

SYNLETT Spotlight 438

Organoindium Reagents

Compiled by Atul Kumar Singh



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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Dedicated to my parents and my honorable mentor, Professor Lal Dhar S. Yadav.

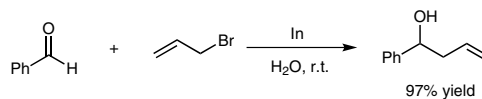
Introduction

From several decades, indium compounds have attracted the attention of a great number of research groups due to their broad chameleonic behavior. These versatile reagents are widely used in organic chemistry as reducing agents,¹ radical initiators,² and Lewis acid catalysts.³ In particular, organoindium compounds are versatile, mild, relatively stable, and non-toxic in nature. In these reactions, various sensitive functional groups can be used di-

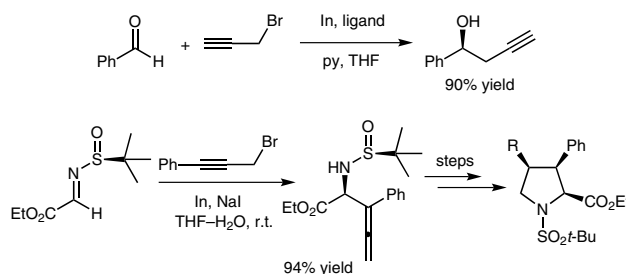
rectly without derivatization. In the context of green chemistry, organoindium reagents can undergo reactions in water, which is attractive from both economic and environmental standpoints. Organoindium compounds are versatile reagents for allylation, propargylation, allenylation, umpolung of enones, benzylation, arylation, alkylation, alkenylation and cross-coupling. Apart from these applications, they are also known for Reformatsky, Henry and Barbier-type reactions.⁴

Abstracts

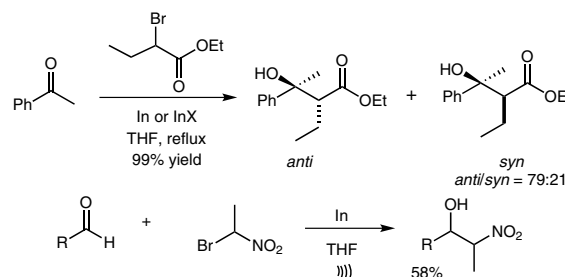
(A) In situ generated allylindium reagents spontaneously react with various carbonyl compounds to give homoallylic alcohols in moderate to good yield.^{5a,b} Indium-mediated allylation can be extended to imines,^{5c} nitriles,^{5d} acid chlorides,^{5e} acyl cyanides,^{5f} α -diazo-ketones^{5g} and α -chlorocarbonyls.^{5h}



(B) Singaram and co-workers reported an indium-mediated enantioselective propargylation of aldehydes with the aid of a chiral promoter.^{6a} Recently, Jin and Xu developed a highly diastereoselective indium-mediated allenylation of chiral (*S*)-*N*-*tert*-butanesulfinyl-imino esters with propargyl halides.^{6b} By taking advantage of the unique reactivity of the allene functionality, several challenging *cis*-substituted proline derivatives could be conveniently accessed.



(C) Indium enolates generated from α -halo esters and indium nitroates generated from 1-bromo-1-nitroalkanes, react with aldehydes to give Reformatsky and Henry-type reactions, respectively. Baba and co-workers established a diastereoselective Reformatsky reaction of aryl ketone with branched α -bromo ester using an indium reagent.^{4a} Soengas and Estévez recently reported a novel method for the preparation of 2-nitroalkan-1-ols by an indium-promoted reaction of bromonitromethane and 2-bromonitropropane with a variety of aldehydes.^{4b}



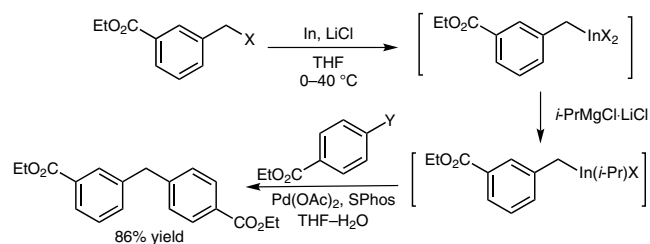
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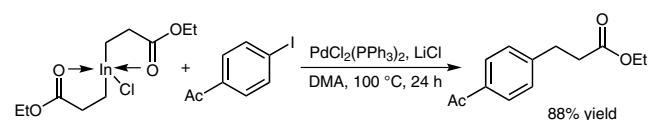
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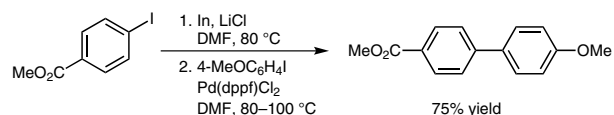
(D) Knochel et al. have prepared a range of highly functionalized benzylic indium compounds, which display an exceptional chemo-selectivity while undergoing palladium-catalyzed cross-coupling reactions with various electrophiles bearing acidic hydrogen atoms, such as amides, alcohols, sulfonamides, unprotected sugars, or uracil derivatives.⁷



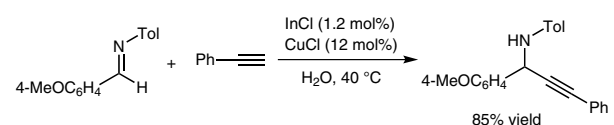
(E) Loh and co-workers developed an efficient method for the synthesis of ester-containing indium compounds which underwent palladium-catalyzed cross-coupling with aryl halides in DMA with wide functional group compatibility.⁸



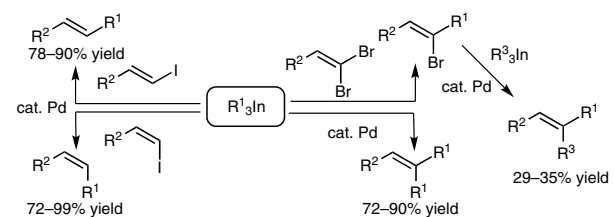
(F) Organoindium halides are capable of participating in cross-coupling reactions under transition-metal catalysis. Combination with aryl halides, acyl halides or allylic acetates/carbonates in the presence of $\text{Cl}_2\text{Pd}(\text{dppf})$ leads to biaryl, arylketone and allylic substitution products, respectively.⁹



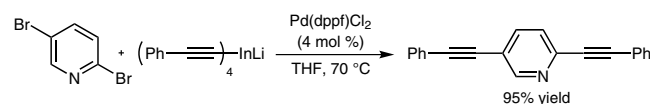
(G) Auge and co-workers reported the first alkylation of carbonyl compounds using alkynylindium reagents,^{10a} which was also extended to carbohydrates,^{10b} Baylis–Hillman acetates,^{10c} N,O-acetals^{10d} and imines.^{10e}



(H) Recently, Sarandeses, Sestelo, and co-workers have studied the regio- and stereoselectivity of the palladium-catalyzed cross-coupling reactions of indium organometallics with stereodefined 1-haloalkenes and 1,1-dihaloalkenes. Triorganoindium reagents (R^1_3In ; $\text{R}^1 = \text{alkyl, alkenyl, aryl and alkynyl}$) can be stereospecifically coupled with stereodefined alkenyl iodides in good yield and short reaction time under palladium catalysis.¹¹



(I) Lee and co-workers have developed an efficient method for the synthesis of various multialkynyl-substituted aromatic compounds using tetraalkynylindate organometallic species.¹²



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