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ORIGINAL ARTICLE

Ionic liquid [tbmim]Cl_2/$AlCl_3$ under ultrasonic irradiation towards synthesis of 1,4-DHP's

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Abstract One pot, three-component synthesis of 1,4-dihydropyridines using ionic liquid 3,3′-thionyl-*bis*-1,1′-methylimidazolium chloroaluminate ([tbmim]Cl_2/$AlCl_3$) was found to be efficient to afford good to excellent yields at room temperature under ultrasonic irradiation. This method has many advantages, which avoids the use of harmful catalysts, occurence of reactions at room temperature, high yields and methodological simplicity.

1. Introduction

It is well known that Hantzsch 1,4-dihydropyridines (1,4-DHP's) exhibit a wide range of biological properties (Mauzeral and Wertheimer, 1955), acting as potent vasodilators, antihypertensives, bronchodilators, heptaprotective, antitumor, antimutagenic, geroprotective and antidiabetic agents (Di Stilo et al., 1998). Moreover a number of DHP's acts as calcium antagonists (Janis and Triggle, 1983; Bocker and Guengerich, 1986; Gordeev et al., 1996) and they have been introduced for the treatment of congestive heart failure. In addition to this 1,4-DHP's exhibit several other medicinal applications like neuroprotectant (Klusa, 1995), platet anti-aggregator activity (Bretzel et al., 1993), as cerebral antiischemic agents in the treatment of Alzheimer's disease (Bretzel et al., 1992) and as a chemosensitizer in tumor therapy (Boer and Gekeler, 1995).

1,4-DHP's are generally synthesized using Hantzsch method (Hantzsch, 1882), which involves one pot cyclocondensation of aldehydes, dicarbonyls/β-ketoesters and ammonium acetate/ammonia/primary amine either in refluxing with acetic acid or alcohol leading to low yields with longer reaction time (Loev and Snader, 1965; Sausins and Duburs, 1988). Recently, a number of modified methods have been developed (Evdokimor et al., 2006). Other procedures comprise the use of microwaves (Khadikar et al., 1995), ionic liquids (Ji et al., 2004), high temperatures at reflux (Phillips, 1949), TMSCl–NaI (Sabitha et al., 2003), $InCl_3$ (Babu and Perumal, 2000), I_2 (Ko et al., 2005), SiO_2/$NaHSO_4$ (Adharvana and Syamasundar, 2005), SiO_2/$HClO_4$ (Maheswara et al., 2006), CAN (Ko and Yao, 2006), Na- and Cs-Norit carbons (Perozo-Rondon et al., 2006), tetrabutylammonium hydrogen sulfate (Tewari et al., 2004), fermenting Baker's yeast (Lee, 2005), organocatalysts (Kumar and Maurya, 2007) and metal triflates (Wang et al.,

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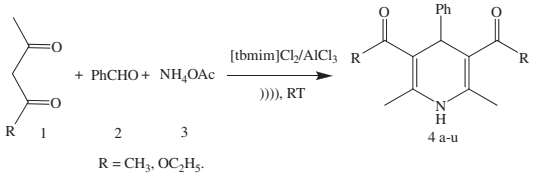

Scheme 1

Table 1 Optimization of reaction conditions for the synthesis of 1,4-DHP's.

Entry	Method	Catalyst $[tbmim]Cl_2/AlCl_3$	Time (min)	Yield (%)
1	Sonication	1 mmol	40	94
2	Sonication	0 mmol	40	70
3	Reflux	0 mmol	180	80
4	Reflux	0.5 mmol	90	89
5	Stirring	0.5 mmol	150	88
6	Sonication	0.5 mmol	40	94

Reaction conditions: benzaldehyde (10 mmol), ethylacetoacetate (20 mmol), ammonium acetate (10 mmol), ionic liquid.

2005). All the above methods are how ever associated with several draw backs, such as unsatisfactory yields, longer duration, difficulty in handling of reagents, toxic solvents, hence the development of an efficient synthesis of Hantzsch 1,4-dihydropyridines seemed to be of prime importance. In green synthesis ionic liquids play a major role. Initially ionic liquids are introduced as alternative green reaction media because of their unique chemical and physical properties of non-volatility, non-flammability, thermal stability, and controlled miscibility. But nowadays ionic liquids have proved to be useful beyond this, showing their importance in controlling reactions as catalysts (Jain et al., 2005).

In organic synthesis ultrasound irradiation has been considered as a clean and useful protocol, compared with the traditional methods. A large number of organic reactions can be carried out in higher yields, shorter reaction time or milder conditions in ultrasonic irradiation (Wilkes, 2002). In continuation of earlier interest on 1,4-DHP's (Rathore et al., 2009; Palakshi Reddy et al., 2009, 2010; Thenmozhi et al., 2009; Fun et al., 2009a,b,c) herein we report an efficient and simple procedure for the synthesis of 1,4-DHP derivatives at room temperature under ultrasonication using ionic liquid $[tbmim]Cl_2/AlCl_3$ as catalyst (see Scheme 1).

2. Experimental

The melting points were recorded in open capillaries and corrected with benzoic acid. Thin-layer chromatography (TLC) was carried out to monitor the course of the reaction and purity of the product. IR spectra recorded in an Avatar-330 FTIR spectrophotometer (Thermo Nicolet), and only noteworthy absorption levels (reciprocal centimeters) were listed. ^1H NMR spectra were recorded on Bruker AMX 400-MHz or 300-MHz spectrometer using $CDCl_3$ or DMSO as solvent and TMS as internal standard. Mass spectra were recorded on a LC-MS. Ionic liquid $[tbmim]Cl_2/AlCl_3$ was prepared according to the literature (Ling et al., 2006).

2.1. General procedure for the synthesis of 1,4-DHP's

A mixture of aromatic aldehyde **1** (1 mmol), ethylacecoacetate/acetylacetone **2** (2 mmol) and ammonium acetate **3** (1 mmol), was taken in a round bottomed flask mixed with $[tbmim]Cl_2/AlCl_3$ (0.5 mmol), which was irradiated under ultrasonic waves at room temperature for an appropriate time as indicated in Table 2. The progress of the reaction was monitored by TLC. The reaction mixture was then extracted with chloroform (10 mL) leaving behind $[tbmim]Cl_2/AlCl_3$. The organic

Table 2 Synthesis of various substituted 1,4-dihydropyridines using ionic liquid.

S. No	Ph	R	US (min)	Yield (%)	M.P (°C)
4a	C_6H_5	OC_2H_5	40	94	158–160
4b	$4\text{-}ClC_6H_4$	OC_2H_5	45	95	145–146
4c	$4\text{-}OCH_3C_6H_4$	OC_2H_5	50	93	153–155
4d	$3\text{-}NO_2C_6H_4$	OC_2H_5	30	96	165–167
4e	4-Pyridyl	OC_2H_5	45	91	185–187
4f	3-Pyridyl	OC_2H_5	50	90	188–190
4g	$4\text{-}BrC_6H_4$	OC_2H_5	45	93	148–150
4h	2-Thienyl	OC_2H_5	50	90	172–173
4i	$4\text{-}CH_3C_6H_4$	OC_2H_5	60	88	142–145
4j	$4\text{-}HOC_6H_4$	OC_2H_5	60	90	227–229
4k	$3\text{-}HOC_6H_4$	OC_2H_5	55	87	172–175
4l	$3\text{-}NO_2C_6H_4$	CH_3	35	94	180–182
4m	$2\text{-}NO_2C_6H_4$	CH_3	35	93	195–197
4n	2-Furyl	CH_3	50	90	169–170
4o	2-Thienyl	CH_3	55	91	170–172
4p	3-Pyridyl	CH_3	50	89	262–263
4q	$3\text{-}ClC_6H_4$	CH_3	40	92	222–224
4r	$3\text{-}OCH_3C_6H_4$	CH_3	50	88	203–205
4s	$4\text{-}C_2H_5C_6H_4$	CH_3	55	87	179–181
4t	4-Pyridyl	CH_3	50	89	245–246
4u	$4\text{-}BrC_6H_4$	CH_3	40	93	109–111

Reaction conditions: aldehyde (10 mmol), ethylaceto acetate/acetylacetone (20 mmol), ammonium acetate (10 mmol), ionic liquid (0.5 mmol).

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layer was then washed with water and dried over anhydrous Na_2SO_4. Organic solvent was evaporated under reduced pressure and a solid compound was crystallized from absolute ethanol to afford the pure corresponding 1,4-dihydropyridine derivatives **4(a–u)** in excellent yields.

3. Results and discussion

Herein, we report a developed a methodology for the synthesis of 1,4-dihydropyridines (1,4-DHP's) in the presence of [tbmim]Cl_2/$AlCl_3$ under ultrasound-irradiation. Herein we have carried out the reaction of benzaldehyde **1**, ethylacetoacetate/acetylacetone **2** and ammonium acetate **3** catalyzed by [tbmim]Cl_2/$AlCl_3$. Different reaction conditions have been studied for optimization (Table 1).

The use of 1 mmol of ionic liquid does not affect the yield even after increase in reaction time. So 0.5 mmol of ionic liquid is sufficient to yield 1,4-DHP's. It is important to note that in the absence of the ionic liquid and without using ultrasound irradiation, the yield of the reactions decreased with increase in time. Using ionic liquid as a promoter for the synthesis of Hantzsch 1,4-DHP's does not only represent a dramatic improvement at room temperature with regard to yield (87–96%) over conventional thermal heating, but the reaction times are also considerably decreased compared to classical synthesis (3–6 h). Ultrasonic irradiation was very simple and convenient for the synthesis of 1,4-DHP's in room temperature using ionic liquid in ultrasonic cleaner with a frequency of 40 kHz and a nominal power 100 W. In this experiment the ultrasonic technique represented a better procedure with respect to time and yield. After optimizing the conditions, the generality of this method was examined by the reaction of several substituted aldehydes, ethylaceto acetate/acetylacetone and ammonium acetate using [tbmim]Cl_2/$AlCl_3$ as a catalyst under ultrasound irradiation, the results are shown in Table 2.

Herein, we have found that the reactions of aromatic aldehydes having electron-withdrawing groups are fast as compared to the reaction of aldehydes having electron donating groups. Unlike those of ethylacetoacetate products, the reaction of acetylacetone products proceeded at lower rate less efficiently to give 1,4-DHP's. The results obtained in the current method are illustrated in Table 2. All the products obtained were fully characterized by spectroscopic methods, such as IR, ^{1}H NMR and mass spectroscopy and also by comparison with the reference compounds. Another advantage of the ionic liquid is that it is recyclable. In view of environmentally friendly methodologies, recovery and reuse of the ionic liquid is highly preferable. [tbmim]Cl_2/$AlCl_3$ is easily separated from reaction medium by washing with water and distillation of the solvent under vacuum and it can be reused for subsequent reactions. Recycled ionic liquid shows no loss of efficiency with regard to yield after four successive runs, hence this method can be regarded as a rapid, convenient and environmentally benign method for the synthesis of 1,4-dihydropyridine derivatives.

4. Conclusion

An efficient and environmentally friendly method has been developed for the synthesis of 1,4-dihydropyridines catalyzed by 0.5 mmol of [tbmim]Cl_2/$AlCl_3$ under ultrasonic irradiation. The use of sonication combining ionic liquid in the three-component condensation at room temperature brings up the merits like milder conditions, low pollution, good yields and simple work-up.

4.1. Spectral data for respective compounds

Compound **4a**: IR (KBr) ν_{max} 3348, 3052, 1692, 1633, 1223. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.26 (t, 6H, J = 8 Hz), δ 2.35 (s, 6H), δ 4.10 (m, 4H, J = 4 Hz), δ 5.93 (s, 1H), δ 5.76 (s, 1H), δ 7.38–8.14 (Aromatic). MS: m/z 329 (M).

Compound **4b**: IR (KBr) ν_{max} 3345, 3091, 1705. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, 6H, J = 6 Hz), δ 2.33 (s, 6H), δ 4.09 (m, 4H, J = 4 Hz), δ 4.96 (s, 1H), δ 5.70 (s, 1H), δ 7.17–7.25 (Aromatic). MS: m/z 363 (M), 364 (M + 1).

Compound **4c**: IR (KBr) ν_{max} 3342, 3094, 1689. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, 6H, J = 8 Hz), δ 2.34 (s, 6H), δ 3.72 (s, 3H), δ 4.09 (m, 4H, J = 4 Hz), δ 4.94 (s, 1H), δ 5.58 (s, 1H), δ 6.76–7.21 (Aromatic). MS: m/z 360 (M).

Compound **4d**: IR (KBr) ν_{max} 3357, 3092, 1692. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, 6H, J = 8), δ 2.33 (s, 6H), δ 4.09 (m, 4H, J = 4 Hz), δ 5.90 (s, 1H), δ 5.73 (s, 1H), δ 7.38–8.14 (Aromatic). MS: m/z 374 (M).

Compound **4e**: IR (KBr) ν_{max} 3378, 3082, 1698. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, 6H, J = 6 Hz), δ 2.30 (*s,* 6H), δ 4.10 (m, 4H, J = 4 Hz), δ 5.00 (s, 1H), δ 6.10 (*s,* 1H), δ 7.20–8.47 (Aromatic). MS: m/z 330 (M).

Compound **4f**: IR (KBr) ν_{max} 3378, 3082, 1698. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (*t,* 6H, J = 6 Hz), δ 2.30 (s, 6H), δ 4.10 (m, 4H, J = 4 Hz), δ 5.00 (s, 1H), δ 6.10 (s, 1H), δ 7.20–8.60 (Aromatic). MS: m/z 330 (M).

Compound **4g**: IR (KBr) ν_{max} 3345, 3091, 1689. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, 6H, J = 6 Hz), δ 2.33 (s, 6H), δ 4.09 (m, 4H, J = 4 Hz), δ 4.96 (s, 1H), δ 5.70 (s, 1H), δ 7.17–7.25 (Aromatic). MS: m/z 409 (M + 2).

Compound **4n**: IR (KBr) ν_{max} 3342, 3094, 1689, 1638. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm):δ 2.28 (s, 6H), δ 2.36 (s, 6H), δ 5.29 (s, 1H), δ 6.05 (s, 1H), δ 7.40–8.04 (Aromatic). MS: m/z 330 (M).

Compound **4o**: IR (KBr) ν_{max} 3342, 3094, 1689. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 6H), δ 2.38 (s, 6H), δ 5.29 (s, 1H), δ 6.10 (s, 1H), δ 7.40–8.10 (Aromatic). MS: m/z 314 (M).

Compound **4p**: IR (KBr) ν_{max} 3332, 3096, 1690. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 6H), δ 2.37 (s, 6H), δ 5.15 (s, 1H), δ 5.80 (s, 1H), δ 6.70–7.54 (Aromatic). ^{13}C NMR ($CDCl_3$): δ 20.0, 29.5, 4.7, 104.5, 141.4, 145.1, 157, 197.8. MS: m/z 259 (M +), 261 (M + 2), 192.

Compound **4q**: IR (KBr) ν_{max} 3332, 3064, 1695. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 6H), δ 2.33 (s, 6H), δ 5.40 (s, 1H), δ 6.10 (s, 1H), δ 6.80–7.80 (Aromatic). ^{13}C NMR (400 MHz, $CDCl_3$): δ 20.6, 29.7, 35.0, 113.0, 123.7, 128.1, 135.1, 144.1, 150.0, 197.2. MS: m/z 274 (M−1), 275 (M), 276 (M + 1).

Compound **4r**: IR (KBr) ν_{max} 3345, 3090, 1685. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (*s,* 6H), δ 2.35 (s, 6H), δ 5.12 (s, 1H), δ 5.80 (s, 1H), δ 6.70–7.29 (Aromatic). ^{13}C NMR ($CDCl_3$, 400 MHz, ppm): δ 20.4, 30.0, 39.92, 113.7, 119.7, 142.8, 197.8. MS: m/z 299 (M).

Compound **4s**: IR (KBr) ν_{max} 3378, 3082, 1698, 963. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 6H), δ 2.20 (s, 6H), δ 5.11 (s, 1H), δ 5.81 (s, 1H), δ 7.16–7.26 (Aromatic). MS: m/z 303 (M), 304 (M + 1).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.arabjc.2011.01.027.

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