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Indium Mediated Pinacol Coupling Reaction of Aromatic Aldehydes in Aqueous Media

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Abstract

The carbon-carbon bond formation reaction of aromatic carbonyl compounds was performed with indium in neutral aqueous media using sonication affording the corresponding diols in moderate to good yields.

Keywords: Coupling reactions ; Diols ; Indium and compounds ; Water, reactions in

Organic reactions in water or aqueous media have attracted increasing interest currently because of environmental issues and understanding biochemical processes.[1-2] The recent development of an aqueous organometallic chemistry has turned considerable attention to indium due to its exceptional stability to air and water compared to other metals.[3-4] In fact indium was found to work effectively for allylation of aldehydes and ketones,[5-7] a reductive coupling of aldimines,[8] Reformatsky and aldol reactions,[9] allenylation of aldehydes,[10] and ring expansion of carbocycles[11] in aqueous conditions without inert atmosphere. Since indium has special properties in water, the application of indium for other carbon-carbon bond formation reaction in aqueous media will be of great interest. In this paper, we wish to report first indium mediated pinacol coupling reaction of aromatic aldehydes in neutral aqueous media using sonication. Although the pinacol coupling reaction of aromatic aldehydes in aqueous media has been described in the literature, these known methods so far suffer from harsh reaction[12-13] and work-up[14] conditions, using an excess amount of metal[15] or a reducing product.[16] In a standard procedure of reductive coupling reaction, the aldehydes (0.1 g) were reacted with In powder (-100 mesh, 150 M%) in H_2O or a 1:1 mixture of H_2O and *t*-BuOH at room temperature under sonication for 8 to 22 hrs to give the corresponding 1,2-diols in moderate to good yields. The results are summarized in the **Table**. The reaction of some liquid aldehydes (Entry 1, 2, 4 and 6) was reacted in H_2O only. In the case of solid aldehydes, the reaction of solid aldehydes with indium did not work in *t*-BuOH at all and was very slow in H_2O. The reactions with aliphatic aldehydes were unsuccessful and ketones are inert to indium under these conditions. A trace amount of acids was observed and no trace of alcohols by unimolecular reduction was detected in the crude reaction mixtures. In the absence of sonic waves, the reaction occurs much more

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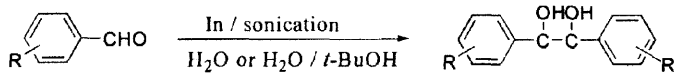
slowly and the yield of the diols is lower by a factor of 2-3. It is interesting to know that the reaction of benzaldehyde in a sealed tube or under a N_2 balloon did not proceed, probably due to the inappropriate vapor pressure. The reason for the effect of the substituents of the aromatic ring on the *dl/meso* ratio is not clear.

Table



Entry	Substrates	Conditions[a]	Time (hr)	Isolated Yield(%)[c]	Recovered SM(%)	Ratio (dl / meso)[d]
1	H	A	8	70.3	0	5 : 3
2	H	A (no sonic)	48	20.0	0	2 : 1
3	3-CH_3	B	11	57.5	20.2	2 : 1
4	4-CH_3	A	9	80.3	0	5.5 : 1
5	2-F	B[b]	10	57.8	0	1 : 2
6	4-F	A	10	50.8	0	2 : 1
7	2-Cl	B	12	50.0	2.3	4 : 1
8	3-Cl	B	12	56.5	13.7	1 : 1
9	4-Cl	B	16	83.1	3.8	1 : 1
10	4-Br	B	20	78.6	5.4	1 : 2
11	4-CF_3	B	22	82.0	1.7	1 : 2

a: Sonications were carried out at room temperature in a BRANSONIC® ultrasonic cleaner bath, which delivered a 47 kHz wave, with a fixed electrical power of 125 Watts; A: H_2O 2ml; B: H_2O/*t*-BuOH (1:1) 2ml; *b*: H_2O/*t*-BuOH (2:1) 2ml; *c:* The analytical data of the diols are all identical with those previously reported; *d*: measured by ^1H NMR Spectroscopy.

In conclusion, a very simple and convenient preparation of pinacols was achieved *via* the indium mediated carbon-carbon bond formation reaction of aromatic aldehydes in neutral aqueous media. Further study on extension of the scope of the utility of indium in aqueous media is in progress.

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