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A New Halogen-Exchange Reaction between Sn–F and Li–X: Selective 1,2- and 1,4-Reductions of α,β-Unsaturated Ketones and Effects of Halogen Substituents on the Regioselectivity of Organotin Hydrides

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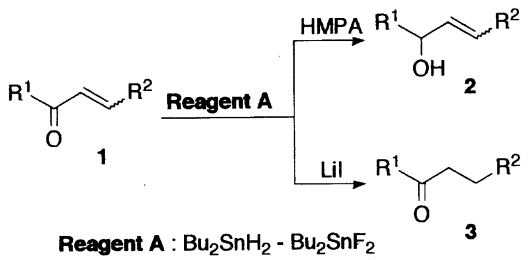
We have found that halogen-exchange occurs effectively between Sn–F and Li–X (X = I, Br, Cl) in tin hydride reagents. This fact induced a complete change in the regiochemistry in the reductions of α,β-unsaturated ketones **1** with Bu_2SnH_2–Bu_2SnF_2 (Reagent A): the use of Reagent A in combination with HMPA performed 1,2-reductions, while the addition of LiI to Reagent A achieved 1,4-reductions. It was demonstrated that the regioselectivity of organotin hydrides greatly depends on the properties of the halogen substituents attached to tin atoms.

The reduction of α,β-unsaturated ketones by metal hydrides is a most interesting reaction in organic synthesis. There are two possible reaction pathways: 1,2- and 1,4-reductions.[1)] It is difficult to control 1,2- and 1,4-reductions by using one metal hydride species, because the regiochemistry is generally dependent on the properties of the reductants.[2)] Although the NaH/*t*-AmONa reducing system can control 1,2- and 1,4-reductions by the addition of $ZnCl_2$ and $Ni(OAc)_2$,[3)] the use of highly basic sodium alkoxide is unavoidable. Organotin hydrides are mild and neutral reagents. The use of triorganotin hydrides usually results in 1,4-reduction prior to 1,2-reduction,[4)] whereas diorganotin hydrides predominantly give 1,2-reduction products.[4c,5)] These facts indicate that the regioselectivity of organotin hydrides should be greatly improved by a change of the substituent on the tin atom. There has been no report that clean control of the regioselectivity in the reduction of α,β-unsaturated ketones can be accomplished by a change of the substituent on metal hydrides. We have focused our attention on this unique specificity of organotin hydrides, and recently found that the transformation of organotin hydride from Bu_2SnH_2 to Bu_2SnIH caused a switching of the regiochemistry in the reduction of α,β-unsaturated ketones.[6)] In this paper we report that a Bu_2SnFH ← HMPA complex[7)] prepared from the Bu_2SnH_2–Bu_2SnF_2 system (Reagent A) and HMPA (hexamethylphosphoric triamide) is an effective reductant for selective 1,2-reduction. Further work spectroscopically reveals that a halogen-exchange reaction from Reagent A to the Bu_2SnIH system proceeds by making use of LiI, and demonstrates that control of exclusive 1,2- and 1,4-reductions can be achieved by using one organotin hydride species, Reagent A (Scheme 1). We also discuss the effects of halogen substituents on the regioselectivity of organotin hydrides. In 1,4-hydrostannations of α,β-unsaturated ketones in the presence of PhCHO, the correlation between the geometry of the generated tin enolates and the diastereoselective formation of aldol-type products is described.

Results and Discussion

Selective 1,2-Reduction. We previously disclosed that Bu_2SnXH (X = Cl, F) acts as an excellent reducing agent for carbonyl compounds.[7,8)] This finding induced us to investigate Bu_2SnXH (X = Cl, F) as 1,2-regioselective reductants for α,β-unsaturated ketones. Table 1 gives the results obtained by the reduction of chalcone **1a** with Bu_2SnXH (X = Cl, F). Contrary to our expectation, the use of Bu_2SnClH, prepared by a redistribution reaction between Bu_2SnH_2 and Bu_2SnCl_2,[9)] gave no carbonyl reduction product (Entry 1). Our previous observation that the reducing power of Bu_3SnH



Scheme 1. Controls of the regiochemistry in reductions of α,β-unsaturated ketones **1**.

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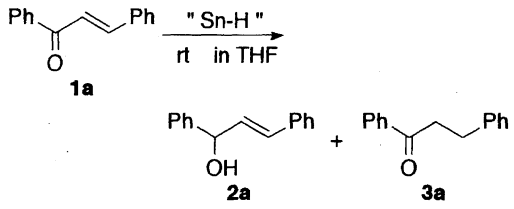
Table 1. Reductions of Chalcone **1a** with Tin Hydride Systems[a)]



Entry	"Sn–H"	Additive	Time h	Yield/% 2a	3a
1	Bu_2SnClH	—	2	0	65
2		HMPA	3	0	45
3	Bu_2SnH_2–Bu_2SnF_2	—	21	49	0
4		HMPA	2	69	0
5		Ph_3PO	3.5	70	Trace
6		$(PhO)_3PO$	36	Trace	5
7		Bu_4NCl	3	0	Trace
8		Bu_4NF	9	22	7
9		LiF	8	54	15
10		LiI	4	0	85
11		LiBr	4	0	78
12		LiCl	4	0	72
13[b)]	Bu_2SnH_2	LiI	3	6	0
14[c)]	—	LiH[d)]	6	8	0

a) Chalcone (**1a**) 1 mmol, Bu_2SnH_2 0.5 mmol, Bu_2SnX_2 0.5 mmol, additive 1 mmol, THF 1 mL. b) Chalcone (**1a**) 1 mmol, Bu_2SnH_2 1 mmol, LiI 1 mmol, THF 1 mL. c) Chalcone (**1a**) 1 mmol, LiH 2 mmol, THF 1 mL. d) LiH was synthesized by the mixing of BuLi (2 mmol) and Bu_3SnH (2 mmol).

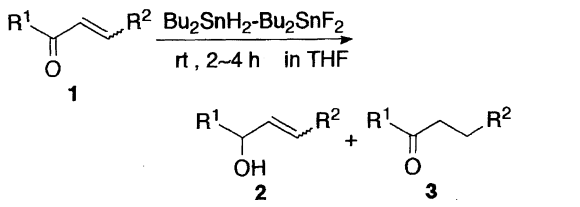
for carbonyl groups can be enhanced by the addition of HMPA[10] strongly motivated us to use such an additive. However, no effect was observed and allylic alcohol **2a** was not detected at all (Entry 2). This result probably means that Bu_2SnClH intrinsically has no reducing ability in 1,2-fashion. On the other hand, the Bu_2SnFH species exhibited remarkable reducing ability; thus, the Bu_2SnH_2–Bu_2SnF_2 system (Reagent A) combined with HMPA reduced **1a** exclusively in a 1,2-fashion to give **2a** in 69% yield within 2 h (Entry 4). In this case, the addition of HMPA is also available for the immediate formation of Bu_2SnFH (Eq. 1).[7]

$$Bu_2SnH_2 + Bu_2SnF_2 \underset{}{\overset{2HMPA}{\rightleftharpoons}} 2\,\underset{\text{HMPA}}{Bu_2SnFH} \qquad (1)$$

Reagent A

Without HMPA, however, the reducing power of Reagent A decreased, and required 21 h to provide **2a** in 49% yield (Entry 3). The addition of Ph_3PO instead of HMPA produced a trace of saturated ketone **3a** (Entry 5). Tetraammonium halides[11] and $(PhO)_3PO$ were no more efficient additives (Entries 6—8). Although DMF[12] and DMSO were employed as solvents and additives, the yield was negligible. As shown in Table 2, high reactivity and 1,2-regioselectivity of Reagent A/HMPA (Bu_2SnFH ← HMPA complex) were also exhibited in the reductions of various α,β-unsaturated ketones **1**, including aromatic ketones (**1b**, **1c**), methyl ketones (**1d**, **1e**) and cyclic one **1f** (Entries 1,3,5,7, and 9). In all cases, allylic alcohols **2b—2f** were effectively provided

Table 2. 1,2- and 1,4-Reductions of α,β-Unsaturated Ketones **1** with Bu_2SnH_2–Bu_2SnF_2[a)]



Entry	R^1	R^2	1	Additive	Yield/% 2	3
1	Ph	Me	**1b**	HMPA	89	0
2				LiI	0	83
3	Ph	H	**1c**	HMPA	75	18
4				LiI	0	70
5	Me	H	**1d**	HMPA	48	0
6				LiI	0	80
7	Me	Ph	**1e**	HMPA	56	0
8				LiI	0	59
9	$-(CH_2)_3-$		**1f**	HMPA	89	0
10				LiI	0	41 (3)[b)]

a) Unsaturated ketone (**1**) 1 mmol, Bu_2SnH_2 0.5 mmol, Bu_2SnF_2 0.5 mmol, additive 1 mmol, THF 1 mL. b) The number in parenthesis is the yield for cyclohexanol.

in 1,2-fashion. The reduction of **1c** was accompanied by 1,4-reduction product **3c** (18%), because of the susceptibility of the terminal conjugated double bond to a nucleophilic attack (Entry 3).

Selective 1,4-Reduction. To develop reductants for a selective 1,4-reduction, we examined the further influence of additives on the regiochemistry. When LiF was added to the Bu_2SnH_2–Bu_2SnF_2 system (Reagent A), because lithium reagents are more frequently used for the preparation of various functionalized organotin reagents,[13] the 1,4-reduction product of **1a** was afforded in 15% yield (Entry 9 in Table 1). Surprisingly, the use of LiCl, LiBr, and LiI dramatically transformed the regiochemistry from 1,2- into 1,4-reduction (Entries 10—12). In particular, the addition of LiI gave excellent 1,4-regioselectivity and yield (Entry 10). No advantageous effect of LiI as an additive was observed in the reduction with Bu_2SnH_2 (Entry 13). It was confirmed that LiH cannot effect 1,4-reduction (Entry 14). No LiH would be generated from the mixture of Reagent A and LiI. This reductant, Reagent A/LiI, also led to an exclusive 1,4-reduction of α,β-unsaturated ketones **1b—1f** (Entries 2,4,6, 8, and 10 in Table 2). In the reduction of **1f**, cyclohexanol was obtained as a minor product (Entry 10). This product presumably arose by sequential 1,4- then 1,2-reduction.[14]

Spectroscopic Studies of Bu_2SnH_2–Bu_2SnF_2 System (Reagent A). A spectral analysis of the resulting solution from the Bu_2SnH_2–Bu_2SnF_2 system (Reagent A) and LiI was carried out by ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR and FT-IR. The spectral data for this reducing system are summarized in Table 3. The obtained spectral data were different from that of the Bu_2SnH_2–Bu_2SnF_2 system (Reagent A) reported previously (IR ν(Sn–H) = 1875 cm^{-1}, ^1H NMR δ = 7.56

Table 3. Spectral Data for Bu_2SnH_2–Bu_2SnF_2 (Reagent A)/LiI, and Bu_2SnIH/LiF in THF-d_8

	Reagent A/LiI[a)]	Bu_2SnIH/LiF[b)]
FT-IR (neat)		
ν(Sn–H)	1846.1 cm^{-1}	1855.7 cm^{-1}
^1H NMR		
δ(Sn–^1H)	6.22 ppm	6.13 ppm
^{119}Sn NMR		
$\delta(^{119}Sn)$	−97.3 ppm	−85.6 ppm
$^1J(^{119}Sn–^1H)$	2156 Hz	2109 Hz
$^1J(^{117}Sn–^1H)$	2059 Hz	2016 Hz
^1J(Sn–$^{13}C_\alpha$)	429 (436/423)[c)] Hz	415 (425/406)[c)] Hz

a) 4.2 mol dm^{-3}. b) 4.1 mol dm^{-3} c) $^{119}Sn/^{117}Sn$ coupling values resolved.

(Sn–H)).[9b)] The ^{119}Sn NMR spectra showed only one Sn–H bond; a doublet peak was observed in the ^1H-coupled spectrum, and the ^1H-decoupled spectrum displayed a singlet signal. The Sn–F bond was not detected in the ^{19}F NMR spectra. The NMR spectra of a solution of Bu_2SnIH in the presence of LiF were similar to that of the Reagent A/LiI system (Table 3), where Bu_2SnIH was prepared from Bu_2SnH_2 and Bu_2SnI_2.[9,15)] These observations indicate the formation of the Bu_2SnIH species.

When an 8 mol dm^{-3} THF solution of the Reagent A/LiI system was left to stand overnight, a white solid was obtained as a precipitate. As illustrated in Fig. 1(a), the powder X-ray spectrum confirmed that this white precipitate was not Bu_2SnF_2, but LiF, by a comparison with standard samples (Figs. 1(b) and 1(c)). From these results, it is proposed that the reaction proceeds as Eq. 2 in the reducing system, Reagent A/LiI. The formation of a stable Li–F bond is perhaps facilitated a halogen-exchange reaction between Sn–F and Li–X. Organotin halide hydrides (Bu_2SnXH) are usually prepared by a redistribution reaction between Bu_2SnH_2 and Bu_2SnX_2.[9)] We have presented a new method for the preparation of Bu_2SnXH by a halogen-exchange reaction.[16)]

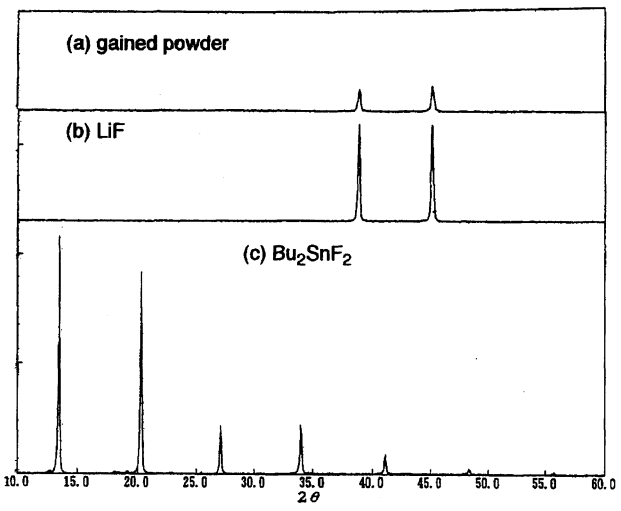


Fig. 1. Powder X-ray spectra of (a) gained powder, (b) LiF, and (c) Bu_2SnF_2.

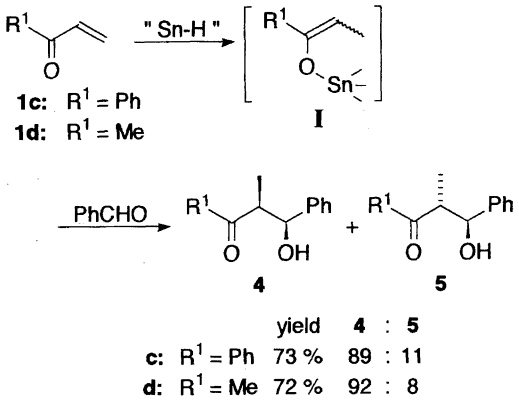
$$Bu_2SnH_2 + Bu_2SnF_2 \xrightarrow{2LiI} 2Bu_2SnIH + 2LiF\downarrow \quad (2)$$

Reagent A

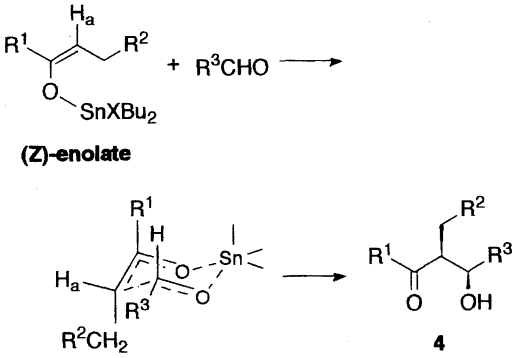
Effects of Halogen Substituents on the Regioselectivity of Organotin Hydrides. The use of Bu_2SnH_2 has provided both 1,2- and 1,4-products in the reduction of α,β-unsaturated ketone **1a** (63% yield, 1,2-**2a** : 1,4-**3a** = 71 : 29).[6)] The present results indicated that the introduction of a fluorine substituent into Bu_2SnH_2 greatly improved the regioselectivity: the Bu_2SnFH ← HMPA complex (Reagent A/HMPA) exhibited clean 1,2-selectivity. This is probably due to the electron-withdrawing ability of the fluorine substituent. The acidity of the tin atom of tin hydride is enhanced by the fluorine substituent attached to the tin atom. When a strong interaction between α,β-unsaturated ketone and the tin atom takes place, 1,2-reduction would be favored.[2)] On the other hand, the introduction of an iodine, bromine or chlorine substituent into Bu_2SnH_2 caused an inversion of the regioselectivity; an exclusive 1,4-reduction was carried out by the Bu_2SnXH species (Reagent A/LiX) (X = I, Br, Cl). This may be attributed to the nucleophilicity of the Sn–X bonds (X = I, Br, Cl). We have already demonstrated that organotin hydrides having a Sn–X bond (X = I, Br, Cl) perform an efficient nucleophilic attack on epoxy compounds.[7,17)] In particular, the Bu_2SnIH species has displayed excellent nucleophilic ability. For example, the nucleophilic attack of a Sn–I bond to epoxy groups of α,β-epoxy ketones proceeded prior to the carbonyl reduction by a Sn–H bond.[7b)] Although no satisfactory evidence is available, the reaction path in the 1,4-reduction of α,β-unsaturated ketones with the Bu_2SnIH species could be explained as follows. At first, an iodine is added at the β position of α,β-unsaturated ketone. The resulting alkyl iodide group is reduced by a Sn–H moiety, giving tin enolate **I**. A saturated ketone is provided by quenching of the tin enolate **I** with MeOH.

Diastereoselective Formation of Aldol Type Products. When a 1 : 1 mixture of α,β-unsaturated ketone **1c** and PhCHO was allowed to react with the Bu_2SnH_2–Bu_2SnF_2 (Reagent A)/LiI system, aldol-type products **4c** and **5c** were provided in good yield at −30 °C → r.t. for 3 h (Scheme 2). Benzyl alcohol, formed by the reduction of PhCHO, was not detected at all. Similarly, the reduction of **1d** in the presence of PhCHO with the Reagent A/LiI system led to the formation of **4d** and **5d**. For these reactions, it seems that the Reagent A/LiI system acts as a chemoselective reductant for α,β-unsaturated ketones **1** in the presence of aldehydes. The resulting tin enolate **I** as an intermediate in 1,4-hydrostannation of **1** presumably reacts with unaffected PhCHO to give aldol-type products **4** and **5**.

Noteworthy is that the predominant formation of products **4** was observed. We monitored the progress of the 1,4-hydrostannation of α,β-unsaturated ketones **1c** in THF-d_8 by NMR spectroscopy.[18)] At −50 °C, a vinyl proton corresponding to the (*Z*)-tin enolate was detected in the ^1H NMR spectrum (δ = 3.91, q, J = 7.33 Hz, H_a).[19)] As the temperature was raised, the (*E*)-tin enolate appeared (δ = 4.87, q, J = 6.96 Hz, H_a).[19)] The final integral ratio of (*Z*)- to (*E*)-tin enolate



Scheme 2. Chemoselective reductions of α,β-unsaturated ketones **1** in the presence of PhCHO with the Bu_2SnH_2–Bu_2SnF_2/LiI system.



Scheme 3. Trasition state of aldol type reactions between tin enolates and aldehydes.

became about 1 : 1. From these facts, it is proposed that the diastereoselective formation of products **4** is probably due to a rapid reaction of the first-formed (*Z*)-tin enolate with the coexistent aldehyde via the conventional cyclic transition state (Scheme 3).

In summary, we have found that a halogen exchange occurred effectively between Sn–F and Li–X (X = I, Br, Cl) in the tin hydride reagents. This fact induced a complete change in the regiochemistry in the reductions of α,β-unsaturated ketones **1** with Bu_2SnH_2–Bu_2SnF_2 (Reagent A): Reagent A/HMPA performed 1,2-reductions, while Reagent A/LiI achieved 1,4-reductions. The present reduction is convenient because the regio-control was accomplished by one reductant.

Experimental

Analysis. ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra were recorded at 400, 100, 376, and 149 MHz, respectively. Samples for the ^{1}H and ^{13}C NMR spectra of the produced alcohols were examined in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Samples for the ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of tin hydrides were examined in tetrahydrofuran-d_8 containing tetramethyltin. Samples for the ^{19}F NMR spectra of tin hydrides were measured relative to external fluorobenzene in tetrahydrofuran-d_8. GLC analyses were performed with a FFAP (2-m×3-mm glass column). Column chromatography was performed by using Wakogel C-200 mesh silica gel. Preparative TLC was carried out on Wakogel B-5F silica gel. The yields were determined by ^{1}H NMR or GLC using internal standards.

Materials. Dibutyltin dihydride (n-Bu_2SnH_2) was prepared by the reduction of dibutyltin dichloride (n-Bu_2SnCl_2) with $LiAlH_4$.[20] Dibutyltin halide hydrides (n-Bu_2SnXH; X = Cl, I) were synthesized by a redistribution reaction between Bu_2SnH_2 and Bu_2SnX_2.[9] THF was freshly distilled over sodium benzophenone ketyl, and HMPA was distilled over finely powdered calcium hydride. All reactions were carried out under dry nitrogen.

Representative Procedure for the 1,2-Reductions of α,β-Unsaturated Ketones. To a solution of Bu_2SnH_2 (0.5 mmol) in 1 mL of THF was added Bu_2SnF_2 (0.5 mmol) and HMPA (1 mmol). The mixture was stirred at room temperature for 10 min. After α,β-Unsaturated ketone **1** (1 mmol) was added at room temperature, the solution was stirred until the Sn–H absorption (1869 cm^{-1}) disappeared in the IR spectrum. After quenching with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column chromatography eluting with hexane–EtOAc (1 : 2) to give a crude product **2**. Further purification of **2** was performed by TLC eluting with hexane–EtOAc (4 : 1).

1,3-Diphenyl-2-propen-1-ol (2a): Colorless liquid; IR (neat) 3200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.12 (br, 1H), 5.37 (dd, 1H, J = 2.44 and 6.35 Hz), 6.38 (dd, 1H, J = 6.35 and 16.11 Hz), 6.68 (d, 1H, J = 16.11 Hz), 7.20—7.44 (m, 10H); ^{13}C NMR ($CDCl_3$) δ = 75.1, 126.3, 126.6, 127.8, 127.8, 128.5, 128.6, 130.5, 131.5, 136.5, 142.8. HRMS Calcd for $C_{15}H_{14}O$: M, 210.1045. Found: m/z 210.1038.

1-Phenyl-2-buten-1-ol (2b): Colorless liquid, purified by TLC eluting with hexane–EtOAc (5 : 1); IR (neat) 3200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.70 (d, 3H, J = 5.86 Hz), 2.29 (br, 1H), 5.11 (d, 1H, J = 6.35 Hz), 5.63—5.77 (m, 1H), 7.22—7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 17.6, 75.0, 126.1, 127.2, 127.4, 128.3, 133.6, 143.3. HRMS Calcd for $C_{10}H_{12}O$: M, 148.0889. Found: m/z 148.0878.

1-Phenyl-2-propen-1-ol (2c): This compound (colorless liquid) was prepared by an another reductant and isolated by TLC as a mixture with **2c** and **3c**; IR (neat) 3380 and 1675 cm^{-1}. HRMS Calcd for $C_9H_{10}O$: M, 134.0732. Found: m/z 134.0724. ^{1}H NMR ($CDCl_3$) **2c** δ = 2.22 (br, 1H), 5.15—5.20 (m, 2H), 5.30—5.38 (m, 1H), 5.98—6.11 (m, 1H) 7.23—7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) **2c** δ = 75.3, 115.0, 126.3, 127.6, 128.5, 140.2, 142.6; ^{1}H NMR ($CDCl_3$) **3c** δ = 1.22 (t, 3H, J = 7.32 Hz), 2.99 (q, 2H, J = 7.32 Hz), 7.39—7.97 (m, 5H); ^{13}C NMR ($CDCl_3$) **3c** δ = 8.2, 31.7, 127.9, 128.5, 132.8, 136.9, 200.9.

4-Phenyl-3-buten-2-ol (2e): Colorless liquid, purified by TLC eluting with hexane–EtOAc (3 : 1); IR (neat) 3380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.36 (d, 3H, J = 6.59 Hz), 4.43—4.51 (qdd, 1H, J = 1.16, 6.22 and 6.59 Hz), 6.25 (dd, 1H, J = 6.22 and 15.76 Hz), 7.20—7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 23.3, 68.8, 126.4, 127.6, 128.5, 129.3, 133.5, 136.7. HRMS Calcd for $C_{10}H_{12}O$: M, 148.0889. Found: m/z 148.0893.

Representative Procedure for the 1,4-Reductions of α,β-Unsaturated Ketones. To a solution of Bu_2SnH_2 (0.5 mmol) and Bu_2SnF_2 (0.5 mmol) in 1 mL of THF was added LiI (1 mmol). The mixture was stirred at room temperature for 10 min. After α,β-Unsaturated ketone **1** (1 mmol) was added, the solution was stirred until the Sn–H absorption (1846 cm^{-1}) disappeared in the IR spectrum. After quenching the reaction with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column chromatography eluting with hexane–EtOAc (9 : 1) to give the product **3**. Further purification was performed by TLC eluting with hexane–EtOAc (10 : 1).

1,3-Diphenyl-1-propanone (3a): White solid; mp 68.7—70.3

°C; IR (KBr) 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.07 (t, 2H, J = 7.32 Hz), 3.30 (t, 2H, J = 7.32 Hz), 7.18—7.97 (m, 10H); ^{13}C NMR ($CDCl_3$) δ = 30.1, 40.4, 126.1, 128.0, 128.4, 128.5, 128.6, 133.0, 136.8, 141.3, 199.2. HRMS Calcd for $C_{15}H_{14}O$: M, 210.1045. Found: *m/z* 210.1024.

3-Buten-2-ol (**2d**) [598-32-3], 2-cyclohexen-1-ol (**2f**) [822-67-3], butyrophenone (**3b**) [495-40-9], propiophenone (**3c**) [93-55-0], 2-butanone (**3d**) [78-93-3], 4-phenyl-2-butanone (**3e**) [2550-26-7], cyclohexanone (**3f**) [108-94-1], cyclohexanol [108-93-0] were identified in comparison with commercially available samples.[21]

Representative Procedure for the Aldol-Type Reactions. To a solution of Bu_2SnH_2 (0.5 mmol) in 1 mL of THF, Bu_2SnF_2 (0.5 mmol) and LiI (1 mmol) were added and cooled at −30 °C. α,β-Unsaturated ketone **1** (1 mmol) and benzaldehyde (1 mmol) were added, and the solution was stirred for 3 h with warming to room temperature. After quenching with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column-chromatography eluting with hexane–EtOAc (1 : 2) to give aldol products **4** and **5**. Further purification was performed by TLC eluting with hexane–EtOAc (1 : 1).

(2*R,3*R**)- and (2*R**,3*S**)-1,3-Diphenyl-3-hydroxy-2-methyl-1-propanone (4c) and (5c):** Colorless liquid, purified by TLC with hexane–EtOAc (1 : 1); IR (neat) 3000 and 1705 cm^{-1}. HRMS Calcd for $C_{16}H_{16}O_2$: M, 240.1151. Found: *m/z* 240.1148. ^1H NMR ($CDCl_3$) **4c** δ = 1.12 (d, 3H, J = 7.33 Hz), 3.63 (qd, 1H, J = 2.93 and 7.33 Hz), 5.17 (d, 1H, J = 2.93 Hz), 7.25—7.95 (m, 10H); ^{13}C NMR ($CDCl_3$) **4c** δ = 11.1, 47.0, 73.1, 126.0, 127.3, 128.2, 128.5, 128.8, 133.6, 135.6, 141.8, 205.8; ^1H NMR ($CDCl_3$) **5c** δ = 1.00 (d, 3H, J = 7.32 Hz), 3.88—4.07 (m, 1H), 4.93 (d, 1H, J = 7.81 Hz), 7.25—7.99 (m, 10H).

^1H NMR data of (2*R**,3*R**)-**4c** and (2*R**,3*S**)-**5c** were consistent with the ones reported previously; R. Noyori, I. Nishida, and J. Sakata, *J. Am. Chem. Soc.*, **105**, 1598 (1983). Registry No. (2*R**,3*R**)-**4c**, 71908-03-7; (2*R**,3*S**)-**5c**, 71908-02-6.[20]

(2*R,3*R**)- and (2*R**,3*S**)-4-Phenyl-4-hydroxy-3-methyl-2-butanone (4d) and (5d):** Colorless liquid, purified by TLC with hexane–EtOAc (1 : 1); IR (neat) 3420 and 1700 cm^{-1}; HRMS Calcd for $C_{11}H_{14}O_2$: M, 178.0994. Found: *m/z* 178.0997. ^1H NMR ($CDCl_3$) **4d** δ = 1.08 (d, 3H, J = 7.33 Hz), 2.13 (s, 3H), 3.63 (qd, 1H, J = 3.90 and 7.33 Hz), 7.21—7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) **4d** δ = 10.1, 29.3, 53.2, 73.0, 125.8, 127.3, 128.2, 141.7, 213.5; ^1H NMR ($CDCl_3$) **5d** δ = 0.92 (d, 3H, J = 6.84 Hz), 2.21 (s, 3H), 2.88—2.99 (m, 1H), 4.72 (d, 1H, J = 8.31 Hz), 7.21—7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) **5d** δ = 14.0, 29.9, 53.6, 76.4, 126.9, 127.5, 128.4, 140.8, 213.5.

^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR Studies. Chemical shifts for ^1H and ^{119}Sn NMR were measured relative to Me_4Sn. Chemical shifts for ^{13}C NMR were measured relative to THF-d_8. Chemical shifts for ^{19}F NMR were measured relative to external fluorobenzene.

Bu_2SnH_2–Bu_2SnF_2/LiI. In a small flask, Bu_2SnH_2 (1.06 mmol), Bu_2SnF_2 (1.06 mmol) and LiI (2.00 mmol) were kept under dry N_2 in 0.5 mL of THF-d_8 containing Me_4Sn; 0.8 mL of the solution was transferred to a 5ϕ NMR tube. NMR spectra were recorded at room temperature (24 °C); ^1H NMR (4.23 mmol in 1 mL of THF-d_8) δ = 6.22 (Sn–H, $^1J(^{119}Sn–^1H)$ = 2156 Hz, $^1J(^{117}Sn–^1H)$ = 2059 Hz); ^{13}C NMR (r.t.) δ = 14.0, 18.9 ($^1J(^{119}Sn–^{13}C_\alpha)$ = 436 Hz, $^1J(^{117}Sn–^{13}C_\alpha)$ = 423 Hz), 26.8 ($^3J(Sn–^{13}C_\gamma)$ = 75 Hz), 29.7 ($^2J(Sn–^{13}C_\beta)$ = 28 Hz); ^{119}Sn NMR (r.t.) δ = −99.1 (d); ^{19}F NMR no peaks was detected; FT-IR (neat) ν(Sn–H) = 1846.1 cm^{-1}.

Bu_2SnH_2–Bu_2SnF_2/LiF: (4.10 mmol in 1 mL of THF-d_8); ^1H NMR (r.t.) δ = 6.13 (Sn–H, $^1J(^{119}Sn–^1H)$ = 2110 Hz, $^1J(^{117}Sn–^1H)$ = 2016 Hz); ^{13}C NMR (r.t.) δ = 14.0, 17.8 ($^1J(^{119}Sn–^{13}C_\alpha)$ = 425 Hz, $^1J(^{117}Sn–^{13}C_\alpha)$ = 406 Hz), 26.9 ($^3J(Sn–^{13}C_\gamma)$ = 76 Hz), 29.9 ($^2J(Sn–^{13}C_\beta)$ = 29 Hz); ^{119}Sn NMR (r.t.) δ = −85.6 (d); FT-IR (neat) ν(Sn–H) = 1855.7 cm^{-1}.

Monitoring of the 1,4-Hydrostannation of 1c with the Bu_2SnClH Species. In a small flask, **1c** (1 mmol) was added to THF-d_8 containing a Me_4Sn solution of Bu_3SnH (1 mmol) and Bu_2SnCl_2 (1 mmol) at −78 °C under dry N_2; 0.8 mL of the solution was transferred to a 5ϕ NMR tube. NMR spectra were recorded from −50 °C to room temperature (20 °C).

Powder X-Ray Analysis. The intensity data ($10° < 2\theta < 70°$) were collected at 293 K on a Mac Science M18XHF diffractometer with graphite monochromated Cu $K\alpha$ radiation. Powder diffraction spectra are shown in Fig. 1. Full details were deposited as Document No. 72008 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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