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Microwave Induced Solvent-free and Catalyst-free Synthesis of 1,4-Dihydropyridine Derivatives using Ammonium Bicarbonate

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ABSTRACT
One-pot synthesis of 1,4-dihydropyridine derivatives by reacting an aldehyde, a β-ketoester and ammonium bicarbonate in the presence of microwaves without a catalyst under solvent-free conditions is described. Using this green method, 1,4-dihydropyridine derivatives can be obtained in good yields in short reaction times.

Keywords*: Hantzsch reaction, dihydropyridines, ammonium bicarbonate, microwave, solvent-free*

1. INTRODUCTION

1,4-Dihydropyridines (1,4-DHPs) and their derivatives have many applications in medicine due to their pharmacological properties. 1,4-DHPs have been explored for their calcium channel blocking activity [1,2] and the compounds are used as vasodilator, bronchodilator, antiatherosclerotic, antitumor, antidiabetic, geroprotective, hepatoprotective [3-6] and radioprotective agents [7]. Conventionally, 1,4-DHPs are synthesized by the Hantzsch method [8,9], involving cyclocondensation of an aldehyde, β-ketoester and ammonia in acetic acid or in refluxing ethanol [10,11]. These reactions are generally carried out in organic solvents like acetic acid and methanol. Scandium(III) triflate [12], $NaHSO_4$-SiO_2 [13], molecular iodine [14,15], ionic liquid [16], microwaves [17,18], iodotrimethylsilane [19] and $Ce(SO_4)_2$-SiO_2 [20] have been used to synthesize 1,4-DHPs. Most of these methods require cumbersome aqueous work-up to isolate the products. Recently, Tamaddon and coworkers [21] have reported Biginelli and Hantzsch reactions using ammonium carbonate in water. However, many methods reported in the literature have been associated with several short comings such as long reaction times, expensive reagents, harsh conditions, low product yields, occurrence of several side products and difficulty in recovery and reusability of the catalysts. Due to these problems, development of an efficient and versatile method for the preparation of Hantzsch 1,4-DHPs is an important aspect and which is an active research area and there is a scope for further improvement towards green reaction conditions with improved yields.

In this paper, we report solvent-free and catalyst-free microwave induced Hantzsch reaction of aldehydes, β-ketoester with ammonium bicarbonate (NH_4HCO_3) as the source of nitrogen. 1,4-DHPs were prepared by the three component reaction of aldehydes, β-ketoesters and ammonium bicarbonate under microwave irradiation conditions (Scheme 1). We have developed a method for the preparation of 1,4-DHPs that involves use of cost effective and less toxic reactants and avoids use of solvent and catalyst. Accordingly, ammonium bicarbonate, used as a reactant in this protocol, is cheaper, less toxic and acts as the source of nitrogen and decomposes to carbon dioxide, ammonia and water vapour on heating.

2. EXPERIMENTAL

2.1 Materials and methods

The reagents were purchased from Sd-fine, Loba, AVRA, and SRL, India. Montmorillonite K10 was purchased from Sigma-Aldrich Company and montmorillonite (Kunipia-F) was purchased from Kunimine Industrial Company, Japan. Aldehydes were purified by distillation and all other reagents were used as-received from commercial sources without further purification. The catalysts were characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), BET analysis, and thermo gravimetric analysis (TGA). The IR spectra were recorded in the range of 450-4000 cm^{-1} on a Perkin-Elmer FTIR spectrometer using KBr pellet. High-resolution mass spectra (HRMS), electron spray ionization (ESI) mode, were obtained on Micro hybrid quadrupole time of flight (Q-Tof)-mass spectrometer. The ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 spectrometer in the indicated solvent.

2.2. Procedures for the preparation of catalysts

2.2.1. 40 wt% $ZrOCl_2$ supported on Montmorillonite K10 (40 wt% $ZrOCl_2$/mont K10)

5 g of mont K10 was dispersed in a 20 ml methanol solution with 2 g of $ZrOCl_2$. $8H_2O$, and stirred for 6 h at room temperature. Methanol was

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evaporated in vacuum to dryness and the catalyst was dried at 110 ˚C for 4 h. BET surface area: 158 m^2/g.

2.2.2. Al^{3+}-exchanged montmorillonite (Al^{3+}-mont)

To 200 ml of a stirred aqueous solution (0.5 M) of $AlCl_3$, 5 g of mont (Kunipia-F) (solution/mont ratio of 40 ml/g) are added. Exchange was then carried out at room temperature for 24 h with constant stirring. The resulting slurry was repeatedly centrifuged in fresh deionised water until free of Cl^- ions [as tested by $AgNO_3$]. The solids obtained were dried overnight at 120 ˚C and subsequently ground to a fine powder. BET surface area: 7 m^2/g.

2.2. $ZnCl_2$ supported on montmorillonite K10 ($ZnCl_2$/mont K10)

5g of mont K10 was mixed with a solution of $ZnCl_2$ (1.3625 g) in methanol (20 ml). The resulting mixture was stirred for 2 h. After removal of methanol under reduced pressure, the solid powder was dried at 120 ˚C for 4 h. BET surface area: 77 m^2/g.

2.3. General procedure for the preparation of 1,4-dihydropyridines

A mixture of aldehyde (2 mmol), ethyl acetoacetate or methyl acetoacetate (4 mmol) and ammonium bicarbonate (3 mmol) was taken in a 10 ml thick-walled glass reaction tube equipped with a magnetic stirrer (Scheme I). The glass reaction tube was then placed inside a CEM Discover microwave reactor, operated at 120 ˚C, power 150 W for 25 or 20 min. After the reaction time, the reaction mixture was dissolved in ethyl acetate, washed with water and concentrated in vacuum. The crude was purified by recrystallisation from ethanol to obtain 1,4–DHPs in 38–90% yields. The products were identified by their IR, HRMS, ^{1}H and ^{13}C NMR spectra.

2.4. Spectral data for selected compounds

Diethyl 2,6-dimethyl-4-(4-hydroxy-3-methoxy phenyl)-1, 4-dihydropyridine-3,5-dicarboxylate, 1g: IR (KBr) υ: 3348, 3094, 2946, 1673, 1647, 1513, 1486, 1379, 1218, 1030 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.42 (t, 6H), 3.62 (s, 6H), 3.94 (s, 3H), 4.26 (m, 4H), 5.01 (s, 1H), 6.85–6.95 (m, 3H), 8.90 (s, 1H), 8.97 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 400 MHz): δ 14.2, 18.1, 38.1, 55.4, 58.9, 102.1, 111.8, 115.1, 119.5, 139.5, 144.7, 144.8, 146.7, 167.1 ppm; HRMS (ESI) *m/z*: calcd for $C_{20}H_{26}NO_6$ [M^++1] 376.1760, found 376.1762.

Dimethyl 2,6-dimethyl-4-(4-hydroxyphenyl)-1,4-dihydropyridine-3,5-dicarboxylate, 2f: IR (KBr) υ: 3336, 2955, 1676, 1655, 1497, 1444, 1349, 1233, 1127, 1021 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 3.69 (s, 6H), 3.79 (s, 6H), 5.02 (s, 1H), 6.83–7.14 (m, 4H), 9.07 (s, 1H), 9.41 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 400 MHz): δ 18.1, 37.4, 50.5, 101.9, 114.6, 127.8, 138.4, 145.1, 155.4, 167.5 ppm; HRMS (ESI) *m/z*: calcd for $C_{17}H_{19}NO_5$ [M^++Na] 340.1161, found 340.1157.

Dimethyl 2,6-dimethyl-4-(2-furyl)-1,4-dihydro pyridine-3, 5-dicarboxylate, 2g: IR (KBr) υ: 3346, 3099, 2949, 1695, 1652, 1491, 1427, 1352, 1213, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.38 (s, 6H), 3.75 (s, 6H), 5.23 (s, 1H), 5.93 (br s, 1H), 5.96–6.25 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 400 MHz): δ 19.6, 33.3, 51.3, 100.5, 104.4, 110.1, 141.1, 145.6, 158.5, 168.0 ppm; HRMS (ESI) *m/z*: calcd for $C_{15}H_{18}NO_5$ [M^++1] 292.1185, found 292.1199.

Dimethyl 2,6-dimethyl-4-(4-hydroxy-3-methoxy phenyl)-1,4-dihydropyridine-3,5-dicarboxylate, 2h: IR (KBr) υ: 3351, 3083, 2955, 1690, 1658, 1486, 1433, 1304, 1218, 1025 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 3.63 (s, 6H), 3.80 (s, 6H), 3.93 (s, 3H), 5.03 (s, 1H), 6.84–6.93 (m, 3H), 8.92 (s, 1H), 9.06 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 400 MHz): δ 18.1, 37.8, 50.6, 55.4, 101.8, 111.4, 115.2, 119.1, 139.1, 144.8, 145.2, 146.9, 167.6 ppm; HRMS (ESI) *m/z*: calcd for $C_{18}H_{22}NO_6$ [M^++1] 348.1447, found 348.1437.

Dimethyl 2,6-dimethyl-4-isopropyl-1,4-dihydropyridine-3,5-dicarboxylate, 2i: IR (KBr) υ: 3339, 3096, 2959, 1711, 1648, 1489, 1331, 1215, 1109, 1014 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.72 (d, 6H), 1.23 (m, 1H), 2.29 (s, 6H), 3.69 (s, 6H), 3.87 (d, 1H), 5.71 (br s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 400 MHz): δ 18.3, 19.4, 29.8, 35.5, 38.8, 51.0, 101.5, 145.0, 169.3 ppm; HRMS (ESI) *m/z*: calcd for $C_{14}H_{22}NO_4$ [M^++1] 268.1549, found 268.1558.

Dimethyl 2,6-dimethyl-4-ethyl-1,4-dihydro pyridine-3,5-dicarboxylate, 2j: IR (KBr) υ: 3352, 3099, 2951, 2877, 1703, 1650, 1481, 1333, 1217, 1016 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.72 (t, 3H), 1.34 (m, 2H), 2.28 (s, 6H), 3.70 (s, 6H), 3.88 (t, 1H), 5.59 (br s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 400 MHz): δ 9.1, 19.5, 29.3, 34.0, 51.0, 102.5, 145.3, 168.7 ppm; HRMS (ESI) *m/z*: calcd for $C_{13}H_{20}NO_4$ [M^++1] 254.1392, found 254.1386.

3. RESULTS AND DISCUSSION

Firstly, the Hantzsch reaction of benzaldehyde, ethyl acetoacetate with different ammonium salts has been investigated under solvent-free microwave conditions. The percentage yields of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate obtained in different reactions carried out using different ammonium salts are summarized in Table 1. No product was obtained in the reactions with ammonium chloride and ammonium sulfate due to their high

melting/decomposition temperatures. When ammonium carbonate and ammonium bicarbonate were reacted with benzaldehyde and ethyl acetoacetate, 73% and 76% of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarb--oxylate (yellow colour) was obtained respectively. The reaction of benzaldehyde, ethyl acetoacetate and ammonium acetate gave 78% of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (pale orange). Therefore, for further studies ammonium bicarbonate, which has lower decomposition temperature, was chosen as the source of nitrogen.

Table 1. Preparation of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5- dicarboxylate using ammonium salts

Entry	Ammonium salt	Yield (%)
1	Ammonium chloride	No reaction
2	Ammonium sulfate	No reaction
3	Ammonium carbonate	73
4	Ammonium bicarbonate	76
5	Ammonium acetate	78

Reaction conditions: Molar ratio (benzaldehyde: ethyl acetoacetate: ammonium salt) = 1:2:1, time = 25 min, temperature = 120 ˚C, microwave power = 150 W.

The model reaction of benzaldehyde, ethyl acetoacetate and ammonium bicarbonate was optimized by investigating different parameters like reaction time and molar ratio of ammonium bicarbonate under solvent-free conditions.

3.1 Effect of time

The Hantzsch reaction has been studied at five different intervals of time. Table 2 shows the effect of reaction time on the diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate for--mation for the reaction of 2 mmol of benzaldehyde, 4 mmol of ethyl acetoacetate and 2 mmol of ammonium bicarbonate. The yield of the diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate increased with increase in reaction time from 05 min (57%) to 25 min (76%). Further increase in the reaction time beyond 25 min resulted in reduced yield of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate. This can be attributed to decomposition of unreacted reactants and product formed due to prolonged heating.

3.2 Effect of molar ratio

The reaction of benzaldehyde, ethyl acetoacetate and ammonium bicarbonate was carried out using equimolar ratio of benzaldehyde and ammonium bicarbonate, wherein the diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate yield was 76% (entry 1, Table 3). When the molar ratio of benzaldehyde to ammonium bicarbonate was increased from 1:1 to 1: 1.5, higher quantities of the diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate were formed (Table 3). This shows that the reaction equilibrium shifts towards the formation of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarb--oxylate when ammonium bicarbonate concentration was increased. However, the percentage yield of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate was reduced when the benzaldehyde to ammonium bicarbonate ratio was 1:2 after 25 min. Higher concentration of ammonium bicarbonate thus inhibited the diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate formation. Therefore, for further studies, the benzaldehyde to ammonium bicarbonate ratio of 1:1.5 was selected.

Table 2. Effect of reaction time on % yield of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate

Entry	Time (min)	Yield (%)
1	05	57
2	15	64
3	25	76
4	35	68
5	45	65

Reaction conditions: Molar ratio (benzaldehyde: ethyl acetoacetate: ammonium bicarbonate)= 1:2:1, temperature= 120 ˚C, microwave power= 150 W.

Table 3. Effect of molar ratio of ammonium bicarbonate on % yield of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate

Entry	Molar ratio (benzaldehyde: ethyl acetoacetate:ammonium bicarbonate)	Yield (%)
1	1:2:1	76
2	1:2:1.5	80
3	1:2:2	76

Reaction conditions: Microwave power= 150 W, temperature= 120 ˚C, time= 25 min.

3.3 Activity of different clay catalysts

Table 4 shows comparison of activity of a few clay catalysts for the synthesis of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate under solvent-free conditions. The Hantzsch reaction of benzaldehyde, ethyl acetoacetate and ammonium bicarbonate has also been tested on a few clay catalysts such as 40 wt% $ZrOCl_2$

supported on montmorillonite K10 (40 wt% $ZrOCl_2$/mont K10), Al^{3+}-exchanged montmorilloni--te (Al^{3+}-mont), and $ZnCl_2$ supported on montmor --illonite K10 ($ZnCl_2$/mont K10) under solvent-free conditions. It is clear from the results that the reaction performed at room temperature in the absence of solvent and catalyst required longer time than microwave assisted reaction (entries 1 & 4, Table 4). Further, there is no significant enhancement in the yield of the product for the reactions catalysed by Al^{3+}-mont and $ZnCl_2$/mont K10 as compared to catalyst-free reaction.

Table 4. Comparison of activity of some clay catalysts for the synthesis of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate

Entry	Catalyst	Time	Yield (%)
1	No catalyst	23 h	65[a]
2	40 wt% $ZrOCl_2$/mont K10 (150 mg)	06 h	52[a]
3	No catalyst	15 min	64
4	Al^{3+}-mont (100 mg)	15 min	69
5	$ZnCl_2$/mont K10 (100 mg)	20 min	72

Reaction conditions: Molar ratio (benzaldehyde: ethyl acetoacetate: ammonium bicarbonate)= 1:2:1, temperature= 120 ˚C, microwave power = 150 W, [a] *performed at room temperature.*

3.4 Synthesis of 1,4-dihydropyridine derivatives

To study scope and generality of the reaction, the optimized conditions were extended to the Hantzsch reaction of aryl, heteroaryl and aliphatic aldehydes with ethyl acetoacetate and 1.5 mmol of ammonium bicarbonate under 150 W microwave power for 25 min at 120 ˚C. Several 1,4-dihydropyridine derivatives have been synthesized in 47-90% yield and the results are summarized in Table 5. Similarly, the Hantzsch reaction of variety of aldehydes with methyl acetoacetate and 1.5 mmol of ammonium bicarbonate under 150 W microwave power for 20 min at 120 ˚C was studied to prepare different 1,4-dihydropyridine derivatives in 38-90% yield and the results are summarized in Table 6. Aromatic (bearing both electron-rich and electron-deficient substituents), heterocyclic (entry 8, Table 5 & entry 7, Table 6) and aliphatic aldehydes (entries 9 & 10, Table 5 & Table 6) underwent smooth transformation to the corresponding 1,4-dihydropyridines in satisfactory yields. However, reduced yields of the corresponding 1,4-dihydropyridines were observed in the reactions with aliphatic aldehydes. This may be attributed to their lower boiling points.

4. CONCLUSION

A convenient and efficient process for the synthesis of 1,4-DHPs through solvent-free and catalyst-free microwave induced three component coupling of aldehydes, ethyl acetoacetate or methyl acetoacetate and ammonium bicarbonate has been developed. The present method offers very attractive features such as reduced reaction times, higher yields and with no catalyst, when compared with any conventional method as well as with other catalysts, which will have wide scope in organic synthesis. The simple procedure combined with easy workup of the reaction mixture makes this method economic, benign and a waste-free chemical process for the synthesis of 1,4-DHPs of biological and medicinal importance.

Acknowledgments

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5. REFERENCES

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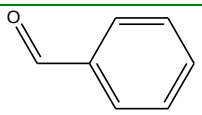
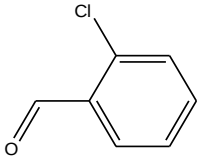
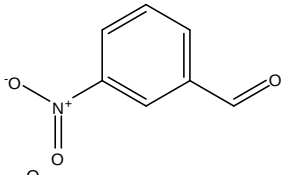
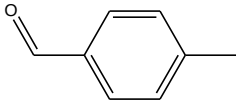
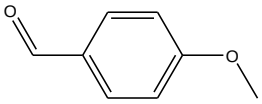
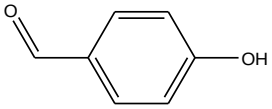
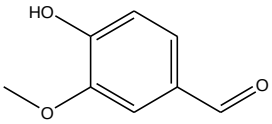
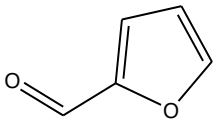
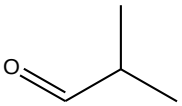
Table 5. Solvent and catalyst-free synthesis of 1,4-dihydropyridine derivatives

Entry	Aldehyde	Product	Yield (%)[a]
1		1a	80 [17]
2		1b	90 [16]
3		1c	82 [17]
4		1d	88 [19]
5		1e	67 [19]
6		1f	81 [19]
7		1g	69 [17]
8		1h	84 [13]
9		1i	47 [19]
10		1j	60 [21]

Reaction conditions: Molar ratio (aldehyde: ethyl acetoacetate: ammonium bicarbonate) = 1:2:1.5, temperature= 120 ˚C, time= 25 min, microwave power= 150 W, [a]isolated yield

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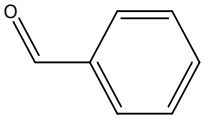
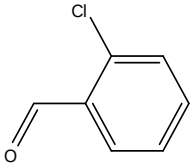
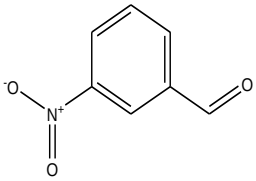
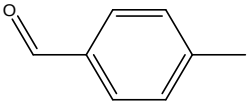
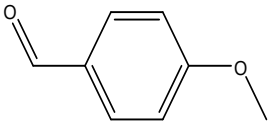
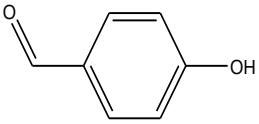
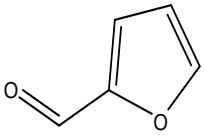
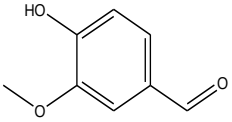
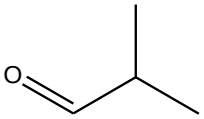
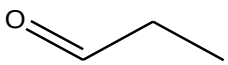
Table 6. Solvent and catalyst-free synthesis of 1,4-dihydropyridine derivatives

Entry	Aldehyde	Product	Yield (%)[a]
1		2a	90 [19]
2		2b	85 [17]
3		2c	89 [17]
4		2d	75 [17]
5		2e	68 [17]
6		2f	70
7		2g	87
8		2h	78
9		2i	38
10		2j	53

Reaction conditions: Molar ratio (aldehyde: methyl acetoacetate: ammonium bicarbonate)= 1:2:1.5, microwave power= 150 W, temperature= 120 ˚C, time= 20 min, [a] isolated yield.

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