This article was downloaded by: [University Of Pittsburgh] On: 30 October 2014, At: 07:00 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

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

PINACOL COUPLING OF AROMATIC ALDEHYDES USING ALUMINIUM UNDER ULTRASOUND IRRADIATION

Yan-Jiang Bian^a, Shu-Ming Liu^a, Ji-Tai Li^a & Tong-Shuang Li^a ^a College of Chemistry and Environmental Science, Hebei University, Baoding, 071002, China

Published online: 16 Aug 2006.

To cite this article: Yan-Jiang Bian , Shu-Ming Liu , Ji-Tai Li & Tong-Shuang Li (2002) PINACOL COUPLING OF AROMATIC ALDEHYDES USING ALUMINIUM UNDER ULTRASOUND IRRADIATION, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:8, 1169-1173, DOI: <u>10.1081/SCC-120003606</u>

To link to this article: http://dx.doi.org/10.1081/SCC-120003606

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

PINACOL COUPLING OF AROMATIC ALDEHYDES USING ALUMINIUM UNDER ULTRASOUND IRRADIATION

Yan-Jiang Bian, Shu-Ming Liu, Ji-Tai Li,* and Tong-Shuang Li

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

ABSTRACT

The pinacol coupling reaction of aromatic aldehydes and ketones was carried out in 26–98% yield with Al in aqueous NaOH–MeOH under ultrasound irradiation at r.t. within 30 min.

Key Words: Pinacol coupling; Ultrasound; Aluminum reagent

Carbon–carbon bond formation is the essence of organic synthesis. One of the most powerful methods for constructing carbon–carbon bond is the pinacol coupling of aromatic aldehydes and ketones. In the last several years, various metals such as Zn,¹ Mn,² Ln,³ Sm,⁴ and Mg⁵ have been developed to mediate the pinacol coupling reaction. Recently, the pinacol coupling of aromatic aldehydes and ketones has been reported to produce 1,2-diols using Al^{6,7} in the presence of potassium hydroxide. However, the base reagent used is much more excessive (substrate/base = 1/9, mole ratio), which will lead to economical and environmental concerns.

1169

Copyright © 2002 by Marcel Dekker, Inc.

www.dekker.com

^{*}Corresponding author. E-mail: orgsyn@mail.hbu.edu.cn

Ultrasound has increasingly been used in organic synthesis.^{8,9} Many metal-involved organic reactions have been accelerated under ultrasound. Recently, we reported that ultrasonic irradiation could promote the pinacol coupling of aromatic aldehydes and ketones by using Zn–ZnCl₂¹⁰ and Mg–NH₄Cl.¹¹ This prompted us to study the possibility of pinacol coupling aromatic aldehydes and ketones with Al using a small amount of sodium hydroxide under ultrasound. Herein, we report the results of pinacol coupling of aromatic aldehydes and ketones with Al in aqueous NaOH–MeOH under ultrasound.

As shown in table and scheme, the coupling of aromatic aldehydes gives pinacols in good yield using the Al–NaOH–MeOH system under ultrasound. The data in the table show that ultrasonic irradiation is a highly chemoselective method. For example, benzaldehyde (1a), *p*-methoxy benzaldehyde (1e) and *p*-methyl benzaldehyde (1g) were reacted with aluminium in aqueous NaOH–MeOH. The corresponding pinacolcoupling products were obtained in 91% (2a), 89% (2e) and 88% (2g) yield respectively, and 3-chlorobenzaldehyde (1d) and 4-chlorobenzaldehyde (1c) gave nearly quantitative yields of 1,2-diols (2d, 2c). The steric hindrance around the carbonyl group may inhibit the coupling reaction, for 2,4-dichlorobenzaldehyde gives only 61% pinacol. When aromatic ketones such as *p*-methoxyacetophenone and *p*-chloroacetophenone were used as substrates, fewer pinacols (2) and more alcohols (3) were obtained. The reaction with cinnamaldehyde was unsuccessful under the same conditions.



In conclusion, we have demonstrated that the Al–NaOH–MeOH system can be used for pinacol coupling reactions of aromatic aldehydes under ultrasound irradiation. Compared with classical methods, the main advantage of the present procedure is that the base used is reduced (substrate/base = 1/3, mole ratio), thus, the environmental concerns are also improved.

1170

Table. Pinacol Coupling Mediated by Al in Aqueous NaOH–MeOH Under Ultrasound*

	Substrate	Reaction Time (min)	Isolated Yield, % (lit. ⁶)		
Entry			2	3	dl/meso
a	О-сно	20	91 (87)	5	51:49
b	сі-О-сно	30	61	0	meso
c	сі(-)-сно	20	98 (93)	0	71:29
d	СІСно	20	98	0	60:40
e	сн30-О-сно	20	89 (98)	8	54:46
f	O CHO	30	60	10	66:34
g	СН3-СНО	20	88 (91)	8	71:29
h	CHO 0	30	70	6	_
i	Cl-O-COMe	30	30	50	_
j	COMe	30	26 (89)	66	_
k	CH ₃ O-COMe	30	41	0	_

*Isolated yield based on the substrate. Ratio of dl/meso was calculated by ¹H NMR.

EXPERIMENTAL

Liquid substrates were purified by distillation prior to use. Melting points were uncorrected. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer (KBr). ¹H NMR spectra were measured on a VXR-300S spectrometer (300 MHz) by using CDCl₃ 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 the water bath was controlled by addition or removal of water.

General Procedure

A 100 ml Pyrex flask was charged with the desired aldehydes or ketone (1, 1 mmol), Al powder (0.1 g, 3.7 mmol), 10% aqueous NaOH (1.5 ml), and methanol (3 ml). The mixture was irradiated in the water bath of an ultrasonic cleaner at room temperature for 20–30 min. 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 NaHCO₃ 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 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: $\delta_{\rm H}$ 2.30 (s, 2H, OH), 4.71 (s, dl) and 4.83 (s, meso) (2H, phCH-), 7.11–7.32 (m, 10H, Ar); m/z (%): 214 (1), 180 (7.6), 167 (12.5), 149 (6.0), 107 (93.8), 79 (100), 77 (73.8); $v_{\rm max}$ (KBr): 3400–3480 cm⁻¹.

2b: $\delta_{\rm H}$ 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); $v_{\rm max}$ (KBr): 3320–3400 cm⁻¹.

2c: $\delta_{\rm H}$ 2.32 (s, 2H, OH), 4.63 (s, dl) and 4.85 (s, meso) (2H, phCH-), 7.02–7.32 (m, 8H, Ar); *m*/*z* (%): 282 (10), 235 (12), 165 (5.5), 141 (100), 107 (19), 77 (10); $v_{\rm max}$ (KBr): 3380–3420 cm⁻¹.

2d: $\delta_{\rm H}$ 2.33 (s, 2H, OH), 4.55 (s, dl) and 4.71 (s, meso) (2H, phCH-), 7.07–7.21 (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); $v_{\rm max}$ (KBr): 3260–3318 cm⁻¹.

2e: $\delta_{\rm H}$ 2.00 (s, 2H, OH), 3.76 (s, dl) and 3.80 (s, meso) (s, 6H, OCH₃), 4.64 (s, dl) and 4.74 (s, meso) (2H, phCH-), 6.74–7.26 (m, 8H, Ar); *m/z* (%): 274 (1), 256 (2), 227 (30), 137 (100), 109 (9), 77 (8); v_{max} (KBr): 3300–3380 cm⁻¹.

2f: $\delta_{\rm H}$ 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); v_{max} (KBr): 3240–3300 cm⁻¹.

2g: $\delta_{\rm H}$ 2.31 (s, 6H, CH₃), 2.51 (s, 2H, OH), 4.67 (s, dl) and 4.75 (s, meso) (2H, -CH-OH), 7.04–7.26 (m, 8H, Ar); m/z (%): 242 (1), 195 (6), 121 (100), 107 (12), 93 (19), 77 (13); $v_{\rm max}$ (KBr): 3280–3450 cm⁻¹.

PINACOL COUPLING OF AROMATIC ALDEHYDES

2h: $\delta_{\rm H}$ 2.20 (s, 2H, OH), 4.57 (s, 2H, phCH-), 5.92 (s, 4H, CH₂) 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); $v_{\rm max}$ (KBr): 3450–3490 cm⁻¹.

2k: $\delta_{\rm H}$ 1.47 (s, dl) and 1.56 (s, meso) (6H, -CCH₃), 2.2 (s, 2H, OH), 3.8 (s, 6H, OCH₃), 6.7–7.3 (m, 8H, Ar), *m*/*z* (%): 302 (1), 151 (100), 135 (5), 109 (4), 77 (3), 43 (60); v_{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).

REFERENCES

- 1. Wang, L.; Sun, X.H.; Zhang, Y.M. J. Chem. Research (S) 1998, 336.
- 2. Rieke, R.D.; Kim, S.H. J. Org. Chem. 1998, 63, 5235.
- 3. Ding, Z.B.; Wu, S.H. You Ji Hua Xue 1997, 17, 165.
- 4. Wang, L.; Zhang, Y.M. Synth. Commun. 1998, 28, 3991.
- 5. Zhang, W.C.; Li, C.J. J. Org. Chem. 1999, 64, 3230.
- 6. Khurana, J.M.; Sehgal, A. J. Chem. Soc., Chem. Commun. 1994, 571.
- Khurana, J.M.; Sehgal, A.; Gogia, A.; Manian, A.; Maikap, G.C. J. Chem. Soc., Perkin Trans. 1 1996, 2213.
- Luche, J.L. Synthetic Organic Sonochemistry. Plenum press: New York, 1998.
- Li, J.T.; Zang, H.J. Hebei Daxue Xuebao (Journal of Hebei University, Natural Science Edition) 2000, 20, 96.
- 10. Zang, H.J.; Li, J.T.; Bian, Y.J.; Li, T.S. Indian J. Chem. (in press).
- 11. Li, J.T.; Bian, Y.J.; Zang, H.J.; Li, T.S. Synth. Commun. 2002, 32, 547.

Received in the Netherlands May 12, 2001

Downloaded by [University Of Pittsburgh] at 07:00 30 October 2014