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**MICROWAVE-INDUCED BISMUTH NITRATE-MEDIATED SELECTIVE
HYDROLYSIS OF AMIDE**

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Abstract: Microwave-induced selective hydrolysis of amide to the corresponding amine has been achieved with bismuth nitrate and montmorillonite KSF clay.

Keywords: Microwave, Clay, Bismuth nitrate

Introduction:

Bismuth nitrate has received extensive recognitions in organic synthesis. Several reactions can be performed using this reagent. The role of bismuth nitrate can be manipulated by the proper selection of the reactions and conditions. This salt is well-tolerated in microwave-induced reactions alone or in the presence of clay. We describe a simple selective hydrolysis of amide to the corresponding amine with bismuth nitrate/montmorillonite KSF clay using microwave-induced reaction.

Results and Discussion:

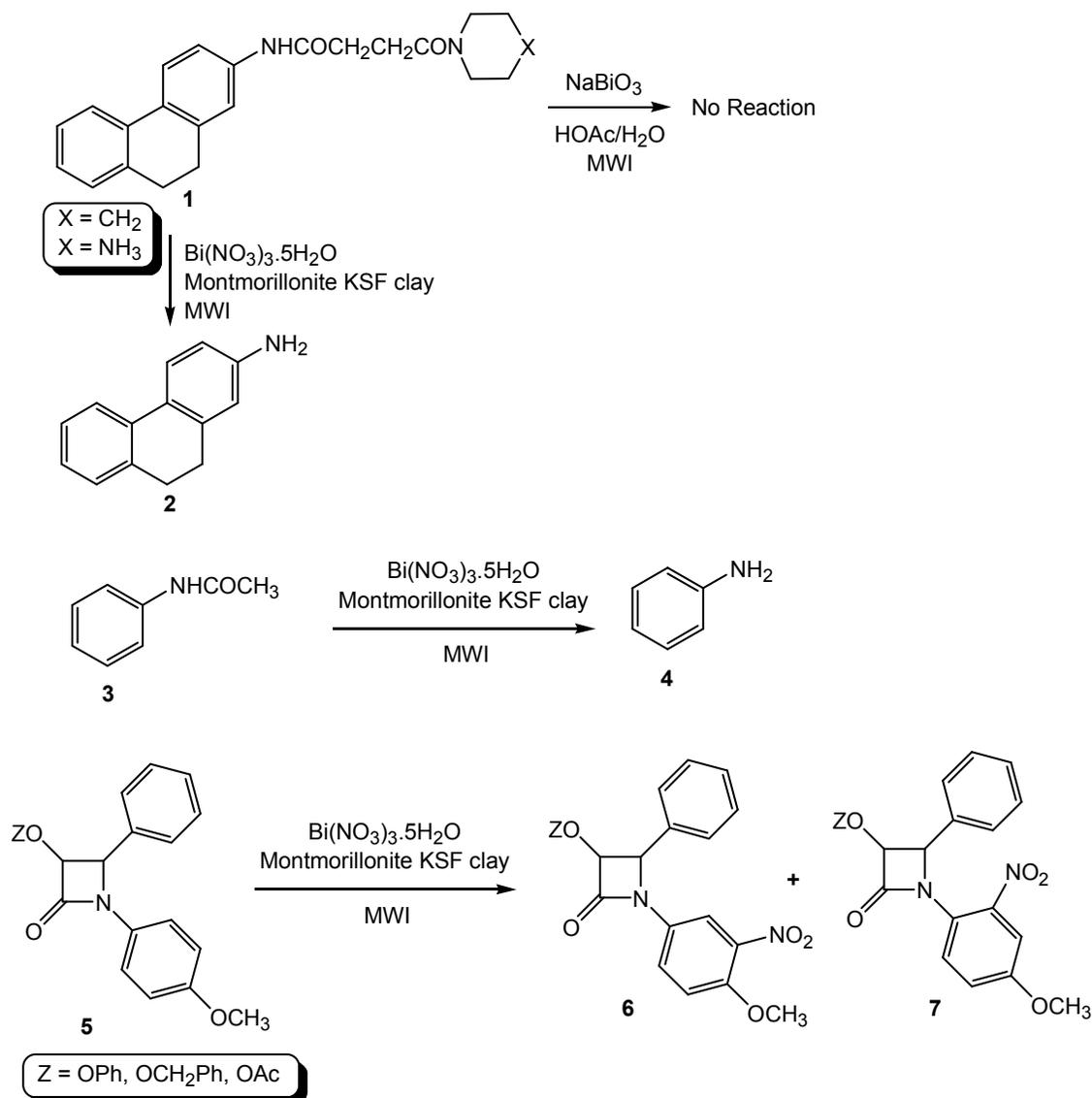
Our research on bismuth nitrate-catalyzed reactions has resulted in various successful methods. For example, a facile nitration of aromatic substrates, synthesis of pyrroles, glycosylation of alcohols, synthesis of dihydropyrimidinones and other heterocycles have been reported from our group. During the course of investigation on polycyclic aromatic compounds and β -lactams, we needed aromatic substitution at the unusual site of the aromatic rings. The keto group present in a molecule has been used to direct electrophile (for example a nitronium ion) in a different location at the aromatic system which could not be achieved by direct nitration of the corresponding hydrocarbon.

Oxidation of polycyclic aromatic derivatives **1** was performed with sodium bismuthate using microwave-induced conditions. However, oxidation of the benzylic methylene could not be detected and starting materials were recovered unchanged. Reaction of the same compound **1** with bismuth nitrate, however, produced amine **2** through hydrolysis of the amide. No nitration of the aromatic systems was observed. Repetition of the reaction with a simple aromatic amide **3** also produced amine **4** as the exclusive product. In contrast to the observation as described above, bismuth nitrate/clay combination produced two nitro β -lactams derivatives **6** and **7** from **5** without hydrolyzing the amide linkage.¹ These observations are very interesting from synthetic chemistry view point. The aromatic group present in strained 4-membered cyclic amide **5** afforded

the nitro derivatives **6** and **7** through electrophilic substitution reaction without hydrolyzing the unstable amide bond whereas amides **1** and **3** with much higher stabilities were cleaved to amines **2** and **4** without giving any nitration reaction under identical conditions. The unusual formation of amines **2** and **4** with amides **1** and **3** by bismuth nitrate-induced conditions is a fascinating observation (**Scheme 1**).

Microwave-induced organic reaction is an established procedure in organic synthesis because of its simplicity.² This method is very appealing because the unconventional set up for conducting the reaction that takes advantage of the specific nature of microwave energy.

Scheme 1



Since this reaction was performed using solid support, no adjustments of temperature of the reaction mixtures was necessary. Medium power level of the microwave was used. These

reactions were performed in unmodified domestic microwave ovens in a matter of minutes. The results described herein clearly suggest that bismuth nitrate is a versatile reagent and can be manipulated to obtain various types of products.³ Hydrolysis of the amide bond with concentrated acid or base is a standard procedure. But, this procedure is time-consuming and requires extensive work-up for the isolation of the products. The present method is much simpler than the existing procedure and requires simple filtration of the solid mass with organic solvent.

Conclusion: A simple microwave-induced method for the preparation of aromatic amine has been demonstrated using bismuth nitrate/clay following domestic microwave-induced reactions in the absence of solvent.

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References:

1. S. Samajdar, F. F. Becker, B. K. Banik, *Arkivoc*, 27, (2001)
2. (a) A.K. Bose, B.K. Banik, N. Lavlinskaia, M. Jayaraman, M.S. Manhas, *Chemtech*. 18 (1997) and references cited therein. (b) L. Perreux, A. Loupy, *Tetrahedron*, 9199 (2001). (c) P. Lidstrom, J. Tierney, B. Wathey, J. Westman, *Tetrahedron* 9225 (2001). (d) A.K. Bose, M.S. Manhas, S.N. Ganguly, A.H. Sharma, B.K. Banik, *Synthesis* 1578 (2002).
3. For related reactions see: (a) N. Srivastava, B. K. Banik, *J. Org. Chem.*, **68**, 2109, (2003). (b) B. K. Banik, I. Garcia, F. Morales, *Heterocycles*, **71**, 919, (2007). (c) B. K. Banik, I. Banik, M. Renteria, S. Dasgupta, S., *Tetrahedron Lett.*, **46**, 2643, (2005). (d) S. Rivera, D. Bandyopadhyay, B. K. Banik, *Tetrahedron Lett.* **50**, 5445, (2009).