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Conjugate Reduction of α,β-Unsaturated Ketones with Hydrosilane Mediated by Copper(I) Salt

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Abstract: Reduction of several α,β-unsaturated ketones with dimethylphenylsilane and 10-100 mol% of $CuF(PPh_3)_3 \cdot 2EtOH$ or $CuCl/PPh_3/Bu_4NF$ proceeds in a 1,4-selective manner to give the corresponding saturated ketones in up to >99% yield. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *copper and compounds; ketones; reduction; silicon and compounds*

Introduction

Introduction of an organic group bonded to silicon into a certain organic molecule serves as one of the significant applications of organosilicon chemistry toward organic synthesis. Since organosilicon reagents, in general, are inert to a variety of organic substrates compared with highly reactive organometallic reagents, it is necessary to activate substrate or the organosilicon reagent for the purpose of such utilization.[1]

Numerous studies on the activation of an organic molecule by a variety of Lewis acids have focused on the reactions, for example, of enol silyl ethers or allylic silanes with carbonyl or the related compounds.[1,2] In contrast, the alternative activation of organosilicon compounds,[3] namely transmetalation, still remains to be exploited. *Transmetalation* has been recognized as a method to activate a less reactive organometallic compound for a reaction with organic substrates. Indeed, a number of metal-mediated synthetic reactions are suggested to involve transmetalation as a key step.[4] The organometallic species thus formed undergo further transformations such as carbon-carbon or carbon-heteroatom bond formations by the reaction with a variety of substrates. To induce transmetalation of an organosilicon compound, it has been considered to be necessary to activate the organosilane by a fluoride ion to form a highly reactive organosilicate. However, we have recently disclosed that alkenyl-, aryl- and alkynylsilanes undergo homo-coupling reactions in the presence of a copper(I) salt in a polar

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solvent to yield symmetric 1,3-dienes, biaryls and 1,3-diynes, respectively.[5] The findings are understood in terms of transmetalation from silicon to copper to generate respective organocopper species. The novel transmetalation is remarkable, since an organic group on silicon is capable of being transferred onto copper without using an additional activator.[6]

Our interest has accordingly been turned to generate *copper hydride* species that will reduce a variety of organic molecules,[7] if the transmetalation of a hydrogen atom on silicon to copper is accessible by mixing a hydrosilane with a copper(I) salt. Although the combination of such system has rarely been studied, the reagents made of a copper salt and a metal hydride such as aluminum or tin are recorded to reduce various types of organic substrates.[8] Hence, we considered that a proper choice of a counter ion and a ligand for copper would also generate similar reactive hydride species, which would serve as a potential reducing agent with high reactivity and selectivity. We herein report that hydrosilanes (**1**) reduce α,β-unsaturated ketones (**2**) in a 1,4-selective manner in the presence of a stoichiometric or a catalytic amount of Cu(I) compound.[9,10]

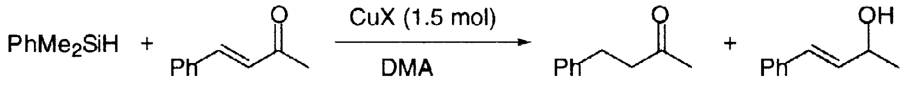
Results and Discussion

A possibility of transmetalation from silicon to copper was first examined by the reaction of phenyldimethylsilane (**1a**) with CuCl as shown in eq 1. Treatment of **1a** with CuCl in DMF at room temperature for 1 h gave the corresponding disiloxane **3** in a quantitative yield. We considered that copper(I) hydride and chlorodimethylphenylsilane (**4**) were first formed; **4** was then converted into **3** via hydrolytic condensation.

$$\underset{\mathbf{1a}}{\mathrm{PhMe_2SiH}} + \mathrm{CuCl} \xrightarrow[\text{DMF, rt, 1 h}]{} \left[\underset{\mathbf{4}}{\mathrm{PhMe_2SiCl}} + \mathrm{CuH}\right] \xrightarrow[\mathrm{H_2O}]{\mathrm{HCl}} \underset{\mathbf{3}\ >99\%}{\mathrm{PhMe_2SiOSiMe_2Ph}} \qquad (1)$$

With this observation in hand, we examined the reaction of the hydride thus formed with 1-phenyl-1-buten-3-one (**2a**) using several copper(I) salts as shown in Table 1.

Table 1. Reduction of **2a** with various copper(I) salts



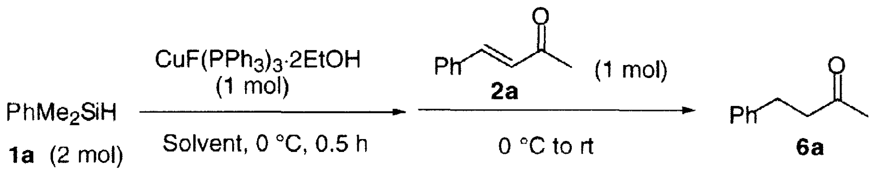
1a (3.0 mol) **2a** (1.0 mol) **6a** **7a**

Run	CuX	Time, h	Temp, °C	Yield, %[a)] **6a**	**7a**	**2a**
1	$\mathrm{CuF(PPh_3)_3 \cdot 2EtOH}$ (**5**)	2	0 to rt	>99	-	-
2	$\mathrm{CuF(PPh_3)_3}$	4		55	-	-
3	CuCl	21		27	-	-
4	$\mathrm{(CuOTf)_2 \cdot C_6H_6}$	12		48	trace	13
5	$\mathrm{Cu_2O}$	21	60	64	-	-
6	CuCN	12	0 to rt	trace	trace	64

a) Yields were estimated by ^{1}H NMR analyses.

Among Cu(I) salts, $CuF(PPh_3)_3 \cdot 2EtOH$ (**5**)[11] was found to be an excellent counterpart of **1a** to give 4-phenyl-2-butanone (**6a**) in >99% yield. When EtOH-free $CuF(PPh_3)_3$ was used as a catalyst, the yield decreased to 55%. The use of 10 mol% of **5** decreased the yield to 63%. Among the solvents examined, *N,N*-dimethylacetamide (DMA) was found to be suitable to give **6a** in an excellent yield within a short period (Table 2).

Table 2. Reduction of **2a** in various solvents

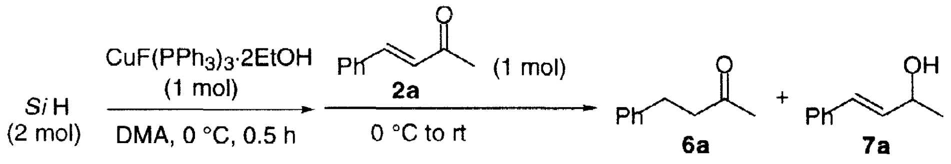


Run	Solvent	Time, h	Yield, %[a]
1	DMA	2	>99 (92)[b]
2	DMF	2.5	40
3	NMP[c]	6	57
4	THF	2.5	42
5	toluene	12.5	80

a) Yields were estimated by ^1H NMR analyses.
b) Isolated yield. c) 1-Methyl-2-pyrrolidinone.

Concerning hydrosilanes, **1a** and triethylsilane (**1b**) exhibited high 1,4-selectivities to give the corresponding ketone in excellent yields, but diphenylsilane (**1d**) considerably decreased the selectivity to give **6a** and **7a** in 49% and 36% yields, respectively, in a sharp contrast with the results on rhodium-catalyzed hydrosilylation of α,β-unsaturated ketones.[12] Alkoxysilane **1c** was also inferior in the regioselectivity. $PhCl_2SiH$ (**1e**) could not reduce **2a**. Results are summarized in Table 3.

Table 3. Reduction of **2a** with hydrosilanes

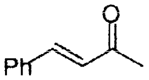
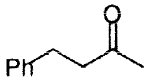
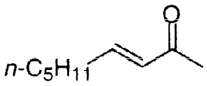
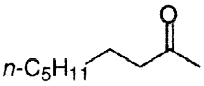
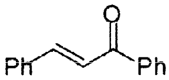
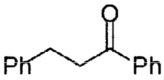
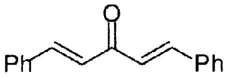
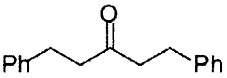
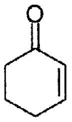
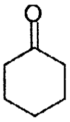
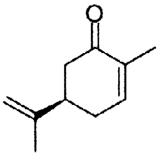
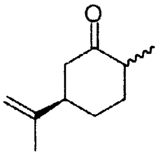


Run	*Si*H	Time, h	Yield, %[a]	
			6a	**7a**
1	$PhMe_2SiH$ (**1a**)	2	>99 (92)[b]	-
2	Et_3SiH (**1b**)	1.5	96	-
3	$(EtO)_3SiH$ (**1c**)	3.5	58	34
4	Ph_2SiH_2 (**1d**)	18	49	36
5[c]	$PhCl_2SiH$ (**1e**)	-	no reaction	

a) Yields were estimated by ^1H NMR analyses.
b) Isolated yield. c) $CuF(PPh_3)_3$ complex was used.

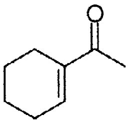
The optimum conditions were applied to reduction of several α,β-unsaturated ketones. The results are shown in Table 4.

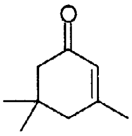
Table 4. Conjugate reduction of α,β-unsaturated carbonyl compounds **2**

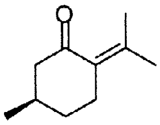
Run	Substrate	Time, h	Product	Yield, %
1	 **2a**	2	 **6a**	>99 (92)
2	 **2b**	2.5	 **6b**	91
3	 **2c**	3	 **6c**	98
4	 **2d**	2	 **6d**	52
5	 **2e**	2	 **6e**	92
6[a)]	 **2f**	24	 **6f**	85[b)]

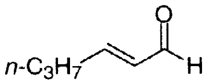
a) Copper(I) salt **1a** (4 mol) was used. b) The isomer ratio was 8 : 1 .

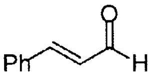
The reactions of 3-nonen-2-one (**2b**), chalcone (**2c**), dibenzylideneacetone (**2d**), 2-cyclohexen-1-one (**2e**), and carvone (**2f**) proceeded in excellent yields with high 1,4-selectivity. However, sterically congested enones such as 1-acetyl-1- cyclohexene (**2g**), isophorone (**2h**), and pulegone (**2i**) were recovered unchanged. Unsaturated aldehydes, **2j** and **2k**, resulted in giving complex mixture.


2g


2h

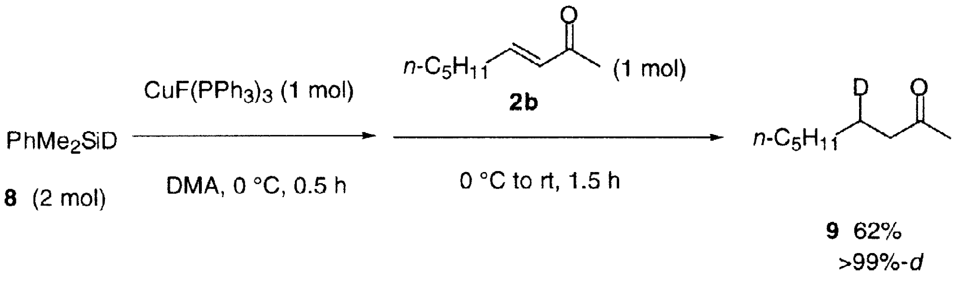

2i


2j


2k

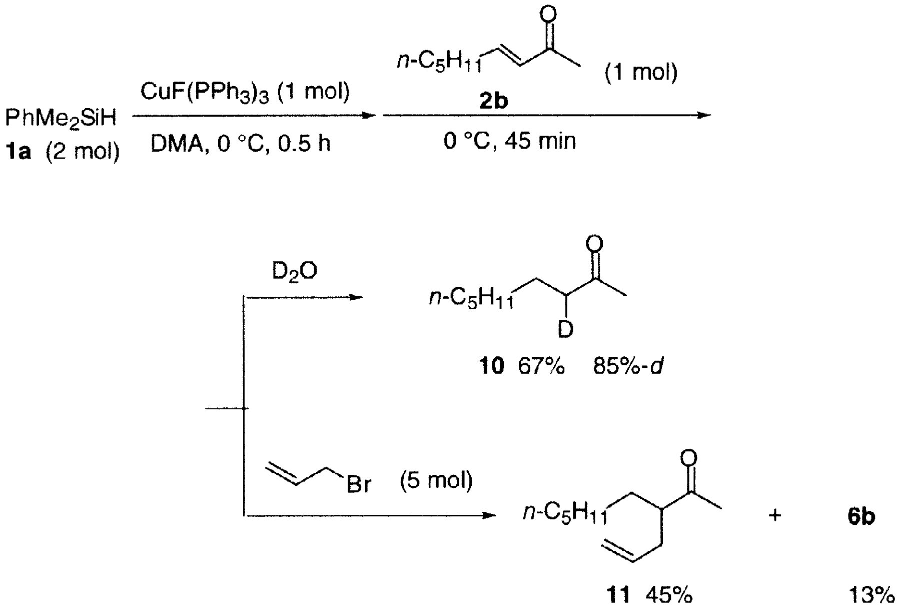
The observed selectivities contrast to those of rhodium complex-catalyzed reduction,[11] which reduces enones

2g-i smoothly in good yields. In this sense, our system appears to be highly chemoselective. The reaction is assumed to proceed via the addition of copper hydride or a related species to the β-position of enones. Indeed, the reaction using deuterosilane (PhMe$_2$SiD: **8**) afforded deuterated product **9** in 62% yield (eq 2).



(2)

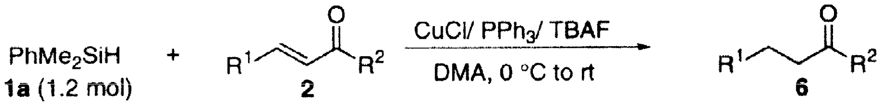
However, neither a copper hydride nor a resulting fluorosilane were observed by NMR experiments. In addition, attempted detection of the adduct of "copper hydride" to an enone, an α-metallo ketone or a corresponding enolate failed except for trapping experiments by the addition of D$_2$O or allyl bromide to give the corresponding deuterated (**10**; 67%) or allylated product (**11**; 45%) as shown in eq 3.

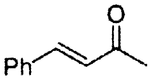
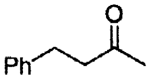
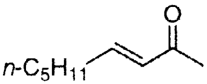
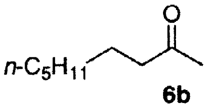
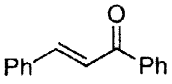
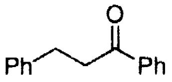
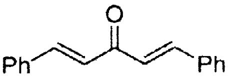
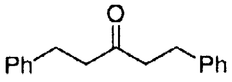
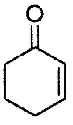
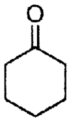
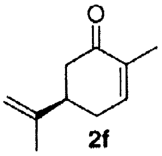
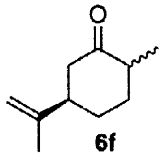
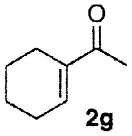
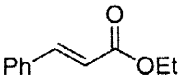
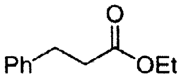
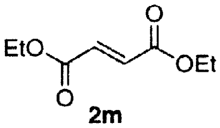
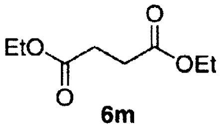


(3)

Since reduction of enones with a hydrosilane proceeds in the presence of CuF(PPh$_3$)$_3$·2EtOH (**5**) highly efficiently, our further interest has thus been centered to a catalytic system for the conjugate addition. Although use of 10 mol% of **5** induced 1,4- reduction of **2a** with moderate reactivity (63% yield of **6a**) under similar conditions, a more efficient catalytic system using readily available reagents needs to be exploited. Since Grignard reagents[13] and aluminum hydrides[14] undergo conjugate addition to α,β-unsaturated carbonyl compounds in the presence of a catalytic amount of copper(I) halide, such combination with hydrosilane was surveyed.

Table 5. Conjugate reduction of α,β-Unsaturated carbonyl compounds



Run	Substrate	CuCl/ PPh$_3$/ TBAF mol%	Time, h	Product	Yield, %[a]
1	 **2a**	20/ 20 /10	2	 **6a**	88
2	 **2b**	25/ 25/ 20	2	 **6b**	77
3	 **2c**	20/ 20/ 10	1	 **6c**	25[b]
4		110/ 110/ 100	2		94
5[c]	 **2d**	25/ 25/ 20	1.5	 **6d**	64
6	 **2e**	50/ 50/ 25	17	 **6e**	67[b]
7[d]	 **2f**	160/ 160/ 150	4.5	 **6f**	87[e]
8	 **2g**	20/ 20/ 10		No Reduction	
9	 **2l**	20/ 20/ 10	4.5	 **6l**	54
10	 **2m**	110/ 110/ 100	2	 **6m**	65[b]

a) Isolated yield. b) NMR yield. c) Hydrosilane **1a** (2.4 mol) was used. d) Hydrosilane **1a** (2 mol) was used. e) A 6 : 1 isomeric mixture of product resulted.

A combination of CuCl, tetrabutylammonium fluoride (TBAF), and triphenylphosphine was revealed to be efficient. When the reduction of **2a** with **1a** was carried out in the presence of CuCl (5 mol%), TBAF (5 mol%), and PPh_3 (5 mol%) at room temperature for 17 h, **6a** was obtained in 64% yield without formation of **7a**. The yield was improved to 95% in the reaction at room temperature for 2 h using 20 mol% of 1:1:1 mixture of the above system with a trace of 1,2-reduction. Other fluorides such as $TBAHF_2$ and $TBAH_2F_3$ were revealed to be less effective.

The 1,4-reduction of a variety of α,β-unsaturated ketones with **1a** in the presence of a $CuCl/PPh_3/TBAF$ system was carried out as shown in Table 5. Various α,β-unsaturated ketones were reduced in a 1,4-manner in good yields. For less reactive ketones, use of the more catalyst was effective to obtain the corresponding product in better yields (e.g. Runs 3 and 4). Unsaturated esters **2l** and **2m** also underwent the 1,4-selective reduction.

Conclusion

Dimethylphenylsilane was revealed to undergo conjugate reduction with the aid of a Cu(I) salt. An efficient 1,4-selective reduction system with the hydrosilane using a stoichiometric amount of $CuF(PPh_3)_3 \cdot 2EtOH$ or a catalytic amount of $CuCl/PPh_3/TBAF$ was achieved to yield the corresponding saturated ketones highly selectively. Since the reactions of the enones with the hydrosilane in the presence of a fluoride ion proceeds in a 1,2-selective manner as we reported previously,[3b] the hydrosilane-based reductions of enones can compensate the mode of 1,2- or 1,4-selective reduction.

Experimental

General. NMR spectra were measured on a Bruker AC-200 (200 MHz) NMR or Varian Mercury 300 NMR spectrometer using $CDCl_3$ as a solvent unless otherwise specified. Tetramethylsilane ($SiMe_4$) and fluorotrichloromethane ($CFCl_3$) were used as an internal standard for ^1H NMR and ^{19}F NMR, respectively. Infrared spectra were recorded on a Shimadzu FTIR-8000A spectrometer. GC/MS analyses were carried out on a Hitachi M-80 spectrometer or a Shimadzu QP-5000 GC-MS system. High-resolution mass spectra were obtained on a JEOL MStation JMS 700 using EI technique. Elemental analyses were carried out at Elemental Analysis Center, Tokyo Institute of Technology, using YANAKO MT2 CHN CORDER. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Silica gel column chromatography was carried out using Merck Kieselgel 60 (70-230 mesh) or Wakogel C-200.

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. *N,N*-Dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP) were distilled from CaH_2 and degassed, if necessary, by carrying out freeze-pump-thaw cycle (3 times) prior to use. THF, toluene, hexane, and diethyl ether were distilled from sodium-benzophenone ketyl prior to use. Triphenylphosphine was recrystallized from hexane. Other chemicals were purchased and used as such.

Preparation of $CuF(PPh_3)_3 \cdot 2EtOH$ (**5**) was carried out according to the procedure described in the literature.[9] The removal of ethanol from $CuF(PPh_3)_3 \cdot 2EtOH$ was carried out under reduced pressure at 90 °C for 12 h and used directly for the following reactions. Decomplexation of ethanol was confirmed by ^1H NMR of an aliquot of the sample.

All ketones synthesized by the 1,4-reduction are known compounds. The registry numbers of these compounds were listed following: 4-phenylbutan-2-one (**6a**); [2550-26-7], 2-nonanone (**6b**); [821-55-6], 1,3-diphenylpropan-1-one (**6c**); [1083-30-3], 1,5-diphenylpentan-3-one (**6d**); [5396-91-8], 2-methyl-5-(1-

methylethenyl)cyclohexanone (**6f**); [619-01-2], 3,5-dimethylcyclohexanone (**6j**); [2320-30-1], ethyl 3-phenylpropanoate (**6l**); [2021-28-5], and ethyl succinate (**6m**); [123-25-1].

General procedure for the reduction of α,β-unsaturated ketones in the presence of $\mathbf{CuF(PPh_3)_3{\cdot}2EtOH}$. Dimethylphenylsilane (**1a**, 0.14 g, 1.0 mmol) was added to a colorless clear solution of $\mathrm{CuF(PPh_3)_3{\cdot}2EtOH}$ (0.48 g, 0.50 mmol) in 2 mL of DMA at 0 °C. The mixture changed to a reddish homogeneous solution. After stirring the resulting mixture at 0 °C for 30 min, 1-phenyl-1-buten-3-one (**2a**; 73 mg, 0.50 mmol) was added. The temperature of the reaction mixture was gradually raised to room temperature, and stirring was continued for 6 h, while color of the solution gradually changed to yellow. The solution was poured into a mixture of diethyl ether (20 mL) and 1*M* HCl (20 mL). The organic phase was separated and the aqueous was extracted twice with diethyl ether (20 mL x 2). The combined extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexanes/EtOAc = 10 : 1) to afford **6a** in 92% yield.

General procedure for the reduction of α,β-unsaturated ketones in the presence of $\mathbf{CuCl/PPh_3/TBAF}$. A mixture of CuCl (10 mg, 0.10 mmol), and TBAF (50 µl of 1.0 *M* THF solution, 0.05 mmol) dissolved in DMA (2 mL) was stirred at 0 °C for 10 min. To the mixture was added $\mathrm{HSiPhMe_2}$ (82 mg, 0.6 mmol) at 0 °C and the resulting mixture was stirred for an additional 30 min. Then, **2a** (73 mg, 0.50 mmol) was added at 0 °C and the mixture was allowed to warm to room temperature. After stirring for 2 h, the reaction mixture was poured into a mixture of diethyl ether (20 mL) and 1*M* HCl (20 mL). The organic phase was separated and the aqueous was extracted with diethyl ether twice (20 mL x 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo to leave a crude oil, which was purified by column chromatography on silica gel (hexanes/EtOAc = 10 : 1) to afford **6a** in 88% yield.

Deuteriodimethylphenylsilane (8). To a suspension of lithium wire cut into small pieces (0.6 g, 90 mmol) in THF (20 mL) was added chlorodimethylphenylsilane (2.6 g, 15 mmol) at -10 °C. Stirring was continued at -10 °C for 20 h before quenching with $\mathrm{D_2O}$ (1 mL). The organic phase was separated and the aqueous was extracted with diethyl ether (30 mL x 3). The combined organic extracts were washed with brine (20 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by distillation under reduced pressure to give **8** (0.90 g, 44%) as a colorless oil. Bp 80 °C (bath temp, 40 Torr). ^{1}H NMR (300 MHz) δ 0.38 (s, 6H), 7.30-7.40 (m, 3H), 7.50-7.60 (m, 2H); ^{13}C NMR (75.5 MHz) δ -3.9, 127.8, 129.2, 134.0, 137.4; IR (neat) 3071, 3019, 2901, 1541, 1427, 1250, 1116, 837, 794, 700 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 139 ($\mathrm{M^+}$+2, 1), 138 ($\mathrm{M^+}$+1, 4) 137 ($\mathrm{M^+}$, 38), 136 ($\mathrm{M^+}$-1, 13), 122 (100), 105 (13), 77 (7), 58 (87). HRMS Calcd for $\mathrm{C_8H_{11}SiD}$: M, 137.0770. Found: *m/z* 137.0777 ($\mathrm{M^+}$).

4-Deuterio-2-nonanone (9). This compound was synthesized by the reaction of 3-nonen-2-one with **8** in a similar manner to the reaction with **1a**. Yield 62% (a colorless oil). ^{1}H NMR (300 MHz) δ = 0.88 (t, *J* = 6.9 Hz, 3H), 1.25-1.35 (m, 8H), 1.50-1.58 (m, 1H), 2.14 (s, 3H), 2.41 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (75.5 MHz) δ = 14.1, 22.6, 23.5 (t, *J* = 19.6 Hz), 29.0, 29.9, 31.7, 43.7, 209.4; IR (neat) 2957, 2926, 2856, 2361, 2156, 1716, 1558, 1508, 1466, 1458, 1412, 1361, 1165, 794 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 144 ($\mathrm{M^+}$+1, 1), 143 ($\mathrm{M^+}$, 3), 128 (1), 110 (1), 72 (15), 59 (23), 58 (100), 57 (11). HRMS Calcd for: $\mathrm{C_9H_{17}OD}$: M, 143.1419. Found: *m/z* 143.1428 ($\mathrm{M^+}$).

Reduction of carbonyl compounds and successive quenching with $\mathbf{D_2O}$. Synthesis of 3-D-2-nonanone (10). Dimethylphenylsilane (0.27 g, 1.0 mmol) was added to a solution of $\mathrm{CuF(PPh_3)_3}$ (0.87 g, 1.0 mmol) in DMA (4 mL) at 0 °C, and the resulting mixture was stirred for 30 min. Then, 3-nonen-2-one (140 mg, 0.5 mmol) was added to the mixture at 0 °C. Stirring was continued at room temperature for further 45 min before $\mathrm{D_2O}$ (1.0 mL) was added to the mixture. The organic phase was separated and aqueous phase was extracted with diethyl ether (30 mL x 3). The combined extracts were washed with $\mathrm{NaHCO_3}$ (20 mL), brine (20 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/$\mathrm{Et_2O}$ = 10 : 1) to give **10** (95 mg, 67% yield, 85%-deuterated) as a colorless oil. ^{1}H NMR (300 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3H), 1.25-1.35 (m, 8H), 1.50-1.62 (m, 2H), 2.13 (s, 3H), 2.39 (tt, *J* = 2.4, 7.5 Hz, $\mathrm{COC\underline{H}D}$ 0.8H), 2.42 (t, *J* = 7.5 Hz, $\mathrm{COC\underline{H}_2}$ 0.4H); ^{13}C NMR (75.5 MHz) δ = 14.0, 22.6, 23.8, 29.0, 29.1, 29.8, 31.7, 43.5 (t, *J* = 19.0 Hz, $\mathrm{CO\underline{C}HD}$), 209.4; IR (neat) 2957, 2928, 2856, 1716, 1466, 1427, 1358, 1174, 1118, 966, 889, 827, 777, 725, 700 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 144 ($\mathrm{M^+}$+1, 1), 143 ($\mathrm{M^+}$, 5), 128 (2), 114

(1), 99 (2), 84 (4), 71 (19), 59 (100). HRMS Calcd for $C_9H_{17}OD$: M, 143.1419. Found: *m/z* 143.1422 (M^+).
3-(2-Propenyl)nonan-2-one (11). Registry No. [75265-81-5]: The reaction of dimethylphenylsilane (0.20 g, 1.5 mmol) and 3-nonen-2-one (70 mg, 0.5 mmol) in the presence of $CuF(PPh_3)_3$ (0.65 g, 0.8 mmol) in DMA (2 mL) was carried out similarly to the synthesis of **6c**. After the reaction was completed, allyl bromide (0.30 g, 2.5 mmol) was added to the mixture. The resulting mixture was allowed to warm to room temperature and quenched with 1 *M* HCl. The organic phase was separated and the aqueous phase was extracted with diethyl ether (30 mL x 3). The combined organic extracts were washed with $NaHCO_3$ (20 mL) and with brine (20 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by silica gel column chromatography to give **11** (41 mg, 45% yield) and 2-nonanone (**6b**, 9 mg, 13% yield) as a colorless oil, respectively. ^1H NMR spectrum of **11** was identical with that of an authentic sample.

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