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PERSPECTIVE

## Versatile Montmorillonite Supported Reagent for the Synthesis of Biologically Active Molecules: Our Own Endeavor

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## ABSTRACT

Montmorillonite in combination with other reagent or itself has been used to perform many organic reactions to obtain diverse organic compounds. The binding of bismuth nitrate to the free hydroxyl group of montmorillonite is crucial for the success of these types of reactions.

## KEYWORDS

Montmorillonite, Bismuth nitrate, Impregnated, Nitration,  $\beta$ -Lactam, Pyrroles, Glycosylation, Microwave.

## INTRODUCTION

Montmorillonite is a mineral of phyllosilicate group. It has two tetrahedral silica systems which form a sandwich with octahedral alumina. Montmorillonite clay is capable of absorbing water and as a result, this process can swell the clay. The exact chemical composition of montmorillonite varies with its origin. However, it is formulated as sodium calcium aluminium magnesium silicate hydroxide  $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ . Bentonite clay is mostly consists of montmorillonite.

Montmorillonite is a stable, economical and readily available solid crystalline clay. We have conducted numerous montmorillonite-mediated or other reagents-impregnated with montmorillonite-mediated reactions successfully. Most of the reactions were performed in dry conditions. It was very interesting to note that bismuth nitrate supported with montmorillonite reactions proceeds faster than montmorillonite-mediated reactions. Microwave-induced reactions help to accelerate montmorillonite-induced or montmorillonite-other reagents supported reactions. We describe here our studies on montmorillonite-supported reactions.

## RESULTS AND DISCUSSION

Solid surface-mediated reactions or surface-bound reagents have been used to study many organic reactions. There are a number of factors that need to address when such a reaction is performed. The pH-value of the solid surface is very crucial. Solid surfaces can act as Lewis acids or bases during the reactions. The most common solid used in laboratory experiment are different forms of clay of which montmorillonite is our choice. Different forms silica gel, florasil, molecular sieves and alumina are also used. In our reactions, we have

identified montmorillonite as our choice for several chemical transformations. A concise description of the methods that are developed in our laboratory is discussed in this perspective. The relationships of the reactions and products with other pertinent methods are also given to understand the goal of this research much more efficiently.

**One-pot synthesis of  $\beta$ -lactams:** Our research group is engaged in the stereoselective and stereospecific synthesis and biological evaluation of new  $\beta$ -lactams for the past many years [1-22]. In continuation of this study, montmorillonite was used for the preparation of imines derived from monocyclic aromatic amines and aromatic aldehydes [23]. The reactants were mixed with montmorillonite effectively without solvent and the formation of imines was observed by the disappearance of carbonyl band in the IR spectrum. The time of the reaction was depended on the nature of the substrates. Electron donating groups at the aromatic compounds were helpful to accelerate the imine formation while electron withdrawing groups at the aromatic rings retarded the formation of imines. The success of this reaction to form imine indicated that montmorillonite acts as dehydrating agent by absorbing water that is formed in this reaction.

The next aim step of the process was to prepare 3,4-disubstituted  $\beta$ -lactams by the reaction of the *in situ* generated imine with acid chloride in the presence of a tertiary base. Acid chloride (for example, acetoxyacetyl chloride, benzyloxyacetyl chloride, crotonyl chloride and phenoxyacetyl chloride) and triethylamine (or N-methylmorpholine) was then added to the clay-containing imine and the reaction mixture was thoroughly mixed. After the completion of the reaction, the reaction mixture was filtered and the solid was washed with dichloromethane. The organic filtrate was collected and washed with dilute hydrochloric acid, brine and evaporated. The crude reaction mixture showed the presence of  $\beta$ -lactams. The stereochemistry of the  $\beta$ -lactams was found to be identical with the compound prepared by classical Staudinger cycloaddition method. This reaction suggests that montmorillonite clay allowed cycloaddition reaction of ketenes and imines to proceed effectively without disturbing it [24-40]. On this basis, it was obvious that  $\beta$ -lactams can be prepared without the isolation of the intermediate imine in the presence of montmorillonite. However, the role of montmorillonite (if there was any) in the cycloaddition reaction was not evaluated.

**Nitration of aromatic hydrocarbons:** Polyaromatic compounds are widely distributed in nature. It was demonstrated by us that suitably functionalized polyaromatic nitrogen-containing compounds can inhibit cancer cell growth *in vitro* and *in vivo* [41-53]. To introduce nitrogen-containing functional group in the aromatic ring, the most widely accepted reaction is nitration. On this basis, electrophilic nitration of the aromatic hydrocarbon is considered to be one of the widely accepted reactions. This reaction required strong nitric acid-sulfuric acid, fuming nitric acid or nitric acid-acetic acid, nitronium fluoride and many other highly corrosive reagents.

It was discovered that montmorillonite-impregnated with bismuth nitrate is able to nitrate numerous aromatic hydrocarbons effectively. For examples naphthalene, anthracene, phenanthrene, pyrene, chrysene and dibenzofluorene were

nitration regioselectively with montmorillonite-impregnated with bismuth nitrate at room temperature [54,55]. Ferric nitrate and cupric nitrate were also used, but the success of nitration was very weak. Silica gel and alumina were used as surface instead of montmorillonite for this reaction. But, the results were not encouraging. Polyaromatic nitro compounds were then converted to a series of new compounds for structure-activity study by our group for the development of novel anticancer agents [40-53]. Bismuth nitrate was found to be an excellent reagent and catalyst not only for the aromatic nitration reaction, but also too many other useful reactions developed at our laboratory [56-72].

**Nitration of estrogens:** Estrone and estradiol control numerous fundamental functions of human life. Nitration of estrone with nitric acid was a complicated process and preparation of nitro derivative in good yield was not possible by this method. Montmorillonite-impregnated with bismuth nitrate was found to be the reagent of choice for the nitration of estrone [73]. Because of the activation created by the phenolic hydroxy group, nitration by this method produced isomeric nitro estrones. No oxidation of the aromatic ring or keto group was observed under this condition.

To functionalize the phenolic hydroxy group of estradiol by alkylation with a strong base and alkylating agent was a problematic procedure. However, nitroestradiol was alkylated easily in the presence of potassium carbonate and a relatively long side chain to produce phenolic ether type of molecules [74]. The ethers with the aromatic nitro group at the 3-position was found to be important anticancer agents. No oxidation of the aromatic ring, alcoholic hydroxyl groups or dehydration and further alkylation at the 5-membered ring of estradiol was observed under these conditions.

**Nitration of  $\beta$ -lactams:** Montmorillonite-bismuth nitrate impregnated method was also applied to nitrate specific aromatic rings that are part in  $\beta$ -lactam rings. It was found that the *p*-anisyl group present in the nitrogen of a  $\beta$ -lactam ring undergoes facile nitration with this reagent combination without rupturing the ring [75]. This study was fascinating since strong nitric acid breaks the ring and preparation of the nitro derivative of the  $\beta$ -lactams is not possible by this method. Oxidation of the *p*-anisyl ring to quinones or N-unsubstituted  $\beta$ -lactam was not observed. Non-activated aromatic rings in  $\beta$ -lactams were not affected.

Nitro  $\beta$ -lactams were important starting materials for the preparation of diverse heterocycles. Indium-induced reduction of the aromatic nitro group in  $\beta$ -lactams was used successfully for the preparation of important heterocyclic molecules through reduction and nucleophilic reaction pathways [76].

**Nitration of eugenol:** Eugenol, a constituent of natural product, clove was nitrated to a single nitro derivative with montmorillonite-bismuth nitrate impregnated method [77]. The 4-position of the aromatic ring with respect to methoxy group present in eugenol was nitrated. It was surprising to note that the phenolic hydroxy group had no effect in this reaction. Under these conditions, no oxidation of the aromatic rings, alkene group, dinitration or non-regioselective nitration was observed. The functionalized eugenol had antibacterial activity similar to that of tetracycline [78].

**Glycosylations:** Ferrier rearrangement is very important for the preparation 2,3-unsaturated oxygen-glycosides. Reaction of glycal and alcohol in the presence of an acid produced 2,3-unsaturated pyranosides. Acidic reagents or catalysts were used for this purpose. Hydrochloric acid, sulfuric acid,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\text{SnBr}_4$ ,  $\text{EtAlCl}_2$  were used in the Ferrier rearrangement with much success. However, this reaction, in general, produced a mixture of isomers. In some examples, the yields were poor. A facile montmorillonite-catalyzed or montmorillonite bound with bismuth nitrate was used for Ferrier rearrangement of numerous alcohols with glycals derived from galactose and glucose [79]. Most of the catalysts or acidic reagents failed to yield products with galactose derivatives [80-87]. It was gratifying to note that alcohols react with glycal obtained from galactose in the presence of montmorillonite and produces glycosides in good yield.

**Paal-Knorr method:** Paal-Knorr method was used for the preparation of pyrroles [88-92]. This reaction required a primary amine, an active diketone and acidic reagents. We demonstrated montmorillonite-mediated pyrrole synthesis starting from primary amines and hexane 2,5-dione [93]. An initial nucleophilic reaction of the amine with the keto group in the presence of a montmorillonite and subsequent dehydration was responsible for the success of this reaction. The time required to complete the reaction was dependent on the basicity of the amine. The more basic amines reacted faster than the less weak amino compounds. Sterically crowded amines reacted slower than non-crowded amines.

**Oxidation:** Montmorillonite-supported bismuth nitrate was able to oxidize diverse allylic and benzylic alcohols to carbonyl compounds. Bismuth nitrate in the absence of montmorillonite was not effective [94].

**Deprotection of oximes:** Oximes were deprotected to carbonyl compounds with montmorillonite-supported bismuth nitrate. In this reaction, molar proportion of bismuth nitrate was required. An excess (3 equivalent) amount bismuth nitrate was required to deprotect oximes to carbonyl compounds in the absence of montmorillonite [95].

**Microwave-Induced method:** Some of the reactions described herein with montmorillonite or montmorillonite-bismuth nitrate were performed in domestic and automated microwave oven. It was also found that montmorillonite-induced reactions under microwave were slower than montmorillonite-bismuth nitrate-induced microwave-mediated reactions. Although the cause of rate acceleration by montmorillonite-bismuth nitrate under microwave or without microwave was not studied systematically, we believe the free hydroxyl group present in montmorillonite can bind bismuth nitrate very effectively. As a result of this binding synergistic effects were possible. An excellent acceleration of reaction rates was understandable under microwave irradiation method. It was argued that microwaves can activate polar reactants very rapidly because of rapid rise in temperature and radiation effects. Moreover, this method was performed in the absence of any solvent in the microwave oven. Earlier methods on microwave-induced reactions required polar solvents. It appeared that the montmorillonite-bound reactants or montmorillonite-bismuth nitrate-bound reactants react at a much rate than those

reactions in which such a suitable solid surface is absent. The presence of solid absorbent (montmorillonite) also inhibited the reactants to decompose in the microwave because of high temperature. Such reductions in the solvent and faster reactions were considered a great way to save energy and environment. In many examples, the isolation of products became much more convenient than the classical procedures methods. Some of the advantages of microwave-mediated reactions were described in our scientific endeavors previously [96-101].

## Conclusion

We demonstrated montmorillonite-supported bismuth nitrate-induced diverse reactions for the synthesis of diverse compounds under environmentally benign conditions [102-104]. Most of the montmorillonite-mediated reactions produced required products in excellent yields. Therefore, products were obtained easily from the reaction mixtures. Montmorillonite and bismuth nitrate are readily available and economical. The reactions were fast since most of these were also tested under microwave-irradiation. The methods described herein are closely related to several of our methods and products: molecular iodine-catalyzed reaction, ketene-imine reaction, azetidinone, heterocycles and polycyclic aromatic compounds.

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