

# Direct Reduction of Alcohols: Highly Chemoselective Reducing System for Secondary or Tertiary Alcohols Using Chlorodiphenylsilane with a Catalytic Amount of Indium Trichloride

Makoto Yasuda, Yoshiyuki Onishi, Masako Ueba, Takashi Miyai, and Akio Baba\*

Department of Molecular Chemistry, Graduate School of Engineering, Osaka University,  
2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

baba@ap.chem.eng.osaka-u.ac.jp

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The direct reduction of alcohols using chlorodiphenylsilane as a hydride source in the presence of a catalytic amount of indium trichloride is described. Benzylic alcohols, secondary alcohols, and tertiary alcohols were effectively reduced to give the corresponding alkanes in high yields. A compound bearing both primary and secondary hydroxyl groups was reduced only at the secondary site to afford the primary alcohol after workup with  $\text{Bu}_4\text{NF}$ . This system showed high chemoselectivity only for the hydroxyl group while not reducing other functional groups that are readily reduced by standard reducing systems. Thus alcohols bearing ester, chloro, bromo, or nitro groups, which are sensitive to  $\text{LiAlH}_4$  or  $\text{Zn}/\text{H}^+$ , were selectively reduced only at the hydroxyl sites by the chlorodiphenylsilane/ $\text{InCl}_3$  system. NMR studies revealed the reaction course. The hydrodiphenylsilyl ether is initially formed and then, with  $\text{InCl}_3$  acting as a Lewis acid, forms an oxonium complex, which accelerates the desiloxylation with donation of the hydrogen to the carbon.

## Introduction

Alcohols are versatile organic compounds reagents and can be used as precursors for other classes of organic molecules in synthetic chemistry. A representative transformation of alcohols is deoxygenation to alkane. Since a hydroxyl group is a poor leaving group, it should be generally activated before treating with a reducing reagent. Tosylation or thiocarboxylation are generally employed for activation.<sup>1,2</sup> Although a few direct reductions of alcohols have been reported, there are some problems to be solved. Nickel-catalyzed hydrogenation of alcohols requires high temperature and pressure (250 °C, 150 atm).<sup>3</sup> Only alcohols that can generate stable carbocations are reduced using strong acidic media.<sup>4</sup> The hydride reagents generally need the aid of excess amounts of Lewis acids.<sup>5</sup> In this context, the development of an efficient reducing system for direct deoxygenation of alcohols under catalytic and mild conditions is strongly desired. We have recently reported the deoxygenation of alcohols using chlorodimethylsilane with a catalytic amount of a Lewis acid.<sup>6</sup> The reducing system is strictly limited to only benzylic alcohols.

In this paper, we report the effective methodology for direct reduction of alcohols, in which a wide variety of secondary or tertiary alcohols are chemoselectively re-

duced to alkanes.<sup>7</sup> Additionally, this direct pathway shows the selective reduction that took place only at the hydroxyl moiety without influence on other functional groups.

## Results and Discussion

**Direct Reduction of Alcohols by Hydrosilane/Indium Chloride.** We chose a simple aliphatic alcohol **1a** for an initial trial to investigate the reducing system. Our previous system,<sup>6</sup> chlorodimethylsilane/ $\text{InCl}_3$ , did not work, as shown in Table 1, entry 7.<sup>8</sup> As the reactivity of hydrosilane strongly depends on the substituent on the silicon center, a variety of hydrosilanes were tested. Among hydrosilanes examined, chlorodiphenylsilane showed high activity with a catalytic amount of  $\text{InCl}_3$  at refluxing temperature in dichloroethane (entry 1).<sup>9</sup> The reaction using chlorodiphenylsilane without  $\text{InCl}_3$  gave a low yield of decane **2** (entry 2).<sup>10</sup> Neither Group 13 catalyst,  $\text{AlCl}_3$ , nor  $\text{BF}_3 \cdot \text{OEt}_2$ , was effective with chlorodiphenylsilane (entries 3 and 4) probably because of their instability to alcohols. Indium trichloride, on the other hand, tolerates protic conditions and can in fact be used

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(2) Hartwig, W. *Tetrahedron* **1983**, *39*, 2609–2645.

(3) Wojcik, B.; Adkin, H. *J. Am. Chem. Soc.* **1933**, *55*, 1293–1294.

(4) Gribble, G. W.; Leese, R. M. *Synthesis* **1977**, 172–176.

(5) For example: (a) Brewster, J. H.; Osman, S. F.; Bayer, H. O.; Hopps, H. B. *J. Org. Chem.* **1964**, *29*, 121–123. (b) Lau, C. K.; Dufresne, C.; Bélanger, P. C.; Piétré, S.; Scheiget, J. *J. Org. Chem.* **1986**, *51*, 3038–3043.

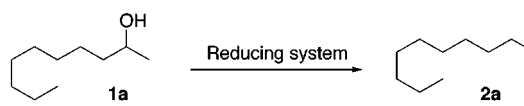
(6) Miyai, T.; Ueba, M.; Baba, A. *Synlett* **1999**, 182–184.

(7) The direct reduction of primary alcohols by hydrosilane with a catalyst was recently reported. (a) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919–8922. (b) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179–6186.

(8) The reaction under higher temperature was not carried out because of the low boiling point of chlorodimethylsilane (ca. 35 °C).

(9) In some cases, phenylsilanes are reported to have higher reactivity than alkylsilanes. Matsuda, I.; Fukuta, Y.; Tsuchihashi, T.; Nagashima, H.; Itoh, K. *Organometallics* **1997**, *16*, 4327–4345.

(10) As is well-known,  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ , or  $\text{Bu}_3\text{SnH}$  were not effective at all as hydride sources, although they are generally used for reduction of the corresponding tosylates or thiocarbonates in an ionic or radical manner. Barton, D. H. R.; McCombie S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574–1585 and ref 1.

**Table 1. Direct Reduction of 2-Decanol<sup>a</sup>**


entry	hydrosilane	catalyst	solvent	<i>T</i> (°C)	yield (%)
1	Ph <sub>2</sub> SiHCl	InCl <sub>3</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	76
2	Ph <sub>2</sub> SiHCl	InCl <sub>3</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	5
3	Ph <sub>2</sub> SiHCl	AlCl <sub>3</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	23
4	Ph <sub>2</sub> SiHCl	BF <sub>3</sub> ·OEt <sub>2</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	tr
5	Ph <sub>2</sub> SiH <sub>2</sub>	InCl <sub>3</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	19
6	Et <sub>3</sub> SiH	InCl <sub>3</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	0
7	Me <sub>2</sub> SiHCl	InCl <sub>3</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	rt	0
8	Ph <sub>2</sub> SiHCl	InCl <sub>3</sub>	hexane	70	33
9	Ph <sub>2</sub> SiHCl	InCl <sub>3</sub>	benzene	80	20
10	Ph <sub>2</sub> SiHCl	InCl <sub>3</sub>	THF	63	0
11	Ph <sub>2</sub> SiHCl	InCl <sub>3</sub>	acetonitrile	80	0

<sup>a</sup> All reactions were carried out in solvent (1 mL) using hydrosilane (2.0 mmol), 2-decanol **1a** (1.0 mmol), and catalyst (0.05 mmol) for 4 h.

even in water.<sup>11</sup> The indium trichloride catalyst was not effective for other silanes (entries 5–7). The choice of solvent is important since hexane, benzene, THF, and acetonitrile gave low yields (entries 8–11). These characteristic results prompted us to develop a Ph<sub>2</sub>SiHCl/InCl<sub>3</sub> system for direct reduction of alcohols.

Table 2 summarizes the direct reduction of various alcohols. Benzhydrol (**1b**) was effectively reduced at room temperature to give diphenylmethane in 87% yield in dichloromethane (entry 1). Reducing the amount of silane to 1 equiv also gave a satisfactory yield (entry 2). With no addition of InCl<sub>3</sub>, the yield was significantly lower (entry 3). Other benzylic alcohols **1c–e** in entries 4–6 were also effectively reduced to give the corresponding alkanes in high yields. The chloride moiety in **1e** was not affected by these conditions, and only the product **2e** via reduction at the hydroxyl site was formed (entry 6). Aliphatic secondary or tertiary alcohols were reduced at 80 °C (entries 7–11). When 1,1-diphenyl-2-propanol (**1j**) was used as a substrate, only the phenyl-rearranged product **2j** was obtained in high yield (entry 12). The phenyl-rearranged product suggests that a carbocationic species may be present in the reduction process. For the primary alcohol **1k**, an ether-type product was detected in the NMR spectra (entry 13). Since the starting alcohol was recovered after workup with Bu<sub>4</sub>NF, the silyl ether would be mainly produced in this case. This result means that the reducing system could distinguish classes of alcohols. In fact, reduction occurred only at the secondary alcohol site in the treatment of 1-phenyl-1,4-butanediol (**11**), and the primary alcohol **2i** was obtained in 53% yield after workup with Bu<sub>4</sub>NF (entry 14). When 4 equiv of the silane was used, the yield was increased to 76% (entry 15).

**Chemoselective Reduction of Functionalized Alcohols.** This reducing system was found to show high chemoselectivity for only hydroxyl groups even in the presence of sensitive functional groups that are readily reduced by standard reducing systems. The reactions in Scheme 1 point out the unique reactivity of the Ph<sub>2</sub>SiHCl/InCl<sub>3</sub> system. While the hydroxyl ester **3** gave the diol **4** in the reaction using LiAlH<sub>4</sub>, the Ph<sub>2</sub>SiHCl/InCl<sub>3</sub> system achieved the deoxygenation without ester reduction to afford ethyl ester **5** without **4**. Interestingly, when our

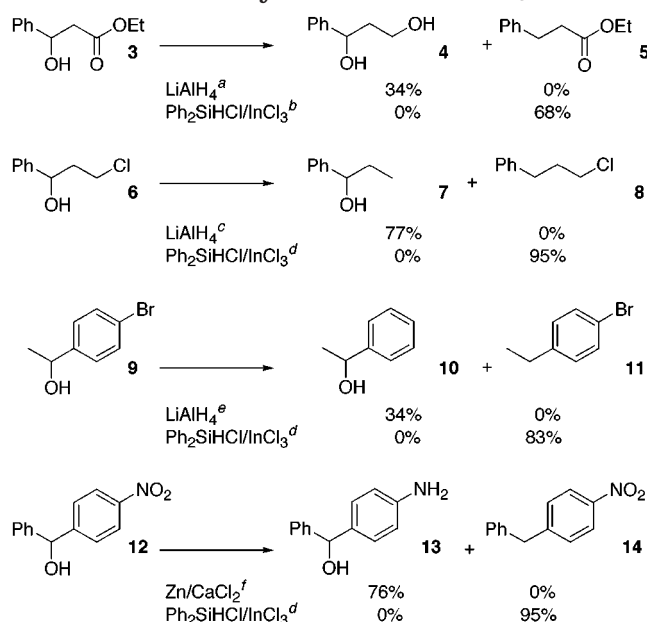
**Table 2. Direct Reduction of Various Alcohols<sup>a</sup>**

entry	R-OH	solvent	<i>T</i> (°C)	<i>t</i> (h)	product	yield (%)
1	Ph <sub>2</sub> CH-OH	CH <sub>2</sub> Cl <sub>2</sub>	rt	2	Ph-CH <sub>2</sub> -Ph	87
2 <sup>b</sup>	Ph <sub>2</sub> CH-OH	CH <sub>2</sub> Cl <sub>2</sub>	rt	2	Ph-CH <sub>2</sub> -Ph	76
3 <sup>c</sup>	Ph <sub>2</sub> CH-OH	CH <sub>2</sub> Cl <sub>2</sub>	rt	2	Ph-CH <sub>2</sub> -Ph	15
4	Ph-CH(OH)-CH <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	rt	1	Ph-CH <sub>2</sub> -CH <sub>3</sub>	88
5	Ph-CH(OH)-CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	rt	1	Ph-CH <sub>2</sub> -CH <sub>2</sub> CH <sub>3</sub>	90
6	Cl-C <sub>6</sub> H <sub>4</sub> -CH(OH)-CH <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	rt	2	Cl-C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub> -CH <sub>3</sub>	77
7	Ph-CH(OH)-CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	6	Ph-CH <sub>2</sub> -CH <sub>2</sub> CH <sub>3</sub>	54
8	Ph-CH(OH)-C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	3	Ph-CH <sub>2</sub> -C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	99
9	Bicyclo[2.2.1]hept-2-yl-OH	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	3	Bicyclo[2.2.1]heptane	99
10	2-decanol	1a	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	decane	<b>2a</b> 76
11	4-decanol	1i	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	decane	<b>2a</b> 74
12	Ph-CH(OH)-CH(Ph)-CH <sub>3</sub>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	1	Ph-CH <sub>2</sub> -CH(Ph)-CH <sub>3</sub>	92
13	Ph-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	5	Ph-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -O-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -Ph	<b>2k</b> 0
14 <sup>d</sup>	Ph-CH(OH)-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	3	Ph-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	53
15 <sup>e</sup>	Ph-CH(OH)-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	CH <sub>2</sub> ClCH <sub>2</sub> Cl	80	3	Ph-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	<b>2i</b> 76

<sup>a</sup> All reactions were carried out in solvent (1 mL) using Ph<sub>2</sub>SiHCl (2.0 mmol), alcohol (1.0 mmol), and InCl<sub>3</sub> (0.05 mmol).

<sup>b</sup> Ph<sub>2</sub>SiHCl (1.0 mmol) was used. <sup>c</sup> InCl<sub>3</sub> was not added. <sup>d</sup> Workup with Bu<sub>4</sub>NF (80 °C, 1 h). <sup>e</sup> Ph<sub>2</sub>SiHCl (4.0 mmol) was used.

previous system, Me<sub>2</sub>SiHCl/InCl<sub>3</sub>,<sup>6</sup> was employed instead of Ph<sub>2</sub>SiHCl/InCl<sub>3</sub>, chlorohydroxylation unexpectedly took place to give ethyl 3-chloro-3-phenylpropanoate as a sole product in 76% yield. Although the difference of the reactivities in these silanes is not clear yet at this stage, this result undoubtedly shows the effectiveness of Ph<sub>2</sub>SiHCl for reduction of alcohols. The reduction of chloro alcohol **6** with LiAlH<sub>4</sub> removed the chlorine and gave only alcohol **7**, and the reduction of the chloro alcohol **6** with Ph<sub>2</sub>SiHCl/InCl<sub>3</sub> removed the hydroxyl group and gave compound **8**. The *p*-bromophenethyl alcohol **9** was debrominated in the reduction with LiAlH<sub>4</sub> to give alcohol **10**. The silane/InCl<sub>3</sub> system, in contrast, afforded chemoselective reduction of the hydroxyl group to give bromo compound **11**. The nitro-substituted benzhydrol **12** was reduced at the nitro group to the corresponding amine by Zn/CaCl<sub>2</sub>,<sup>12</sup> while the treatment with LiAlH<sub>4</sub> resulted in recovery of **12**. The

**Scheme 1. Direct Chemoselective Reduction of Alcohols by Ph<sub>2</sub>SiHCl/Cat. InCl<sub>3</sub>**


<sup>a</sup> THF, 0 °C, 0.5 h. <sup>b</sup> CH<sub>2</sub>ClCH<sub>2</sub>Cl, 50 °C, 0.5 h. <sup>c</sup> THF, 0 °C, 1 h → 63 °C, 2 h. <sup>d</sup> CH<sub>2</sub>Cl<sub>2</sub>, rt, 3 h. <sup>e</sup> THF, 0 °C, 1 h → 63 °C, 2 h. <sup>f</sup> EtOH/H<sub>2</sub>O, 80 °C, 3 h.

Ph<sub>2</sub>SiHCl/InCl<sub>3</sub> system smoothly reduced only the alcohol and provided only the nitro diarylmethane **14** in high yield. These results show that the Si–In system provides an unusual and useful reducing reagent in selective organic syntheses.

**NMR Study of Hydrosilane/InCl<sub>3</sub> System.** NMR studies were performed to examine the reaction course. The mixing of benzhydrol and chlorodiphenylsilane in CD<sub>2</sub>Cl<sub>2</sub> spontaneously led to disappearance of the signals of benzhydrol with generation of new signals at δ(<sup>1</sup>H) 6.07 ppm and δ(<sup>13</sup>C) 64.15 ppm, which were correlated in the C–H COSY spectrum.<sup>13</sup> In <sup>29</sup>Si NMR, this solution showed two doublet signals at –5.81 ppm (*J* = 235 Hz) and –19.30 ppm (*J* = 220 Hz).<sup>14</sup> Since the former is ascribed to unreacted chlorodiphenylsilane, the latter was found to correspond to a new species. These results clearly suggest the formation of the hydrodiphenylsilyl ether **15** and HCl<sup>15</sup> and not the chlorodiphenylsilyl ether caused by dehydrogenation.<sup>16</sup> The insolubility of HCl in dichloromethane or dichloroethane caused the fine bubbles of HCl that evaporated from the reaction system.<sup>17</sup> This phenomenon explains the interesting solvent effect shown in Table 1. The addition of 5 mol % of InCl<sub>3</sub> to this mixture gave diphenylmethane (**2b**). InCl<sub>3</sub>, acting as a Lewis acid, could accelerate the desiloxylation by forming

(12) Nitroaryl compounds can be reduced by a Zn/H<sub>2</sub>O/EtOH system. *Organic Syntheses*, Wiley: New York, 1943; Collect. Vol. II, pp 447–448.

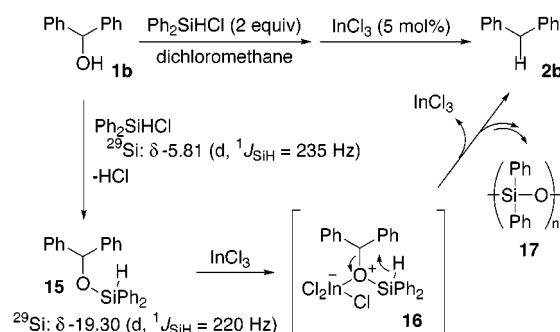
(13) The signals for the methine moiety in benzhydrol are 6.03 and 75.64 ppm in <sup>1</sup>H and <sup>13</sup>C NMR, respectively.

(14) In <sup>1</sup>H NMR, the corresponding signals of hydrogens on silicons were observed at 5.72 ppm with satellite peaks (*J* = 235 Hz) and at 5.65 ppm with satellite peaks (*J* = 220 Hz).

(15) Tamao, K.; Tohma, T.; Inui, N.; Nakayama, O.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 7333–7336.

(16) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887–4892 and references therein.

(17) The generated HCl was found not to catalyze the reaction because the addition of MgO, which can trap HCl as a base, did not affect the yield in the reaction of **1b**. Nakano, M.; Matsuo, J.-i.; Mukaiyama, T. *Chem. Lett.* **2000**, 1352–1353.

**Scheme 2**


the oxonium complex **16**. InCl<sub>3</sub> could be regenerated with the formation of the siloxane, which in fact was isolated and showed good agreement by MS with the compound **17** (*n* = 4). The moderate oxophilicity of InCl<sub>3</sub> contributes to its catalytic use.<sup>18</sup> A similar hydrosilyl ether was detected in the mixture of chlorodiphenylsilane with 2-decanol (**1a**) at 80 °C by <sup>29</sup>Si NMR. The <sup>29</sup>Si NMR showed a signal at –15.18 ppm (*d*, *J* = 216 Hz), while no reaction was observed at room temperature. After cooling to room temperature, the addition of a catalytic amount of InCl<sub>3</sub> to the mixture gave the corresponding decane (**2a**) in quantitative yield. These results suggest that the rate-determining step is the formation of silyl ether from the alcohol with the chlorohydrosilane. It is important that the facile transformation of silyl ether to alkane is accelerated by catalytic amount of InCl<sub>3</sub>.

**Conclusions**

The direct reduction of secondary, benzyl, and tertiary alcohols proceeds by chlorodiphenylsilane with a catalytic amount of indium trichloride, in which a hydrosilyl ether is a key intermediate. InCl<sub>3</sub> acts as Lewis acid to accelerate the deoxygenation of the resulting intermediate that accompanies the hydride transfer. This system attains high chemoselectivity for only the hydroxyl group in multifunctional compounds. Indium trichloride is considered as a unique Lewis acid because of its low affinity to oxygen compared to that of aluminum or boron compounds. This character causes the catalytic activity of indium trichloride in this reducing process.

**Experimental Section**

**General.** IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were obtained with a 270, 67.9, and 53.7 MHz spectrometer, respectively, with TMS as internal or external standard. Mass spectra were recorded on a JEOL JMS-DS303 or a Shimadzu GCMS-QP2000A spectrometer. GLC analyses were performed on a Shimadzu GC-8A with FID using a 2 m × 3 mm column packed with SE-52. Column chromatography was performed on silica gel (Wakogel C-300). Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by GLC or <sup>1</sup>H NMR using internal standards.

**Materials.** Dichloromethane and 1,2-dichloroethane were distilled from CaH<sub>2</sub>. THF was distilled from sodium and benzophenone. All reducing reagents and catalysts in Table 1 were commercially available. The starting alcohols, 1-phenylbutane-1,4-diol (**11**) and **12** were prepared, and the experi-

(18) Yasuda, M.; Onishi, Y.; Ito, T.; Baba, A. *Tetrahedron Lett.* **2000**, *41*, 2425–2428.

mental details are described in Supporting Information. These preparation methods were not optimized. The compound **3** was prepared by a known method [*Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 408]. All other starting alcohols are commercially available.

**General Procedure (I) for Reduction of Alcohols Using  $\text{Ph}_2\text{SiHCl}/\text{InCl}_3$  System (Table 2 and Scheme 1).** To a mixture of  $\text{InCl}_3$  (0.05 mmol) and the alcohol (1.0 mmol) in dry dichloromethane or 1,2-dichloroethane (1 mL) was added chlorodiphenylsilane (2.0 mmol) under nitrogen. The reaction mixture was stirred under the reaction conditions noted in the text. The resulting mixture was poured into  $\text{Et}_2\text{O}$  (50 mL) and water (30 mL). The homogeneous solution was extracted with  $\text{Et}_2\text{O}$ , and the organic layer was dried over  $\text{MgSO}_4$ . The evaporation of the ether solution gave the crude product, which was analyzed by GLC and NMR. The details of further purification performed for the new compound are described in Supporting Information.

**General Procedure (II) for Reduction of Alcohols (3, 6, and 9) Using  $\text{LiAlH}_4$  (Scheme 1).** To a solution of the alcohol (1.0 mmol) in dry THF (1 mL) was added  $\text{LiAlH}_4$  (2.0 mmol) under nitrogen (4 mmol of  $\text{LiAlH}_4$  was used in the reaction with **9**). The reaction mixture was stirred under the conditions described in the text. The resulting mixture was quenched by ethyl acetate (10 mL) and aq HCl (1 M, 30 mL). The resultant mixture was extracted with  $\text{Et}_2\text{O}$ , and the organic layer was dried over  $\text{MgSO}_4$ . The evaporation of the ether solution gave the crude product, which was analyzed by

GLC and NMR. The details of further purification performed for the new compound are described in Supporting Information.

**Reduction of Alcohol 12 Using Zn (Scheme 1).** To a solution of **12** (1 mmol) in mixed solvent ( $\text{EtOH}$ , 8 mL and  $\text{H}_2\text{O}$ , 2 mL) was added a solution of 3.0 g of zinc dust and 0.1 g of calcium chloride in 0.15 mL of water. The mixture was refluxed for 3 h. After filtration of zinc compound, the filtrate was extracted with diethyl ether. The organic layer was dried over  $\text{MgSO}_4$  and evaporated to give the crude product, which was analyzed by GLC and NMR. Further purification was performed by washing with hexane to give the pure product as a yellow solid [*Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, pp 447–448].

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**Supporting Information Available:** Characterization data of all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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