

Indium-Catalyzed Reductive Coupling of Aromatic Carbonyl Compounds and Imines in the Presence of Aluminum and Chlorosilanes

Seiji Ohtaka, Kenji Mori, and Sakae Uemura

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Received 4 January 2001; revised 16 February 2001

ABSTRACT: Reductive homocoupling of aromatic aldehydes, ketones, and imines has been achieved in tetrahydrofuran (THF) at room temperature using a catalytic amount of InCl_3 (0.5–3.0 mol %) under a nitrogen atmosphere in the presence of chlorotrimethylsilane (TMSCl) and aluminum metal (Al) to provide the corresponding 1,2-diols and 1,2-diamines, respectively, in good to moderate yields. Other indium compounds such as $\text{In}(\text{NO}_3)_3$, cyclopentadienylindium, and indium metal have also been revealed to be effective as catalysts. The catalytic effect of the indium compound is remarkable, and, thus, without it, no reaction occurs in the case of aromatic aldehydes and aldimines, and an induction period is quite long in the case of aromatic ketones. Without either TMSCl or Al, no reaction proceeds even in the presence of the catalyst. Unfortunately, the diastereoselectivity of the products (dl and meso) is not high. Although the precise reaction scheme is not yet clear, we tentatively propose that a redox-active In-Al alloy might be formed on the surface of aluminum in the presence of TMSCl, and an electron transfer from the alloy to substrate might

occur. © 2001 John Wiley & Sons, Inc. *Heteroatom Chem* 12:309–316, 2001

INTRODUCTION

The organic chemistry of indium is of current interest from the viewpoint of organic synthesis [1]. Thus, indium and its compounds have worked as reagents as well as catalysts in some carbon–carbon bond-forming reactions, such as allylation of carbonyl compounds [2], Reformatsky reactions [3], aldol reactions [4], Diels-Alder reactions [5], Michael reactions [6], Friedel-Crafts reactions [7], and reductive coupling reactions [8]. In the cases of catalytic reactions, however, a rather large amount of indium salts (10–20 mol %) has normally been employed. We have now disclosed a new and quite efficient catalytic activity of indium(III) chloride (0.5–3.0 mol %) in reductive homocoupling of carbonyl compounds and imines. It has so far been reported that the use of a stoichiometric amount of indium metal induced the reductive homocoupling of aromatic aldehydes [8a] and imines [8b] in water or water-alcohol mixture. Our new system consists of the combination of chlorotrimethylsilane (TMSCl), aluminum (Al), and a catalytic amount of an indium compound for this reductive coupling reaction. It is worth noting that catalytic systems for the reductive coupling using a catalytic amount of transition metal complex (mainly Ti and V), and TMSCl with a co-reductant

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

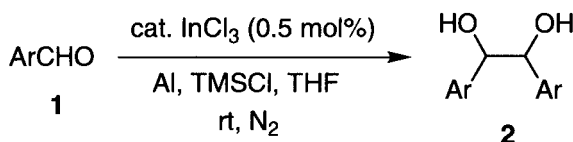
Correspondence to: Sakae Uemura.
© 2001 John Wiley & Sons, Inc.

metal such as Zn, Al, and Mg have recently been developed by several groups [9].

RESULTS AND DISCUSSION

Reductive Homocoupling of Aromatic Aldehydes

Treatment of benzaldehyde (**1a**) with aluminum metal (Al, 4 equiv), chlorotrimethylsilane (TMSCl, 4 equiv), and a catalytic amount of InCl₃ (5 mol %) in tetrahydrofuran (THF) under a nitrogen atmosphere at room temperature for 2 hours afforded 1,2-diphenyl-1,2-ethanediol (**2a**) in 45% yield (*dl/meso* = 52/48) (Scheme 1). Without either Al or TMSCl, the reaction did not occur even in the presence of InCl₃. On the other hand, without the addition of InCl₃, no reaction proceeded in the presence of both TMSCl and Al [10] even under sonication. It was found that the amount of InCl₃ can be reduced to 0.5 mol % with the yield of **2a** being increased to 61%. The yield of the expected diols was somewhat low despite a complete conversion of **1a**, and a small amount of benzyl alcohol and small amounts of many unidentified compounds were detected. It was also disclosed that other several indium(III) and (I) compounds and indium metal (powder) work as effective catalysts like InCl₃ (Table 1). We examined the effect of other metals such as Zn [11], Mg [12], and In [8] as a reductant. In the cases of Zn and Mg, the reaction proceeded to give **2a** in moderate yield (up to 45%), but no catalytic effect of InCl₃ was observed in the cases of Zn and In, as shown in Table 1. The diastereoselectivity was not affected much by changing the reaction temperature in the range between reflux (58/42) to 0°C (61/39), while the reaction did not proceed at much lower temperature. Similarly, a great change of selectivity was not observed when the reaction was carried out in a variety of solvents, such as dimethylformamide, 1,4-dioxane, acetonitrile, and dichloromethane, as shown in Table 2, the product yield being highest in the reaction using THF. Many chlorosilanes, such as chlorotriisopropylsilane, chlorodiphenylmethylsilane, chlorotriphenylsilane, dichlorodimethylsilane and bis(dimethyl-



- 1a** Ar = Ph
1b Ar = *p*-ClC₆H₄
1c Ar = *p*-CH₃C₆H₄
1d Ar = *p*-CH₃OC₆H₄

SCHEME 1

TABLE 1 Effect of Reductant for Reductive Coupling of Benzaldehyde (**1a**)^a

Entry	Reductant (equiv) ^b	Time (h) ^c	Yield (%) of 2a ^d	<i>dl/meso</i> ^e
1	Al (4)	24 ^f	0	—
2 ^g	Al (4)	5 ^f	0	—
3 ^h	InCl ₃ (0.001) + Al (4)	8	39	59/41
4 ^h	InCl ₃ (0.005) + Al (4)	2	61	57/43
5	InCl ₃ (0.01) + Al (4)	2	56	55/45
6	InCl ₃ (0.02) + Al (4)	2	52	54/46
7	InCl ₃ (0.05) + Al (4)	2	45	52/48
8	InCl ₃ (0.1) + Al (4)	2	18	55/45
9 ^h	In (0.005) + Al (4)	2	54	53/47
10 ^{g,h}	In (0.005) + Al (4)	4	34	59/41
11 ^h	InCl (0.005) + Al (4)	2	59	56/44
12 ^h	InCp (0.005) + Al (4)	5	54	57/43
13 ^h	In(NO ₃) ₃ (0.005) + Al (4)	5	57	57/43
14	Zn (4)	1	43	52/48
15	Mg (4)	20	42	59/41
16	In (4)	24 ⁱ	0	—
17 ^h	InCl ₃ (0.005) + Zn (4)	4	40	59/41
18 ^h	InCl ₃ (0.005) + In (4)	7	0	—

^aReaction conditions: **1a** (0.106 g, 1 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N₂.

^bAl, foil; In, powder; Zn, powder; Mg, ribbon.

^cThe time for 100% conversion of **1a**.

^dIsolated yield. The formation of 0.5 mmol of **2a** corresponds to 100% yield.

^eDetermined by ¹H NMR.

^fNo reaction.

^gUnder sonication in a BRANSONIC ultrasonic cleaner bath, which delivered a 47 kHz wave, with a fixed electrical power of 125 W.

^hFive-fold scale reaction.

ⁱThe conversion was not determined.

TABLE 2 Effect of Solvent for Reductive Coupling of Benzaldehyde (**1a**)^a

Entry	Solvent	Time (h) ^b	Yield (%) of 2a ^c	<i>dl/meso</i> ^d
1	THF	2	45	52/48
2	Et ₂ O	48 ^e	18	24/76
3	1,4-dioxane	24	21	48/52
4	DME	18	14	45/55
5	DMF	6	33	60/40
6	MeCN	6	21	49/51
7	CH ₂ Cl ₂	2	18	27/73
8	CHCl ₃	24 ^f	0	—
9	toluene	24 ^f	0	—

^aReaction conditions: **1a** (0.106 g, 1 mmol), InCl₃ (11 mg, 0.05 mmol), Al (0.108 g, 4 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N₂.

^bThe time for 100% conversion of **1a**. The formation of 0.5 mmol of **2a** corresponds to 100% yield.

^cIsolated yield.

^dDetermined by ¹H NMR.

^eThe conversion was not determined.

^fNo reaction.

chlorosilyl)ethane, could be used in the place of TMSCl, but the product yield was somewhat lower with almost the same diastereoselectivity. From all these experiments, we decided the optimum condition for this coupling reaction to be the use of the combination of TMSCl, Al, cat InCl₃ (0.5 mol %), and THF at room temperature. The results of the application of this optimized condition to *p*-substituted benzaldehydes are shown in Table 3. In these cases, although the reaction became slow, the corresponding coupling product was obtained in 50–68% yields. Without the addition of InCl₃, no reaction occurred in all these cases.

Since Nicholas et al. have reported the enantioselective reductive coupling of benzaldehyde using a stoichiometric amount of a chiral titanium complex [13], we attempted the above reductive coupling in the presence of either chiral monophosphine ((*R*)-MeO-MOP), diphosphine ((*R*)-BINAP), diphosphine oxide ((*R*)-BINAPO), diphosphinite or bisoxazoline (*i*Pr-Phebox), but enantioselectivity was not observed in the formation of the *dl*-isomer.

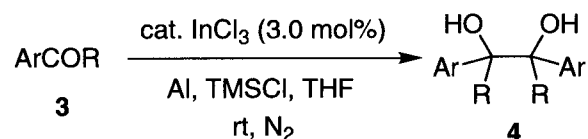
Reductive Homocoupling of Aromatic Ketones

Reductive coupling similarly proceeded with acetophenone (**3a**) as a substrate to afford 2,3-diphenyl-2,3-butanediol (**4a**) in good yield, the use of 3 mol % InCl₃ being revealed to be the best (Scheme 2, Table 4). In this case, the reaction occurred even in the absence of InCl₃ catalyst, but a long induction period was observed, and also, the product yield was much lower. Figure 1 shows the relationship between the reaction time and the isolated yield of **4a** in this coupling. Here, Zn and Mg were also revealed to work

as a reductant, but the catalytic effect of InCl₃ was not observed in the Zn case (Table 4). Results of the reductive coupling of various aromatic ketones are summarized in Table 5 where the effect of InCl₃ was generally remarkable.

Reductive Homocoupling of Aliphatic Carbonyl Compounds and Aromatic Imines

In the cases of aliphatic carbonyl compounds, such as *n*-octanal (**5a**), cyclohexanone (**5b**), and 3-phenylpropanal (**5c**), the corresponding 1,2-diols could not be formed (Table 6). However, α,β -unsaturated carbonyl compounds, such as *trans*-cinnamaldehyde (**5d**) and crotonaldehyde (**5e**), yielded the corresponding 1,2-diols in moderate yields. Next, we performed the reductive coupling of various aromatic imines (Scheme 3), typical results of which are sum-



- 3a** Ar = Ph, R = CH₃
3b Ar = *p*-ClC₆H₄, R = CH₃
3c Ar = *p*-BrC₆H₄, R = CH₃
3d Ar = *p*-CH₃C₆H₄, R = CH₃
3e Ar = Ph, R = Ph
3f Ar = 2-naphthyl, R = CH₃

SCHEME 2

TABLE 4 Effect of Reductant for Reductive Coupling of Acetophenone (**3a**)^a

Entry	Reductant (eq)	Time (h) ^b	Yield (%) of 4a ^c	<i>dl</i> / <i>meso</i> ^d
1	Al (4)	24 ^e	29	68/32
2 ^f	Al (4)	18 ^e	13	74/26
3 ^g	InCl ₃ (0.005) + Al (4)	8	57	71/29
4 ^g	InCl ₃ (0.01) + Al (4)	7	58	70/30
5	InCl ₃ (0.03) + Al (4)	4	74	62/38
6	InCl ₃ (0.05) + Al (4)	2	64	64/36
7	InCl ₃ (0.10) + Al (4)	2	51	57/43
8	Zn (4)	9	65	49/51
9	Mg (4)	24 ^e	29	52/48
10	InCl ₃ (0.03) + Zn (4)	4	45	56/44

^aReaction conditions: **3a** (0.12 g, 1 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N₂.

^bThe time for 100% conversion of **3a**.

^cIsolated yield. The formation of 0.5 mmol of **3a** corresponds to 100% yield.

^dDetermined by ¹H NMR.

^eThe conversion was not determined.

^fUnder sonication in a BRANSONIC ultrasonic cleaner bath, which delivered a 47 kHz wave, with a fixed electrical power of 125 W.

^gFive-fold scale reaction.

TABLE 3 InCl₃-Catalyzed Reductive Coupling of Aromatic Aldehydes (**1**)^a

Entry	Substrate	Product	Time (h) ^b	Isolated Yield (%)	<i>dl</i> / <i>meso</i> ^c
1	1a	2a	4	61	57/43
2 ^d	1a	2a	24 ^e	0	—
3	1b	2b	18	68	41/59
4 ^d	1b	2b	24 ^e	0	—
5	1c	2c	20	56	62/38
6 ^d	1c	2c	24 ^e	0	—
7	1d	2d	17	50	59/41
8 ^d	1d	2d	24 ^e	0	—

^aReaction conditions: **1** (5 mmol), InCl₃ (5.5 mg, 0.025 mmol), Al (0.54 g, 20 mmol), TMSCl (2.5 mL, 20 mmol), THF (50 mL), rt, N₂.

^bThe time for 100% conversion of **1**. The formation of 2.5 mmol of **2** corresponds to 100% yield.

^cDetermined by ¹H NMR.

^dReaction without InCl₃.

^eNo reaction.

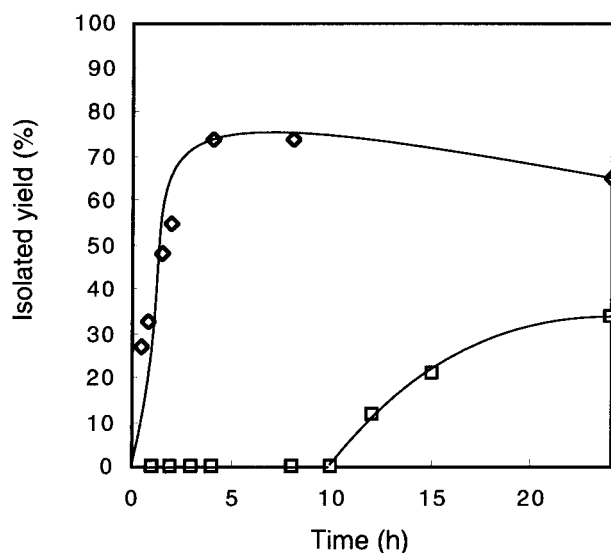


FIGURE 1 Yield of **4a** in the Coupling of Acetophenone in the Presence (◇) and Absence (□) of InCl_3 .

TABLE 5 InCl_3 -Catalyzed Reductive Coupling of Aromatic Ketones (**3**)^a

Entry	Substrate	Product	Time (h) ^b	Isolated Yield (%) ^c	dl/meso ^d
1	3a	4a	4	74	68/32
2 ^e	3a	4a	24 ^f	29	62/38
3	3b	4b	10	76	58/42
4 ^e	3b	4b	10 ^g	9	64/36
5	3c	4c	5 ^h	62	61/39
6 ^e	3c	4c	5 ^h	48	53/47
7	3d	4d	5	72	65/35
8 ^e	3d	4d	5 ⁱ	0	—
9	3e	4e	6 ^h	56	—
10 ^e	3e	4e	6 ^h	42	—
11	3e	4e	20	91	—
12 ^e	3e	4e	24	90	—
13	3f	4f	4	67	58/42
14 ^e	3f	4f	48 ^h	34	50/50

^aReaction conditions: **3** (1 mmol), InCl_3 (6.6 mg, 0.03 mmol), Al (0.18 g, 4 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N_2 .

^bThe time for 100% conversion of **3**.

^cThe formation of 0.5 mmol of **4** corresponds to 100% yield.

^dDetermined by ^1H NMR.

^eReaction without InCl_3 .

^fThe conversion was not determined.

^gAbout 20% conversion of **3**.

^hAbout 70–80% conversion of **3**.

ⁱNo reaction.

marized in Table 7. In the cases of aromatic aldimines such as **6a–6f**, the effect of InCl_3 catalyst (3 mol %) was remarkable, while, in the cases of aromatic ketimines such as **6g**, the addition of InCl_3 decreased the product yield unexpectedly because of the rapid decomposition of **6g** to the starting ketone (**3a**), probably catalyzed by InCl_3 .

TABLE 6 InCl_3 -Catalyzed Reductive Coupling of Aliphatic Aldehydes and Ketones^a

Entry	Substrate	Time (h) ^b	Isolated Yield (%) ^c	dl/meso ^d
1		5a	24 ^e	0 —
2		5b	24 ^e	0 —
3		5c	18	0 ^f —
4		5d	2	27 60/40
5 ^g			2 ^h	0 —
6		5e	3	45 64/36
7 ^g			2 ^e	0 —

^aReaction conditions: substrate (1 mmol), InCl_3 (6.6 mg, 0.03 mmol), Al (0.108 g, 4 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N_2 .

^bThe time for 100% conversion of **5**.

^cThe formation of 0.5 mmol of 1,2-diol corresponds to 100% yield.

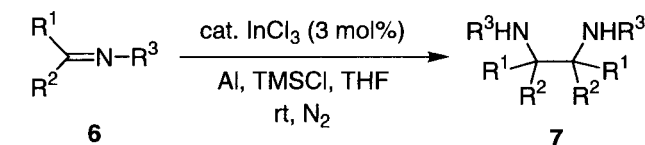
^dDetermined by ^1H NMR.

^eThe conversion was not determined.

^f3-Phenylpropanol (23% yield) was obtained.

^gReaction without InCl_3 .

^hNo reaction.



6a $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$

6b $\text{R}^1 = p\text{-ClC}_6\text{H}_4$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$

6c $\text{R}^1 = p\text{-CH}_3\text{C}_6\text{H}_4$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$

6d $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = p\text{-ClC}_6\text{H}_4$

6e $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = p\text{-CH}_3\text{C}_6\text{H}_4$

6f $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Bn}$

6g $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{CH}_3$, $\text{R}^3 = \text{Ph}$

SCHEME 3

Plausible Reaction Scheme

Although the precise reaction scheme is not yet clear, we tentatively propose Scheme 4 for this catalytic homocoupling by consideration of the generally accepted scheme for reductive coupling of carbonyl compounds [14] and also by the known fact of activation of aluminum by indium ions in chloride solutions [15]. First, a redox-active In–Al alloy might be formed on the surface of aluminum in the presence of TMSCl. An electron transfer from the alloy to aldehydes generates ketyl radicals, and the carbon–carbon bond formation takes place by the radical coupling. When the coupling was attempted in the presence of *m*-dinitrobenzene (0.5 equiv to **1a**),

TABLE 7 InCl₃-Catalyzed Reductive Coupling of Aromatic Imines (**6**)^a

Entry	Substrate	Product	time (h) ^b	Isolated Yield (%) ^c	dl/meso ^d
1	6a	7a	9	71	45/55
2 ^e	6a	7a	12	0	—
3	5b	7b	8	36	43/57
4 ^e	6b	7b	2	0	—
5	6c	7c	6	28	42/58
6 ^e	6c	7c	2	0	—
7	6d	7d	2	48	42/58
8 ^e	6d	7d	4 ^f	0	—
9	6e	7e	2	63	38/62
10 ^e	6e	7e	2 ^f	0	—
11	6f	7f	2	41	— ^g
12 ^e	6f	7f	1	0	—
13	6g	7g	2	40	50/50
14 ^e	6g	7g	2	79	47/53

^aReaction conditions: **6** (1 mmol), InCl₃ (6.6 mg, 0.03 mmol), Al (0.108 g, 4 mmol), TMSCl (0.5 mL, 4 mmol), THF (10 mL), rt, N₂.

^bThe time for 100% conversion of **6**.

^cThe formation of 0.5 mmol of **7** corresponds to 100% yield.

^dDetermined by ¹H NMR.

^eReaction without InCl₃.

^fThe conversion was not determined.

^gNot determined.

which is considered to be a radical scavenger, the product yield was greatly decreased (45% to 5%) (Table 1, entry 7), suggesting the intervention of a ketyl radical species. Finally, metal–oxygen bond cleavage occurs by the reaction with TMSCl to afford the 1,2-bis(trimethylsiloxy) derivative of the diol, which might be hydrolyzed to the product by the work-up procedure. At this stage, cleavage by the action of a proton, which may be present in TMSCl in a small concentration as HCl, might also be operative to some extent, competitively to afford the diol directly. In fact, a pH indicator showed the reaction mixture to be acidic, and also when the coupling of **1a** or **3a** was attempted using aqueous HCl in the place of TMSCl, the product **2a** or **4a**, respectively, was formed, although the yield was low (see Experimental). Since In(O) metal and In(I) compounds were also effective as catalysts in this system, as recorded in Table 1, we consider that a similar redox-active Al–In species might also be formed from these indium compounds and aluminum.

EXPERIMENTAL

¹H and ¹³C NMR spectra were measured on JEOL EX-400, JNM-AL300, and JEOL GSX270 spectrometers for solutions in CDCl₃ with Me₄Si as an internal standard. Analytical thin-layer chromatography (TLC) was performed with Merck silica gel 60 F-254

plates. Column chromatography was performed with Merck silica gel 60.

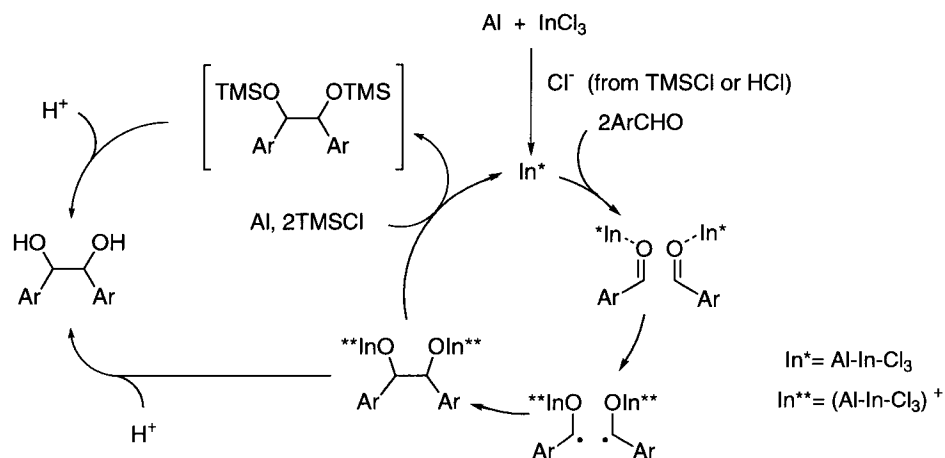
InCl₃ was purchased from Aldrich and used without further purification. Aluminum metal (Al foil, 0.1 mm × 0.8 mm) was purchased from Nacalai Tesque and used without further purification. Chlorotrimethylsilane and THF were distilled before use. All of the carbonyl compounds were commercially available and used without further purification. All of the imines were prepared by the condensation of carbonyl compounds with amines. The structures of 1,2-diols and 1,2-diamines were determined by comparison of spectral data with those of the authentic samples reported. The structures of **7e** and **7g** were determined by analogy with other compounds [11,16–26].

Typical Procedure for Reductive Homocoupling of Benzaldehyde (**1a**) (Table 1, Entry 4)

To a mixture of InCl₃ (5.5 mg, 0.025 mmol), aluminum (0.54 g, 20 mmol), TMSCl (2.5 mL, 20 mmol), and THF (40 mL) in a 200 mL two-necked flask was added **1a** (0.53 g, 5 mmol) in THF (10 mL) at room temperature under N₂. The mixture was kept at room temperature with magnetic stirring for 2 hours. Diethyl ether (100 mL) and aqueous HCl (1.2 M, 50 mL) were added to the resulting mixture, and the organic layer was separated, washed with saturated aqueous NaHCO₃ (50 mL × 3), dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel (eluent, hexane/ethyl acetate) to obtain 1,2-diphenyl-ethanediol **2a** (325 mg, 1.52 mmol, 61% yield; *dl/meso* = 57/43) and a complex mixture containing benzyl alcohol and many unidentified compounds (56 mg).

Reductive Homocoupling of Benzaldehyde (**1a**) or Acetophenone (**3a**) in the Presence of HCl in the place of TMSCl

To a mixture of InCl₃ (5.5 mg, 0.025 mmol), aluminum (0.54 g, 20 mmol), and THF (30 mL) in a 200 mL two-necked flask were added a THF (10 mL) solution containing HCl (aqueous 35% HCl, 0.5 mL, 5 mmol) and **1a** (0.53 g, 5 mmol) in THF (10 mL) at room temperature under N₂. The mixture was kept at room temperature with magnetic stirring for 24 hours and treated as described previously in a typical procedure. The product **2a** was obtained in 19% yield (100 mg, 0.467 mmol; *dl/meso* = 58/42) together with benzyl alcohol (60 mg, 0.555 mmol, 11% yield), and **1a** (161 mg, 1.52 mmol) was recovered. When a similar reaction was carried out using 1 mmol of HCl, no reaction occurred.



SCHEME 4 Plausible reaction scheme.

In the case of the coupling of **3a**, using **3a** (1 mmol), InCl_3 (0.03 mmol), Al (4 mmol), aqueous 35% HCl (0.1 mL, 1 mmol), and THF (10 mL) at room temperature for 24 hours, **4a** was obtained in 55% yield (67 mg, 0.276 mmol; *dl/meso* = 58/42), and **3a** (39 mg, 0.330 mmol) was recovered. Similarly, the reaction using 0.2 mmol HCl did not give any **4a**.

1,2-Diphenyl-1,2-ethanediol (*dl* and *meso*) (**2a**)

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.28 [2.91] (2H, s, br), 4.59 [4.72] (2H, s), 7.01–7.23 (10H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 79.0 [78.0], 126.9 [127.0], 127.9 [128.0], 128.2 [128.1], 139.7 [139.8]. The values in brackets are of the *meso*-isomer. The reported ^1H NMR data of the benzylic C–H hydrogens are 4.59 and 4.72 for *dl* and *meso*-isomers, respectively [16,17].

1,2-Bis(4-chlorophenyl)-1,2-ethanediol (*dl* and *meso*) (**2b**) [16]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.55 [3.10] (2H, s, br), 4.56 [4.78] (2H, s), 6.97–7.32 (8H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 78.4 [77.1], 128.2, 128.3, 133.8, 137.7 [137.9].

1,2-Bis(4-methylphenyl)-1,2-ethanediol (*dl* and *meso*) (**2c**) [16]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.22 [2.26] (6H, s), 2.07 [2.77] (2H, s, br), 4.57 [4.65] (2H, s), 6.95–7.18 (8H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 21.1 [21.1], 78.8 [78.0], 126.8 [127.0], 128.8 [129.0], 137.0, 137.4 [137.8].

1,2-Bis(4-methoxyphenyl)-1,2-ethanediol (*dl* and *meso*) (**2d**) [16]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.10 [2.80] (2H, s, br), 3.75 [3.79] (6H, s), 4.63 [4.72] (2H, s), 6.73–7.26 (8H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 55.1 [55.2], 78.7 [77.7], 113.5 [113.6], 128.1 [128.3], 132.0, 159.1 [159.4].

2,3-Diphenyl-2,3-butanediol (*dl* and *meso*) (**4a**) [16,17]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 1.35 [1.46] (6H, s), 2.23 [2.52] (2H, s, br), 7.06–7.11 (10H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 24.9 [25.1], 78.8 [78.6], 126.9, 127.1 [127.0], 127.3 [127.2], 143.4 [143.7].

2,3-Bis(4-chlorophenyl)-2,3-butanediol (*dl* and *meso*) (**4b**) [18]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 1.39 [1.47] (6H, s), 2.23 [2.55] (2H, s, br), 7.00–7.15 (8H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 24.7 [25.0], 78.5 [78.2], 127.3 [127.3], 128.8 [128.4], 133.1 [133.0], 141.7 [142.2].

2,3-Bis(4-bromophenyl)-2,3-butanediol (*dl* and *meso*) (**4c**) [16]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 1.38 [1.46] (6H, s), 2.05 [2.35] (2H, s, br), 6.94–7.30 (8H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 24.6 [25.0], 78.4 [78.2], 121.4 [121.2], 129.2 [128.8], 130.2 [130.3], 142.2 [142.7].

2,3-Bis(4-methylphenyl)-2,3-butanediol (*dl* and *meso*) (**4d**) [18]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 1.44 [1.51] (6H, s), 2.26 [2.52] (2H, s, br), 2.32 [2.31] (s,

6H), 7.04–7.11 (8H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 20.9, 25.0 [25.2], 78.7 [78.5], 127.3 [126.8], 127.8 [128.0], 136.5 [136.3], 140.5 [140.9].

1,1,2,2-Tetraphenyl-1,2-ethanediol (4e) [17]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 2.96 (2H, s, br), 7.05–7.25 (20H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 83.0, 126.9, 127.3, 128.6, 144.1.

2,3-Bis(2-naphthyl)-2,3-butanediol (dl and meso) (4f) [19]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 1.54 [1.61] (6H, s), 2.35 [2.75] (2H, s, br), 7.15–7.77 (14H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 25.2 [25.5], 79.2 [78.8], 125.5, 125.8 [125.8], 125.9, 126.4, 126.7, 127.3, 128.3, 132.3 [132.4], 141.0, 141.0.

1,6-Diphenyl-1,5-hexadiene-3,4-diol [20]

White solid; *dl*-isomer: ^1H NMR (CDCl_3 , 400 MHz) δ = 4.27 (2H, d, J 5.86 Hz), 6.26 (2H, dd, J 5.86 Hz, 15.9 Hz), 6.71 (2H, d, J 15.9 Hz), 7.22–7.38 (14H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 75.8, 126.6, 127.0, 127.9, 128.6, 132.7, 136.4. *meso*-isomer: ^1H NMR (CDCl_3 , 400 MHz) δ = 4.43 (2H, d, J 6.11 Hz), 6.28 (2H, dd, J 6.11 Hz, 15.6 Hz), 6.69 (2H, d, J 15.6 Hz), 7.22–7.38 (14H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 75.7, 126.6, 127.0, 127.6, 128.6, 133.1, 136.4.

2,6-Octadiene-4,5-diol (dl and meso) [11]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 1.66–1.74 (6H, m), 2.94 (2H, s, br), 3.88 [4.04] (2H, m), 5.35–5.50 (2H, m), 5.63–5.79 (2H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 17.8 [17.8], 75.7 [75.5], 128.9 [129.1], 129.7 [129.5].

N,N'-Diphenyl-1,2-diphenyl-1,2-ethanediamine (dl and meso) (7a) [21,22]

White solid; ^1H NMR [CDCl_3 + D_2O (few drops), 400 MHz] δ = 4.54 [4.96] (2H, s), 6.49–7.23 (20H, m); ^{13}C NMR [CDCl_3 + D_2O (few drops), 75.5 MHz] δ = 63.9 [61.9], 114.2 [113.7], 118.2 [117.8], 127.5, 127.3 [127.5], 128.3 [128.2], 129.0 [129.2], 139.7, 146.8 [146.4].

N,N'-Diphenyl-1,2-bis(4-chlorophenyl)-1,2-ethanediamine (dl and meso) (7b) [23]

White solid; ^1H NMR [CDCl_3 + D_2O (few drops), 400 MHz] δ = 4.46 [4.91] (2H, s), 6.49–7.23 (18H, m); ^{13}C NMR [CDCl_3 + D_2O (few drops), 75.5 MHz] δ = 61.2

[63.4], 114.1 [113.7], 118.6 [118.3], 128.6 [128.6], 128.7 [128.8], 129.2 [129.3], 133.3 [133.5], 138.2 [136.5], 146.4 [145.9].

N,N'-Diphenyl-1,2-bis(4-methylphenyl)-1,2-ethanediamine (dl and meso) (7c) [23]

White solid; ^1H NMR [CDCl_3 + D_2O (few drops), 400 MHz] δ = 2.27 [2.28] (6H, s), 4.52 [4.90] (2H, s), 6.50–7.08 (m, 18H); ^{13}C NMR [CDCl_3 + D_2O (few drops), 75.5 MHz] δ = 21.0, 63.3 [61.5], 114.0 [113.6], 117.8 [117.6], 127.2 [127.4], 129.0 [128.9], 129.1 [129.1], 147.1 [146.5].

N,N'-Bis(4-chlorophenyl)-1,2-diphenyl-1,2-ethanediamine (dl and meso) (7d) [24]

White solid; ^1H NMR [CDCl_3 + D_2O (few drops), 400 MHz] δ = 4.49 [4.88] (2H, s), 6.40–7.19 (18H, m); ^{13}C NMR [CDCl_3 + D_2O (few drops), 75.5 MHz] δ = 63.8 [61.8], 115.2 [114.9], 122.8 [122.5], 127.2 [127.3], 127.7 [127.7], 128.4 [128.3], 128.9 [128.9], 139.1, 145.4 [144.8].

N,N'-Bis(4-methylphenyl)-1,2-diphenyl-1,2-ethanediamine (dl and meso) (7e) [25]

White solid; ^1H NMR [CDCl_3 + D_2O (few drops), 400 MHz] δ = 2.14 [2.15] (s, 6H), 4.49 [4.91] (2H, s), 6.40–7.19 (18H, m); ^{13}C NMR [CDCl_3 + D_2O (few drops), 75.5 MHz] δ = 20.3, 64.2 [62.1], 114.2 [113.8], 127.2 [126.9], 127.3 [127.4], 127.4 [127.5], 128.3 [128.2], 129.5 [129.7], 140.1 [138.4], 144.8 [144.2].

N,N'-Dibenzyl-1,2-diphenyl-1,2-ethanediamine (dl and meso) (7f) [21]

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ = 3.42 (4H, AB system, J_{AB} 13.7 Hz), 3.76 (2H, s), 6.96–7.30 (20H, m); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ = 50.9, 67.1, 126.6, 127.6, 127.9, 128.2, 128.3, 128.6, 140.3, 140.7.

2,3,N,N'-tetraphenyl-2,3-butanediamine (dl and meso) (7g) [26]

White solid; ^1H NMR [CDCl_3 + D_2O (few drops), 400 MHz] δ = 1.64 [1.81] (6H, s), 6.17–7.56 (20H, m); ^{13}C NMR [CDCl_3 + D_2O (few drops), 75.5 MHz] δ = 20.8, 116.2, 127.4, 127.6, 128.2, 128.5, 128.6, 128.9, 141.2, 145.4.

REFERENCES

- [1] (a) For reviews of the application of indium compounds in organic chemistry, see: Li, C. J.; Chan,

- T. H. *Tetrahedron* 1999, 55, 11149–11176; (b) Cintas, P. *Synlett* 1995, 1087–1096; (c) Chauhan, K. K.; Frost, C. G. *J Chem Soc Perkin Trans 1* 2000, 3015–3019; (d) Ranu, B. C. *Eur J Org Chem* 2000, 2347–2356.
- [2] For example, see: (a) Li, C. J.; Chan, T. H. *Tetrahedron Lett* 1991, 32, 7017–7020; (b) Miyai, T.; Inoue, K.; Yasuda, M.; Baba, A. *Synlett* 1997, 699–700; (c) Chan, T. H.; Yang, Y. *J Am Chem Soc* 1999, 121, 3238–3239 and references cited therein.
- [3] Hirashita, T.; Kinoshita, K.; Yamaura, H.; Kawai, M.; Araki, S. *J Chem Soc Perkin Trans 1* 2000, 825–828 and references cited therein.
- [4] Kobayashi, S.; Busujima, T.; Nagayama, S. *Tetrahedron Lett* 1998, 39, 1579–1582 and references cited therein.
- [5] (a) Loh, T. P.; Pei, L.; Lin, M. *Chem Commun* 1996, 2315–2316; (b) Ali, T.; Chauhan, K. K.; Frost, C. G. *Tetrahedron Lett* 1999, 40, 5621–5624; (c) Babu, G.; Perumal, P. *Tetrahedron* 1999, 55, 4793–4802 and references cited therein.
- [6] (a) Loh, T. P.; Wei, L. L. *Tetrahedron Lett* 1998, 54, 7615–7624; (b) Loh, T. P.; Wei, L. L. *Synlett* 1998, 975–976.
- [7] (a) Miyai, T.; Onishi, Y.; Baba, A. *Tetrahedron* 1999, 55, 1017–1026; (b) Tsuchimoto, T.; Maeda, T.; Shirakawa, E.; Kawakami, Y. *Chem Commun* 2000, 1573–1574.
- [8] (a) Kalyanam, N.; Venkateswara, R. G. *Tetrahedron Lett* 1993, 34, 1647–1648; (b) Lim, H. J.; Keum, G.; Kang, S. B.; Chung, B. Y.; Kim, Y. *Tetrahedron Lett* 1998, 39, 4367–4368; (c) Baek, H. S.; Lee, S. S.; Yoo, B. W.; Ko, J. J.; Kim, S. H.; Kim, J. H. *Tetrahedron Lett* 2000, 41, 8097–8099.
- [9] Ti: (a) Fürstner, A.; Hupperts, A. *J Am Chem Soc* 1995, 117, 4468–4475; (b) Lipski, T. A.; Hilfiker, M. A.; Nelson, S. G. *J Org Chem* 1997, 62, 4566–4567; (c) Gansäuer, A.; Bauer, D. *J Org Chem* 1998, 63, 2070–2071; (d) Yamamoto, Y.; Hattori, R.; Itoh, K. *Chem Commun* 1999, 825–826; (e) Bandini, M.; Cozzi, P. G.; Morganti, S.; Umani-Ronchi, A. *Tetrahedron Lett* 1999, 40, 1997–2000; V: (f) Hirao, T.; Hasegawa, T.; Muguruma, Y.; Ikeda, I. *J Org Chem* 1996, 61, 366–367; (g) Hirao, T.; Asahara, M.; Muguruma, Y.; Ogawa, A. *J Org Chem* 1998, 63, 2812–2813; (h) Hirao, T.; Hatano, B.; Imamoto, Y.; Ogawa, A. *J Org Chem* 1999, 64, 7665–7667; (i) Hirao, T.; Takeuti, H.; Ogawa, A.; Sakurai, H. *Synlett*, 2000, 1658–1660; Sm: (j) Nomura, R.; Matsuno, T.; Endo, T. *J Am Chem Soc* 1996, 118, 11666–11667; Ce: (k) Groth, U.; Jeske, M. *Angew Chem Int Ed Engl* 2000, 39, 574–576.
- [10] The reaction proceeds with Al (Hg) or Al metal in the basic condition, see: (a) Schreiber, A. A. P. *Tetrahedron Lett* 1970, 11, 4271–4272; (b) Hulce, M.; LaVaute, T. *Tetrahedron Lett* 1988, 29, 525–528; (c) Khurana, J. M.; Sehgal, A.; Gogia, A.; Manian, A.; Maikap, G. C. *J Chem Soc Perkin Trans 1* 1996, 2213–2215; (d) Sahada, D. A.; Kawaji, T.; Sawada, T.; Matoka, S.; Thiemann, T.; Tsukinoki, T.; Tashiro, M. *J Chem Res (S)* 1999, 210–211.
- [11] Reductive coupling of carbonyl compounds with Zn and TMSCl, see: So, J. H.; Park, M. K.; Boudjouk, P. *J Org Chem* 1988, 53, 5871–5875.
- [12] Reductive coupling of carbonyl compounds with Mg, TMSCl, and hexamethylphosphoramide, see: Chan, T.-H.; Vinokur, E. *Tetrahedron Lett* 1972, 13, 75–78.
- [13] Halterman, R. L.; Zhu, C.; Chen, Z.; Dunlap, M. S.; Khan, M. A.; Nicholas, K. M. *Organometallics* 2000, 19, 3824–3829.
- [14] March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley Interscience: New York, 1992; Chapter 19, pp 1225–1226.
- [15] Saidman, S. B.; Bessone, J. B. *Electrochim Acta* 1997, 42, 413–420.
- [16] Wang, L.; Zhang, Y. *Synth Commun* 1998, 28, 3991–3997 and references cited therein.
- [17] Fürstner, A.; Csuk, R.; Rohrer, C.; Weidmann, H. *J Chem Soc Perkin Trans 1* 1988, 1729–1734.
- [18] Matsuura, T.; Kitaura, Y. *Bull Chem Soc Jpn* 1968, 41, 2483–2485.
- [19] Rieke, R. D.; Kim, S. H. *J Org Chem* 1998, 63, 5235–5239.
- [20] Reductive coupling of *trans*-cinnamaldehyde has been carried out, see for example: (a) Barden, M. C.; Schwartz, J. *J Am Chem Soc* 1996, 118, 5484–5485; (b) Mukaiyama, T.; Yoshimura, N.; Igarashi, K. *Chem Lett* 2000, 838–839.
- [21] Talukdar, S.; Banerji, A. *J Org Chem* 1998, 63, 3468–3470 and references cited therein.
- [22] Eisch, J. J.; Kaska, D. D.; Peterson, C. J. *J Org Chem* 1966, 31, 453–456.
- [23] Smith, J. G.; Ho, I. *J Org Chem* 1972, 37, 653–656.
- [24] Periasamy, M.; Srinivas, G.; Karunakar, G. V.; Bharathi, P. *Tetrahedron Lett* 1999, 40, 7577–7580.
- [25] Reductive coupling of *N*-benzylidene-*p*-toluidine has been carried out, see for example: Imamoto, T.; Nishimura, S. *Chem Lett* 1990, 1141–1142.
- [26] Reductive coupling of *N*-(1-phenylethylidene)-aniline has been carried out, see for example: (a) Sato, T.; Inoue, T.; Mukaiyama, T. *Chem Lett* 1975, 637–640; (b) Tsukinoki, T.; Mitoma, Y.; Nagashima, S.; Kawaji, T.; Hashimoto, I.; Tashiro, M. *Tetrahedron Lett* 1998, 39, 8873–8876.