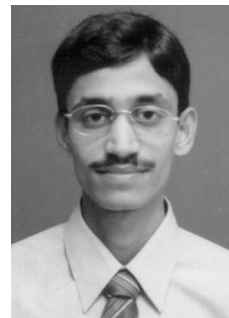


SYNLETT Spotlight 39

InCl₃: A Mild Lewis Acid but Efficient Reagent in Organic Synthesis

Compiled by Srinivasarao Arulananda Babu



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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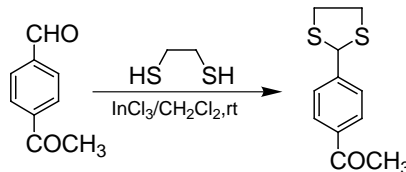
Introduction

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 AlCl₃, BF₃·Et₂O, ZnCl₂, TiCl₄ and SnCl₂. Even though indium belongs to the same group in the periodic table as boron and aluminium, InCl₃ 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 InCl₃ 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 InCl₃ as an efficient Lewis acid catalyst presents new and exciting opportunities for organoindium chemis-

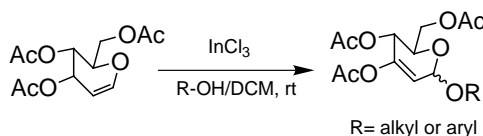
try. It has been used as a catalyst for a wide variety of organic transformations and reactions since its emergence as a catalyst. InCl₃ was used in the synthesis of aryl hydrazides,² 2-haloamines,³ *cis*-aziridine carboxylates,⁴ chiral furan diol,⁵ quinolines,⁶ and homoallyl acetates.⁷ Also it has been 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 acids¹⁹ etc.

Abstracts

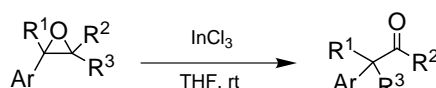
An efficient, mild and highly chemoselective thioacetalization of carbonyl compounds using InCl₃ as the catalyst was developed.¹²



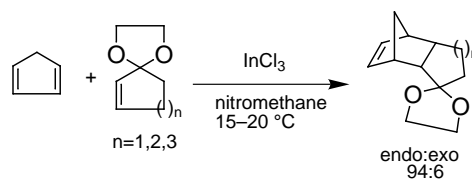
Treatment of tri-*O*-acetyl-D-glucal with various alcohols and phenols in the presence of InCl₃/DCM at ambient temperature gave the corresponding alkyl aryl 2,3-unsaturated glycopyranosides in excellent yields with good anomeric selectivity.¹³



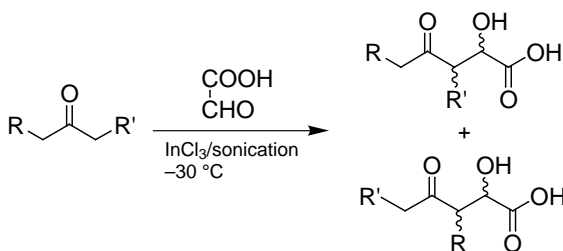
A simple and efficient procedure for the rearrangement of substituted epoxides catalyzed by InCl_3 was developed and selectivity was observed in the case of aryl-substituted epoxides.¹⁴



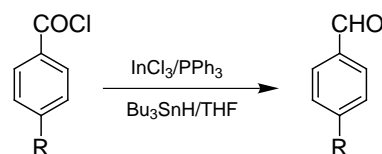
InCl_3 (20 mol%) in nitromethane permits ionic Diels-Alder reaction of a variety of 2,3-olefinic acetals to form the respective cycloadducts in good yields with good *endo* selectivity.¹⁵



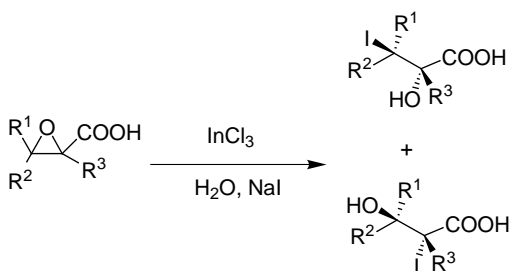
The direct aldol reactions of various ketones with glyoxylic and glyoxylic acids in the presence of InCl_3 afforded the α -hydroxy acid and α -hydroxy esters in good yields with high regioselectivities.¹⁶



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