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$NaBH_4$/C: A Convenient System for Reductive Amination of Aldehydes

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ABSTRACT

In this context, $NaBH_4$ in the presence of activated charcoal has been used for thereductive aminationofa varietyof aldehydes withanilines. The reductive amination reactions have been performed within 60-100 min in THFunder reflux conditionsin high to excellent yields of products (85-90%).

Key words: $NaBH_4$, Charcoal, Reductive amination, Aldehydes, Amines

INTRODUCTION

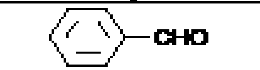
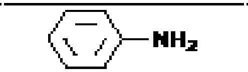
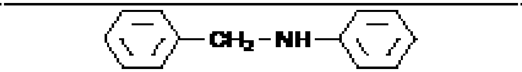
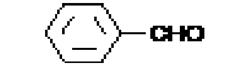
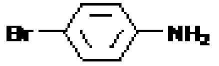
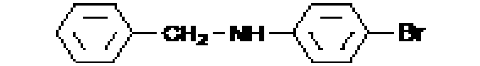
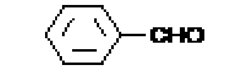
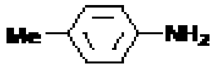
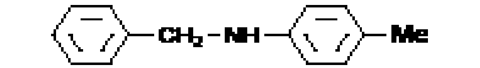
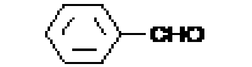
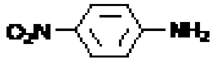
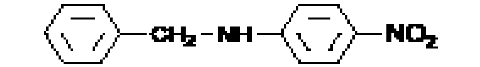
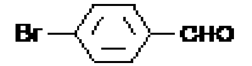
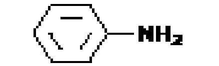
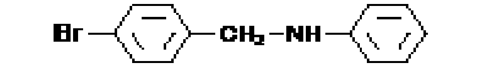
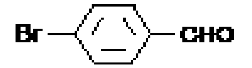
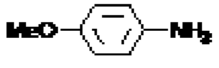
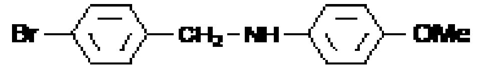
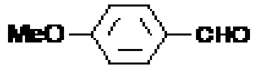
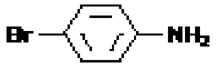
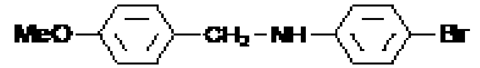
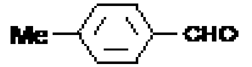
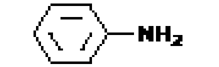
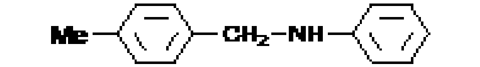
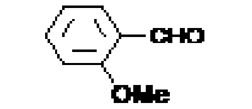
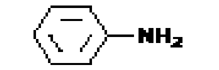
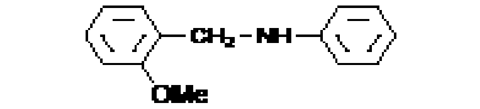
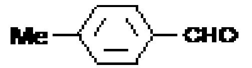
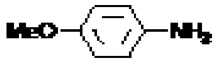
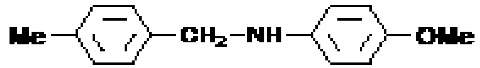
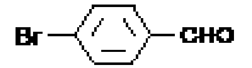
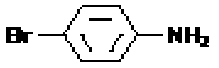
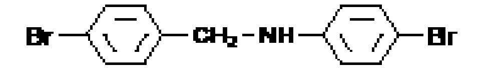
The reductive aminationreaction is a suitable procedure for the preparation of amines from their corresponding of aldehydes. Because, other approaches such as: the reduction of nitro, cyano, azide, carboxamide compounds or the alkylation of amines are often problemssuch as: harsh reaction conditions, overalkylation, low chemical selectivity and generally poor yields. The reductive aminationreactionhas been carried out by sodium borohydridewith different reducing system[1-15].But, in continuing our efforts for the development of new reducing systems [16-28],in this context, we have reported the reductive amination reaction of aldehydes with anilines by $NaBH_4$/C system in THF.

RESULTS AND DISCUSSIONS

In the past, we have distributed some application of activated charcoal as catalyst in different reducing system such as: $NaBH_4$/C for the reduction of carbonyl compounds[27]and the reduction of nitro arenes[28].Recently, we have reported $Zn(BH_4)_2$/C is an efficient reducing system for the reduction of carbonyl compounds[20]. Here in, we have used $NaBH_4$/C as convenient system for reductive amination of aldehydes with anilines.

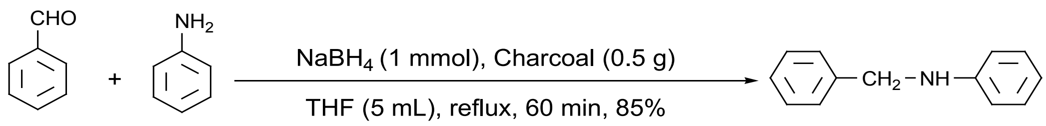
For this goal, the model reaction has been performed by reductive amination of benzaldehydeand aniline. This reaction was carried outwith different molar ratio of the benzaldehyde/ aniline/charcoal/$NaBH_4$in different solvents for the

Table 1. Reductive Amination of Aldehydes (1 mmol) with Anilines (1 mmol) by $NaBH_4$ (1 mmol) in the presence of charcoal (0.5 g) in THF (5 mL) under reflux conditions

Entry	Aldehydes	Anilines	Products	Time/min	Yield[a]/%
1				60	85
2				60	88
3				60	90
4				65	88
5				60	88
6				90	90
7				100	85
8				100	87
9				100	85
10				70	90
11				60	90

[a]Yields refer to isolated pure products (±5%).

optimazition reaction conditions. Our experiments have been shown that using 0.5 gof activated charcoalin THF (5 mL) under reflux conditions is the best conditions to complete the reductive amination of benzaldehye (1 mmol) and aniline (1 mmol) to *N*-benzylaniline. The reductive aminationwas completed within 60 min with 85% yields of product as shown in scheme 1.



Scheme 1

The various structurally different aldehydes and anilines have been used by this reducing system.Experiments have been shown the correspondingsecondary amines were obtained in excellent yields (85-90%) within 60-100 min(Table 1); therefore the efficiency of this protocol was further examined for the reductive amination of aldehydes. The influence of activated charcoal is not clear but we have reported [26-27] sodium borohydride is slowly decomposed by activated charcoal. Consequently, it is liberated hydrogen gas *in situ*. Thus, the generated molecular hydrogen accelerate the reduction reaction.

EXPERIMENTAL

The products were characterized by their ^{1}H NMR (400 MHzBruker)or IR (PerkinElmer FT-IR RXI) and comparison with authentic samples (melting or boiling points). TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

Reductive amination of banzaldehyde and aniline with $NaBH_4$/Charcoal system (typical procedure)

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of benzaldehyde (0.106 g, 1 mmol), aniline (0.093 g, 1 mmol) and activated charcoal(0.5 g) was preparedin THF (5 mL). Then the $NaBH_4$ (0.036 g, 1 mmol) was added to the reaction mixture and stirred under reflux conditions. TLC monitored the progress of the reaction (eluent; CCl_4/Ether: 5/2). The reaction was filtered after completion within 60 min. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (eluent; CCl_4/Ether: 5/2) afforded the *N*-benzylaniline (0.l53 g, 85% yield, Table 1, entry 1).

CONCLUSION

In this research, we have shown that the $NaBH_4$/charcoalis convenient system for the reductive amination of a variety of aldehydes and anilines to their corresponding secondary amines. The reduction reactions were accomplished with $NaBH_4$ (1 mmol) and activated charcoal (0.5 g) in THFunder reflux conditions.High efficiency of the reduction reactions and easy work-up procedure makes as an attractive new protocol for reductive amination of aldehydes.

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