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# Reductive Coupling Reaction of Carbonyl Compounds Using Al Powder in 10% aq NaOH/MeOH/THF Solution<sup>1),2)</sup>

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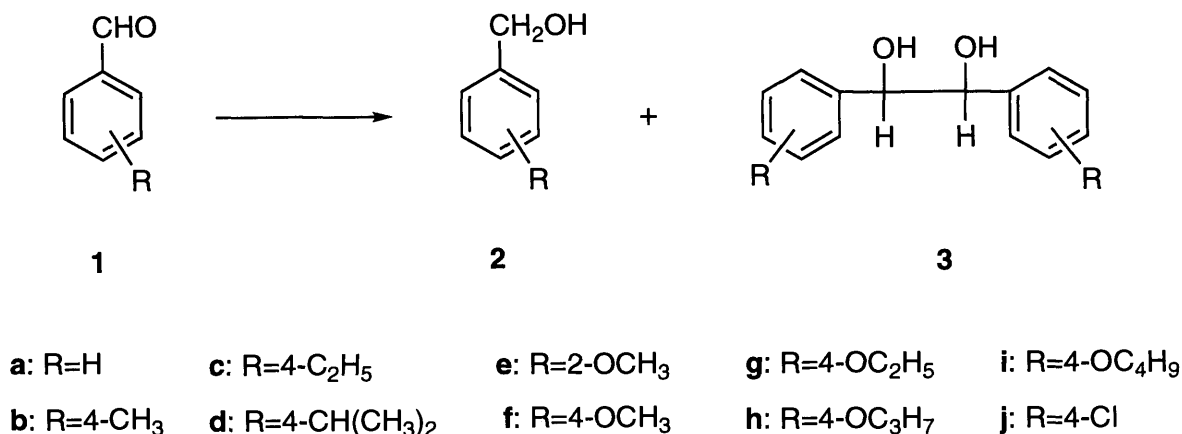
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Reductive coupling reaction of benzaldehydes, acetophenone, ethyl phenyl ketone and 1-tetralone using Al powder in 10% aq NaOH/MeOH/THF solution afforded the corresponding ethane-1,2-diols.

## Introduction

The reductive C-C coupling reaction of carbonyl compounds<sup>3)</sup> is an important method for the preparation of ethane-1,2-diols and Al(Hg)<sup>4)</sup>, TiCl<sub>4</sub>-Zn<sup>5)</sup>, Ce-I<sub>2</sub><sup>6)</sup>, SmI<sub>2</sub><sup>7)</sup>, Mg-Graphite<sup>8)</sup>, Me<sub>3</sub>SiCl/NaI/Sm<sup>9)</sup> and Sm(OTf)<sub>2</sub><sup>10)</sup> have been widely used. These reagents are moisture-sensitive and have to be handled under dry inert atmosphere with tedious procedures. Only a few metallic reagents such as TiCl<sub>3</sub><sup>11)</sup>, Al(Hg)<sup>12)</sup>, and Zn-ZnCl<sub>2</sub><sup>13)</sup> have been reported for the reductive coupling reactions under aqueous conditions. Recently, pinacolization of aromatic carbonyl compounds with Al powder and KOH in MeOH was reported.<sup>14)</sup>

We previously reported that the treatment of benzaldehyde (**1a**) with Raney Cu-Al alloy in 10% aq NaOH solution afforded 1,2-diphenyl-1,2-ethanediol (**3a**) in poor to moderate yields (5-32%), besides benzyl alcohol<sup>15)</sup> and that **3a** was selectively obtained in a low yield (30%) by using Al powder under the same conditions with the recovery (50%) of **1a**.<sup>15)</sup> We now report the treatment of carbonyl compounds using Al powder in an alkaline media to afford 1,2-ethanediol derivatives in good yields.



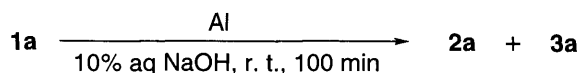
Scheme 1

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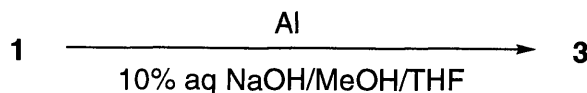


Scheme 2

**Table 1** Solvent Effect on the Reductive Coupling Reaction of (1).<sup>a)</sup>

solvent <sup>b)</sup>	Product (%) <sup>c)</sup>		Recovery of <b>1a</b>
	<b>2a</b>	<b>3a</b>	<b>1a</b>
MeOH	8 (trace <sup>d)</sup> )	92 (46 <sup>d)</sup> )	0
THF	9	9	82
THF/MeOH	7 (trace <sup>d)</sup> )	93 (75 <sup>d)</sup> )	0
THF/EtOH	1	3	96
THF/ <i>i</i> -PrOH	2	2	96

a) **1a**/Al/10% aq NaOH = 50mmol/1.25g/20ml.r.t., 100min. b) MeOH, EtOH, or *i*-PrOH/THF = 35mmol/10ml. c) Relative yields determined by G.C. d) Isolated yield.



Scheme 3

**Table 2** The Reductive Coupling Reaction of (1) in an Alkaline Solution.<sup>a)</sup>

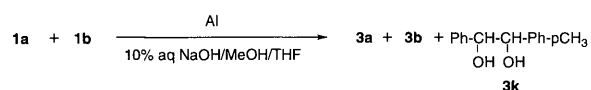
Substrate	Product	Yield (%) <sup>b)</sup>	dl/meso <sup>c)</sup>
<b>1a</b>	<b>3a</b>	75	46/54
<b>1b</b>	<b>3b</b>	81	57/43
<b>1c</b>	<b>3c</b>	75	58/42
<b>1d</b>	<b>3d</b>	72	50/50
<b>1e</b>	<b>3e</b>	62	60/40
<b>1f</b>	<b>3f</b>	66	88/12
<b>1g</b>	<b>3g</b>	91	55/45
<b>1h</b>	<b>3h</b>	86	57/43
<b>1i</b>	<b>3i</b>	80	60/40
<b>1j</b>	<b>3j</b>	47	67/33

a) r.t., 100min. b) Isolated yield. c) Ratios determined from the intensities of benzylic protons in <sup>1</sup>H-NMR spectra, in which the protons of dl form appeared at a higher magnetic field, compared to the one of meso isomer.<sup>8), 16)–18)</sup>

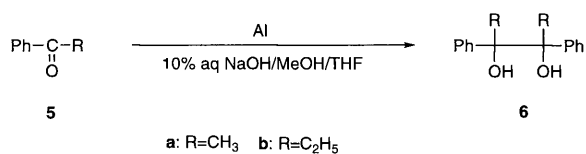
## Results and Discussion

The coupling reaction of **1a** using Al powder in 10% aq NaOH-MeOH alkaline gave **3a** in 46% yield (Scheme 2 and Table 1). Though THF itself is less effective, a mixed solvent of MeOH and THF gave **3a** in 75% yield. It was found that MeOH is essential for the reaction and that EtOH and *iso*-PrOH are ineffective. As alkaline solutions, a 10% aq KOH solution afforded the expected **3a** just as a 10% aq NaOH solution, but a 10% aq LiOH solution gave a little of **3a**. The coupling reaction of **1a** did not proceed in a 10% aq CsOH or a 10% aq Na<sub>2</sub>CO<sub>3</sub> solution.

From the results above mentioned, the coupling reactions of **1b-j** were carried out using Al powder in a mixed solvent of 10% aq NaOH, MeOH and THF and the corresponding 1,2-ethanediols **3b-j** were given in good yields (Scheme 3 and Table 2). The (dl/meso) ratios of **3a-j** were determined by <sup>1</sup>H-NMR<sup>8), 16)–18)</sup> to be almost 1 : 1. Attempted cross coupling reac-



Scheme 4

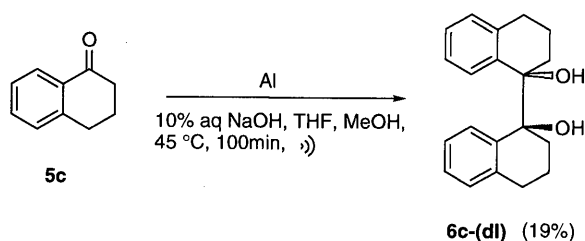


Scheme 5

Table 3 Coupling Reaction of Ketone (5).<sup>a)</sup>

Substrate	Temp.	Isolated yield (%) of <b>6</b> <sup>c)</sup>
<b>5a</b>	room temp.	<b>6a</b> (35)
<b>5a</b> <sup>b)</sup>	room temp.	<b>6a</b> (75)
<b>5b</b> <sup>b)</sup>	45°C	<b>6b</b> (43)

a) 100min. b) Under ultrasonic irradiation. c) *dl/meso* Ratios were determined by <sup>1</sup>H-NMR<sup>8),19)</sup> as 51/49 for **6a** and 79/21 for **6b**, respectively.



Scheme 6

tion of **1a** and **1b** gave the expected **3a**, **3b** and cross-coupled **3k** in a 1 : 1 : 1 ratio (Scheme 4).

The reductive coupling reaction of acetophenone (**5a**) gave **6a** in 35% yield. Ultrasonic irradiation increased the yield of **6a** to 75%. The reaction of ethyl phenyl ketone (**5b**) proceeded at a elevated temperature (45°C) under sonication to afforded **6b** in 43% yield (Scheme 5 and Table 3).

Similarly tetralone (**5c**) gave *dl*-1,1'-dihydroxy-octahydro-1,1'-binaphtalin **6c**, but in poor 19% yield (Scheme 6).

Aldehydes such as 2-hydroxy-, 4-hydroxy-, 4-phenyl- and 4-benzyl-oxybenzaldehyde, 1- and 2-napthaldehyde as well as cyclohexanone and 9-fluorenone are inert towards the treatment with Al powder under the similar conditions.

Finally, Al powder is useful for the reductive coupling reaction of carbonyl compounds in a mixed solvent system of 10% aq NaOH solution, MeOH and THF under mild conditions with easy operations.

## Experimental

**General.** Vapor-phase chromatography was performed on a Yanagimoto Gas Chromatograph G-2800 instrument equipped with a fused-silica capillary column (Quadrex corporation, 007-1-25-0.25F, 0.25 mm i. d. X 25 m, liquid phase: methyl silicone). Product identification was carried out based on the retention time of standard materials (**1a**, **2a**, and **3a**). An ultrasonic cleaner (Elma Transsonic T 460, frequency 35 KHz, acoustic power 68 W, capacity 2L) was used for sonication durring coupling reaction. Column chromatography was carried out on silica gel

(Wako-gel, C-300).

**Materials.** Benzaldehydes **1a-j** and ketones such as **5a-5c** are commercially available. Commercially available Al powder was used for the reaction (mesh 150, Kishida Chemical Co.).

**Reductive Coupling Reaction of Benzaldehydes: General Procedure.**— To a stirred mixture of benzaldehyde (**1a**) (5.30g, 50mmol), Al powder (1.25g), MeOH (35ml) and THF (10ml) at room temperature was added gradually 10 % aq NaOH solution<sup>20)</sup> (20ml) for 10 min. After the reaction mixture was stirred for 90 min at room temperature, Al powder was filtered off with filter aid and the filtrate was extracted with dichloromethane. The extracts were washed with water, dried (MgSO<sub>4</sub>) and evaporated *in vacuo* to leave a residue. Recrystallization (hexane-ethyl acetate) of the residue gave 1,2-diphenyl-1,2-ethanediol (**3a**) (4.01g, 75%) as a mixture of dl<sup>-21)</sup> and meso<sup>-8)</sup> isomer (dl/meso=46/54).

**Reductive Coupling Reaction of Ketones: General Procedure.**— To a stirred mixture of acetophenone (**5a**) (6.00g, 50mmol), Al powder (1.25g), MeOH (35ml) and THF (10ml) at room temperature was added gradually 10% aq NaOH solution (20ml) for 10 min under ultrasonic irradiation.<sup>22)</sup> Then the reaction mixture was stirred for 90 min under the same reaction conditions. The work-up, as described above, gave 2,3-diphenyl-2,3-butanediol (**6**) (4.53g, 75%) as a mixture<sup>8)</sup> of dl and meso form (dl/meso=51/49).

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