A Novel Method for Synthesis of 1,4-Dihydropyridines Using Robust Laterite Catalyst under Ultrasonic Irradiation

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An efficient method for the synthesis of 1,4-dihydropyridine derivatives from various aryl or heteroaryl aldehydes, β -ketoester and ammonium acetate in presence of laterite catalyst in ethanol under ultrasonication is reported. Catalyst study done with wet chemical analysis, FT-IR, XRD, SEM and EDS techniques. The catalyst can be recovered and reused without noticeable loss of activity even after five cycles.

Keywords: Laterite, Wet chemical analysis, Ultrasonication, Heterogeneous catalysis.

INTRODUCTION

1,4-Dihydropyridine (DHP) belongs to the class of nitrogen containing heterocycles and exhibits significant biological activities. Out of five regioisomers only 1,2-dihydropyridine and 1,4-dihydropyridine have gained significant attention because of their utility in the synthesis of various natural products [1]. 1,4-Dihydropyridine derivatives have been used as potential drug in the form of nifedipine, amlodipine, isradipine, feldopine, nicardipine for the treatment of hypertension [2,3]. 1,4-Dihydropyridines also act as antidepressive, hypnotic, antitubercular [4] and anticancer agent [5,6].

1,4-Dihydropyridines normally synthesized by Hantzsch method. 1,4-Dihydropyridine-3,5-dicarboxylates are called Hantzsch dihydropyridines or Hantzsch esters. It involves condensation of aryl aldehydes, β -ketoester and ammonium acetate or ammonia in presence of acetic acid or refluxing in alcohol [7,8]. This needs longer reaction time and gave low to reasonable yield of product [2,9]. Literature reveals that till today various attempts have been made to improve the Hantzsch synthesis using alternative catalyst and greener protocols [10].

These methods involves use of microwave [11,12], $\text{Cu}(\text{OTf})_2$ [13], hydrotalcites [14], $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ [2], silica/sulphuric acid [15], $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ [16], $\text{Y}(\text{OTf})_3$ [17], nickel nanoparticles [18], silica gel-supported polyphosphoric acid (PPA- SiO_2) [19], L-proline [20], ionic liquids [21], $([\text{BPy}][\text{BF}_4])$ [22], alumi-

nium phosphate [23], diphenyl ammonium triflate [24], nano crystalline solid acid catalyst [25], melamine trisulfonic acid [26], visible light [27], eutectic solvent [28], perchloric acid resting on magnetic Fe_3O_4 nano-particles [29], graphene oxide nanoparticles [30], $\text{CsCl}_3 \cdot 7\text{H}_2\text{O}$ [31], ceric ammonium nitrate [32], $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ [33], $[\text{Tb}(\text{mim})]\text{Cl}_2/\text{AlCl}_3$ [34], benzyl-triphenylphosphonium chloride (BTTPC) [35], TiCl_4 [1], ultrasound irradiation [36], functionalize multi-walled carbon nanotube (MWCNTs) [37], etc. The most part of accessible methods of 1,4-dihydropyridines synthesis bear with drawbacks such as less yield, inconsiderate reaction conditions, expensive catalyst and long reaction time.

Hence, in context of green chemistry to develop novel catalytic scheme in an environmentally compassionate fashion is the real challenge to organic chemists. Therefore, we wish to report the synthesis of 1,4-dihydropyridines catalyzed by laterite clay under ultrasound irradiation. Laterite is abundantly available in nature and contains significant amount of SiO_2 , Fe_2O_3 and Al_2O_3 , etc. It showed application as an adsorbent in the removal of heavy metal ions from waste water [38]. Recently, iron rich laterite has been reported as heterogeneous catalyst in the photo fenton process [39].

EXPERIMENTAL

All the chemicals used without further purification and were of AR grade. Ultrasonication was done in sonicator with a

frequency of 25 KHz. Synthesized products were characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy data and melting points. Perkin Elmer spectrometer with ATR technology was used to record IR spectra. ^1H NMR and ^{13}C NMR spectra were recorded on 500 MHz Bruker FT NMR spectrometer using CDCl_3 solvent. Melting points were determined by an open capillary method and were uncorrected.

Catalyst preparation: In order to prepare catalyst the collected natural laterite sample was milled. It was then sieved through various mesh sizes to remove coarser particles and to get the particles with the average diameter 50 μm . The catalyst was then rinsed with distilled water. It was then dried and calcined at 300 $^\circ\text{C}$ for 3 h. The screened catalyst was stored in polythene for further application. Chemical composition of collected laterite was calculated by wet chemical analysis method reported in Table-1.

TABLE-1
LATERITE COMPOSITION BY WET CHEMICAL ANALYSIS

Constituent	Laterite (%)
SiO_2	47.17
Al_2O_3	39.20
Fe	11.95
Mg	0.33

Synthesis of 1,4-dihydropyridines: In a 50 mL round bottom flask aromatic/heteroaromatic aldehyde (1 mmol), ethyl acetoacetate (2 mmol), ammonium acetate (1.5 mmol), in ethanol (5 mL), catalyst (20 wt % with respect to aldehyde) was added and the solution was sonicated for appropriate time. Advancement of reaction was observed by TLC. After completion of reaction the mixture was poured into cold water. Solid product was obtained by filtration and then purified by recrystallization (**Scheme-I**). The catalyst was recovered during recrystallization and reused without appreciable loss of activity up to six cycles. The elemental analysis of the synthesized compounds are shown in Table-2.

Scheme-I: Synthesis of 1,4-DHPs using laterite catalyst

RESULTS AND DISCUSSION

Catalyst has been characterized using XRD, FTIR, SEM and EDS techniques.

X-ray diffraction pattern analysis: This study was done in order to determine various minerals and inorganic phases present in laterite. X-ray diffraction study was carried out on Philips, Holland X-ray diffractometer. Fig. 1 represents XRD peaks of laterite sample. By correlating the results with JCPDS, laterite consists of SiO_2 , Al_2O_3 , Fe_2O_3 , $\text{FeO}(\text{OH})$ and FeO . The diffraction peaks in this pattern at 2θ values 19, 20.76, 25.04, 29.46, 35.16, 49, 53.81, 66.67 are associated with SiO_2 and matches with literature values [39-41]. The diffraction peaks at 2θ 31°, 33°, 62.69°, 64.23°, 66° represents Al_2O_3 and matches with (JCPDS100425) [38,42,43]. The peaks at 2θ 24.25°, 32°, 33.02°, 67° are due to presence of hematite phase (Fe_2O_3) [38]. The diffraction peaks at 2θ 21°, 26° and at 2θ 36°, 42°, 61° are related to $\text{FeO}(\text{OH})$ and FeO , respectively [38].

Fig. 1. XRD pattern of catalyst-laterite

Infrared spectroscopy (FT-IR): FT-IR study of catalyst was done to confirm presence of silica, iron and aluminum. The distinct band at 3694.7 and 3621 cm^{-1} indicate existence of isolated OH group of Si, Al. The band at 461.93 cm^{-1} indicates O-Si-O bending mode whereas band at 1029.51, 911.47 and 793.85 cm^{-1} signify occurrence of Si-O-Fe, Al-OH, Fe-OH vibrations. The bands at 538.87, 469.43 and 450.09 cm^{-1} are due to Fe-O bond stretching.

SEM and EDS: Scanning electron microscopy (SEM) and energy dispersive spectroscopy were performed in a JEOL

TABLE-2
ELEMENTAL ANALYSIS OF SYNTHESIZED COMPOUNDS

Entry	m.f.	Elemental analysis (%): Calcd. (Found)			
		C	H	N	X
1	$\text{C}_{19}\text{H}_{21}\text{NO}_4\text{Cl}$	62.89 (62.90)	5.79 (5.81)	3.86 (3.88)	9.79 (9.81)
2	$\text{C}_{20}\text{H}_{24}\text{NO}_5$	67.04 (67.08)	6.70 (6.72)	3.91 (3.93)	—
3	$\text{C}_{19}\text{H}_{25}\text{NO}_5$	66.28 (66.30)	6.39 (6.41)	4.07 (4.08)	—
4	$\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_6$	61.13 (61.11)	5.63 (5.64)	7.51 (7.50)	—
5	$\text{C}_{19}\text{H}_{22}\text{NO}_4$	69.51 (69.49)	6.71 (6.71)	4.27 (4.26)	—
6	$\text{C}_{19}\text{H}_{21}\text{NO}_4\text{Br}$	55.03 (55.07)	5.16 (5.16)	3.44 (3.45)	19.64 (19.66)
7	$\text{C}_{26}\text{H}_{26}\text{N}_3\text{O}_4\text{S}$	65.55 (65.58)	5.46 (5.47)	8.82 (8.83)	6.72 (6.74)
8	$\text{C}_{28}\text{H}_{27}\text{N}_3\text{O}_4\text{Cl}$	66.60 (66.62)	5.35 (5.38)	8.32 (8.34)	7.04 (7.06)
9	$\text{C}_{29}\text{H}_{30}\text{N}_3\text{O}_4$	71.90 (71.93)	6.19 (6.21)	8.68 (8.70)	—

6360A scanning electron microscope working at 20 kV, with an energy dispersive X-ray spectrometer.

The SEM photographs of the laterite particles are shown in Fig. 2. The prepared particles were highly agglomerated with homogeneous distribution. Formation of agglomerated particles may arise due to calcinations. The surface appears like a “platelet” type of morphology, as shown in Fig. 2. The particles were of irregular shapes and different sizes.

All these characterization data clearly demonstrate morphology and composition of catalyst [38,44].

Optimization of reaction conditions: Optimization of reaction conditions with respect to catalyst and solvent amount was investigated on selected model reaction of 4-chloro benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol) and NH_4OAc (1.5 mmol). All reactions for optimization were performed under ultrasonication.

Optimization of catalyst amount: In the beginning reaction was performed without catalyst in presence of ethanol and only trace amount of product was obtained after 55 min (Table-3, entry1). The same reaction was done with 10 wt % of catalyst, 69 % of product obtained after 40 min (Table-3, entry 2). As the catalyst amount increased from 10 to 20 wt % the time of reaction was reduced from 40 to 30 min and yield of product increased from 69 to 92 %. Further increase in the catalyst amount to 30 wt % no increase in yield of product

Entry	Catalyst (wt %)	Time (min)	Yield (%) ^a
1	–	55	Trace
2	10	40	69
3	20	30	92
4	30	30	85

^aIsolated yields

observed (Table-3, entry 4). From these observations 20 wt % of catalyst can be considered as optimized amount in EtOH as solvent.

Effect of solvent: We examined solvent effect on yield of product and time of reaction using several solvents. Initially reaction was performed without solvent and yields only 25 % of product. Later on the same reaction was performed in presence of water, ethanol and then in toluene. It was found that comparatively ethanol is an efficient solvent which yields 92 % product in short reaction time (Table-4).

Synthesis of 1,4-dihydropyridines using laterite under ultrasonication: After the optimization of reaction conditions, we investigated the synthesis of 1,4-dihydropyridines using aryl/heteroaryl aldehyde (1 mmol), ethyl acetoacetate (2 mmol) and ammonium acetate (1.5 mmol) with 20 wt % catalyst in EtOH solvent under ultrasonic irradiation. From the results

Fig. 2. SEM and EDS images of catalyst laterite

TABLE-4
EFFECT OF SOLVENT ON PRODUCT
YIELD AND REACTION TIME^a

Entry	Solvent	Time (min)	Yield (%) ^b
1	—	90	25
2	Water	45	80
3	Ethanol	30	92
4	Toluene	55	65

^aModel reaction in the presence of 20 wt % catalyst; ^bIsolated yields.

depicted in Table-5, products were obtained in good to excellent yields. It is also observed that the conversions including aldehydes with electron donating group complete in short reaction time than aldehydes with electron donating group.

Diethyl 1,4-dihydro-2,6-dimethyl-4-(1-phenyl-3-thio-phen-2-yl)pyridine-3,5-dicarboxylate (entry 7): m.p.: 212 °C; FTIR (cm⁻¹): 3319, 1692, 1635, 1488, 1299, 1211, 1096, 961, 827, 757, 694; ¹H NMR (500 MHz, CDCl₃, δ ppm): 1.06 (bs, 6H, -CH₃), 2.21 (s, 6H, -CH₃), 2.38 (s, 3H, Ar-CH₃), 3.76 (bs, 2H, -CH₂-), 4.01 (bs, 2H, -CH₂-), 5.28 (s, 1H, -CH-), 5.6 (s, 1H, -NH), 7.20-7.21 (m, 5H, Ar-H), 7.65-7.71 (m, 5H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): 167.62, 151.21, 143.35, 140.13, 137.01, 131.92, 129.20, 128.80, 128.65, 128.55, 127.04, 125.89, 118.78, 104.44, 59.70, 29.65, 21.30, 19.47, 14.28.

Diethyl 4-(3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)-1,4-dihydro-2,6-dimethyl pyridine-3,5-dicarboxylate

TABLE-5
SYNTHESIS OF 1,4-DIHYDROPYRIDINES USING LATERITE UNDER ULTRASONICATION

Entry	Aldehyde	Product	Time (min)	Yield ^a (%)	m.p. (°C)
1			30	92	145
2			40	85	154
3			40	82	229
4			35	92	130

5			35	87	155
6			30	88	150
7			35	89	212
8			30	90	166
9			35	87	180

Reaction condition: Aryl/hetero aryl aldehyde (1.0 mmol), EAA (2.0 mmol), ammonium acetate (1.5 mmol) and catalyst (20 wt %) in ethanol (5 mL, ^aIsolated yields.

(entry 8): m.p.: 166 °C; FTIR (cm⁻¹): 3312, 3092, 1696, 1632, 1488, 1299, 1211, 1096, 962, 841, 758, 738, 694; ¹H NMR (500 MHz, CDCl₃, δ ppm): 1.06-1.09 (t, 6H, -CH₃), 2.26 (s, 6H, -CH₃), 3.78-3.81 (m, 2H, -CH₂), 4.01-4.04 (m, 2H, -CH₂), 5.26 (s, 1H, -CH-), 5.51 (s, 1H, -NH), 7.23-7.26 (t, 1H, Ar-H), 7.39-7.42 (t, 4H, Ar-H), 7.65-7.66 (d, 2H, Ar-H), 7.73 (s, 1H, Ar-H), 7.84-7.86 (d, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): 167.47, 149.82, 143.29, 139.99, 130.40, 130.24, 129.27, 128.86, 128.07, 127.37, 126.18, 118.87, 104.56, 59.81, 29.68, 19.63, 14.31.

Diethyl 1,4-dihydro-2,6-dimethyl-4-(1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl)pyridine-3,5-dicarboxylate (entry 9): m.p.: 180 °C; FTIR (cm⁻¹): 3312, 1696, 1648, 1486, 1368, 1304, 1204, 1095, 961, 878, 822, 82, 754, 720, 686; ¹H NMR (500 MHz, CDCl₃, δ ppm): 1.22-1.25 (t, 6H, -CH₃), 2.08 (s, 6H, -CH₃), 4.09-4.11 (m, 4H, -CH₂), 5.8 (s, 1H, -CH-), 5.14 (s, 1H, -NH), 7.19-7.21 (d, 1H, Ar-H), 7.24-7.27 (t, 2H, Ar-H), 7.40-7.43 (t, 2H, Ar-H), 7.48-7.49 (d, 1H, Ar-H), 7.65-7.66 (d, 2H, Ar-H), 7.84 (s, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): 167.30, 157.04, 155.06, 143.64, 139.89, 134.39, 131.07, 130.24, 129.36, 30.43, 19.42, 14.41

Recycling study of laterite catalyst: The recycling of heterogeneous catalyst was studied by separation of catalyst during recrystallization. It was washed with distilled water, dried and calcined. The recovered catalyst was examined under optimized reaction conditions. From the recycling experiments, the catalyst can be reused without appreciable loss of activity even after five cycles (Fig. 3).

Fig. 3. Recycling of catalyst

Conclusion

We have developed nonconventional, greener synthetic protocol for synthesis of 1,4-dihydropyridines using robust laterite catalyst under ultrasonic irradiation at room temperature. Laterite catalyst was prepared by simple procedure and it could be recycled for at least six cycles without appreciable loss of reactivity. The significant features of this protocol are use of naturally available, inexpensive, reusable, efficient catalyst, sonication, short reaction time and good to excellent yields of product.

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CONFLICT OF INTEREST

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

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