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Aromatic Aldehydes from Benzylbromides via Cobalt(I) Mediated Benzyl Radicals in the Presence of Aerial Oxygen: a Mild Oxidation Reaction in Neutral Condition

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Abstract : $Co(PPh_3)_3Cl$ has been shown to be a novel mediator for the conversion of benzylic bromides to aromatic aldehydes under mild conditions in the presence of aerial oxygen probably via benzylic radicals. In the absence of oxygen, the carbon-carbon coupling reactions have been utilised to afford a series of functionalised benzylic dimers. © 1998 Elsevier Science Ltd. All rights reserved.

The conversion of benzylic halides to aromatic aldehydes is an important fundamental organic reaction.[1,2] We report here for the first time, the synthesis of aromatic aldehydes from benzylbromides by $Co(I)(PPh_3)_3Cl$[3] in the presence of aerial oxygen under mild conditions (< 0 °C) where a number of functional groups or protected functional groups in the aromatic rings survive. Thus this new reaction is suitable for the synthesis of functionalised aldehydes under mild conditions from benzylic bromides.

Cobalt mediated reactions[4,5,6] have become very important in chemical and biochemical reactions (vitamin B_{12}). Cobalt (I) mediated benzylic or allylic carbon-carbon coupling reactions[7,8] have been previously shown to occur under mild conditions and has been particularly useful in the synthesis of functionalised heterocyclic dimers[8] which are difficult molecules for synthesis by other coupling reactions[4] because of the necessity of more vigorous reaction conditions intolerable for the pendant functional groups. This coupling reaction probably occurs through the benzylic or allylic radicals generated by $Co(I)(PPh_3)_3Cl$ resulting carbon-carbon bond formation. We have explored the possibility of trapping this radical, easily available under mild conditions mediated by this Co(I) complex, with molecular oxygen to form the benzylperoxyl radical favouring carbon-oxygen bond formation in contrast to carbon-carbon coupling reaction, and we have achieved the synthesis of aromatic aldehydes by this new method.

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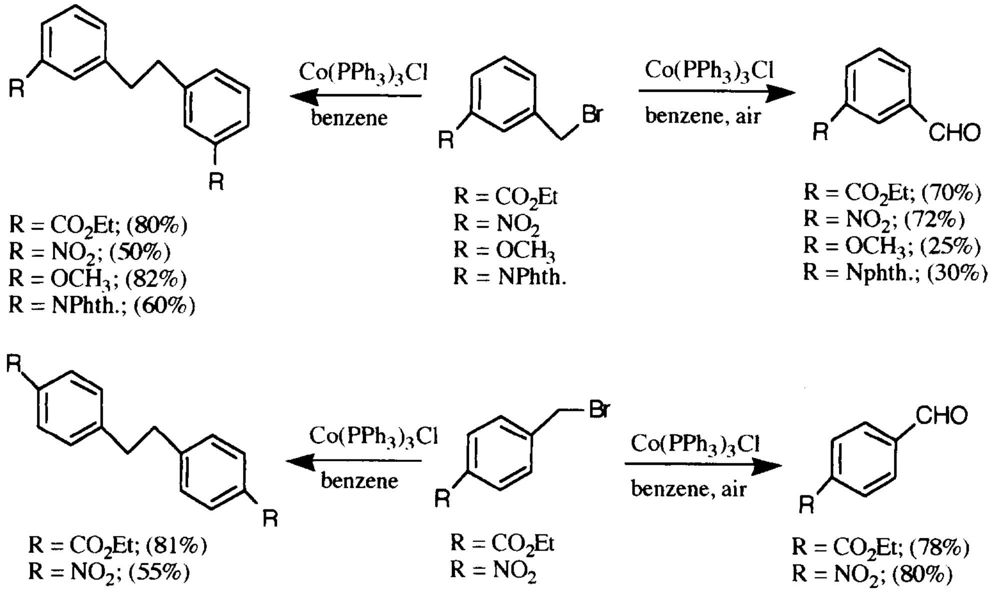
The required substituted benzylic bromides were prepared by suitable protection of carboxyl, hydroxyl or amino groups of the corresponding methyl substituted benzenes followed by NBS bromination. All the reactions were carried out in the presence of anhydrous Co(I)$(PPh_3)_3Cl$ and the substrate (1:1) in dry benzene/ethylacetate by air bubbling at 0 ° to -10 °C for 15 to 30 min. The same reaction of functionalised benzylic bromides is also shown to be useful for the carbon-carbon bond formation[7,8] by Co(I) in the absence of oxygen resulting in the convenient synthesis of a variety of functionalised benzylic dimers suitable for new functionalised spacers for molecular recognition research.[9]

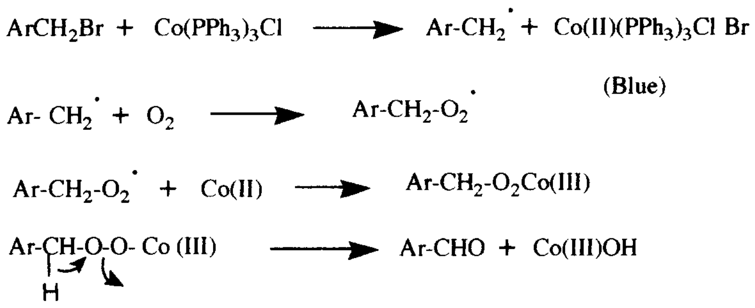


Scheme 1

A series of substituted benzyl bromides having various type of functional groups like nitro, carbethoxy, methoxy and phthalimido etc. in the benzene rings have been transformed below room temperature into the corresponding aldehydes and carbon-carbon coupled products without affecting the functional groups via Co(I) mediated reactions under the different conditions as mentioned in Scheme 1.

When the reaction was carried out under nitrogen, but not in degassed solvent, both carbon-carbon coupled products as well as a small amount of aldehyde was obtained in some cases. But when the reaction was carried out under nitrogen in carefully degassed solvent, only carbon-carbon coupled product but no aldehyde was obtained as expected. Thus the unprecedented formation of aldehydes must occur through the oxygen capture of the benzylic radical and this reaction was found to be a new general reaction of benzylic halides when carried out by $Co(I)(PPh_3)_3Cl$ in the presence of aerial oxygen. However some traces of carboxylic acids were also obtained as minor side products. In the case of benzylbromide itself an appreciable amount of benzoic acid was obtained.

The possible mechanism may be similar to the conversion of toluene to benzaldehyde by $Co(OAc)_3$. However toluene cannot be oxidised by $Co(I)(PPh_3)_3Cl$ in our method. Also benzylbromide cannot be oxidised by $Co(OAc)_2$[10] in acetic acid in the presence of oxygen and NaBr. Thus Co (I) is a specific mediator for this reaction due to the facile formation of the benzylic radical from the benzylbromides followed by oxygen capture to give the intermediate benzylperoxyl radical. This peroxy radical is captured by Co(II) which facilitates the removal of acidic hydrogen from the activated benzylic position with the cleavage of the peroxide bond to produce the aromatic aldehyde. However we are yet to obtain any definite evidence regarding the trapping of the peroxy radicals by Co(II) or for the subsequent elimination of the proton from the peroxy-cobalt species to produce the aldehydes. All the steps of this reaction occur at low temperature within a few minutes to half an hour. The change of colours from green Co (I) complex to blue Co (II) complex and finally to grey Co(III) oxide indicates the completion of the reaction. The possible mechanism[10] is suggested in Scheme 2.



Scheme 2

In conclusion, oxidation mediated by $Co(I)(PPh_3)_3Cl$ in the presence of aerial oxygen at low temperature is the first report of the synthesis of aromatic aldehydes from benzylic bromides where the functional groups or the masked functional groups survive. The combination of Co(I) complex and air makes a new and convenient oxidation of benzylic bromides to aromatic aldehydes under mild and neutral conditions. This method is highly suitable for the synthesis of aromatic aldehydes containing nitro, phthalimido and ester groups. The subsequent hydrolysis of phthalimido or ester groups in the products constitutes a useful new synthesis of the amino or carboxylic aromatic aldehydes. In our molecular recognition research, the use of the functionalised benzylic spacers, synthesised by carbon-carbon coupling reactions of the same benzylic radicals mediated by Co(I) in the absence of oxygen is in progress.

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All the products were satisfactorily characterised by ^{1}H NMR and IR data.

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