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Original Research Article

# Highly effective synthesis of 3, 4-dihydropyrimidin-2 (1*H*)-ones using pyridinium-*N*-sulfonic acid bisulfate as a dual-functional catalyst

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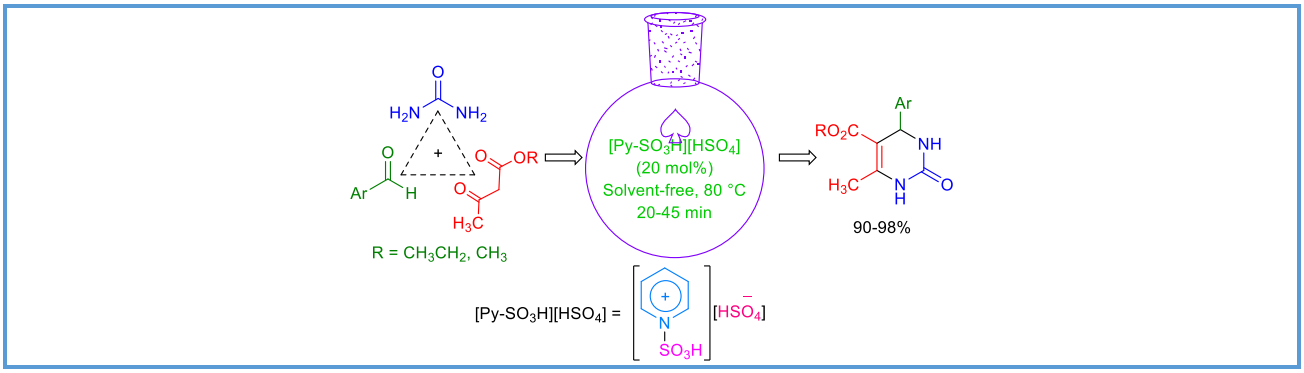
Acidic ionic liquid
Dual-functional catalyst
Pyridinium-*N*-sulfonic acid bisulfate (Py-$SO_3H$][$HSO_4$])
Solvent-free

**ABSTRACT**

Acidic ionic liquid pyridinium-*N*-sulfonic acid bisulfate ([Py-$SO_3H$][$HSO_4$]) has effectively catalyzed the production of 3, 4-dihydropyrimidin-2 (1*H*)-ones *via* the condensation reaction of the arylaldehydes with β-ketoesters and urea under solvent-free conditions. Due to the dual-functionality of [Py-$SO_3H$][$HSO_4$] (bearing acidic and basic sites), it was highly effective and general catalyst for the reaction. Additionally, an attractive mechanism for the dual-functionality of the catalyst was proposed.

## Graphical Abstract

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## Introduction

Room-temperature ionic liquids (RTILs) have extensive applications in industry and chemistry due to their benefit properties including, negligible vapor pressure, non-flammability, reasonable thermal and chemical stability, excellent ionic conductivity, wide electrochemical windows, large liquid range, tunable hydrophobicity, and green nature. Physical properties of the RTILs are adaptable by judicious selection of the cation and anion [1]. In view of the excellent physicochemical characteristics of the ionic liquids, they have been used in lithium batteries [2], electrode position [3], solar cells [4], and electric double layer capacitors [5], and as solvent, reagent and catalyst in organic synthesis [6–23]. Among the ionic liquids, protic acidic ones act as catalysts for a variety of organic transformations [9–23].

Solvent-free conditions has been applied as a valuable technique in green chemistry, as many compounds could be prepared in an efficient and environmentally benign manner by that. Synthesizing compounds under solvent-free conditions has numerous benefits relative to the classical synthetic techniques, which include: (i) shorter reaction time, (ii) higher yield of product, (iii) maximum incorporation of the reactants into the aim product, (iv) higher selectivity in many reactions, (v) easier workup, (vi) fewer energy requirement to promote reaction, (vii) prevention of using harmful and volatile solvents, (viii) safer reaction profile, and (ix) prevention or minimization of waste/by-products [24–28].

3,4-Dihydropyrimidin-2 (1*H*)-one derivatives have various pharmaceutical and biological activities, and have been used as antihypertensive [29], antibacterial [30], antitumor [31], antiviral [32], calcium channel blockers [33], neuropeptide antagonist [34], $\alpha_{1a}$-adrenergic antagonists [35], and anti-inflammatory [36] agents. The general method which has been utilized for production of this class of compounds consists of the condensation reaction of arylaldehydes with β-ketoesters (or compounds containing active methylene) and urea in the presence of a catalyst; for example Mg-Al-$CO_3$ and Ca-Al-$CO_3$ hydrotalcite [37] nano-γ-$Fe_2O_3$@$SiO_2$ [38], 1-butyl-1,3-thiazolidine-2-thione *p*-toluenesulfate [39], $H_4SiMO_{12}O_{40}$ [40], 3D printed α-$Al_2O_3$ [41], silica-supported imidazolium salt [42], $TiCl_3OTf$-1-butyl-3-methylimidazolium chloride [43], [Co $(BPO)_2$ $(H_2O)_4$] $(BS)_2$ $(H_2O)_2$ [44], chitosan/graphene oxide [45], (-)-4, 5-dimethyl-3, 6-bis(*o*-tolyl)-1,2-benzenedisulfonimide [46], and $Fe_3O_4$@mesoporous SBA-15 [47]. Although some catalysts for the synthesis of 3,4-dihydropyrimidin-2 (1*H*)-ones are known, newer catalysts continue to attract attention for solving the drawbacks accompanied with the reported ones, such as harsh conditions, long reaction times, moderate yields, the use of expensive, non-available or toxic catalysts, difficulty in catalyst preparation, and performing the reaction in volatile and toxic organic solvents.

Bearing the above-mentioned subjects in mind, we report here a highly effective and dul-functional ionic-liquid catalyst namely pyridinium-*N*-sulfonic acid bisulfate (Py-$SO_3H$] [$HSO_4$]) to produce 3, 4-dihydropyrimidin-2 (1*H*)-ones *via* the condensation reaction between arylaldehydes, β-ketoesters and urea in the absence of solvent. Interestingly, our procedure hasn't the mentioned disadvantages at all.

## Experimental

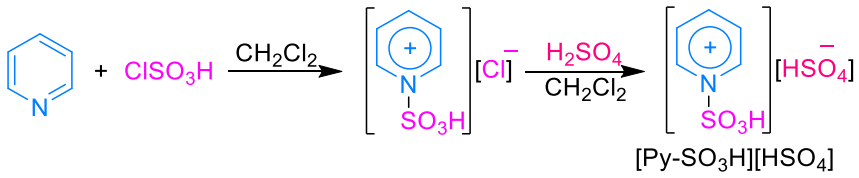
### *Materials and methods*

All the chemicals were purchased from Merck and Fluka Chemical Companies. All

known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Progress of the reactions was monitored by thin layer chromatography (TLC) using silica gel SIL G/UV 254 plates. The $^{1}$H NMR (250 or 400 MHz) and $^{13}$C NMR (62.5 or 100 MHz) were run on a Bruker Avance DPX, FT-NMR spectrometers.

*Procedure for preparation of [Py-$SO_3$H][$HSO_4$]*

A solution of pyridine (0.395 g, 5 mmol) in dry $CH_2Cl_2$ (15 mL) was added dropwise to a stirring solution of chlorosulfonic acid (0.580 g, 5 mmol) in dry $CH_2Cl_2$ (15 mL) over a period of 10 min in an ice-bath. After the addition was completed, the reaction mixture was stirred for 60 min at room temperature [13], and then sulfuric acid (0.490 g, 5 mmol) was added dropwise over a period of 3 min. The resulting mixture was stirred for 4 h at room temperature under nitrogen atmosphere (to remove the produced HCl), and for 1 h in refluxed $CH_2Cl_2$. Afterward, the mixture was stand for 3 min, the $CH_2Cl_2$ was decanted, and the residue was washed with dry $CH_2Cl_2$ (3×10 mL), and dried under vacuum to give [Py-$SO_3$H][$HSO_4$] as a viscous pale yellow oil in 97 % yield (Scheme 1) [14].




**Scheme 1**. The synthesis of pyridinium-*N*-sulfonic acid bisulfate

*General procedure for production of 3, 4-dihydropyrimidin-2 (1H)-ones*

A mixture of arylaldehyde (1 mmol), β-ketoester (1 mmol), urea (0.078 g, 1.3 mmol) and [Py-$SO_3$H][$HSO_4$] (0.052 g, 0.2 mmol) was initially stirred magnetically at 80 °C, and after solidification of the reaction mixture, it was stirred by a small rod at same temperature. Progress of the reaction was followed by TLC; after completion of the reaction, the mixture was cooled to room temperature, and the resultant solid was purified by recrystallization from ethanol (95%) to give the pure product.

*Selected spectroscopic data of 3, 4-dihydropyrimidin-2 (1H)-ones*

*Ethyl 6-methyl-2-oxo-4-p-tolyl-1, 2, 3, 4-tetrahydropyrimidine-5-carboxylate (**4**)*

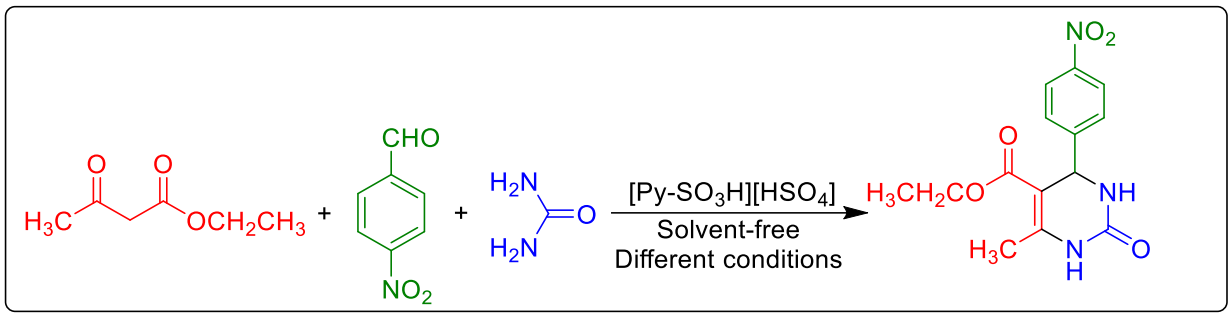
$^{1}$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 1.1 (3H, t, $J$ = 7.2 Hz), 2.2 (3H, s), 2.2 (3H, s), 3.9 (2H, q, $J$ = 7.2 Hz), 5.12 (1H, s), 7.1 (4H, s), 7.7 (1H, br.), 9.1 (1H, br.). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 14.6, 18.2, 21.1, 54.1, 59.6, 99.9, 126.6, 129.4, 136.8, 142.4, 148.6, 152.7, 165.8.

*Ethyl 6-methyl-2-oxo-4-(4 dimethylaminophenyl)-1, 2, 3, 4-tetrahydropyrimidine-5-carboxylate (**5**)*

$^{1}$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 1.1 (3H, t, $J$ = 7.2 Hz), 2.2 (3H, s), 2.86 (6H, s), 3.97 (2H, q, $J$ = 7.0 Hz), 5 (1H, s), 6.6 (2H, d, $J$ = 8.8 Hz), 7 (2H, d, $J$ = 8.8 Hz), 7.5 (1H, br.), 9.1 (1H, br.). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 14.6, 18.2, 40.7, 53.8, 59.6, 100.4, 112.7, 127.4, 133.1, 148.0, 150.2, 152.8, 165.9.

## Results and Discussion

To obtain the appropriate reaction temperature and catalyst amount, the condensation between the 4-nitrobenzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), and urea (1.3 mmol) was chosen as a model reaction (Scheme 2), and examined at the presence of different molar ratios of [Py-$SO_3H$][$HSO_4$] at 70-90 °C in the absence of solvent. The main results are presented in Table 1. As can be seen in Table 1, the suitable temperature and catalyst amount were 70 °C and 20 mol%, correspondingly (Table 1, Scheme 2).




**Scheme 2.** The model reaction for the production of 3, 4-dihydropyrimidin-2 (1*H*)-one

**Table 1.** Optimizing temperature and the catalyst amount on the model reaction

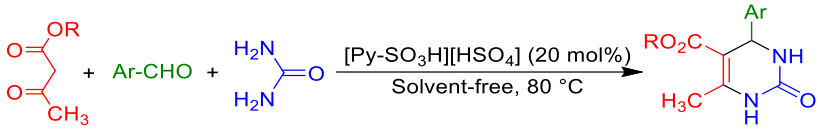
| Entry | Temperature (°C) | Mol% of [Py-$SO_3H$][$HSO_4$] | Time (min) | Yielda (%) |
|---|---|---|---|---|
| 1 | 70 | 20 | 30 | 97 |
| 2 | 80 | 20 | 20 | 98 |
| 3 | 90 | 20 | 20 | 98 |
| 4 | 80 | 17 | 30 | 95 |
| 5 | 80 | 25 | 20 | 97 |

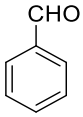
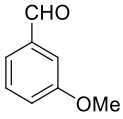
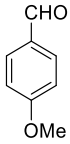
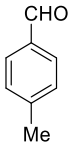
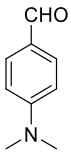
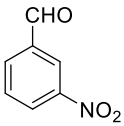
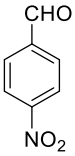
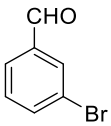
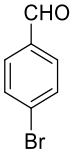
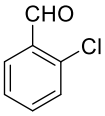
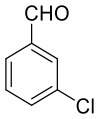
[a] Yields refer to isolated pure product

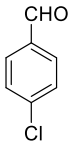
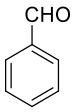
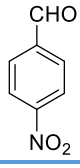
With the aim of recognizing the generality and effectiveness of the catalyst for producing the 3,4-dihydropyrimidin-2 (1*H*)-ones, the reaction of different arylaldehydes (benzaldehyde and electron-rich as well as electron-deficient arylaldehydes) with β-ketoesters and urea was examined in the presence of [Py-$SO_3H$][$HSO_4$] in the optimal conditions; the relevant results are summarized in Table 2. As shown in Table 2, the ionic-liquid efficiently catalyzed all reactions to produce the related products in excellent yields and in short reaction times. Thus, [Py-$SO_3H$][$HSO_4$] was general and highly efficient catalyst for the synthesis.

In another study, our catalyst was compared with the more recently reported catalysts for the production of 3,4-dihydropyrimidin-2(1*H*)-ones. The results for the synthesis of compounds **3** and **7** were displayed in Table 3. As demonstrated in Table 3, the [Py-$SO_3H$][$HSO_4$] was superior related to the reported catalysts in terms of reaction time, yield and/or reaction conditions as well as temperature. Moreover, the purification of the products in our method was easy (recrystallization). The amount of urea used in our protocol was also fewer than most of the reported protocol.

**Table 2.** The synthesis of 3, 4-dihydropyrimidin-2 (1*H*)-ones using [Py-$SO_3H$][$HSO_4$]




| Product | Aldehyde | R | Time (min) | Yield[a] (%) | M.p. °C (Lit.) |
|---|---|---|---|---|---|
| **1** |  | Et | 35 | 90 | 202-204 (202-204) [38] |
| **2** |  | Et | 35 | 91 | 205-207 (207-209) [43] |
| **3** |  | Et | 40 | 97 | 203-205 (201-202) [43] |
| **4** |  | Et | 35 | 94 | 216-218 (216-218) [38] |
| **5** |  | Et | 45 | 97 | 251-253 (250-253) [39] |
| **6** |  | Et | 30 | 98 | 224-226 (225-227) [39] |
| **7** |  | Et | 20 | 98 | 205-207 (207-209) [40] |
| **8** |  | Et | 40 | 97 | 184-186 (183-185) [39] |
| **9** |  | Et | 30 | 98 | 211-213 (210-212) [43] |
| **10** |  | Et | 30 | 93 | 221-223 (222-224) [38] |
| **11** |  | Et | 35 | 90 | 194-196 (193-195) [43] |

| | | | | | |
|---|---|---|---|---|---|
| **12** |  | Et | 35 | 98 | 205-207 (207-210 ) [39] |
| **13** |  | $CH_3$ | 30 | 91 | 212-214 (211-213) [38] |
| **14** |  | $CH_3$ | 20 | 97 | 236-238 (233-236) [40] |

[a] Yields refer to isolated pure product

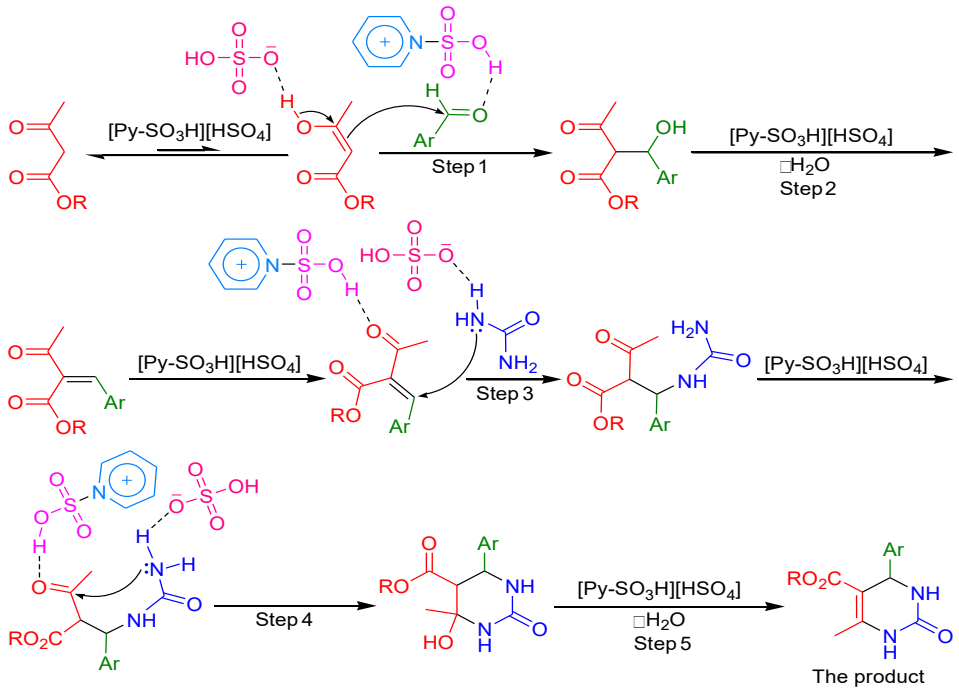
**Table 3.** Comparison of [Py-$SO_3H$][$HSO_4$] catalyzed 3,4-dihydropyrimidin-2(1*H*)-ones synthesis with the recently reported catalyzed process

| Catalyst (mol%) | Conditions | Time (min) | | Yield (%) | | Ref |
|---|---|---|---|---|---|---|
| | | 3[a] | 7[b] | 3[a] | 7[b] | |
| [Pyridine-$SO_3H$]$HSO_4$ | Solvent-free (80 °C) | 40 | 20 | 97 | 98 | - |
| Mg-Al-$CO_3$ hydrotalcite | Solvent-free (80 °C) | 30 | 60 | 82 | 81 | [37] |
| Ca-Al-$CO_3$ hydrotalcite | Solvent-free (80 °C) | 45 | 60 | 61 | 64 | [37] |
| Mg-Al-$CO_3$ hydrotalcite | Solvent-free, MW (390 W) | 6 | 6 | 82 | 83 | [37] |
| Ca-Al-$CO_3$ hydrotalcite | Solvent-free, MW (390 W) | 8 | 8 | 63 | 67 | [37] |
| Nano- γ -$Fe_2O_3$@$SiO_2$ | Solvent-free (60 °C) | -[c] | 90 | -[c] | 82 | [38] |
| Nano- γ -$Fe_2O_3$@$SiO_2$ | Solvent-free, MW (60 °C, 250 W) | -[c] | 30 | -[c] | 95 | [38] |
| [Btto][*p*-TSA][d] | Solvent-free (90 °C) | 30 | -[c] | 97 | -[c] | [39] |
| $H_4SiMO_{12}O_{40}$ | Reflux in $CH_3CN$ | 90 | 90 | 75 | 80 | [40] |
| $H_4SiMO_{12}O_{40}$ | Reflux in EtOH | 90 | 90 | 69 | 78 | [40] |
| 3D printed α-$Al_2O_3$ | Solvent-free, MW (100 °C) | 15[e] | -[c] | 95[e] | -[c] | [41] |
| Silica-supported imidazolium salt | Ethanol, reflux | 40 | 20 | 88 | 95 | [42] |
| $TiCl_3OTf$-ionic liquid | Solvent-free (140 °C) | -[c] | 20 | -[c] | 95 | [43] |
| $[Co(BPO)_2(H_2O)_4](BS)_2(H_2O)_2$ | Solvent-free (80 °C) | 120 | -[c] | 98.55 | -[c] | [44] |
| Chitosan/graphene oxide | Solvent-free (110 °C) | 50 | 65 | 75 | 78 | [45] |

| | | | | | | |
|---|---|---|---|---|---|---|
| (-)-4,5-dimethyl-3,6-bis(*o*-tolyl)-1,2-benzene disulfonimide | Solvent-free (50 °C) | 120 | 360 | 90 | 85 | [46] |
| $Fe_3O_4$@mesoporous SBA-15 | Ethanol, reflux | 420 | 300 | 82 | 84 | [47] |

[a] Compound **3**
[b] Compound **7**
[c] In the paper, the synthesis of this compound has not been reported
[d] 1-Butyl-1,3-thiazolidine-2-thione *p*-toluenesulfate
[e] The results are related to

A plausible mechanism considering the dual-functionality of the catalyst is illustrated in Scheme 3, which supported by some research studies [43, 47]. The acidic site of the [Py-$SO_3H$][$HSO_4$] assists to promote the reaction by activating the carbonyl groups to accept a nucleophilic attack (steps 1, 3 and 4), and activation of hydroxyl group for removing $H_2O$ molecule (steps 2 and 5). The weak basic site of the catalyst (negative oxygen of bisulfate) accelerates the reaction by abstracting a proton (steps 1, 3 and 4). High efficacy of the [Py-$SO_3H$][$HSO_4$] can be attributed to the dual-functionality, and also having two acidic sites.




**Scheme 3**. The proposed mechanism for the preparation of 3, 4-dihydropyrimidin-2(1*H*)-ones

## Conclusions

In this work, we introduced a new acidic ionic-liquid catalyst namely pyridinium-*N*-sulfonic acid bisulfate for the reaction of arylaldehydes with β-ketoesters and urea to produce 3,4-dihydropyrimidin-2(1*H*)-ones, with the following benefits: generality, effectiveness, excellent yields, short reaction times, easy workup and purification of the

products, easy preparation of the catalyst from available reactants, clean reaction, dual-functionality of the catalyst, avoid of using organic solvents as reaction media, and goof agreement with green chemistry protocols.

**Acknowledgements**

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**Disclosure statement**

No potential conflict of interest was reported by the author.

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