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Silica gel supported $AlCl_3$ catalyzed Friedel-Crafts acylation of aromatic compounds

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Abstract

Silica gel supported aluminium trichloride (SiO_2-$AlCl_3$) has been shown to be a mild, efficient, and chemoselective heterogeneous Lewis acid catalyst for the acylation of aromatic compounds with acid chlorides. The catalyst can be reused up to five times after simple washing with ether and is stable (as a bench top catalyst).

Keywords: Acylation; Ketones; Aluminium trichloride; Silica gel

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Friedel-Crafts acylation is a fundamental and important process in organic synthesis as well as in industrial chemistry [1,2]. Protic acids and Lewis acids have been used as catalysts in conventional Friedel-Crafts acylation reactions [3–19]. The major disadvantages associated with the reported methods for the acylation of arenes are a need for the use of stoichiometric or excess amounts of catalyst in reactions (due to consumption of the catalyst by complexation to starting materials and/or products), the use of unrecyclable catalysts which eventually result in generation of a large amount of environmentally hazardous waste materials, less selectivity of *para*/*ortho* isomers, tedious work-up, and the use of moisture-sensitive, expensive, hazardous or difficult to handle catalysts. Furthermore, in most of these methods applicable substrate range is very limited.

Over the last years, SiO_2-$AlCl_3$ has been reported to catalyze several organic reactions [20–22]. In a previous study, we also reported the use of SiO_2-$AlCl_3$ as a remarkably efficient heterogeneous catalyst for the Friedel-Crafts sulfonylation of arenes [23]. Along this line, we now wish to report that SiO_2-$AlCl_3$ is also highly chemoselective catalyst for the acylation of aromatic compounds with acid chlorides in solvent-free conditions (Scheme 1).

1. Experimental

Chemicals were either prepared in our laboratory or were purchased from Merck and Fluka. Capacity of the catalyst was determined by gravimetric method and atomic absorption technique using a Philips atomic absorption instrument.

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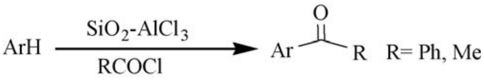
Reaction monitoring and purity determination of the products were accomplished by GLC or TLC on silica gel polygram SILG/UV_{254} plates. Gas chromatography was recorded on Shimadzu GC 14-A. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Advance DPX-300 spectrometer.



Scheme 1.

Anhydrous $AlCl_3$ (5.1 g) was added to silica gel (Merck grade 60, 230–400, washed with 1 mol/L HCl and dried under vacuum at 80 °C for 72 h, 10.2 g) in CCl_4 (30 mL). The mixture was stirred using a magnetic stirrer under reflux condition for two days under N_2 atmosphere and filtered and washed with 50 mL of dry CCl_4, and then dried under vacuum at 60 °C for 3 h. The loading of $AlCl_3$ determined was 1.3 mmol/g [23].

To a solution of anisole (5 mmol) and benzoyl chloride (4 mmol) was added 0.4 mmol of SiO_2-$AlCl_3$ and the reaction mixture was stirred magnetically at room temperature. After completion of the reaction (monitored by TLC), the catalyst was filtered off and washed with CH_2Cl_2. The filtrate was washed with aqueous solution of sodium bicarbonate and water and the organic layer was dried (Na_2SO_4) and concentrated on a rotary evaporator under reduced pressure to give the corresponding ketone. Whenever required, the products were purified by column chromatography (silica gel) using petroleum ether-ethyl acetate as eluent so as to afford the pure ketone.

2. Results and discussion

SiO_2-$AlCl_3$ was prepared by reaction of silica gel with aluminium trichloride in refluxing carbon tetrachloride. By using this catalyst various substituted benzenes were converted into their corresponding ketones with benzoyl chloride and acetyl chloride as acylating agents in high to excellent yields at room temperature in solvent-free conditions (Table 1). The optimum molar ratio of SiO_2-$AlCl_3$ to acid chloride was 0.1:1. The methodology showed the excellent positional selectivity as the *para* substituted product was formed almost exclusively. Naphthalene, 2-methoxy-naphthalene, and anthracene underwent acylation with high regioselectivity in 89–91% yields (see the supporting information). Acylation of furan, thiophene, and pyrrole is not a straightforward reaction and usually in the presence of acid catalysts undergo polymerization reactions. We found that SiO_2-$AlCl_3$ is a suitable catalyst for such important acylation reactions. These reactions were regioselective and produced only the 2-acyl product in 89–92% yields. The acylation of indoles with acid chlorides in the presence of SiO_2-$AlCl_3$ was also studied and the corresponding indolyl aryl ketones were obtained with high regioselectivity. For example, indole was converted to its corresponding ketone with acetyl chloride in 91% yield. No *N*-substituted products were observed under these reaction conditions. Acylation of highly deactivated arenes such as nitrobenzene and 1,2-dichlorobenzene failed. SiO_2-$AlCl_3$ was stable under the reaction conditions and during reactions no leaching of acid moieties was observed due to being chemically bonded to the support.

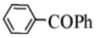
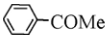
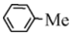
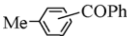
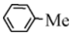
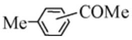
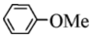
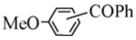
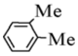
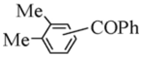
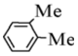
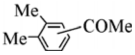
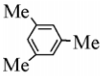
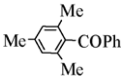
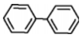
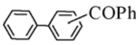
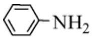
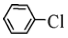
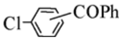
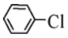
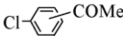
It was observed that, 4-phenylbutanoic acid chloride cyclized in nitrobenzene at 40 °C in the presence of SiO_2-$AlCl_3$ to give the desired 1-tetralone in 94% yield (Scheme 2).

The feasibility of recycling the catalyst was also examined. After each reaction the catalyst was washed with ether and reused. As it is shown in Scheme 3 the efficiency of the recycled catalyst did not change appreciably after five cycles.

As shown in Table 2, SiO_2-$AlCl_3$ has a good efficiency compared to other recently reported catalysts.

In conclusion we have introduced a highly efficient solid catalyst for the acylation of arenes with acid chlorides to afford ketones in high to excellent yields. The mild reaction conditions, short reaction times, easy work-up, high to excellent yields, chemoselectivity, reuse of the catalyst for at least five times without significant change in its catalytic activity, low cost, and easy preparation and handling of the catalyst are the obvious advantages of the present method.

Table 1
Acylation of arenes with acid chlorides catalyzed by SiO_2-$AlCl_3$.[a].

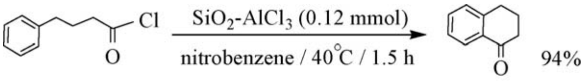
Entry	Arene	Acid chloride	Product	Time (h)	Yield (%) (*o:m:p*)[b]
1		PhCOCl		1	91 [7]
2		MeCOCl		1.1	92 [7]
3		PhCOCl		0.9	92 (6:3:91) [19]
4		MeCOCl		0.9	92 (5:4:91) [7]
5		PhCOCl		0.8	95 (5:3:92) [19]
6		PhCOCl		0.9	92 (95:5)[c] [7]
7		MeCOCl		0.9	92 (95:5)[c] [7]
8		PhCOCl		0.9	92 [19]
9		PhCOCl		1	89 (4:3:93)[d] [7]
10		PhCOCl		1.1	91 (6:0:94) [7]
11		PhCOCl		1.2	89 (6:4:90) [7]
12		MeCOCl		1.3	90 (6:4:90) [7]

[a] All reactions carried out at room temperature in the absence of solvent, unless otherwise indicated. The molar ratio of SiO_2-$AlCl_3$:acid chloride is 0.1:1.

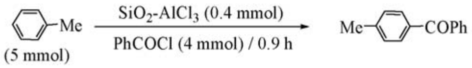
[b] Isolated yields. Isomer distribution based on ^1H-NMR spectroscopy and GC. All products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples.

[c] Isomer distribution of 3,4-dimethylphenyl isomer to 2,3-dimethylphenyl isomer.

[d] The reaction was performed in 1,2-dichloroethane.



Scheme 2.



Use[a]	1	2	3	4	5
Yield (%)	92	92	91	90	89

[a]Recovered catalyst was used successively (Use 2,3,…)

Scheme 3.

Table 2
Comparison of the catalytic activity of SiO_2-$AlCl_3$ against other reported catalysts for the acylation of anisole with benzoyl chloride.

Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%) (*o*:*p*)
SiO_2-$AlCl_3$	Neat	r.t	0.8	95 (5:92)
$Sc(OTf)_3$	CH_3NO_2	50	18	79 [4]
$BiCl_3$	Neat	110	6	96 [6]
Zn powder	Neat (MW)	120	10 (s)	71 [7]
$AlPW_{12}O_{40}$	Neat	60–70	2	94 (20:80) [8]
Al metal powder	Neat	82 (MW)	10	81 [11]
$InCl_3$-$[C_4mim]Cl$[a]	Neat	100	18	94 (6:94) [12]
SmI_3	CH_3CN	45	4	61 [13]

[a] Chloroindate(III) ionic liquid.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2010.07.024.

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