

SYNLETT Spotlight 140

Bismuth(III) Nitrate Pentahydrate – A Versatile Reagent in Organic Synthesis



Compiled by Varughese Alexander Mulamoottil

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Varughese Alexander received his M.Sc. (organic chemistry) in 2000 from the University of Mumbai, India. He then joined Prof. Shrinivas D. Samant's research group in the Department of Chemistry, at the Institute of Chemical Technology, University of Mumbai, Mumbai, India to pursue his doctoral studies. His research interests include development of new synthetic strategies, catalysis, use of supported reagents, microwaves and ionic liquids for achieving organic transformations.

Department of Chemistry, Institute of Chemical Technology,
University of Mumbai, N. M. Parekh Road, Matunga, Mumbai -
400 019 India

E-mail: mva_sds@yahoo.co.in

This Spotlight is dedicated to the late Dr. B. M. Khadilkar.

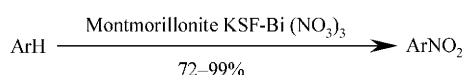
Introduction

The use of bismuth(III) derivatives as catalysts in organic synthesis has increased considerably. This new interest in bismuth is easily justified by its user-friendly ecological behavior.¹ The catalytic properties of bismuth(III) compounds have been investigated during the past few years.

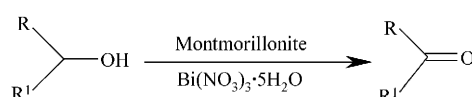
Bismuth nitrate pentahydrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ is one such addition to the list of compounds exploited under this class. It is relatively nontoxic and insensitive to air. It is commercially available and inexpensive.

Abstracts

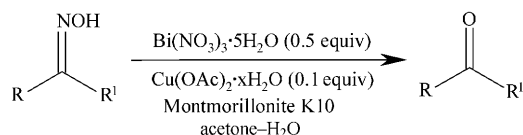
(A) Montmorillonite impregnated with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was found to be an excellent reagent for aromatic nitration in high yield.² The same group has also explored the nitration of few phenolic compounds and β -lactams.³



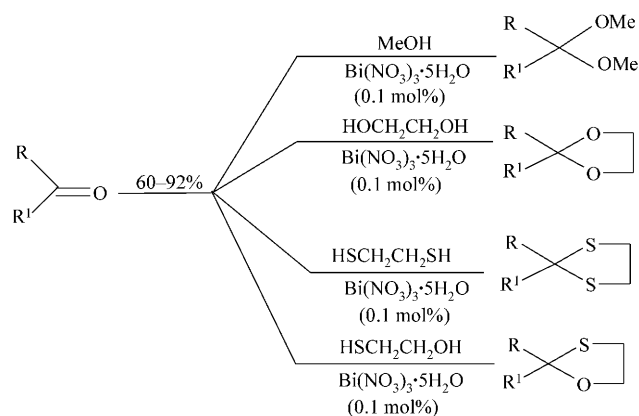
(B) Montmorillonite impregnated with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was also found to be an excellent reagent for the oxidation of a variety of alcohols in excellent yield.⁴



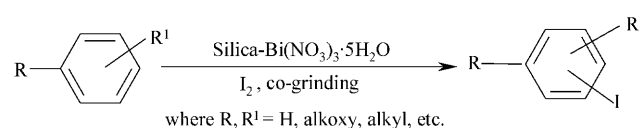
(C) Ketoximes undergo facile deprotection in acetone– H_2O (9:1) in the presence of 0.5 equivalent of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.⁵ This method is an attractive alternative to existing routes for the deprotection of oximes. Banik and co-workers have also demonstrated the utility of this reagent for the facile deprotection of various hydrazones and oximes.⁶



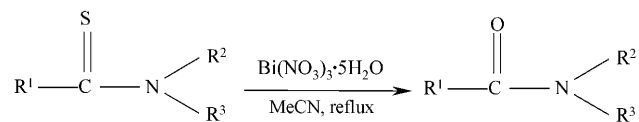
(D) $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ has been found to be an outstanding catalyst for the protection of carbonyl compounds such as acetals, ketals, mixed ketals and thioketals with an excellent yield.⁷



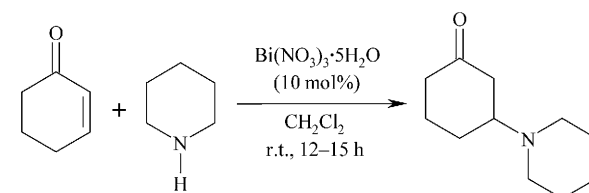
(E) Silica-supported $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ [BNP-silica] was prepared under simple co-grinding conditions. The iodination of aromatic compounds using [BNP-silica] and molecular iodine under solvent-free conditions has been described. The reaction occurs in the solid state at room temperature, yielding the corresponding mono-iodo derivatives in good yields. However, less activated aromatics required longer reaction time with comparatively lesser yield.⁸



(F) A variety of thioamides and thioureas are rapidly transformed to their oxo derivatives with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in excellent yields.⁹ However, thiono esters and thioketones are converted to the corresponding carbonyl compounds in only poor yields. The selective deprotection of thioamides and thioureas in the presence of thiono esters and thioketones make this method an attractive alternative to the existing routes for deprotection of thiocarbonyl compounds.



(G) A $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ -catalyzed versatile Michael reaction, developed to reduce the complications that characterize the current standard Michael reaction, has been used for facile preparation of organic compounds of widely different structures.¹⁰ For example, several substituted amines, imidazoles, thio compounds, indoles and carbamates were prepared at room temperature by this method. In contrast to the existing methods using acidic catalysts, this method is very general, simple, high yielding, environmentally friendly, and oxygen- and moisture-tolerant. However, the promoting role of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in this reaction is not understood at this time.



References

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