Rapid Pinacolization of Carbonyl Compounds with Aluminium–KOH

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A rapid and convenient method is reported for the quantitative pinacolization of aromatic carbonyl compounds with aluminium powder and potassium hydroxide in methanol at ambient temperature.

1,2-Diols are very useful synthons for a variety of organic synthesis.[1] The formation of 1,2-diols has been attempted using a number of reagents such as Mg–MgI_2,[2] Zn–$ZnCl_2$,[3] a number of transition metals,[4] lanthanides[4] and actinides.[4] Ti^{II} and Ti^{III} reagents have received considerable attention,[5,6] although olefin formation is a competing reaction with these reagents.[7]

We report here a very rapid procedure for the pinacolization of aromatic carbonyl compounds using inexpensive reagents, aluminium powder and potassium hydroxide. We have observed that aromatic aldehydes and ketones undergo coupling rapidly in the presence of aluminium powder and potassium hydroxide at ambient temperature in methanol [eqn. (1)]. The molar ratio of substrate : aluminium powder : potassium hydroxide varies with the carbonyl compound. The progress of the reactions was monitored by the absence of starting material by TLC. No significant change in ± : *meso* ratio was observed when the molar ratio of ArCOR : Al : KOH was increased to 1 : 3 : 9. No alcohol or carboxylic acid (due to competing Cannizaro reaction) was observed to have been formed in these reactions. Our results are shown in Table 1.

$$\mathrm{ArCOR} \xrightarrow[\text{MeOH, room temp.}]{\text{Al, KOH}} \mathrm{Ar{-}RC(OH){-}C(OH)R\,Ar} \qquad (1)$$

A mixture of products was produced in the case of 4-nitrobenzaldehyde due to competing reduction of the nitro group as observed by the reduction of nitrobenzene in an independent experiment and also with aliphatic aldehydes. No coupling of 4-chlorobenzaldehyde took place when methanol was replaced by THF, but when methanol was replaced by MeCN, a mixture containing starting aldehyde, the corresponding alcohol and the diol was obtained.

In a typical procedure benzaldehyde (0.53 g, 5 mmol) was dissolved in methanol (10 ml). Aluminium powder (0.269 g, 10 mmol) and KOH (1.68 g, 30 mmol) were added and the reaction mixture was stirred. The reaction became vigorous immediately after the addition of KOH. The reaction mixture was filtered to remove the aluminium powder and water (*ca.* 50 ml) was added to the filtrate. A white solid precipitated out which was filtered off under pressure. Some of the diol was also obtained by extracting the filtrate with CH_2Cl_2 (3 × 10 ml), drying with anhydrous $MgSO_4$ and then concentrated using a vacuum rotatory evaporator.

This method has many advantages over other methods as it is a very fast reaction. We are investigating further the application of this reagent (Al–KOH–MeOH) on a variety of carbonyl compounds and the effect of chiral additives on the stereoselectivity, as well as establishing the probable reaction pathway.

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Table 1 Coupling of carbonyl compounds with Al–KOH in methanol

	ArCOR		Reaction	Molar ratio	
Run	Ar	R	time/ min[a]	ArCOR : Al : KOH	% Yield[b] (± : *meso*[c])
1	Ph	H	5	1 : 2 : 6	87 (50 : 50)
2	4-ClC_6H_4	H	5	1 : 2 : 6	93 (48 : 52)
3	4-MeC_6H_4	H	5	1 : 3 : 9	91 (50 : 50)
4	4-$MeOC_6H_4$	H	5	1 : 2 : 6	98 (52 : 48)
5	3,4$(OMe)_2C_6H_3$	H	5	1 : 2 : 6	90 (50 : 50)
6	Ph	Me	10	1 : 3 : 9	89 (—)[d]
7	4-MeC_6H_4	Me	10	1 : 5 : 15	87 (—)[d]

[a] Monitored by complete disappearance of starting material using TLC. [b] Isolated yields; spectral data (IR, ^1H NMR) are in agreement with the structure. [c] Ratio of ± : *meso* as calculated from ^1H NMR. [d] ^1H NMR shows it to be a pure *meso*-stereoisomer.[8]

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