

SYNLETT Spotlight 8

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

Indium

Compiled by Dramane Lainé

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

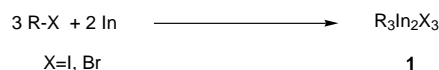
Dramane Lainé worked for Exchem Industries Limited, Essex, and Pfizer Central Research, Kent, after graduating from ENSC Montpellier in France in 1991. He is currently a third year Ph.D. student with Professor S.V. Ley at the University of Cambridge.



Since the beginning of the nineties, the use of metallic indium in organic synthesis has provoked widespread interest.¹ What makes this metal particularly attractive is its relative non-toxicity, its inertia to air and more importantly to water.² This compatibility allows reactions involving water soluble molecules, such as unprotected carbohydrates, to be carried out in a simple, straightforward manner, thus avoiding protection-deprotection protocols. The lower first ionisation potential of indium (5.8 eV) relative to similarly water resistant metals such as tin (7.3 eV) and zinc (9.4 eV) makes it a very mild and useful reactant for single electron transfer processes. Thus the main use of indium has been to mediate Reformatsky and

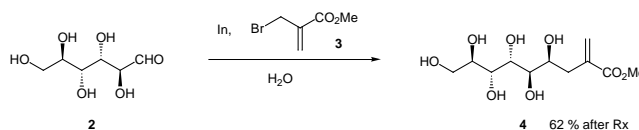
Barbier-type reactions³ in polar solvents (water, DMF) under very mild conditions.

Preparation: Indium is commercially available as a powder. Organo-indium compounds are usually formed *in situ* by reacting, at room temperature, metallic indium with alkyl or allyl halides and exists as the corresponding sesqui-halides **1**.

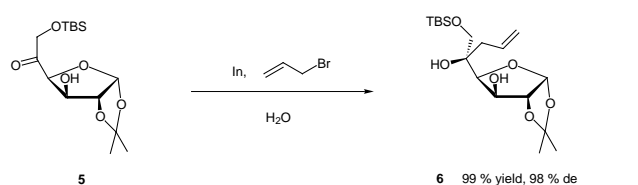


Abstracts

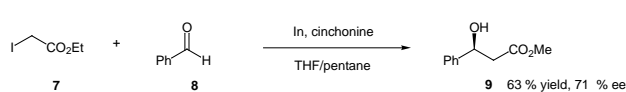
A) The coupling of D-(+)-mannose **2** with methyl 2-(bromomethyl)acrylate **3** was carried out efficiently in aqueous media with indium.⁴ No protection was required under such conditions and a pure product was obtained in 62 % yield after recrystallisation



B) An efficient indium-mediated allylation of a sugar-derived ketone **5** in water affords the corresponding chiral tertiary alcohol **6** with excellent diastereoselectivity.⁵ The stereoselectivity is thought to arise from the chelation of indium between the carbonyl group and the oxygen atom of the tetrahydropyran ring, with addition occurring from the least hindered face.



C) Indium was used to mediate a chiral Reformatsky reaction between ethyl iodoacetate **7** and benzaldehyde **8**.⁶ The asymmetry of the reaction was induced by the chiral amino alcohol cinchonine and the active β -hydroxy ester **9** was obtained in 63 % yield and 71 % ee.



References

- (1) For a recent review see Cintras P. *Synlett* **1995**, 1087 and also Sullivan A.C. in *Dictionary of Organometallic compounds*, Vol. 2, Chapman and Hall, London, **1995**, 1975.
- (2) Li C-J. *Tetrahedron* **1996**, 52(16), 5643; Lubineau A.; Augé J.; Queneau Y. *Synthesis* **1993**, 741.
- (3) For a review of the addition of allylic indium reagents to aldehydes see Marshall J.A. *Chemtracts, Org. Chem.* **1997**, 10, 481.

- (4) Chan T-H.; Li C-J. *J. Chem. Soc., Chem. Comm.* **1992**, 747.
- (5) Loh T-P.; Ho D. S-C.; Chua G-L.; Kim K-Y. *Synlett* **1997**, 563.
- (6) Johar P.S.; Araki S.; Butsugan Y. *J. Chem. Soc., Perkin Trans. 1* **1992**, 711.

Article Identifier:

1437-2096,E;1999,0,08,1331,1331,ftx,en;V00599ST.pdf