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Synthesis of *N*-citralbenzenamines by $NaBH_4/B(OH)_3$System

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ABSTRACT

Citral as α, β-unsaturated carbonyl compound has been reacted with structurally different anilines with sodium borohydride in the presence of boric acid for the synthesis of their corresponding *N*-citralbenzenamineswith good yields (75-85%)within 5 min in CH_3CNat room temperature.

Key words: $NaBH_4$, $B(OH)_3$, Citral, *N*-citralbenzenamines.

INTRODUCTION

Reduction of α, β-unsaturated carbonyl compounds can follow two pathways: addition to carbonyl group (1,2-reduction) to give allylicproducts or addition to the conjugated double bond (1,4-reduction) to give saturated carbonyl compounds. $NaBH_4$ (common reducing agent) uses for the 1,2-reduction of conjugated carbonyl compounds under different reducing system[1-9]. On the other hands, in the synthetic project we needed some *N*-citralbenzenamines.Also, recently we reported a convenient system for direct reductive amination of aldehydes by $NaBH_4/B(OH)_3$ system[10]. Therefore we decide to use of this reducing system for the synthesis of *N*-citralbenzenamines with this hope,the reductive amination of citralas an α, β-unsaturated carbonyl compoundfollow addition to carbonyl group (1, 2-addition) to give the corresponding α, β-unsaturated*N*-benzenamines.

RESULTS AND DISCUSSIONS

We have done the reductive amination reactions based on the optimized reaction that has been reported in the literature [7]. These reactions were carried out with molar ratio of citral (1 mmol), anilines (1 mmol), $B(OH)_3$ (1 mmol) and $NaBH_4$ (1 mmol) in CH_3CN (3 mL) at room temperature. The reactionswere completed within 5 min with 75-85% yields of product as shown in scheme 1. In this reactions *N*-(3,7-dimethylocta-2,6-dienyl) benzenamines (*N*-citralbenzenamines) as major products have been produced more than

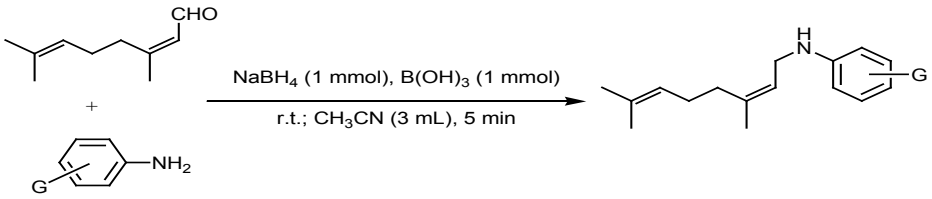
75%;butgeraniol and unreacted anlinesas by-products less than 15%.

EXPERIMENTAL

The products were characterized by their ^{1}H NMR (400 MHz Bruker) 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 citral and aniline with $NaBH_4/Al(OH)_3$, A typical procedure

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of citral (0.152 g, 1 mmol), aniline (0.093 g, 1 mmol) and $Al(OH)_3$ (0.078, 1 mmol) in CH_3CN (3 mL) was prepared. The resulting mixture was stirred for 5 min at room temperature. Then the $NaBH_4$ (0.036 g, 1 mmol) was added to the reaction mixture and stirred at room temperature. TLC monitored the progress of the reaction (eluent; CCl_4/Ether: 5/2). The reaction was



G: H (85%), 4-Br (80%), 4-Me (80%), 2-MeO (75%), 4-MeO (80%), 4-NO_2 (75%)

Scheme 1:

filtered after completion within 5 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*-(3,7-dimethylocta-2,6-dienyl)benzenamine(0.l95 g, 85%).

CONCLUSION

In this investigation, we have shown that the combination reducing system of $NaBH_4/B(OH)_3$ in CH_3CN can be used for reductive amination of citral with a variety of anilines to their corresponding *N*-citralbenzenaminesin good yields (75-80%) within 5 min at room temperature. Reduction reactions were carried out with 1 molar equivalents of $NaBH_4$ in the presence of 1molar amounts of $B(OH)_3$.

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