Tris(trifluoromethanesulfonato)indium

Compiled by Ashim Jyoti Thakur

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Introduction

Tris(trifluoromethanesulfonato)indium or indium(III) triflate [In(OTf)3] constitute one of the most important catalyst among the lanthanide triflates and indium based reagents. In recent years, indium(III) triflate has received increasing attention both as a reagent and catalyst for organic reactions.1 It is a mild, selective, and water tolerant Lewis acid in several C–C and C-heteroatom bond forming reactions. In contrast to classical Lewis acids, which often are required in stoichiometric quantities, In(OTf)3 readily promotes a range of reactions in catalytic quantities soluble both in organic solvents and aqueous media. In some cases the presence of water even improves their activity. Moreover, the solubility of this reagent in water means that they can be readily recovered unchanged from the aqueous phase of reaction mixtures on work up and subsequently reused, a very crucial point as far as green chemistry is concerned, for which it is gaining popularity and momentum in current research. This catalyst finds application in thioacetalization and transthioacetalization of carbonyl compounds,12 acylation of alcohols and amines,13 tetrahydropyranylation and depyranylation of alcohols,14 regioselective ring opening of activated aziridines with arenes.15

Preparation: In(OTf)3 is prepared from the corresponding oxide (In2O3) and triflic acid (TfOH) in water.2 The water formed in the reaction is evaporated under reduced pressure after filtering the unreacted oxide. The resulting white powder is dried in vacuo.

Abstracts

(A) Loh et al.3 have reported the In(OTf)3 catalyzed conversion of branched homoallylic alcohols to the thermodynamically preferred linear regioisomers followed by it’s utilization for the construction of steroidal side chains with anti-Cram stereoselectivity.

(B) Intramolecular 3,5-oxonium-ene cyclization reaction catalyzed by In(OTf)3 in dichloromethane afford both tetrahydropyran and tetrahydrofuran rings.4 A tandem 2-oxonia[3,3]-sigmatropic rearrangement/cyclization reaction of homoallylic alcohols with the corresponding aldehydes catalyzed by In(OTf)3 selectively afford dimethylethyltetrahydrofurans and methylenedimethylethyltetrahydrofurans.5
(C) An atom economic and efficient synthetic construction of tetrahydro-
pyran rings using In(OTf)₃ – catalyzed self-tandem carbonyl-ene, in-
tramolecular (2,5)-oxonium-ene cyclization between aldehydes and
methylenecyclohexane is reported. This method provides a facile as-
sembly of tetrahydrodopyran units for the synthesis of natural products
containing tetrahydrodopyran groups.⁶

(D) Facile O–H insertion reactions of α-diazo ketones with aliphatic/ar-
omatic alcohols or benzenethiol have been developed in the presence of
In(OTf)₃ as a catalyst. These reactions provide good yields of α-alkoxy
ketones. A comparative study with other Lewis acids establishes the re-
activity of indium triflate in O–H insertion reactions of α-diazo ketones
with no Wolf rearrangement product.⁷

(E) In(OTf)₃ is found to be an effective (reusable) catalyst for one step
intramolecular Diels–Alder reaction of furans in the solid state under
Microwave irradiation (8–10 mins, 80–90% yields). The reaction is less
effective under thermal conditions (20–30 mins, 40–45% yields) and
takes several days at room temperature, and undergo retro Diels–Alder
reaction when purified by distillation. It should be noted that the yield of
second (83%) and even third (80%) runs are comparable to that of first
run (85%).

(F) At a loading as low as 0.5 mol% it can catalyse the hetero Diels–Al-
der reaction of Danishefsky’s diene and imines. A three component cou-
pling reaction between aldehydes, amines, and Danishefsky’s diene to
afford tetrahydropyridine derivatives proceeds similarly in high yields.⁹

(G) A practical synthesis of sulfonamides is achieved through this in-
dium catalyst by the sulfamoylation of aromatics. The reaction gives
consistently good results with activated aromatics across a range of sul-
famoyl chlorides but isolated yields are low with deactivated substrates
such as chlorobenzenes. An intramolecular sulfamoylation is also possible.

(H) This catalyst finds important applications in protection-deprotection
chemistry also. In the presence of 5 mol% of this catalyst both activated
and deactivated aromatic aldehydes including a sterically hindered one
such as mesitaldehyde, aliphatic aldehydes and cinnamaldehyde react
rapidly with 2-mercaptoethanol (1.5 equiv) in dichloromethane as the
solvent at 15 °C to afford the corresponding 1,3-oxathiolanes in good to
excellent yields.¹¹

References