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ULTRASOUND-INDUCED MONTMORILLONITE-IMPREGNATED BISMUTH NITRATE-MEDIATED AROMATIC NITRATION

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Abstract
Ultrasound-induced montmorillonite-impregnated with bismuth nitrate-mediated reaction of aromatics produces aromatic nitro compounds in excellent yield. This method for the preparation of aromatic nitro compounds is very effective in a small to medium scale reaction.

Key words
Ultrasound, Montmorillonite, Bismuth Nitrate Aromatic Nitration

Introduction

Aromatic nitration of benzene and heterocycle derivatives has been extensively used for the synthesis of functionalized aromatic compounds. The most common method for the aromatic nitration is nitric acid-mediated reaction [1]. Our studies on aromatic nitration have culminated in bismuth nitrate-induced reaction under classical conditions. It was found that the yield of the nitro compound depends on the dry conditions of the reaction mixture [2]. As an extension of this method, we have developed a simple procedure for the aromatic nitration mediated by ultrasound. Ultrasound-mediated montmorillonite clay-impregnated bismuth nitrate is an ideal reagent combination for aromatic nitration in wet conditions. Therefore, high vacuum drying of the reaction mixture is not necessary to yield the products in excellent yield.

Results and Discussions

Nitric acid or nitric acid-sulfuric acid mixture-mediated aromatic nitration is extremely hazardous [2]. This reaction can cause serious accident. Nitronium tetrafluoborate is an excellent reagent. However, the toxicity and associated hazards of this reagent is also very high. To overcome the limitation, we reported surface-mediated efficient nitration of aromatic compounds with bismuth nitrate [3]. The success of this reaction depends on extremely dry conditions. If the reaction mixture is not dried with high vacuum pump, the yield of the products becomes low to medium. The reasons for the low yield under these conditions are not known. On the basis of this observation and to overcome this limitation,

we have conducted ultrasound-mediated montmorillonite clay-impregnated bismuth nitrate-induced aromatic nitration in wet conditions and identified products in excellent yield [4]. This reaction requires 10-30 minutes for completion. Aromatic hydrocarbons, ethers, phenols and heterocycles were nitrated under these conditions effectively (Table 1).

Table 1: Ultrasound-Induced Montmorillonite-impregnate Bismuth Nitrate-Mediated Aromatic Nitration

Entry	Starting Compounds	Products	Yield (%)	Time (min)
1	Anisole	4-Nitroanisole and 2-Nitroanisole (4:1)	90	10
2	Naphthalene	1-Nitronaphthalene	88	20
3	Anthracene	9-Nitroanthracene	85	20
4	Chrysene	6-Nitrochrysene	88	30
5	Phenanthrene	9-Nitrophenanthrene	85	25
6	Fluorene	2-Nitrofluorene	90	15
7	Phenol	4-Nitrophenol and 2-Nitrophenol (4:1)	85	10
8	2-Naphthol	1,6-Dinitro-2-naphthol	85	15
9	Pyridine	3-Nitropyridine	40	15
10	Furan	2-Nitrofuran	50	15
11	Thiophene	2-Nitrothiophene	75	15

Table 1 suggests that nitration works well with high yield through ultrasonic exposure. An excellent regioselectivity with diverse aromatic compounds is also observed. The reaction produces a mixture of products with reactive substrates (phenols) as expected. Notable, some less reactive aromatic compounds (chrysene) can also be nitrated following this method.

Experimental

The reaction was conducted using aromatic starting compound (1.0 mmol), montmorillonite (1 g) and bismuth nitrate pentahydrate (1.5 mmol) in THF (1 mL) as the solvent. These reagents and reactants are then sonicated at room temperature for 10 min to 30 min. The solvent was then evaporated. The reaction mixture was filtered and it was washed with THF (10 mL). The filtrate was evaporated and the solid reside was crystallized from diethylether. The compounds reported herein are all known and available from different vendors. Furthermore, these were characterized by comparison with the available physical and spectroscopy data of authentic samples.

Conclusion

A simple preparation of aromatic nitro compounds by ultrasound-induced montmorillonite-impregnated bismuth nitrate-mediated reaction was performed without drying the reactants and using undistilled solvent. These nitro derivatives are precursors of several organic heterocyclic compounds that are reported from our laboratory [5]. This method is simple since it can be applied to any research laboratory where facilities are not adequate.

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