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An effective method for the selective synthesis of geminal diacetates (acylals) from aromatic aldehydes using alumina-supported $InCl_3$

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Abstract

Aliphatic and aromatic aldehydes can be converted to acylals in mild conditions by a treatment with acetic anhydride in the presence of $InCl_3/Al_2O_3$ (indium chloride loading = 1.2 mmol g^{-1}). For all reactions, $InCl_3/Al_2O_3$ is the best catalyst with reusable and highly activity.

Keywords: Acylal; Acylation; Alumina-supported; Protecting groups

1. Introduction

Acylals have been used as protecting groups for carbonyl compounds because of their stability in neutral and basic media as well as aqueous acids [1,2]. The acylals are important starting materials for the synthesis of valuable intermediates in the Diels-Alder cycloaddition reactions [3]. Acylals have been applied as crosslinking reagents for cellulose in cotton [4]. Hence, there are considerable methods for synthesis of acylals. Some of the catalysts which have been developed for this purpose are including: sulfuric acid [5a], triflic acid [5b], PCl_3 [5c], TMSCl–NaI [5d], $ZnCl_2$ [5e], I_2 [5f], anhydrous ferrous sulfate [5g], $FeCl_3$ [5h], NBS [5i], zeolites [6a], sulfated zirconia [6b], montmorillonite clay [6c], expansive graphite [6d], aluminum dodecatungstophosphate [6e], zeolite HSZ-360 [6f], layered zirconium sulfophenyl phosphonate [6g], $Cu(OTf)_2$ (2.5 mol%) [7a], $Sc(OTf)_3$ (2 mol%) [7b], $Bi(OTf)_3$ (0.1 mol%) [7c], $Zn(BF_4)_2$ [7d], $ZrCl_4$ [7e] and bismuth nitrate [7f] which are also efficient for this conversion.

Many of the reported methods, however, involve strongly acidic or oxidising conditions, corrosive reagents, high temperature, high catalyst loading, longer reaction time and cumbersome procedures. Moreover, some of these are not selective in terms of aldehydes and keto carbonyl functional groups. In view of these, the search for finding a cost effective, mild and simple selective protocol for synthesis of acylals from aldehydes is still relevant. In recent years, indium compound has been used as a potential Lewis acid for many organic transformations [8]. In continuation of our research programmed on In(III) mediated organic reactions [9], we herein report the results of $InCl_3/Al_2O_3$ catalysed expedient, simple and cost effective, selective conversion of aldehydes to acylals (Table 1).

2. Experimental

2.1. Preparation of heterogeneous catalyst

Heterogeneous catalysts were prepared by impregnating acidic alumina (Merck: Art No. 1078, aluminium oxide 90 active acidic, 0.063–0.200 mm, it was activated at 500 °C for 8 h before use) with anhydrous indium(III) chloride (purity 99.99% Aldrich) from their acetonitrile solution by incipient wetness technique [12e], and evaporating the solvent in vacuum oven at 120 °C for 10 h (loading of metal chloride = 1.2 mmol g^{-1}). At the end of the reaction, the catalyst was separated by filtration, thoroughly washed with solvent

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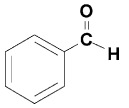
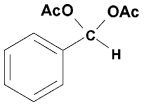
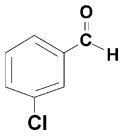
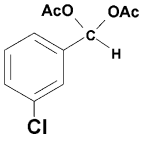
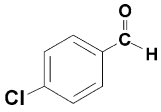
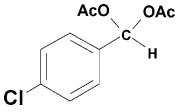
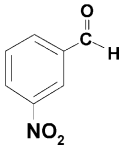
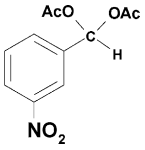
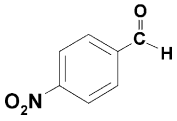
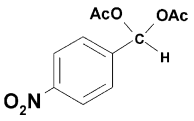
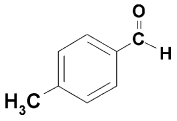
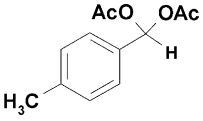
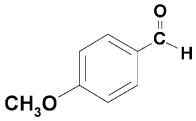
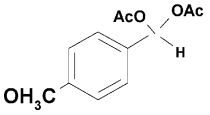
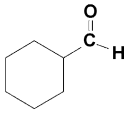
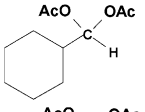
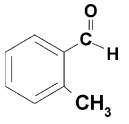
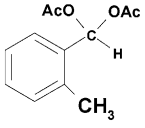
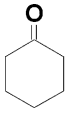
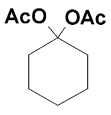
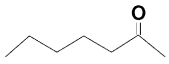
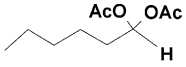
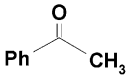
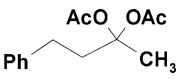
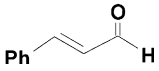
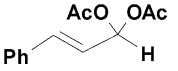
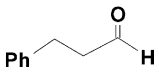
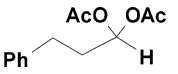
Table 1
Alumina-supported indium chloride acylal formation and deprotection

Entry	Substrate	1,1-Diacetates[a]	Preparation		Deprotection	
			Yield (%)[b]	Time	Yield (%)[b]	Time (h)
1			86	10 min	87	3
2			88	10 min	88	3
3			91	10 min	90	3
4			89	10 min	89	3
5			94	10 min	91	3
6			99	10 min	93	3
7			97	10 min	92	3
8			82	50 min	36	6
9			80	30 min	79	3
10			9	24 h	[c]	24
11			8	24 h	[c]	24
12			7	24 h	[c]	24
13			73	3 h	85	3
14			35	4 h	72	6

[a] All the products were characterized by comparison (TLC and physical constant) with authentic samples prepared by the conventional method [2,7,11].
[b] Isolated yields.
[c] No reaction.