Mercuric Triflate
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Dedicated with best wishes to Dr. Ani Deepthi.

Introduction

Mercuric triflate or mercury(II) trifluoromethane sulfonate, Hg(CF₃SO₂)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 instantaneously by the reaction of mercury(II) oxide and triflic anhydride in acetonitrile (Scheme 1). Mercuric triflate is a very versatile reagent 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.

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\begin{align*}
\text{HgO} + (\text{CF}_3\text{SO}_2)\text{O} & \rightarrow \text{Hg(OSO}_2\text{CF}_3) \quad \text{(A)} \\
\text{Hg(OTf)}_2 & \rightarrow \text{Hg(OSO}_2\text{CF}_3) \\
\end{align*}
\]

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. 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.

(C) Cyclization of Alkynes:
Mercuric triflate is reported to efficiently catalyze the hydroxylative carbacyclization of 1,6-ynes and can cause aryl alkyn cyclization. In addition, it also catalyzes tandem cyclizations yielding polycarbacycles.
(D) Cyclization of Alkenes:

Mercuric triflate can also catalyze the cyclization of allylic alcohol tethered substrates. The initial event involves the protonation of the allylic hydroxyl group by TIOH 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. The same strategy was also used for the total synthesis of the irregular sesquiterpenoid heliannuol as well.

(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.

(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.

(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.

(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. It showed remarkable catalytic activity for heterocycle as well as polycarbocycle synthesis. They also applied this in pyrrole synthesis by azide cyclization.

References