

SYNLETT Spotlight 31

Bismuth(III) Derivatives: New Catalysts

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Sébastien Vidal was born in Montpellier (France) in 1974. He received his Ph. D. in Organic Chemistry (2000) from the University of Montpellier (France). He studied under the direction of Professor Jean-Louis Montero and synthesized new mannose 6-phosphate analogs. He then moved to the United States and is carrying out his postdoctoral studies involving the synthesis and characterization of glycodendrimers with Professor J. Fraser Stoddart at UCLA.

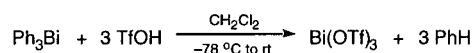


This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Introduction

Since the beginning of the 1980s, the use of bismuth(III) derivatives as catalysts in organic synthesis has increased considerably. This new interest in bismuth is easily justified by its friendly ecological behavior.¹ Bismuth is a relatively rare metal present in the earth's crust at about the same abundance as silver and is almost never found in its native state. It is usually associated with copper, lead, tin, tungsten, silver, and gold ores. Bismuth is the heaviest of the heavy metals and the only non-toxic heavy metal.¹ Bismuth catalysts are used in industry for the production of acrylonitrile and acrolein.² The catalytic properties of bismuth(III) compounds have been investigated during the past twenty years.³ Applications of bismuth(V) in organic chemistry are also well known.⁴ Although these reactions typically involve bismuth(III) halides (BiX₃ where

X = F, Cl, Br, I), bismuth(III) trifluoromethanesulfonate (Bi(OTf)₃) have also been discovered recently in numerous reactions. The main advantages of using these catalysts are their strong activities and their low cost with respect to most other known catalysts, and their easy removal by filtration, simplifying the purification of the product.

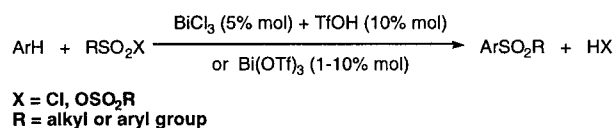


Preparation

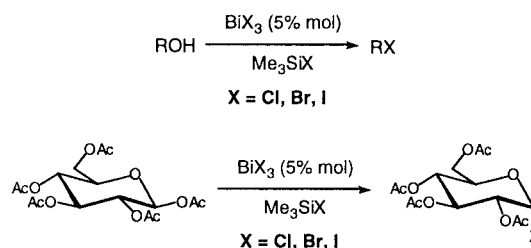
Bismuth(III) halides (BiF₃, BiCl₃, BiBr₃ and BiI₃) are commercially available. Bismuth(III) trifluoromethanesulfonate can be easily prepared according to Dubac's procedure⁵ in which commercially available triphenylbismuth is reacted with trifluoromethanesulfonic acid.

Abstracts

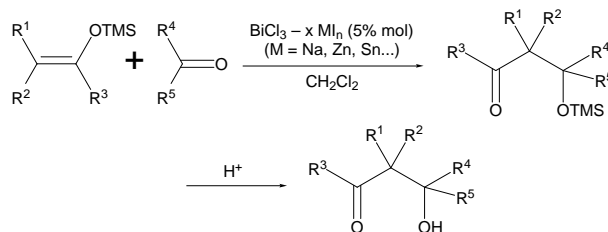
(A) Sulfonylation of arenes can be catalyzed by either Bi(OTf)₃⁶ or by BiCl₃ in the presence of trifluoromethanesulfonic acid.⁷ The mechanism of this reaction has been proposed⁶ to involve the transfer of the triflate from Bi(OTf)₃ to the sulfonyl compound (RSO₂X). The resulting activated sulfonyl moiety (RSO₂OTf) then reacts with the arene (ArH) to give the final product (ArSO₂R) by displacement of the triflate. For the BiCl₃/TfOH reagent, the trifluoromethanesulfonic acid is necessary to transform in situ BiCl₃ into BiCl_n(OTf)_{3-n} (n = 1, 2) in order to proceed in a similar way as for Bi(OTf)₃.⁷ Moreover, the BiF₃/TfOH, BiBr₃/TfOH and BiI₃/TfOH reagents were also shown to display the same catalytic activities.



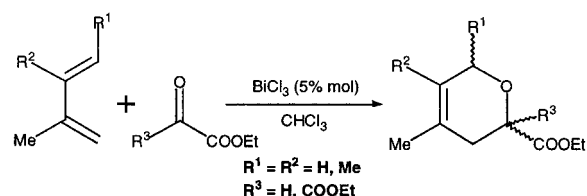
(B) The association of bismuth(III) halides with halogenosilanes was shown to lead to very effective halogenating agents.^{8,9} The first application was reported for the conversion of secondary and tertiary alcohols into the corresponding chlorides in near-quantitative yields by using BiCl₃ as a catalyst and chlorotrimethylsilane in a 1:1 molar ratio with the alcohol. More generally, the BiBr₃/Me₃SiBr and BiI₃/Me₃SiI reagents were shown to afford the corresponding halogens.⁸ The conversion of peracetylated glycosides into the corresponding halides can also be accomplished by using bismuth(III) halides as catalysts in the presence of halogenosilanes⁹ in a procedure which has led to a new and efficient one-pot synthesis of nucleosides.¹⁰



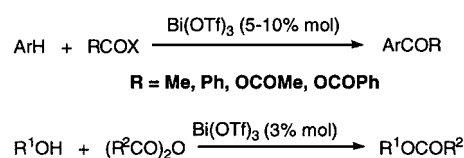
(C) Bismuth(III) chloride was shown to catalyze the Mukaiyama–aldol and –Michael reactions,¹¹ and some metallic iodides can activate strongly its catalytic power.¹² The silylated intermediate can be isolated.



(D) Lewis acid catalysis is among the most important ways to activate the Diels–Alder reaction. As bismuth(III) derivatives display Lewis acidity, BiCl_3 and $\text{Bi}(\text{OTf})_3$ have been shown to catalyze the carbonyl- and aza-Diels–Alder reactions.¹³ These catalysts allow a lower reaction temperature and avoid diene polymerization.



(E) Bismuth(III) derivatives, as Lewis acids, also catalyze acylation reactions.^{14–17} $\text{Bi}(\text{OTf})_3$ has been used for Friedel–Crafts acylation of aromatic compounds,¹⁴ and also for acylation of alcohols.¹⁵ BiCl_3/NaI and $\text{BiCl}_3/\text{ZnI}_2$ reagents catalyze the acylation of allylsilanes.¹⁶ They also display catalytic activity in the C-acylation of enoxysilanes with or without metallic iodide (NaI , ZnI_2) addition.¹⁷



References and Notes

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