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ONE-POT THREE-COMPONENT SYNTHESIS OF 4-ARYL-3,4-DIHYDRO-PYRIMIDIN-2(1*H*)-THIONES CATALYZED BY Ni LOADED SiO_2

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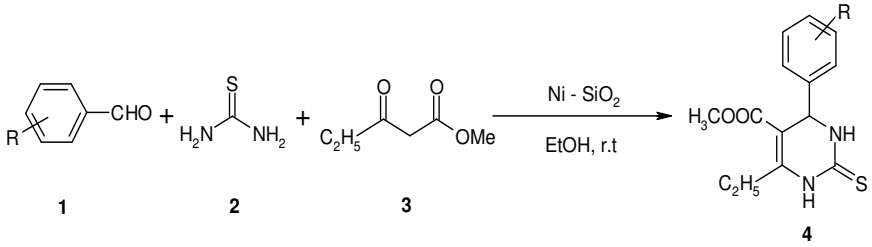
ABSTRACT. A simple and efficient method has been developed for the synthesis of 4-aryl-3,4-dihydropyrimidin-2(1H)-thiones from methyl 3-oxopentanoate, aldehydes and thiourea in the presence of a catalytic amount of Ni loaded SiO_2 at room temperature.

KEY WORDS: Ni loaded SiO_2, 4-Aryl-3,4-dihydropyrimidin-2(1*H*)-thiones, One-pot three-component synthesis, Methyl 3-oxopentanoate, Aldehydes, Thiourea

INTRODUCTION

In recent years, dihydropyrimidinones (DHPMs) and their derivatives have occupied an important position in natural and synthetic organic chemistry because of their wide range of biological activities, such as calcium channel blockers, antiviral, antihypertensive, antifilarial, antibacterial [1-4], and antagonists [5]. Several alkaloids which contain the dihydropyrimidine core unit that have been isolated from marine sources also showed interesting biological properties. Most notable among these are the batzelladine alkaloids, which were found to be potent as HIV gp-120-CD4 inhibitors [6].

In 1893, Biginelli reported the first synthesis of DHPM by a simple one-pot condensation reaction of ethyl acetoacetate, benzaldehyde, and thiourea [7]. However, this method often suffers from drawbacks such as harsh conditions, long reaction times and low yields, particularly when aliphatic and substituted aromatic aldehydes are used. Recently, several synthetic procedures for preparing of DHPMs have been reported, such as the use of a number of Lewis acid catalysts as well as protic acids including $Y(NO_3)_3.6H_2O$ [8], $Cu(BF_4)_2$ [9], $KAl(SO_4)_2.12H_2O$ [10], $Mg(ClO_4)_2$ [11], triphenylphosphine [12], $Ca(NO_3)_2$ [13], and H_3BO_3 [14]. In addition, microwave irradiation [15], ultrasound irradiation [16], and ionic liquid [17] have also been utilized to improve and modify this reaction. As part of our current studies on the development of new catalysts [18, 19], herein, we report an efficient and environmentally friendly method for the synthesis of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones catalyzed by Ni on SiO_2 at room temperature (Scheme 1).



Scheme 1. The synthetic route of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones.

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We studied the possibility to synthesize 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones by the Biginelli reaction using methyl 3-oxopentanoate, aldehydes and thiourea using Ni-SiO_2 as the catalyst (Scheme 1). Here, an efficient and simple method for the synthesis of target compounds is described and the synthesis of some compounds has been reported in our previous studies [20, 21].

EXPERIMENTAL

All reagents and solvents were purchased and used without further purification. Melting points were determined on a Fisher–Johns melting point apparatus were uncorrected. Crude products were purified by column chromatography on silica gel of 60–120 mesh. The NMR spectra were recorded on a Varian 300 MHz spectrometer for ^{1}H NMR. The chemical shifts were reported as ppm down field using TMS as an internal standard. LC–MS Mass spectra were recorded on a MASPEC low resolution mass spectrometer operating at 70 eV.

To conclude, we have shown that the Ni loaded SiO_2 is a highly active catalyst for the synthesis of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones. General procedure for the preparation of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones: A mixture of thiourea (1 mmol), substituted benzaldehyde (1 mmol) and methyl 3-oxopentanoate (1.5 mmol) with Ni loaded SiO_2 (20 mol%) in EtOH (1 mL) was stirred at ambient temperature for an appropriate time (Table 1). After completion of the reaction as indicated by TLC, the Ni–SiO_2 was filtered and washed with 50% EtOH (2 × 10 mL). The crude product was purified by recrystallization from diethyl ether (solid products) or by chromatography using silica gel and mixtures of hexane/ethyl acetate of increasing polarity. The physical data (mp, IR, ^{1}H NMR, LCMS) of known compounds were found to be identical with those reported in the literature [20, 21]. Some selected product characterization data.

RESULTS AND DISCUSSION

Methyl 3-oxopentanoate, aldehydes and thiourea were selected as the model reaction to examine catalytic activity of Ni on SiO_2 at ambient temperature. We observed that the model reaction did not proceed in the absence of SiO_2 even after 24 h (Table 1, entry 1). When using catalytic amount of 10 mol% Ni SiO_2, the reaction gave a 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones with 70% yield in 1.5 h in EtOH (Table 1, entry 3), and further lowering the catalyst loading up to 5 mol% led to lower yield of 55% in 1.5 h (Table 1, entry 2). In the presence of 20 mol% catalyst the reaction affords the corresponding 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones in 98% yield within 1.5 h (Table 1, entry 4), and Ni SiO_2 (25 mol%) also gives 98% yield in 1.5 h (Table 1, entry 5). The solvents examined were trichloromethane, acetonitrile and ethanol, among which ethanol is shown to be the best (Table 1). Accordingly, 20 mol% Ni-SiO_2 catalyst loading in EtOH is considered optimal for the synthesis of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones.

We prepared a range of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones under the optimized conditions (Table 2). Methyl 3-oxopentanoate, different aldehydes were coupled with thiourea under these reaction conditions. The reactions are clean and highly selective affording exclusively 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones in high yields in a short reaction time. The reaction of methyl 3-oxopentanoate, thiourea with with 2,4-dimethoxy, 3-hydroxy-4-methoxy and 3-nitro-4-ethyl benzaldehyde is completed within 1.5 h with 98%, 96% and 94% yield, respectively (Table 2, entries 1 and 3). Similarly, the reaction of methyl 3-oxopentanoate and thiourea with *o*-methoxy, *o*-ethoxy and *o*-nitro benzaldehydes produce the corresponding products in excellent yields of 93, 89 and 98% in 1.5, 2.0 and 1.5 h, respectively (Table 2, entries 4–6). This method is equally effective with electron-withdrawing *o*-chloro, *m*-chloro, *o*-fluoro, *m*-bromo *p*-bromo and 2-hydroxy-5-bromobenzaldehydes (Table 2, entries 7–12). The

reaction of methyl 3-oxopentanoate and thiourea with *o*-methyl, *m*-methyl and *m,p*-dimethyl benzaldehyde produce the corresponding products in 84%, 82% and 86% yields, respectively, with 'longer' reaction time (3 h) (Table 2, entries 13 and 15).

Table 1. Three-component synthesis of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones under various conditions[a].

Entry	Catalyst (%)	Time (h)	Yield[b] (%)
1	No catalyst	24	0
2	5	1.5	55
3	10	1.5	70
4	20	1.5	98
5	25	1.5	98
6	20	2	86[c]
7	20	2.5	90[d]

[a]Ni-SiO_2 was added to a mixture of 1.5 mmol of methyl 3-oxopentanoate, 1 mmol of aldehyde and 1 mmol of thiourea. [b]Isolated yield. [c]In the presence of $CHCl_3$. [d]In the presence of CH_3CN.

Table 2. Preparation of various 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones in the presence of Ni-SiO_2 in EtOH at room temperature[a].

Product	R	Time (h)	Yield (%)
1	2-OCH_3, 4-OCH_3	1.5	98
2	3-OH, 4-OCH_3	1.5	96
3	3-NO_2, 4-C_2H_5	1.5	94
4	2-OCH_3	1.5	93
5	2-OC_2H_5	2	89
6	2-NO_2	1.5	98
7	2-Cl	1.5	92
8	3-Cl	1.5	93]
9	2-F	2	91
10	3-Br	2	94
11	4-Br	2	90
12	2-OH, 5-Br	1.5	92
13	2-CH_3	3	84
14	4-CH_3	3	82
15	3-CH_3, 4-CH_3	3	86

[a]Reaction conditions: thiourea (1 mmol), substituted benzaldehyde (1 mmol), ethyl 3-oxopentanoate (1.5 mmol), Ni-SiO_2 (20 mol%), room temperature, EtOH.

6-Ethyl-4-(2,4-dimethoxyphenyl)–5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione ***(1)***. Mp 189–191 °C; ^{1}H NMR: δ = 1.10 (t, 3H, CH_3), 2.45 (m, 2H, CH_2), 3.58 (s, 3H, OCH_3), 3.72 (s, 6H, Ar-2OCH_3), 4.80 (d, 1H, CH), 6.40–6.65 (m, 2H, C_6H_3), 9.45 (s, 1H, NH), 9.85 (s, 1H, NH); IR (KBr): 3315, 3180, 3120, 2980, 1662, 1571, 1460, 1435, 1348, 1282, 1199, 1180, 1121, 765 cm^{-1}; MS (70 eV, EI): *m/z* (%): 337 (M+1); Anal. calcd for $C_{16}H_{20}N_2O_4S$: C, 57.31; H, 5.74; N, 8.37. Found: C, 57.16; H, 5.64; N, 8.45.

6-Ethyl-4-(3-hydroxy-4-methoxyphenyl)–5-(methoxycarbonyl)-3,4-dihydro-pyrimidin-2(1H)-thione ***(2)***. Mp 159-161 °C; ^{1}H NMR: δ = 1.14 (t, 3H, CH_3), 2.55-3.00 (m, 2H, CH_2), 3.58 (s, 3H, OCH_3), 3.79 (s, 3H, Ar-OCH_3), 5.42 (d, 1H, CH), 6.55–6.95 (m, 3H, C_6H_3), 9.05 (s, 1H, OH), 9.65 (s, 1H, NH), 10.25 (s, 1H, NH); IR (KBr): 3318, 3190, 3120, 2990, 1667, 1583,

1471, 1431, 1345, 1292, 1201, 1184, 1121, 762 cm^{-1}; MS (70 eV, EI): *m/z* (%): 322 (M^+); Anal. calcd for $C_{15}H_{18}N_2O_4S$: C, 55.88; H, 5.65; N, 8.70. Found: C, 55.98; H, 5.51; N, 8.93.

6-Ethyl-4-(4-ethyl-3-nitrophenyl)–5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***3***). Mp 190-191 °C; ^1H NMR: δ = 1.10-1.21 (t, 6H, $2CH_3$), 2.45–2.85 (m, 4H, CH_2), 3.54 (s, 3H, OCH_3), 5.40 (d, 1H, CH), 7.55–8.10 (m, 3H, C_6H_3), 9.75 (s, 1H, NH), 10.32 (s, 1H, NH); IR (KBr): 3293, 3181, 3101, 2979, 2921, 1729, 1678, 1571, 1549, 1476, 1439, 1349, 1322, 1281, 1194, 1164, 1109, 755 cm^{-1}; MS (70 eV, EI): *m/z* (%): 349 (M^+); Anal. calcd for $C_{16}H_{19}N_3O_4S$: C, 55.10; H, 5.25; N, 12.14. Found: C, 55.38; H, 5.64; N, 12.01.

6-Ethyl-4-(2-methoxyphenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***4***). Mp 231 °C, lit.[20] 234–236 °C; ^1H NMR: δ = 1.11 (t, 3H, CH_3), 2.45–3.00 (m, 2H, CH_2), 3.54 (s, 3H, Ar-OCH_3), 3.78 (s, 3H, OCH_3), 5.55 (d, 1H, CH), 6.48–7.95 (m, 4H, C_6H_4), 9.28 (s, 1H, NH), 10.30 (s, 1H, NH); IR (KBr): 3201, 2978, 2944, 1721, 1668, 1585, 1492, 1478, 1433, 1284, 1258, 1179, 1141, 1105, 760 cm^{-1}; MS (70 eV, EI): *m/z* (%): 306 (M^+).

6-Ethyl-4-(2-ethoxyphenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***5***). Mp 204–206 °C; ^1H NMR: δ = 1.08 (t, 3H, CH_3), 1.42 (t, 3H, Ar-CH_3), 2.51–2.74 (m, 2H, CH_2), 3.45 (s, 3H, OCH_3), 3.85–4.10 (m, 2H, Ar-OCH_2), 5.43 (d, 1H, CH), 6.68–7.38 (m, 4H, C_6H_4), 9.21 (s, 1H, NH), 10.27 (s, 1H, NH); IR (KBr): 3315, 3181, 3118, 2975, 2942, 1719, 1655, 1585, 1482, 1431, 1328, 1299, 1261, 1236, 1186, 1131, 1101, 1008, 758 cm^{-1}; MS (70 eV, EI): *m/z* (%): 320 (M^+); Anal. calcd for $C_{16}H_{20}N_2O_3S$: C, 59.98; H, 6.29; N, 8.74. Found: C, 59.32; H, 6.81; N, 8.64.

6-Ethyl-4-(2-nitrophenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***6***). Mp 158–160 °C; ^1H NMR: δ = 1.12 (t, 3H, CH_3), 2.58–2.95 (m, 2H, CH_2), 3.45 (s, 3H, OCH_3), 5.58 (d, 1H, CH), 7.35–7.64 (m, 4H, C_6H_4), 9.64 (s, 1H, NH), 10.50 (s, 1H, NH); IR (KBr): 3274, 3173, 2974, 2949, 1718, 1654, 1558, 1523, 1470, 1438, 1351, 1309, 1270, 1200, 1180, 1127, 1101, 750 cm^{-1}; MS (70 eV, EI): *m/z* (%): 322 (M+1); Anal. calcd for $C_{14}H_{15}N_3O_4S$: C, 52.33; H, 4.71; N, 13.07. Found: C, 52.87; H, 4.74; N, 12.99.

6-Ethyl–4-(2-chlorophenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***7***). Mp 183–184 °C, lit.[21] 196–198 °C; ^1H NMR: δ = 1.10 (t, 3H, CH_3), 2.38–2.95 (m, 2H, CH_2), 3.45 (s, 3H, OCH_3), 5.61 (d, 1H, CH), 7.15–7.55 (m, 4H, C_6H_4), 9.60 (s, 1H, NH), 10.40 (s, 1H, NH); IR (KBr): 3265, 3170, 3012, 2945, 1707, 1640, 1592, 1468, 1433, 1314, 1269, 1187, 1137, 1105, 774 cm^{-1}; MS (70 eV, EI): *m/z* (%): 311 (M+1).

6-Ethyl–4-(3-chlorophenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***8***). Mp 169–170 °C, lit.[21] 175-177 °C; ^1H NMR: δ = 1.09 (t, 3H, CH_3), 2.42–2.84 (m, 2H, CH_2), 3.51 (s, 3H, OCH_3), 5.24 (d, 1H, CH), 7.10-7.45 (m, 4H, C_6H_4), 9.58 (s, 1H, NH), 10.45 (s, 1H, NH); IR (KBr): 3321, 3184, 3110, 2994, 1684, 1574, 1442, 1280, 1191, 1109, 762 cm^{-1}; MS (70 eV, EI): *m/z* (%): 311 (M+1).

6-Ethyl-4-(2-fluorophenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***9***). Mp 183–185 °C; ^1H NMR: δ = 1.10 (t, 3H, CH_3), 2.67–2.73 (m, 2H, CH_2), 3.49 (s, 3H, OCH_3), 5.43 (d, 1H, CH), 7.14–7.22 (m, 4H, C_6H_4), 9.56 (s, 1H, NH), 10.39 (s, 1H, NH); IR (KBr): 3265, 3179, 2934, 1699, 1642, 1576, 1485, 1462, 1436, 1313, 1273, 1225, 1189, 1149, 1132, 1105, 759 cm^{-1}; MS (70 eV, EI): *m/z* (%): 294 (M^+); Anal. calcd for $C_{14}H_{15}N_2O_2SF$: C, 57.13; H, 5.14; N, 9.52. Found: C, 56.59; H, 4.47; N, 9.47.

6-Ethyl–4-(3-bromophenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***10***). Mp 185–187 °C, lit.[21] 195–197 °C; ^{1}H NMR: δ = 1.10 (t, 3H, CH_3), 2.45–3.00 (m, 2H, CH_2), 3.48 (s, 3H, OCH_3), 5.24 (s, 1H, CH), 7.15–7.60 (m, 4H, C_6H_4), 9.64 (d, 1H, NH), 10.45 (s, 1H, NH); IR (KBr): 3320, 3177, 3121, 2991, 2936, 1672, 1588, 1471, 1438, 1368, 1291, 1194, 1175, 1132, 779 cm^{-1}; MS (70 eV, EI): *m/z* (%): 358 (M+2).

6-Ethyl-4-(4-bromophenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***11***). Mp 181–183 °C, lit.[21] 178–179 °C; ^{1}H NMR: δ = 1.09 (t, 3H, CH_3), 2.36–2.95 (m, 2H, CH_2), 3.52 (s, 3H, OCH_3), 5.20 (d, 1H, CH), 7.20–7.60 (m, 4H, C_6H_4), 9.70 (s, 1H, NH), 10.45 (s, 1H, NH); IR (KBr): 3172, 2984, 1681, 1582, 1468, 1441, 1351, 1279, 1199, 1110, 764 cm^{-1}; MS (70 eV, EI): *m/z* (%): 358 (M+2).

6-Ethyl-4-(5-bromo-2-hydroxyphenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***12***). Mp 207–209 °C; ^{1}H NMR: δ = 1.04 (t, 3H, CH_3), 1.86–2.48 (m, 2H, CH_2), 3.38 (s, 3H, OCH_3), 3.64 (s, H, OH), 4.74 (s, 1H, CH), 6.76–7.49 (m, 3H, C_6H_3), 9.12 (s, 1H, NH), 10.15 (s, 1H, NH); IR (KBr): 3315, 3183, 3121, 2979, 2943, 1724, 1655, 1585, 1479, 1446, 1329, 1301, 1262, 1238, 1187, 1141, 1112, 986, 760 cm^{-1}; MS (70 eV, EI): *m/z* (%): 374 (M+2), 372 (M^+); Anal. calcd for $C_{14}H_{16}N_2O_3SBr$: C, 45.17; H, 4.33; N, 7.52. Found: C, 45.59; H, 4.46; N, 7.59.

6-Ethyl-4-(2-methylphenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***13***). Mp 181–183 °C, lit.[20] 192–193 °C; ^{1}H NMR: δ = 1.12 (t, 3H, CH_3), 2.40 (s, 3H, Ar-CH_3), 2.48-2.75 (m, 2H, CH_2), 3.48 (s, 3H, OCH_3), 5.30 (d, 1H, CH), 7.10-7.35 (m, 4H, C_6H_4), 9.50 (s, 1H, NH), 10.30 (s, 1H, NH); IR (KBr): 3270, 3169, 3009, 2972, 1690, 1631, 1580, 1461, 1434, 1311, 1187, 1136, 1101, 755 cm^{-1}; MS (70 eV, EI): *m/z* (%): 290 (M^+).

6-Ethyl-4-(4-methylphenyl)-5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***14***). Mp 177–179 °C; ^{1}H NMR: δ = 1.10 (t, 3H, CH_3), 2.15 (s, 3H, Ar-CH_3), 2.45–2.75 (m, 2H, CH_2), 3.51 (s, 3H, OCH_3), 5.25 (d, 1H, CH), 6.90–7.24 (m, 4H, C_6H_4), 9.60 (s, 1H, NH), 10.35 (s, 1H, NH); IR (KBr): 3188, 2988, 1679, 1651, 1592, 1518, 1473, 1349, 1282, 1199, 1121, 765 cm^{-1}; MS (70 eV, EI): *m/z* (%): 290 (M^+). Anal. calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.24; N, 9.64. Found: C, 62.31; H, 6.19; N, 9.47.

6-Ethyl-4-(3,4-dimethylphenyl)–5-(methoxycarbonyl)-3,4-dihydropyrimidin-2(1H)-thione (***15***). Mp 145-147 °C; ^{1}H NMR: δ = 1.07 (t, 3H, CH_3), 2.20-2.30 (s, 6H, Ar-2CH_3), 2.60-2.72 (m, 2H, CH_2), 3.51 (s, 3H, OCH_3), 5.12 (d, 1H, CH), 7.02–7.15 (m, 3H, C_6H_3), 9.65 (s, 1H, NH), 10.35 (s, 1H, NH); IR (KBr): 3170, 3018, 2995, 1674, 1652, 1599, 1518, 1468, 1430, 1348, 1290, 1150, 1110, 761 cm^{-1}; MS (70 eV, EI): *m/z* (%): 305 (M+1); Anal. calcd for $C_{16}H_{20}N_2O_2S$: C, 63.15; H, 6.60; N, 9.20. Found: C, 63.28; H, 6.49; N, 9.10.

CONCLUSIONS

In conclusion, we have developed a novel and highly efficient method for the synthesis of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones by treatment of methyl 3-oxopentanoate, aldehydes and thiourea with Ni loaded silica as catalyst, which acts an effective Lewis acid. The significant advantages of this method are good yields, short reaction times and simple workup procedure, plus easy preparation and handling of the catalyst. This methodology may find wide uses in organic synthesis for preparation of the 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thiones.

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