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# Montmorillonite Impregnated with Bismuth Nitrate: A mild and efficient reagent for the synthesis of gem-dinitro compounds from oximes

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**Abstract**— The reaction of Oximes with Montmorillonite Impregnated with Bismuth Nitrate generates corresponding gem-dinitro compounds in good yield under mild reaction conditions.

**Keywords:** Synthesis, Montmorillonite, Bismuth Nitrate, Oximes, gem-dinitro compounds

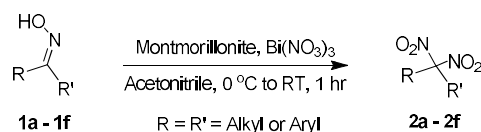
## I. INTRODUCTION

The Synthesis of High energy materials with Nitro functional groups is a challenging area for the chemists because of the hazardous and sensitive nitrating conditions. The well-known and common reagents for the nitration are Nitric acid and Nitronium tetrafluoroborate [1]. However, the nitration using Nitric acid generates lot of fumes and also highly corrosive. On the other hand, Nitronium tetrafluoroborate used for nitration is highly hygroscopic and expensive. Hence, the development of eco-friendly and simple method for the synthesis of High energy materials with Nitro functionality is demanding topic of interest for energy materials community. In the recent years, Bismuth (III) nitrate has been found as potential reagent in various organic reactions due to their low toxicity, low cost, good stability and eco-friendly nature [2]. Montmorillonite has found as efficient eco-friendly solid supported catalyst in various organic transformations [3]. In the literature, Montmorillonite Impregnated with Bismuth Nitrate has been used for nitration of various electron rich aromatic systems [4]. Herein, we report the synthesis of gem-dinitro compounds from oximes using Montmorillonite Impregnated with Bismuth Nitrate reagent system.

## II. RESULTS AND DISCUSSION

The required oximes were prepared by oximation of the corresponding ketones using reported method [5]. The reagent has been prepared by mixing Montmorillonite K10 and Bi(NO<sub>3</sub>)<sub>3</sub> in anhydrous tetrahydrofuran followed by evaporation of solvent [6]. In order to delineate the standard reaction conditions, a stirred solution of Benzophenone Oxime in acetonitrile was treated with Montmorillonite Impregnated with Bismuth Nitrate reagent system at room temperature for 1hr. After workup and purification, the corresponding gem-dinitro compound was isolated in 60 % yield. By spectroscopic

analysis the product was confirmed as **2a** and compared with the literature data [7] (Scheme 1).



Scheme 1. Bi(NO<sub>3</sub>)<sub>3</sub>/Montmorillonite mediated conversion of Oximes to gem-dinitro compounds

The method was applied to wide range of oximes including aromatic and aliphatic oximes and observed the same results with yield ranging from 40% to 60%. However, the reaction of aliphatic oximes with Montmorillonite Impregnated with Bismuth Nitrate reagent system observed lower yield compared to aromatic oximes. In order to see the optimum reaction conditions, the reaction was performed at different temperature ranging from -10 °C to 80 °C and observed low yield at lower temperature and more by products at higher temperature. Hence, it is observed that the optimum temperature for this conversion is 35-40 °C. The reaction has also been tried without using MontmorilloniteK10 and observed the unreacted starting material by TLC, indicating the essentiality of using Montmorillonite K10.

## III. CONCLUSION

In summary, we have demonstrated mild and efficient method for the conversion of oximes to gem dinitro products using Montmorillonite Impregnated with Bismuth Nitrate reagent system. The attractive features of this process are ambient temperature conditions, simple, easy handling and nonhazardous nature of reagents makes it useful process for the conversion of oximes to gem dinitro products.

## IV. ACKNOWLEDGEMENT

RK, RN and RG thank DRDO for financial assistance

## V. EXPERIMENTAL

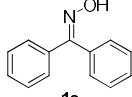

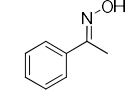
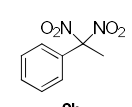
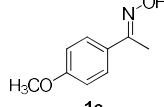
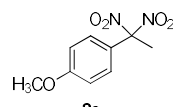
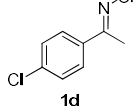
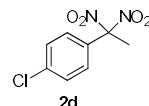
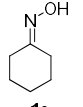
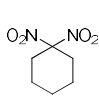
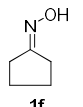
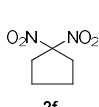
To a stirred solution of Benzophenone oxime (0.5 g, 2.53 mmol) in anhydrous acetonitrile (10 mL), was added

Montmorillonite Impregnated with Bismuth Nitrate (2.5 g) at 0-10 °C under Nitrogen atmosphere. Then the reaction mixture was allowed to room temperature and stirred for 1hr. After completion of starting materials by TLC, the reaction mixture was filtered and the filtrate was concentrated to get the crude product. The crude product was extracted with ethyl acetate, concentrated and purified over Silicagel (100-200 mesh) column chromatography and product eluted with 1:9 ethyl acetate and Hexane to afford pure product **2a** in 60 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.62 (m, 2H), 8.25 (m, 4H), 8.51 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ 131.56, 131.22, 130.26, 128.58, 126.62; mp 78.5-79.0 °C (lit. [8] 79-79.5 °C)

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**Table 1.** Bi(NO<sub>3</sub>)<sub>3</sub>/Montmorillonite mediated conversion of Oximes to gem-dinitro compounds

Entry	Oxime	Product <sup>a</sup>	Yield (%) <sup>b</sup>
1			60
2			50
3			40
4			55
5			45
6			40

a: All the products were characterized by <sup>1</sup>H NMR and mass spectroscopy.  
b: Isolated yields after column chromatography.