

EFFICIENT AND GREEN CATALYTIC SYNTHESIS OF DIHYDROPYRIMIDINONE (THIONE) DERIVATIVES USING COBALT NITRATE IN SOLVENT-FREE CONDITIONS

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ABSTRACT

A series of 3,4-dihydropyrimidin-2(1H)-one(thione) derivatives was synthesized using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in solvent-free condition. Avoiding organic solvents during the chemical reactions leading to an economic approach is effective. The reaction is characterized by high efficiency, short reaction time, high yields, simple experimental procedure, availability of catalyst and environmentally friendly reaction conditions.

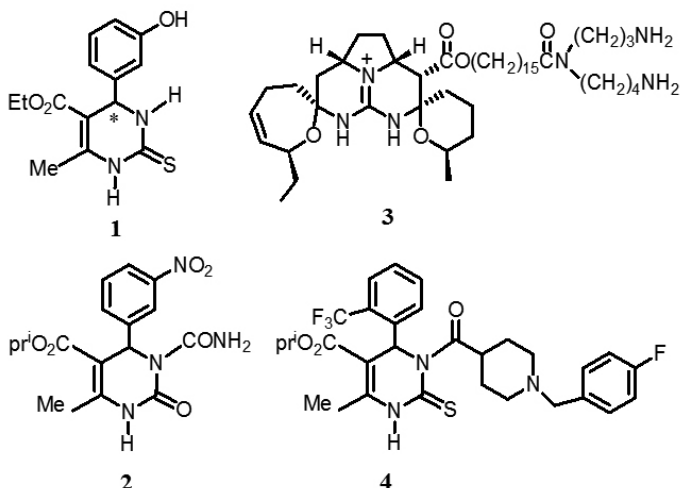
Keywords: Dihydropyrimidinone, Dihydropyrimidinethione, Cobalt(II) Nitrate, Solvent-free, One-pot synthesis

INTRODUCTION

Synthesis of 3,4-dihydropyrimidin-2(1H)-Ones (DHPMs) through one-pot reaction of aromatic aldehyde, urea and ethyl acetoacetate in acid ethanol solution was initiated by Biginelli in 1893¹. These compounds occupied an important place in medicinal and synthetic organic chemistry, mainly because of their wide range of biological activities².

Notably, monastrol (**1**) is the only cell-permeable molecule that blocks normal bipolar spindle assembly in mammalian cells causing cell cycle arrest³, and is considered a lead for the development of new anticancer drugs⁴, while the appropriately functionalized DHPM analogs have emerged as orally active antihypertensive agents (**2**, **4**)⁵.

Many biological activities such as anticancer, antifungal, anti HIV have been exhibited using the representatives such as batzelladines, pitomycalines (**3**) and crambescidines (Fig. 1)⁶.



<<Fig. 1>>

The Biginelli method was developed⁷ and many catalysts such as CaF_2 ⁸, $\text{Sr}(\text{OTf})_2$ ⁹, PPh_3 ¹⁰, tetrabutylammonium bromide (TBAB)¹¹, copper(II) sulfamate¹², phenyl phosphonic acid¹³, $\gamma\text{-Fe}_2\text{O}_3/\text{CuO}$ (on the nanoscale)¹⁴ and so on have been used in the Biginelli reaction. Also microwave irradiation¹⁵, ultrasound irradiation¹⁶ and/or ionic liquids¹⁷ have been used. However, many of these methods suffer from drawbacks such as the use of expensive reagents, strong acidic conditions, long reaction times and use of expensive and poisonous solvents. Therefore, the introduction of a more efficient and milder methods accompanied with higher yields are in demand yet. In recent years with the development of green chemistry technology, multi components reactions under solvent-free conditions with a solid catalyst are considered as

an important subject¹⁸. Solid acids have emerged as potential alternate catalysts to the common liquid acids due to their safe natures, enhanced selectivity, requirements in catalytic amounts and easier work up¹⁹.

Solid catalysts are harmless to the environment due to safety, no corrosion and reduction of the amount of waste residuals. So many reactions in organic chemistry of the solid catalyst are used. Following our interest in producing 3,4-dihydropyrimidin-2(1H)-ones²⁰, a study to revisit this reaction in a parallel combinatorial fashion using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a solvent-free synthesis approach was initiated.

EXPERIMENTAL

Chemicals were purchased from Merck, Fluka and Aldrich chemical companies. Melting points were determined using a Barnstead/Electothermal (BI) capillary apparatus and are uncorrected. IR spectra were recorded from KBr discs on a JASCO FT-IR-680. ¹H NMR spectra were recorded with Bruker ultrasheild NMR 400 machines. NMR spectra were obtained on solution in DMSO-d_6 using TMS as internal standard.

General procedure for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones(thiones)

A mixture of aldehyde (1.0 mmol), β -dicarbonyl (1.0 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 mmol) and urea or thiourea (1.5 mmol) was magnetically stirred at 80 °C in solvent-free condition. After completion of the reaction, as indicated by TLC ($\text{EtOAc}/n\text{-hexane}$, 1:4), the reaction mixture was filtered and the residue recrystallized from ethanol to afford the pure product. All products were characterized by mp, IR and ¹H NMR spectra. The physical and spectroscopic data of new compounds is given below:

Methyl 4-(2,6-dichlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (8q): Mp: 292-294 °C; R_f = 0.43 ($n\text{-hexane}$:ethyl acetate = 4:1); IR ($\bar{\nu}$, cm^{-1}): 3320, 3227, 2976, 1698, 1652, 1661, 1577, 1497, 1284, 1236; ¹H NMR (400 MHz, DMSO-d_6) δ (ppm) : 2.06 (s, 3H), 2.19 (s, 3H), 6.18 (s, 1H), 7.26 (t, 1H, J = 7.6 Hz), 7.40 (d, 2H, J = 8.0 Hz), 7.62 (s, 1H), 9.25 (s, 1H); Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_5$: C, 49.54; H, 3.84; Cl, 22.50; N, 8.89; O, 15.23; found: C 49.45, H 3.90, N 8.80.

Methyl 4-(2-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (8r): Mp: 249-251 °C; R_f = 0.33 ($n\text{-hexane}$:ethyl acetate = 4:1); IR ($\bar{\nu}$, cm^{-1}): 3363, 3249, 2929, 1703, 1623, 1458, 1381, 1229; ¹H NMR (400 MHz, DMSO-d_6) δ (ppm) : 2.05 (s, 3H), 2.34 (s, 3H), 5.63 (s, 1H), 7.20 (t, 1H, J = 6.0 Hz), 7.26 (d, 1H, J = 6.4 Hz), 7.37 (t, 1H, J = 7.2 Hz), 7.61 (d, 1H, J = 7.2 Hz), 7.71 (s, 1H), 9.30 (s, 1H); Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{BrN}_2\text{O}_5$: C, 48.02; H, 4.03; Br, 24.57; N, 8.62; O, 14.76; found: C 47.93, H 4.10, N 8.54.

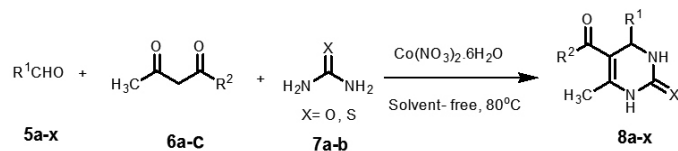
Methyl 4-(2,4-dichlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (8y): Mp: 214-215 °C; R_f = 0.50 ($n\text{-hexane}$:ethyl acetate = 4:1); IR ($\bar{\nu}$, cm^{-1}): 3406, 3179, 2949, 1678, 1652, 1563, 1464, 1203; ¹H NMR (400 MHz, DMSO-d_6) δ (ppm) : 2.30 (s, 3H), 3.34 (s, 3H), 5.58 (s, 1H), 7.28 (d, 1H, J = 8.8 Hz), 7.43 (d, 1H, J = 8.0 Hz), 7.58 (s, 1H, J = 7.2 Hz), 9.65 (s, 1H), 10.45 (s, 1H); Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_2\text{S}$: C, 47.14; H, 3.65; Cl, 21.41; N, 8.46; O, 9.66; S, 9.68; found: C 47.03, H 3.72, N 8.39.

Methyl 4-(3-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (8z): Mp: 248-249 °C; R_f = 0.35 ($n\text{-hexane}$:ethyl acetate = 4:1); IR ($\bar{\nu}$, cm^{-1}): 3316, 3176, 2968, 1678, 1662, 1574, 1434, 1385,

1285; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm): 2.29 (s, 3H), 3.56 (s, 3H), 5.17 (s, 1H), 7.17-7.36 (m, 4H), 9.71 (s, 1H), 10.45 (s, 1H); Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{ClN}_2\text{O}_5\text{S}$: C, 52.61; H, 4.42; Cl, 11.95; N, 9.44; O, 10.78; S, 10.80; found: C 52.53, H 4.50, N 9.37.

RESULTS AND DISCUSSION

In this paper, we report synthesis of the dihydropyrimidinones and dihydropyrimidinethiones using cobalt nitrate hexahydrate as catalyst at 80 °C in solvent-free condition (Scheme 1).



Scheme 1. Synthesis of DHPMs **8a-x**.

Effect of catalyst concentration and solvent

The catalyst concentration was varied over a range of 5–25 mol% of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on the basis of the total volume of the reaction mixture. Table 1 shows the effect of catalyst concentration on the reaction of benzaldehyde, ethylacetoacetate and urea. The yield of the corresponding dihydropyrimidinone increased with increasing catalyst concentration from 5 to 15 mol%. Further addition of catalyst had no noticeable effect on the yield. This was due to over an obvious concentration, there have an excess of catalyst sites beyond what is actually required by the reactant substrates, and the additional catalyst does not increase the rate of the reaction. Therefore, in all further reactions 15 mol% were used.

Table 1. Investigation of catalyst effects in the synthesis of 5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one under solvent-free conditions^a

Entry	Amount of catalyst (mol%)	Time (min)	Yields (%) ^b
1	5	80	85
2	10	65	90
3	15	40	93
4	20	40	94
5	25	50	94

^bIsolated yields

Then, the solvent effect in the condensation of benzaldehyde (1 mmol), urea (1.5 mmol) and ethyl acetoacetate (1 mmol) in the presence of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 mmol) as a model has been studied. As shown in Table 2, among the tested solvents, such as ethanol, methanol, acetonitrile, water, chloroform and a solvent-free system, the best result was obtained after 40 min under solvent-free conditions in excellent yield (90%).

Table 2. Solvent effect on the reaction of benzaldehyde, urea and ethyl acetoacetate catalyzed by $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

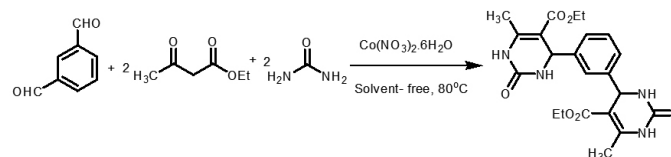
Entry	Solvent (reflux)	Time(h)	Yield ^a (%)
1	CH_3OH	20	68
2	$\text{CH}_3\text{CH}_2\text{OH}$	20	70
3	CH_3CN	20	60
4	CH_2Cl_2	20	55
5	H_2O	20	65
6	Solvent-free ^b	0.6	90

^a Isolated yields

^b At 80 °C

We began our studies with the reaction of benzaldehyde (**5a**), ethylacetoacetate (**6a**) and urea (**7a**) as a model reaction. For this purpose, various parameters such as molar ratio of reactants, catalyst and reaction

temperature were optimized. The results showed that use of 1 mmol benzaldehyde, 1 mmol ethylacetoacetate, 1.5 mmol of urea or thiourea and 1.5 mmol catalyst under solvent-free condition at 80 °C, the product of dihydropyrimidinone (thiones) with 90% efficiency was achieved. Then under this condition, dihydropyrimidinones and dihydropyrimidinethiones by various aromatic and aliphatic aldehydes were synthesized. The results were presented in table 3. As shown, various aromatic aldehydes bearing either electron-releasing or electron-withdrawing substituents can lead to high yields. The use of methyl acetoacetate or acetylacetone as 1,3-dicarbonyl moiety in place of ethyl acetoacetate also gave similar results (Table 3, entries 16–21, 25–27). Furthermore, substrate with two formyl group (entry 10) was produced the corresponding bis-dihydropyrimidinone in short time and excellent yield (Scheme 2).

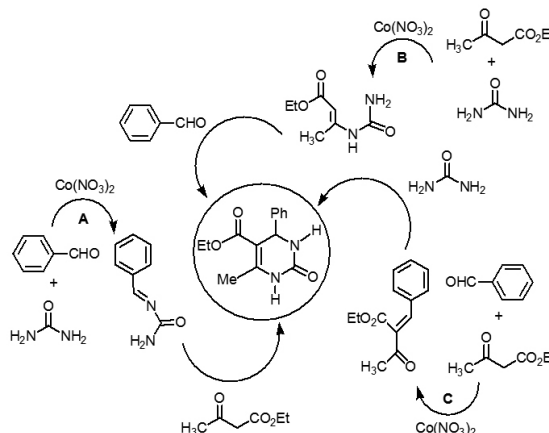


Scheme 2. Synthesis of ethyl-4-(3-(5-(ethoxycarbonyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-4-yl)-Phenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate.

The reactions of acid-sensitive substrates such as 2-thiophenecarbaldehyde and cinnamaldehyde also proceeded well to give the dihydropyrimidinone without any side products (entry 11 and 12). However, aliphatic aldehydes such as butanal, as observed previously, reacted over longer times with a reduced yield (entry 13, 80 min time, 35% yield) compared with the aromatic compounds under our reaction conditions²⁰.

To use of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in large scale synthesis especially in chemical laboratory, a typical reaction was performed for synthesis of **8a** with tenfold amounts of reactants and catalyst with respect to one mentioned in the experimental section. The result showed that the yield of 87% in these conditions that is comparable with one in table 3.

Three possible mechanisms are proposed for Biginelli reaction according to the literature but generally accepted reaction mechanism includes the acid-catalyzed formation of C-N bond from the benzaldehyde and urea (pathway A, Scheme 3)³⁶. According to reported results the pathway A is characteristic for the Brønsted type of catalysts whereas Lewis acid type of catalysts follows the pathway B (ureido-crotonate mechanism)³⁷. For clarifying the role of the catalyst, three separated reactions were performed (pathways A-C, Scheme 3) under the optimized reaction conditions (15 mol% of cobalt(II) nitrate at 80 °C in solvent-free condition and reflux temperature in acetonitrile during 30 min and 20 h, respectively). The prolonged heating of benzaldehyde and ethyl acetoacetate (pathway C) or benzaldehyde and urea (pathway A) did not undergo the expected reactions to yield of products whereas the reaction of ethyl acetoacetate and urea furnished the ureido-crotonate (pathway B). These observations clearly indicate that Biginelli reaction catalyzed by cobalt(II) nitrate proceeds predominately.



Scheme 3. Three proposed possible mechanisms for Biginelli reaction.

Comparative results

In order to show the ability of our method with respect to previous reports, our result for synthesis of 5-(ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-ones (**8a**) in comparison to other methods for preparation of this compound have been summarized in table 4. As shown in table 4, the yield/time ratio of the present method is better or comparable with the other reported results.

Table 3. Synthesis of 3,4-dihydropyrimidin-2-(1H)-ones(thiones) Catalyzed by $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ under solvent-free Conditions^a

entry	R ¹	R ²	X	Product	Time (min)	Yield(%) ^b	Mp (°C)	Ref
1	C ₆ H ₅	OEt	O	8a	40	90	208-209	21
2	4-CH ₃ OC ₆ H ₄	OEt	O	8b	40	92	205-207	13
3	4-CH ₃ C ₆ H ₄	OEt	O	8c	50	90	215-217	13
4	3-BrC ₆ H ₄	OEt	O	8d	65	79	185-187	22
5	4-ClC ₆ H ₄	OEt	O	8e	65	80	212-214	13
6	2-CH ₃ OC ₆ H ₄	OEt	O	8f	55	85	257-259	24
7	2-ClC ₆ H ₄	OEt	O	8g	70	85	216-218	13
8	4-NO ₂ C ₆ H ₄	OEt	O	8h	75	80	207-209	13
9	2-NO ₂ C ₆ H ₄	OEt	O	8i	35	88	208-209	25
10	3-CHOC ₆ H ₄	OEt	O	8j	24	90	212-214	26
11	2-Thienyl	OEt	O	8k	65	85	213-215	23
12	C ₆ H ₅ -CH=CH	OEt	O	8l	40	75	230-232	27
13	<i>n</i> -Pr	OEt	O	8m	80	35	178-180	23
14	2,4-Cl ₂ C ₆ H ₃	OEt	O	8n	50	80	251-252	22
15	3-NO ₂ C ₆ H ₄	OEt	O	8o	14	93	227-228	28
16	C ₆ H ₅	OMe	O	8p	40	88	191-193	29
17	2,6-Cl ₂ C ₆ H ₃	OMe	O	8q	45	80	292-294	-
18	2-BrC ₆ H ₄	OMe	O	8r	50	85	249-251	-
19	C ₆ H ₅	Me	O	8s	45	90	232-234	30
20	4-CH ₃ C ₆ H ₄	Me	O	8t	45	85	250-253	31
21	4-CH ₃ OC ₆ H ₄	Me	O	8u	50	90	171-169	30
22	4-CH ₃ OC ₆ H ₄	OEt	S	8v	70	90	191-194	32
23	4-HOC ₆ H ₄	OEt	S	8w	80	85	197-199	33
24	2-CH ₃ OC ₆ H ₄	OEt	S	8x	30	90	200-202	34
25	2,4-Cl ₂ C ₆ H ₃	OMe	S	8y	55	90	254-255	-
26	3-ClC ₆ H ₄	OMe	S	8z	60	84	248-249	-
27	4-ClC ₆ H ₄	OMe	S	8a'	60	85	241-243	35

^a Reaction conditions: aldehyde (1 mmol), β -dicarbonyl (1 mmol), urea or thiourea (1.5 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 mmol), 80 °C; ^b Isolated yield

Table 4. Comparison of efficiency of various catalysts in synthesis of 5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-ones

Entry	Catalyst	Amount of catalyst ^b	Conditions	Yield/Time ^a	Ref
1	Sr(OTf) ₂	5	Solvent-free/70 °C	97/4	38
2	[Al(H ₂ O) ₆](BF ₄) ₃	10	CH ₃ CN (reflux)	81/20	39
3	Zr(H ₂ PO ₄) ₂	7	Solvent-free/90 °C	88/1	40
4	LiBr	10	CH ₃ CN (reflux)	92/3	41
5	SbCl ₃	100	CH ₃ CN (reflux)	90/18	42
6	CaF ₂	10	C ₂ H ₅ OH/(reflux)	98/2	43
7	Chloroacetic acid	10	Solvent-free/90°C	92/3	44
8	NH ₄ Cl	40	Solvent-free/100 °C	90/3	45
9	Triphenylphosphine	10	Solvent-free/100 °C	70/10	46
10	TiCl ₄ -MgCl ₂	10	Solvent-free/100 °C	90/3	47
11	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	15	Solvent free/80 °C	90/0.6	-

^a Values refer to yield(%) / time(h)

^b Amount of catalysts are in mol%

CONCLUSIONS

In summary, we have described an improved procedure for the synthesis of dihydropyrimidinones and dihydropyrimidinethiones using cobalt(II) nitrate hexahydrate as heterogeneous catalyst. For clarifying the role of the catalyst, three separated reactions were performed that the results clearly indicated that the reaction catalyzed by $\text{Co}(\text{NO}_3)_2$ proceeds predominately through ureido-crotonate intermediate, which this achievement well supports the necessity of Lewis type catalyst for the Biginelli reaction. The mild reaction conditions, rapid conversion, high yields, simple experimental procedure, availability of catalyst are some notable advantages of the present method. Moreover, compatibility with the environment, more efficiency and easy separation after synthesis are considered as another advantages of this catalyst loading. Most importantly, absence of organic solvents in this method contributes it to the development of green technology.

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