Original Article

Bulletin of Pure and Applied Sciences.
Vol.38 C (Chemistry), No.1, 2019: P.27-32
Print version ISSN 0970 4620
Online version ISSN 2320 320X
DOI 10.5958/2320-320X.2019.00003.7
http://www.bpasjournals.com/chemistry/

Indium modified AlMCM-41 catalyzed synthesis of 2,4,5-triaryl-1H-imidazole derivatives

Abstract

We have presented a very simple, fast, general and efficient method for synthesis of 2,4,5-triarylimidazole derivatives *via* condensation of aldehydes, benzil/benzoin and ammonium acetate in the presence of In/AlMCM-41. All the synthesized compounds have been characterized on the basis of elemental analysis, IR, ^{1}H NMR, and ^{13}C NMR spectral studies.

Keywords: 2,4,5-Triaryl-1*H*-Imidazole, Mesoporous zeolite In/AlMCM-41, Heterogeneous catalyst

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Received on 16.08.2018
Accepted on 03.10.2018

1. Introduction

In modern preparative synthetic chemistry, multicomponent reactions (MCRs) have great importance. By combining several operational steps without isolation of intermediates or change of the conditions, these reactions increase the efficiency [1-6]. No of reactants viz more than three are combined in a single chemical step to produce products. 2,4,5-triaryl-1*H*-imidazole compounds are well known as inhibitors of P38MAP kinase [7], herbicides [8], anti-inflammatory [9,10] anti-thrombotic [11], plant growth regulators [12] and therapeutic agents [13]. In addition to this, imidazoles are substantially used in the synthesis of ionic liquids [14,15] that have been given a new approach to the green chemistry. These are also used in photography as a photosensitive compound [16].

The applications of zeolites in the field of catalysis are growing continuously. Zeolites possess unique properties such as Bronsted and Lewis acidity, possibility to modify their acid:base and redox properties by changing their chemical composition by using different metals, ability to accept and release electrons, high proton mobility, easy work-up procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of these catalysts. Because of their stronger acidity, they generally exhibit higher catalytic activity than conventional catalysts such as mineral acids, ion exchange resins, and mixed oxides. In the context of green chemistry, the substitution of harmful liquid acids by solid reusable zeolites or mesoporous materials as catalysts in organic synthesis is the most promising application. Recently the 2,4,5-triaryl-1*H*-imidazole derivatives synthesized by using homogeneous and heterogeneous catalysts such as $InCl_3.3H_2O$ [17], alum [18], $ZrCl_4$ [19], zeolite HY [20], *L*-proline [21], $[(Hmim)HSO_4]$ [22], *p*-TSA [23], iodine [24], $Eu(OTf)_3$ [25],

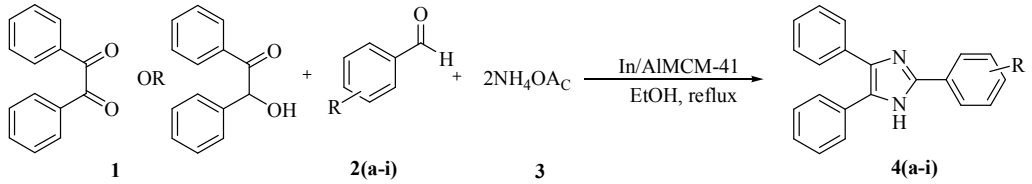
sulphanilic acid [26]. A major drawback of these classical methods is the poor yields, use of expensive and hazardous reagents and solvents, tedious work-up procedure, and in some cases failure of the method. In addition, the synthesis of fine chemicals under environmentally friendly conditions represents a challenging goal in the field of synthetic organic chemistry.

In continuation of our ongoing research on zeolite as a solid as a solid catalyst for organic transformations [27-31], herein we report, the efficient method for the synthesis of various 2,4,5-triaryl-1*H*-imidazole derivatives using heterogeneous catalyst indium modified mesoporous zeolite AlMCM-41.

2. Result and discussion

2.1 Effect of catalyst loading

The catalyst indium modified mesoporous zeolite AlMCM-41 was prepared by using our reported method [32]. For establishing the best reaction conditions, an optimization study was performed using the reaction of benzaldehyde, benzil and ammonium acetate as a model reaction (Scheme1) in the presence of varying amounts of catalyst (0, 0.01, 0.05, 0.1, 0.15 and 0.2 gm) and the results were given in Table 1. Various catalytic amounts was used, the 0.1 gm of a catalyst proved superior and generated the desired product in 93% (Table 1, entry 4). Further, increase in the amount of catalyst (0.15 and 0.2 gm) does not show any variation in time and product yield (Table 1, entries 5 and 6). In the absence of catalyst, no product was formed (Table 1, entry 1).



1 2(a-i) 3 4(a-i)

Scheme 1: Synthesis of 2,4,5-triarylimidazole derivatives under reflux condition catalyzed by In/AlMCM-41.

Table 1: Effect of catalyst loading in the synthesis of 2,4,5-triphenyl-1*H*-imidazole[a].

Entry	Catalyst amount (gm)	Time (min)	Yield[b] (%)
1	None	90	-
2	0.01	90	45
3	0.05	90	78
4	0.10	90	93
5	0.15	90	93
6	0.20	90	93

[a]Reaction condition: Benzaldehyde (10 mmol), benzil (10 mmol), ammonium acetate (20 mmol) at reflux condition, [b]Isolated yields.

2.2 Effect of various solvent

Further optimization of the reaction by using same model reaction for the effect of different solvents, such as dichloromethane (DCM), dimethylformamide (DMF), methanol (MeOH), acetonitrile (MeCN) and ethanol (EtOH). In the initial stage, we select dichloromethane (DCM), afforded only 45% product yield (Table 2, entry 1). Furthermore, by using DMF, MeOH and MeCN, gave 61%, 72% and 79% product yields (Table 2, entries 2, 3 and 4) respectively. Moreover, when the reaction is carried out in ethanol, gave excellent product yield (93%) within 90 min. (Table 2, entry 5). This indicates that reaction in ethanol gave the best results with respect to product yield and time.

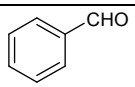
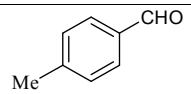
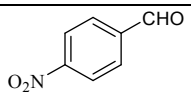
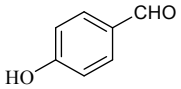
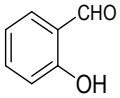
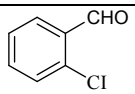
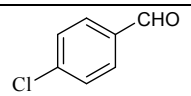
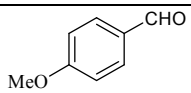
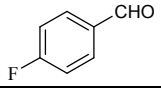
Table 2: Screening of various solvent in the synthesis of 2,4,5-triphenyl-1*H*-imidazole (Table 3, entry 4a).[a]

Entry	Solvent	Time (min)	Yield[b] (%)
1	DCM	130	45
2	DMF	120	61
3	MeOH	90	72
4	MeCN	90	79
5	EtOH	90	93

[a]Reaction condition: Benzaldehyde (10 mmol), benzil (10 mmol), ammonium acetate (20 mmol) and In/AlMCM-41 catalyst (0.1 gm) at reflux condition, [b]Isolated yields.

Based upon the above findings, we further studied the synthesis of 2,4,5-triarylimidazole derivatives from different aromatic aldehydes with benzil/benzoin and ammonium acetate using In/AlMCM-41 as catalyst. As shown in Table 3, it can be seen that a variety of aldehydes, including those having electron-donating or electron-withdrawing groups the reaction could be completed in shorter time with good to excellent yields (Table 3, entries 4a-i).

Table 3: Synthesis of 2,4,5-triaryl-1*H*-imidazole derivatives using indium modified AlMCM-41 catalyst in ethanol.

Entry	Ar-CHO	Reaction time (min)		Yield (%)[a]		M.P. (°C)
		Benzil	Benzoin	Benzil	Benzoin	
4a		90	120	93	87	274-276
4b		110	130	93	85	231-232
4c		125	150	90	82	231-232
4d		90	110	89	83	269-270
4e		90	125	90	85	201-202
4f		90	110	93	91	183-184
4g		90	110	93	87	262-263
4h		120	140	89	82	232-233
4i		100	125	89	84	261-262

[a]All yield refers to isolated yield.

2.3 Recovery and reusability of catalyst

Finally, we studied the recovery and reusability of In/AlMCM-41 catalyst by using same model reaction. The catalyst was separated by directly filtering from the reaction mixture, washed with n-hexane and dried at 120°C for 1 h. The catalyst was reused for subsequent reactions and did not show any significant decrease in catalytic activity even after four runs (Table 4).

Table 4: Reusability of In/AlMCM-41 catalyst in the synthesis of 2,4,5-triphenyl-1*H*-imidazole.[a]

Entry	Run	Yield[b] (%)
1	1st	93
2	2nd	93
3	3rd	92
4	4th	91

[a]Reaction condition: Benzaldehyde (10 mmol), benzil (10mmol), ammonium acetate (20 mmol) and ethanol (10 mL) at reflux condition for 90 min, [b]Isolated yields.

In order to show the merits of In/AlMCM-41 in comparison with other reported catalysts. As Table 5 demonstrates, our method afforded the better results to those previously reported.

Table 5: Comparisons of results of other reported procedures with the present method.

Entry	Catalyst	Reaction condition	Time (h)	Yield (%)
1	In/AlMCM-41	EtOH/reflux	1.5-2.5	82-93
2	$InCl_3.H_2O$	MeOH/ rt	8.3-9.4	54-82
3	*L*-proline	EtOH/reflux	2-5	75-94
4	Excess H_2SO_4	150-200°C	4	40-90

2.4 Experimental

All chemicals are purchased from Aldrich and Rankem chemical suppliers and used as received. The uncorrected melting points of compounds were taken in an open capillary in a paraffin bath. 1H NMR spectra were recorded on an 300 MHz FT-NMR spectrometer in CDCl3 as a solvent and chemical shifts values are recorded in δ (ppm) relative to tetramethylsilane (Me4Si) as an internal standard.

2.5 General procedure for the synthesis of 2,4,5-triaryl-1*H*-imidazoles

A mixture of an aldehyde (10 mmol), benzil/benzoin (10 mmol), ammonium acetate (20 mmol) In/AlMCM-41 (0.1 gm) and ethanol (10 mL) was refluxed up to completion of reaction. The progress of the reaction was monitored by thin layer chromatography, using petroleum ether/ethyl acetate (7:3) as a solvent system. After completion of the reaction, In/AlMCM-41 was filtered and the filtrate was concentrated under reduced pressure. The solid product obtained was crystallized from ethanol to afford the pure products **(4a-i)**.

2.6 Spectral data of representative compound (4i):

^{1}H NMR ($CDCl_3$, δ in ppm): 6.75 (s, 1H, NH), 7.34-7.78 (m, 10H, ArH), 7.20 (d, 2H), 8.69 (d, 2H). IR (KBr): 3051, 1888, 1811, 1764, 1698, 1600, 1509, 1443, 1231, 1109 cm^{-1}.

3. Conclusions

In summary we have developed highly efficient method for the synthesis of 2,4,5-triaryimidazole derivatives. This method has the ability to tolerate the variety of other functional groups such as methoxy, hydroxyl, nitro, halides etc. The method offers simple experimental and isolation procedure and catalyst is easily recovered and recycled.

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