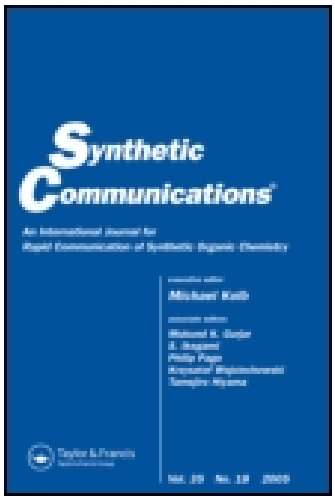

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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

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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

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

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

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

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ABSTRACT

The pinacol coupling reaction of aromatic aldehydes and ketones was performed in 8–95% yield with magnesium in 0.1 M aqueous NH_4Cl 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, Al(Hg),[1] Ln,[2] Mn,[3] Sm,[4] Te,[5] Al,[6] and Mg[7] have been used to carry out the pinacol coupling. Recently, Zn-Cu[8] or In[9] 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.

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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,[7] a suspension of benzaldehyde and magnesium turning in aqueous 0.1 M NH_4Cl 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,[7] 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_4Cl under ultrasound.

EXPERIMENTAL

Liquid substrates were purified by distillation prior to use. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer (KBr). ^{1}H NMR spectra were measured on VXR-300S spectrometer (300 or 200 MHz) by using $CDCl_3$ 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_4Cl (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 $NaHCO_3$ 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

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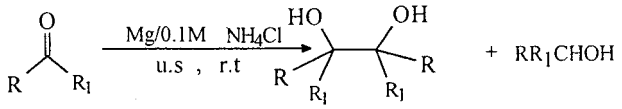

1 2 3

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: δ_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); ν_{max} (KBr): 3400–3800 cm^{-1}.

2b: δ_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); ν_{max} (KBr): 3320–3400 cm^{-1}.

2c: δ_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); ν_{max} (KBr): 3380–3420 cm^{-1}.

2d: δ_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); ν_{max} (KBr): 3260–3318 cm^{-1}.

2e: δ_H 1.79 (s, 2H, OH), 4.44 (8, dl) (2H, -*CH*-OH), 6.29 (t, 2H, -CH=C*H*-), 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); ν_{max} (KBr): 3300–3380 cm^{-1}.

2f: δ_H 2.90 (s, 2H, OH), 3.77 (s, dl) and 3.81 (s, meso) (s, 6H, OCH_3), 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); ν_{max} (KBr): 3300–3380 cm^{-1}.

2g: δ_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); ν_{max} (KBr): 3240–3300 cm^{-1}.

2h: δ_H 2.29 (s, 6H, CH_3), 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); ν_{max} (KBr) 3280–3450 cm^{-1}.

2i: δ_H 2.20 (s, 2H, OH), 4.57 (s, 2H, phCH-), 5.92 (s, 4H, CH_2), 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); ν_{max} (KBr): 3450–3490 cm^{-1}.

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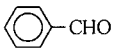
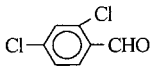
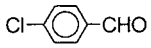
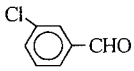
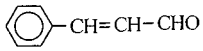
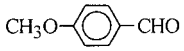
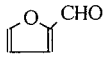
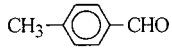
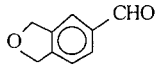
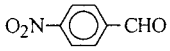
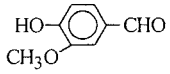
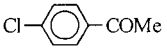
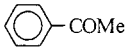
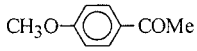
Table. Pinacol-Coupling Mediated by Mg in 0.1 M Aqueous NH_4Cl Under Ultrasound*

Entry	Substrate	Isolated yield, % (lit.[7])		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}HNMR.

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2j: δ_H 2.52 (s, 6H, CH_3), 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); ν_{max} (KBr): 3360–3450 cm^{-1}.

2n: δ_H 1.47 (s, dl) and 1.56 (s, meso) (6H, -CCH_3), 2.2 (s, 2H, OH), 3.8 (s, 6H, OCH_3), 6.7–7.3 (m, 8H, Ar), *m*/*z* (%): 302 (1), 151 (100), 135 (5), 109 (4), 77 (3), 43 (60); ν_{max} (KBr): 3200–3600 cm^{-1}.

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).

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Received in the Netherlands March 19, 2001

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