SYNLETT Spotlight

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

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

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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 chemistry. 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,¹² for the bromolysis or iodolysis of α,β-,epoxycarboxylic acids¹³ etc.

**Abstracts**

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

![Thioacetalization Reaction](image)

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

![Thioacetalization Reaction](image)

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A simple and efficient procedure for the rearrangement of substituted epoxides catalyzed by InCl₃ was developed and selectivity was observed in the case of aryl-substituted epoxides.¹⁴

InCl₃ (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 InCl₃ 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

References


(3) Yadav, J. S.; Reddy, B. V. S.; Kumar, G. M. *Synlett* 2001, 1417.


