Pinacolic Coupling of Aromatic Carbonyl Compounds Using Zn Powder in Aqueous Basic Media without Organic Solvents

Takehito Tsukinoki,* Takatoshi Kawaji,[†] Iwao Hashimoto,[†] Shuntaro Mataka,[††] and Masashi Tashiro[††]
Tohwa Institute for Science, Tohwa University, 1-1-1, Chikushigaoka, Minami-ku, Fukuoka 815
[†]*Department of Industrial Chemistry, Wakayama National College of Technology, Nojima 77, Nata-machi, Goboh, Wakayama 644*
[††]*Institute of Advanced Material Study, and Department of Molecular Science and Technology, Graduate School of Kyushu University, 6-1, Kasuga-koh-en, Kasuga, Fukuoka 816*

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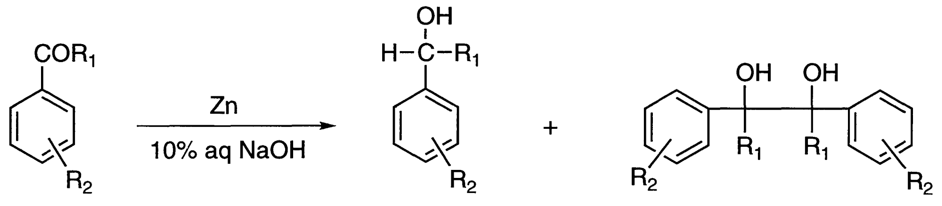
Treatment of aromatic carbonyl compounds with Zn powder in 10% aq NaOH solution *without using any organic solvents* under the mild conditions afforded the corresponding 1,2-diols in good yields.

The reductive coupling reaction of carbonyl compounds is an important method for the formation of carbon-carbon bonds,[1] and many reagents[2] have been developed, which are usually used under anhydrous conditions. Metallic reagents such as $TiCl_3$,[3] Al(Hg),[4] Zn-$ZnCl_2$[5] and Al powder[6] are reported to be effective for the coupling reactions under aqueous conditions. However, an organic co-solvent such as MeOH or THF is necessary in these reactions. Recently, due to environmental protection requirements, much attention has been focused on reactions carried out in an aqueous solution without any organic solvents. We report here our findings that in 10% aq NaOH solution *without any organic solvents*, Zn powder is effective for the reductive coupling reaction of aromatic aldehydes (**1a**-**h**) and acetophenone (**1i**) to afford the corresponding 1,2-diarylethane-1,2-diols **3** under mild conditions.[7]

When substituted benzaldehydes **1a**-**h** were treated with Zn powder in 10% aq NaOH solution at ambient temperature for 100 min, the coupling reaction products **3a**-**h** were obtained in 67-82% yields (Table 1). Except for that of **3g**, the dl/meso-ratios of **3a**-**f** and **3h** are nearly 1:1 (^{1}H-NMR).[8-11] The reason for the effect of the methoxy group in *p*-position of the aromatic ring on the dl/meso ratio is not clear. A small amount of alcohols **2** was formed as a by-product. Zinc powder is also effective for the reductive coupling of **1a** in 10% aq LiOH, 10% aq KOH, and 10% aq CsOH, as well as 10% aq NaOH, giving **3a** in 75~81% yields, but ineffective in 10% aq Na_2CO_3 and 10% aq K_2CO_3; **1a**

Table 1. Coupling reaction of aromatic carbonyl compounds **1** with Zn powder in 10% aq NaOH solution[a]



1 **2** **3**

a: R_1=H, R_2=H **b**: R_1=H, R_2=2-CH_3 **c**: R_1=H, R_2=3-CH_3 **d**: R_1=H, R_2=4-CH_3
e: R_1=H, R_2=2-OCH_3 **f**: R_1=H, R_2=3-OCH_3 **g**: R_1=H, R_2=4-OCH_3 **h**: R_1=H, R_2=4-F
i: R_1=CH_3, R_2=H

Run	Substrate	Temp/°C	Reaction time/min	Product/%[b]		dl/meso ratio[c] **3**
1	**1a**	r. t.	100	**2a** (4)	**3a** (82)	53/47
2	**1b**	r. t.	100	**2b** (10)	**3b** (68)	59/41
3	**1c**	r. t.	100	**2c** (7)	**3c** (81)	50/50
4	**1d**	r. t.	100	**2d** (5)	**3d** (82)	50/50
5	**1e**	r. t.	100	**2e** (1)	**3e** (67)	49/51
6	**1f**	r. t.	100	**2f** (8)	**3f** (81)	52/48
7	**1g**	r. t.	100	**2g** (3)	**3g** (78)	75/25
8	**1h**	r. t.	100	**2h** (2)	**3h** (81)	50/50
9[d]	**1i**	45	370	–	**3i** (77)	58/42

[a] Substrate/Zn powder/10% aq NaOH solution=10 mmol/5 g/20 ml. [b] Isolated yields. [c] Ratios determined from the intensities of benzylic protons in ^{1}H-NMR spectra, in which the protons of dl isomer appeared at a higer magnetic field, compared to the one of meso isomer.[8-11] [d] Recovery of **1i** was 3%.

was quantitatively recovered.

The expected 2,3-diphenyl-2,3-butanediol (**3i**) was obtained in 77% yield in the reaction of acetophenone (**1i**) with Zn powder in 10% aq NaOH at an elevated temperature (45 °C) for a prolonged reaction time (370 min). For the coupling reaction of **1i**, 5% aq NaOH (20 ml) is as effective as 10% aq NaOH (20 ml), giving **3i** in 75% yield, but 1% aq NaOH (20 ml) was ineffective. Sonication did not accelerate the reaction.

In conclusion, the reductive coupling reaction of aromatic aldehydes and acetophenone was carried out using inexpensive Zn powder in an aqueous basic solution *without any organic solvents.*

References and Notes

1 See for example, B. E. Kahn and R. D. Rieke, *Chem. Rev.*, **88**, 733 (1988); J.-M. Pons and Santelli, *Tetrahedron,* **44**, 4295 (1988).

2 G. M. Robertson,'' Comprehensive Organic Synthesis,'' ed by B. M. Trost, Pergamon Press, Oxford (1991), vol 3, pp563 - 610.

3 A. Clerici and O. Porta, *Tetrohedron Lett.*, **23**, 3517 (1982).

4 M. Hulce and T. LaVaute, *Tetrohedron Lett.,* **29**, 525 (1988).

5 K. Tanaka, S. Kishigami, and F. Toda, *J. Org. Chem.*, **55**, 2981 (1990).

6 T. Tsukinoki, Y. Nagano, T. Kawaji, I. Hashimoto, T. Etoh, S.Mataka, and M. Tashiro, submitted for publication in Org. Prep. Proced. Int.

7 General coupling procedures: To a stirred mixture of **1** (10 mmol) and Zn powder (5.00 g) at room temperature was gradually added dropwise 10% aq NaOH solution (20 ml) for 10 min. After the reaction mixture was stirred for 90 min at room temperature, insoluble materials were filtered off and the filtrate was extracted with dichloromethane (30 ml x 3). The extract was washed with water, dried over ($MgSO_4$) and evaporated *in vacuo* to give a residue, which was washed with hexane, giving **3**. From the hexane solution, **2** was obtained. In runs 2, 5, 6, and 9 (Table 1), **2** and **3** were purified by column chromatography (silica gel; Wakogel, C-300). Addition of Zn powder to a stirred mixture of **1** and 10% aq NaOH gave similar results.

8 A. Fürstner, R. Csuk, C. Rohrer, and H. Weidmann, *J. Chem. Soc., Perkin Trans. 1,* **1988**, 1729.

9 J. H. Stocker, D. H. Kern, and R. M. Jenerein, *J. Org. Chem.,* **33**, 412 (1968).

10 M. Imuta and H. Ziffer, *J. Org. Chem.*, **43**, 3319 (1978).

11 R. E. Balsells and A. R. Frasca, *Tetrahedron,* **38**, 2525 (1982).