

SYNLETT Spotlight 402

Mercuric Triflate

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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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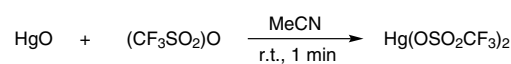
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Dedicated with best wishes to Dr. Ani Deepthi.

Introduction

Mercuric triflate or mercury(II) trifluoromethane sulfonate, $\text{Hg}(\text{CF}_3\text{SO}_3)_2$ is a white powdery solid, hygroscopic in nature and soluble in water. It belongs to the chemical family of metal triflate compounds and is toxic upon inhalation, contact or ingestion. It has a melting point of 350°C above which it decomposes to a mixture of carbonyl fluoride, carbon monoxide, hydrogen fluoride, sulfur dioxide and metal salts. Mercuric triflate is commercially available and can as well be prepared in-

stantaneously by the reaction of mercury(II) oxide and triflic anhydride in acetonitrile (Scheme 1).¹ Mercuric triflate is a very versatile reagent² and has been used for several organic catalytic transformations including C–C bond forming cyclizations, alkyne hydrations, heterocycle synthesis and very recently in C–N bond forming reactions.

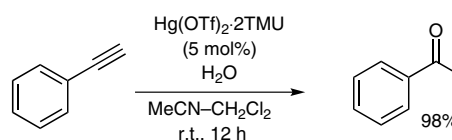


Scheme 1

Abstracts

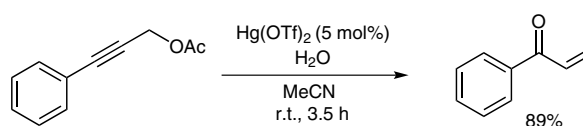
(A) Hydration of Terminal Alkynes:

Nishizawa and co-workers successfully utilized mercuric triflate for the synthesis of a wide range of methyl ketones.³ The products were obtained in excellent yield and high chemoselectivity. Functional groups as well as long chains on the substrate are tolerated in this *modus operandi*.



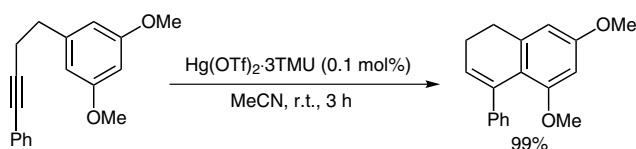
(B) Hydration of Propargyl Acetates:

The same group synthesized enones by the hydration of propargyl acetates, which serves as an alternative to the well-known Meyer–Schuster and Rupe rearrangements. Also α,β -unsaturated esters were synthesized with high catalytic turnover up to 1000 times.⁴



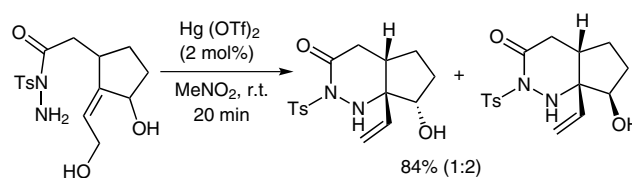
(C) Cyclization of Alkynes:

Mercuric triflate is reported to efficiently catalyze the hydroxylative carbacyclization of 1,6-enynes^{5a} and can cause aryl alkyne cyclization.^{5b} In addition, it also catalyzes tandem cyclizations yielding polycarbacycles.^{5c,d}

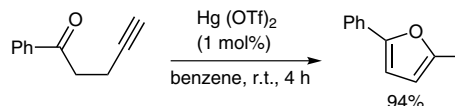


(D) *Cyclization of Alkenes:*

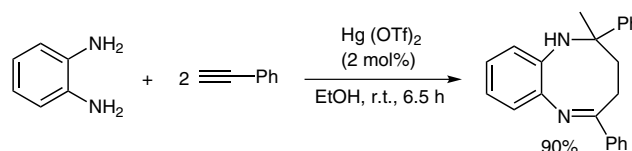
Mercuric triflate can also catalyze the cyclization of allylic alcohol tethered substrates.⁶ The initial event involves the protonation of the allylic hydroxyl group by TfOH formed in situ generating a cationic species, which subsequently undergoes demercuration. The cyclopentane derivative, which corresponds to the core of palau'amine, a well-known marine natural product, was synthesized by this protocol.^{7a} The same strategy was also used for the total synthesis of the irregular sesquiterpenoid heliannuol as well.^{7b}

(E) *Heterocyclic Synthesis by Alkyne Cyclizations:*

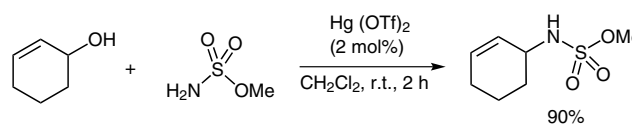
An array of heterocycles including furans, indoles, cyclic enol carbonates, benzoazepines, etc., was synthesized by suitable alkyne cyclization catalyzed by mercuric triflate.⁸

(F) *One-Pot Protocol:*

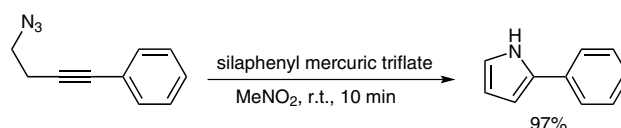
Biologically important benzodiazepines were synthesized in excellent yields by the one-pot protocol in which the terminal alkyne serves as the keto methyl equivalent.⁹

(G) *Allylic Amination:*

The allylic amination of allyl alcohols and soft nitrogen nucleophiles such as sulfamates or sulfonamides under very mild conditions has been developed.¹⁰

(H) *Silaphenyl Mercuric Triflate:*

The recent development of solid-supported catalyst viz, silaphenyl mercuric triflate makes this unique reagent suitable for industrial organic synthesis as well.¹¹ It showed remarkable catalytic activity for heterocycle as well as polycarbocycle synthesis. They also applied this in pyrrole synthesis by azide cyclization.¹²



References

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