SYNLETT Spotlight 62

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

Tris(trifluoromethanesulfonato)indium
Compiled by Ashim Jyoti Thakur

Ashim Jyoti Thakur was born in Diphu, a small hilly town in Assam, India in 1974. He received a BSc (Chemistry) degree in 1995 and MSc (Chemistry) degree in 1997 from Gauhati University, Guwahati, India and was awarded a PhD (2002) from Dibrugarh University, Dibrugarh, India working in the Medicinal Chemistry Division of Regional Research Laboratory (CSIR), Jorhat 785 006, India under the guidance of Dr. J. S. Sandhu, FNA. During doctoral tenure he worked on synthetically modified pyrimidine moiety and development of synthetic methods. Currently he is a Senior Research Fellow (CSIR) in the same institution working in the same area under the supervision of Dr. Dipak Prajapati, Sc. E-II. His research interests include asymmetric synthesis of bio-potent molecules and green chemistry.

Medicinal Chemistry Division, Regional Research Laboratory, Jorhat 785 006, India
E-mail: ajthax@yahoo.com

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. 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 recov-ered 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 thiaacetalization and thioacetalization of carbonyl compounds, acylation of alcohols and amines, tetrahydropyranylation and depyranylation of alcohols, regioselective ring opening of activated aziridines with arenes.

Preparation: In(OTf)₃ is prepared from the corresponding oxide (In₂O₃) and triflic acid (TfOH) in water. 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. have reported the In(OTf)₃ catalyzed conversion of branched homoallylic alcohols to the thermodynamically preferred linear regiosomers 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. A tandem 2-oxonia-[3,3]-sigmatropic rearrangement/cyclization reaction of homoallylic alcohols with the corresponding aldehydes catalyzed by In(OTf)₃ selectively afford dimethyltetrahydrofurans and methylenedimethyltetrahydrofurans.

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(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 tetrahydrodropyan units for the synthesis of natural products 
containing tetrahydrodropyan groups.⁶

(D) Facile O–H insertion reactions of α-diazoketones with aliphatic/ar- 
aromatic 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-diazoketones 
with no Wolf rearrangement product.⁷

(E) In(OTf)₃ is found to be an effective (reusable) catalyst for one step 
imtramolecular Diels–Alder reaction of furans ⁸ 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- 
ping reaction between aldehydes, amines, and Danishefsky’s diene to 
afford tetrahydropyridine derivatives proceeds similarly in high yields.⁹

(G) A practical synthesis of sulfonamides¹⁰ 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 possi- 
bile.

(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 
good yields.¹¹

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