Reductive Coupling of Aromatic Carbonyl Compounds to Pinacols Using Zinc Powder in Aqueous Media†

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Lei Wang, Xinghua Sun and Yongmin Zhang*

Department of Chemistry, Hangzhou University, Hangzhou, 310028, P.R. China

Zinc-mediated reductive coupling of aromatic carbonyl compounds occurs to give corresponding 1,2-diols in moderate to good yields in saturated $NH_4Cl(aq)$–THF solution at room temperature.

1,2-Diols are very useful synthons for a variety of organic syntheses.[1] The reductive coupling of carbonyl compounds is an important method for the formation of 1,2-diols,[2] and is usually carried out under anhydrous conditions. On the other hand, many reagents such as $TiCl_3$,[3] Zn–$ZnCl_2$,[4] Al(Hg),[5] Cp_2TiCl[6] and Mn[7] have been developed for pinacolic coupling reactions in aqueous media because organic reactions in aqueous media offer a number of advantages over conventional organometallic reactions in organic solvents.[8] As a cheap and efficient reagent, metallic zinc powder has been used for the preparation of homoallylic alcohols by the coupling of allylic halides with carbonyl compounds in aqueous media.[9] To the best of our knowledge there are no literature examples of pinacolic coupling using zinc powder in saturated $NH_4Cl(aq)$–THF solution. We therefore report herein that zinc-mediated reductive coupling of aromatic carbonyl compounds to pinacols can be carried out in aqueous media at room temperature. The results are summarized in Table 1.

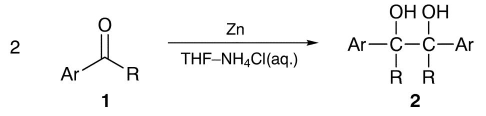

Table 1 shows that aromatic aldehydes undergo coupling in the presence of zinc powder in THF–$NH_4Cl(aq)$ solution to give pinacolic coupling products (1,2-diols) in moderate to good yields at ambient temperature. Except for that of **2 g**, the DL : *meso* ratio of diols (entries **a**–**f**, **h**) is nearly 1 : 1 (^1H NMR). The reason for the effect of the trifluoromethyl group in the 4-position of the aromatic ring (entry **g**) on the DL:*meso* ratio is not clear. Unfortunately, the aromatic ketone (entry **h**) gives the pinacolic coupling product in poor yield.

We have tried to use anhydrous THF, THF–water (4:1) or water in place of THF–$NH_4Cl(aq)$ (4:1) respectively. However, no product was formed under these conditions. Also, other metal powders such as tin and indium in place of zinc gives no reaction.

In summary, zinc is a useful metal to mediate the reductive coupling of aromatic carbonyl compounds in aqueous media at room temperature. The advantages of this reaction are mild and neutral reaction conditions, simple operation and good yields.

Experimental

^1H NMR spectra were recorded on a JEOL PMX 60 SI instrument. All NMR samples were measured in $CDCl_3$ using TMS as internal standard. IR spectra were obtained on a Perkin-Elmer 683 spectrophotometer as KBr plates.

General Procedure for the Preparation of Pinacols.—The aromatic carbonyl compound (1.0 mmol) and metallic zinc powder (1.2 mmol) were added to saturated aqueous NH_4Cl–THF (1:4, 5 ml) solution. The resulting mixture was stirred at room temperature for 8 h, then dilute hydrochloric acid (0.5 mol l^{-1}, 2 ml) was added to quench the reaction and the mixture was extracted with diethyl ether (20 ml × 2). The extracts were washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel with light petroleum–ether as the eluent to give the product.

Table 1 Zinc-mediated reductive coupling of aromatic carbonyl compounds

Entry	Ar	R	Yield(%)[a]	DL:*meso*[b]	^1H NMR(δ)	IR($\tilde{\nu}$/cm^{-1})
a	C_6H_5	H	65	55:45	3.78 (2 H, s, OH),[c] 4.40 (s, DL) and 4.60 (s, *meso*) (2 H, 2 Ph*CH*), 6.50–7.30 (10 H, m, Ph)	3100–3600(s)
b	*p*-ClC_6H_4	H	77	58:42	2.85 (2 H, s, OH),[c] 4.40 (s, DL) and 4.63 (s, *meso*) (2 H, 2 Ph*CH*), 6.60–7.30 (8 H, m, Ar)	3200–3600(s)
c	*p*-BrC_6H_4	H	76	50:50	2.46 (2 H, s, OH),[c] 4.50 (s, DL) and 4.60 (s, *meso*) (2 H, 2 Ph*CH*), 6.60–7.60 (8 H, m, Ar)	3100–3600(s)
d	*p*-FC_6H_4	H	73	55:45	3.15 (2 H, s, OH),[c] 4.55 (s, DL) and 4.70 (s, *meso*) (2 H, 2 Ph*CH*), 6.60–7.50 (8 H, m, Ar)	3150–3620(s)
e	*m*-BrC_6H_4	H	70	52:48	3.33 (2 H, s, OH),[c] 4.33 (s, DL) and 4.50 (s, *meso*) (2 H, 2 Ph*CH*), 6.70–7.40 (8 H, m, Ar)	3100–3500(s)
f	*o*-BrC_6H_4	H	68	50:50	2.90 (2 H, s, OH),[c] 4.55 (s, DL) and 4.65 (s, *meso*) (2 H, 2 Ph*CH*), 6.70–7.50 (8 H, m, Ar)	3100–3600(s)
g	*p*-$CF_3C_6H_4$	H	82	74:26	3.04 (2 H, s, OH),[c] 4.45 (s, DL) and 4.66 (s, *meso*) (2 H, 2 Ph*CH*), 6.65–7.50(8 H, m, Ar)	3100–3600(s)
h	C_6H_5	CH_3	32	51:49	1.42 (s, DL) and 1.55 (s, *meso*) (6 H, 2 CH_3), 2.40 (2 H, s, OH),[c] 6.80–7.30 (10 H, m, Ph)	3100–3600(s)

[a] Isolated yields. [b] Ratios determined from the intensities of benzylic protons in ^1H NMR spectra(entries **a**–**g**), in which the protons of the DL isomer appeared at a higher magnetic field compared to that of the *meso* isomer, or from the intensities of methyl protons in ^1H NMR spectra(entry **h**), in which the methyl protons of the DL isomer appeared at higher magnetic field compared to that of the *meso* isomer.[10] [c] In all examples this signal disappeared on adding D_2O.

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*To receive any correspondence.

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