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Original article

1-Sulfopyridinium chloride: Green and expeditious ionic liquid for the one-pot synthesis of fused 3,4-dihydropyrimidin-2(1*H*)-ones and thiones under solvent-free conditions

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ABSTRACT

1-Sulfopyridinium chloride portrayed as an efficient and recyclable ionic liquid for the synthesis of fused 3,4-dihydropyrimidin-2(1*H*)-ones and thiones *via* a modified Biginelli reaction involving one-pot three component condensation of 6-methoxy-1-tetralone, arylaldehydes and urea/thiourea under solvent-free conditions. Analytically pure products are formed within 10–20 min in excellent yields.

1. Introduction

The development of cleaner technologies is a major subject in green chemistry [1]. Among the several aspects of green chemistry, the reduction or replacement of volatile organic solvents from the reaction medium is of greatest concern. Ionic liquids (ILs) have received considerable interest as eco-friendly solvents, catalysts and reagents in the context of green synthesis because of their unique properties such as low volatility, non-flammability, high thermal stability, negligible vapour pressure and ability to dissolve a wide range of materials [2].

Dihydropyrimidinones (DHPMs) were found to possess several biological activities such as antimicrobial, antiviral, antimalarial, anticancer, antihypertensive, anti-inflammatory, calcium channel modulators, mitotic kinesin inhibitors, α_{1A}-antagonists and neuropeptide Y(NPY) antagonists [3–7]. Several biologically active marine alkaloids were also found to contain the dihydropyrimidinone-5-carboxylate core. Most notable among them are batzelladine alkaloids, which have been found to be potent HIVgp-120-CD4 inhibitors [8]. Some of the biologically active dihydropyrimidine derivatives have shown in Fig. 1.

3,4-Dihydropyrimidin-2(1*H*)-ones was first reported by Pietro Biginelli in 1893 *via* a three component condensation of benzaldehyde, β-ketoester and urea under strongly acidic conditions [9]. However, it often requires harsh reaction conditions, longer reaction time and affords low yields, particularly when substituted aromatic and aliphatic aldehydes are employed. To avoid these limitations, several methods were reported utilizing different catalytic systems such as CaF_2 [10], PPh_3 [11], $BF_3(OEt)_2$ [12], $FeCl_3{\cdot}6H_2O$ [13], $InCl_3$ [14], $YbCl_3$ [15], $BiCl_3$ [16], $Fe(OTs)_3{\cdot}6H_2O$ [17], $Ce(C_{12}H_{25}SO_3)_3$ [18], HCl/EtOH [19], chloroacetic acid [20], 1-carboxymethyl-3-methylimidazolium hydrogen sulfate [21], silica sulfuric acid [22], cellulose sulfuric acid [23], silica-bonded *N*-propyl sulfamic acid [24], potassium phthalimide [25] and acidic ionic liquids [26]. Nevertheless, many of the reported methods suffer from one or several drawbacks such as longer reaction time, low yield of the products, complex isolation procedure, harsh reaction conditions and use of large amount of expensive reagents. Therefore, the present communication aims to introduce a mild, efficient and eco-friendly protocol for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones and thiones in the presence of acidic ionic liquid, 1-sulfopyridinium chloride [pyridine-SO_3H]Cl under solvent-free conditions.

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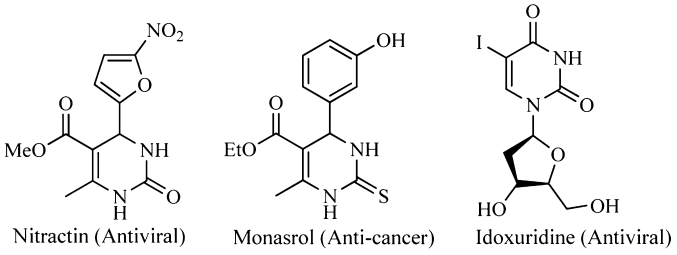


Fig. 1. Some of the biologically potent DHPMs.

2. Experimental

All the solvents and chemicals were purchased from Aldrich/Merck and used without further purifications. Melting points were obtained in open capillaries using Stuart SMP30 melting point apparatus and are uncorrected. The progress of the reactions as well as purity of the compounds was monitored by thin layer chromatography, and the developed chromatogram was visualized with UV light and iodine vapors. IR spectra were recorded on Perkin-Elmer 100S spectrophotometer using KBr disk. ^{1}H NMR spectra were recorded on Bruker-400 MHz spectrometer using TMS as an internal standard. The C, H and N analyses of the compounds were done on a Carlo Erba EA1108 analytical unit and mass spectra were recorded on a JEOL JMSD-300 spectrometer.

General procedure for the synthesis of fused 3,4-dihydropyrimidine-2(1*H*)-ones (**4a–l**) and thiones (**5a–l**): Ionic liquid [pyridine-SO_3H]Cl (10 mol%) was added to a mixture of 6-methoxy-1-tetralone (**1**, 1 mmol), aromatic aldehydes (**2a–l**, 1 mmol) and urea/thiourea (**3a**/**b**, 1.2 mmol), and heated at 80 °C under solvent-free conditions for an appropriate time. After completion of the reaction (monitored by TLC), the product was extracted by the warm ethyl acetate and purified by recrystallization from ethanol. The recovered catalyst was washed with ethyl acetate, dried under vacuum at 90 °C for about 3 h and reused for subsequent reaction.

4-(3-Bromophenyl)-8-methoxy-3,4,5,6-tetrahydrobenzo[h]-quinazolin-2(1*H*)-one (**4d**): Pale yellow solid; IR (KBr, cm^{-1}): υ_{max} 3237 (NH), 1681 (C=O), 1178 (C–O–C), 764 (C–Br); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.71–1.79 (m, 1H), 2.07–2.15 (m, 1H), 2.54–2.60 (m, 1H), 2.65–2.72 (m, 1H), 3.73 (s, 3H), 4.93 (s, 1H), 6.76 (t, 2H, J = 6.4 Hz), 7.29–7.34 (m, 3H), 7.47–7.53 (m, 3H), 8.54 (s, 1H); MS (ESI): m/z 385 [M+1]$^+$; Anal. calcd. for $C_{19}H_{17}BrN_2O_2$: C, 59.23; H, 4.45; N, 7.27. Found: C, 59.38; H, 4.36; N, 7.12.

4-(3-Ethoxy-4-hydroxyphenyl)-8-methoxy-3,4,5,6-tetrahydrobenzo[h]quinazolin-2(1*H*)-one (**4l**): Pale yellow solid; IR (KBr, cm^{-1}): υ_{max} 3359 (OH), 3180 (NH), 1686 (C=O), 1172 (C–O–C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.30 (t, 3H, J = 6.8 Hz), 1.73–1.81 (m, 1H), 2.02–2.10 (1H), 2.54–2.69 (m, 2H), 3.73 (s, 3H), 3.94–3.99 (m, 2H), 4.78 (s, 1H), 6.68–6.75 (m, 4H), 6.84 (d, 1H, J = 6.4 Hz), 7.07 (s, 1H), 7.49 (d, 1H, J = 9.6 Hz), 8.39 (s, 1H), 8.86 (s, 1H); MS (ESI): m/z 367 [M+1]$^+$; Anal. calcd. for $C_{21}H_{22}N_2O_4$: C, 68.84; H, 6.05; N, 7.65. Found: C, 68.95; H, 5.91; N, 7.35.

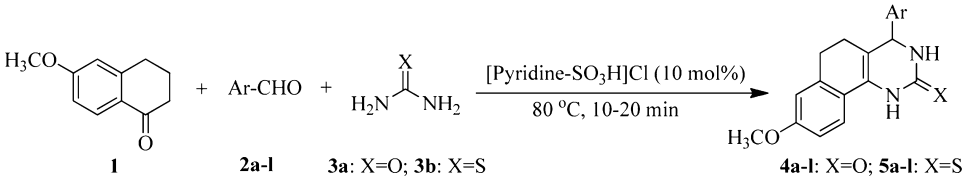
4-(3-Bromophenyl)-8-methoxy-3,4,5,6-tetrahydrobenzo[h]-quinazoline-2(1*H*)-thione (**5d**): Pale yellow solid; IR (KBr, cm^{-1}): υ_{max} 3179 (NH), 1251 (C=S), 1185 (C–O–C), 741(C–Br); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.79–1.87 (m, 1H), 2.14–2.21 (m, 1H), 2.56–2.61 (m, 1H), 2.67–2.73 (m, 1H), 3.75 (s, 3H), 4.96 (s, 1H), 6.78 (s, 2H), 7.30–7.38 (m, 2H), 7.50 (t, 2H, J = 7.6 Hz), 7.63 (d, 1H, J = 9.2 Hz), 9.08 (s, 1H), 9.78 (s, 1H); MS (ESI): m/z 402 [M+1]$^+$; Anal. calcd. for $C_{19}H_{17}N_2OS$: C, 56.86; H, 4.27; N, 6.98. Found: C, 56.75; H, 4.41; N, 6.79.

4-(3-Ethoxy-4-hydroxyphenyl)-8-methoxy-3,4,5,6-tetrahydrobenzo[h]quinazolin-2(1*H*)-thione (**5l**): Pale yellow solid; IR (KBr, cm^{-1}): υ_{max} 3354 (OH), 3183 (NH), 1262 (C=S), 1171 (C–O–C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.31 (t, 3H, J = 6.8 Hz), 1.81–1.88 (m, 1H), 2.08–2.16 (m, 1H), 2.54–2.71 (m, 2H), 3.74 (s, 3H), 3.94–4.00 (m, 2H), 4.79 (s, 1H), 6.68 (t, 1H, J = 8.4 Hz), 6.76 (d, 3H, J = 7.6 Hz), 6.84 (s, 1H), 7.61 (d, 1H, J = 9.2 Hz), 8.92 (s, 1H), 8.95 (s, 1H), 9.61 (s, 1H); MS (ESI): m/z 383 [M+1]$^+$; Anal. calcd. For $C_{21}H_{22}N_2O_3S$: C, 65.95; H, 5.80; N, 7.32. Found: C, 65.82; H, 5.89; N, 7.09.

3. Results and discussion

Fused 3,4-dihydropyrimidin-2(1*H*)-ones (**4a–l**) and thiones (**5a–l**) were obtained by the one-pot three component condensation of 6-methoxy-1-tetralone (**1**), aromatic aldehyde (**2a–l**) and urea (**3a**)/thiourea (**3b**) utilizing acidic ionic liquid, [pyridine-SO_3H]Cl as a catalyst under solvent-free conditions in excellent yields. The schematic representation has shown in Scheme 1. The ionic liquid, [pyridine-SO_3H]Cl has prepared according to the literature procedure [27].

To evaluate the feasibility of 1-sulfopyridinium chloride, a modal reaction involving benzaldehyde (**2a**), 6-methoxy-1-tetralone (**1**)



[Pyridine-SO_3H]Cl =

4a: Ar = C_6H_5, X = O
4b: Ar = 2-ClC_6H_4, X = O
4c: Ar = 4-ClC_6H_4, X = O
4d: Ar = 3-BrC_6H_4, X = O
4e: Ar = 4-$OCH_3C_6H_4$, X = O
4f: Ar = 3,4-$(OCH_3)_2C_6H_3$, X = O
4g: Ar = 4-$CH_3C_6H_4$, X = O
4h: Ar = 4-OHC_6H_4, X = O
4i: Ar = 3-$NO_2C_6H_4$, X = O
4j: Ar = 4-$N(CH_3)_2C_6H_4$, X = O
4k: Ar = 4-OH-3-$OCH_3C_6H_3$, X = O
4l: Ar = 4-OH-3-$OC_2H_5C_6H_3$, X = O

5a: Ar = C_6H_5, X = S
5b: Ar = 2-ClC_6H_4, X = S
5c: Ar = 4-ClC_6H_4, X = S
5d: Ar = 3-BrC_6H_4, X = S
5e: Ar = 4-$OCH_3C_6H_4$, X = S
5f: Ar = 3,4-$(OCH_3)_2C_6H_3$, X = S
5g: Ar = 4-$CH_3C_6H_4$, X = S
5h: Ar = 4-OHC_6H_4, X = S
5i: Ar = 3-$NO_2C_6H_4$, X = S
5j: Ar = 4-$N(CH_3)_2C_6H_4$, X = S
5k: Ar = 4-OH-3-$OCH_3C_6H_3$, X = S
5l: Ar = 4-OH-3-$OC_2H_5C_6H_3$,X=S

Scheme 1. 1-Sulfopyridinium chloride catalyzed synthesis of fused 3,4-dihydropyrimidine-2(1*H*)-ones and thiones.

Table 1
Optimizing the reaction conditions.[a]

Entry	Amount of IL (mol%)	Conditions	Time (min)	Yield (%)[b]
1	–	r.t./Solvent-free	120	–
2	–	40 °C/Solvent-free	120	Trace
3	–	80 °C/Solvent-free	120	10
4	–	120 °C/Solvent-free	120	10
5	5	r.t./Solvent-free	120	–
6	5	40 °C/Solvent-free	90	23
7	5	80 °C/Solvent-free	60	48
8	5	120 °C/Solvent-free	60	49
9	10	40 °C/Solvent-free	60	62
10	10	80 °C/Solvent-free	15	96
11	10	120 °C/Solvent-free	15	95
12	15	80 °C/Solvent-free	15	96
13	10	Reflux/ethanol	30	79
14	10	Reflux/acetic acid	30	82
15	10	Reflux/water	30	73

[a] Reaction conditions: 6-methoxy-1-tetralone (1 mmol), benzaldehyde (1 mmol) and thiourea (1.2 mmol).
[b] Isolated yields.

Table 2
1-Sulfopyridinium chloride catalyzed synthesis of fused 3,4-dihydropyrimidine-2(1*H*)-ones and thiones under solvent-free conditions.[a]

Analog	Aldehyde	Time (min)	Yield (%)[b]	Melting Points (°C)	
				Found	Reported [Ref.]
4a	Benzaldehyde	10	97	254–256	255–258 [28]
4b	2-Chloro benzaldehyde	15	92	295–297	297–299 [28]
4c	4-Chloro benzaldehyde	15	93	261–263	260–263 [28]
4d	3-Bromo benzaldehyde	10	94	261–263	–
4e	4-Methoxy benzaldehyde	15	96	199–201	199–201[28]
4f	3,4-Dimethoxy benzaldehyde	15	96	146–148	148–150 [28]
4g	4-Methyl benzaldehyde	15	92	259–261	258–260 [28]
4h	4-Hydroxy benzaldehyde	10	91	276–278	275–277 [28]
4i	3-Nitro benzaldehyde	20	90	255–257	254–256 [28]
4j	4-(Dimethylamino) benzaldehyde	20	91	297–299	298–300 [28]
4k	4-Hydroxy-3-methoxy benzaldehyde	15	94	271–273	271–273 [28]
4l	4-Hydroxy-3-ethoxy benzaldehyde	20	92	277–279	–
5a	Benzaldehyde	15	96	271–273	272–274 [28]
5b	2-Chloro benzaldehyde	15	97	270–271	270–272 [28]
5c	4-Chloro benzaldehyde	10	98	241–243	240–243 [28]
5d	3-Bromo benzaldehyde	10	91	274–276	–
5e	4-Methoxy benzaldehyde	10	94	234–236	234–237 [28]
5f	3,4-Dimethoxy benzaldehyde	10	93	254–256	253–255 [28]
5g	4-Methyl benzaldehyde	15	92	247–249	248–251 [28]
5h	4-Hydroxy benzaldehyde	10	92	269–271	268–270 [28]
5i	3-Nitro benzaldehyde	20	90	245–247	244–246 [28]
5j	4-(Dimethylamino) benzaldehyde	20	91	273–275	274–276 [28]
5k	4-Hydroxy-3-methoxy benzaldehyde	15	94	265–267	264–266 [28]
5l	4-Hydroxy-3-ethoxy benzaldehyde	15	95	256–258	–

[a] Reaction conditions: 6-methoxy-1-tetralone (1 mmol), aryl aldehyde (1 mmol), urea/thiourea (1.2 mmol) and [Pyridine-SO_3H]Cl (10 mol%), 80 °C, neat conditions.
[b] Yields refer to pure isolated products.

and thiourea (**3b**) with a building block ratio of 1:1:1.2 was carried out at different temperatures (r.t., 40, 80 and 120 °C) in the absence as well as in the presence of different amount of catalyst (5–15 mol%) under solvent-free conditions (Table 1). At room temperature, with and without catalyst product (**5a**) formation was not observed. In absence of catalyst, as the temperature increases the yield of the product has slightly increased and observed maximum yield (10%) at 80 °C. In the presence of catalyst, maximum yield (96%) was observed at 80 °C with 10 mol% of the catalyst. Further increment of temperature and amount of catalyst has not shown any affect on product yield and reaction time. The same reaction was also carried out with 10 mol% of catalyst in different solvents like ethanol, acetic acid and water under reflux conditions. But the yield of the product (**5a**) obtained was lower compare to the reaction under solver-free conditions (Table 1).

At these optimistic conditions (10 mol% of catalyst, solvent-free conditions, 80 °C), a series of 3,4-dihydropyrimidine-2(1*H*)-ones (**4a–l**) and thiones (**5a–l**) were obtained by varying the aromatic aldehyde and urea/thiourea with excellent yields in shorter reaction time (Table 2). After completion of the reaction the catalyst was recovered from the reaction mixture by washing with warm ethyl acetate, dried under vacuum at 90 °C and reused for subsequent reactions. For example, the reaction of 6-methoxy-1-tetralone (**1**), benzaldehyde (**2a**) and thiourea (**3b**) gave the corresponding 3,4-dihydropyrimidin-2(1*H*)-thione (**5a**) in 96%, 94%, 91%, 90% and 90% yields over additional five cycles.

4. Conclusion

In conclusion, we have developed a facile route for the synthesis of fused 3,4-dihydropyrimidine-2(1*H*)-ones and thiones in the presence of ionic liquid [pyridine-SO_3H]Cl under solvent-free conditions. This method has several advantages such as simple work-up procedure, involving short reaction time, high yields of the product formation, eco-friendly and reusability of catalyst.

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