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MONTMORILLONITE-IMPREGNATED SAMARIUM-MEDIATED REDUCTION OF AROMATIC NITRO COMPOUNDS TO AROMATIC AMINES

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Abstract
Montmorillonite-impregnated with samarium metal-induced reaction of commercially available aromatic and heteroaromatic nitro compounds produced corresponding amino compounds in excellent yield. This method for the preparation of amines is very effective in a small to medium scale reaction.

Key words
Montmorillonite, Samarium, Aromatic amine, Reduction

Introduction

Surface-mediated reactions have received significant attention [1]. Montmorillonite clay has found to be suitable in many studies [2]. Perhaps aromatic and heteroaromatic amines are most versatile organic compounds for research and development purposes. Therefore, many methods are known for the preparation of amino compounds starting from aromatic and heteroaromatic nitro compounds [3]. This subject is so commendable that these methods are described in text books.

Our previous results described samarium metal and indium metal-induced reduction of aromatic nitro compounds [3, 4]. In continuation of our study, we report here a convenient study of montmorillonite impregnated samarium-induced reduction of aromatic and heteroaromatic nitro compounds to aromatic amines.

Results and Discussions

Our research on aromatic amines has resulted in a few derivatives that have demonstrated anticancer activities [3, 4, 5]. Therefore, we have explored numerous possibilities to obtain diverse aromatic amines following different methods. In our earlier studies, we demonstrated surface mediated efficient aromatic nitration and reduction of the aromatic nitro derivatives to aromatic amines. We develop a simple method for the reduction of aromatic nitro compounds to aromatic amines by combining these approaches.

Samarium metal is used in the presence of different Lewis acids for the preparation of numerous compounds. We found that samarium metal impregnated with montmorillonite is an effective reagent combination for the reduction of nitro compounds. The results are given in Table 1.

Table 1: Montmorillonite-impregnate samarium metal-induced reduction of nitro compounds

Entry	Starting Compounds	Products	Yield (%)
1	4-Methoxynitrobenzene	4-Methoxyaniline	90
2	4-Methylnitrobenzene	4-Methylaniline	88
3	2-Methoxynitrobenzene	2-Methoxyaniline	85
4	2-Methylnitrobenzene	4-Methylaniline	88
5	2,4-Dimethoxynitrobenzene	2,4-Dimethoxyaniline	85
6	1-Nitronaphthalene	1-Aminonaphthalene	85
7	2-Nitronaphthalene	2-Aminonaphthalene	85
8	1-Nitroanthracene	1-Aminoanthracene	85
9	3-Nitropyridine	3-Aminopyridine	50
10	2-Nitrofuran	2-Aminopyridine	75
11	2-Nitrothiophene	2-Aminothiophene	75

As can be seen from the above table, commercially available important aromatic nitro compounds with methoxy and methyl substituents afforded the products in excellent yield. However, the reaction became sluggish when chloro, bromo, iodo, and cyano groups are present along with the nitro group in the same molecule. The compounds described herein have been used for the synthesis of useful heterocyclic compounds [6].

Experimental

The reaction was conducted using nitro compound (1.0 mmol), montmorillonite (1 g) and samarium metal (50 mg) in THF (1 mL) as the solvent. These reagents and reactants are mixed thoroughly. The solvent was then evaporated under reduced pressure and dried in a high vacuum pump for 10 min. The mixture was then washed three times with dichloromethane (10 mL) and filtered through a filter paper. The pure product was isolated on evaporation of the solvent (filtrate) and crystallization. The products are all known and commercially available. These were compared with authentic samples with respect to physical and spectroscopy data.

Conclusion

Synthesis of aromatic and heteroaromatic amines by montmorillonite-impregnated samarium metal-induced reaction was accomplished in excellent yield.

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