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Research Article

Benign Methodology and Efficient Catalysis for the One-Pot Multicomponent Synthesis of Dihydropyrimidinones and Thiones: A New Key for Old Lock

Parvez Ali,[1] Naziyanaz Pathan,[2] and Taibi Ben Hadda[3]

[1] *Center for Health Studies, Prince Sultan Military Medical City, Riyadh 11159, Saudi Arabia*
[2] *Institute of Science, Nagpur University, Nagpur 440001, India*
[3] *Laboratoire de Chimie des Matériaux, Université Mohammed Premier, 6000 Oujda, Morocco*

Correspondence should be addressed to Parvez Ali; parvezali_81@yahoo.com

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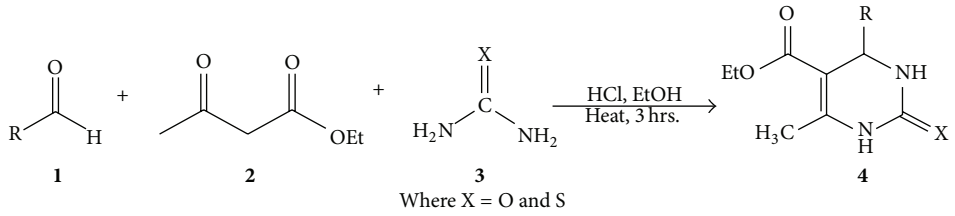
In the present communication, under the influence of microwaves, cuprous chloride has been demonstrated to be safe, mild, efficient, and inexpensive catalyst for the Biginelli discovered multicomponent reaction (MCR) between aromatic aldehydes, urea/substituted urea, and ethyl acetoacetate to produce structurally diverse dihydropyrimidin-2(1H)-ones (DHPMs) and thiones in an ecofriendly solvent-free protocol. The practical and simple protocol led to excellent yields of the dihydropyrimidin-2(1H)-one derivatives under mild reaction conditions and within short span of reaction times with easy reaction workup by maintaining excellent atom economy.

1. Introduction

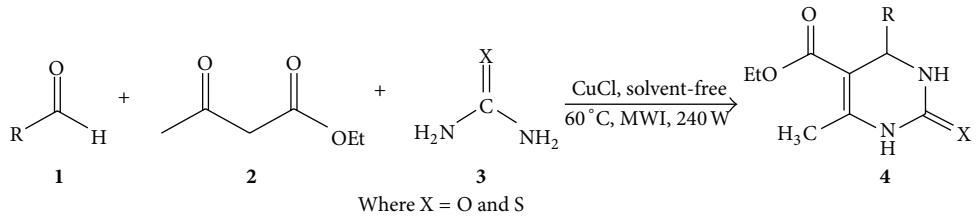
In multicomponent reactions (MCRs), three or more reactants come together in a single reaction vessel to form new products that contain portions of all the components [1–5]. In this dynamic era of chemistry where a premium effort is put on speed, diversity, and efficiency in the drug discovery process [6], MCR strategies offer significant advantages over conventional linear-type synthesis [1–5]. One such MCR that belongs to this category is the venerable Biginelli dihydropyrimidinones synthesis. In 1893, Italian chemist Pietro Biginelli reported the acid catalyzed cyclocondensation reaction of ethyl acetoacetate (**1**), benzaldehyde (**2**), and urea (**3**) [7]. The reaction was carried out by heating a mixture of the three components by dissolving it in ethanol with a catalytic amount of HCl at reflux temperature. The product of this novel one-pot, three-component synthesis that precipitated on cooling of the reaction mixture was identified correctly by Biginelli as 3,4-dihydropyrimidin-2(1H)-one **4** (Scheme 1) [8, 9].

Owing to their remarkable pharmacological properties such as calcium channel blockers, antitumor, and anti-inflammatory activities, dihydropyrimidinones and their derivatives have increasingly attracted the attention of synthetic chemists [10–15]. Moreover, the dihydropyrimidine-5-carboxylate core has been found in several marine natural products which are potent HIVgp-120-CD4 inhibitors [16, 17]. However, despite the potential utility of dihydropyrimidinones as bioactive compounds, their antifungal activities are also studied [18]. Thus, due to immense pharmacological profile of this class of compounds, research interest towards this area is growing day by day. This in turn increases the attempts to develop various versatile, safe, and quick processes for their synthesis. The classical Biginelli condensation protocol suffers from the drawbacks like harsh reaction conditions, high reaction times, and frequently low yields. This has led to multistep synthetic strategies that produce somewhat better yields but lack the simplicity of one-pot synthesis. In recent years, new methods for the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones have been developed



1 2 3 4

Scheme 1: Traditional Biginelli reaction.



1 2 3 4

Scheme 2: CuCl catalysed Biginelli condensation.

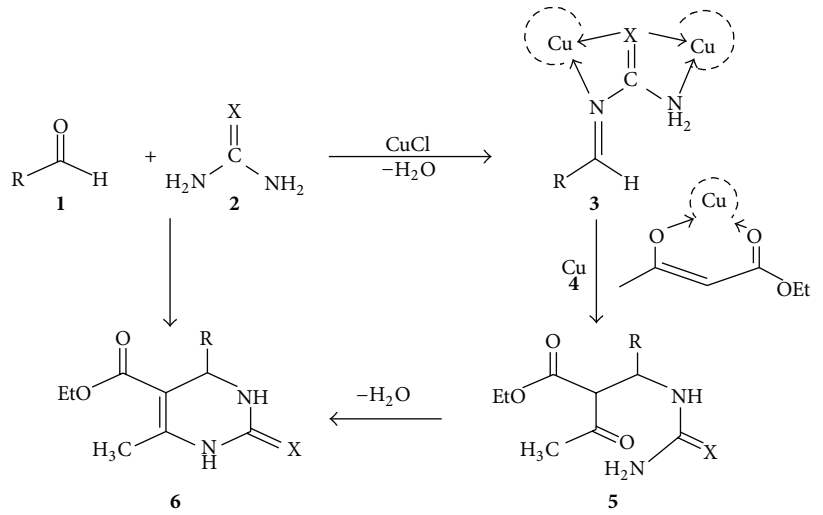
by different groups. In order to improve the efficiency of the Biginelli reaction, different Lewis catalysts such as $ZrCl_4$ [19], $BiCl_3$ [20], LiBr [21] $Mn(OAc)_3{\cdot}2H_2O$ [22], $InCl_3$ [23], $Cu(OTf)_2$ [24], $Zn(OTf)_2$ [25], $FeCl_3{\cdot}H_2O$ [26], $LiClO_4$ [27], $CuCl_2$ [28] chloroacetic acid and $LaCl_3$ as $BF_3{\cdot}OEt_2$, $La(OTf)_3$, $Yb(OTf)_3$ silica sulfuric acid, $H_3PW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ [29] have been developed. Some of them are really fascinating from the synthetic chemist's points of view; however, some drawbacks still remain. For example, some catalysts are expensive, complex, or unavailable and organic solvents are always used. Furthermore, many heavy metallic salts were used which resulted in the pollution of the environment to some extent. Previous reported protocols normally required prolonged reaction times and high temperature with moderate yields; so there has been considerable interest in exploring mild, rapid, and high yielding protocol at ambient temperature. Recently, there were some reports which utilized phenylboronic acid [30], triphenylphosphine [31], phosphate ester [32], calcium fluoride [33], and ammonium carbonate in water [34]. But some of these protocols suffered from longer reaction times and requirement of solvents. Thus due to the immense biological importance of dihydropyrimidinones, it is essential to search for catalysts which can provide excellent yield in a short reaction time and can be used effectively for the preparation of a wide variety of functional dihydropyrimidinones under solvent-free conditions.

In the recent years, microwave heating has emerged out as a powerful technique to promote a variety of chemical reactions [35]. Microwave reactions under solvent-free conditions and/or in the presence of a solid support, such as clays, alumina, silica, and graphite, resulting in shorter reaction times and higher product yields than those obtained by using conventional heating offer low cost together with simplicity in processing and handling [36]. Keeping in mind all these parameters and in continuation of our interest in heterocyclic compounds [37, 38], microwave-assisted [39, 40], and solvent-free synthesis [41], we wish to report the CuCl catalyzed synthesis of dihydropyrimidinones and thiones under microwave conditions (Scheme 2).

2. Materials and Methods

2.1. General. The solvents and reagents used in the synthetic work were of analytical grade obtained from Qualigens, India, and were purified by distillation or crystallization where necessary and their boiling or melting points were compared with the available literature values. Melting points were determined in open capillaries and are uncorrected. ^{1}H-NMR spectra were recorded on a Perkin Elmer FT-NMR Cryomagnet Spectrometer 400 MHz (Bruker) instrument using tetramethylsilane (TMS) as an internal standard and DMSO-d_6 as a solvent. Chemical shifts are given in parts per million (ppm). Infrared spectra were recorded on Shimadzu-IR Prestige 21. Mass spectra were recorded on a Waters Micromass Q-T of Microspectrometer. The microwave-assisted reactions were carried out in a "CEM DISCOVER" manufactured by CEM Technologies Corporation. In this unit, microwaves are generated by magnetron at a frequency of 2450 MHz having an output energy range of 100 to 500 W. The reactions were monitored and the purity of products was checked out on precoated TLC plates (Silica gel 60 F254, Merck), visualizing the spots under ultraviolet light and iodine chamber.

2.2. General Procedure for the Synthesis of Dihydropyrimidinones and Thiones. In a typical solventless preparation, mixture of aldehyde (25 mmol), ethyl acetoacetate (27.5 mmol), urea or thiourea (37.5 mmol), and cuprous chloride (1.25 mmol, 5 mol%) in a reaction flask was stirred well, kept in the microwave generator, and allowed to irradiate with microwaves at MW, 60°C, 240 W for the required time as mentioned in Table 1 based on reaction monitoring by TLC. After completion of the reaction, it was allowed to cool and the reaction was quenched with 5% NH_4OH solution



Where X = O and S

Scheme 3: Plausible reaction mechanism.

Table 1: Comparison of catalyst loading with percent yield for the model reaction (Scheme 2).

Catalyst loading (mol%)	% yield
20	96
15	95
10	95
5	94

and stirred for 15 min. The solid was filtered under suction, washed with ice cold water twice, and then recrystallized from ethanol to afford pure products **4** (**a**–**m**).

2.3. Spectral Data

2.3.1. ***4d****: Mp 200–202°C (Lit. Mp 198–200°C) [29].* IR (KBr): ν = 3520, 3230, 3150, 1705, 1690 cm^{-1}. ^1H NMR (DMSO-d_6): 1.18 (t, J = 7.5 Hz, 3H, CH_3), 2.28 (s, 3H, CH_3), 4.0 (q, J = 7.5 Hz, 2H, $-OCH_2$), 5.18 (s, 1H), 6.7 (d, J = 8.9 Hz, 2H, Ar), 7.09 (d, J = 8.9 Hz, 2H, Ar), 7.25 (s, 1H), 8.95, and 9.0 (2s, 2H, brs. NH). MS: m/z(%) = 276 (15) (M^+), 248 (100), 231 (28), 204 (80), 168 (87), 136 (48). Anal. calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14; O, 23.16. Found: C, 60.89; H, 5.86; N, 10.19; O, 23.19.

2.3.2. ***4j****: Mp 201–203°C (Lit. Mp 202–204°C) [29].* IR (KBr): ν = 3260, 3198, 3100, 1720, 1690 cm^{-1}. ^1H NMR (DMSO-d_6): 1.20 (t, J = 7.3 Hz, 3H, CH_3), 2.29 (s, 3H, CH_3), 4.10 (q, J = 7.3 Hz, 2H, $-OCH_2$), 5.22 (s, 1H, CH), 7.25 (m, 5H, Ar), 9.25, and 9.9 (2s, 2H, 2brs. NH). MS: m/z(%) = 276 (65) (M^+), 237 (45), 204 (100), 172 (35), 142 (20). Anal. calcd for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14, S, 11.60. Found: C, 60.88; H, 5.86; N, 10.16, S, 11.65.

3. Result and Discussion

Copper is one of the oldest transition metals used in organic synthesis and copper salts are still broadly employed nowadays [42, 43]. Among these copper salts, CuCl is a special choice of chemists due to its inexpensiveness, lack of toxicity, and easy handling. It is a well-known soft Lewis acid catalyst which has been used for several important organic transformations. It is a weak Lewis acid capable of catalyzing the reaction under mild conditions as compared to other acids. Carrying out reactions under solvent-free conditions coupled with microwaves is an important strategy in organic synthesis which significantly reduces the production of waste and precludes postsynthesis steps such as product isolation solvent recycling and reaction time. This employed system of catalysis under microwaves is extremely new for the Biginelli type of condensation.

To establish the reaction conditions for the CuCl catalyzed Biginelli condensation under microwaves, the reaction of benzaldehyde with ethyl acetoacetate and urea was taken as model reaction as shown in Scheme 2.

We have tried to optimize the reaction conditions by taking various amounts of CuCl in the range of 5–20 mol% at room temperature. It was observed that the condensation reaction can be efficiently carried out by taking 5 mol% of the catalyst at 240 W, in a short time span of just 2.0 to 3.5 minutes which is much lesser as compared to other catalysts using more than 5 to 20 mol%. Further increase in the catalyst amount does not show any marked increase in the product yield (Table 1).

To ascertain the generality of the protocol, a series of aromatic aldehydes carrying both electron-donating or -withdrawing substituent and heterocyclic aldehydes were subjected to reaction with β-ketoesters, urea, and thiourea under the optimized reaction conditions. Thiourea has been used with similar success to provide the corresponding dihydropyrimidin-2(1H)-thiones which are also of much

Table 2: CuCl catalysed solvent-free synthesis of dihydropyrimidin-2(1H)-ones and thiones under microwaves (Scheme 2).

Compound	R	X	Time (min)	isolated yield (%)	MP (°C)	
					Found	Reported
4a	C_6H_5	O	2.5	94	197–199	200–202 [29]
4b	2-Cl C_6H_5	O	2.0	98	215–217	216–218 [44]
4c	4-Cl C_6H_5	O	2.4	97	210–212	211–213 [44]
4d	4-HO C_6H_5	O	2.5	96	200–202	198–200 [29]
4e	2-NO_2 C_6H_5	O	2.5	90	207–209	206–208 [44]
4f	3-NO_2 C_6H_5	O	2.0	89	226–228	229-230 [44]
4g	4-OMe	O	2.5	96	203-204	201-202 [29]
4h	$CH_3CH_2CH_2$	O	2.5	70	178–180	180–182 [44]
4i	$(CH_3)_2CH$	O	2.5	88	195–197	196-197 [44]
4j	C_6H_5	S	3.0	89	201–203	202–204 [29]
4k	3-NO_2 C_6H_5	S	3.5	85	203–205	206-207 [29]
4l	4-Cl C_6H_5	S	3.0	92	181–183	184-185 [29]
4m	4-HO C_6H_5	S	3.5	88	192–194	193-194 [29]

interest with regard to biological activity. It is pleasing to observe the remarkable stability of a variety of functional groups under the established reaction conditions.

The authors investigated the mechanism of the Biginelli reaction in the literature and proposed an N-acyliminium ion formed in situ by reaction of the aldehyde with urea as the key intermediate followed by metal ligation to generate the target things. That is, this reaction may proceed via generation of acyl imine intermediate formed by the reaction of the aldehyde and urea which was stabilized by CuCl. Subsequent addition of β-ketoester enolate to the acylimine, followed by cyclization and dehydration, afforded the corresponding dihydropyrimidinones (Scheme 3).

Table 2 shows the generality of the present protocol, which is equally effective for urea or thiourea and also for aromatic and aliphatic aldehydes. Under these conditions, the yields were significantly better in comparison with the classical Biginelli procedure. Several aromatic aldehydes carrying either electron-releasing or electron-withdrawing substituents in the *ortho*, *meta,* and *para* positions afforded high yields of the products.

An important feature of this procedure is the survival of a variety of functional groups such as ethers, nitro groups, hydroxy groups, and halides, under these reaction conditions. Another advantage of this method is its efficiency for the high yield synthesis of DHPMs from aliphatic aldehydes.

4. Conclusion

In conclusion, the present protocol provides a benign, high yielding, efficient, and improved route for the synthesis of Biginelli discovered dihydropyrimidinones and thiones. Mild reaction conditions, solvent-free protocol, ease of workup, high yields, stability, cost reduction, and quick reaction execution are the features of this new protocol. Moreover, this method has an ability to tolerate a wide variety of substituent in all three components.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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