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Ionic liquid catalyzed formation of 3, 4-dihydropyrimidine 2(1H)-ones

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ABSTRACT

In green synthesis using ionic liquids as a recyclable eco- friendly reaction medium to enhance rates and selectivity we report here in a one pot synthesis of dihydropyrimidinones catalyzed by specific acidic ionic liquids [B min] HSO₄ which is found to be a simple, highly yielding time saving and environmentally friendly method. © 2011 Trade Science Inc. - INDIA

KEYWORDS

3, 4-dihydropyrimidine
2(1H)-ones;
Ionic liquid;
Catalyst;
Green chemistry.

INTRODUCTION

In recent years dihydropyrimidinones and their derivatives have been shown to display a range of useful physiological and pharmacological properties. They have emerged as integrals backbones of several calcium channel blockers, antagonists, antihypersensitive agents and anticancer drugs. Thus synthesis of the dihydropyrimidinone derivative has received much attention continuously. In 1893 Biginelli reported a simple and straightforward procedure starting from aromatic aldehydes, β- dicarbonyl compounds and thiourea under strong acidic conditions with low yield and time Therefore the development of an efficient and versatile catalyst for Biginelli reaction is an active ongoing research area and there is scope for further improvements towards milder reaction conditions and better yields. Many improved procedure have been reported using PPA lanthanide compounds and various Lewis acid as promoters. Recently NH₄Cl Ionic liquids and hetero poly acid have also been for Biginelli reaction. However, some of the methods employed have drawbacks, for example using expensive reagents, prolonged reaction

time, unsatisfactory yield, etc. Therefore the development of an inexpensive and facile and effective method for the synthesis of dihydropyrimidinone derivatives is desirable.

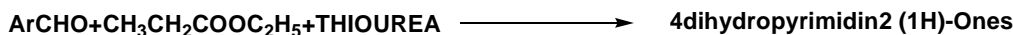
Room temperature ionic liquids (RTILs) have received increasing attention as potential “greener” alternative to volatile organic solvent, and they have been used as catalyst in reaction

Investigated extensively as solvent or catalyst for many important organic reactions because of their special properties such as negligible vapor pressure, tunable polarity, high thermal stability, good solvating ability, ease of recyclables and potential to enhance reaction rates and selectivity. They have also been referred as designer solvents as their properties can be altered by the fine tuning of parameters such as the choice of organic cation. These structural variations offer flexibility to the chemist to device the most idealized solvent and catalyst catering for the needs of a particular process. The task specific ionic liquids which have a functional group in their framework, have been successfully employed as efficient catalyst as dual catalyst solvent for a variety of reactions.

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In continuing our work in green synthesis & using ionic liquids as a recyclable eco- friendly reaction medium to enhance rates & selectivity we report here in a one pot synthesis of dihydropy-

rimidinones [Scheme 1] catalyzed by specific acidic ionic liquids [bmim] HSO₄ which is found to be a simple, highly yielding time saving and environmentally friendly method.



Scheme 1

IR 3426, 3335, 2977, 1660, 1616, 1524 cm⁻¹

EXPERIMENTAL

General M.P. determined on Buchi M.P. apparatus and were resuspended. ¹H NMR spectra were recorded on INM- PMX 60 NMR spectrometer (60MHz) in CDCl₃ using tetramethyl silane as internal standard; and IR spectras in KBR disc, reaction were monitored by T.L.C. A mixture of aromatic aldehyde 1mm, ethylacetoacetate 2mm of urea or thiourea 1mm and ionic liquid 0.2ml was heated at 80-85^o c for 20-50 min. after completion of reaction, the mixture was cooled to room temperature washed with 5ml of water and filtered. the solid was recrystallised from 95% ethanol. 3, 4-dihydropyrimidine 2(1H)-ones are synthesized and characterized by melting point, IR, H1 NMR.

TABLE 1 : Result table for acidic ionic liquid (himm) HSO₄

Sr. No.	ALDEHYDE	TIME min	M.P. 0c	Yield %
1	2 chloro benza dehyde	20	217	90
2	4 chloro benzadehyde	22	215	91
3	4 hydroxy benzadehyde	25	227	93
4	4 methyl benzadehyde	15	204	88
5	3 nitro benzadehyde	20	228	87
6	benzadehyde	40	188	88
7	2 nitro benzadehyde	35	228	87
8	4 methoxy benzadehyde	30	210	96
9	2 methyl benza dehyde	40	218	87
10	4 bromo benzadehyde	25	240	89
11	2 bromo benzadehyde	27	232	90

Spectral data for some pyimidones

- 2 chloro benzaldehyde:** (DMSO 400MHz) NMR 1.08δ(t,3H), 2.29(s 3H) 3.91(q 2H), 5.65(d 1H) 7.3(m 4H), 7.73(s 1H), 9.28 (s 1H)
IR 3426, 3335, 2977, 1660, 1616, 1524 cm⁻¹
- 4 chloro benzaldehyde:** (DMSO 400MHz) NMR 1.08δ(t,3H), 2.26(s 3H) 3.95(q 2H), 5.16(d 1H) 7.25(m 4H), 7.79(s 1H), 9.28 (s 1H)

CONCLUSION

In our initial study, we used 4-chlorobenzaldehyde as a representative reactant in order to optimize the reaction conditions. The reaction proceed efficiently in acidic ionic liquids. [bmim] HSO₄, good yield were obtained, in green synthesis using ionic liquids as a recyclable eco- friendly reaction medium to enhance rates and selectivity we report here in a one pot synthesis of dihydropyrimidinones catalyzed by specific acidic ionic liquids [B min] HSO₄ which is found to be a simple, highly yielding time saving and environmentally friendly method

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