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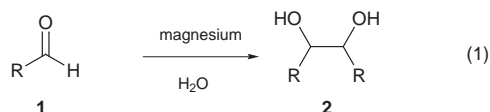
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A simple and effective pinacol-coupling has been carried out with magnesium. The reaction is highly effective in water in the presence of a catalytic amount of ammonium chloride. Under these conditions, various aromatic aldehydes and ketones undergo carbonyl coupling, generating 1,2-diols in good yields. The effectiveness of the reaction is strongly influenced by the steric environment surrounding the carbonyl group. Aliphatic aldehydes appear inert under the reaction conditions.

Discovered well over a century ago, the pinacol-coupling reaction is still one of the most important reactions for the formation of carbon-carbon bonds.¹ Previously, pinacol-couplings have been effected by using metals such as sodium,² lithium,³ or magnesium(I) iodide⁴ (and Reike Mg⁵) under strictly anhydrous conditions. Other reagents used for such a reaction include chromium or vanadium,⁶ SmI₂,⁷ Ce-I₂,⁸ Yb,⁹ Bu₃SnH,¹⁰ Al(Hg),¹¹ as well as the versatile TiCl₃ based reducing agents (the McMurry pinacol-coupling).¹² Recently, pinacol coupling reactions mediated by Ti(III) in aqueous media have been intensively investigated.¹³ Other metals like Zn-Cu¹⁴ or In¹⁵ have also been found to promote the aqueous reaction under ultrasonic radiation and manganese in acidic conditions.¹⁶ Herein we report a simple and effective pinacol-coupling mediated by magnesium in water.¹⁷

When benzaldehyde was reacted with magnesium in 0.1 M ammonium chloride aqueous solution, the corresponding pinacol-coupling product was obtained in high yield. The use of water alone as the reaction solvent was also effective; however, it resulted in a low conversion of the starting material. The use of 0.1 M HCl aqueous solution as solvent also decreased the yield of the desired pinacol-coupling product. Other aryl aldehydes **1** [eqn. (1)] were coupled similarly to obtain the corre-



sponding diols **2** (Table 1). It is noteworthy that aromatic aldehydes bearing halogens (bromo, chloro, fluoro) were coupled without any complications in product formation. Furfural coupled equally well under the reaction conditions. The coupling of aryl ketones was also successful (entries 15 and 16). On the other hand, an aliphatic aldehyde was inert under the reaction conditions (entry 14). The magnesium mediated pinacol-coupling in water appears strongly affected by steric effects. The positions of substituents present on the aromatic rings show a dramatic effect on the course of the reaction. While no substantial difference was observed between *meta*- or *para*-substituted aromatic aldehydes (compare entries: 2 and 3, 4 and 7, 6 and 9), the presence of *ortho*-substituents increased the formation of reduced product (entries 5, 10 and 12). A similar increase in the amount of the reduced product was observed on increasing the size of the *ortho*-substituents. When two substituents were present (entry 11), no pinacol-coupling product was obtained; complete reduction of the aldehyde was observed.

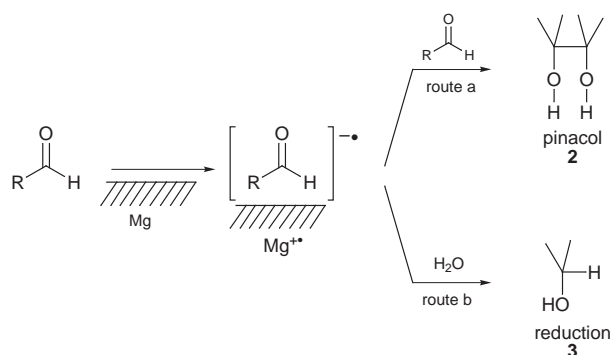
In the notable report by Gomberg and Bachmann,⁴ the use of a Mg-MgI₂ (1:1) mixture in anhydrous benzene or ether for carbonyl coupling was rationalized through the formation of MgI and the coupling of radical intermediates. In the present

Table 1 Pinacol-coupling mediated by magnesium in aqueous medium

Entry	Substrate (1)	Yield (%) ^a of pinacol product 2	Yield (%) ^a of reduced product 3	<i>threo</i> : <i>erythro</i> ^b
1		88(80)	1	59:41
2		93(87)	0	80:20
3		90(83)	6	54:46
4		56(42)	11	54:46
5		61(50)	27	52:48
6		96(89)	0	61:39
7		(90)	(7)	50:50
8		(65)	(8)	61:39
9		(78)	0	54:46
10		73(67)	10	51:49
11		0	(74)	na
12		(62)	(30)	30:70
13		quant. (92)	0	64:36
14		0	0	na
15		66(59)	8	53:47
16		(41)	na	53:47
17		0	0	na

Reactions were carried out with carbonyl compound (1.89 mmol), magnesium turnings (1 g) in 0.1 M aqueous ammonium chloride 10 mL at r.t. for 12–24 h. ^a Measured by ¹H NMR (isolated yields in parentheses). ^b *threo*:*erythro* Ratios were measured by ¹H NMR based on the intensities of benzylic protons. For entry 15, 26% of the starting material was recovered.

investigation, no magnesium salt was present, thus indicating, apparently, the occurrence of the reaction through a different mechanism. We tentatively rationalize the experimental results



Scheme 1 Postulated mechanism for magnesium-mediated pinacol coupling and reduction of carbonyl compounds.

as shown in Scheme 1. During the reaction, there are two potential pathways competing with each other; generating either pinacol-coupling product (route a) or reduced product (route b). The increase in steric hindrance around the carbonyl would destabilize the transition-state in route a, thus favoring the formation of the reduced product. The presence of NH_4Cl would clean the metal surface to effect further reactions.

In conclusion, we found magnesium to be effective for mediating pinacol-coupling reactions in 0.1 M aqueous NH_4Cl . The product formation was strongly influenced by steric effects. We are presently exploring this new reactivity in synthetic applications.

Experimental

A sample experimental procedure follows. A suspension of benzaldehyde (200 mg, 1.89 mmol) and magnesium turnings (1 g, 41.67 mmol) in 0.1 M aqueous ammonium chloride (10 mL) was stoppered and stirred overnight (vigorously) under an atmosphere of air and at room temperature. The reaction was quenched with 3 M aqueous HCl and extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with saturated aqueous NaHCO_3 solution and brine, dried over magnesium sulfate and filtered. The filtrate was concentrated *in vacuo* to give a crude material, which was purified by flash chromatography on silica gel to afford the pinacol product (162 mg, 80%) as a white crystalline solid.

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