerization of the double bond achieved by the addition-elimination process of H–Rh.

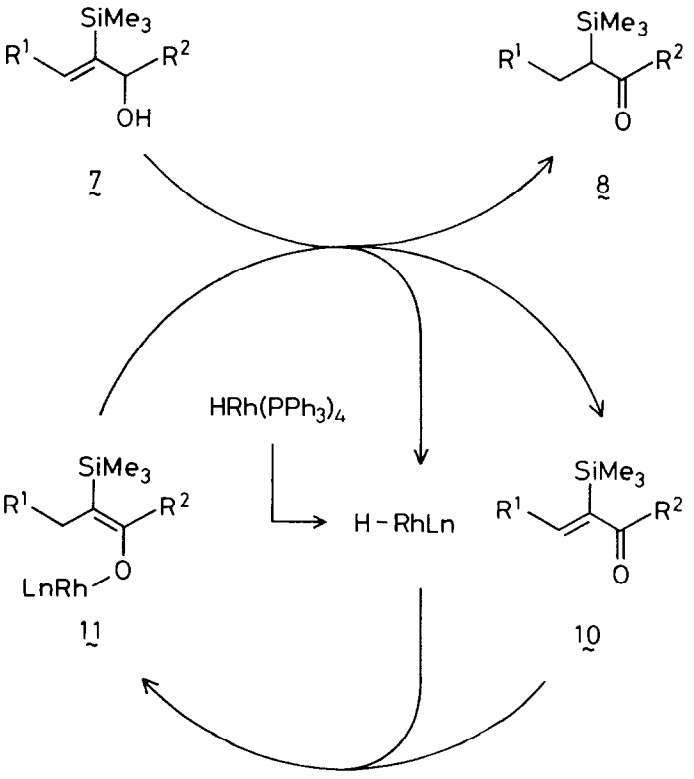
Some types of allyl alcohols [19b] and allyl trimethylsilyl ethers [19f] isomerize to give corresponding ketones and trimethylsilyl enol ethers, respectively, by the catalytic action of $HRh(CO)(PPh_3)_3$ or $H_2Ru(PPh_3)_4$. By contrast, **7** themselves

Table 1

α-Trimethylsilyl ketones **8** from **7**

Entry	Allyl alcohol **7**	R^1	R^2	Conditions		Silyl ketone **8**	Yield (Isolated) (%)
				Temp. (°C)	Time (min)		
1	**7b**	H	n-C_5H_{11}	105	60	**8b**	60
2	**7c**	H	n-C_6H_{13}	105	40	**8c**	98
3	**7d**	H	n-C_8H_{17}	105	30	**8d**	90
4	**7e**	H	n-$C_{10}H_{21}$	108	15	**8e**	96
5	**7f**	H	2-phenylethyl	105	30	**8f**	94
6	**7g**	H	phenyl	105	5	**8g**	56 [a]
7	**7h**	H	1-ethylpentyl	103	60	**8h**	82
8	**7i**	H	cyclohexyl	107	15	**8i**	81
9	**7j**	H	1-pentenyl	105	30	**8j**	82 [b]
10	**7k**	CH_3	n-C_5H_{11}	105	30	**8k**	72
11	**7l**	n-C_4H_9	n-C_5H_{11}	105	30	**8l**	87
12	**7m**	n-C_4H_9	H	105	88	**8m**	0
13	**7n**	$-(CH_2)_3-$		107	40	**8n**	0

[a] 17% of 1-phenyl-1-trimethylsiloxy-1-propene was included. [b] 7% of 2-trimethylsilyl-1-octen-3-one (**10j**) was included.



Scheme 1

and trimethylsilyl ethers of **7** did not at all isomerize to the corresponding enol ethers in the presence of a catalytic amount of $HRh(CO)(PPh_3)_3$, $HRh(PPh_3)_4$, or $H_2Ru(PPh_3)_4$. These findings can be explained in terms of the steric constraint present in the intermediate under isomerization of the double bond via addition-elimination process of H–M in which the bulky trimethylsilyl group and the transition metal atom must be bound onto the same carbon atom. Despite the steric congestion, the isomerization of allyl alcohol **7** to **8** was realized by the serendipitous addition of **10g** as a cocatalyst. This strongly suggests that the interaction of H–Rh with **10g** by a Michael type addition plays an important role in the incorporation of rhodium complex into the catalytic cycle. Thus, a plausible pathway for the isomerization of **7** is illustrated in Scheme 1.

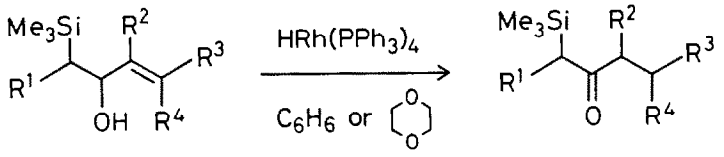
Thus it can be seen that rhodium enolate complex **11** is generated by Michael type addition of HRhLn to **10** in the first stage, to afford **8** by interaction with **7**. Then HRhLn and **10** are regenerated and the catalytic cycle is accomplished. Although direct evidence for the formation of **11** was not obtained, it is noteworthy that a rhodium enolate complex such as **11** has been proposed in the interaction of 4-phenyl-3-buten-2-one with $HRh(PPh_3)_4$ [22].

This type of transformation was not undergone by **7m** and **7n**, either because of secondary interaction between relatively unstable product **8m** and catalyst, or because of the severe steric congestion, to form intermediate **11n** where bulky trimethylsilyl group and rhodium atom have to be located in *cis* geometry.

Isomerization of β′-trimethylsilyl allyl alcohols (12)

Although a novel method to form **8** was exploited in the foregoing transformation (eq. 3), it is not applicable to the synthesis of trimethylsilylmethyl ketones because of the structural restrictions of **7**. Thus β′-trimethylsilyl allyl alcohol (**12**) was designed and used for the isomerization, catalyzed by $HRh(PPh_3)_4$, in order to circumvent this.

In spite of the possible β-elimination of Me_3SiOH from **12**, rhodium catalyzed isomerization proceeded smoothly to give **13** in excellent yield (eq. 5). In contrast to the isomerization of **7**, the presence of **10g** as a cocatalyst is not required for the case of **12** which is analogous to that for non-silylated allyl alcohol reported previously [19b].



(5)

12 13

Catalytic efficiency of $HRh(PPh_3)_4$ in the isomerization is much higher than that in eq. 3. The turnover number of the catalyst increases to 450 within 1 h. The rate of isomerization is almost equal in the solvents, 1,4-dioxane and benzene. The results are listed in Table 2. The reaction of trisubstituted allyl alcohol **12f**, however led only to recovery of starting allyl alcohol. This suggests that the substitution pattern around the double bond plays an important role for smooth isomerization of **12**.

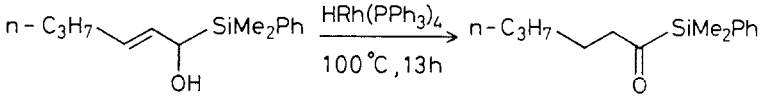
Table 2

α-Trimethylsilyl ketones **13** from **12**

Entry	Allyl alcohol **12**	R^1	R^2	R^3	R^4	Solvent	Conditions		Silyl ketone **13**	Yield (Isolated) (%)
							Temp. (°C)	Time (min)		
1	**12a**-A	H	H	H	H	benzene	105	40	**13a**-A	95
2	**12a**-B [a]	H	H	H	H	dioxane	110	20	**13a**-B	82
3	**12a**-C [b]	H	H	H	H	benzene	105	30	**13a**-C	88
4	**12b**	H	H	CH_3	H	dioxane	107	30	**13b**	67
5	**12c**	H	CH_3	H	H	dioxane	107	30	**13c**	65
6	**12d**	H	H	n-C_3H_7	H	dioxane	102	30	**13d**	90
7	**12e**	H	H	n-C_5H_{11}	H	dioxane	105	20	**13e**	88
8	**12e**	H	H	n-C_5H_{11}	H	benzene	105	40	**13e**	95
9	**12f**	H	H	CH_3	CH_3	dioxane	106	30	**13f**	0 [c]
10	**12g**	CH_3	H	n-C_3H_7	H	dioxane	106	40	**13g**	99
11	**12h**	n-C_5H_{11}	H	H	H	dioxane	106	40	**13h**	92
12	**12i**	n-C_5H_{11}	H	CH_3	H	dioxane	115	60	**13i**	95
13	**12j**	n-C_5H_{11}	CH_3	H	H	dioxane	106	60	**13j**	90
14	**12k**	n-C_5H_{11}	H	n-C_3H_7	H	dioxane	109	55	**13k**	99

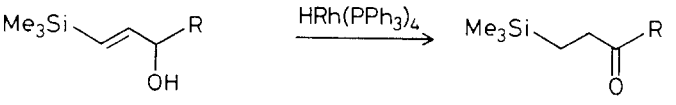
[a] Phenyldimethylsilyl group was used instead of trimethylsilyl group. [b] t-Butoxydimethylsilyl group was used instead of trimethylsilyl group. [c] Starting allyl alcohol was recovered.

This type of double bond migration was extended to other silylated allyl alcohols, **14** and **16**. Although both alcohols required relatively longer reaction times for complete isomerization compared with **12**, ketones **15** and **17** were obtained in good yields after bulb-to-bulb distillation (eqs. 6 and 7).The structures of **15** and **17** were confirmed by elemental analyses and from their IR and ^1H NMR spectra. Thus, the present transformation which involves the migration of a double bond can also be applied to the synthesis of various types of acylsilanes [23], and β-trimethylsilyl ketones [24].



(6)

14 15 81 %



(7)

16a R = n-C_8H_{17} 100°C, 16h 17a 83 %

16b R = Cyclohexyl 100°C, 72h 17b 92 %

Table 3

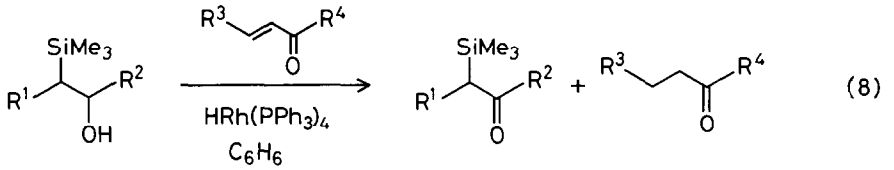
α-Trimethylsilyl ketones **19** from **18**

Entry	Alcohol **18**	R^1	R^2	Hydrogen acceptor [a]	Conditions		Silyl ketone **19**	Yield (Isolated) (%)
					Temp. (°C)	Time (min)		
1	**18a**	H	n-C_7H_{15}	A	105	60	**19a**	23 [b]
2	**18a**	H	n-C_7H_{15}	B	107	240	**19a**	83
3	**18b**	H	1-ethylpentyl	A	105	60	**19b**	82
4	**18c**	n-C_4H_9	n-C_3H_7	C	94	30	**19c**	71
5	**18d**	n-C_5H_{11}	CH_3	A	90	30	**19d**	60 [b]
6	**18d**	n-C_5H_{11}	CH_3	C	90	20	**19d**	75
7	**18e**	n-C_5H_{11}	2-methylpropyl	C	100	30	**19e**	95
8	**18f**	n-C_6H_{13}	CH_3	C	90	30	**19f**	97
9	**18g**	n-C_5H_{11}	H	A	105	20	**19f**	0 [c]
10	**18h**	H	H	A	90	20	**19h** [d]	36
11	**18i**	$-(CH_2)_4-$		A	104	20	**19i**	71

[a] A: 3-buten-2-one, B: 3-trimethylsilyl-3-buten-2-one, C: 2-cyclohexenone. [b] Significant amount of protodesilylated ketone was obtained. [c] A mixture of 1-trimethylsiloxy-1-heptene and 1-heptanal was obtained. [d] Triphenylsilyl group was used instead of trimethylsilyl group.

*Oxidation of β-trimethylsilyl alcohol (**18**) by transfer hydrogenation*

Rhodium-catalyzed isomerizations of the allyl alcohols **7** and **12** offer facile and versatile tools for the synthesis of the α-trimethylsilyl ketones **8**, and **13**. In certain cases, however, the preparation of the starting substrates of **7** and **12** is extremely difficult or impossible. An alternative rhodium-catalyzed route is desirable for simple purification. Mechanistic considerations (shown in Scheme 1) strongly suggest the involvement of an intermolecular transfer hydrogenation process [20] in the isomerization of **7**. This process, thus, could be applied to the oxidation of β-trimethylsilyl alcohols **18** (eq. 8).



(8)

18 **19** **20**

In fact the reaction of **18d** with an equivalent of 2-cyclohexenone (90 °C, 30 min) proceeded smoothly to give **19d** in 75% yield by the aid of a catalytic amount of $HRh(PPh_3)_4$. The isolation of **19** was accomplished by simple distillation during the transformation. The results of the reactions of the remaining **18** are summarized in Table 3.

Unlike the previous two transformations (eqs. 3 and 5), this reaction inevitably produces an equivalent amount of ketone **20** as a result of hydrogen abstraction from **18**. It is therefore extremely important to protect **19** from the protodesilylation which is caused by interaction with **20** in the presence of the rhodium catalyst. The correct combination of **18** and an α,β-unsaturated ketone as a hydrogen acceptor is necessary to retain the satisfactory purity of **19**. When 3-buten-2-one was used, **19**

was contaminated with an appreciable amount of the corresponding protodesilylated ketone (entries 1 and 5 in Table 3). Such undesirable protodesilylation of **19** was prevented completely when 2-cyclohexenone or 3-trimethylsilyl-3-buten-2-one (**10a**) were used as the hydrogen acceptor (entries 2 and 6 in Table 3). Thus, the reaction can be used to form cyclic **19i** and **19e** which cannot be obtained by the isomerization of **7** or **12**. Furthermore, it is noteworthy that α-silyl aldehyde, **19h**, can be isolated from the present route despite the indispensable requirement of triphenylsilyl group. Although a similar transformation can be achieved using chromic acid oxidation [7a,12], the present method eliminates the serious problems associated with the chromic acid oxidation.

In conclusion, new procedures catalyzed by $HRh(PPh_3)_4$ for the regiodefined synthesis of α-trimethylsilyl ketones as shown in eqs. 3, 5, and 8 have been found. Compared with known methods, these new procedures have the advantage of non-aqueous treatment to isolate product, and ready availability of starting materials.

Experimental

All reactions were carried out in an atmosphere of argon or nitrogen. Boiling points shown are bath temperatures for bulb-to-bulb distillations. IR spectra were recorded on a JASCO DS-403G or JASCO IRA-1 spectrometer. Proton NMR spectra were recorded on a JEOL-C60HL instrument using tetramethylsilane as internal standard. Dry solvents were distilled under dry N_2 and degassed under vacuum just before use: tetrahydrofuran (THF) and 1,4-dioxane were distilled from sodium metal in the presence of benzophenone.

Hydridotetrakis(triphenylphosphine)rhodium [25], trimethylvinylsilane [26], 1-bromovinyltrimethylsilane [26], (*E*)-1-iodopropenyltrimethylsilane [27], (*E*)-1-iodohexenyltrimethylsilane [27], 3-trimethylsilyl-3-buten-2-ol (**7a**) [26], 2-trimethylsilyl-2-cyclohexenol (**7n**) [28], 3-trimethylsilyl-3-buten-2-one (**10a**) [26], and 1-phenyl-2-trimethylsilyl-2-propen-1-one (**10g**) [26] were prepared by standard procedures.

Preparation of β-trimethylsilyl allyl alcohols (7)

Procedures for **7b** and **7k** are described as typical examples. Spectral and analytical data for **7** are listed in Table 4.

*2-Trimethylsilyl-1-octen-3-ol (**7b**).* To a solution of 1-trimethylsilylvinylmagnesium bromide (40.4 mmol) formed from Mg (0.98 g, 40.4 mmol) and 1-bromovinyltrimethylsilane (8.38 g, 46.8 mmol) in 100 ml of tetrahydrofuran was added hexanal (5.93 g, 41.8 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature and quenched with aqueous NH_4Cl (30 ml). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3 × 30 ml). The combined organic portions were washed with brine (3 × 50 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel, a mixed solvent (hexane/ethyl acetate, 95/5) was used as eluent and bulb-to-bulb distillation gave 3.66 g (37%) of **7b** as a colorless oil.

*3-Trimethylsilyl-2-nonen-4-ol (**7k**).* (*E*)-1-Iodo-1-trimethylsilylpropene (2.18 g, 9.02 mmol) was added to 6.5 ml of hexane solution of n-butyllithium (1.5 *M*, 9.75 mmol) at −78 °C and the mixture was stirred for 1 h at the same temperature. A

Table 4

Spectral and analytical data for β-trimethylsilyl allyl alcohols 7

Entry	Allyl alcohol 7	Yield (%)	B.p. (°C/Torr)	IR (CCl_4)		^1H NMR (CCl_4) [a]			Analysis (Found (calc)(%))		Formula
				ν(OH) (cm^{-1})	δ($SiMe_3$)	$SiCH_3$	CH(OH)	C=CH	C	H	
1	**7b**	37	88/2	3630	1252	0.13(s, 9H)	4.34(m, 1H)	5.51(d of d, *J* 3.0, 1.4, 1H) 5.87(d of d, *J* 3.0, 1.4, 1H)	65.69 (65.93)	12.11 (12.07)	$C_{11}H_{24}OSi$
2	**7c**	79	105/0.4	3630	1250	0.12(s, 9H)	4.32(m, 1H)	5.47(d of d, *J* 3.0, 1.4, 1H) 5.81(d of d, *J* 3.0, 1.4, 1H)	67.39 (67.22)	12.28 (12.22)	$C_{12}H_{26}OSi$
3	**7d**	52	143/0.4	3630	1250	0.13(s, 9H)	4.30(m, 1H)	5.39(d of d, *J* 3.0, 1.5, 1H) 5.73(d of d, *J* 3.0, 1.5, 1H)	69.21 (69.35)	12.32 (12.47)	$C_{14}H_{30}OSi$
4	**7e**	67	124/0.03	3630	1250	0.13(s, 9H)	4.27(m, 1H)	5.43(d of d, *J* 2.9, 1.4, 1H) 5.78(d of d, *J* 2.9, 1.4, 1H)	71.14 (71.04)	12.52 (12.67)	$C_{16}H_{34}OSi$
5	**7f**	53	88/0.05	3610	1245	−0.11(s, 9H)	4.12(t, *J* 6.2, 1H)	5.31(d of d, *J* 3.0, 1.4, 1H) 5.69(d of d, *J* 3.0, 1.4, 1H)	71.88 (71.73)	9.74 (9.46)	$C_{14}H_{22}OSi$
6	**7g**	45	103/0.05	3600	1240	−0.07(s, 9H)	5.20(t, *J* 1.5, 1H)	5.43(d of d, *J* 3.0, 1.5, 1H) 5.73(d of d, *J* 3.0, 1.5, 1H)	69.61 (69.84)	8.70 (8.79)	$C_{12}H_{18}OSi$
7	**7h**	35	102/0.1	3630	1245	0.10(s, 9H)	4.30(m, 1H)	5.35(d of d, *J* 3.0, 1.3, 1H) 5.65(d of d, *J* 3.0, 1.3, 1H)	68.63 (68.35)	12.22 (12.35)	$C_{13}H_{28}OSi$
8	**7i**	41	68/0.01	3630	1248	0.12(s, 9H)	3.84(m, 1H)	5.56(d of d, *J* 2.8, 1.3, 1H) 5.80(d of d, *J* 2.8, 1.3, 1H)	68.07 (67.86)	11.45 (11.39)	$C_{12}H_{24}OSi$
9	**7j**	61	86/2	3620	1243	0.10(s, 9H)	4.70(m, 1H)	5.65(m, 4H)	66.41 (66.60)	11.32 (11.18)	$C_{11}H_{22}OSi$
10	**7k**	48	97/0.4	3630	1245	0.17(s, 9H)	4.00(m, 1H)	6.24(q, *J* 6.9, 1H)	67.25 (67.22)	12.09 (12.22)	$C_{12}H_{26}OSi$
11	**7l**	45	106/0.03	3630	1245	0.17(s, 9H)	4.05(m, 1H)	6.16(t, *J* 7.4, 1H)	70.41 (70.24)	12.52 (12.57)	$C_{15}H_{32}OSi$
12	**7m**	47	97/4	3630	1243	0.18(s, 9H)	4.10(s, 1H)(*E*) 4.54(s, 1H)(*Z*)	6.07(t, *J* 8.3, 0.5H)(E) 6.19(t, *J* 8.3, 0.5H)(Z)	64.12 (64.45)	11.81 (11.90)	$C_{10}H_{22}OSi$

[a] Shifts are in ppm, coupling constants in Hz; relative to $SiMe_4$ at 60 MHz and 25 °C.

diethyl ether (1 ml) solution of hexanal (0.96 g, 9.61 mmol) was added slowly at $-78°C$. The resulting solution was then stirred for 3 h at $-20°C$ and quenched with aqueous NH_4Cl (30 ml).The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3×30 ml). The combined organic portions were washed with water (2×30 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was chromatographed on silica gel, a mixed solvent (hexane/EtOAc, 180/11) was used as eluent to give 0.92 g (48%) of **7k** as a colorless oil.

*Preparation of β′-silylated allyl alcohols (**12**)*

Procedures for **12a**-A, **12g**, and **12h** are described as typical examples. The data for **12** are listed in Table 5. These alcohols were used immediately after distillation since β-elimination of Me_3SiOH from **12** took place at room temperature before elemental analysis.

*1-Trimethylsilyl-3-buten-2-ol (**12a**-A).* To a solution of trimethylsilylmagnesium chloride (18.7 mmol) formed from Mg (0.45 g, 18.7 mmol) and chloromethyltrimethylsilane (2.42 g, 19.8 mmol) in 40 ml diethyl ether was added 1.12 g (20.0 mmol) of acrolein in 5 ml of Et_2O at 0 °C. The reaction mixture was stirred for 2 h at room temperature, and quenched with aqueous NH_4Cl (20 ml). The organic phase was then separated off, and the aqueous phase was extracted with Et_2O (3×30 ml). The combined organic portions were washed with brine (3×40 ml), dried over anhydrous $MgSO_4$, and concentrated. The resulting crude product was distilled to give 2.24 g (83%) of **12a**-A as a colorless oil.

*2-Trimethylsilyl-4-octen-3-ol (**12g**).* A suspension of lithium 1.35 g (195 mmol) and 1-chloroethyltrimethylsilane 2.65 g (19.3 mmol) in pentane (35 ml) was refluxed for 1.5 h, cooled to room temperature, and kept for 2 h. The gray powder (LiCl) which precipitated and the excess lithium were filtered from the suspension under argon. The filtrate was cooled to $-78°C$ and diluted with 30 ml of THF. A THF (10 ml) solution of (*E*)-2-hexenal (0.97 g, 9.83 mmol) was added to the above solution at $-78°C$, and the mixture was stirred for 4 h at the same temperature, then quenched with aqueous NH_4Cl (20 ml). The organic phase was separated and the aqueous layer was extracted with Et_2O (3×30 ml). The organic layer and the extracts were combined, washed with brine (2×30 ml) and dried over anhydrous $MgSO_4$. After evaporation of solvent under reduced pressure, the residual oil was distilled to give 1.85 g (94%) of **12g** as a colorless oil.

*4-Trimethylsilyl-1-nonen-3-ol (**12h**).* To a THF (1000 ml) solution of trimethylvinylsilane (20.8 g, 0.21 mol) was added 128 ml of a hexane solution of n-butyllithium (1.5 *M*, 0.20 mol) at $-78°C$ and the mixture was stirred for 1.5 h at 0 °C. A THF (80 ml) solution of acrolein (11.0 g, 0.20 mol) was added slowly to the resulting yellow solution at $-78°C$. The mixture was then stirred for 2 h at the same temperature and quenched with aqueous NH_4Cl (300 ml). The organic phase was separated and the aqueous phase was extracted with Et_2O (3×150 ml). The combined organic portions were washed with brine (3×200 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Bulb-to-bulb distillation of the residual oil gave 28.7 g (71%) of **12h** as a colorless oil.

*Preparation of 1-dimethylphenylsilyl-2-buten-1-ol (**14**)*

To a suspension of lithium (0.22 g, 32.4 mmol) in THF (20 ml) was added slowly chlorodimethylphenylsilane (2.45 g, 14.3 mmol) and the mixture was stirred for 15 h

Table 5

Spectral data for β'-trimethylsilyl allyl alcohols **12**

Entry	Allyl alcohol **12**	Yield (%)	B.p. (°C/Torr)	IR (CCl_4)		^{1}H NMR (CCl_4) [a]		
				ν(OH) (cm^{-1})	δ($SiMe_3$)	$SiCH_3$	CH(OH)	C=CH
1	**12a**-A	83	72/30	3605	1240	0.05(s, 9H)	4.58(t of d, J 7.5, 7.5, 1H)	5.3–6.6 (m, 3H)
2	**12a**-B	84	110/0.6	3620	1245	0.33(s, 6H)	4.12(t of d, J 6.8, 6.8, 1H)	4.8–6.2 (m, 3H)
3	**12a**-C	50	88/0.3	3630	1250	0.17(s, 6H)	4.0–4.4(m, 1H)	4.7–6.1 (m, 3H)
4	**12b**	51	84/27	3605	1240	0.06(s, 9H)	4.3–4.8(m, 1H)	5.7–6.2 (m, 2H)
5	**12c**	70	80/20	3605	1240	0.03(s, 9H)	4.16(d, J 4.9, 1H)	4.66(m, 1H) 4.85(m, 1H)
6	**12d**	94	65/0.2	3610	1249	0.00(s, 9H)	3.8–4.4(m, 1H)	5.3–5.5 (m, 2H)
7	**12e**	86	68/0.8	3620	1249	0.00(s, 9H)	3.7–4.5(m, 1H)	5.1–5.4 (m, 2H)
8	**12f**	47	78/10	3610	1240	0.01(s, 9H)	4.37(d of t, J 8.3, 7.2, 1H)	4.9–5.2 (m, 1H)
9	**12g**	94	80/2	3630	1245	0.00(s, 9H)	3.8–4.2(m, 1H)	5.3–5.6 (m, 2H)
10	**12h**	71	70/0.1	3605	1243	0.04(s, 9H)	4.1–4.4(m, 1H)	4.9–6.2 (m, 3H)
11	**12i**	69	83/0.7	3610	1243	0.00(s, 9H)	3.9–4.3(m, 1H)	5.4–5.7 (m, 2H)
12	**12j**	78	88/0.3	3610	1246	0.03(s, 9H)	4.0–4.3(m, 1H)	4.8–5.0 (m, 2H)
13	**12k**	87	87/0.1	3615	1246	0.03(s, 9H)	4.0–4.3(m, 1H)	5.5–7.7 (m, 2H)

[a] Shifts are in ppm, coupling constants in Hz; relative to $SiMe_4$ at 60 MHz and 25 °C.

at room temperature. The resulting solution of dimethylphenylsilyllithium was added to a THF (10 ml) solution of 2-butenal (0.87 g, 12.4 mmol) at −78 °C. After the addition, the temperature of the cooling bath was raised to room temperature for 5 h. The resulting mixture was cooled to −78 °C again, and quenched with aqueous NH_4Cl (20 ml) at the same temperature. The organic phase was separated and the aqueous layer was extracted with Et_2O (3 × 20 ml). The combined organic phases were washed with brine (3 × 30 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. After bulb-to-bulb distillation of the residual oil, 0.25 g (20%) of **14** was obtained as a pale yellow oil. B.p.: 78 °C/0.1 Torr. Anal. Found: C, 70.02; H, 8.65. $C_{12}H_{18}OSi$ calc: C, 69.84; H, 8.79%. IR (CCl_4): 3580 (OH), 1241 (SiC) cm^{-1}. ^{1}H NMR (CCl_4): δ 0.50 (s, 6H, H_3CSi), 2.05 (d of d, J 5.2, 1.9 Hz, 3H, =CCH_3), 2.35 (broad s, 1H, OH), 4.2–4.4 (m, 1H, O–CH), 5.4–5.6 (m, 2H, CH=CH), 7.2–7.7 (broad m, 5H, Ph).

*Preparation of 1-trimethylsilyl-1-undecen-3-ol (**16a**)*

To a THF (30 ml) solution of ethylmagnesium bromide (25.3 mmol) formed from 0.62 g (25.3 mmol) of Mg and 3.02 g (27.7 mmol) of ethyl bromide was added 2.58 g

(26.3 mmol) of ethynyltrimethylsilane at room temperature. After the mixture had been refluxed for 2 h, a THF (10 ml) solution of 3.66 g (25.8 mmol) of nonanal was added to the solution. The resulting solution was stirred for 2 h at room temperature and quenched with aqueous NH_4Cl (40 ml). The organic phase was separated and the aqueous layer was extracted with Et_2O (3×30 ml). The combined organic portions were washed with brine (3×30 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was submitted to bulb-to-bulb distillation to give 4.53 g (74%) of 1-trimethylsilyl-1-undecyn-3-ol. B.p.: 93°C/0.9 Torr. Anal. Found: C, 69.65; H, 11.70. $C_{14}H_{28}OSi$ calc: C, 69.93; H, 11.74%. IR (CCl_4): 3610 (OH), 2160 (C≡C), 1242 (SiC) cm^{-1}. ^1H NMR (CCl_4): δ 0.19 (s, 9H, H_3CSi), 0.7–1.8 (broad m, 17H, $7 \times CH_2$, CH_3), 2.0–2.3 (broad s, 1H, O*H*), 4.20 (t, *J* 6.1 Hz, 1H, O–C*H*).

To a solution of $LiAlH_4$ (0.32 g, 8.4 mmol) in THF (50 ml) was added 2.00 g (8.3 mmol) of 1-trimethylsilyl-1-undecyn-3-ol in 2 ml of THF at room temperature and refluxed for 2.5 h. The resulting solution was cooled to room temperature, quenched with ethyl acetate (8 ml) and aqueous NH_4Cl (30 ml). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3×40 ml). The combined organic portions were washed with brine (3×40 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was chromatographed on silica gel, a mixed solvent (hexane/EtOAc, 90/10) was used as eluent to give 1.65 g (83%) of **16a** as a yellow oil. B.p.: 80°C/0.4 Torr. Anal. Found: C, 69.31; H, 12.40. $C_{14}H_{30}OSi$ calc: C, 69.35; H, 12.47%. IR (CCl_4): 3610 (OH), 1603 (C=C), 1240 (SiC) cm^{-1}. ^1H NMR (CCl_4): δ 0.07 (s, 5.8 H, H_3CSi, *E*-isomer), 0.14 (s, 3.2H, H_3CSi, *Z*-isomer), 0.87 (t, *J* 4.4 Hz, 3H, CH_3), 1.1–1.7 (broad m, 15H, $7 \times CH_2$, O*H*), 3.7–4.2 (broad m, 1H, O–C*H*), 5.4–6.4 (m, 2H, C*H*=C*H*).

*Preparation of 1-cyclohexyl-3-trimethylsilyl-2-propen-1-ol (**16b**)*

In a procedure analogous to that for **16a**, 1.47 g (13.2 mmol) of cyclohexanecarboxaldehyde gave 2.10 g (77%) of 1-cyclohexyl-3-trimethylsilyl-2-propyn-1-ol. B.p.: 82°C/0.2 Torr. Anal. Found: C, 68.25; H, 10.57. $C_{12}H_{22}OSi$ calc: C, 68.51; H, 10.54%.

IR (CCl_4): 3610 (OH), 2150 (C≡C), 1239 (SiC) cm^{-1}. ^1H NMR (CCl_4): δ 0.18 (s, 9H, H_3CSi), 0.7–2.2 (broad m, 11H, cyclohexyl), 1.88 (broad s, 1H, O*H*), 3.7–4.1 (broad m, 1H, O–C*H*).

1-Cyclohexyl-3-trimethylsilyl-2-propyn-1-ol, 2.10 g (10.0 mmol), then yielded 1.90 g (90%) of **16b** as a yellow oil. B.p.: 155°C/1.7 Torr. Anal. Found: C, 67.92; H, 11.43. $C_{12}H_{24}OSi$ calc: C, 67.86; H, 11.39%. IR (CCl_4): 3630 (OH), 1605 (C=C), 1241 (SiC) cm^{-1}. ^1H NMR (CCl_4): δ 0.10 (s, 5.8H, H_3CSi, *E*-isomer), 0.15 (s, 3.2H, H_3CSi, *Z*-isomer), 0.6–2.2 (broad m, 12H, cyclohexyl, O*H*), 3.6–4.2 (broad m, 1H, O–C*H*), 5.5–6.5 (m, 2H, C*H*=C*H*).

*Preparation of β-silylated alcohols (**18**)*

Procedures for **18a, 18h**, and **18i** are described as typical examples. The data of **18** are listed in Table 6.

*1-Trimethylsilyl-2-nonanol (**18a**).* To a solution of trimethylsilylmethylmagnesium chloride (23.7 mmol) formed from Mg (0.58 g, 23.7 mmol) and chloromethyltrimethylsilane (2.93 g, 23.9 mmol) in 60 ml of THF was added octanal (2.99 g, 23.4 mmol) in 10 ml of THF at 0°C. The reaction mixture was stirred for 1.5 h at

room temperature and quenched with aqueous NH_4Cl (30 ml). The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 30 ml). The combined organic phases were washed with brine (3 × 40 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was submitted to bulb-to-bulb distillation to give 3.61 g (71%) of **18a** as a colorless oil.

*2-Triphenylsilylethanol (**18h**) [29].* A suspension of lithium 0.29 g (41.7 mmol) and chlorotriphenylsilane 3.51 g (11.9 mmol) in THF (20 ml) was stirred for 14 h at room temperature. The resulting brown solution was added to a solution of ethylene oxide 4 ml (81 mmol) in THF (10 ml) at −55°C. The mixture was stirred for 20 min at the same temperature and for 1 h at room temperature. The resulting pale brown mixture was quenched with aqueous NH_4Cl (20 ml) at −78°C. The organic phase was separated and the aqueous layer was extracted with Et_2O (3 × 30 ml). The combined organic phases were washed with brine (3 × 30 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual solid was purified by recrystallization from Et_2O/hexane solvent to give 2.45 g (68%) of **18h** as orange block-like crystals.

*2-Trimethylsilyl-1-cyclohexanol (**18i**) [12b].* A THF (10 ml) solution of 1-trimethylsilylcyclohexene oxide (0.71 g, 4.2 mmol) was added to a THF (30 ml) solution of lithium aluminium hydride (0.28 g, 7.5 mmol) at room temperature. The mixture was refluxed for 30 min, and quenched with ethyl acetate (10 ml) and aqueous NH_4Cl (20 ml) at room temperature. The organic phase was separated and the aqueous layer was extracted with ethyl acetate (2 × 20 ml). The combined organic phases were washed with brine (3 × 30 ml), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give 0.61 g (86%) of **18i** as a clear solid.

(*Continued on p. 86*)

Table 6

Spectral and analytical data for β-trimethylsilyl alcohols **18**

Entry	Silyl alcohol **18**	Yield (%)	B.p. (°C/Torr)	IR (CCl_4)		^{1}H NMR (CCl_4)		[a]Analysis (Found (calc) (%))		Formula
				ν(OH) (cm^{-1})	δ($SiMe_3$)	$SiCH_3$	CH(OH)	C	H	
1	**18a**	71	90/0.2	3605	1240	0.05 (s, 9H)	3.4–3.9 (m, 1H)	66.77 (66.59)	13.19 (13.04)	$C_{12}H_{28}OSi$
2	**18b**	80	88/0.2	3605	1240	0.03 (s, 9H)	3.6–4.0 (m, 1H)	66.82 (66.59)	13.08 (13.04)	$C_{12}H_{28}OSi$
3	**18c**	73	100/0.35	3650	1250	0.03 (s, 9H)	3.6–3.9 (m, 1H)	66.51 (66.59)	13.11 (13.04)	$C_{12}H_{28}OSi$
4	**18d**	75	80/0.2	3660	1245	0.05 (s, 9H)	3.7–4.2 (m, 1H)	65.02 (65.27)	12.84 (12.95)	$C_{11}H_{26}OSi$
5	**18e**	81	113/0.2	3660	1245	0.05 (s, 9H)	3.8–4.2 (m, 1H)	68.51 (68.78)	13.25 (13.19)	$C_{14}H_{32}OSi$
6	**18f**	82	105/0.5	3660	1247	0.05 (s, 1H)	3.5–4.2 (m, 1H)	66.86 (66.59)	13.33 (13.04)	$C_{12}H_{28}OSi$
7	**18g**	47	89/0.2	3650	1240	0.05 (s, 1H)	3.7–3.9 (m, 1H)	63.49 (63.76)	12.71 (12.84)	$C_{10}H_{24}OSi$
8	**18h**	68	[b]	3620	–	–	–	ref. [29]		
9	**18i**	86	[c]	3630	1241	0.00 (s, 1H)	4.0–4.2 (m, 1H)	ref. [12b]		

[a] Shifts are in ppm, relative to $SiMe_4$ at 60 MHz and 25°C. [b] M.p. 99–102°C. [c] M.p. 53–55°C.

Table 7

Spectral and analytical data for α-trimethylsilyl ketones

Entry	Silyl ketone	B.p. (°C/Torr)	IR (CCl_4)		^1H NMR (CCl_4) [a]			Analysis (Found (calc)(%))		Formula
			ν(C=O) (cm^{-1})	δ($SiMe_3$)	$SiCH_3$	(C=O)C*H*	$SiCH$(C=O)	C	H	
1	**8b**	77/1.5	1691	1250	0.05(s, 9H)	2.25(t, *J* 7.1, 2H)	2.31(q, *J* 7.1, 1H)	66.01 (65.93)	12.11 (12.07)	$C_{11}H_{24}OSi$
2	**8c**	95/0.1	1700	1260	0.05(s, 9H)	2.24(t, *J* 6.6, 2H)	2.33(q, *J* 6.6, 1H)	67.46 (67.22)	12.39 (12.22)	$C_{12}H_{26}OSi$
3	**8d**	97/0.05	1681	1243	0.05(s, 9H)	2.22(t, *J* 6.7, 2H)	2.28(q, *J* 6.7, 1H)	69.24 (69.35)	12.68 (12.47)	$C_{14}H_{30}OSi$
4	**8e**	119/0.05	1694	1250	0.05(s, 9H)	2.23(t, *J* 6.8, 2H)	2.28(q, *J* 6.8, 1H)	71.29 (71.04)	12.65 (12.67)	$C_{16}H_{34}OSi$
5	**8f**	75/0.1	1694	1252	0.00(s, 9H)	2.69(t, *J* 5.3, 2H)	2.23(q, *J* 7.2, 1H)	71.72 (71.73)	9.58 (9.46)	$C_{14}H_{22}OSi$
6	**8g**	75/0.1	1670	1250	−0.07(s, 9H)	–	3.47(q, *J* 6.5, 1H)	[b]		
7	**8h**	64/0.1	1691	1252	0.05(s, 9H)	2.0–2.5(m, 1H)	2.38(q, *J* 6.8, 1H)	68.19 (68.35)	12.28 (12.35)	$C_{13}H_{28}OSi$
8	**8i**	80/1.0	1695	1251	0.03(s, 9H)	[d]	2.37(q, *J* 6.9, 1H)	67.87 (67.86)	11.54 (11.39)	$C_{12}H_{24}OSi$
9	**8j**	77/1.5	1670	1240	0.03(s, 9H)	5.6–6.1(m, 1H)	[d]	[c]		
10	**8k**	125/1.2	1692	1248	0.03(s, 9H)	[d]	[d]	67.09 (67.22)	12.14 (12.22)	$C_{12}H_{26}OSi$
11	**8l**	105/0.03	1691	1248	0.00(s, 9H)	[d]	[d]	70.49 (70.24)	12.85 (12.57)	$C_{15}H_{32}OSi$
12	**13a-A**	65/30	1694	1251	0.10(s, 9H)	2.28(q, *J* 7.5, 2H)	2.10(s, 2H)	ref. [13d]		
13	**13a-B**	112/0.9	1685	1248	0.38(s, 6H)	2.14(q, *J* 7.5, 2H)	2.33(s, 2H)	69.88 (69.84)	8.90 (8.79)	$C_{12}H_{18}OSi$
14	**13a-C**	82/0.2	1692	1255	0.15(s, 6H)	2.29(q, *J* 7.2, 2H)	2.05(s, 2H)	59.06 (59.35)	11.15 (10.96)	$C_{10}H_{22}O_2Si$
15	**13b**	82/25	1688	1250	0.10(s, 9H)	2.24(t, *J* 6.4, 2H)	2.07(s, 2H)	60.43 (60.69)	11.36 (11.46)	$C_8H_{18}OSi$

16	**13c**	72/21	1688	1250	0.09(s, 9H)	2.43(septet, *J* 7.1, 1H)	2.10(s, 2H)	60.81 (60.69)	11.58 (11.46)	$C_8H_{18}OSi$
17	**13d**	65/0.4	1685	1250	0.10(s, 9H)	2.24(t, *J* 6.3, 2H)	2.06(s, 2H)	64.17 (64.45)	12.20 (11.90)	$C_{10}H_{22}OSi$
18	**13e**	88/0.15	1690	1250	0.09(s, 9H)	2.25(t, *J* 6.9, 2H)	2.08(s, 2H)	67.10 (67.22)	12.50 (12.22)	$C_{12}H_{26}OSi$
19	**13g**	(identical with **8b**)								
20	**13h**	75/1.5	1688	1245	0.00(s, 9H)	2.21(q, *J* 7.5, 2H)	2.18(t, *J* 7.5, 1H)	67.13 (67.22)	12.50 (12.22)	$C_{12}H_{26}OSi$
21	**13i**	99/0.3	1690	1250	0.03(s, 9H)	[d]	[d]	ref. [15b]		
22	**13j**	85/4.5	1689	1250	0.00(s, 9H)	[d]	[d]	68.51 (68.35)	12.56 (12.35)	$C_{13}H_{28}OSi$
23	**13k**	(identical with **8l**)								
24	**19a**	(identical with **13e**)								
25	**19b**	80/0.2	1678	1245	0.09(s, 9H)	[d]	2.09(s, 2H)	67.44 (67.22)	12.50 (12.22)	$C_{12}H_{26}OSi$
26	**19c**	85/0.2	1693	1257	0.06(s, 9H)	[d]	[d]	67.56 (67.22)	12.21 (12.22)	$C_{12}H_{26}OSi$
27	**19d**	77/0.2	1690	1250	0.05(s, 9H)	2.00(s, 3H)	[d]	ref. [15b]		
28	**19e**	109/0.2	1681	1247	0.04(s, 9H)	1.9–2.5(*m*, 3H)		69.49 (69.35)	12.41 (12.47)	$C_{14}H_{30}OSi$
29	**19f**	86/0.2	1685	1245	0.05(s, 9H)	1.96(s, 3H)	[d]	67.16 (67.22)	12.39 (12.22)	$C_{12}H_{26}OSi$
30	**19h**	[e]	1707	–	–	–	2.92(d, *J* 4.2, 2H)	ref. [29]		
31	**19i**	90/0.5	1676	1242	0.06(s, 9H)	[d]	[d]	ref. [12b]		

[a] Shifts are in ppm, coupling constants in Hz, relative to $SiMe_4$ at 60 MHz and 25° C. [b] 1-Trimethylsilyl-1-phenyl-1-propene was included. [c] 2-Trimethylsilyl-1-octen-3-one (**10j**) was included. [d] Indistinguishable. [e] Pale yellow block-like crystals. M.p. 99–102° C.

*Synthesis of α-trimethylsilyl ketones **8** by the isomerization of 7*

The procedure for the isomerization of **7c** is described as a typical example. The data of **8** listed in Tables 1 and 7.

*2-Trimethylsilyl-3-nonanone (**8c**).* A benzene (5 ml) solution of 3.00 g (14.0 mmol) of **7c**, 6.7 mg (0.033 mmol, 0.24 mol%) of **10g**, and 0.51 g (0.44 mmol, 3 mol%) of $HRh(PPh_3)_4$ was placed in a 25 mm ∅ Pyrex tube, under argon atmosphere. The tube was sealed and heated at 105 °C in an oil bath for 1 h. The resulting dark red solution was concentrated under reduced pressure, and subsequent bulb-to-bulb distillation gave 2.95 g (98%) of **8c** as a colorless oil.

*Synthesis of α-trimethylsilyl ketones **13** by the isomerization of **12***

The procedure for the isomerization of **12a**-A is described as a typical example. The data of **13** are listed in Tables 2 and 7.

*1-Trimethylsilyl-2-butanone (**13a**-A) [13d].* A benzene (7 ml) solution of 4.96 g (34.3 mmol) of **12a**-A, 0.48 g (0.41 mmol, 1.2 mol%) of $HRh(PPh_3)_4$ was placed in a 25 mm ∅ Pyrex tube under argon. The tube was sealed and heated at 105 °C in an oil bath for 40 min. The resulting orange solution was concentrated under reduced pressure, and the subsequent bulb-to-bulb distillation gave 4.69 g (95%) of **13a**-A as a colorless oil.

*Synthesis of 1-dimethylphenylsilyl-1-butanone (**15**)*

In a procedure analogous to that for the isomerization of **12a**-A, 109.6 mg (0.53 mmol) of **14** and 19.2 mg (0.017 mmol) of $HRh(PPh_3)_4$ gave 88.8 mg (81%) of **15** as a yellow oil. B.p.: 74 °C/0.1 Torr. Anal. Found: C, 69.88; H, 8.86. $C_{12}H_{18}OSi$ calc: C, 69.84; H, 8.79%. IR (CCl_4): 1630 (C=O), 1240 (SiC) cm^{-1}. ^1H NMR (CCl_4): δ 0.44 (s, 6H, H_3CSi), 0.79 (t, *J* 6.5 Hz, 3H, CH_3), 1.1–1.7 (broad m, 2H, CH_2), 2.47 (t, *J* 6.5 Hz, 2H, $COCH_2$), 6.1–6.7 (broad m, 5H, Ph).

*Synthesis of 1-trimethylsilyl-3-undecanone (**17a**)*

Similarly, 110.1 mg (0.45 mmol) of **16a** and 13.3 mg (0.012 mmol) of $HRh(PPh_3)_4$ gave 91.4 mg (83%) of **17a** as a colorless oil. B.p.: 81 °C/0.5 Torr. Anal. Found: C, 69.12; H, 12.46. $C_{14}H_{30}OSi$ calc: C, 69.35; H, 12.47%. IR (CCl_4): 1715 (C=O), 1240 (SiC) cm^{-1}. ^1H NMR (CCl_4): δ 0.00 (s, 9H, H_3CSi), 0.4–1.8 (broad m, 17H, $7 \times CH_2$, CH_3), 2.1–2.5 (broad m, 4H, CH_2COCH_2).

*Synthesis of 1-cyclohexyl-3-trimethylsilyl-1-propanone (**17b**)*

Similarly, 215 mg (1.02 mmol) of **16b** and 11.5 mg (0.010 mmol) of $HRh(PPh_3)_4$ gave 198 mg (92%) of **17b** as a colorless oil. B.p.: 78 °C/0.1 Torr. Anal. Found: C, 68.03; H, 11.45. $C_{12}H_{24}OSi$ calc: C, 67.86; H, 11.39%. IR (CCl_4): 1700 (C=O), 1241 (SiC) cm^{-1}. ^1H NMR (CCl_4): δ 0.01 (s, 9H, H_3CSi), 0.5–2.6 (broad m, 10H, $5 \times CH_2$), 0.71 (t, *J* 8.3 Hz, 2H, $SiCH_2$), 2.2–2.6 (broad m, 1H, COCH), 2.38 (t, *J* 8.3 Hz, 2H, $COCH_2$).

*Catalytic transfer dehydrogenation of **18***

The procedure for dehydrogenation of **18a** is described as a typical example. The data for **19** are listed in Tables 3 and 7.

*1-Trimethylsilyl-2-nonanone (**19a**)*

A solution of 104.8 mg (0.48 mmol) of **18a** in benzene (1 ml), 160.1 mg (1.14 mmol) of 3-trimethylsilyl-3-buten-2-one, and 27.6 mg (0.024 mmol, 5 mol%) of $HRh(PPh_3)_4$ was placed in a 10 mm ∅ Pyrex tube under argon. The tube was sealed and heated at 107 °C in an oil bath for 4 h. The resulting orange solution was concentrated under reduced pressure, and subsequent bulb-to-bulb distillation gave 87.0 mg (83%) of **19a** (identical with **13e**) as a colorless oil.

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