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Highly *meso*-Diastereoselective Pinacol Coupling of Aromatic Aldehydes Mediated by Al Powder/Copper Sulfate in Water

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Abstract: Pinacol-type coupling reaction products presenting a high *meso*-diastereoselectivity (the ratio *dl/meso* was 4/96 up to 1/99) were obtained in fair to good yields (24–69%) using several aromatic aldehydes as starting materials and aluminium powder/copper sulfate as catalysts, in water, under reflux conditions.

Keywords: Aqueous media, *meso*-diastereoselectivity, reductive coupling

INTRODUCTION

Organic syntheses in aqueous media present many advantages in terms of safety and economical or environmental aspects compared to syntheses in organic solvents.^[1] Starting from this perspective, we have

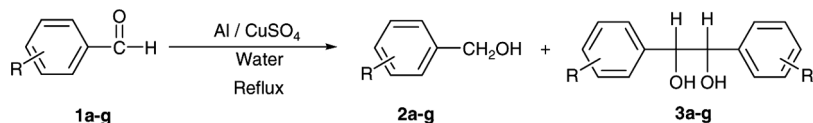
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investigated the reduction of some functional groups linked to aromatic rings using different types of Raney alloys in an aqueous alkaline solution.^[2] As a result of prior investigations, we showed that aromatic aldehydes yielded their corresponding benzyl alcohol, in high yields, when Raney Ni-Al or Co-Al alloys were used in a tetrahydrofuran (THF)/water solution with slight addition of alkali.^[2d] Interestingly, the use of Raney Cu-Al alloy, in the same conditions described previously, also promoted the pinacol coupling reaction between 2 equivalents of aldehyde, in contrast to the use of Raney Ni-Al or Co-Al alloy, which afforded reduction-type products. Therefore, we decided to investigate the differences between the reactivities of Raney alloys toward the behavior of aldehydes in such reaction conditions.

The well-known pinacol reaction^[3] using reductive reagents e.g., metals, their salts, or complexes), in different reaction media such as dry organic solvents, aqueous organic solvents, or simply water, is an important and convenient method to achieve C-C bond formation in organic synthesis. In recent decades, several reports have described different investigations of pinacol condensation, most of these reports being related to complex catalysts based on vanadium,^[4] titanium,^[5] samarium,^[6] chromium,^[7] indium,^[8] manganese,^[9] magnesium,^[10] nickel,^[11] aluminium,^[12] cerium,^[13] niobium,^[14] zinc,^[15] or zirconium,^[16] either as simple metals or in different types of combinations. Although many different methods have been developed for the pinacol reductive coupling process, examples of diastereoselective processes are scarce, showing mostly a *dl*-stereochemistry of reductive coupling reaction products.^[4b,c;5c-i;6a,d;7a-c;8b;9b-e] Quite surprisingly, there are very few examples of a *meso*-diastereoselectivity.^[6a] Moreover, although the aldehydes by coupling gave a *dl*-diastereoisomer, their imine parent compounds yield a *meso*-isomer in identical conditions.^[4d] To the best of our knowledge, no reports have described a highly stereoselective coupling method in an aqueous solution yielding large amounts of *meso*-1,2-diols, although Aspinall et al. presented a 20:80 *dl:meso* ratio for hydrobenzoin obtained by reductive coupling of benzaldehyde.^[6a]

Throughout our investigations of the reduction processes of aldehydes using the Raney Cu-Al alloy, we found that, along with the corresponding benzyl alcohol, a low diastereoselective pinacol coupling reaction of the aromatic aldehydes also occurred. On replacing the Cu-Al alloy with a mixture of Al powder and CuSO₄ and using only water as a solvent (without any alkali), a much higher diastereoselectivity was obtained, although yields dropped. We report here a convenient and simple coupling method that yields a highly *meso*-diastereoselective coupling product starting from aromatic aldehydes (Scheme 1).



Scheme 1. a: R=H, b: R=4-CH₃-, c: R=4-CH₃O-, d: R=3-CH₃O-, e: R=2-CH₃O-, f: R=4-Cl-, g: R=4-F-.

RESULTS AND DISCUSSION

As mentioned previously, we successfully found that the use of Raney Cu-Al alloy in a mixture of an aqueous alkaline solution and organic solvents as well as in a totally aqueous alkaline media promoted the pinacol reaction of aromatic aldehyde. Consequently, the treatment of benzaldehyde **1a** with Raney Cu-Al alloy in a 10% NaOH solution afforded benzylalcohol **2a** and hydrobenzoin **3a**, as shown in entry 1 (Table 1). Through a series of experiments, we investigated the importance of the contribution of each participant in this process. Therefore, when copper powder was used alone in an alkaline solution, the transformation of benzaldehyde was complete

Table 1. Reaction of **1a** with Raney Cu-Al alloy, Al, Cu, and CuSO₄ in aqueous solution without any added organic solvent

Entry ^a	Alloy or metal (g) Additive (g)	Temp. ^b (°C)	Time (h)	Solution	Products (%) ^c				
					1a	2a	3a	<i>dl:meso</i>	4a
1	Cu-Al alloy/5.0 g	rt	1.5	10% NaOH	0	24	67	(46:54)	9
2	Cu/2.5 g	rt	1.5	10% NaOH	0	52	0	—	48
3	Al/2.5 g	rt	1.5	10% NaOH	19	0	81	(56:44)	0
4	Al/2.5 g	Reflux	24	Water	58	9	33	(12:88)	0
5	Cu-Al alloy/5.0 g	Reflux	1.5	Water	100	0	0	—	0
6	Al/2.5 g–CuSO ₄ /1.0 g	Reflux	1.5	Water	86	2	12	(8:92)	0
7	CuSO ₄ /1.0 g	Reflux	6	Water	86	1	0	—	13

^aThe reaction conditions were 50 mmol as substrate and 40 ml as solution in entries 1–7.

^bIn entries 1, 3, and 4, the temperature of the reaction solution increased up to 90 °C.

^cThe products were determined by melting point (*meso*: 139–140 °C), GC, and ¹H NMR spectra. The chemical shifts of methine proton in *dl*- and *meso*-isomer were δ 4.73 and 4.83 ppm, respectively.

through a simple Cannizzaro reaction (entry 2). When replacing copper powder with aluminium powder, **3a** was obtained in high yields without any by-product (entry 3), but the *dl/meso* ratio of **3a** was almost 1:1. No recorded transformations of benzaldehyde **1a** occurred in water at room temperature, even at prolonged reaction times or at reflux for periods of time up to 120 min (those entries are not depicted in Table 1). Only when the mixture of benzaldehyde and Al powder was refluxed in water for 1 day did we notice the presence of a reductive coupling product in fair yields, but the diastereoselectivity was substantially improved (entry 4). Comparing entries 1–4, we noticed that the presence of copper enhances the formation of the reactive coupling product, whereas the absence of alkali favors a high diastereoselectivity. Therefore, we tried the use of Co–Al alloy in water, but even at reflux conditions there was no transformation of the starting benzaldehyde (entry 5). The next step was to replace copper with one of its salts to enhance both the yield and the diastereoselectivity. The use of Al powder and CuSO₄ in water at reflux allowed aldehyde **1a** to transform to the highly *meso*-diastereoselective diol **3a** along with the reduced compound **2a**. Diol **3a** was identified as the *meso*-isomer by its melting point (138–140 °C, lit. 137–139 °C^[17]) and ¹H NMR spectra. The corresponding diol was not obtained at all when only copper sulfate was used; instead, the corresponding oxidation product, benzoic acid **4a**, was formed (paradoxically in higher yields at a lower temperature). We may conclude that the reaction in water requires a certain amount of copper sulfate as a catalyst.

The typical procedure is the following: to a mixture of benzaldehyde (10.6 g, 100 mmol) in 50 mL of water, at room temperature, copper sulfate 5-hydrate (5.00 g, 20.0 mmol) and aluminium powder (150 mesh, 10.8 g, 400 mmol) were added in one portion. The reaction mixture was stirred vigorously under reflux for 8 h. The mixture was extracted with ether (3 × 10 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated. Compound **3a** was obtained in a 51% yield (5.46 g).

Table 2 summarizes the reactions performed using several differently substituted aromatic aldehydes, **1a–g**, and one aliphatic aldehyde, heptanal **5**. The *meso*-diastereoselectivity is excellent in each case, even though the yields in reductive coupling product, irrespective of the nature or position of the substituent, are lower than that for benzaldehyde.

Taking for a fact that the first step of the reductive coupling process is the nucleophilic attack of an electron (donated by the metal) at the carbon atom of the carbonyl moiety,^[3] the electronic effects and the

Table 2. Effect of substituent on the coupling reaction of aldehydes

Entry	Substrate	Products (%) ^a		
		Monoalcohol	Diol	<i>dl/meso</i> -ratio ^b
1	1a	2a (15)	3a (69)	1:99
2	1b	2b (6)	3b (24)	4:96
3	1c	2c (81)	3c (0)	—
4	1d	2d (48)	3d (47)	>99
5	1e	2e (38)	3e (24)	>99
6	1f	2f (82)	3f (2)	—
7	1g	2g (97)	3g (0)	—
8	CH ₃ (CH ₂) ₅ -CHO	2h (97)	3h (0)	—

^aSubstrate is 5 mmol; the obtained products were identified by GC-MS.^bThe *dl/meso* ratio was determined by ¹H NMR spectra.

electronic densities at this particular atom can explain the lower yields in runs 2–8 (Table 2). Thus, in run 8, when no coupling occurs, the donor effect of the aliphatic group enhances the electronic density at the carbon atom of the carbonyl group. Paradoxically, the same effect (a higher electronic density) is obtained in runs 6 and 7 because of the powerful electron-withdrawing effect of the halogen atom (Cl-, respectively F-), which enhances the conjugation between the aromatic nucleus and the >C=O double bond, diminishing in the same time the electronic displacement toward the oxygen atom. An interesting situation is that of the three isomers of anisaldehyde: in *m*-anisaldehyde, the electron donor effect of the methoxy group has little or no influence on the electronic density of the carbon atom in the carbonyl group or on the conjugation between the aromatic nucleus or the carbon–oxygen double bond (delocalization shows high electronic densities on both *ortho*-carbon atoms). Consequently, the main effect is the withdrawal effect of the oxygen atom; the electronic density is subsequently lowered and the reductive coupling process can occur. In *p*-anisaldehyde, the negatively charged atom is located on the quaternary atom in the immediate proximity of the carbonyl group. An extended conjugation is present, and the electronic density is therefore very high, which explains the absence of a reductive coupling product. More interesting is the situation of *o*-anisaldehyde: although its behavior should have resembled that of its *para*-isomer, the formation of a reductive coupling product can be explained by an unfavorable limit structure for the extended conjugation, with two vicinal exocyclic double bonds.

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