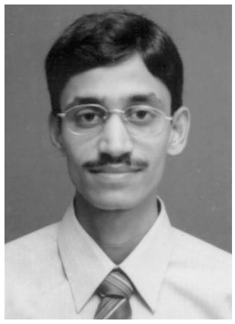
SYNLETT
Spotlight 39

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

$InCl_3$: A Mild Lewis Acid but Efficient Reagent in Organic Synthesis

Compiled by Srinivasarao Arulananda Babu



S. Arulananda Babu was born in 1976, received his BSc degree in Chemistry (1996) and MSc degree in Organic Chemistry (1998) from University of Madras, Chennai, India. He joined as CSIR-JRF (Junior Research Fellow) at CSMCRI; currently he is working as CSIR-SRF under the supervision of Dr. S. Muthusamy, CSMCRI, Bhavnagar, India, for his Ph.D degree on tandem cyclization-cycloaddition reactions of rhodium carbenoids. His present research interest involves on the application of tandem/cascade cycloaddition reactions for the synthesis of architecturally complex polycyclic and natural product frameworks using diazo ketones; Lewis acid catalysis, cycloaddition chemistry; application of new, resourceful and environmentally benign catalysts for various organic transformations.

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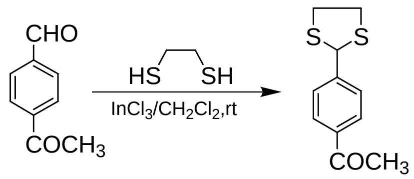
Introduction

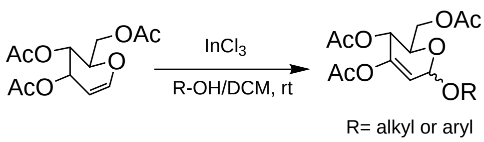
Lewis acids play a vital role in synthetic organic reactions since their use avoids the conventional, traditional and corrosive or harsh acid catalytic route. Lewis acids most habitually encountered in organic synthesis are $AlCl_3$, $BF_3{\cdot}Et_2O$, $ZnCl_2$, $TiCl_4$ and $SnCl_2$. Even though indium belongs to the same group in the periodic table as boron and aluminium, $InCl_3$ as a Lewis acid for organic reactions has been not exploited unlike the other Lewis acids during past decades. But recently, it has been proven that $InCl_3$ is a mild, worthwhile Lewis acid; which is stable in aqueous medium, effectively and selectively catalyzes various important organic reactions.[1] The recent emergence of $InCl_3$ as an efficient Lewis acid catalyst presents new and exciting opportunities for organoindium chemistry. It has been used as a catalyst for a wide variety of organic transformations and reactions since its emergence as a catalyst. $InCl_3$ was used in the synthesis of aryl hydrazides,[2] 2-haloamines,[3] *cis*-aziridine carboxylates,[4] chiral furan diol,[5] quinolines,[6] and homoallyl acetates.[7] Also it has been used in reductive Friedel-Crafts alkylation of aromatics with ketones or aldehydes,[8] for the reaction of acid chlorides with allylic tins,[9] for the insertion reactions of α-diazo ketones,[10] Biginelli reaction,[11] Mukaiyama aldol reactions,[1] imino Diels-Alder reactions,[1] in the conjugate addition of indoles with electron-deficient olefins,[18] for the bromolysis or iodolysis of α,β-epoxycarboxylic acids[19] etc.

Abstracts

An efficient, mild and highly chemoselective thioacetalization of carbonyl compounds using $InCl_3$ as the catalyst was developed.[12]



Treatment of tri-*O*-acetyl-D-glucal with various alcohols and phenols in the presence of $InCl_3$/DCM at ambient temperature gave the corresponding alkyl aryl 2,3-unsaturated glycopyranosides in excellent yields with good anomeric selectivity.[13]



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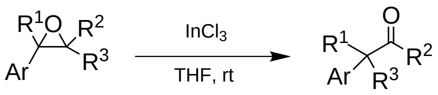
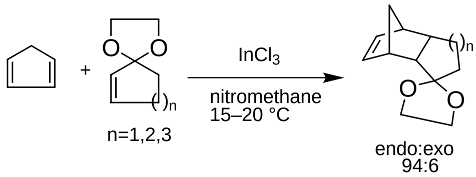
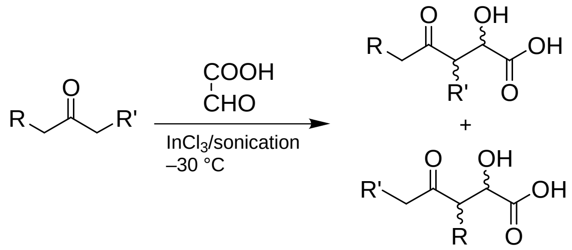
A simple and efficient procedure for the rearrangement of substituted epoxides catalyzed by $InCl_3$ was developed and selectivity was observed in the case of aryl-substituted epoxides.[14]



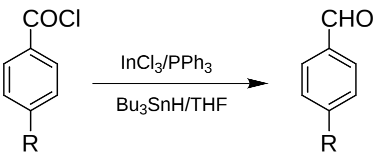
$InCl_3$ (20 mol%) in nitromethane permits ionic Diels-Alder reaction of a variety of 2,3-olefinic acetals to form the respective cycloadducts in good yields with good *endo* selectivity.[15]



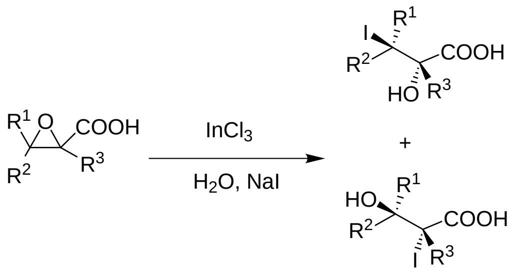
The direct aldol reactions of various ketones with glyoxylic and glyloxylates in the presence of $InCl_3$ afforded the α-hydroxy acid and α-hydroxy esters in good yields with high regioselectivities.[16]



The reduction of a wide range of acid chlorides to the corresponding aldehydes was carried out using indium trichloride in the presence of triphenylphosphene.[17]



The ring opening of α,β-epoxycarboxylic acids by bromide and iodide ions has been efficiently carried out in water in a high regio- and stereoselective fashion in the presence of indium trichloride as catalyst.[18]



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