

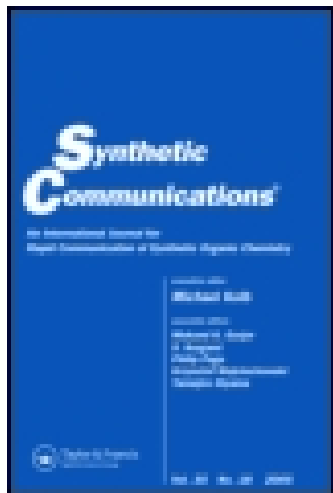
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Carbon-Carbon Bond Formation Reaction Promoted by Cadmium In Aqueous Media

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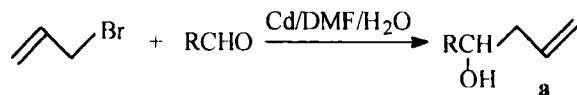
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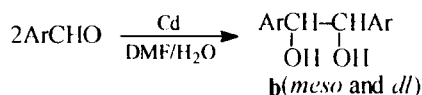
Abstract: Promoted by metallic cadmium allylic and propargyl bromides react smoothly with aldehydes in aqueous DMF to give homoallylic and homopropargyl alcohols in moderate to good yields. It can also promote pinacol coupling of aromatic aldehydes. The metallic cadmium is produced *in situ* by the reduction of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ with samarium metal.

Although organocadmium compounds were discovered in as early as 19th century, their use as synthetic reagents was initiated much later and has been largely restricted to the preparation of ketones from acid chlorides and anhydrides.¹ Also there are some reports about metallic cadmium in organic synthesis. For example, carbonyl group in many kinds of ketones could be reduced in Cd-Mg-H₂O systems.² Nitro aromatics could be selectively reduced to azoxy compounds in CdCl₂-Zn-CH₃CN system³. But to the best of our knowledge there are no reports on carbon-carbon bond formation promoted by metallic cadmium in aqueous media.

Due to the theoretical and practical interests, much enthusiasm has been devoted recently to the performing of organometallic reactions in aqueous media since Wolinsky's pioneering work in 1977.⁴ We are also engaged in the area. The choice of metals in organometallic reactions in aqueous media is quite limited, however. The metals which have been used in aqueous organometallic reactions are zinc, indium, tin and bismuth. Usually the reactions were carried out in aqueous THF solutions. We report herein that metallic cadmium can also promote an aqueous organometallic reaction of allyl and propargyl bromides with aldehydes in DMF-H₂O solutions:



The metallic cadmium we used was produced by reduction of CdCl₂ • H₂O with powdered samarium in DMF-H₂O solution in situ before allylic bromide and aldehyde were added to the reaction mixture. Also these materials could be added to DMF-H₂O solution in sequence continuously. Though the yield was not ideal when the reaction was carried out in the THF-H₂O solution (entry 1), we got satisfactory results in DMF-H₂O solutions for aromatic aldehydes (entry 2a-6a). When the ratio of H₂O to DMF was raised to 1/5 the result was almost the same with 1/10 (entry 13a and 14a). Without the presence of H₂O the yield was comparatively low (entry 12a), probably because CdCl₂ was not soluble enough in DMF to be reduced to Cd. At room temperature the reaction was relatively slow. The weak acid usually needed in the Zinc promoted reactions was not necessary in the reactions here reported. For ketones the results were not good under the same conditions and for aliphatic aldehyde the yield was low (entry 7a). It can also promote coupling reaction of aromatic aldehydes to pinacols, which was composed mainly of *dl* isomers. The reaction condition was almost the same with the above.

**Table.** Reaction Conditions and Yields

Entry	RCHO	RBr	Solvents (ml.)	Y(%)
1a	C ₆ H ₅ CHO	Allyl Bromide	THF/H ₂ O: 10/0.5	51
2a	C ₆ H ₅ CHO	Allyl Bromide	DMF/H ₂ O: 10/0.5	86
3a	<i>m</i> -BrC ₆ H ₄ CHO	Allyl Bromide	DMF/H ₂ O: 10/0.5	85
4a	<i>p</i> -ClC ₆ H ₄ CHO	Allyl Bromide	DMF/H ₂ O: 10/0.5	78
5a	<i>p</i> -CH ₃ C ₆ H ₄ CHO	Allyl Bromide	DMF/H ₂ O: 10/0.5	80
6a	2,4-Cl ₂ C ₆ H ₃ CHO	Allyl Bromide	DMF/H ₂ O: 10/0.5	75
7a	CH ₃ (CH ₂) ₃ CHO	Allyl Bromide	DMF/H ₂ O: 10/0.5	50
8a	<i>m</i> -BrC ₆ H ₄ CHO	3-Bromocyclohexene	DMF/H ₂ O: 10/0.5	79
9a	<i>p</i> -ClC ₆ H ₄ CHO	3-Bromocyclohexene	DMF/H ₂ O: 10/0.5	76
10a	<i>m</i> -BrC ₆ H ₄ CHO	Propargyl Bromide	DMF/H ₂ O: 10/0.5	78
11a	<i>p</i> -ClC ₆ H ₄ CHO	Propargyl Bromide	DMF/H ₂ O: 10/0.5	74
12a	C ₆ H ₅ CHO	Allyl Bromide	DMF: 10	62
13a	C ₆ H ₅ CHO	Allyl Bromide	DMF/H ₂ O: 10/1	84
14a	C ₆ H ₅ CHO	Allyl Bromide	DMF/H ₂ O: 10/2	76
1b	C ₆ H ₅ CHO		DMF/H ₂ O: 10/0.5	81*
2b	<i>m</i> -BrC ₆ H ₄ CHO		DMF/H ₂ O: 10/0.5	72*
3b	<i>o</i> -BrC ₆ H ₄ CHO		DMF/H ₂ O: 10/0.5	70*

* The ratio of *meso:dl*: 1b 22/78, 2b 31/69, 3b 11/89(from NMR).

Experimental

¹H NMR spectra were recorded in CCl₄ on Bruker AC-80 spectrometer using TMS as internal standard. IR spectra were obtained on a P-E 683 spectrometer (neat).

The general procedure is as follows. In a round bottomed flask fitted with a reflux condenser, and in N₂ atmosphere, were placed 3 mmol CdCl₂ • H₂O, 3 mmol Sm powder, 10 mL DMF, 0.5 mL H₂O, 2 mmol aldehyde and 3–4 mmol allylic bromide. The mixture was stirred first at the room temperature for 5h, then at 50 ° C for another 12h. The solution was cooled down to room temperature and

extracted with ether (30mL × 2) after brine (10mL) and a little dilute hydrochloric acid were added. The organic layer was dried (MgSO₄) and solvents evaporated in vacuo. The product was separated from the residue through preparative TLC (silica gel) with petroleum ether / ether as eluent.

1-Phenyl-3-buten-1-ol: [M⁺] m/z: 148(C₁₀H₁₂O); ¹H NMR: 2.27(t, 2H, J=6.4Hz), 2.50(s, 1H, OH), 4.47(t, 1H, J=6.4Hz), 4.76-5.05(m, 2H), 5.31-5.98(m, 1H), 7.11(s, 5H); IR: 3400(br)

1-(3'-Bromophenyl)-3-buten-1-ol: [M⁺] m/z: 227(C₁₀H₁₁BrO); ¹H NMR: 2.23(t, 2H, J=6.2Hz), 3.28(s, 1H, OH), 4.38(t, 1H, J=6.2Hz), 4.72-5.01(m, 2H), 5.26-5.92(m, 1H), 6.95-7.16(m, 3H), 7.27(d, 1H, J=2Hz); IR: 3400(br)

1-(4'-Methylphenyl)-3-buten-1-ol: [M⁺] m/z: 162(C₁₁H₁₄O); ¹H NMR: 2.18(s, 3H), 2.23(t, 2H, J=6.8Hz), 3.06(s, 1H, OH), 4.35(t, 1H, J=6.8Hz), 4.68-4.97(m, 2H), 5.25-5.92(m, 1H), 6.80-7.10(m, 4H); IR: 3420(br).

1-(4'-Chlorophenyl)-3-buten-1-ol: [M⁺] m/z: 182(C₁₀H₁₁ClO); ¹H NMR: 2.25(t, 2H, J=6.2Hz), 2.87(s, 1H, OH), 4.46(t, 1H, J=6.2Hz), 4.78-5.07(m, 2H), 5.31-5.98(m, 1H), 7.00-7.28(m, 4H); IR: 3400cm⁻¹(br).

1-(2', 4'-Dichlorophenyl)-3-buten-1-ol: [M⁺] m/z: 216(C₁₀H₁₀Cl₂O); ¹H NMR: 2.21(t, 2H, J=7.0Hz), 3.00(s, 1H, OH), 4.82-5.10(m, 3H), 5.40-6.06(m, 1H), 7.03-7.40(m, 4H); IR: 3400cm⁻¹(br).

1-Decen-4-ol: [M⁺] m/z: 156(C₁₀H₂₀O); ¹H NMR: 0.83(t, 3H, J=5Hz), 1.17-1.76(m, 8H), 2.00-2.37(m, 4H), 3.00(s, 1H, OH), 3.43-3.68(m, 1H), 4.80-5.20(m,

Acknowledgements

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