

# 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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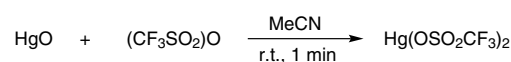
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Dedicated with best wishes to Dr. Ani Deepthi.

### 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  $350^\circ\text{C}$  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).<sup>1</sup> Mercuric triflate is a very versatile reagent<sup>2</sup> 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.

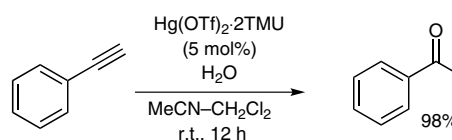


Scheme 1

### Abstracts

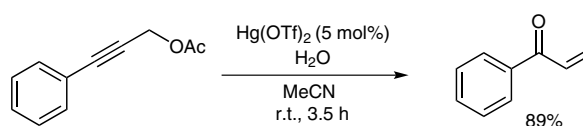
#### (A) Hydration of Terminal Alkynes:

Nishizawa and co-workers successfully utilized mercuric triflate for the synthesis of a wide range of methyl ketones.<sup>3</sup> 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*.



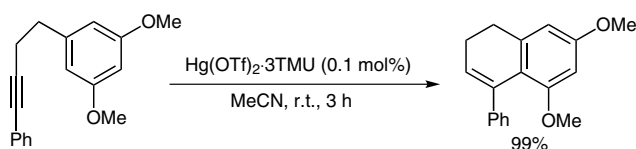
#### (B) Hydration of Propargyl Acetates:

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  $\alpha,\beta$ -unsaturated esters were synthesized with high catalytic turnover up to 1000 times.<sup>4</sup>



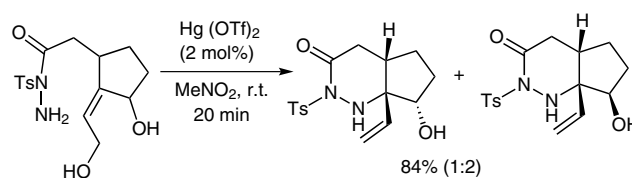
#### (C) Cyclization of Alkynes:

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

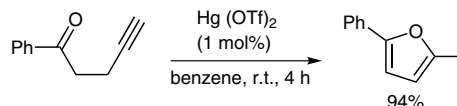


(D) *Cyclization of Alkenes:*

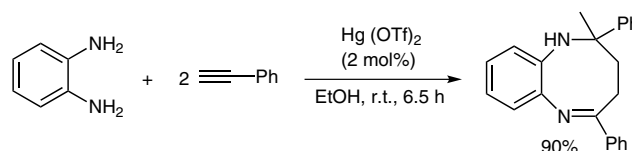
Mercuric triflate can also catalyze the cyclization of allylic alcohol tethered substrates.<sup>6</sup> The initial event involves the protonation of the allylic hydroxyl group by TfOH formed in situ generating a cationic species, which subsequently undergoes demercuration. The cyclopentane derivative,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

(E) *Heterocyclic Synthesis by Alkyne Cyclizations:*

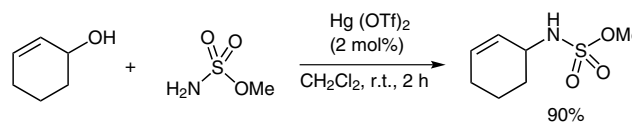
An array of heterocycles including furans, indoles, cyclic enol carbonates, benzoazepines, etc., was synthesized by suitable alkyne cyclization catalyzed by mercuric triflate.<sup>8</sup>

(F) *One-Pot Protocol:*

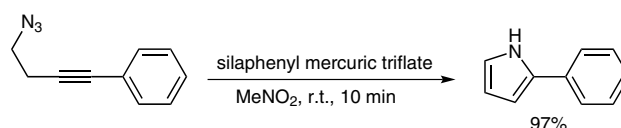
Biologically important benzodiazepines were synthesized in excellent yields by the one-pot protocol in which the terminal alkyne serves as the keto methyl equivalent.<sup>9</sup>

(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.<sup>10</sup>

(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.<sup>11</sup> It showed remarkable catalytic activity for heterocycle as well as polycarbocycle synthesis. They also applied this in pyrrole synthesis by azide cyclization.<sup>12</sup>



## References

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