

SYNLETT Spotlight 67

Bismuth(III) *tris*(trifluoromethanesulfonate)

Compiled by Sylvain Antoniotti



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

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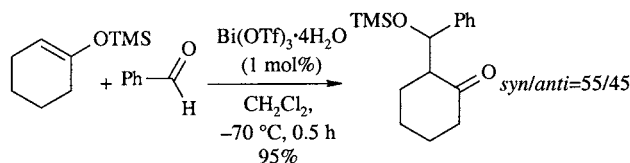
Introduction

Among several bismuth compounds described for their use in organic synthesis,¹ bismuth(III) *tris*(trifluoromethanesulfonate), commonly called bismuth triflate, has received increasing interest over the last few years, and many publications have reported its powerful Lewis acidity, offering a new reagent for various catalytic reac-

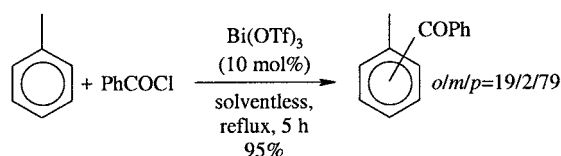
tions. Bismuth(III) triflate can be prepared from cheap triphenylbismuth² or bismuth(III) oxide Bi_2O_3 ,³ and triflic acid. The displacement of trifluoroacetate groups of bismuth(III) trifluoroacetate by an excess of triflic acid has also been reported.⁴

Abstracts

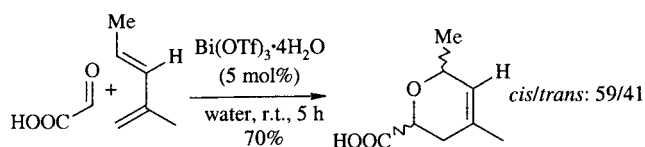
(A) Bismuth(III) triflate is an efficient catalyst for the Mukaiyama aldol-type reaction and shows higher catalytic activity than other metallic triflates such as scandium, ytterbium, or cerium.⁵ Ketones, aldehydes, and acetals may be used as electrophiles with aromatic and aliphatic silyl enol ethers to lead to the corresponding β -hydroxycarbonyl compounds in the presence of 1–5 mol% of catalyst.



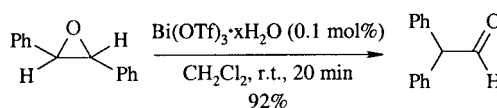
(B) Friedel–Crafts acylation of monosubstituted benzene derivatives by acetyl and benzoyl chlorides catalyzed by bismuth(III) triflate has been reported to occur in 75–96% yields. Good selectivities for the *para* product were observed.⁶



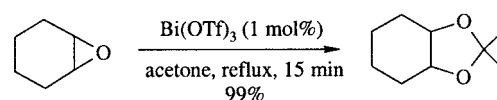
(C) Bismuth triflate catalyses both classical and non-classical Diels–Alder reactions involving conjugated olefins,⁷ carbonyl compounds,⁸ and imines,⁹ e.g. the reaction of various unfunctionalized dienes and glyoxilic acid in water.^{8a}



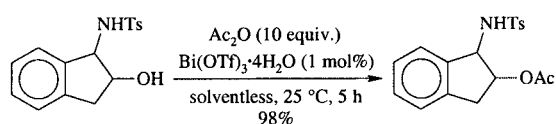
(D) The rearrangement of aryl epoxides has been reported to lead to aldehydes and ketones in 73–92% yields by using 0.1 mol% of bismuth triflate as catalyst.¹⁰ The reaction was found to be regioselective, particularly for stilbene oxide, for which only the phenyl group migration was observed.



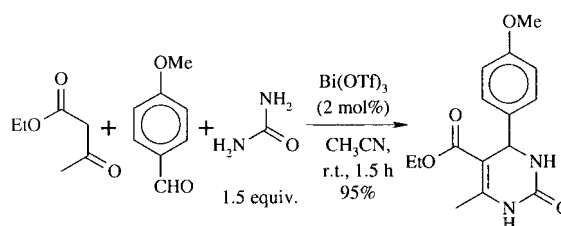
(E) Bismuth triflate catalyses the conversion of epoxides to 1,3-dioxolanes in the presence of acetone in 94–99% yields.¹¹ The activity of bismuth triflate, compared to those of bismuth trifluoroacetate and bismuth trichloride, was shown to be superior.



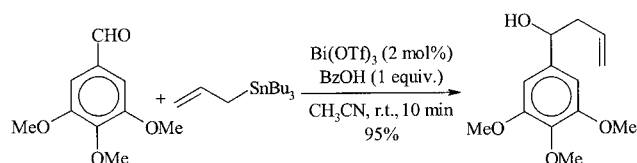
(F) The use of bismuth(III) triflate in acetylation of alcohols and diols by acetic anhydride has been reported simultaneously by several research groups.¹² From Otera's group^{12a} acetylation of various functionalized primary and secondary alcohols is easily carried out in the presence of small amounts of bismuth triflate (0.01–1 mol%) in yields of 80–99%.



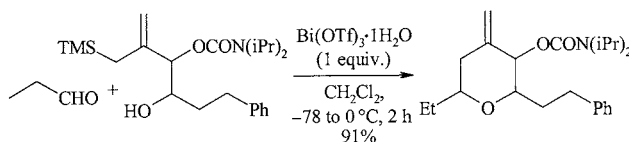
(G) Bismuth(III) triflate catalyses the three-component reaction through the Biginelli reaction, where urea, a β -ketoester and an aldehyde are assembled into a dihydropyrimidinone in 58–95% yields.¹³



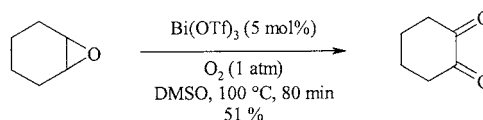
(H) $\text{Bi}(\text{OTf})_3$ catalyses the allylation of aldehydes and aldimines using allyltributylstannane.¹⁴ The catalyst is re-usable without loss of activity during four cycles. Acetals, in the presence of allyltrimethylsilane as the allyl donor, undergo also an allylation reaction to homoallylic ethers.¹⁵



(I) Bismuth(III) triflate promotes the intramolecular Sakurai cyclisation (IMSC) of homoallylic alcohols and aldehydes leading to the corresponding 4-methylidenetetrahydropyran derivatives in 84–98% yields.¹⁶



(J) The first example of bismuth(III) triflate-catalysed oxidation of organic compounds has been reported in the one-pot selective oxidation of internal epoxides to α -diketones.¹⁷ The reaction proceeds in DMSO under an oxygen atmosphere (1 atm).



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