Indium(III) Acetate-Catalyzed 1,4-Reduction and Reductive Aldol Reactions of α-Enones with Phenylsilane

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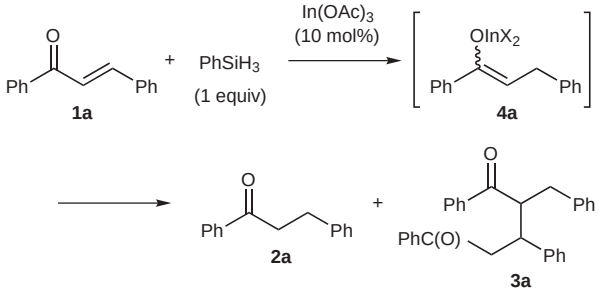
Abstract: A catalytic amount of $In(OAc)_3$ smoothly promoted 1,4-reduction of certain α-enones with $PhSiH_3$ in ethanol at ambient temperature. The intermediary enolates could be used for inter- and intramolecular aldol reactions and intramolecular Michael addition.

Key words: indium, reductions, enones, silicon, aldol reactions

Catalytic 1,4-hydrometalation of α-enones provides a reliable and efficient method for regioselective formation of metal enolates.[1–4] Recently, much attention has been given to the development of catalytic systems effecting both the enolate formation and the subsequent reaction with coexistent carbon electrophiles.[5–7] Some transition metal salts and complexes work as effective catalysts of this tandem process. All catalytic systems except those reported by Krische's group[5,7] were utilized only for reductive aldol reactions of α-enones with aldehydes. We herein disclose that $In(OAc)_3$ efficiently catalyzes the 1,4-reduction of certain α-enones with $PhSiH_3$, and the intermediary enolates can be used for carbon-carbon bond-forming reactions with aldehydes, ketones, and α-enones.[8,9]

The reduction of (*E*)-1,3-diphenyl-2-propen-1-one (chalcone, **1a**) with $PhSiH_3$ was initially examined for optimization of the reaction conditions (Table 1). The $In(OAc)_3$-catalyzed reaction in THF at 70 °C gave the desired ketone **2a** as the major product; however, a significant amount of dimerization product **3a** was also obtained (entry 1).[10] The formation of **3a** is attributable to the Michael addition of indium enolate intermediate **4a** to **1a**. Proton sources such as water and EtOH were used to suppress this side reaction by protonation of **4a** (entries 2 and 3). As a result, the addition of EtOH was found to be effective not only in suppressing the formation of **3a** but also in accelerating the 1,4-reduction of **1a**. The use of EtOH as solvent further enhanced the reaction rate to enable the reduction at room temperature (entry 4).[11] Thus the $In(OAc)_3$-catalyzed reduction of **1a** in EtOH was completed in 1.5 hours at room temperature to give **2a** in 90% yield.[12] Indium metal was deposited under these reaction conditions. Since indium trihydride is known to easily decompose to indium metal and H_2,[13] this observation is indicative of the formation of indium hydride species.

Table 1 Optimization of Reaction Conditions for $In(OAc)_3$-Catalyzed 1,4-Reduction[a]



Entry	Solvent	Additive	Temp (°C)	Time (h)	Isolated yield (%) 2a	3a
1	THF	None	70	24	56	26
2	THF	H_2O[b]	70	24	67	Trace
3	THF	EtOH[b]	70	3	76	Trace
4	EtOH	None	r.t.	1.5	90	0
5[c]	EtOH	None	r.t.	1.5	0	0

[a] Unless otherwise noted, all reactions were carried out with **1a** (208 mg, 1.00 mmol), $PhSiH_3$ (108 mg, 1.00 mmol), and $In(OAc)_3$ (30 mg, 0.10 mmol) in solvent (2.0 mL).
[b] One equivalent (1.00 mmol) of H_2O or EtOH was used.
[c] Without $In(OAc)_3$.

Without $In(OAc)_3$, the reduction of **1a** did not proceed at all (entry 5). Accordingly, indium hydride species would act as the actual reductant.

The $In(OAc)_3$-catalyzed system using EtOH as solvent was applied to the reduction of some α,β-unsaturated carbonyl compounds (Table 2).[14] Similar to **1a**, (*E*)-1-phenyl-2-buten-1-one (**1b**), 1-phenyl-2-propen-1-one (**1c**), and (*E*,*E*)-1,5-diphenyl-1,4-pentadien-3-one (**1d**) underwent 1,4-reduction to give the corresponding ketones **2** in good yields (entries 1–4). In the case of **1d**, a small amount of 1,5-diphenyl-3-pentanone was formed by double 1,4-reduction. The reduction of (*E*)-4-phenyl-3-buten-2-one (**1e**) gave 1,4- and 1,2-reduction products, **2e** and **5e**, in low yields and **1e** was recovered in 75% yield (entry 5). Similarly, (*E*)-3-decen-2-one (**1f**) was less reactive than **1a**–**d**. Slow addition of $PhSiH_3$ slightly improved the yield of **2f** (entry 6). 5-Phenyl-1-penten-3-one (**1g**), a vinyl ketone, showed high reactivity, but low chemoselec-

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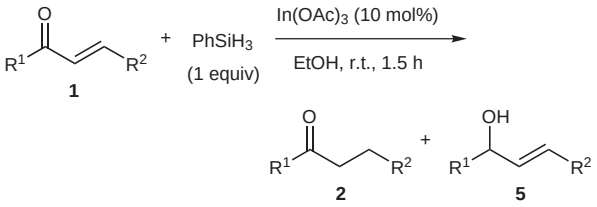
Table 2 $In(OAc)_3$-Catalyzed Reduction of α,β-Unsaturated Carbonyl Compounds with $PhSiH_3$[a]

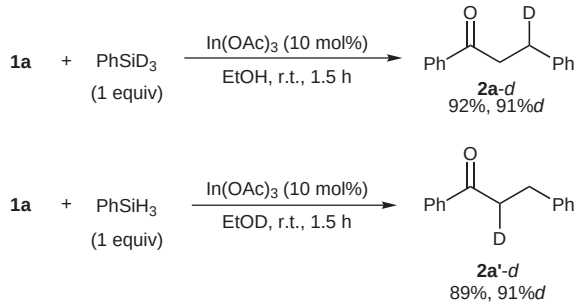


Entry	Substrate			Isolated yield (%)	
	R^1	R^2		**2**	**5**
1	Ph	Ph	(**1a**)	90	0
2	Ph	Me	(**1b**)	84	0
3	Ph	H	(**1c**)	93	0
4	(*E*)-PhCH=CH	Ph	(**1d**)	72[b]	0
5	Me	Ph	(**1e**)	15[c]	8[c]
6	Me	*n*-Hex	(**1f**)	30[c,d] 54[c,e]	0
7	$PhCH_2CH_2$	H	(**1g**)	63	23
8	EtO	Ph	(**1h**)	0	0
9	H	Ph	(**1i**)	0	80

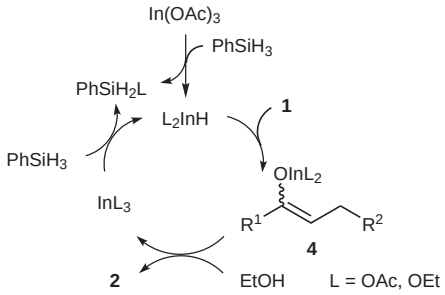
[a] Unless otherwise noted, all reactions were carried out with **1** (0.50 mmol), $PhSiH_3$ (54 mg, 0.50 mmol), and $In(OAc)_3$ (15 mg, 0.05 mmol) in EtOH (1.0 mL) at r.t. for 1.5 h.
[b] 1,5-Diphenyl-3-pentanone also was obtained in 14% yield.
[c] The yield was determined by ^1H NMR analysis using benzyl acetate as the internal standard.
[d] The reaction was run for 24 h.
[e] The enhanced yield was obtained by the following method: $PhSiH_3$ was added dropwise to the mixture of **1f**, $In(OAc)_3$, and EtOH over 1 h. The resultant mixture was stirred for 24 h.

tivity (entry 7). The present catalytic system was ineffective in the reduction of ethyl cinnamate (**1h**, entry 8). In the case of cinnamaldehyde (**1i**), only the 1,2-reduction was observed (entry 9).

Dichloroindium hydride (Cl_2InH) has been reported to be valuable for radical reduction of alkyl halides.[15] The $In(OAc)_3$-catalyzed reaction of **1a** with $PhSiH_3$ gave **2a** efficiently even in the presence of galvinoxyl, a radical scavenger. The present 1,4-reduction would therefore not involve a radical chain mechanism although the deposition of indium metal suggests the presence of indium hydride species. In the 1,4-reduction of **1a**, the use of $PhSiD_3$ instead of $PhSiH_3$ provided **2a**-*d* by β-deuteration, while the use of EtOD as solvent resulted in α-deuteration (Scheme 1). Judging from these results, the present 1,4-reduction could proceed via the following mechanism (Scheme 2): (1) transmetalation between $In(OAc)_3$ and $PhSiH_3$ in EtOH forms an indium hydride species ($HInL_2$, L = OAc, OEt), (2) 1,4-addition of the hydride to an α-enone **1** leads to the corresponding indium enolate **4**, (3) solvolysis of **4** gives the 1,4-reduction product **2** and InL_3, (4) transmetalation between InL_3 and $PhSiH_3$ regenerates $HInL_2$.



Scheme 1

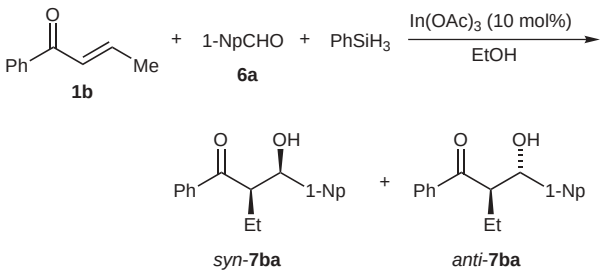


Scheme 2

The mechanistic consideration induced us to utilize the indium enolate intermediate **4** for carbon-carbon bond formation. We thus examined the $In(OAc)_3$-catalyzed reductive aldol reaction of α-enones, aldehydes, and $PhSiH_3$. Initially, enone **1b** and 1-naphthaldehyde (**6a**) were selected as the substrates for optimization of the reaction conditions (Table 3). Expectedly, the reaction of **1b**, **6a**, and $PhSiH_3$ (molar ratio = 1:1:1) at room temperature gave the desired aldol **7ba** in 65% yield along with **2b** (32%) and 1-naphthylmethanol (ca. 30%, entry 1).[16] This result indicates that the $In(OAc)_3$-catalyzed reduction of **1b** is faster than that of **6a**.[17] The use of an excess amount of **6a** improved the yield of **7ba** (entry 2). Lowering the reaction temperature brought about high *syn*-selectivity although the reaction rate became much slower (entry 3). With a decreased amount of EtOH, **7ba** was obtained in high yield with high *syn*-diastereoselectivity (entries 4 and 5).[18]

The optimized conditions were applied to other combinations of enones **1** and aldehydes **6** (Table 4).[19] The reductive aldol reaction of phenyl ketones **1a**–**c** with aromatic aldehydes proceeded in high yields with high *syn*-diastereoselectivity except the case with *p*-cyanobenzaldehyde (entries 1–4, 7, 8, and 11). The use of aliphatic aldehydes lowered the reaction efficiency and the *syn*-selectivity (entries 5, 6, 9, and 10).[20] Aliphatic α-enones also underwent the reductive coupling to give the corresponding aldol products in moderate yields (entries 12–14).

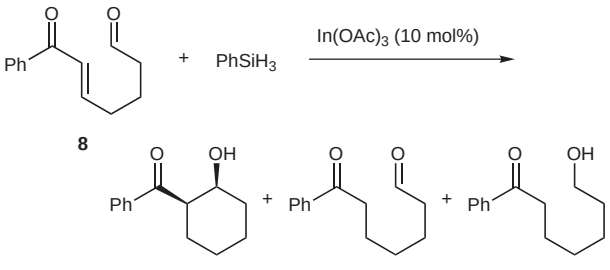
Table 3 Optimization of Reaction Conditions for $In(OAc)_3$-Catalyzed Reductive Aldol Reaction[a]



Entry	EtOH (mL)	Temp (°C)	Time (h)	Isolated yield (%)	*syn*:*anti*
1[b]	1.0	r.t.	24	65	74:26
2	1.0	r.t.	13	82	84:16
3	1.0	0	60	45	92:8
4	0.5	0	60	82	92:8
5	0.25	0	36	83	92:8

[a] Unless otherwise noted, all reactions were carried out with **1b** (73 mg, 0.50 mmol), **6a** (102 mg, 0.65 mmol), $PhSiH_3$ (54 mg, 0.50 mmol), and $In(OAc)_3$ (15 mg, 0.05 mmol) in EtOH.
[b] With **6a** (0.50 mmol).

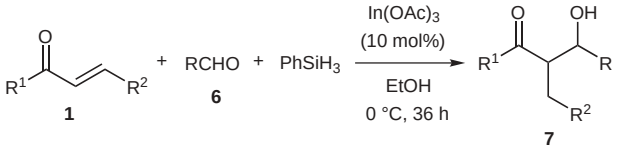
Our attention was next focused on intramolecular reductive coupling by the $In(OAc)_3$–$PhSiH_3$ system. The $In(OAc)_3$-catalyzed reaction of α-enone **8**,[21] bearing a formyl group, with $PhSiH_3$ was performed under similar conditions as those used for the intermolecular reductive aldol reaction (Scheme 3, method A). However, the desired cyclized product **9** was obtained in only a poor yield. The formation of reduction products **10** and **11** was favored over the intramolecular aldol reaction. As the result of various attempts, it was found that the reaction of **8** in THF containing EtOH at reflux gave *cis*-**9** in 77% yield (Scheme 3, method B).[22,23] The *trans* isomer of **9** was not obtained.



Method A: EtOH (0.1 M), r.t., 4 h.
Method B: THF (0.1 M), EtOH (1 equiv), reflux, 8.5 h.

Scheme 3

Table 4 $In(OAc)_3$-Catalyzed Reductive Aldol Reaction of α-Enones **1**, Aldehydes **6**, and $PhSiH_3$[a]

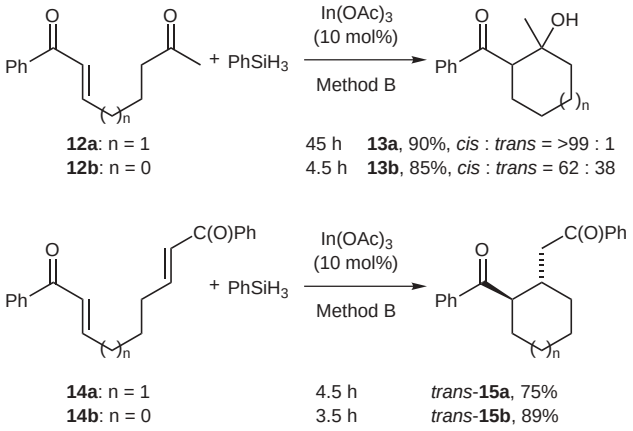


Entry	Substrates R[1]	R[2]		R	Yield[b] (%)	*syn*:*anti*
1	Ph	Me	(**1b**)	1-Np	83	92:8
2[c]				Ph	84	92:8
3				*p*-$MeOC_6H_4$	96	96:4
4				*p*-NCC_6H_4	85	69:31
5[c]				*n*-C_7H_{15}	66	77:23
6				*c*-Hex	37	72:28
7	Ph	Ph	(**1a**)	1-Np	86	86:14
8[c]				Ph	94	87:13
9[c]				*n*-C_7H_{15}	71	70:30
10[c]				*c*-Hex	53	71:29
11	Ph	H	(**1c**)	1-Np	92	92:8
12[c]	Me	*n*-Hex	(**1f**)	1-Np	49	87:13
13	Me	H	(**1j**)	1-Np	47	88:12
14				Ph	60	85:15

[a] Unless otherwise noted, all reactions were carried out with **1** (0.50 mmol), **6** (0.65 mmol), $PhSiH_3$ (54 mg, 0.50 mmol), and $In(OAc)_3$ (15 mg, 0.05 mmol) in EtOH (0.25 mL) at 0 °C for 36 h.
[b] Isolated yield.
[c] The reaction time is 72 h.

The cyclizations of enones **12** and bis-enones **14** also were efficiently promoted by method B (Scheme 4).[21,22] The reductive aldol reaction of **12a** afforded *cis*-**13a** with complete stereocontrol.[23] Enone **12b** showed much higher reactivity than **12a**, but the cyclization resulted in low diastereoselectivity. The reductive Michael reaction of **14** leading to 1,5-diketones **15** proceeded with complete *trans* selectivity.[23]

In conclusion, we have found that the combination of $In(OAc)_3$ and $PhSiH_3$ is quite useful for both 1,4-reduction of certain α-enones and their intermolecular reductive aldol reaction under mild conditions.[9] The $In(OAc)_3$–$PhSiH_3$ system is rather neutral (less Lewis acidic) and it works well in EtOH, a less harmful solvent, at room temperature or 0 °C. This catalytic system is applicable to intramolecular reductive aldol and Michael reactions with some modifications of the reaction conditions. We are now studying further application of the $In(OAc)_3$–$PhSiH_3$ system, and the results will be reported in due course.



Scheme 4

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(9) Quite recently, Baba et al. have reported a similar catalytic system for reductive aldol reaction, in which $InBr_3$ and Et_3SiH are used as catalyst and reducing agent, respectively. See: Shibata, I.; Kato, H.; Ishida, T.; Yasuda, M.; Baba, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 711.

(10) The use of $In(acac)_3$ (acac = acetylacetonate) instead of $In(OAc)_3$ gave **2a** and **3a** in 34% and 65% yields, respectively. $InCl_3$ also promoted the reaction of **1a** with $PhSiH_3$ in Et_2O at r.t. (**2a**, 29%; **3a**, 49%).

(11) The use of other hydrosilanes [Et_3SiH, $PhMe_2SiH$, poly(methylhydrosiloxane)] instead of $PhSiH_3$ resulted in no reduction under the same conditions.

(12) The use of a half amount of $PhSiH_3$ lowered the yield to 62%.

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(14) **General Procedure for the $In(OAc)_3$-Catalyzed 1,4-Reduction of α-Enones with $PhSiH_3$:** Under N_2, α-enone **1** (0.50 mmol) and $PhSiH_3$ (54 mg, 0.50 mmol) were added to a suspension of $In(OAc)_3$ (15 mg, 0.05 mmol) in EtOH (1.0 mL). The mixture was stirred at r.t. for 1.5 h and quenched with sat. aq $NaHCO_3$. The extract with *t*-BuOMe was dried over Na_2SO_4 and evaporated. The residual oil was purified by silica gel column chromatography.

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(16) As shown here, the reductive aldol reaction is much slower than the 1,4-reduction. This observation is attributable to slow regeneration of the indium hydride species from the indium aldolate intermediate.

(17) The $In(OAc)_3$-catalyzed reduction of **6a** with $PhSiH_3$ (r.t., 1.5 h) gave 1-naphthylmethanol in 82% yield.

(18) As proposed by Baba et al. (ref.[9]), the *syn*-selectivity can be attributed by the formation of *Z*-**4b** by a concerted hydroindation and the subsequent aldol addition via a cyclic transition state. However, we have no evidence of the selective formation of *Z*-**4b**.

(19) **Typical Procedure for the $In(OAc)_3$-Catalyzed Reductive Aldol Reaction of α-Enones with Aldehydes:** Under N_2, α-enone **1b** (73 mg, 0.50 mmol), **6a** (102 mg, 0.65 mmol), and $PhSiH_3$ (54 mg, 0.50 mmol) were added to a suspension of $In(OAc)_3$ (15 mg, 0.05 mmol) in EtOH (0.25 mL). The mixture was stirred at 0 °C for 36 h. The work-up and purification were performed by the procedure described in ref.[14]. Compound **7ba** (*syn*:*anti* = 92:8): IR (neat): 3540 (br s, OH), 1680 (C=O) cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ = 0.69 (t, *J* = 7.6 Hz, 2.76 H), 0.86 (t, *J* = 7.6 Hz, 0.24 H), 1.63–1.79 (m, 1 H), 1.89–2.08 (m, 1 H), 3.52 (d, *J* = 5.9 Hz, 0.08 H), 3.80 (d, *J* = 1.7 Hz, 0.92 H), 3.96 (ddd, *J* = 9.1, 3.8, 3.6 Hz, 0.92 H), 4.11 (ddd, *J* = 8.2, 6.2, 5.9 Hz, 0.08 H), 5.82 (dd, *J* = 6.2, 5.9 Hz, 0.08 H), 5.85 (br s, 0.92 H), 7.31–7.96 (m, 12 H). ^{13}C NMR (68 MHz, $CDCl_3$) for the major isomer: δ = 12.25 (CH_3), 20.17 (CH_2), 51.62 (CH), 70.12 (CH),

122.49 (CH), 124.51 (CH), 125.28 (CH), 125.34 (CH), 126.04 (CH), 127.94 (CH), 128.38 (CH × 2), 128.75 (CH × 2), 129.14 (CH), 129.86 (C), 133.63 (CH), 133.73 (C), 136.69 (C), 137.22 (C), 206.37 (C). For the minor isomer (only well-resolved peaks): δ = 11.88 (CH_3), 24.18 (CH_2), 53.14 (CH), 72.85 (CH), 123.01 (CH), 124.37 (CH), 125.48 (CH), 126.17 (CH), 128.07 (CH), 128.43 (CH), 129.03 (CH), 130.53 (C), 133.16 (CH), 138.15 (C), 206.08 (C).

(20) The reaction of **1b** with octanal was carried out in THF containing an equimolar amount of EtOH at 70 °C. However, both the yield of **7** and the *syn*-selectivity dropped to 52% and 56% *syn*, respectively.

(21) According to the method reported by Montgomery et al., **8** and **14a** were prepared by ozonolysis of cyclopentene and the subsequent Wittig olefination with $Ph_3PCHC(O)Ph$. This method was used also for the preparation of **12a**, **12b**, and **14b** from 1-methylcyclopentene, 1,5-dimethyl-1,5-cyclooctadiene, and 1,5-cyclooctadiene, respectively. See: (a) Montgomery, J.; Savchenko, A. V.; Zhao, Y. *J. Org. Chem.* **1995**, *60*, 5699. (b) See also the following paper for the preparation of **12a** and **12b**: Huddleston, R. R.; Cauble, D. F.; Krische, M. J. *J. Org. Chem.* **2003**, *68*, 11.

(22) For the stereochemical assignment of **9**, **15a**, and **15b**, see ref.[7a]. The relative configurations of **13a** and **13b** were determined by their NMR data reported in ref.[21b].

(23) Krische et al. have reported *cis*-selective reductive aldol reactions of **8** and **12a**, and *trans*-selective reductive Michael reaction of **14**. See ref.[7] and ref.[21b]