J. Iran. Chem. Soc., Vol. 8, No. 2, June 2011, pp. 545-552.

JOURNAL OF THE
Iranian
Chemical Society

A Simple Green Approach to the Synthesis of 2-Amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile Derivatives Catalyzed by 3-Hydroxypropanaminium Acetate (HPAA) as a New Ionic Liquid

H.R. Shaterian* and A.R. Oveisi

Department of Chemistry, Faculty of Sciences, the University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran

(Received 19 September 2010, Accepted 29 October 2010)

A new ionic liquid, 3-hydroxypropanaminium acetate (HPAA) [H_3N^+-CH_2-CH_2-CH_2-OH][CH_3COO^-], was synthesized for the first time and used as an efficient and recoverable catalyst in the synthesis of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile derivatives by condensing together 4-hydroxycoumarin, aldehydes and malononitrile at room temperature. The catalyst can be reused for four times without noticeable loss of activity.

Keywords: 2-Amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile, Ionic liquid, Multi-component reaction, Catalysis

INTRODUCTION

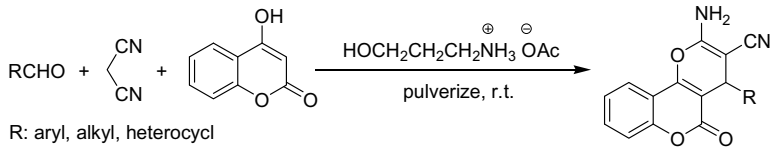
Multi-component reactions (MCRs) are very important in organic synthesis due to the formation of carbon-carbon and carbon-hetero atom bonds in one pot [1-3]. Simple procedures, high bond forming efficiency, time and energy saving and low expenditures are among the advantages of these reactions [4]. Recently, Shaabani *et al*. reported the synthesis of functionalized benzo[g]- and dihydropyrano[2,3-g]chromene derivatives *via* a novel one-pot three- and pseudo-five-component reaction [5].

Ionic liquids are salts consisting of ions, which exist in the liquid state at ambient temperatures [6]. Although the first ionic liquid, ethylammonium nitrate (m.p.: 12 °C) was reported as early as 1914 [7], ionic liquids have gained great significance only recently. More than 40 reviews have been published on ionic liquids between 2003 and 2008 [8]. The use of ionic liquids has received special attention for being eco-friendly, reusable and alternative reaction media in organic synthesis because of their unique properties such as high thermal and chemical stability, negligible vapor pressure, no flammability, high loading capacity and excellent electrical conductivity [9-12]. Ionic liquids have shown great promise not only as alternative green solvents, but also as reagents or catalysts in organic transformations [9,13-20].

Green chemistry is destined to be of global concern in the near future. In this context, a convenient and rapid synthetic procedure is highly desirable. To be of practical value, such a procedure should be suitable for large-scale operations as well [21]. The pioneering work of Toda *et al.* has shown that many reactions (but not all) can be produced in high yields just by grinding solids together [22,23]. Traditionally, these reactions were carried out on a very small scale in an agate mortar and pestle. To conduct grindstone chemistry on a large scale a simple and inexpensive expedient is to use a hand-held electric food mixer with stainless steel rotors for grinding the reagents in a large glass or porcelain bowl [21].

Pyrano[3,2-c]chromene derivatives belong to a class of

*Corresponding author. E-mail: hrshaterian@chem.usb.ac.ir



Scheme 1. Synthesis of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile derivatives

important heterocycles with a wide range of biological properties [24] such as spasmolytic, diuretic, anticoagulant, anti-cancer, and anti-anaphylactic activity [25]. In addition, aminochromene derivatives exhibit a wide spectrum of biological activities including antihypertensive and anti-ischemic behavior [26-28]. Also, a number of 2-amino-4*H*-pyrans are useful as photoactive materials [29].

2-Amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitriles have previously been prepared in the presence of organic bases like piperidine or pyridine in an organic solvent i.e. ethanol and pyridine [30]. They have also been prepared in the presence of diammonium hydrogen phosphate in aqueous ethanol [31] and K_2CO_3 under microwave irradiation [32]. Some of the reported procedures require long reaction times, multi-step reactions and complex synthetic pathways, having drawbacks such as modest yields, and non-reusability of the catalyst [33-39]. Also, 1,1,3,3-N,N,N',N'-tetramethyl-guanidinium trifluoroacetate (TMGT) as an ionic liquid was used for the preparation of this class of compounds [40].

In continuation of our work [41-46], here we wish to report a new room temperature task-specific ionic liquid, 3-hydroxypropanaminium acetate (HPAA) as an efficient and reusable catalyst for one-pot synthesis of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitriles derivatives by 'Grindstone Chemistry' (Scheme 1).

EXPERIMENTAL

Materials

All reagents were purchased from Merck and Sigma-Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparing the physical data with those of authentic samples and spectroscopic (IR and NMR) data. The NMR spectra were recorded on a Bruker Avance DPX 500 MHz instrument. The spectra were measured in DMSO relative to TMS (0.00 ppm). IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. Mass spectra were recorded on an Agilent technologies 5973 network mass selective detector (MSD) operating at an ionization potential of 70 eV. Conductivities were measured by a WTW Multiline P3 with TetraCon 325 electrode. Cyclic Voltammetry (CV) traces were obtained by an EG and G Parstat 2263 model potentiostat-galvanostat. Thermo-gravimetric Analysis (TGA) (which was performed by a Shimadzu TG-50 at 10 °C min^{-1}. heating rate, under nitrogen flow, 23 ml min^{-1}) curve shows a sharp decline around 150 °C and an inflection at about 190 °C. Hundred percent mass losses occur at 277 °C. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica-gel polygram SILG/UV 254 plates.

Preparation of Task-Specific Ionic Liquid (HPAA)

To a 250 ml three-necked flask was added 30.5 g (0.5 mol) of 3-propanolamine and 25 ml of ethanol. To the solution 30 g (0.5 mol) of acetic acid in 25 ml of ethanol was added dropwise at room temperature within 60 min with magnetic stirring. The resultant solution was stirred at room temperature for 24 h. Ethanol was removed and the oil residual was dried *in vacuo* at 50 °C for 48 h to give [H_3N^+-CH_2-CH_2-CH_2-OH] [CH_3COO^-] as a colorless, viscous liquid. ^{1}H NMR (DMSO-d_6, 500 Hz): δ 1.52-1.67 (m, 5H, CH_3-COO, -CH_2-), 2.79 (t, J = 7.40 Hz, 2H, -O-CH_2-), 3.41 (t, J = 6.10 Hz, 2H, -CH_2-N), 4.24-4.82 (broad singlet, 4H, -NH_3^+, -OH) ppm; ^{13}C NMR (DMSO-d_6, 125 Hz): δ 22.8 (CH_3-), 28.5 (-CH_2-), 36.7 (-CH_2-N), 58.3 (-CH_2-O), 180.5 (-CO_2-) ppm.

FT-IR spectrum showed a broad band in the 3700-2300 cm^{-1} that is indicative of zwitterionic quaternary ammonium carboxylates character. The OH stretching vibration is embedded in this band. A broad band centered at 1628 cm^{-1} is

a combined band of the carbonyl stretching and N-H plane bending vibrations. Literature survey confirms this interpretation as beingconsistent with [H_3N^+-CH_2-CH_2-OH] [$HCOO^-$] [47].

General Procedure for the Synthesis of 2-Amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile Derivatives Catalyzed by 3-Hydroxypropanaminium Acetate

A mixture of aldehydes (3 mmol), malononitrile (3 mmol) and 4-hydroxycoumarin (3 mmol) in the presence of 6 drops (0.12 g) of ionic liquid was pulverized in a mortar at room temperature for appropriate time (Table 2). The reaction was monitored by TLC. After completion of the reaction, H_2O was added and the mixture was filtered to separate the ionic liquid. The solvent (H_2O) was evaporated under reduced pressure and the ionic liquid was recovered and reused (Fig. 1). For the purification of the product, the precipitate was washed with aqueous ethanol or recrystallized from EtOH/H_2O to give the pure products. All the desired products were characterized by comparing their physical data with those of the known compounds [31,48-50]. Characterization data for the new products are given below.

2-Amino-5-oxo-4-phenethyl-4,5-dihydropyrano[3,2-c] chromene-3-carbonitrile (Table 2, entry 14). ^{1}H NMR (DMSO-d_6, 500 Hz): δ 1.81-1.88 (m, 1H, CH_2), 2.08-2.17 (m, 1H, CH_2), 2.44-2.62 (m, 2H, CH_2), 3.50 (t, J = 4.3 Hz, 1H, CH), 7.00 (t, J = 8.1 Hz, 1H, Ar), 7.08 (d, J = 7.0 Hz, 2H, Ar), 7.13 (t, J =7.5 Hz, 3H, Ar), 7.34-7.45 (m, 4H, NH_2 & Ar), 7.62-7.67 (m, 1H, Ar), 7.76 (dd, J = 5.9, 1.2 Hz, 1H, Ar) ppm; ^{13}C NMR (DMSO-d_6, 125 Hz): δ 30.3, 30.7, 34.6, 54.8, 103.7, 112.9, 116.3, 119.5, 122.1, 124.3, 125.5, 127.9, 128.1, 132.5, 141.2, 152.0, 154.0, 159.4, 159.8 ppm; IR (KBr, cm^{-1}): 3382, 3315, 3189, 2198, 1694, 1671, 1608, 1396, 1315, 1179, 1211, 1112, 759; MS (EI, 70 eV) m/z (%) = 344 (M^+, 7), 240 (20), 239 (100), 187 (8), 138 (21), 91 (10), 43 (17). Anal. Calcd. for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13%. Found: C, 73.28; H, 4.70; N, 8.20%.

2-Amino-4-(3-flourophenyl)-5-oxo-4,5-dihydropyrano [3,2-c] chromene-3-carbonitrile (Table 2, entry 15). ^{1}H NMR (DMSO-d_6, 500 Hz): δ 4.50 (s, 1H, CH), 7.01-7.14 (m, 3H, Ar), 7.31-7.41 (m, 5H, NH_2 & Ar), 7.63-6.69 (m, 1H, Ar), 7.87 (dd, J = 7.9, 1.2 Hz, 1H, Ar) ppm; ^{13}C NMR (DMSO-d_6, 125 Hz): δ 36.6, 57.5, 103.2, 112.9, 113.8, 113.9, 114.4, 114.5, 116.4, 119.0, 122.5, 123.7, 124.5, 130.3, 130.3, 132.8, 146.1, 146.2, 152.1, 153.6, 157.9, 159.5, 161.2, 163.1 ppm; IR (KBr, cm^{-1}): 3375, 3315, 3191, 2195, 1711, 1675, 1619, 1489, 1370, 1252, 1062, 763; MS (EI, 70 eV) m/z (%) = 334 (M^+, 22), 267 (13), 239 (100), 121 (21), 92 (8). Anal. Calcd. for $C_{19}H_{11}FN_2O_3$: C, 68.26; H, 3.32; N, 8.38%. Found: C, 68.35; H, 3.30; N, 8.40%.

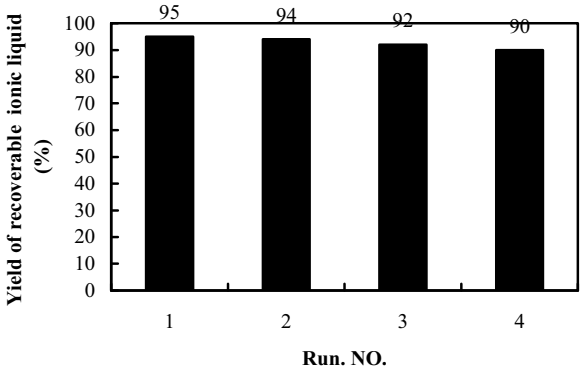


Fig. 1. The reusability of the catalyst.

2-Amino-5-oxo-4-*o*-tolyl-4,5-dihydropyrano[3,2-c] chromene-3-carbonitrile (Table 2, entry 16). ^{1}H NMR (DMSO-d_6, 500 Hz): δ 2.48 (s, 3H, CH_3), 4.73 (s, 1H, CH), 6.90-7.20 (m, 4H, Ar), 7.34 (s, 2H, NH_2), 7.41 (d, J = 8.3 Hz, 1H, Ar), 7.46 (t, J = 7.6 Hz, 1H, Ar), 7.66-7.73 (m, 1H, Ar), 7.89 (d, J = 7.8 Hz, 1H, Ar) ppm; ^{13}C NMR (DMSO-d_6, 125 Hz): δ 19.0, 32.4, 57.9, 104.5, 122.8, 116.4, 119.1, 122.3, 124.6, 126.6, 126.7, 127.8, 130.0, 132.7, 135.2, 142.2, 152.0, 153.4, 157.7, 159.5 ppm; IR (KBr, cm^{-1}): 3400, 3283, 3179, 2202, 1709, 1675, 1637, 1603, 1490, 1457, 1377, 1171, 1059, 957, 753; MS (EI, 70 eV) m/z (%) = 330 (M^+, 18), 249 (24), 240 (17), 239 (100), 121 (21). Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48%. Found: C, 72.80; H, 4.30; N, 8.50%.

2-Amino-5-oxo-4-(pyridin-2-yl)-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 17). ^{1}H NMR (DMSO-d_6, 500 Hz): δ 4.61 (s, 1H, CH), 6.26 (d, J = 3.0 Hz, 1H, Ar), 6.32-6.39 (m, 1H, Ar), 7.42-7.50 (m, 5H, NH_2 & Ar), 7.52 (s, 1H, Ar), 7.69 (t, J = 7.5 Hz, 1H, Ar), 7.85 (d, J = 7.7 Hz, 1H, Ar) ppm; ^{13}C NMR (DMSO-d_6, 125 Hz): δ 30.6, 55.3, 101.5, 106.4, 110.6, 112.8, 116.6, 118.9, 122.3, 124.6, 133.0,

142.3, 144.5, 152.1, 153.8, 154.1, 158.7, 159.3 ppm; IR (KBr, cm^{-1}): 3368, 3282, 3169, 2201, 1704, 1672, 1604, 1376, 1268, 1171, 1111, 1056, 957, 757; MS (EI, 70 eV) m/z (%) = 317 (M^+, 0.2), 306 (60), 278 (100), 239 (54), 158 (41), 121 (67), 92 (13), 63 (11). Anal. Calcd. for $C_{18}H_{11}N_3O_3$: C, 68.14; H, 3.49; N, 13.24%. Found: C, 68.20; H, 3.54; N, 13.35%.

2-Amino-4-(2,5-dimethoxyphenyl)-5-oxo-4,5-dihydro-pyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 18). ^1H NMR (DMSO-d_6, 500 Hz): δ 3.63 (s, 3H, CH_3), 3.64 (s, 3H, CH_3), 4.64 (s, 1H, CH), 6.66 (d, J = 2.3 Hz, 1H, Ar), 6.75-6.79 (m, 1H, Ar), 6.90 (d, J = 8.8 Hz, 1H, Ar), 7.25 (s, 2H, NH_2), 7.41-7.49 (m, 2H, Ar), 7.67 (t, J = 7.7 Hz, 1H, Ar), 7.89 (d, J = 7.7 Hz, 1H, Ar) ppm; ^{13}C NMR (DMSO-*d6*, 125 Hz): δ 32.6, 55.2, 56.4, 56.8, 103.1, 112.2, 112.9, 113.1, 115.7, 116.4, 119.2, 122.2, 124.5, 131.9, 132.6, 151.5, 152.0, 153.1, 153.9, 158.5, 159.4 ppm; IR (KBr, cm^{-1}): 3403, 3322, 3192, 2195, 1708, 1672, 1605, 1501, 1380, 1224, 1054, 959, 620; MS (EI, 70 eV) m/z (%) = 376 (M^+, 23), 361 (14), 345 (42), 279 (100), 239 (26), 215 (13), 121 (24). Anal. Calcd. for $C_{21}H_{16}N_2O_5$: C, 67.82; H, 4.28; N, 7.44%. Found: C, 67.92; H, 4.36; N, 7.55%.

RESULTS AND DISCUSSION

The reaction of 3-propanolamine with acetic acid is highly exothermic, and efficient cooling is essential throughout the reaction. A simple acid-base reaction occurred and formed ionic liquid, *i.e.* acetate salt of 3-propanolamine (Scheme 2).

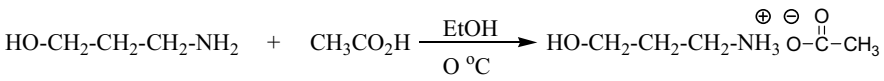
Dropwise addition of acetic acid to 3-propanolamine under continuous stirring at 0 °C, gives a viscous clear liquid which remains non-frozen when stored in a deep-freeze compartment of a refrigerator (-20 °C) for over 6 months. The liquid freezes at -88 °C, as estimated from the DSC curve. Otherwise, vigorous heat evolution may result in following dehydration of the salt to give the corresponding amide. Dehydration of the liquid salt commences around 104.67 °C, as estimated from the TGA curve. The TGA shows 95.7% of mass loss at 226.86 °C. This implies that evaporation of the dehydration product, 3-hydroxyepropyl acetamide or its decomposition products occurs at this temperature.

Conductivity of the liquid at room temperature is 0.123 ms cm^{-1}. The ionic conductivity depends largely on the temperature and rises exponentially as the temperature increases. This can be ascribed to the fast ion mobilities at elevated temperatures.

Electrochemical stability of the ionic liquid is important when redox reactions take place in such a medium. The electrochemical stability was inspected by the cyclic voltammetry. Redox stability of the ionic liquid must be imposed by the reduction potential of the ammonium cation and oxidation potential of the acetate anion. The cyclic voltammetry indicates a useful stability range of 0.1-1.28 V. The ionic liquid showed weak basic character, pH = 7.14. Some common physical characteristics of the ionic liquid have been tabulated in Table 1.

Both ^1H NMR and FT-IR spectra indicate simple salt structure of the liquid. Thus, in IR spectrum, the broad band at 3700-2300 cm^{-1} range implies typical ammonium structure. The carbonyl stretching and N-H plane bonding vibrations are observed as a combined band centered around 1628 cm^{-1}. In ^1H NMR spectra, the integral of the broad singlet in the 4.24-4.82 ppm range represents four protons belonging to the sum of ammonium and OH protons. When the spectrum was determined in D_2O as the solvent, these four protons having hydrogen bonding character disappeared. In ^{13}C NMR spectra, the carbon atom of the acetate group exhibited a singlet at 180.5 ppm.

To optimize the amount of the catalyst, the reaction of benzaldehyde (3 equiv.), malononitrile (3 equiv.), and 4-hydroxycoumarin (3 equiv.) under grinding conditions was selected as a model reaction at room temperature. The best result was obtained by causing the reaction using 6 drops (0.12 g) of 3-hydroxypropanaminium acetate HPAA at room temperature.



Scheme 2. Preparation of task-specific ionic liquid, 3-hydroxypropanaminium acetate (HPAA)

Table 1. Some Common Physical Characteristics of the Ionic Liquid, 3-Hydroxypropanaminium Acetate (HPAA)

Density	1.205 g cm^{-3} at (25 °C)
Refractive index	1.4705 at (25 °C)
conductivity	0.123 ms cm^{-1} at (25 °C)
Decomposition Temperature	226.86 °C by (TGA)
Freezing point	-88 °C by (DSC)
pH	7.14 at 25 °C, concentration: 0.2 M in water
Electrochemical stability	0.1-1.28 V

Table 2. Synthesis of 2-Amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile Derivatives in the Presence of HPAA

Entry	Aldehyde(s)	Time (min)/Yield (%)[a]	M.p. (°C)/(M.p.)[Lit]
1	Benzaldehyde	4/91	245-246/245-247[40]
2	2-Chlorobenzaldehyde	7/88	263-264/266-268[48]
3	3-Chlorobenzaldehyde	5/87	243-244/247-248[49]
4	4-Chlorobenzaldehyde	5/90	263-264/263-265[31]
5	3-Nitrobenzaldehyde	6/90	261-262/262-264[31]
6	4-Nitrobenzaldehyde	4/90	251-252/250-252[40]
7	4-Fluorobenzaldehyde	4/90	263-264/260-262[48]
8	4-Hydroxybenzaldehyde	9/92	259-260/261-262[49]
9	4-Methylbenzaldehyde	6/90	258-259/254-255[31]
10	4-Methoxybenzaldehyde	5/91	229-230/226-228[50]
11	2,3-Dichlorobenzaldehyde	4/78	282-283/280-282[31]
12	2,4-Dichlorobenzaldehyde	5/89	255-256/257-259[31]
13	cinnamaldehyde	5/88	182-185/185-188[52]
14	3-Phenylpropanal	5/89	187-188[b]
15	3-Fluorobenzaldehyde	5/88	243-244[b]
16	2-Methylbenzaldehyde	6/91	264-265[b]
17	Pyridine-2-carboxaldehyde	5/70	246-247[b]
18	2,5-Dimethoxybenzaldehyde	4/91	247-248[b]

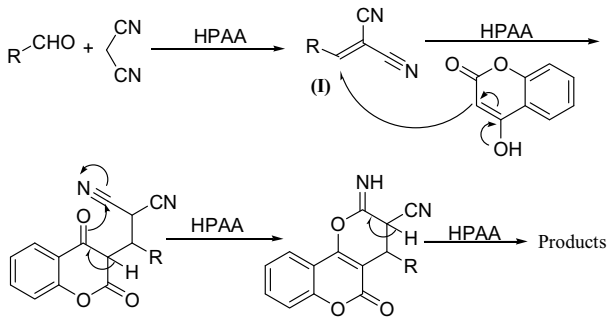
[a]Yields refer to the isolated pure products. All of the desired product(s) were characterized by comparison of their physical and spectroscopic data with those of known compounds [31,48-50,52]. [b]The spectral patterns of the new products showed similar peaks and fragmentations according to analogous compounds which reported in the literature.

Using these optimized reaction conditions, the scope and efficiency of the reactions were explored for the synthesis of a wide variety of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c] chromene-3-carbonitriles using various aldehydes, 4-hydroxycoumarin and malononitrile at room temperature. The results are summarized in Table 2.

As shown in Table 2, the direct three-component reactions worked well with cinnamaldehyde (entry 13), aliphatic aldehydes (entry 14), heterocyclic 2-pyridinecarbaldehyde (entry 17) and a variety of aryl aldehydes including the ones carrying electron-withdrawing and -donating groups such as OMe, OH, Cl, F and NO_2. The desired compounds were obtained in good to high yields. Also, we prepared 5 new analogues of this class of compounds (entries 14-18). In the case of aliphatic aldehydes such as *n*-heptaldehyde and *n*-octaldehyde, the reactions were not completed after 24 h and the desired products were obtained in low yields.

The suggested mechanism for the HEAA-catalyzed transformations is shown in Scheme 3. As reported in the literature [47], the Knoevenagel coupling of aldehydes with malononitrile gives intermediate (I) and 3-hydroxypropan-aminium acetate (HPAA) with weak basic character (Table 1, pH = 7.14) acting as a catalyst. Then, the subsequent 1,4-conjugate addition of 4-hydroxycoumarin to the intermediate (I) followed by cyclization, affords the corresponding products [51,52].

Ionic liquid (HPAA) is a weak basic catalyst and also plays a solvent role. The HPAA effects as a solvent can be explained in terms of solvophobic interactions that generate an internal pressure, which promotes the association of the reactants in a solvent cavity during the activation process and shows an acceleration of the multi-component reactions (MCRs) in comparison to the conventional solvents [40].



Scheme 3. The suggested mechanism for preparation of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile derivatives

The reusability of the catalyst was tested in the synthesis of 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile, as shown in Fig. 1. The catalyst was recovered after each run (Section 2.3), and used for checking its activity in the subsequent run. The catalyst was tested for 4 runs. It was revealed that the catalyst displayed very good reusability. In addition, the difference between the FT-IR spectrum of the reused task-specific ionic liquid compared with the newly synthesized ionic liquid, was so subtle, that confirmed no change in the structure of the catalyst.

Table 3. Comparison Results of 3-Hydroxypropanaminium Acetate (HPAA) with other Catalysts Reported in the Literature

Entry	Conditions	Time (min)/Yield (%)
1	HPAA (0.12 g), r.t.	4-9 min/70-92; present work
2	DAHP (10 mol%), H_2O/EtOH (1:1), r.t.	4 h/81-95
	(S)-Proline (10 mol%), H_2O/EtOH (1:1), Reflux	3 h/72-88
3	$H_6[P_2W_{18}O_{62}].18H_2O$ (1 mol%), H_2O: EtOH (1:1), Reflux	30-85/86-90
4	TBAB (10 mol%), H_2O, Reflux	45-60/84-93
	TBAB (10 mol%), Solvent-free, 120 °C	40/75-89
5	KF-Al_2O_3 (0.125 g), EtOH, 80 °C	4-7 h/80-90
6	Piperidine (0.5 ml), EtOH, Δ	30/70-90
7	TEBA (0.07 g), H_2O, 90 °C	7-18 h/85-96

To demonstrate the effectiveness of the present work in comparison with the previously reported results, we compared the results of diammonium hydrogen phosphate and (S)-proline [29], triethylbenzylammonium chloride [45], KF-Al_2O_3 [46], piperidine [47], $H_6[P_2W_{18}O_{62}]$ $18H_2O$ [48] and tetrabutylammonium bromide [49] in the synthesis of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbo-nitriles derivatives. As shown in Table 3, HPAA was found to be an effective catalyst with respect to reaction time, yield, and the resulting products.

CONCLUSIONS

In summary, the new ionic liquid exhibited a low melting temperature (-88 °C) which seems to be promising for use in low temperature reactions. In addition, showing electrochemical stability (0.1-1.28 V) and being obtainable from commercially available low-cost chemicals, this ionic liquid is expected to be useful as solvent for various reactions. Moreover, an efficient protocol for the one-pot preparation of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbo-nitriles from the three-component condensation reaction of 4-hydroxycoumarin, aldehydes and malononitrile using a room temperature task-specific ionic liquid, 3-hydroxypropan-aminium acetate (HPAA) as a reusable catalyst under grinding conditions was described.

ACKNOWLEDGEMENTS

The authors are thankful to the Sistan and Baluchestan University Research Council for the partial support of this work.

REFERENCES

[1] A. Domling, Chem. Rev. 106 (2006) 17.
[2] I. Ugi, Adv. Synth. Catal. 339 (1997) 499.
[3] N.K. Terret, M. Gardener, D.W. Gordon, R.J. Kobylecki, J. Steele, Tetrahedron 51 (1995) 8135.
[4] A. Domling, I. Ugi, Angew. Chem., Int. Ed. 39 (2000) 3168.
[5] A. Shaabani, R. Ghadari, S. Ghasemi, M. Pedarpour, A.H. Rezayan, A. Sarvary, S.W. Ng, J. Comb. Chem. 11 (2009) 956.
[6] D. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 74 (2002) 157.
[7] W. Lu, A.G. Fadaev, B. Qu, E. Smela, B.R. Mattes, J. Ding, G.M. Spinks, J. Mazurkiewicz, D. Zhou, G.G. Wallace, D.R. MacFarlane, S.A. Forsyth, M. Forsyth, Science 297 (2002) 983.
[8] H. Olivier-Bourbigou, L. Magna, D. Morvan, Appl. Catal. A-Gen. 373 (2010) 1.
[9] P. Wasserscheid, W. Keim, Angew. Chem., Int. Ed. 39 (2000) 3772.
[10] J. Dupont, R.F. Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667.
[11] J.S. Wilkes, Green Chem. 4 (2002) 73.
[12] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, Germany, 2003.
[13] D. Fang, Q.-R. Shi, J. Cheng, K. Gong, Z.-L. Liu, Appl. Catal. A-Gen. 345 (2008) 158.
[14] A. Chrobok, S. Baj, W. Pudło, A. Jarzebski, Appl. Catal. A-Gen. 366 (2009) 22.
[15] S. Luo, X. Mi, L. Zhang, S. Liu, H. Xu, J.-P. Cheng, Angew. Chem., Int. Ed. 45 (2006) 3093.
[16] K. Fukumoto, M. Yoshizawa, H. Ohno, J. Am. Chem. Soc. 127 (2005) 2398.
[17] Q. Yao, Y. Zhang, Angew. Chem., Int. Ed. 42 (2003) 3395.
[18] G. Song, Y. Cai, Y. Peng, J. Comb. Chem. 7 (2005) 561.
[19] J.-C. Xiao, B. Twamley, J.M. Shreeve, Org. Lett. 6 (2004) 3845.
[20] J.D. Holbrey, W.M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R.D. Rogers, Chem. Commun. (2003) 28.
[21] A.K. Bose, S. Pednekar, S.N. Ganguly, G. Chakrabortyb, M.S. Manhas, Tetrahedron Lett. 45 (2004) 8351.
[22] F. Toda, K. Tanaka, A. Sekikawa, J. Chem. Soc., Chem. Commun. (1987) 279.
[23] K. Tanaka, Solvent-Free Organic Synthesis, Wiley-VCH, Weinheim, 2003.
[24] G.R. Green, J.M. Evans, A.K. Vong, in: A.R. Katritzky, C.W. Rees, E.F. Scriven (Eds.), In Comprehensive Heterocyclic Chemistry II, 5, Pergamon Press, Oxford,

1995, p. 469.
[25] W.O. Foye, Principi Di Chemica Frmaceutica, Piccin, Padova, Italy, 1991.
[26] A. Burgard, H.-J. Lang, U. Gerlach, Tetrahedron 55 (1999) 7555.
[27] J.M. Evans, C.S. Fake, T.C. Hamilton, R.H. Poyser, G.A. Showell, J. Med. Chem. 27 (1984) 1127.
[28] J.M. Evans, C.S. Fake, T.C. Hamilton, R.H. Poyser, E.A. Watts, J. Med. Chem. 26 (1983) 1582.
[29] D. Arnesto, W.M. Horspool, N. Martin, A. Ramos, C. Seaone, J. Org. Chem. 54 (1989) 3069.
[30] R.M. Shaker, Pharmazie 51 (1996) 148.
[31] S. Abdolmohammadi, S. Balalaie, Tetrahedron Lett. 48 (2007) 3299.
[32] M. Kidwai, S. Saxena, Synth. Commun. 36 (2006) 2737.
[33] C. Wiener, C.H. Schroeder, B.D. West, K.P. Link, J. Org. Chem. 27 (1962) 3086.
[34] B.H. Rizkalla, A.D. Broom, J. Org. Chem. 37 (1972) 3980.
[35] A.D. Broom, J.L. Shim, G.L. Anderson, J. Org. Chem. 41 (1976) 1095.
[36] V.K. Ahluwalia, R. Kumar, A. Khurana, R. Bhatla, Tetrahedron 46 (1990) 3953.
[37] E.V. Stoyanov, I.C. Ivanov, D. Heber, Molecules 5 (2000) 19.
[38] P. Srivastava, A.S. Saxena, V.J. Ram, Synthesis (2000) 541.
[39] Y.-M. Ren, C. Cai, Catal. Commun. 9 (2008) 1017.
[40] A. Shaabani, S. Samadi, Z. Badri, A. Rahmati, Catal. Lett. 104 (2005) 39.
[41] H.R. Shaterian, A. Hosseinian, M. Ghashang, Tetrahedron Lett. 49 (2008) 5804.
[42] H.R. Shaterian, A. Hosseinian, H. Yarahmadi, M. Ghashang, Lett. Org. Chem. 5 (2008) 290.
[43] H.R. Shaterian, A. Hosseinian, M. Ghashang, Synth. Commun. 38 (2008) 3766.
[44] H.R. Shaterian, A. Hosseinian, M. Ghashang, Can. J. Chem. 86 (2008) 376.
[45] H.R. Shaterian, A. Hosseinian, M. Ghashang, ARKIVOC ii (2009) 59.
[46] H.R. Shaterian, A. Hosseinian, M. Ghashang, Synth. Commun. 39 (2009) 2560.
[47] N. Bicak, J. Mol. Liq. 116 (2005) 15.
[48] S. Da-Qing, W. Jing, Z. Qi-Ya, W. Xiang-Shan, Chin. J. Org. Chem. 26 (2006) 643.
[49] W. Xiang-Shan, Z. Zhao-Sen, S. Da-Qing, W. Xian-Yong, Z. Zhi-Min, Chin. J. Org. Chem. 25 (2005) 1138.
[50] A.M. El-Agrody, M.S.A. El-Latif, A.H. Fakery, A.H. Bedair, J. Chem. Res (S) (2000) 26.
[51] M.M. Heravi, B. Alimadadi-Jani, F. Derikvand, F.F. Bamoharram, H.A. Oskooie, Catal. Commu. 10 (2008) 272.
[52] J.M. Khurana, S. Kumar, Tetrahedron lett. 50 (2009) 4125.