SILT TOWARDS HETEROGENEOUS CATALYSIS

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Abstract: Biginelli compounds are influential heterocyclic compounds because of their role in the development of important therapeutic agents. Synthesis of 3, 4- dihydropyrimidinones using different aldehydes, β ketoesters, urea/thiourea in presence of silty soil as green catalyst under solvent free conditions and MW irradiation. It is an ecofriendly process.

Keywords: Biginelli, silty soil, solvent free, microwave, multicomponent

1. Introductioin: Biginelli compounds are important class of heterocyclic compounds in the field of pharmaceutics. They manifest vast range of biological activities and their applications in the field of medicinal research [1]. Literature study reveals that different methods have been developed for the synthesis of biginelli compounds and their derivatives.

The most common method for the preparation of biginelli compounds is condensation of an aryl aldehyde, β-ketoesters, urea/thiourea[2-3]. Furthermore, improved methods have been reported using lewis acids, bronsted acids, polyacids, Baker's yeast, citric acid[4], heterogeneous catalyst such as scolecite[5], zeolite[6], Zirconia/H_2SO_4 [7] Nano composite ferrites[8] etc. Use of HCl[9], NH_4VO_3[10], I_2[11] under MWI. The literature also reveals the biginelli reaction conditions using ionic liquid Bronsted acid [12], Benzotriazolium[13] as catalyst under solvent free conditions.

However many of these reported catalytic processes involve strong acidic conditions, expensive ragents, catalyst, multistep preparation of catalyst, long reaction time etc. Therefore development of more competent, less expensive, high yielding, environment friendly method is still required.

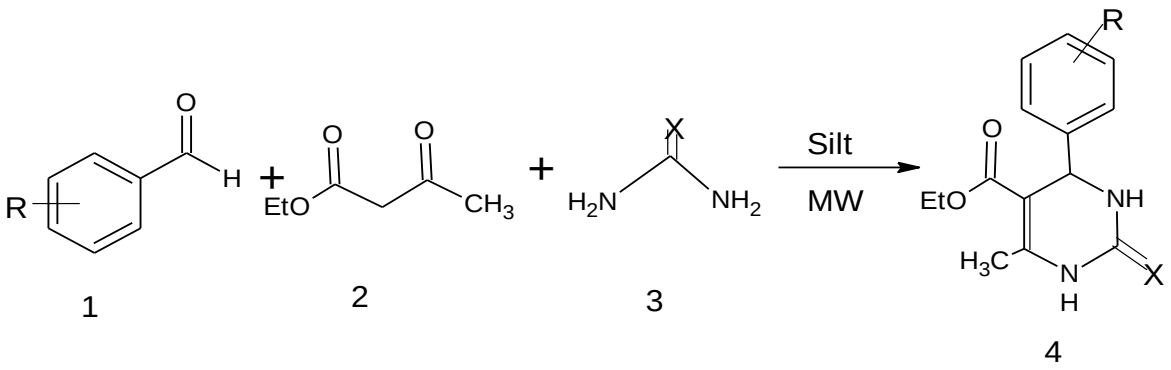
The organic reactions run under solvent free conditions are beneficial due to their increased selectivity, efficiency, easy work up procedure and more purity of product. MWI method reduce reaction time, allow control of temperature, pressure and increase in yield of product[14].Thus in continuation of our research we use silty soil to catalyze the reactions under MWI ,without solvent.

2. Experimental section:

2.1. General Remarks: All chemicals used in synthesis were of AR grade. Melting points of all synthesized compounds were taken in an open capillary and uncorrected. IR spectra were recorded on Perkin Elmer spectrophotometer with ATR technology. H^1NMR and CMR spectra were recorded on 500 MHz Bruker FT-NMR spectrometer using $CDCl_3$ as a solvent.

2.2. General Procedure for the synthesis of 3, 4-dihydropyrimidinones:

Synthesis of 3, 4-dihydropyrimidinones were done using a mixture of aromatic aldehyde (1.0mmol), EAA (1.0mmol) and urea/thiourea (1.5mmol) and silt (20 wt %) taken in round bottom flask and kept in MW at 180W for required time (Table 4). The progress of reaction was monitored by thin layer chromatography using ethyl acetate: hexane solvent system. On completion of reaction, the reaction mass was filtered and concentrated. Isolation of catalyst and purification of product was done by recrystallisation using ethanol (Scheme1).



Scheme1. Synthesis of 3, 4-dihydropyrimidinones

3. Result and Discussion:

3.1 Catalyst- Silt: The silty soil collected from bed of Godavari River, Kopargaon, A.Nagar, India was utilized for catalyzing the reactions. The silt is naturally available granular brown colour material having particle size (0.05-0.002mm) between clay and sand, it may occur as soil [15] .Chemical composition of silt is quartz and feldspar. The diameter of silt used is 50 µm.

3.2. Optimization of reaction conditions:

Optimization of reaction conditions were done on model reaction of benzaldehyde(1mmol), EAA(1mmol) and urea(1.5mmol), with silt catalyst under microwave irradiation.

3.2.1 Effect of catalyst on model reaction:

Influence of catalyst concentration on model reaction was studied. Catalyst concentration was varied from 10 wt% to 30 wt%. Initially reaction was carried out with 10 wt% catalyst, more time required for completion of reaction and gave fewer yields (Entry1). When catalyst concentration was increased to 20 wt% it leads to considerable decrease in reaction time and increase in yield of product (Entry2). Then reaction was performed with 30 wt% catalyst, the reaction time and product yield almost remain constant (Entry3). Thus for this reaction optimum concentration of catalyst was considered 20 wt%. The results are summarized in Table 1.

Table1: Effect of catalyst concentration on model reaction

Entry	Catalyst amount (Wt %)	Time in minutes	Yield %
1	10	15	80
2	20	7	97
3	30	7	97

3.2.2 Effect of MWI powers on model reaction:

The influence of microwave power settings such as 100W, 180W, 360W on model reaction was studied. It was found that irradiation at lower power required more time and at high power leads to lower yield. It reveals that irradiation at 180W gives better result Table2 (entry2).

Table 2: Effect of MWI powers for synthesis of 3, 4 dihydropyrimidin-2-ones

Entry	Power(W)	Time(minutes)	Yield%

1	100	15	80
2	180	7	97
3	360	7	82

The generability of this method was studied by performing the reaction of several substituted aromatic aldehyde , EAA and Urea/thiourea using silt as a catalyst under MWI without solvent. The results are summarized in Table 3

Table 3.Synthesis of 3,4 Dihydropyrimidin-2-(1H)-ones catalyzed by silt under MWI at 180W

Entry	Aldehyde	Urea/ Thiourea	β ketoester	Reaction time (minutes)	Yield (%)	M.P^{0}C	
						Found	Literature
4a	Benzaldehyde	Urea	EAA	6	97	202	200-202
4b	Benzaldehyde	Thiourea	EAA	6	98	203	202-204
4c	4-methoxy benzaldehyde	Urea	EAA	4	92	202	201-203
4d	4-methoxy benzaldehyde	Thiourea	EAA	4	94	154	150-152
4e	4-methyl benzaldehyde	Urea	EAA	5	86	215	215-216
4f	4-methyl benzaldehyde	Thiourea	EAA	5	86	214	214-215
4g	4-hydroxy benzaldehyde	Urea	EAA	5	90	236	237-238
4h	4-hydroxy benzaldehyde	Thiourea	EAA	5	92	202	202-203
4i	4-chlorobenzaldehyde	Urea	EAA	6	96	215	215-216
4j	4-chlorobenzaldehyde	Thiourea	EAA	6	97	207	208-210

3.2.3. Spectral Data:

4a: 5-Ethoxy carbonyl-6-methyl-4- phenyl-3, 4 – dihydropyrimidin-2(1H)-one

M.P. 202^{0}C, IR (cm^{-1}): 3239 and 3069 (-N-H str.), 1697 and 1636 (C=O str.), 755,698. ^{1}HNMR (500MHz, $CDCl_3$): 7.99 (s, 1H, NH), 7.32(s, 1H, NH), 7.31-7.26(m, 5H, ArH), 5.69 (s, 1H, CH), 4.08(q, 2H, O CH_2 CH_3, J=5Hz), 2.53(s, 3H, CH_3), 1.16(t, 3H, O CH_2 CH_3, J=5Hz), CMR(500MHz, $CDCl_3$): 165.63, 153.19, 146.23, 143.69, 128.73, 127.99, 126.62, 101.41, 60.06, 55.78, 18.73, 14.15.

4b: 5-Ethoxy carbonyl-6-methyl-4- phenyl-3, 4 – dihydropyrimidin-2(1H)-thione

M.P. 203^{0}C, IR (cm^{-1}): 3236 and 3114 (-N-H str.), 1697 (C=O str.), 1640 (C=S str.), 697, 661, ^{1}HNMR (500MHz, $CDCl_3$): 7.91 (s, 1H, NH), 7.30(s, 1H, NH), 7.29-7.23(m, 5H, ArH), 5.38 (s, 1H, CH), 4.05(q, 2H, O CH_2 CH_3, J=5Hz), 2.32(s, 3H, CH_3), 1.15(t, 3H, O CH_2 CH_3, J=5Hz), CMR(500MHz, $CDCl_3$): 165.63, 153.19, 146.23, 143.69, 128.73, 127.99, 126.62, 101.41, 60.06, 55.78, 18.73, 14.15.

Conclusion:

The most important advantage of this method is use of liberally available, economical and competent silt catalyst. It works without solvent under microwave irradiation in short time. This implicates fruitful addition to the nonconventional methods for the synthesis of 3, 4-dihydropyrimidinones.

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