Iranian Journal of Catalysis 6(2), 2016, 153-159

IRANIAN JOURNAL OF CATALYSIS

Polyvinylpolypyrrolidone supported chlorosulfonic acid: An efficient catalyst for the one-pot synthesis of hexahydroquinolines

Mahshid Yosefzadeh, Masoud Mokhtary*

Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran.

Received 16 July 2015; received in revised form 13 November 2015; accepted 20 December 2015

ABSTRACT

Polyvinylpolypyrrolidone supported chlorosulfonic acid ([PVPP-SO_3H]$^+Cl^-$) was synthesized and evaluated as a recoverable catalyst for the one-pot synthesis of hexahydroquinolines by reaction of arylaldehydes, dimedone (5,5-dimethylcyclohexane-1,3-dione) or 1,3-cyclohexanedione, ethylacetoacetate and ammonium acetate in high to excellent yield in ethanol at 70 °C. The [PVPP-SO_3H]$^+Cl^-$ catalyst was characterized via Fourier transform infrared spectroscopy (FT-IR) and thermal gravimetric analysis (TGA). The acidity strength of the catalyst was determined by titration and found to be 12 mmol/g, which shows a high loading of H^+ per gram of the catalyst. Moreover, the catalyst could be recycled several times without significant loss of its catalytic activity. Clean methodologies, easy work-up procedure, high yield and simple preparation of the catalyst are some advantages of this work.

***Keywords**: Polyvinylpolypyrrolidone, Chlorosulfonic acid, Multicomponent reaction, Hexahydroquinolines.*

1. Introduction

1,4-Dihydropyridines (1,4-DHPs) have shown a variety of biological activities such as, antiangin [1], anti-inflammatory activity [2], antitumor [3], antitubercular activity [4], analgesic activity [5] and antithrombotic [6]. Commercial drugs such as Nifedipine which are a prototype of the 1,4-DHP structure have been used extensively in both antianginal and antihypertensive treatment. 1,4-DHPs are used as the most popular drug as calcium channel blockers and also possess the disordered heart ratio as a chain cutting agent of factor IV channel [7]. Also, 1,4-DHPs exhibits several medicinal applications which include neuroprotectant [8] and cerebral antischemic activity in the treatment of Alzheimer's disease [9]. These examples clearly demonstrate the remarkable potential of 1,4-dihydropyridine derivatives as a source of valuable drugs. One of the commonly used methods reported for the synthesis of symmetrical 1,4- dihydropyridines (1,4-DHPs) involves the one-pot, four component condensation of two molecules of ethylacetoacetate, aromatic aldehyde and ammonia which was first established by Hantzsch in 1881 [10].

*Corresponding author email: mmokhtary@iaurasht.ac.ir
Tel: +98 13 3342 4307; Fax: +98 13 3342 3621

In order to improve the efficiency of Hantzsch DHPs synthesis, different catalysts such as $Yb(OTf)_3$ [11], ionic liquid [12], $Sc(OTf)_3$ [13], iron(III) trifluoroacetate [14], heteropolyacid [15], Baker's yeast [16], L-proline [17], cerium(IV) ammonium nitrate [18], $Hf(NPf_2)_4$ [19], ANP [20], Pd-nanoparticles [21], $Bi(NO_3)_3.5H_2O$ [22], FeF_3 [23], TiO_2 NPs [24], [pyridine-SO_3H]Cl [25], 1,3-di(bromo or chloro)-5,5-dimethylhydantoin (DBH or DCH) [26], [Dsim]HSO_4 [27], [NMP]HSO_4 [28] and Fe_3O_4 NPs [29] have been explored. However, some drawbacks still exist, such as the use of expensive or toxic catalyst, longer reaction time, corrosive, hazardous reaction condition, tedious work-up procedures, unsatisfactory yields, and non-recyclable catalysts. Therefore, it seems that a major task of current research is to replace less efficient and traditional catalysis procedures with more acceptable method based on improved, stable, and recoverable catalyst. There are a number of advantages in using polymer-supported catalysts over conventional catalysis; the reactions can be performed under mild conditions, and purification of the product is simplified because of the use of an insoluble solid support. Polymer supported catalysts can also be recycled after use [30]. Following our interest in the use of polyvinyl polypyrrolidone as

support for the preparation of polyvinyl polypyrrolidone-bromine (PVPP-Br_2) [31], polyvinyl polypyrrolidone-boron trifluoride (PVPP-BF_3) [32] and application of these reagents for some organic reactions [33,34], herein, polyvinylpolypyrrolidone supported chlorosulfonic acid has been successfully applied to perform the reaction of arylaldehydes, dimedone (5,5-dimethylcyclohexane-1,3-dione) or 1,3-cyclohexanedione, ethylacetoacetate and ammonium acetate in ethanol at 70°C to provide a series of hexahydroquinolines in good to excellent yields (Scheme 1).

2. Experimental

2.1. General

High-purity chemical reagents were purchased from the Merck Chemical Company. Melting points were determined using an Electrothermal Mk3 apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ on a Bruker Avance DRX-400 MHz instrument spectrometer using TMS as internal standard. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm^{-1} with a Perkin-Elmer 780 spectrometer. Thermal gravimetric analysis (TGA) was recorded on a Shimadzu-50 system at a heating rate of 10 °C/min.

2.2. Preparation of the catalyst

To a suspension of PVPP (3 g) in CH_2Cl_2 (25 mL), a solution of chlorosulfonic acid (3 mL) in CH_2Cl_2 (15 mL) was added dropwise and the mixture stirred for 2 h at room temperature. The resulting resin was filtered and washed with CH_2Cl_2 (2×10 mL) and dried in a vacuum desiccator to give $[PVPP\text{-}SO_3H]^+Cl^-$ as a pale yellow stable powder.

2.2.1. General synthesis of hexahydroquinolines

A mixture of aromatic aldehyde (1 mmol), dimedone (5,5-dimethylcyclohexane-1,3-dione) (1 mmol, 0.14 g) or 1,3-cyclohexanedione (1 mmol, 0.112 g), ethylacetoacetate (1 mmol, 0.126 mL) and ammonium acetate (1.2 mmol, 0.092 g) in the presence of $[PVPP\text{-}SO_3H]^+$ Cl^- (0.05 g) was stirred in ethanol (5 mL) at 70°C for the appropriate time, as shown in Table 1. Completion of the reaction was indicated by TLC monitoring. Then, the reaction mixture was cooled to ambient temperature, and the crude solid residue was recrystallized from ethanol and water (10 mL, 50% V/V) to afford pure crystals of the proper hexahydroquinolines in 80-96% yields. The products were characterized by FT-IR, ^{1}HNMR, ^{13}CNMR and by comparison with authentic samples reported in the literature.

Selected spectral data

*Ethyl2,7,7-trimethyl-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquin-oline-3-carboxylate (**5c**):*

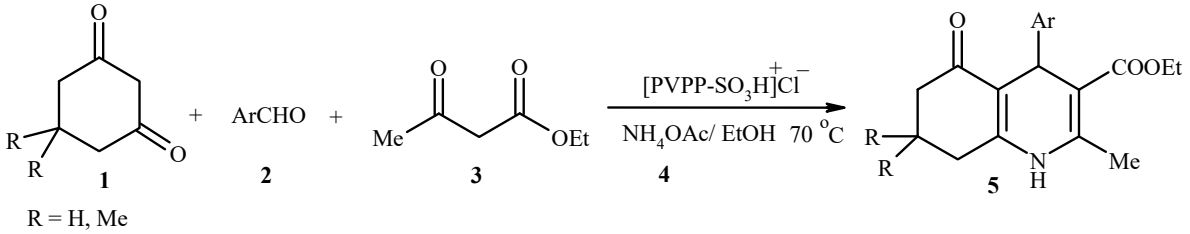
Yellow solid. m.p.= 175-177°C. FT-IR (KBr): $\bar{\nu}$ = 3275, 2958, 1702, 1608, 1529, 1485, 1347, 1232, 1073, 687 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 3H), 1.11 (s, 3H), 1.21 (t, 3H, *J* = 7.2 Hz), 2.14–2.43 (m, 7H), 4.08 (q, *J*= 7.1 Hz, 2H), 5.17 (s, 1H), 5.79 (s, 1H), 7.36 (t, *J*= 7.9 Hz, 1H),7.74 (d, *J*= 7.9 Hz, 1H), 7.98 (d, *J*= 8.1, 1H), 8.11 (s,1H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ = 14.0, 18.4, 26.5, 29.0, 32.2, 36.6, 50.0, 59.4, 102.4, 109.0, 121.0, 121.9, 129.7, 134.2, 145.6, 146.0, 150.0, 154.9, 166.5, 194.2 ppm.

*Ethyl4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahy-droquinoline-3-carboxylate (**5e**):*

Yellow solid. m.p.= 244-246°C. FT-IR (KBr): $\bar{\nu}$ = 3270, 3195, 3070, 2945, 1670, 1604, 1475, 1367, 1227, 1105, 857 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 0.96 (s, 3H), 1.04 (s, 3H), 1.11 (t, 3H, *J*= 7.2 Hz), 2.12–2.35 (m, 4H), 2.36 (s, 3H), 4.05 (q, 2H, *J*= 7.1 Hz), 5.03 (s, 1H), 6.46 (s, 1H), 7.15 (d, *J*= 8.4 Hz, 2H), 7.25 (d, *J*= 8.4 Hz, 2H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 14.1, 18.4, 26.6, 29.1, 32.2, 35.6, 50.2, 59.0, 103.3, 109.6, 127.8, 129.2, 130.4, 145.4, 146.5, 149.6, 166.5, 194.2 ppm.

*Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(2-chlorolphenyl)-5(6H)-oxo-quinolin-3-arboxylate (**5f**):*

Yellow solid. m.p.= 208-209°C. FT-IR (KBr): $\bar{\nu}$ = 3063, 2956, 1721, 1640, 1611, 1467, 1384, 1227, 1021, 745 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): δ= 0.97 (s, 3H), 1.09 (s, 3H), 1.20 (t, *J*= 7.2 Hz, 3H), 2.11-2.24 (m, 4H), 2.32 (s, 3H), 4.05 (q, *J*= 7.2 Hz, 2H), 5.04 (s, 1H), 5.74 (s, 1H), 7.02-7.42 (m 4H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ = 13.1, 18.3, 26.1, 28.3, 31.5, 34.9, 40.0, 49.6, 58.8, 104.1, 110.1, 125.2, 126.2, 128.6, 131.0, 132.1, 142.6, 142.9, 147.5, 166.4, 194.3 ppm.



Scheme 1. Synthesis of hexahydroquinolines catalyzed by $[PVPP\text{-}SO_3H]^+Cl^-$.

*2-Methyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (**5j**):*

Yellow solid. m.p.= 240-242°C. FT-IR (KBr): $\bar{\nu}$ = 3276, 2960, 1681, 1603, 1487, 1380, 1276, 1217, 1074, 814 cm^{-1}. ^{1}HNMR ($CDCl_3$, 400 MHz): δ= 1.18 (t, 3H, *J*= 6.8 Hz), 1.80–2.10 (m, 2H), 2.30–2.44 (m, 7H), 4.06 (q, 2H, *J*= 6.8 Hz), 5.07 (s, 1H), 6.17 (s, 1H), 7.10 (t, 1H, *J*= 7.6 Hz), 7.20 (t, 2H, *J*= 7.6 Hz), 7.30 (d, 2H, *J*= 7.6 Hz) ppm. ^{13}CNMR ($CDCl_3$, 100 MHz): δ = 14.1, 19.4, 21.0, 27.6, 36.4, 37.0, 59.8, 106.6, 113.4, 125.9, 127.9, 127.8, 143.3, 147.1, 149.5, 167.4 ppm.

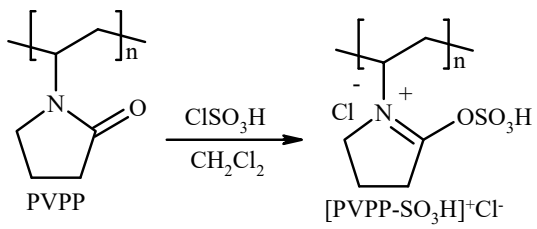
*Ethyl 2-methyl-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, (**5l**):*

Yellow solid. m.p.= 199-201°C. FT-IR (KBr): $\bar{\nu}$ = 3297, 2940, 1703, 1608, 1527, 1480, 1346, 1222, 1182, 1076, 718 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): δ= 1.19 (t, *J*= 7.2 Hz, 3H), 2.05–1.92 (m, 2H), 2.36–2.32 (m, 2H), 2.42 (s, 3H), 2.50–2.47 (m, 2H), 4.08 (q, *J*= 7.2 Hz, 2H), 5.18 (s, 1H), 6.06 (s, 1H), 7.39 (m, 1H), 7.74 (d, *J*= 7.6 Hz, 1H), 7.99 (dd, *J*= 8.0, 2.0 Hz, 1H), 8.09 (m, 1H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ = 14.2, 19.2, 21.1, 27.2, 36.8, 60.0, 104.9, 112.2, 121.2, 122.8, 128.6, 134.8, 144.6, 148.2, 149.4, 150.8, 167.0, 195.8 ppm.

3. Results and Discussion

In this study, $[PVPP\text{-}SO_3H]^+Cl^-$ is obtained by simple reaction of chlorosulfonic acid with the cross-linked PVP (Scheme 2). Characterization of $[PVPP\text{-}SO_3H]^+Cl^-$ was performed by recording the Fourier transform infrared spectroscopy (FT-IR), which shows the O–H stretching vibration at 3394 cm^{-1}, the SO_2 asymmetric and symmetric stretching at 1176 and 1072 cm^{-1} respectively and S–OH bending at 1007 cm^{-1} and symmetric S–O stretching at 883 cm^{-1} (Fig. 1). In addition, the band at 1442 (C–N) cm^{-1} in PVPP is disappeared and a moderate absorption at 1643 cm^{-1} that corresponds to the internal imine groups in catalyst is appeared. These results provided the evidences that chlorosulfonic acid was successfully attached to the polyvinylpolypyrrolidone.

The acidity strength of the catalyst was determined by titration and found to be 12 mmol/g, which shows a high loading of H^+ per gram of the catalyst.



Scheme 2. Preparation of $[PVPP\text{-}SO_3H]^+Cl^-$.

The thermal behavior of PVPP and $[PVPP\text{-}SO_3H]^+Cl^-$ are shown in Fig. 2. The thermal analysis $[PVPP\text{-}SO_3H]^+Cl^-$ showed two decreasing peaks. First peak appears at temperature around 100–120°C due to desorption of water molecules from the catalyst surface. This is followed by a second peak at 220–270°C, corresponding to the loss of the sulfonic group. The thermal analysis data showed that the catalyst is stable up to 200°C.

In order to optimize the reaction conditions, the effect of temperature, the amount of catalyst, and the reaction time were examined. It was found that the condensation reaction of benzaldehyde, dimedone (5,5-dimethylcyclohexane-1,3-dione), ethylacetoacetate and ammonium acetate as a model reaction was affected by various solvents. Also, the model reaction was performed under solvent-free conditions. Among them, ethanol (96%) provided the highest yield at 70°C after 2 h (Table 1, entry 1). In addition, very low conversion to the product was observed in the absence of the catalyst even after 12 h. Next, we examined the optimal amount of catalyst using the same model reaction. It was observed that 50 mg $[PVPP\text{-}SO_3H]^+Cl^-$ was sufficient to catalyze the reaction smoothly. Using these optimized reaction conditions, a variety of hexahydroquinolines was prepared from arylaldehydes, dimedone (5,5-dimethylcyclohexane-1,3-dione) or 1,3-cyclohexanedione, ethylacetoacetate and ammonium acetate in the presence of polyvinylpolypyrrolidone supported chlorosulfonic acid in ethanol at 70°C in good to excellent yields (Table 1). Surprisingly, the corresponding hexahydroquinolines was isolated by crystallization from the crude filtrate. As shown in Table 1, aromatic aldehydes bearing electron-deficient substituents on the aromatic ring reacted in shorter time and the desired product obtained in better yields.

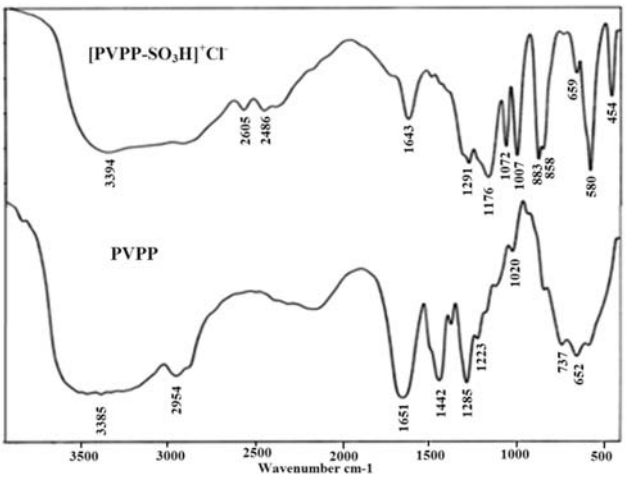


Fig. 1. The FT-IR spectrum of PVPP and $[PVPP\text{-}SO_3H]^+Cl^-$.

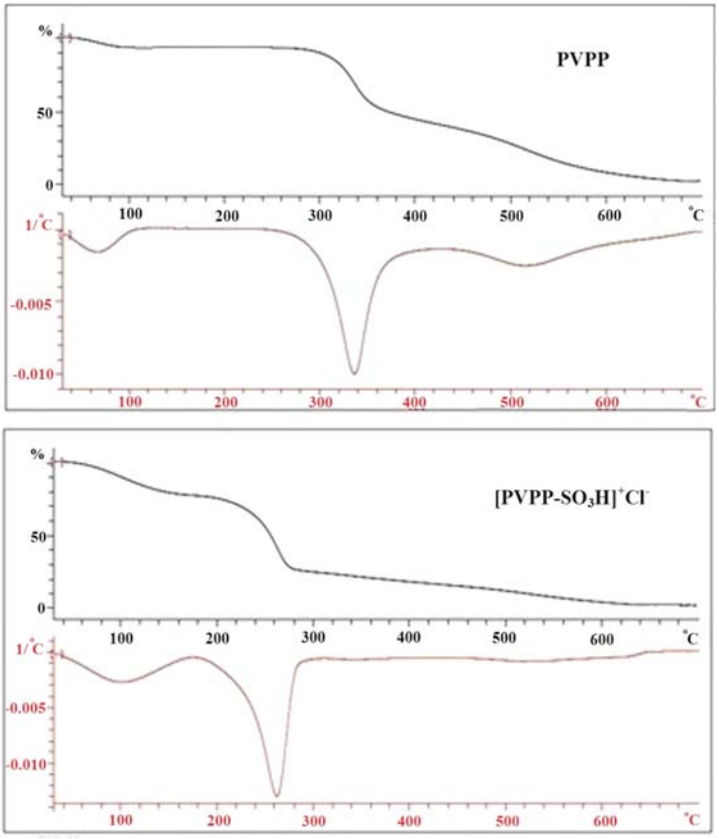


Fig. 2. The thermal analysis of PVPP and $[PVPP\text{-}SO_3H]^+Cl^-$.

Table 1. Synthesis of hexahydroquinolines derivatives by $[PVPP\text{-}SO_3H]^+Cl^-$.[a]

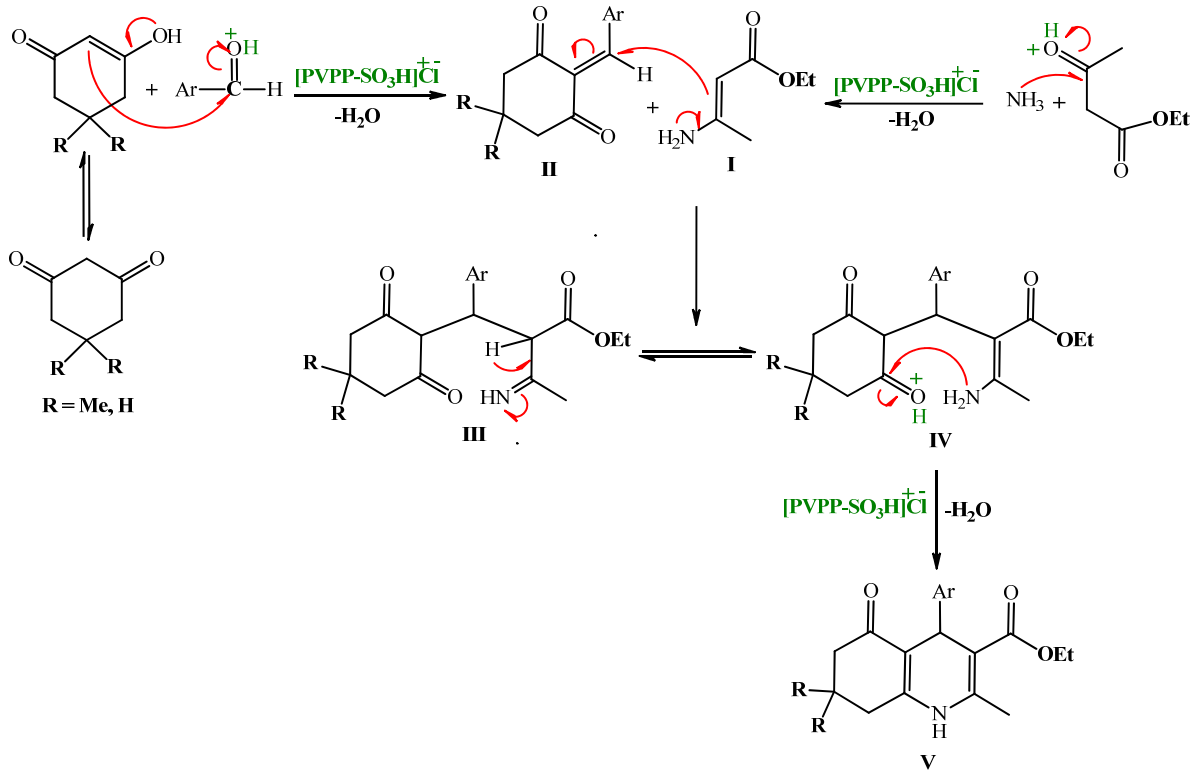
Entry	R	Aryl	Product	Time (h)	Yield (%)[b]	m.p. (°C)	
						Found	Reported[c]
1	Me	C_6H_5	**5a**	2	95	226-228	225-227
2	Me	4-NO_2-C_6H_4	**5b**	1.75	96	242-244	242-243
3	Me	3-NO_2-C_6H_4	**5c**	2	94	175-177	174-173
4	Me	2-NO_2-C_6H_4	**5d**	2	93	203-205	204-206
5	Me	4-Cl-C_6H_4	**5e**	2	96	244-246	243-244
6	Me	2-Cl-C_6H_4	**5f**	2	92	208-209	208-210
7	Me	3-HO-C_6H_4	**5g**	4	87	220-221	218-220
8	Me	3-MeO-C_6H_4	**5h**	4.5	82	202-204	201-203
9	Me	4-Me-C_6H_4	**5i**	4.5	80	260-262	261-263
10	H	C_6H_5	**5j**	3	90	240-242	239-240
11	H	2-NO_2-C_6H_4	**5k**	2.5	94	190-192	189-190
12	H	3-NO_2-C_6H_4	**5l**	2.5	92	199-201	198-200
13	H	4-Cl-C_6H_4	**5m**	4	90	234-235	233-234
14	H	4-MeO-C_6H_4	**5n**	4.5	80	192-194	192-193
15	H	4-Me-C_6H_4	**5o**	4.5	81	241-243	239-240

[a]Reaction and conditions: aldehyde (1 mmol), dimedone (5,5-dimethylcyclohexane-1,3-dione) or 1,3-cyclohexanedione (1 mmol), ethylacetoacetate (1 mmol), ammonium acetate (1.2 mmol) and $[PVPP\text{-}SO_3H]^+ Cl^-$ (0.05 g) in EtOH (5 mL) at 70 °C.
[b]All yields refer to isolated products.
[c]From refs. [12,15,19].

A plausible mechanism for the formation of hexahydroquinolines catalyzed by $[PVPP\text{-}SO_3H]^+Cl^-$ is shown in Scheme 3. Formation of the hexahydroquinolines **V** takes place through a Hantzsch-type mechanism via conjugate addition of the enamine intermediate **I** obtained from ethylacetoacetate and ammonium acetate (the catalyst facilitates the formation of enamine intermediate **I** by increasing the electrophilicity of the carbonyl group of ethylacetoacetate) to the Knoevenagel product **II** obtained from dimedone or 1,3-cyclohexanedione and the corresponding aromatic aldehyde. Then, intermediate **III** is converted to **IV** by imino-enamino tautomerization. Finally, hexahydroquinonine **V** forms by intramolecular nucleophilic attack of the NH_2 group to the activated carbonyl group and then removes one molecule H_2O.

To check the reusability of the catalyst, it was employed in the synthesis of 3-acetyl-2,7,7-trimethyl-4-phenyl-4,6,7,8-tetrahydroquinolin-5(1*H*)-one (**5a**) six cycles under the optimum conditions. The catalyst powder was recovered by simple filtration and washed with dichloromethane, taking into account the partial loss of catalyst during the recovery. Afterward, according to the amount of catalyst the required amount of fresh dimedon, benzaldehyde, ethylacetoacetate and ammonium acetate were added. The results showed that the catalyst can be reused six consecutive times without significant loss of its catalytic activity and the yield was changed from 95% (first run) to 89% (sixth run).

In order to examine the efficiency of the present method for the synthesis of hexahydroquinolines, compound **5a** was compared with some of those reported in the literature (Table 2). As one can see, our results show good comparability with previously reported data when all terms including yields, reaction times, and reaction conditions are taken into account. Although ILs possessed such promising advantages and this reaction with ionic liquids has been reported in shorter reaction times [27,28], but, their widespread practical application was still prevented by several disadvantages such as high viscosity and homogeneous reaction, which was difficult for separation and reuse procedures and consequently high cost for the use of relatively large amounts of ILs as opposed to economic criteria [35,36]. Polyvinylpyrrolidone is used as a binder in many pharmaceutical tablets [37]; it simply passes through the body when taken orally. However, autopsies have found that crospovidone (PVPP) contributes to pulmonary vascular injury in substance abusers who have injected pharmaceutical tablets intended for oral consumption [38]. $[PVPP\text{-}SO_3H]^+Cl^-$ is a biocompatible and reusable polymeric catalyst. Clean methodologies, easy workup procedure, good to high yields and simple preparation of the catalyst are some advantages of this work.



Scheme 3. The proposed mechanism for the synthesis of hexahydroquinolines catalyzed by $[PVPP\text{-}SO_3H]^+Cl^-$.

Table 2. Comparison of our results with previously reported data for the synthesis of **5a**.

Entry	Catalyst	Reaction conditions	Time/min	Yield (%)	Ref.
1	$Yb(OTf)_3$	EtOH/ r.t.	300	90	[11]
2	$Sc(OTf)_3$	EtOH/ r.t.	240	93	[13]
3	Baker's yeast	Phosphate buffer /r.t.	1440	79	[16]
4	L-proline	EtOH/ reflux	360	92	[17]
5	CAN	EtOH/ r.t.	120	94	[18]
6	$Hf(NPf_2)_4$	$(C_{10}F_{18})$/ 60°C	180	95	[19]
7	ANP	EtOH/ r.t.	240	88	[20]
8	Pd-nanoparticles	THF/ reflux	240	89	[21]
9	$Bi(NO_3)_3.5H_2O$	EtOH/ 80°C	240	92	[22]
10	$[Dsim]HSO_4$	50°C	35	94	[27]
11	$[NMP]HSO_4$	r.t.	9	91	[28]
12	$[PVPP\text{-}SO_3H]^+Cl^-$	EtOH/ 70°C	120	95	This work

4. Conclusions

In summary, we have developed a simple, clean, efficient and one-pot procedure for the synthesis of hexahydroquinolines using $PVPP\text{-}SO_3H]^+Cl^-$ as a reusable heterogeneous catalyst in ethanol at 70°C. Simple performance and work-up procedure and high yields are some of advantages of this method. The catalyst is recyclable and could be reused without significant loss of activity. The $[PVPP\text{-}SO_3H]^+Cl^-$ is also stable, non-corrosive, easy to prepared and handle, and represent effective activity after several months of storage.

Acknowledgements

Financial support by Rasht Branch, Islamic Azad University Grant No. 4.5830 is gratefully acknowledged.

References

[1] F. Bossert, H. Meyer, E. Wehinger, Angew. Chem. Int. Ed. 20 (1981) 762-769.
[2] B. Sushilkumar, S. Devanand, Acta Pharm. (Zagreb, Croatia) 52 (2002) 281-287.
[3] R. Boer, V. Gekeler, Drugs Future 20 (1995) 499-509.
[4] G.A. Wachter, M.C. Davis, J. Med. Chem. 41 (1998) 2436-2438.
[5] S. Gullapalli, P. Ramarao, Neuropharmacology 42 (2002) 467-475.
[6] C.E. Sunkel, M. De casa Juana, L. Santos, J. Med. Chem. 33 (1990) 3205-3210.
[7] R. Shan, C. Velazquez, E. Knaus, J. Med. Chem. 47 (2004) 254-261.
[8] V. Klusa, Drugs Future 20 (1995) 135-138.
[9] R.G. Retzel, C.C. Bollen, E. Maeser, K.F. Drugs Future 17 (1992) 465-468.
[10] A. Hantzsch, Chem. Ber. 14 (1881) 1637-1638.
[11] L.M. Wang, J. Sheng, L. Zhang, J.W. Han, Z.Y. Fan, H. Tian, C.T. Qian, Tetrahedron 61 (2005) 1539-1543.
[12] S.J. Ji, Z.Q. Jiang, J. Lu, T.P. Loa, Synlett (2004) 831-835.
[13] J.L. Donelson, A. Gibbs, S.K. De, J. Mol. Catal. A: Chem. 256 (2006) 309-311.
[14] H. Adibi, H.A. Samimi, M. Beygzadeh, Catal. Commun. 8 (2007) 2119. 2119-2124.
[15] M.M. Heravi, K. Bakhtiri, N.M. Javadi, F.F. Bamoharram, M. Saeedi, H.A. Oskooi, J. Mol. Catal. A: Chem. 264 (2007) 50-52.
[16] A. Kumar, R.A. Maurya, Tetrahedron Lett. 48 (2007) 3887-3890.
[17] N.N. Karade, V.H. Budhewara, S.V. Shindeb, W.N. Jadhav, Lett. Org. Chem. 4 (2007) 16-19.
[18] C.S. Reddy, M. Raghu, Chin. Chem. Lett. 19 (2008) 775-779.
[19] M. Hong, C. Cai, W.B. Yi, J. Fluorine Chem. 131 (2010) 111-114.
[20] S.J. Song, Z.X. Shan, Y. Jin, Synth. Commun. 40 (2010) 3067-3077.
[21] M. Saha, A.K. Pal, Tetrahedron Lett. 52 (2011) 4872-4877.
[22] S. Sheik Mansoor, K. Aswin, K. Logaiya, S.P.N. Sudhan, J. Saudi Chem. Soc. (2012) in press, doi: 10.1016/j.jscs. 2012.09.010.
[23] R. Surasani, D. Kalita, A.V. Dhanunjaya Rao, K. Yarbagi, K.B. Chandrasekhar, J. Fluorine Chem. 135 (2012) 91-96.
[24] M. Tajbakhsh, E. Alaee, H. Alinezhad, M. Khandan, F. Jahani, S. Khaksar, P. Rezaee, M. Tajbakhsh, Chin. J. Catal. 33 (2012) 1517-1522.

[25] A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, J. Afsar, A. Zare, V. Khakyzadeh, M.H. Beyzavi, Chin. J. Catal. 34 (2013) 1936-1944.
[26] B. Maleki, R. Tayebee, M. Kermanian, S.S. Ashrafi, J. Mex. Chem. Soc. 57 (2013) 290-297.
[27] A. Zare, F. Abi, A.R. Mossavi-Zare, M.H. Beyzavi, M.A. Zolfigol, J. Mol. Liq. 178 (2013) 113-121.
[28] M. Ghorbani, H.R. Shaterian, S. Noura, F. Khammar, K. Behbodi, B. Reisi, M. Oftadeh, J. Mol. Liq. 204 (2015) 15-20.
[29] M. Nasr-Sefahani, S.J. Hoseini, M. Montazerozohori, R. Mehrabi, H. Nasrabi, J. Mol. Catal. A: Chem. 382 (2014) 99-105.
[30] S.V. Ley, I.R. Baxendale, R.N. Bream, P.S. Jackson, A.G. Leach, D.A. Longbottom, M. Nesi, J.S. Scott, R.I. Storer, S.J. Taylor, J. Chem. Soc. Perkin. Trans 1 (2000) 3815-4195.
[31] M. Mokhtary, M.M. Lakouraj, Chin. Chem. Lett. 22 (2011) 13-17.
[32] M. Mokhtary, F. Najafizadeh, C. R. Chim. 15 (2012) 530-532.
[33] M. Mokhtary, S. Refahati, Dyes Pigm. 99 (2013) 378-381.
[34] M. Mokhtary, S.A. Mirfarjood Langroudi, Monatsh Chem. 145 (2014) 1489-1494.
[35] S. Sahoo, P. Kumar, F. Lefebvre, S.B. Halligudi, Appl. Catal. A 354 (2009)17-25.
[36] L.L. Zhu, Y.H. Liu, J. Chen, Ind. Eng. Chem. Res. 48 (2009) 3261-3267.
[37] V. Bühler, Polyvinylpyrrolidone Excipients for Pharmaceuticals: Povidone, Crospovidone and Copovidone, Berlin, Heidelberg, New York: Springer. (2005) 1–254.
[38] S. Ganesan, J. Felo, M. Saldana, V.F. Kalasinsky, M.R. Lewin-Smith, J.F. Tomashefski Jr, Mod. Pathol. 16 (2003) 286–292.