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Silica-based sulfonic acid (SiO_2-Pr-SO_3H): an efficient catalyst in the green one-pot synthesis of 3,4-dihydropyrimidinones/thiones

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SiO_2-Pr-SO_3H efficiently catalyzes the three-component coupling of ethyl acetoacetate, aldehydes, and urea (or thiourea) under solvent-free conditions to afford the corresponding dihydropyrimidinones. Compared with the classical Biginelli reaction conditions, this protocol has the advantage of very short reaction time (2 minutes), good to excellent yields, recyclable catalyst, and simple experimental procedure.

Keywords: Sulfonic acid functionalized silica; 3,4-Dihydropyrimidinones, Biginelli reaction; Heterogeneous catalyst, Green conditions.

INTRODUCTION

Dihydropyrimidinones (DHPMs), the so called *Biginelli compounds* [1], and their derivatives are very well known for their diverse biological activities such as antifungal [2], antibacterial [3], antihypertensive [4], anti-HIV [5] and anti-tumor effects [6]. DHPMs were recently developed as calcium channel modulators, α_{1a} adrenoceptor-selective antagonists and compounds that target the mitotic machinery [7]. Moreover, several marine alkaloids with interesting biological activities containing the dihydropyrimidine-5-carboxylate core have been isolated [8, 9]. Therefore, this heterocyclic nucleus has gained great importance and several improved methodologies for the original Biginelli protocol have recently been reported in the literature [10-18]. Although these methods have their own merits, they also suffer from drawbacks such as use of solvents, expensive reagents or catalysts, drastic reaction conditions, long reaction times and unsatisfactory yields.

The development of efficient and versatile catalytic systems for the Biginelli reaction is an active ongoing research area and thus, there is scope for further improvement toward milder reaction conditions, variations of substituents in all three components, shorter reaction times, and better yields. In 2007, Paul and coworkers developed a simple procedure for the synthesis of 3,4-dihydropyrimidinones/thiones in CH_3CN using re-usable covalently anchored sulfonic acid onto the surface of silica gel solid acid catalyst with long reaction times (7-12 h) [19]. In continuation of our studies on the application of heterogeneous solid catalysts to organic synthesis [20-23], herein we developed a green, rapid, efficient and inexpensive procedure for the synthesis of 3,4-dihydropyrimidinones using SiO_2-Pr-SO_3H under solvent-free conditions.

EXPERIMENTAL

Materials

All chemicals were obtained commercially and used without further purification. Melting points were measured by the capillary tube method with an Electrothermal 9200 apparatus.

Instruments

IR spectra were recorded from KBr disks using a FT-IR Bruker Tensor 27 instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX spectrometer (250 MHz for ^{1}H, 62 MHz for ^{13}C) in DMSO-d_6 solutions. GC-mass analysis was performed on a model 5973/6890 network mass-selective detector (Agilent).

Preparation of catalyst: synthesis of 3-mercaptopropylsilica (MPS) and its oxidation

To 20 g of SiO_2 in dry toluene, 25 ml of (3-mercaptopropyl)trimethoxysilane was added, and the reaction mixture was refluxed for 24 h. Then, the mixture was filtered to obtain 3-mercaptopropylsilica (MPS) which was washed with acetone and dried. MPS (20 g) was oxidized with H_2O_2 (50 ml) and one drop of H_2SO_4 in methanol (20 ml) for 24 h at room temperature,

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then the mixture was filtered and washed with H_2O and acetone to obtain SiO_2-Pr-SO_3H. The modified SiO_2-Pr-SO_3H was dried and used as a solid acid catalyst in the following reaction.

General procedure for the synthesis of 3,4-dihydropyrimidinones/thiones

SiO_2-Pr-SO_3H (0.02 g) was activated in vacuum at 100°C, and after cooling the catalyst to room temperature, aldehyde (1 mmol), urea or thiourea (1 mmol), and ethyl acetoacetate (1 mmol) were added. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature, poured into ice-water and filtered. The crude product was dissolved in EtOAc, filtered off for removing the unsolved material and the filtrate was cooled to afford the pure product.

Selected Spectral Data

5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-(1H)-one (4a)

m.p.: 203-204°C; IR (KBr): 3244, 3116, 1725, 1701, 1646 cm^{-1}; Mass: m/z (%) 260 [$M^{+\cdot}$], 245, 231, 215, 183 (100), 169, 155; ^{1}H NMR (DMSO-d_6): δ = 1.10 (t, *J* = 5.8 Hz, 3H, CH_3-CH_2O), 2.25 (s, 3H, CH_3), 3.97 (q, *J* = 5.8 Hz, 2H, CH_3-CH_2O), 5.14 (d, *J* = 2.7 Hz, 1H, CH), 5.41 (s, 1H, NH), 7.21-7.35 (m, 5CH, ArH), 7.74 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6): δ = 14.1, 17.8, 53.9, 59.2, 99.2, 126.2, 127.2, 128.4, 144.8, 148.3, 152.1, 165.3 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(2-thienyl)-3,4-dihydropyrimidin-(1H)-one (4c)

m.p.: 205-207°C; IR (KBr): 3333, 3245, 1700, 1650, 1594 cm^{-1}; Mass: m/z (%) 266 [$M^{+\cdot}$], 251, 237 (100), 221, 193, 178, 110; ^{1}H NMR (DMSO-d_6): δ = 1.22 (t, *J* = 4.5 Hz, 3H, CH_3-CH_2O), 2.30 (s, 3H, CH_3), 4.11 (q, *J* = 7.2 Hz, 2H, CH_3-CH_2O), 5.58 (d, *J* = 3.5 Hz, 1H, CH), 6.88-6.96 (m, 3H, 3CH), 7.43 (s, 1H, NH), 9.02 (s, 1H, NH) ppm.

4-(4-Chlorophenyl)-5-(ethoxycarbonyl)-6-methyl-3,4-dihydropyrimidin–(1H)–one (4e)

m.p: 210°C; IR (KBr): 3242, 3116, 1706, 1647 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 1.17 (t, *J* = 7.0 Hz, 3H, CH_3-CH_2O), 2.34 (s, 3H, CH_3), 4.10 (q, *J* = 7.2 Hz, 2H, CH_3-CH_2O), 5.37 (d, *J* = 2.7 Hz, 1H, CH), 5.56 (s, 1H, NH), 7.23-7.31 (m, 4CH, ArH), 7.48 (s, 1H, NH) ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-(1H)-one (4m)

m.p.: 211-213°C; IR (KBr): 3309, 3243, 1704, 1650 cm^{-1}; Mass: m/z (%) 274 [$M^{+\cdot}$], 259, 245, 229,215, 201, 215, 183 (100), 155, 91; ^{1}H NMR (DMSO-d_6): δ = 1.17 (t, *J* = 7.5 Hz, 3H, CH_3-CH_2O), 2.33 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 4.07 (q, *J* = 7.5 Hz, 2H, CH3-CH_2O), 5.32 (d, *J* = 5.0 Hz, 1H, CH), 6.02 (s, 1H, NH), 7.08 (d, *J* = 7.5 Hz, 2CH, ArH), 7.20 (d, *J* = 7.5 Hz, 2CH, ArH), 8.05 (s, 1H, NH) ppm.

4-(4-N,N-Dimethylaniline)-5-(ethoxycarbonyl)-6-methyl-3,4-dihydropyrimidin-(1H)–one (4o)

m.p.: 248-250°C; IR (KBr): 3241, 3112, 1720, 1702, 1646 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 1.18 (t, *J* = 7.0 Hz, 3H, CH_3-CH_2O), 2.32 (s, 3H, CH_3), 2.92 (s, 6H, $2CH_3$), 4.06 (q, *J* = 7.0 Hz, 2H, CH_3-CH_2O), 5.25 (s, 1H, CH), 6.19 (s, 1H, NH), 6.63 (d, *J* = 8.5 Hz, 2CH, ArH), 7.16 (d, *J* = 8.5 Hz, 2CH, ArH), 8.27 (s, 1H, NH) ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(2-methylphenyl)-3,4-dihydropyrimidin-(1H)-one (4q)

m.p.: 201-203°C; IR (KBr): 3237, 3104, 1702, 1642 cm^{-1}; Mass: m/z (%) 274 [$M^{+\cdot}$], 259, 245, 229, 201, 183 (100), 155, 91; ^{1}H NMR (DMSO-d_6): δ = 0.97 (t, *J* = 5.9 Hz, 3H, CH_3-CH_2O), 2.28 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.86 (q, *J* = 4.0 Hz, 2H, CH_3-CH_2O), 5.39 (d, *J* = 2.1 Hz, 1H, CH), 7.09-7.16 (m, 4CH, ArH), 7.61 (s, 1H, NH), 9.14 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6): δ = 13.9, 17.6, 18.6, 54.4, 59.0, 99.1, 126.5, 127.1, 130.0, 134.6, 143.2, 148.4, 151.5, 165.2 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(2-methoxyphenyl)-3,4-dihydropyrimidin-(1H)-one (4r)

m.p.: 258-260°C; IR (KBr): 3255, 3107, 1726, 1701 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 1.10 (t, *J* = 7.5 Hz, 3H, CH_3-CH_2O), 2.42 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 4.05 (q, *J* = 7.5 Hz, 2H, CH_3-CH_2O), 5.67 (d, *J* = 2.5 Hz, 1H, CH), 5.89 (s, 1H, NH), 6.84-7.79 (m, 4CH, ArH), 8.46 (s, 1H, NH) ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-(1H)-one (4s)

m.p.: 208°C; IR (KBr): 3243,3110, 1705, 1648 cm^{-1}; Mass: m/z (%) 290 [$M^{+\cdot}$], 261 (100), 245, 217, 183, 155,77; ^{1}H NMR (DMSO-d_6): δ = 1.17 (t, *J* = 7.5 Hz, 3H, CH_3-CH_2O), 2.34 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 4.06 (q, *J* = 7.5 Hz, 2H, CH_3-CH_2O), 5.35 (d, *J* = 2.5 Hz, 1H, CH), 5.48 (s, 1H, NH), 6.82 (d, *J* = 7.5 Hz, 2CH, ArH), 7.25 (d, *J* = 7.5 Hz, 2CH, ArH), 7.49 (s, 1H, NH) ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(2,3-dimethoxyphenyl)-3,4-dihydropyrimidin-(1H)-one (4t)

m.p.: 199-200°C; IR (KBr): 3232, 3104, 1705. 1645 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 1.11 (t, *J* = 7.5 Hz, 3H, CH_3-CH_2O), 2.41 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 4.04 (q, *J* = 7.5 Hz, 2H, CH_3-CH_2O), 5.52 (s, 1H, NH), 5.71 (d, *J* = 2.5 Hz, 1H, CH), 6.69-7.01 (m, 3CH, ArH), 7.53 (s, 1H, NH) ppm.

Table 1. SiO_2-Pr-SO_3H catalyzed synthesis of 3,4-dihydropyrimidinones/thiones **4** under solvent-free conditions

Entry	R	X	Product	Time (min)	[a]Yield (%)	m.p (˚C)	m.p. (Ref.)
1	C_6H_5-	O	**4a**	2	95	203-204	204-205[24]
2	2,3-$Cl_2C_6H_3$-	O	**4b**	2	100	236-238	244-246[25]
3	2-Thienyl-	O	**4c**	3	100	205-207	207-208[13]
4	4-OHC_6H_4-	O	**4d**	20	99	241-244	237-238[26]
5	4-ClC_6H_4-	O	**4e**	3	99	210	208-211[24]
6	CH_3-	O	**4f**	90	99	180-182	188-189[12]
7	2,6-$Cl_2C_6H_3$-	O	**4g**	1	99	230-232	226[14]
8	2-FC_6H_4-	O	**4h**	2	99	231-233	233-235[24]
9	2,4-$Cl_2C_6H_3$-	O	**4i**	7	98	235-237	238-240[27]
10	i-Pr	O	**4j**	2	98	198-200	194-195[27]
11	2-Furyl-	O	**4k**	210	95	205-208	202-204[14]
12	4-$NO_2C_6H_4$-	O	**4l**	2	92	209-211	209-212[24]
13	4-MeC_6H_4-	O	**4m**	5	85	211-213	214-215[15]
14	3-$NO_2C_6H_4$-	O	**4n**	2	80	228-230	226-228[12]
15	4-$NMe_2C_6H_4$-	O	**4o**	4	80	248-250	253-254[26]
16	3-MeC_6H_4-	O	**4p**	2	77	203-206	204-205[13]
17	2-MeC_6H_4-	O	**4q**	15	76	201-203	208-210[28]
18	2-$OMeC_6H_4$-	O	**4r**	4	70	258-260	262-265[24]
19	4-$OMeC_6H_4$-	O	**4s**	3	62	208	206-208[24]
20	2,3-$OMe_2C_6H_3$-	O	**4t**	8	61	199-200	New
21	3,4-$OMe_2C_6H_3$-	O	**4u**	2	42	188-190	192-194[29]
22	C_6H_5CH=CH-	O	**4v**	15	30	230-232	234-236[30]
23	4-ClC_6H_4-	S	**4w**	180	61	194	191-192[10]
24	C_6H_5-	S	**4x**	180	44	202-204	206-208[30]
25	4-$OMeC_6H_4$-	S	**4y**	180	40	151-153	153-156[10]
26	C_6H_5CH=CH-	S	**4z**	120	30	238-240	243-245[30]
27	3-$NO_2C_6H_4$-	S	**4aa**	180	20	203-205	206-207[26]
28	4-$NO_2C_6H_4$-	S	**4bb**	180	35	107-109	109-111[28]
29	i-Pr	S	**4cc**	20	30	188-190	191-192[31]

[a] Isolated yield.

5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-(1H)-thione (4x)

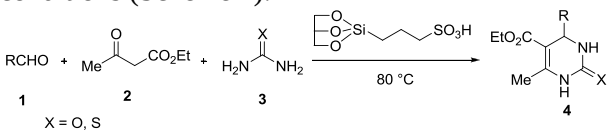
m.p.: 202-204°C; IR (KBr): 3172, 3106, 2981, 1670, 1618, 1196 cm^{-1}; Mass: m/z (%) 276 [$M^{+\cdot}$], 247, 231, 199 (100), 171; ^{1}H NMR (DMSO-d_6): δ = 1.08 (t, *J* = 5.9 Hz, 3H, CH_3-CH_2O), 2.28 (s, 3H, CH_3), 4.01 (q, *J* = 5.9 Hz, 2H, CH_3-CH_2O), 5.16 (d, *J* = 3.0 Hz, 1H, CH), 7.20-7.36 (m, 5CH, ArH), 9.63 (s, 1H, NH), 10.31 (s, 1H, NH) ppm; ^{13}C NMR: δ = 14.0, 17.1, 54.0, 59.6, 100.7, 126.4, 127.7, 128.5, 143.5, 145.0, 165.1, 174.2 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-(1H)-thione (4y)

m.p.: 151-153°C; IR (KBr): 3173, 3105, 1674, 1575 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 1.17 (t, *J* = 7.0 Hz, 3H, CH_3-CH_2O), 2.34 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 4.07 (q, *J* = 7.0 Hz, 2H, CH_3-CH_2O), 5.29 (d, *J* = 3.0 Hz, 1H, CH), 7.08 (d, *J* = 8.0 Hz, 2CH, ArH), 7.17 (d, *J* = 8.0 Hz, 2CH, ArH), 8.84 (s, 1H, NH), 9.51 (s, 1H, NH) ppm.

RESULTS AND DISCUSSION

A model reaction of benzaldehyde **1a** ethyl acetoacetate **2**, and urea **3** was carried out in the presence of SiO_2-Pr-SO_3H as a highly efficient heterogeneous acid catalyst under solvent-free conditions (Scheme **1**).



Scheme 1

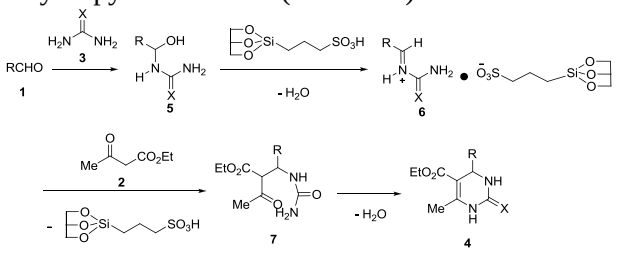
It was found that the reaction took place smoothly and the corresponding product **4a** was obtained in high yield (100%) when the mixture was stirred at 80°C for only 2 min. Encouraged by this result, various types of substituted aldehydes were examined under solvent-free conditions.

Aromatic aldehydes carrying either electron-donating or electron-withdrawing substituents reacted very well, giving moderate to excellent yields (Table **1**). Even for aliphatic aldehydes, which normally show extremely poor yields in the Biginelli reaction, better yields of the

corresponding dihydropyrimidinones could be obtained.

After reaction completion (monitored by TLC), the mixture was cooled to room temperature and poured into ice-water and filtered. The crude product was dissolved in hot EtOAc, filtered for removing the unsolved material and then the filtrate was cooled to afford the pure product. The catalyst could be recycled by subsequent washing with dilute acid solution, water, and then acetone, and after drying could be reused without loss of reactivity.

The most probable mechanism of this reaction includes acid catalyzed *in situ* formation of an *N*-acyliminium ion intermediate **6** by the reaction of urea and aldehyde, which undergoes subsequent addition to ethyl acetoacetate followed by cyclization and dehydration to yield dihydropyrimidinone **4** (Scheme **2**).



Scheme **2**

For preparation of the catalyst, functionalization of SiO_2 with $–SO_3H$ group was performed by direct synthesis or post-grafting [32, 33]. SiO_2 was functionalized with (3-mercaptopropyl) trimethoxysilane (MPTS), then the thiol groups of the product were oxidized to sulfonic acid by hydrogen peroxide. The catalyst surface was analyzed by different methods such as thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET), and CHN methods, which demonstrated that the organic groups (propyl sulfonic acid) were immobilized into the pores [34]. Pore volume and average pore diameter of SiO_2-Pr-SO_3H are smaller than those of SiO_2 due to the immobilization of organic groups (propyl sulfonic acid) into the pores.

CONCLUSIONS

In conclusion, we have developed a simple, efficient and mild protocol for the synthesis of dihydropyrimidinones in excellent yields. The use of SiO_2-Pr-SO_3H under solvent-free conditions has the advantages of being a reusable and environmentally benign catalyst. Excellent yields of the products, very short reaction times, and simplicity of the system make it an improved protocol in comparison with existing methods.

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ЕФЕКТИВЕН КАТАЛИЗАТОР (SiO_2-Pr-SO_3H) ЗА ЕДНОСТАДИЙНА ЗЕЛЕНА СИНТЕЗА НА 3,4-ДИХИДРОПИРИМИДИНОНИ/ТИОНИ

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(Резюме)

SiO_2-Pr-SO_3H ефективно катализира свързването на етил-ацетоацетат, алдехиди и карбамид (тиокарбамид) в отсъствие на разтворител за получаването на съответните дихидропиримидинони. В сравнение с класическите реакционни условия по Biginelli този протокол има предимствата на много кратко време за реакция (2 минути), добри до отлични добиви, рециклируем катализатор и проста експериментална процедура.