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Choline chloride based eutectic solvent: a highly efficient reaction media for the synthesis of 3,4-dihydropyri midin-2(1H)-thiones

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ABSTRACT

A mild and green protocol was developed for three-component, one pot synthesis of 3,4-dihydropyrimidin-2(1H)-thione derivatives in a deep eutectic solvent (DES) without the use of a catalyst or any other additive. DES based on choline chloride (ChCl) and urea offered high reaction yield and was proper for a wide range of aromatic aldehydes. In addition, after 3,4-dihydropyrimidin-2(1H)-thione synthesis, DES could be easily recycled and reused five times without any obvious changes in catalytic activity. In general, the procedure offers a number of benefits, including clean reaction profile, avoiding the use of typical toxic catalysts, an easy workup procedure, short reaction times, and low prices.

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1. Introduction

Recently, deep eutectic solvents (DESs) have attracted much consideration as a chemical reaction media in place of conventional volatile organic solvents, in organic synthesis for the construction of new materials [1-3]. These solvents are generally less expensive, biodegradable, [4] biocompatible, and non-toxic,[5] reinforcing the greenness of these media and can be used under less demanding reaction conditions, like anaerobic conditions or rigorously anhydrous [6-13]. In addition, DESs have been studied for their usage in pharmaceutical applications,[5] surfactant chemistry [14], and extraction [14].

Abbott et al. established the solvent foundation in 2003 [15] and reported that a blend of ChCl and urea could produce a DES by hydrogen bond interactions, which appeared as a liquid state under typical conditions (Fig.1). Owing to its low toxicity, biodegradability, low cost, ChCl has been widely employed as the acceptor of hydrogen bond to prepare DES with inexpensive hydrogen bond donor including glycerol, carboxylic acids, or urea [16].

Pyrimidine derivatives including 3,4-dihydropyrimidin-2(1H)-thiones and 3,4-dihydropyrimidin-2(1H)-ones are Biginelli reaction products [17]. Due to their broad spectrum of biological activities [18], they are used in medicinal chemistry [19]. These compounds [20] possess various biological activities [21] like antibacterial, antiviral, calcium channel blockers, anti-tumor, neuropeptide Y (NPY) antagonists, α-1-antagonists, etc [22, 23].

Various other synthetic analogs such as monastrol [24], L-771,688 [25], and SQ 32926 [26] have been developed (Fig. 1). Monastrol was identified as a potent anticancer agent and has an ability to cross the cell membrane by special preventing the motor activity of mitotic kinesin Eg5. In addition, monastrol is considered as a lead for the expansion of newer anti-cancer drugs [27, 28]. Promising activity against cancer also is observed with Piperastrol and Mon-97 [13].

In view of these useful properties, there has been a continuous interest in the expansion of facile synthetic protocols for the construction of pyrimidine derivatives. Three-component one-pot condensation of β-ketoester, aldehyde, and thiourea/ urea proposed by Biginelli is the straightforward and most simple route to synthesize dihydropyrimidines [29]. Nonetheless, the low yields, prolonged reaction durations, and severe conditions of this reaction—especially when substituted aliphatic and aromatic aldehydes are used—limit its practical use [30]. To address these drawbacks, different methodologies for the synthesis of dihydropyrimidines have been reported to modify [31] and improve this reaction by ionic liquids, ultrasound irradiation, microwave irradiation, different types of phase transfer, enzyme, nanoparticle [32], metal oxide [33], base, and acidic catalysts [34-44]. However, some of the recent literature techniques have shortcomings such as prolonged reaction times, use of expensive, corrosive/toxic, metal-based catalysts [45], unsatisfactory yields, and extractive isolation of the product using hazardous organic solvents, which restricts their application owing to environmental [46] and financial concerns. Therefore, the development of new effective

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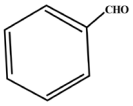
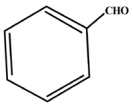
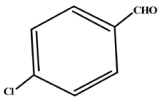
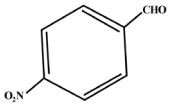
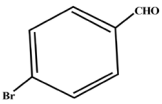
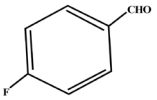
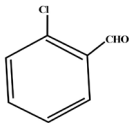
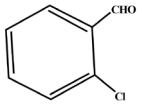
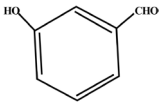
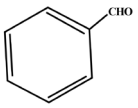
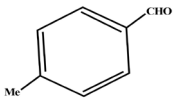
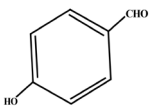
Table 1.
Synthesis of 3,4-dihydropyrimidin-2(1H)-thiones in DES.

Entry	Carbonyl group	R_1	Time(min)	Product	Yield	mp°C[ref]
1		Me	60	**4a**	90	220-222[30]
2		Et	60	**4b**	88	207-209[33]
3		Et	50	**4c**	91	192-194[33]
4		Et	50	**4d**	85	111-113[32]
5		Et	60	**4e**	88	190-191[33]
6		Et	50	**4f**	90	186-187[30]
7		Et	90	**4g**	93	216-218[26]
8		Me	90	**4h**	90	176-178[26]
9		Et	100	**4k**	92	181-183[26]
10		Et	110	**4l**	90	210-212[30]
11		Et	120	**4m**	92	150-152[33]
12		Et	120	**4n**	92	204-206[33]

synthetic protocols is highly desirable.

In continuation of research interest in the development of greener and more efficient protocols for organic synthesis [47-51], we report the application of a urea and ChCl-based DES as media to synthesize 3,4-dihydropyrimidin-2(1H)-thiones compound through a three-component, one-pot reaction of an aldehyde, a *β*-ketoester, and ammonium thiocyanate (NH_4SCN) in place of thiourea (Scheme 2). The weakly acidic nature of NH_4SCN has been reported to cause the acceleration of

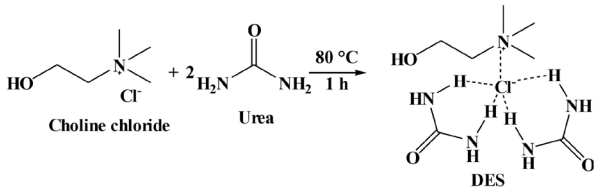
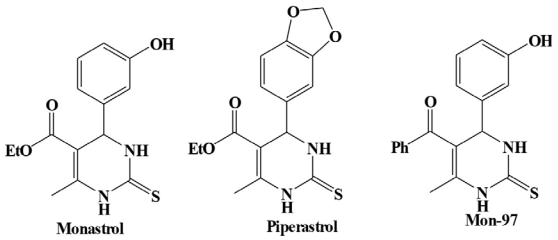


Fig. 1. DES ChCl/urea preparation.



Scheme 1. Examples of biologically and pharmaceutically important 3, 4-dihydropyrimidin-2(1H)-thiones.

reaction rate, providing higher yields, and shorter reaction time. Being safer, cheaper, and readily available are the other reasons for the usage of NH_4SCN in the synthesis of 3,4-dihydropyrimidin-2(1H)-thiones compound [52, 53].

2. Experimental

2.1. Method for preparing 3,4-dihydropyrimidin-2(1H)-thiones

All the analytical grade chemicals with the purity of ≥ 95 were purchased from Merck (Darmstadt, Germany) and used without additional purification.

An aldehyde (2 mmol), a *β*-ketoester (2 mmol), ammonium thiocyanate (2.4mmol), and DES (choline chloride/urea 1:2) were mixed under continuous and vigorous stirring at 80 °C. Thin layer chromatography was used to monitor the reaction progress. The product was extracted with ethyl acetate and dried over sodium sulphate before being vacuum evaporated. To obtain the required 3,4-dihydropyrimidin-2(1H)-thione, the residue was purified on a silica gel using an ethyl acetate/hexane combination [54].

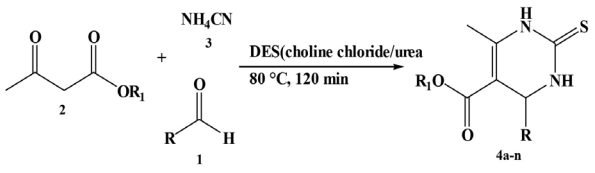
The product was characterized by comparing the physical and spectral data of the products to those of authentic samples [53].

3. Results and discussion

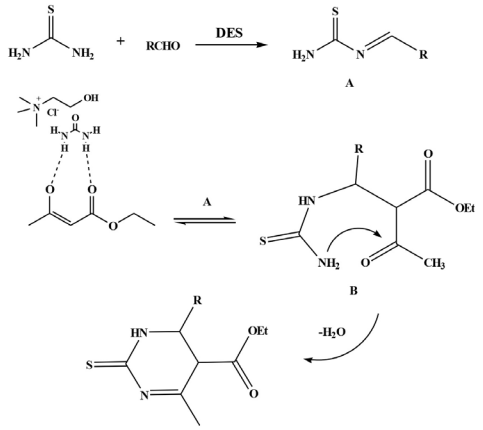
Initial preparation of DES (ChCl / Urea) involved mixing ChCl and urea at 80˚C until a bright solution was formed (Scheme 1). The produced transparent homogeneous liquid was then progressively cooled to ambient temperature. The prepared DES was used as a solvent for the

Table 1.
Effect of different solvent on formation of 4a.

Entry	Temperature °C	Solvent	Time (min/yield)
1	reflux	Isopropyl alchol	180/80
2	reflux	CH_3CN	240/82
3	reflux	Water	350/30
4	reflux	THF	300/75
5	110	DMF	180/85
6	reflux	Toluence	240/80
7	80	DES	60/90



Scheme. 2. Synthesis of 3,4-dihydropyrimidin-2(1H)-thiones via a three-component Biginelli reaction in DES.



Scheme. 3. Proposed mechanism for the synthesis of 3,4-dihydropyrimidin-2(1H)-thiones.

Biginelli reaction.

Promisingly, it was discovered that with the simple blending of ethyl acetoacetate (2 mmol), ammonium thiocyanate (2.4 mmol), and benzaldehyde (2 mmol) in Urea/ChCl (2 mL), the reaction proceeded rapidly, producing the equivalent 5-Methoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione compound with 90% efficiency within 60 minutes (Table 1, entry1). The positive impact of DEC on the reaction yield was also reported by Cui et al. [55] (yield 88%) and Pawar et al. [56] (yield 81%).

The influence of several solvents (e.g., Isopropyl alcohol, CH_3CN, THF, DMF, toluene, and H_2O) on the reaction time and yield was also examined (Table 2, entries1–7). DES offered the greatest yield at 80°C after 60 minutes (Table 2, entry 7).

To investigate the applicability of reaction, we employed a wide range of substituted aromatic aldehydes with *β*-ketoesters for preparing a vast type of 3, 4-dihydropyrimidin-2(1*H*)-thiones compound (Table 1).

As listed in the Table 1, aromatic aldehydes having either electron-withdrawing or electron- donating substituents at the ortho–para positions reacted quickly and smoothly to give 3,4-dihydropyrimidin-2(1*H*)-thiones compound in high purity and yield. It was demonstrated that the electronic effects of the substituents on the aromatic ring had very little impact on the reaction yield. Aldehydes with electron-withdrawing groups was also found to consume less reaction times than those with electron-donating groups (Table 1 entries 9-12), in addition, ortho substituted aldehydes time (Table 1 entries 7,8) did the reactions in longer times than para substituted ones, which can be described by the steric hindrance effect. This is in accordance with previous report [57]. This observation demonstrated that 3, 4-dihydropyrimidin-2(1H)-thione compound material can be formed with the variation of time.

For environmental and economic considerations, it is also important

Table 3.
Recyclability of DES for one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-thione.

Run	1	2	3	4	5
Yield	90	90	88	85	85

to take the recycling and reuse of DESs into account. In the present study, DES was reused to synthesize 3, 4-dihydropyrimidin-2(1H)-thiones from benzaldehyde and methyl acetoacetate under optimized reaction parameters. To recycle DES, water was added to the reaction mixture (4a). Then the unrefined insoluble product was separated and DES was obtained after water evaporation at 90 °C temperature under vacuum conditions. The recycled DES was reused for another reaction under the same condition. As can be observed in Table 3, DES could be reused four times without substantial activity loss.

The reaction mechanism for the synthesis of 3, 4-dihydropyrimidin-2(1*H*)-thione is presented in Scheme 3. Regarding the reaction mechanism, isomerization of ammonium thiocyanate to thiourea would be the first step. The aldehyde activated by DES undergoes nucleophilic addition by thiourea, leading to intermediate **A**. Thereafter, the intermediate **A** reacts with the enolate form of ethyl acetoacetate to give intermediate **B,** followed by intramolecular cyclization to afford the final product.

4. Conclusion

In summary, we have demonstrated an effective and green process for the 3,4-dihydropyrimidin-2(1*H*)-thiones synthesis employing an eutectic strong solvent as a green reaction medium. The important features of this protocol are: (1) using DES as a readily available, inexpensive, and efficient medium, (2) simple reaction condition (3) green and recyclable solvent system, (4) easy purification, and high yields. The primary process for making 3,4-dihydropyrimidin-2(1H)-thione compound derivatives is described here, and we wish to emphasize that it is an environmentally benign process.

Spectroscopic data for selected examples follow:

5-Methoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione: (**4a**) ^{1}HNMR (DMSO-d_6, 400 MHz): δ 2.2 (s, 3H), 5.3 (d, J = 4.0 Hz, ^{1}H), 6.2 (s, 1H), 7.0-7.2 (m, 5H); ^{3}CNMR (DMSO-d_6, 100 MHz): δ 18.5, 51.3, 54.8, 101.2, 116.1, 128.1, 128.3, 139.5, 146.8, 153.6, 161.1, 163.5, 168.8.

5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione: **(4b)** ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.11 (t, J = 7.1 Hz, 3H), 2.20 (s, 3H), 4.02 (q, J = 7.1 Hz, 2H), 5.30 (s, 1H), 7.99 (s, 1H), 8.17-7.62 (m, 4H), 9.38 (brs,1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz); δ 14.3, 18.3, 54.0, 59.8, 98.7, 121.5, 122.8, 131.1, 133.5, 146.3, 153.1, 167.5, 175.1.

5-ethoxycarbonyl-4(4-chloroyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione **(4c)** 1H NMR (400 MHz, DMSO-d6): δ 1.10 (t, J = 7.0 Hz, 3H), 2.28 (s, 3H), 3.95–4.04 (m, 2H), 5.17 (s, 1H), 7.23 (d, J = 8.3 Hz,2H), 7.42 (d, J = 8.3 Hz, 2H), 9.65 (brs, 1H, NH), 10.36 (brs, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz); δ 14.5, 18.2, 53.7, 59.8, 99.4, 128.4, 128.8, 132.3, 142.3, 142.5, 149.2, 153.5, 169.6.

5-ethoxycarbonyl-4(3-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione: (**4k**) ^{1}HNMR (DMSO-d_6, 400 MHz): δ 1.1 (t, J = 7.2 Hz), 2.2 (s, 3H), 4.0 (q, 2H), 5.0 (d, 1H), 6.6 (d, 3H), 7.1 (m, 1H), 9.4(s, 1H), 9.5 (d, 1H), 10.2 (s, 1H); ^{13}CNMR (DMSO-d_6, 100 MHz): δ 14.0, 53.9, 100.6, 113.3, 114.5, 117.1, 129.5, 144.8, 157.5, 165.1, 174.1.

5-ethoxycarbonyl-4(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione **(4m)** ^{1}H NMR (400 MHz, DMSO-d6): δ 1.11 (t, J = 7.1 Hz, 3H,), 2.28 (s, 3H), 3.72 (s, 3H), 4.00 (q, J = 7.1 Hz, 2H), 5.11 (d, J = 3.6 Hz, 1H), 6.89 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 8.6 Hz, 2H), 9.57 (s, 1H, NH), 10.26 (brs,1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz); δ 14.5, 18.1, 53.8, 55.5, 59.8, 100.1, 114.2, 127.8, 137.6, 148.5, 153.5, 158.8, 172.8.

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