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SYNTHESIS OF 2-SUBSTITUTED BENZIMIDAZOLES AND 1,5-DISUBSTITUTED BENZODIAZEPINES USING ALUM

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ABSTRACT

Alum, have been investigated for their catalytic activity in the condensation reaction between *o*-phenylenediamine and an aldehyde or a ketone to synthesizes 2-substituted benzimidazole and 1,5-disubstituted benzodiazepines respectively. The isolated yields of 2-substituted benzimidazole and 1,5-disubstituted benzodiazepines are in the range of 30% to 95%. This method has been found to be simple and economical. The solid supports could be regenerated and reused without much loss in their activity. Further, the solid supports have been also found to be effective as general catalysts in the condensation of *o*-phenylenediamine with other substituted aldehydes and ketones.

Keywords: 2-substituted benzimidazole, 1,5-disubstituted benzodiazepines, alum.

INTRODUCTION

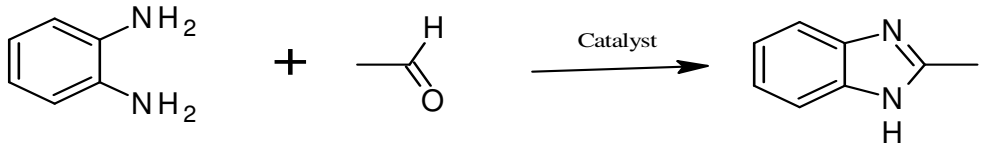
For several decades there has been a concern for improving the chemical processes in the industry, with regard to environmental and health related issues, which would also eventually reduce chemical waste. Catalytic activation of substrates under heterogeneous conditions using solid acids and bases as catalysts or catalyst supports has been identified as one of the important ways to make the given process environmentally benign and efficient.[1-2] Thus over the years a lot of research has been focused on the development of greener processes.[3] Benzimidazole derivatives exhibit various biological and pharmaceutical properties [4-7]. Recently it has been found that benzimidazole derivatives are useful as fluorescent chemo sensors for Cu^{2+}.[8] Benzodiazepine and their derivatives are also interesting class of bioactive compounds widely used in therapeutics as anti-conversant, analgesics, anti-anxiety drugs, sedatives, anti-depressants, and hypnotics.[9-11] One of the methods commonly reported by several groups for the synthesis of benzimidazole and benzodiazepines is the condensation reaction between *o*-phenylenediamine (OPDA) and an aldehyde or a ketone respectively.

Catalytic activities of different Lewis acids have been investigated in the synthesis of benzimidazole and benzodiazepines by different groups highlighting the advantages of their protocol over the other methods.[12-18] However, to the best of our knowledge no attempt has been made to correlate the surface properties of the catalysts and their catalytic activity in the condensation of aldehydes/ketones with OPDA to synthesizes benzimidazole and benzodiazepines Metal oxides and supported metal oxides are known to possess surface acidity and/or basicity and activate a number of industrially important organic transformations.[19-24] We have developed new method of synthesis of benzimidazole using green approach and alum as catalyst.

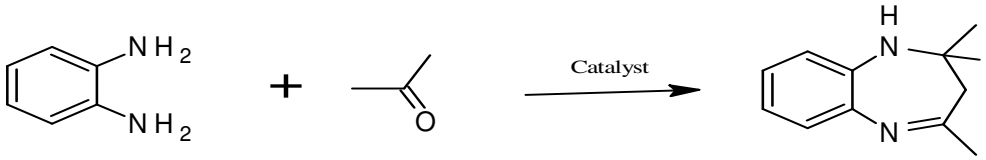
EXPERIMENTAL

The catalytic activity of the catalysts, dried at 120^0C and calcined at 450^0C, was investigated in the condensation reaction between OPDA and benzaldehyde or acetophenone (Scheme 1). This is used as a

model reaction. In a typical procedure a mixture of OPDA (1 mmol), benzaldehyde (1mmol) or acetophenone (2.2 mmol), ethanol (5 ml), and the catalyst (0.2 g) taken in a 100 ml RB flask was heated to 80^0C. The progress of the reaction was monitored periodically by analyzing the reaction mixture by thin layer chromatography using a mixture of petroleum ether and ethyl acetate in 8:2 ratio. After completion of the reaction, the reaction mixture was diluted with 10 ml of ethanol and filtered to recover the solid catalyst. The filtrate was poured into a beaker containing crushed ice. The solid product was separated and purified by column chromatography using silica gel [100-200 mesh] with petroleum ether and ethyl acetate as solvent. The products were further analyzed by IR, 1H NMR.



Scheme-1



Scheme-2

Table-1: Observation for benzimidazole

Entry I	Aldehyde	Time (min)	Yields in %	M.P. ^{o}C
1	Benzaldehyde	7	90	289
2	Anisaldehyde	9	95	234
3	4-methyl benzaldehyde	9	94	224
4	4-chlorobezaldehyde	7	95	291
5	4-flurobenzaldehyde	7	97	245
6	3-bromobenzaldehyde	7	96	265
7	Furan-2carbaldehyde	7	95	285
8	Cinnamaldehyde	12	95	199-201
9	3-nitrobanzaldehyde	10	90	309-310

Table-2: Observation for benzopines

Entry I	Aldehyde	Time (min)	Yields in %
1	Benzaldehyde	9	85
2	Anisaldehyde	10	80
3	4-methyl benzaldehyde	11	74
4	4-chlorobezaldehyde	15	75
5	4-flurobenzaldehyde	20	80
6	3-bromobenzaldehyde	18	85
7	Furan-2carbaldehyde	17	90
8	Cinnamaldehyde	16	94
9	3-nitrobanzaldehyde	15	90

Spectral Analysis

Phenyl-1H-benzimidazole

Pale yellow solid: mp: 293–296ºC; **IR** (KBr) 3042, 1440, 1403, 1271, 971 cm^{-1}; **MS:** *m*/*z* = 193(M+); **1H NMR** (300 Hz, DMSO): δ 7.22 (m, 2H), 7.48 (m, 5H), 7.58 (s, 1H), 8.04 (d, 2H, *J* = 1.6 Hz).

Benzopines 2-(4-Methoxyphenyl)-1H-benzimidazole
Yellow solid: **MP:** 225–226ºC; **IR** (KBr) 3478, 2985, 1625, 1537, 1341, 1127, 1038, 835 cm^{-1}: **MS:** *m/z* =224(M+): **1H NMR** (300 Hz, DMSO): δ 8.00–8.08 (m, 2H), 7.20–7.60 (m, 6H), 3.52 (m, 3H).

CONCLUSION

Synthesis of 2-substituted benzimidazole and 1,5-disubstituted benzodiazepines by the condensation of *o*-phenylenediamine with different substituted aldehydes and ketones reported well. Mild reaction conditions, easily work up, and high yields along with reusability of the catalyst make it a valuable alternative to the existing catalysts in the literature. The importance of the amount of surface acid sites and the morphology of the catalysts in activating the condensation reaction between OPDA and an aldehyde/ketone is made clear.

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