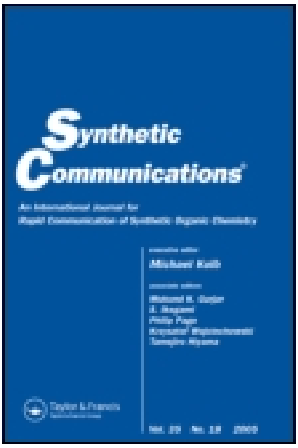

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Zinc Promoted Regioselective Friedel-Crafts Acylation of Electron Rich Arenes

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ZINC PROMOTED REGIOSELECTIVE FRIEDEL-CRAFTS ACYLATION OF ELECTRON RICH ARENES

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Abstract : A simple and convenoent zinc promoted selective Friedel-Crafts acylation is described. The inexpensive metal grade catalyst and minimum waste effluent are the important features of the procedure.

Friedel-Crafts acylation is an useful reaction in organic synthesis[1] and it is a boon to organic chemistry for the preparation of ketones. The classical catlysts[1] like $AlCl_3$ and other metal halides generally empolyed in more than stoichiometric amounts encounters the problems of corrosivity and effluent pollution. Considering the importance of the reaction, several methods[2] have been developed but some of them lacks the selectivity while the others have difficulty in catalyst preparation.[3] Moreover, the acylation using anhydrides produces one molecule of acid as a waste. Today the goal is to evolve a procedure to minimize the amount of waste-byproducts. Considerable success has already been achieved using improved reagents and strong solid acids[4] which could eliminate the hazards of HF. Zeolites[5] (120-250°C) have also been used for acylation but their utility is limited to smaller molecules.

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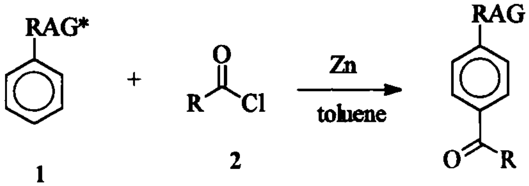
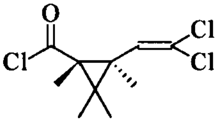
Recently, the metal catalysed[6] reactions have gained wide popularity because of their easy handling and seclctivity. The observation prompted us to employ the inexpensive metal catalyst for acylation to satisfy the criteria of less waste byproducts and the use of stoichimoetric amount of catalyst. In continuation of our work in developing new methodologies using metals[7] and solid supported reagents,[8] herein we wish to report a zinc promoted convenient simple and selective Friedel-Crafts acylation of electron rich arenes. We beleive that our procedure is an useful addition to the array of Friedel-Crafts acylation reaction.

The general experimental procedure is as follows : A solution of acid chloride (4 mmol in 50 ml toluene) was stirred with activated zinc (4 mmol) at r.t. for 15 minutes. To this was added a toluene solution of arene (4 mmol in 30 ml) and the mixture was heated at 70°C for stipulated time (see table). The completion of the reaction was followed by tlc. The used up catalyst was removed by filtration, filtrate washed with sodium bicarbonate (10%) and organic phase dried over sodium sulphate. The evaportion of solvent gave essentially pure product in good yield. If necessary the further purification can be done by passing through a small bed of neutral alumina using hexane:ethylacetate (80:20) as eluent.

The method selictively and efficiently proceeds with active arenes. However, the efforts failed to acylate benzene, chlorobenzene and toluene in the identical condition. Further, it was observed that increasing the alkyl chain on benzene ring facilitate the reaction (entry-9,10,11,12). This finding supports the selectivity of this method for electron donating substrates. We presume that the electrophilic character of acyl chlorides is enhanced by the zinc which in turn reacts at the ectron rich position of arenes. This effect may be explained by assuming that the polar groups complexes efficiently to the zinc surface.[9] Though the reaction proceeds 0.5 eq. of zinc, the rate of the reaction is enhanced by employing by 1 eq. of zinc. It is important to note that the unused zinc is recovered at the end of the reaction, which can be resused again after activation. It shows the economical and environmental consciousness of the



1 2

1a.	Anisole	2a.	Pivaloyl chloride
1b.	N-2,6-dichlorophenyl aniline	2b.	Palmitoyl chloride
1c.	Isobutyl benzene	2c.	p-Chlorobenzoyl chloride
1d.	Thiophene	2d.	

* RAG = Ring activating group

Table : Acylation of electron rich arenes with acid chlorides

Entry	Arenes	Acid chlorides	Time/h	Yield[a,b]
1.	1a	2a	6	90
2.	1a	2b	5	91
3.	1a	2c	7	85
4.	1a	2d	8	89
5.	1b	2a	6	90
6.	1b	2b	6	93
7.	1b	2c	7	85
8.	1b	2d	6	88
9.	1c	2a	6	90
10.	1c	2b	7	83
11.	1c	2c	7	80
12.	1c	2d	8	86
13.	1d	2a	6	93
14.	1d	2b	7	89
15.	1d	2c	8	92
16.	1d	2d	7	94

[a] : Yields are obtained after column chromatography purification.

[b] : Products are characterised based on NMR, IR and Mass spectral data.

method and offers advantages over the existing methods. The importance of the procedure can be seen by its application to a variety of substrates using different acid chlorides and leading to selective acylated products.

In conclusion we have demonstrated a simple and convenient zinc promoted Friedel-Crafts acylation. The inexpensive and reusable catalyst with less waste effluent allows the method to transform into economically viable procedure.

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