

REDUCTIVE AMINATION OF CARBONYL COMPOUNDS USING LIGNIN SULFONIC ACID AS CATALYST AND BOROHYDRIDE EXCHANGE RESIN

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Abstract : An efficient and mild method for reductive amination of a variety of aldehydes with amines in presence of lignin sulphonic acid as catalyst and borohydride exchange resin at room temperature was explored. Borohydride exchange resin was utilized successfully for the reductive amination of saturated as well as unsaturated aldehydes.

Key words: amination, lignin sulphonic acid, Borohydride exchange resin

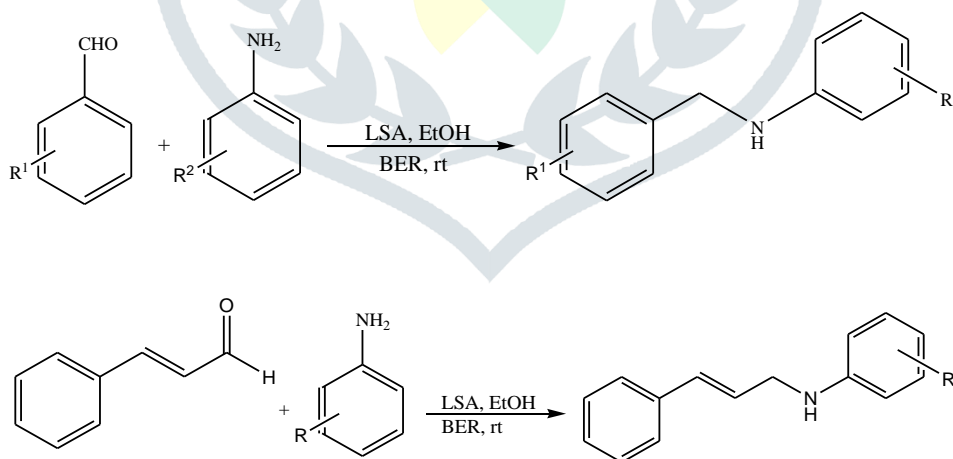
I. INTRODUCTION

The selective reduction of functional groups is a common need in organic synthesis. Polymer supported borohydride exchange resin (BER) was first synthesized by Gibson and Baily.¹ They reported BER as a reducing agent for the reduction of benzaldehyde to benzyl alcohol. BER has several advantages over other polymer supported reagents.² As compared to sodium borohydride, BER is highly stable and easy to handle.³

A number of reagents⁴ were developed for the selective reduction of carbonyl compounds to the corresponding products. These reagents used have some disadvantages like complex reaction work up, low yields, etc. BER was extensively used in the reduction of carbonyl compounds in alcohol solvents.⁵ Aromatic as well as aliphatic aldehydes and ketones reduced using BER as a reducing agent. Selective reduction of α,β -unsaturated aldehydes and ketones was done using BER.^{5b}

Several reducing systems were developed using BER in combination with catalysts such as phenyl disulfide,⁶ 2,4 Ionene,⁷ Et₃NHCl,³ NiCl₂·6H₂O.⁸ BER reduces conjugated ethylenic linkage selectively.⁹ It was used as reducing agent for the reduction of conjugated acid chlorides,¹⁰ aryl and sulfonyl,^{5c} benzonitriles,¹¹ oximes,¹² alkynes,¹³ nitroso amines,¹⁴ selenium.¹⁵ BER as a mild, efficient and selective reducing agent than NaBH₄ for the reduction of carbonyl compounds without being reduction of α, β -unsaturation was reported.

In the present work, we herein report the application of BER as a mild and selective reducing agent for the reductive amination of aldehydes I with amines II using lignin sulphonic acid in ethanol at room temperature. (Scheme 1)



Scheme 1

II. EXPERIMENTAL PROCEDURE

I. Preparation of Borohydride exchange resin (BER)

To 5 g of resin (Amberlyte IRA-400) 100 mL of 10% HCl was added and the contents were kept overnight. The resin was transferred into 500 mL beaker and washed with distilled water 4-5 times, filtered and wet resin was obtained (the filtrate was checked with AgNO₃). To this resin NaBH₄ (1 g) was added in distilled water (80 mL) and kept overnight. Water was removed from the beaker 3-4 times, further washed 2-3 times till it is free from excess of NaBH₄. After washings and testing with HCl, it is dried in vacuum oven at 65 °C for five hours.

II. General procedure

Aromatic aldehyde (1 mmol), aniline (1 mmol) and catalyst lignin sulphonic acid in solvent ethanol (5 mL) were stirred at room temperature for about 10 minutes. Sodium borohydride exchange resin (2 mmol) was then added to the reaction mixture and stirring was continued. After completion of the reaction as judged by TLC, the contents of flask were filtered, washed with dichloromethane (2 x 15 mL), evaporated and concentrated. The solid obtained was then purified by column chromatography (petroleum ether : ethylacetate = 9:1 V/V).

III. RESULTS AND DISCUSSION

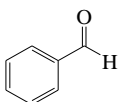
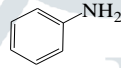
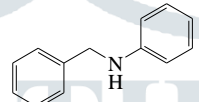
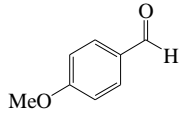
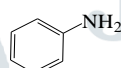
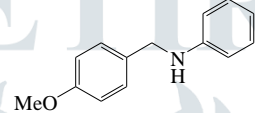
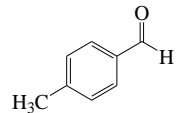
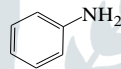
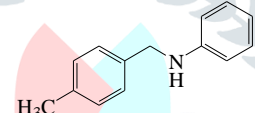
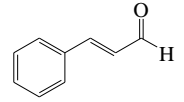
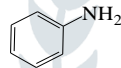

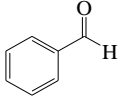
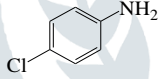
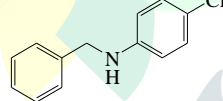
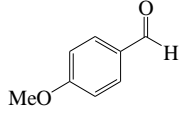
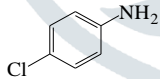
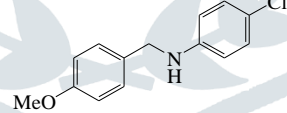
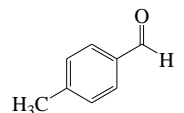
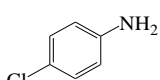
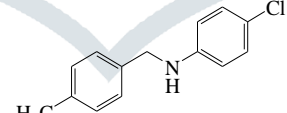
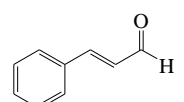
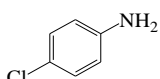
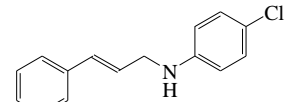
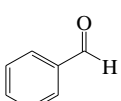
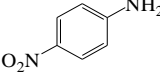
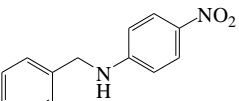
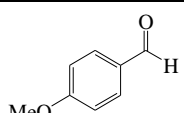
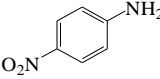
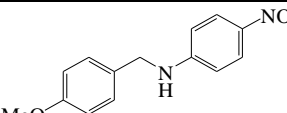
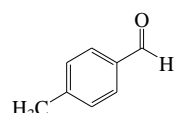
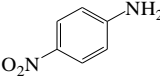
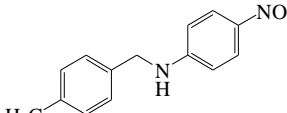
The reductive amination of a variety of aldehydes by lignin sulphonic acid as catalyst with a mild reducing agent BER was studied. The results are summarized in Table 1. It was observed that the aromatic aldehydes having different substituents underwent the reduction in 2-2.5 h. affording the corresponding amines in good yields.

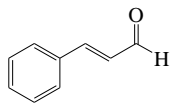
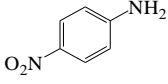
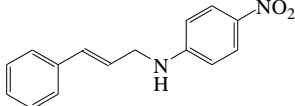
Entries (4, 8, 12) clearly demonstrate that the olefinic functionality is stable to the present experimental conditions. Thus as compared to NaBH₄, BER was found to be specific reagent for the α , β -unsaturated aldehyde.

IV. CONCLUSION

An efficient method for the reductive amination of carbonyl compounds using lignin sulfonic acid as a catalyst and BER as mild reducing agent with different amines has been reported. BER was found to be an interesting chemoselective reducing agent for carbonyl compounds especially for α , β -unsaturated aldehyde which was sensitive to NaBH₄.

Table 1 : Reductive amination of carbonyl compounds using LSA and BER

Entry	Aldehyde	Amine	Product	Time (h)	Isolated yield (%)
1				2	90
2				2.5	89
3				2.5	88
4				2.5	90
5				2	91
6				2.5	88
7				2	91
8				2	90
9				2	92
10				2.5	89
11				2	91

12				2	92
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