

## Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

### PINACOL COUPLING OF AROMATIC ALDEHYDES AND KETONES USING MAGNESIUM IN AQUEOUS AMMONIUM CHLORIDE UNDER ULTRASOUND

Ji-Tai Li <sup>a</sup>, Yan-Jiang Bian <sup>a</sup>, Hong-Jun Zang <sup>a</sup> & Tong-shuang Li

<sup>a</sup> Department of Chemistry, Hebei University, Baoding, 071002, P. R. China

Published online: 16 Aug 2006.

To cite this article: Ji-Tai Li, Yan-Jiang Bian, Hong-Jun Zang & Tong-shuang Li (2002) PINACOL COUPLING OF AROMATIC ALDEHYDES AND KETONES USING MAGNESIUM IN AQUEOUS AMMONIUM CHLORIDE UNDER ULTRASOUND, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 32:4, 547-551, DOI: [10.1081/SCC-120002400](https://doi.org/10.1081/SCC-120002400)

To link to this article: <http://dx.doi.org/10.1081/SCC-120002400>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

SYNTHETIC COMMUNICATIONS, 32(4), 547–551 (2002)

## PINACOL COUPLING OF AROMATIC ALDEHYDES AND KETONES USING MAGNESIUM IN AQUEOUS AMMONIUM CHLORIDE UNDER ULTRASOUND

Ji-Tai Li,\* Yan-Jiang Bian, Hong-Jun Zang,  
and Tong-shuang Li

Department of Chemistry, Hebei University,  
Baoding 071002, P. R. China

### ABSTRACT

The pinacol coupling reaction of aromatic aldehydes and ketones was performed in 8–95% yield with magnesium in 0.1 M aqueous  $\text{NH}_4\text{Cl}$  under ultrasound irradiation at r.t. for 3 h.

The reductive coupling of carbonyl compounds is an important method for the formation of 1,2-diols. A number of types of metal reagents, such as Zn,  $\text{Al}(\text{Hg})$ ,<sup>1</sup> Ln,<sup>2</sup> Mn,<sup>3</sup> Sm,<sup>4</sup> Te,<sup>5</sup> Al,<sup>6</sup> and Mg<sup>7</sup> have been used to carry out the pinacol coupling. Recently, Zn-Cu<sup>8</sup> or In<sup>9</sup> has also been found to promote the pinacol-coupling under ultrasound irradiation. Herein, we report the studies of using Mg for pinacol coupling of aromatic aldehydes and ketones in aqueous media under ultrasound.

---

\*Corresponding author. E-mail: orgsyn@mail.hbu.edu.cn

As shown in table and scheme, *p*-methoxy benzaldehyde and *p*-methyl benzaldehyde were reacted with magnesium in 0.1 M ammonium chloride aqueous solution, the corresponding pinacol-coupling products were obtained in high yield (**2f**, **2h**) under ultrasound. In the absence of ultrasound,<sup>7</sup> a suspension of benzaldehyde and magnesium turning in aqueous 0.1 M NH<sub>4</sub>Cl were stirred vigorously at room temperature overnight to furnish 1,2-bis(4-methoxyphenyl)-1,2-diol (**2f**) and 1,2-bis(4-methylphenyl)-1,2-diol (**2h**) in 89 and 65% yield respectively. Our procedure both results in 95% yield within 3 h. The yield of pinacol-coupling product from some carbonyl compounds (**2c**, **2g**, **2m**, and **2n**) was lower than reported in above literature. According postulated mechanism for magnesium-mediated pinacol coupling and reduction of carbonyl compounds,<sup>7</sup> ultrasonication was favorable for single electron transfer reaction of the aldehydes, resulting in diols. At the same condition, ultrasonication was favorable for reduction of ketones, resulting in reduction product.

In conclusion, we found magnesium to be effective for mediating pinacol-coupling reactions in aqueous NH<sub>4</sub>Cl under ultrasound.

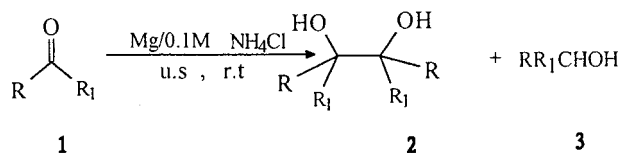
## EXPERIMENTAL

Liquid substrates were purified by distillation prior to use. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer (KBr). <sup>1</sup>H NMR spectra were measured on VXR-300S spectrometer (300 or 200 MHz) by using CDCl<sub>3</sub> as solvent and TMS as internal standard. Mass spectra were determined on an AEI MS-50 SD90 spectrometer (EI, 70 eV). Sonication was performed in a Shanghai Branson-CQX ultrasonic cleaner with a frequency of 25 kHz and a nominal power 500 W. The reaction flask was located at the maximum energy area in the cleaner and the temperature of water bath was controlled by addition or removal of water.

### General Procedure

A 100 mL Pyrex flask was charged with the desired aldehyde or ketone (1, 1 mmol) Mg powder (0.55 g, 22 mmol), and 0.1 M aqueous NH<sub>4</sub>Cl (6 mL). The mixture was irradiated in the water bath of an ultrasonic cleaner at room temperature for 3 h. The reaction was quenched with 3 M aqueous HCl and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with saturated aqueous NaHCO<sub>3</sub> solution and brine, dried over magnesium sulfate and filtered. The filtrate was concentrated in vacuum to give a crude material, which was separated by column





*Scheme.*

chromatography on silica (200–300 mesh), eluted with petroleum ether (b.p. 60–90°C) or a mixture of petroleum ether and diethyl ether. The authenticity of the product was established by their spectra.

**2a:**  $\delta_{\text{H}}$  2.26 (s, 2H, OH), 4.70 (s, dl) and 4.83 (s, meso) (2H, phCH-), 7.10–7.32 (m, 10H, Ar);  $m/z$  (%): 214 (1), 180 (7.6), 167 (12.5), 149 (6.0), 107 (93.8), 79 (100), 77 (73.8);  $\nu_{\text{max}}$  (KBr): 3400–3800  $\text{cm}^{-1}$ .

**2b:**  $\delta_{\text{H}}$  2.98 (s, 2H, OH), 5.49 (s, meso) (2H, phCH-), 7.00–7.26 (m, 6H, Ar);  $m/z$  (%): 352 (1), 305 (1.4), 233 (10), 175 (100), 145 (10), 111 (25), 77 (15);  $\nu_{\text{max}}$  (KBr): 3320–3400  $\text{cm}^{-1}$ .

**2c:**  $\delta_{\text{H}}$  2.98 (s, 2H, OH), 5.19 (s, dl) and 5.49 (s, meso) (2H, phCH-), 7.10–7.26 (m, 8H, Ar);  $m/z$  (%): 282 (10), 235 (12), 165 (5.5), 141 (100), 107 (19), 77 (10);  $\nu_{\text{max}}$  (KBr): 3380–3420  $\text{cm}^{-1}$ .

**2d:**  $\delta_{\text{H}}$  2.89 (s, 2H, OH), 4.62 (s, dl) and 4.79 (s, meso) (2H, phCH-), 7.12–7.20 (m, 8H, Ar);  $m/z$  (%): 263 (1.2), 251 (1.6), 178 (4.6), 165 (4.6), 141 (100), 113 (23.8), 77 (71.0);  $\nu_{\text{max}}$  (KBr): 3260–3318  $\text{cm}^{-1}$ .

**2e:**  $\delta_{\text{H}}$  1.79 (s, 2H, OH), 4.44 (s, dl) (2H, -CH-OH), 6.29 (t, 2H, -CH=CH-), 6.71 (d, 2H, -CH=CH-), 7.24–7.41 (m, 10H, Ar);  $m/z$  (%): 264 (1.0), 248 (6.2), 232 (3.6), 219 (3.0), 157 (6.7), 134 (21.4), 133 (100), 115 (24.7), 91 (27.8), 77 (19.9), 55 (37.0);  $\nu_{\text{max}}$  (KBr): 3300–3380  $\text{cm}^{-1}$ .

**2f:**  $\delta_{\text{H}}$  2.90 (s, 2H, OH), 3.77 (s, dl) and 3.81 (s, meso) (s, 6H, OCH<sub>3</sub>), 4.64 (s, dl) and 4.75 (s, meso) (2H, phCH-), 6.73–7.21 (m, 8H, Ar);  $m/z$  (%): 274 (1), 256 (2), 227 (30), 137 (100), 109 (9), 77 (8);  $\nu_{\text{max}}$  (KBr): 3300–3380  $\text{cm}^{-1}$ .

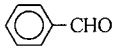
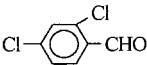
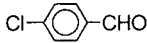
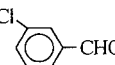
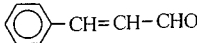
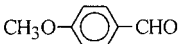
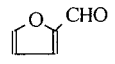

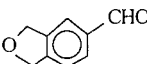

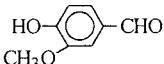
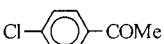
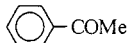

**2g:**  $\delta_{\text{H}}$  2.04 (s, 2H, -OH), 5.00 (s, dl) and 5.02 (s, meso) (2H, fur-CH-), 6.27 (m, 2H, 3,4-fur-H), 7.26 (m, 1H, 5-fur-H);  $m/z$  (%): 196 (10), 178 (25), 152 (73), 137 (33), 98 (100), 84 (22), 49 (30);  $\nu_{\text{max}}$  (KBr): 3240–3300  $\text{cm}^{-1}$ .

**2h:**  $\delta_{\text{H}}$  2.29 (s, 6H, CH<sub>3</sub>), 2.58 (s, 2H, OH), 4.65 (s, dl) and 4.72 (s, meso) (2H, -CH-OH), 7.02–7.20 (m, 8H, Ar);  $m/z$  (%): 242 (1), 195 (6), 121 (100), 107 (12), 93 (19), 77 (13);  $\nu_{\text{max}}$  (KBr) 3280–3450  $\text{cm}^{-1}$ .

**2i:**  $\delta_{\text{H}}$  2.20 (s, 2H, OH), 4.57 (s, 2H, phCH-), 5.92 (s, 4H, CH<sub>2</sub>), 6.64–6.71 (m, 6H, Ar);  $m/z$  (%): 302 (1), 284 (2.5), 268 (5.0), 255 (11.8), 151 (100), 123 (32), 93 (77.1), 65 (39.0);  $\nu_{\text{max}}$  (KBr): 3450–3490  $\text{cm}^{-1}$ .



**Table.** Pinacol-Coupling Mediated by Mg in 0.1 M Aqueous  $\text{NH}_4\text{Cl}$  Under Ultrasound\*

Entry	Substrate	Isolated yield, % (lit. <sup>7</sup> )		dl/meso
		2	3	
a		75(80)	5(0)	55:45
b		8	7	meso
c		58(90)	10(7)	49:51
d		44(42)	12(11)	51:49
e		39	28	—
f		95(89)	13(0)	66:34
g		39(92)	5(0)	66:34
h		95(65)	5(8)	90:10
i		72	10	—
j		9	5	—
k		51	8	—
l		55	15	—
m		19(59)	57(8)	—
n		35(41)	4(0)	79:21

\* Reactions were carried out at room temperature for 3h. Isolated yield based on the substrate. Ratios of dl/meso as calculated by  $^1\text{H}$ NMR.



## PINACOL COUPLING OF ALDEHYDES AND KETONES

551

**2j:**  $\delta_{\text{H}}$  2.52 (s, 6H, CH<sub>3</sub>), 6.11 (s, 2H, OH), 6.82–6.85 and 7.85–7.89 (m, 8H, Ar);  $m/z$  (%): 282 (1), 266 (15), 221 (12), 177 (24), 162 (26), 151 (30), 135 (23), 120 (70), 85 (38), 77 (17), 57 (90);  $\nu_{\text{max}}$  (KBr): 3360–3450 cm<sup>-1</sup>.

**2n:**  $\delta_{\text{H}}$  1.47 (s, dl) and 1.56 (s, meso) (6H, -CCH<sub>3</sub>), 2.2 (s, 2H, OH), 3.8 (s, 6H, OCH<sub>3</sub>), 6.7–7.3 (m, 8H, Ar),  $m/z$  (%): 302 (1), 151 (100), 135 (5), 109 (4), 77 (3), 43 (60);  $\nu_{\text{max}}$  (KBr): 3200–3600 cm<sup>-1</sup>.

## ACKNOWLEDGMENTS

The project was supported by National Natural Science Foundation of China (29872011), Educational Ministry of China and Educational Department of Hebei Province (99014). The project was supported by Natural Science Foundation of Hebei Province (299080).

## REFERENCES

1. Wang, L.; Sun, X.H.; Zhang, Y.M. J. Chem. Research (S) **1998**, 336.
2. Ding, Z.B.; Wu, S.H. YouJi HuaXue **1997**, 17, 165.
3. Rieke, R.D.; Kim, S.H. J. Org. Chem. **1998**, 63, 5235.
4. Wang, L.; Zhang, Y.M. Synth. Commun. **1998**, 28, 3991.
5. Khan, R.H.; Mathur, R.K.; Ghosh, A.C. Synth. Commun. **1997**, 27, 2193.
6. Khurana, J.M.; Sehgal, A. J. Chem. Soc., Chem. Commun. **1994**, 5, 571.
7. Zhang, W.C.; Li, C.J. J. Org. Chem. **1999**, 64, 3230.
8. Li, C.J.; Meng, Y.; Yi, X.H.; Ma, J.H.; Chan, T.H. J. Org. Chem. **1998**, 63, 7498.
9. Lim, H.J.; Keum, G.; Kang, B.Y.; Chung, B.Y.; Kim, T. Tetrahedron Lett. **1998**, 39, 4367.

Received in the Netherlands March 19, 2001



## **Request Permission or Order Reprints Instantly!**

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the [U.S. Copyright Office](#) for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on [Fair Use in the Classroom](#).

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our [Website User Agreement](#) for more details.

**[Order now!](#)**

Reprints of this article can also be ordered at

<http://www.dekker.com/servlet/product/DOI/101081SCC120002400>