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ORIGINAL PAPER

Synthesis of pyranopyrazoles, benzopyrans, amino-2-chromenes and dihydropyrano[*c*]chromenes using ionic liquid with dual Brønsted acidic and Lewis basic sites

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An efficient ionic liquid with both Brønsted acidic and Lewis basic sites, namely 1,4-dimethyl-1-(4-sulphobutyl)piperazinium hydrogen sulphate (*IL1*), was synthesised and characterised. *IL1* is a "green", homogeneous and reusable catalyst for: *i*) the synthesis of pyranopyrazoles (*Va–Vj*) and benzopyrans (*VIa–VIj* and *VIIa–VIIf*) at ambient temperature under solvent-free conditions and *ii*) the synthesis of amino-2-chromenes (*VIIIa–VIIIi* and *IXa–IXi*) and dihyropyrano[*c*]chromenes (*Xa–Xi*) at 80 °C under solvent-free conditions. The reactions were rapid with excellent product yields. In addition, the double Brønsted acid, 1,4-dimethyl-1,4-bis(4-sulphobutyl)piperazinium hydrogen sulphate (*IL2*), was prepared to evaluate the cooperation efficiency of their Brønsted acidic and Lewis basic sites as compared with the double Brønsted acidic sites in *IL1*.

Keywords: ionic liquid, synthesis, pyranopyrazoles, benzopyrans, amino-2-chromenes, dihydropyrano[*c*]chromenes

Introduction

Ionic liquids (ILs) have received increased attention as "green" solvents and environmentally friendly catalysts. ILs possess remarkable properties; they are non-flammable, non-corrosive and are liquid at ambient temperature with low vapour pressure (Dupont et al., 2002; Sheldon, 2001; Welton, 1999). ILs successfully have been used as dual solvent-catalysts in many reactions since they possess the advantages of both solid and liquid acids such as stability in water and air, easy separation and reusability (Gupta et al., 2007).

More specifically, research efforts into ILs have been directed towards Brønsted acidic ILs. Some recent work focuses on chloride ILs as strong acids in various organic reactions. However, further developments are required to decrease the sensitivity of the catalysts to water. The functionalised sulphoalkyl groups have been used effectively and have attracted increased attention with a view to overcoming these problems (Cole et al., 2002). They have a high catalytic activity and are non-volatile, non-corrosive and can be used as dual solvents and catalysts (Firouzabadi et al., 2006; Kamal & Chouhan, 2004; Sugimura et al., 2007; Wu et al., 2004). Also, the base catalysts can be used in different organic syntheses (Bartók et al., 1999; Niknam et al., 2013; Yokoi et al., 2012), and different basic ILs have recently been prepared (Davis, 2004).

In addition, modern syntheses need to be rapid and efficient, in order to avoid toxic solvents and tedious procedures (Banerjee & Sereda, 2009; Banerjee et al., 2011). Multi-component reactions (MCRs) are, therefore, ideally suited for this purpose and have been shown to be valuable methods in organic and medicinal chemistry (Bräse et al., 2002; Ganem, 2009). Hence, the development of MCRs in the presence of ILs would be most beneficial, both economically and environmentally.

Furthermore, many biological systems have the pyranopyrazole structure and many methods for their

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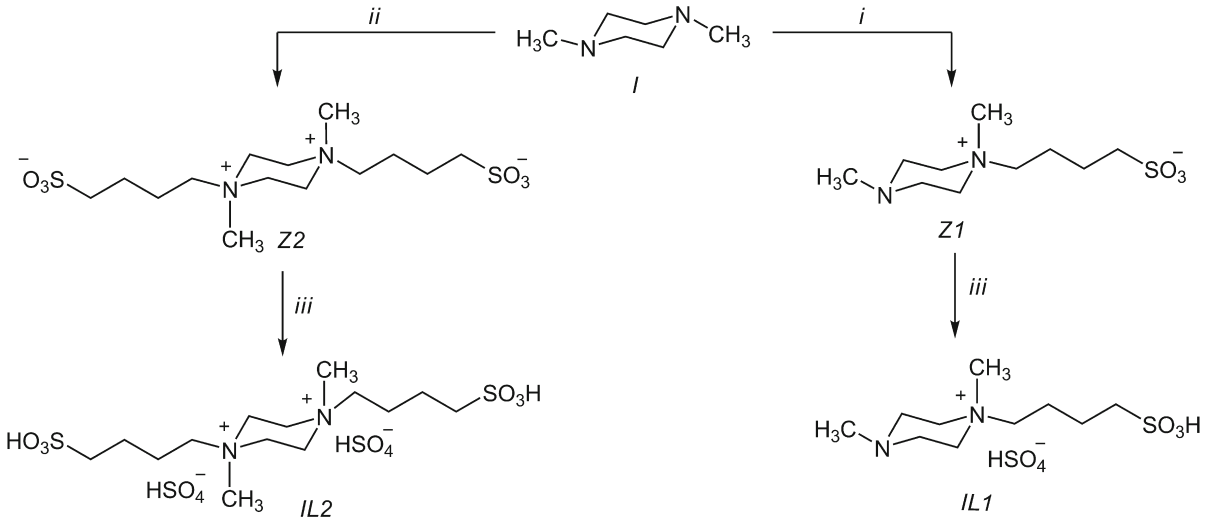

Fig. 1. Synthesis of two novel ionic liquids. Reaction conditions: *i*) 1,4-butane sultone (*II*) (1 mmol), solvent-free, ambient temperature, 10 h; *ii*) *II* (excess), toluene, reflux, 60 h; *iii*) H_2SO_4, 80 °C.

syntheses have been reported (Bonsignore et al., 1993). Benzopyran derivatives are found in a variety of important biological products such as pheromones, antibiotics and antimicrobial agents (Al-Haiza et al., 2003; Darbarwar & Sundaramurthy, 1982). A variety of methods including the use of microwave (Al'-Assar et al., 2002), [bmim]OH (Ranu et al., 2008), DMF (Singh et al., 1996), acetic acid (Wang et al., 2003), and (*S*)-proline (Balalaie et al., 2006) have been used in the syntheses of benzopyrans.

Due to the distinctive properties of 2-amino-2-chromenes and dihydropyrano[*c*]chromenes, which can be used in spasmolytic, diuretic, anticancer, anticoagulant and anti-HIV treatments, they have attracted a great deal of research. They have also been shown to act as cognitive enhancers for the treatment of neurodegenerative diseases including Parkinson's disease, Down's syndrome, schizophrenia, Alzheimer's disease and AIDS-associated dementia (Hafez et al., 1987; Konkoy et al., 2000). Recently, several catalysts such as KF/Al_2O_3 (Ballini et al., 2000), basic alumina (Maggi et al., 2004), tetrabutylammonium bromide (TBAB) (Khurana & Kumar, 2009) potassium phthalimide (Kiyani & Ghorbani, 2014) and sodium dodecyl sulphate (Mehrabi & Abusaidi, 2010) were applied to synthesise chromene derivatives. However, some of these procedures have been limited by the use of toxic organic solvents, expensive catalysts and tedious workup.

In continuation of our researches into the synthesis of different oxygen- and nitrogen-containing heterocycles (Habibi et al., 2007, 2013; Habibi & Shamsian, 2013), this paper describes the synthesis of novel and efficient ionic liquids *IL1* and *IL2* (Fig. 1) for the production of different pyranopyrazoles, benzopyrans, amino-2-chromenes and dihyropyrano[*c*]chromenes.

Experimental

All chemicals purchased from the Aldrich and Merck chemical companies were of high-grade quality and used without further purification. Melting points were taken in open capillary tubes using a BUCHI 510 melting point apparatus and are uncorrected. NMR spectra were recorded in DMSO-d_6 using Bruker AM 400, Bruker AM 300 and Jeol FT 90 MHz spectrometers. FTIR spectra (KBr discs or Nujol techniques) were recorded on a Perkin–Elmer 781 spectrometer. Mass spectra (70 eV) were obtained using a Shimadzu GC-MS-QP 1100 EX instrument.

General procedures for synthesis of IL1 and IL2

1,4-Dimethylpiperazine (*I*) (10.0 mmol, 1.4 mL) was added to 1,4-butane sultone (*II*) (10.0 mmol, 1.0 mL) and the mixture was stirred under solvent-free conditions at ambient temperature for 10 h. The white solid zwitterion *Z1* (formed early in the reaction) was filtered, washed with diethyl ether (3 × 5 mL) to remove any impurities and dried under diminished pressure at 110 °C (yield 95 %). Sulphuric acid was added to *Z1* (mole ratio of 1 : 1) and the mixture was stirred at 80 °C for 6 h to form *IL1* (yield of 92 %). The *IL1* so obtained was then washed with ether (3 × 5 mL) to remove the non-ionic residues and dried under diminished pressure at 110 °C.

Analogously, *I* (10.0 mmol, 1.4 mL) was added to *II* (50.0 mmol, 5 mL) in toluene (5 mL) and the mixture was heated under reflux for 60 h. The white solid zwitterion *Z2* was filtered, washed with diethyl ether (3 × 5 mL) to remove any impurities and dried under diminished pressure at 110 °C (yield of 92 %).

Sulphuric acid was added to *Z2* (mole ratio of 2 : 1)

Table 1. Optimisation of reaction conditions for preparation of *Z1*, *Z2*, *IL1* and *IL2*

Entry	*I*/*II* ratio	Conditions	Zwitterion/yield[a] /%	Ionic liquid/yield[a] /%
1	1 : 1	Solvent-free, r.t., 5 h	*Z1*/70	–
2	1 : 1	Solvent-free, r.t., 10 h	*Z1*/95	*IL1*/92
3	1 : 1	Solvent-free, r.t., 10 h	*Z1*/95	–
4	1 : 5	Solvent-free, r.t., 10 h	*Z1*/95	–
5	1 : 5	Toluene, reflux, 24 h	*Z1*/96	–
6	1 : 5	Toluene, reflux, 60 h	*Z2*/92	*IL2*/90

a) Isolated yields; r.t. refers to ambient temperature.

and the mixture was stirred at 80 °C for 8 h. The *IL2* thus obtained (yield of 90 %) was then washed repeatedly with diethyl ether (3 × 5 mL) to remove non-ionic residues and dried under diminished pressure at 110 °C.

General procedure for synthesis of pyranopyrazoles and benzopyrans

To a mixture of aldehyde (1.0 mmol), malononitrile (1.0 mmol) and 3-methyl-1-phenyl-2-pyrazolin-5-one/dimedone/1,3-cyclohexane-dione (1.0 mmol), *IL1* (0.03 mmol, 0.01 g) was added as catalyst and the reaction carried out at ambient temperature under solvent-free conditions for a certain time. The contents of the flask solidified, the solid was washed with H_2O (2 × 5 mL), filtered and the crude products purified by recrystallisation from ethanol/water (φ_r = 7 : 3).

All products were characterised by comparing their physical and spectral data with those of known compounds.

General procedure for synthesis of chromenes

The reaction of aldehyde (1 mmol), malononitrile (1 mmol), α- or β-naphthol or 4-hydroxycoumarin (1 mmol) and *IL1* (0.03 mmol, 0.01 g) was performed at 80 °C under solvent-free conditions for a certain time (monitored by TLC) until the contents of the flask solidified. The reaction mixture was cooled to ambient temperature, the solid was washed with H_2O (2 × 5 mL), filtered and the crude product was recrystallised from ethanol/water (φ_r = 7 : 3).

The catalyst-containing aqueous filtrate was reused in subsequent runs without further purification.

Results and discussion

1,4-Dimethylpiperazine (*I*) and 1,4-butane sultone (*II*) were used under different conditions in order to synthesise *IL1* and *IL2* (Fig. 1). In the first step, the reaction conditions were optimised for the preparation of zwitterions, *Z1* and *Z2* (Table 1). For *Z1*, the optimal conditions were found to be the 1 : 1 mole ratio of *I* and *II* under solvent-free conditions and ambient temperature (entry 2). It was expected that

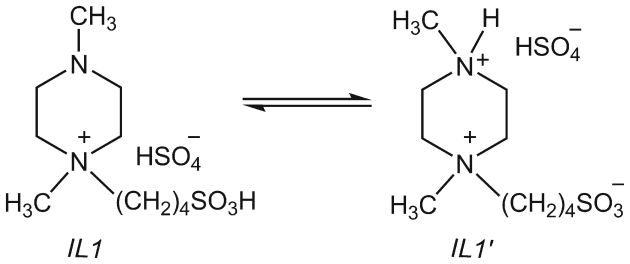

Fig. 2. Possible formation of *IL1* and *IL1′*.

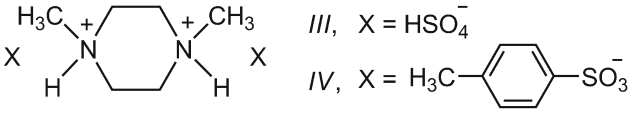

Fig. 3. Structure of acidic catalysts *III* and *IV*.

zwitterion *Z2* would be produced with a mole ratio of 1 : 2; however, the ring conformational flexibility of *Z1* which related to the pyramidal properties of the piperazine cycle, apparently inhibited its attack to *II*, hence more sultone molecules were required. Even at a 1 : 5 mole ratio, *Z2* was not formed at ambient temperature, but it was eventually formed by changing the conditions to a 1 : 5 mole ratio in refluxed toluene (entry 6). Compounds *IL1* and *IL2* were synthesised from purified *Z1* and *Z2*, respectively, by the addition of the appropriate amount of sulphuric acid at 80 °C (Table 1).

During the protonation stage of *Z1* with sulphuric acid, the equilibrium would have occurred for *IL1* and both *IL1* and *IL1′* could theoretically be formed (Fig. 2).

To investigate whether the protonated nitrogen could catalyse the reaction or the SO_3H group, two acidic catalysts were synthesised. Sulphuric acid or *p*-toluenesulphonic acid (PTSA) (2 mmol) were added to *I* (1 mmol) to prepare *III* and *IV* (Fig. 3). The ^{1}H NMR spectrum of *I* showed two peaks at δ 1.57 (6H, 2 × CH_3) and δ 1.72 (8H, 4 × CH_2) while the ^{1}H NMR spectrum of the new compound *III* showed three peaks at δ: 2.48 (6H, 2 × CH_3), 3.13 (8H, 4 × CH_2) and 8.63 (2H, NH). The signals at δ 1.57–2.48 and δ

Table 2. Effect of different amounts of catalyst on two sets of reactions

Entry	Catalyst/mole %	Reaction conditions A[a]			Reaction conditions B[b]		
		Time/min	Yield[c]/%	TF[d]/min^{-1}	Time/min	Yield[c]/%	TF[d]/min^{-1}
1	*IL1*/3	4	96	8	5	94	6.3
2	*IL1*/4	4	95	6	5	95	4.7
3	*IL1*/5	4	94	4.7	5	93	3.7
4	*IL2*/3	6	92	5.2	5	92	6.0
5	*III*/5	15	76	1.7	20	68	0.7
6	*IV*/5	15	78	1.7	20	70	0.7
7	No catalyst	30	–	–	30	–	–

a) 4-Chlorobenzaldehyde (1.0 mmol), malononitrile (1.0 mmol), dimedone (1.0 mmol), ambient temperature, solvent-free; *b*) 4-chlorobenzaldehyde (1.0 mmol), malononitrile (1.0 mmol), β-naphthol (1.0 mmol), 80 °C, solvent-free; *c*) isolated yields; *d*) TF = turnover frequency.

Table 3. Spectral data of zwitterions and ionic liquids

Compound	Spectral data
Z1	IR (KBr), $\tilde{\nu}$/cm^{-1}: 898, 1039 (SO_3), 1179 (C—N) ^{1}H NMR (400 MHz, D_2O), δ: 1.82–1.88 (m, 2H, CH_2), 1.94–2.02 (m, 2H, CH_2), 2.39 (s, 3H, NCH_3), 2.82–2.92 (m, 4H, $H_{piperazinium}$), 3.00 (t, J = 7.6 Hz, 2H, NCH_2), 3.14 (s, 3H, NCH_3), 3.45–3.50 (m, 6H, SCH_2 and $H_{piperazinium}$) ^{13}C NMR (100 MHz, D_2O), δ: 20.18, 21.38, 44.00, 46.98, 47.53, 50.30, 59.75, 63.92 MS (70 eV), m/z (I_r/%): 250 (M^+, 5), 173 (100), 157 (12), 127 (25), 114 (14)
IL1	IR (Nujol), $\tilde{\nu}$/cm^{-1}: 901, 1040, (SO_3), 1182 (C—N(, 3100–3500 (br, O—H) ^{1}H NMR (400 MHz, D_2O), δ: 1.72–1.78 (m, 2H, CH_2), 1.84–1.92 (m, 2H, CH_2), 2.29 (s, 3H, NCH_3), 2.74–2.80 (m, 4H, $H_{piperazinium}$), 2.90 (t, J = 7.6 Hz, 2H, NCH_2), 3.04 (s, 3H, NCH_3), 3.35–3.39 (m, 6H, SCH_2 and $H_{piperazinium}$) ^{13}C NMR (100 MHz, D_2O): δ: 19.82, 21.03, 43.64, 46.61, 47.18, 49.93, 53.60, 59.40, 63.56 MS (70 eV), m/z (I_r/%): 348 (M^+, 5), 251 (25), 170 (12), 157 (8), 129 (22), 114 (100)
Z2	IR (KBr), $\tilde{\nu}$/cm^{-1}: 898, 1041 (SO_3), 1179 (C—N) ^{1}H NMR (400 MHz, D_2O), δ: 1.81–1.90 (m, 4H, CH_2), 1.89–2.09 (m, 4H, CH_2), 3.01 (t, J = 7.6 Hz, 4H, NCH_2), 3.35 and 3.36 (6H, 2 × NCH_3), 3.65–3.70 (m, 4H, SCH_2), 3.93–4.02 (m, 8H, $H_{piperazinium}$) ^{13}C NMR (100 MHz, D_2O), δ: 20.16, 20.91, 45.33, 49.81, 53.85, 67.33 MS (70 eV), m/z (I_r/%): 386 (M^+, 5), 228 (20), 187 (10), 114 (12), 55 (100)
IL2	IR (Nujol), $\tilde{\nu}$/cm^{-1}: 905, 1050 (SO_3), 1200 (C—N), 2680–3550 (br, O—H) ^{1}H NMR (400 MHz, D_2O), δ: 1.72-1.80 (m, 4H, CH_2), 1.91-1.95 (m, 4H, CH_2), 2.91 (t, J = 7.6 Hz, 4H, NCH_2), 3.25 and 3.26 (6H, 2 × NCH_3), 3.55–3.60 (m, 4H, SCH_2), 3.83–3.92 (m, 8H, $H_{piperazinium}$) ^{13}C NMR (100 MHz, D_2O), δ: 20.05, 20.83, 46.32, 49.76, 53.82, 66.01

1.72–3.13 as well as the new peak at δ 8.63 indicated the formation of *III*. In addition, the ^{1}H NMR spectrum of *IV* (δ: 2.22 (s, 3H, NCH_3), 2.83 (s, 3H, CH_3), 3.43 (s, 4H, 2 × CH_2), 7.15 (d, 2H, H_{aryl}) and 7.52 (d, 2H, H_{aryl}) confirms its formation.

Unfortunately, catalysts *III* and *IV* were not capable of promoting the synthesis of two different sets of pyran derivatives and the yields were appropriately low (Table 2). Accordingly, it was concluded that the protonated nitrogen could not promote the reactions, apparently for the following two reasons: *i*) the conjugate acid of a strong base is a weak acid and *ii*) the steric hindrance of the tertiary amine apparently prevents the acidic proton from catalysing the reactions. It was noted that the prepared ionic liquids with the long sulphonated alkyl chain were more active in catalysing the reactions.

Structure confirmation of ionic liquids

The structures of compounds *Z1*, *Z2*, *IL1*, and *IL2* were confirmed by IR, NMR and mass spectra (Table 3). The presence of the SO_3H group was indicated by the broad peaks at 3500–3100 cm^{-1} and 3550–2680 cm^{-1} in the IR spectra of *IL1* and *IL2*. In addition, the peaks at 1040 cm^{-1} for *IL1* and 1050 cm^{-1} for *IL2* corresponded to the vibrational modes of the O—SO_2 bonds. The ^{1}H NMR spectra showed two separated singlets of NCH_3 at δ 2.29 and δ 3.04 for *IL1* and a split singlet at δ 3.25 and δ 3.26 for *IL2*.

As can be seen from the diagrams of thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG) of *IL1* and *IL2* (Figs. 4 and 5), both ionic liquids show high thermal stability with thermal decomposition of above 270 °C.

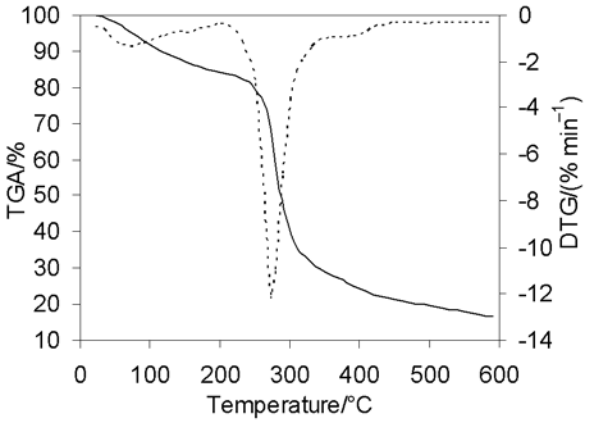

Fig. 4. TGA/DTG diagram (TGA curve – solid line; DTG curve – dashed line) of *IL1*.

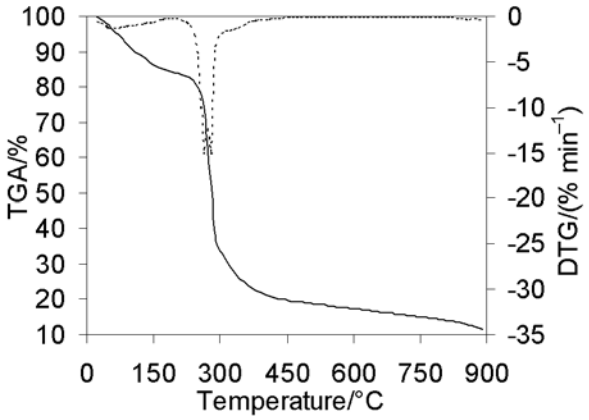

Fig. 5. TGA/DTG diagram (TGA curve – solid line; DTG curve – dashed line) of *IL2*.

Efficiency and applications of ionic liquids

Two sets of model reactions were selected to optimise the reaction conditions (Table 2): reaction of 4-chlorobenzaldehyde (1.0 mmol) and malononitrile (1.0 mmol) with dimedone (1.0 mmol) at ambient temperature and under solvent-free conditions (reaction conditions A) and reaction of 4-chlorobenzaldehyde (1.0 mmol) and malononitrile (1.0 mmol) with β-naphthol (1 mmol) at 80 °C under solvent-free conditions (reaction conditions B). According to Table 2, *IL1* is an effective catalyst for the synthesis of pyranopyrazoles, benzopyrans and amino-2-chromenes. The best yield was obtained with 0.03 mmol of *IL1* (entry 1) and increasing the amount of the catalyst had no significant effect on the yield or time (entries 2 and 3). Also, the model reactions were carried out with *IL2* (entry 4); although the results were acceptable with high yields, it was decided to restrict the study to the use of *IL1* since preparation of the zwitterion *Z1*, which is an intermediate for *IL1,* requires less time and lower concentrations of *II* and is synthesised at ambient temperature, in contrast with preparation of the zwitterion *Z2*, as an intermediate for *IL2* which requires higher concentrations of *II* as well as reflux conditions. In addition, the use of *III* and *IV* resulted in long reaction times and low yields (Table 2, entries 5 and 6). As shown in entry 7, in the absence of the catalyst, the yield was very low.

The catalytic efficiency can be described by the turnover frequency (TF) (Jiménez-González & Constable, 2011), hence the TF of all the catalysts were calculated (Table 2). *IL1* had the highest TF, indicating a greater efficiency than the other catalysts.

Four different categories of oxygen- and nitrogen-containing heterocycles were synthesised in the presence of *IL1* (Fig. 6): *i*) pyranopyrazoles were synthesised by the reaction of different aldehydes (RCHO), malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one (*V*) at ambient temperature and under solvent-free conditions; *ii*) benzopyrans were synthesised by the reaction of different aldehydes (RCHO), malononitrile and dimedone (*VI*) or 1,3-cyclohexanedione (*VII*) at ambient temperature and solvent-free conditions; *iii*) amino-4*H*-chromenes were synthesised by the reaction of different aldehydes (RCHO), malononitrile and α-naphthol (*VIII*) or β-naphthol (*IX*) at 80 °C and under solvent-free conditions; *iv*) dihyropyrano[*c*]chromenes were synthesised by the reaction of different aldehydes (RCHO), malononitrile and 4-hydroxycoumarin (*X*) at 80 °C and under solvent-free conditions.

The experimental procedure was highly efficient, convenient, rapid and tolerated a variety of functional groups under different reaction conditions. As shown by the synthesis of pyranopyrazoles (*Va–Vj*) and benzopyrans (*VIa–VIj* and *VIIa–VIIf*), the aromatic aldehydes carrying either electron-donating or electron-withdrawing substituents reacted efficiently affording excellent yields (Table 4).

All the synthesised compounds are known and were characterised by comparing their melting points and spectral data with authentic samples.

In addition, amino-2-chromenes (*VIIIa–VIIIi*, *IXa–IXi*) and 3,4-dihydropyrano[*c*]chromenes (*Xa–Xi*) were efficiently synthesised in the presence of *IL1* (Table 5).

All the synthesised compounds are known and were characterised by comparing their melting points and spectral data with authentic samples.

Tables 4 and 5 show that the reactions were more rapid with aromatic aldehydes bearing the electron-withdrawing groups such as nitro or halogen, while the reactions were slower with those containing the electron-donating groups such as methyl or methoxy. Electron-withdrawing groups decrease the electron density on the carbon of the carbonyl group, facilitating the nucleophilic attack, while the converse is true for the electron-donating groups.

The main advantages of this protocol are the sim-

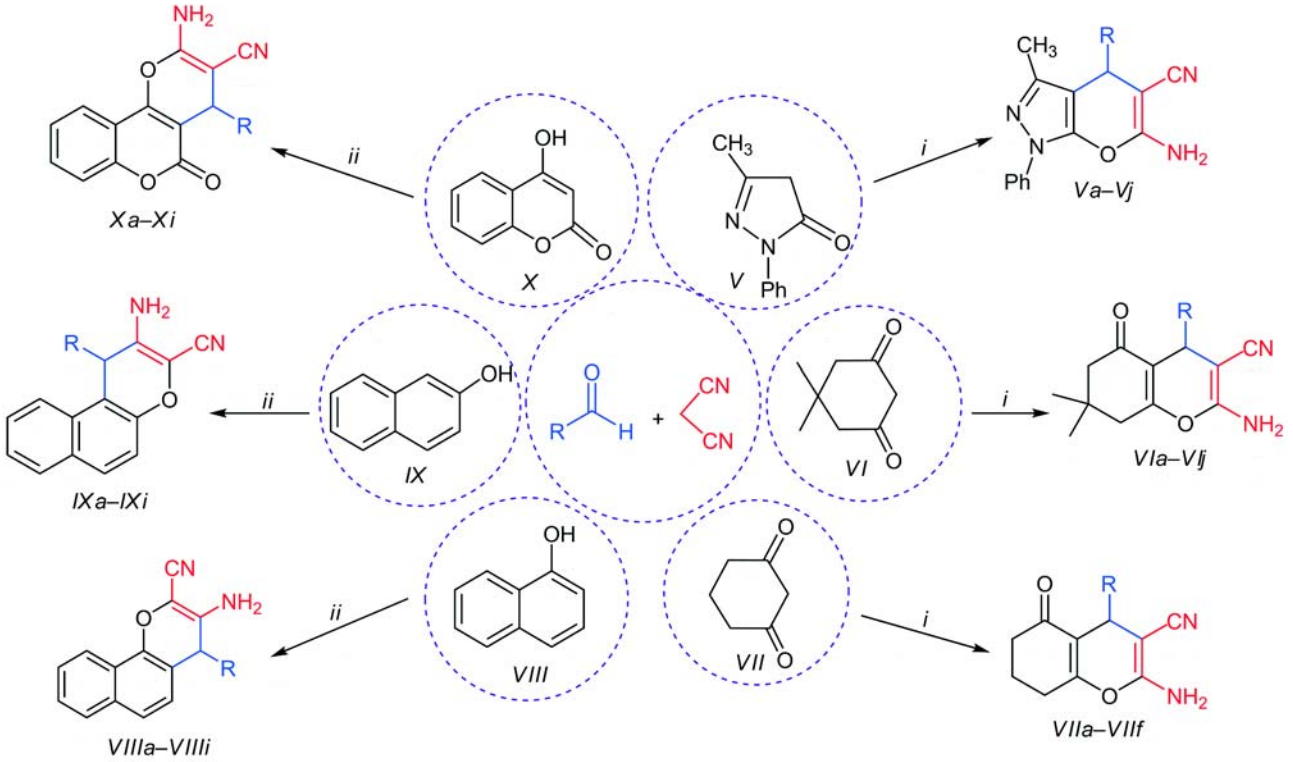

Fig. 6. Synthesis of various pyran and chromene derivatives. Reaction conditions: *i*) *IL1* (3 mole %), solvent-free, ambient temperature; *ii*) *IL1* (3 mole %), solvent-free, 80 °C.

Table 4. Synthesis of pyranopyrazoles (*Va–Vj*) and benzopyrans (*VIa–VIj* and *VIIa–VIIf*) from aldehyde RCHO, malononirile and cyclic ketone *V* or *VI* or *VII* in the presence of *IL1* (see Fig. 6)

Entry	R	Ketone	Product[a]	Time/min	Yield[b]/%
1	C_6H_5	*V*	*Va*	10	90
2	4-Cl-C_6H_4	*V*	*Vb*	8	92, 92, 90, 89[c]
3	4-F-C_6H_4	*V*	*Vc*	12	90
4	2,4-Cl_2-C_6H_3	*V*	*Vd*	8	93
5	3-Cl-C_6H_4	*V*	*Ve*	13	90
6	3-NO_2-C_6H_4	*V*	*Vf*	10	92
7	2-Naphthyl	*V*	*Vg*	15	90
8	4-Ph-C_6H_4	*V*	*Vh*	15	89
9	4-(O=CH)-C_6H_4	*V*	*Vi*	20	90
10	3-EtO-4-HO-C_6H_3	*V*	*Vj*	15	88
11	C_6H_5	*VI*	*VIa*	5	96
12	4-Me-C_6H_4	*VI*	*VIb*	10	88
13	2-Cl-C_6H_4	*VI*	*VIc*	4	93
14	4-Cl-C_6H_4	*VI*	*VId*	4	96, 96, 95, 93[c]
15	4-MeO-C_6H_4	*VI*	*VIe*	10	89
16	4-F-C_6H_4	*VI*	*VIf*	7	90
17	2,4-Cl_2-C_6H_3	*VI*	*VIg*	3	96
18	3-NO_2-C_6H_4	*VI*	*VIh*	2	92
19	2-NO_2-C_6H_4	*VI*	*VIi*	5	90
20	1-Naphthyl	*VI*	*VIj*	10	88
21	2,4-Cl_2-C_6H_3	*VII*	*VIIa*	5	92
22	4-MeO-C_6H_4	*VII*	*VIIb*	7	85
23	3-NO_2-C_6H_4	*VII*	*VIIc*	4	90
24	4-Me-C_6H_4	*VII*	*VIId*	5	87
25	4-Cl-C_6H_4	*VII*	*VIIe*	3	93, 91, 90, 89[c]
26	2-Cl-C_6H_4	*VII*	*VIIf*	5	88

a) See Fig. 6; *b*) isolated yiels; *c*) isolated yields from recovered *IL1* used in four successive runs.

Table 5. Synthesis of amino-2-chromenes (*VIIIa–VIIIi*, *IXa–IXi*) and dihydropyrano[*c*]chromenes (*Xa–Xi*) from aldehyde RCHO, malononitrile and aromatic hydroxy compounds (ArOH) *VIII* or *IX* or *X* in the presence of *IL1* (see Fig. 6)

Entry	R	ArOH	Product[a]	Time/min	Yield[b]/%
1	C_6H_5	*VIII*	*VIIIa*	3	94
2	2-Furyl	*VIII*	*VIIIb*	9	91
3	4-HO-C_6H_4	*VIII*	*VIIIc*	13	82
4	4-Cl-C_6H_4	*VIII*	*VIIId*	2	94, 94, 92, 90[c]
5	4-MeO-C_6H_4	*VIII*	*VIIIe*	7	89
6	2-Cl-C_6H_4	*VIII*	*VIIIf*	4	90
7	2,4-Cl_2-C_6H_3	*VIII*	*VIIIg*	2	94
8	3-NO_2-C_6H_4	*VIII*	*VIIIh*	2	95
9	4-Me-C_6H_4	*VIII*	*VIIIi*	8	87
10	C_6H_5	*IX*	*IXa*	4	95
11	2-Furyl	*IX*	*IXb*	12	88
12	4-Me-C_6H_4	*IX*	*IXc*	10	86
13	4-Cl-C_6H_4	*IX*	*IXd*	3	94, 93, 91, 89[c]
14	2-Cl-C_6H_4	*IX*	*IXe*	4	95
15	4-MeO-C_6H_4	*IX*	*IXf*	8	88
16	4-F-C_6H_4	*IX*	*IXg*	5	90
17	2,4-Cl_2-C_6H_3	*IX*	*IXh*	3	94
18	3-NO_2-C_6H_4	*IX*	*IXi*	2	93
19	C_6H_5	*X*	*Xa*	6	94
20	4-Cl-C_6H_4	*X*	*Xb*	5	95, 93, 91,89[c]
21	4-Br-C_6H_4	*X*	*Xd*	6	91
22	3-NO_2-C_6H_4	*X*	*Xe*	5	94
23	4-NO_2-C_6H_4	*X*	*Xf*	6	90
24	4-MeO-C_6H_4	*X*	*Xg*	8	88
25	3,4-$(MeO)_2$-C_6H_3	*X*	*Xh*	15	84
26	4-Me_2N-C_6H_4	*X*	*Xi*	15	88

a) See Fig. 6; *b*) isolated yields; *c*) isolated yields from recovered *IL1* used in four successive runs.

Table 6. Spectral data of selected pyranopyrazoles, benzopyrans and chromenes

Compound	Spectral data
Vd	IR (KBr), $\tilde{\nu}$/cm^{-1}: 1529, 1660, 2198, 3322, 3456 ^{1}H NMR (400 MHz, DMSO-d_6), δ: 1.78 (s, 3H, CH_3), 5.10 (s, 1H, H-4), 7.32–7.8 (m, 10H, ArH and NH_2) ^{13}C NMR (100 MHz, DMSO-d_6), δ: 12.5, 34.9, 56.0, 97.7, 120.9, 120.1, 126.8, 129.0, 129.8, 130.6, 132.2, 137.8, 143.5, 144.6, 145.2, 160.2, 160.5
VIc	IR (KBr), $\tilde{\nu}$/cm^{-1}: 1606, 1637, 1676, 2190, 3185, 3382 ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.95 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 2.18 (d, J = 16.4 Hz, 2H, CH_2), 2.50 (s, 2H, CH_2), 4.21 (s, 1H, H-4), 7.04–7.32 (m, 6H, ArH and NH_2) ^{13}C NMR (100 MHz, DMSO-d_6), δ: 27.3, 28.8, 32.2, 35.4, 50.4, 58.6, 113.1, 115.4, 115.5, 120.2, 129.4, 129.5, 141.4, 159.1, 160.1, 162.1, 195.4
VIIb	IR (KBr), $\tilde{\nu}$/cm^{-1}: 750, 770, 840, 1026, 1245, 1368, 1450, 1510, 1600, 1700, 2220, 3320, 3460 ^{1}H NMR (400 MHz, DMSO-d_6), δ: 1.93–1.96 (m, 2H, H-7), 2.26–2.30 (m, 2H, H-8), 2.58–2.62 (m, 2H, H-6), 3.74 (s, 3H, OCH_3), 4.20 (s, 1H, H-4), 6.82 (d, 2H, J = 8.0 Hz, ArH), 6.98 (s, 2H, NH_2), 7.06 (d, 2H, J = 8.0 Hz, ArH) ^{13}C NMR (100 MHz, DMSO-d_6), δ: 20.7, 27.5, 33.9, 37.3, 60.2, 114.4, 119.2, 127.3, 128.2, 130.5, 130.4, 133.5, 141.1, 157.6, 164.5, 196.1
VIIIi	IR (KBr), $\tilde{\nu}$/cm^{-1}: 1379, 1507, 1605, 1677, 2194, 3322, 3416 ^{1}H NMR (400 MHz, DMSO-d_6), δ: 2.61(s, 3H, CH_3), 4.88 (s, 1H, CH), 7.01 (s, 2H, NH_2), 7.07 (d, J = 8.7 Hz, 1H, ArH), 7.17–7.32 (m, 5H, ArH), 7.42–7.53 (m, 2H, ArH), 7.89 (d, J = 7.2 Hz, 1H, ArH), 8.26 (d, J = 8.1 Hz, 1H, ArH) ^{13}C NMR (100 MHz, DMSO-d_6), δ: 32.3, 54.4, 57.9, 112.2, 116.3, 117.8, 120.9, 121.5, 125.3, 127.6, 128.4, 128.9, 129.0, 129.6, 130.1, 131.4, 134.9, 147.5, 159.1, 160.7
IXi	IR (KBr), $\tilde{\nu}$/cm^{-1}: 1302, 1529, 1590, 1659, 2191, 3356, 3464 ^{1}H NMR (400 MHz, DMSO-d_6), δ: 5.6 (s, 1H, CH), 7.1 (s, 2H, NH_2), 7.4–7.7 (m, 5H, ArH), 7.34 (d, J = 8.7 Hz, 1H, ArH), 7.42–7.47 (m, 3H, ArH), 8.09 (s, 1H, ArH) ^{13}C NMR (100 MHz, DMSO-d_6), δ: 37.8, 57.4, 115.2, 117.4, 120.4, 121.9, 122.3, 123.9, 125.6, 127.8, 129.0, 130.4, 130.5, 130.9, 131.3, 134.7, 147.7, 148.4, 148.5, 160.5
Xb	IR (KBr), $\tilde{\nu}$/cm^{-1}: 1379, 1507, 1605, 1677, 1716, 2194, 3292, 3378 ^{1}H NMR (400 MHz, DMSO-d_6), δ: 5.1 (s, 1H, H-4), 7.01–8.03 (m, 12H, ArH and NH_2) ^{13}C NMR (100 MHz, DMSO-d_6), δ: 36.3, 57.9, 103.8, 112.9, 115.0, 116.6, 119.1, 123.0, 130.0, 133.0, 139.5, 152.1, 153.4, 157.9, 159.5, 160.2, 162.2

Table 7. Comparison of 4*H*-benzo[*b*]pyrans synthesis catalysed by *IL1* with methods reported in the literature

Entry	Catalysts and conditions[a]	Time/min	Yields[b]/%	TN	TF/min^{-1}	Reference
1	$[PhCH_2Me_2N^+\ CH_2CH_2NMe_2]Cl^-$ (5 mole %), solvent free, 60 °C	30	76	15	0.5	Chen et al. (2009)
2	[TETA]TFA (5 mole %), EtOH/H_2O, reflux	20	85	17	0.9	Zheng and Li (2011)
3	[ADPPY]OH (10 mole %), H_2O, r.t.	15	95	9.5	0.6	Salvi et al. (2011)
4	SB-DABCO (6 mole %), EtOH, r.t.	35	96	16	0.45	Hasaninejad et al. (2011)
5	$[TEBSA]HSO_4$ (5 mole %), solvent-free, 90 °C	60	89	18	0.3	Fang et al. (2010)
6	*IL1* (3 mole %), solvent-free, r.t.	4	96	32	8	present work

a) Reactants: dimedone, benzaldehyde, malononitrile in a mole ratio of 1 : 1 : 1; *b*) isolated yields; r.t. means ambient temperature.

Table 8. Comparison of dihydropyrano[*c*]chromenes synthesis catalysed by *IL1* with methods reported in the literature

Entry	Catalysts and conditions[a]	Time/min	Yield[b]/%	TN	TF/min^{-1}	Reference
1	CuO nanoparticle (15 mole %), H_2O, reflux	6	93	6.3	1.05	Mehrabi and Kazemi-Mireki (2011)
2	$H_6[P_2W_{18}O_{62}] \cdot 18H_2O$ (1 mole %), EtOH/H_2O, reflux	30	89	89	3	Heravi et al. (2008)
3	TBAB (10 mole %), water/neat	45	91	9.1	0.2	Khurana and Kumar (2009)
4	*IL1* (3 mole %), solvent-free, 80 °C	6	94	31	5.2	present work

a) Reactants: 4-hydroxycoumarin, benzaldehyde, malononitrile in a mole ratio of 1 : 1 : 1; *b*) isolated yields.

ple procedure and purification of the product, since *IL1*, but not the products, is fully miscible with water. After product separation, the catalyst was readily recovered by the removal of water.

The reusability of *IL1* was investigated in four different reaction categories. The catalyst was recovered from the aqueous medium, dried under vacuum and reused in four successive runs, (Table 4, entries 2, 14 and 25) and (Table 5, entries 4, 13 and 20), showing the capacity of the applied catalyst without significant loss of activity.

In general, a slight decrease in the activity of the catalyst is common and has been reported in several studies (Fang, et al., 2006; Han, et al., 2012; Liu, et al., 2013; Luo, et al., 2014; Wang, et al., 2008). In the current work, although there is no clear explanation for the slight loss of activity, it might be due to the ion exchanges.

Selected spectroscopic data for several known products are given in Table 6.

In addition, the turnover number (TN) and turnover frequency (TF) values of the present catalyst were compared with those of the catalysts reported as used in the reaction of 4*H*-benzo[*b*]pyrans (Table 7) and dihydropyrano[*c*]chromenes (Table 8). The TN and TF values showed *IL1* to be a more effective catalyst than those reported in the literature.

Conclusions

To summarise, a new efficient ionic liquid *IL1*, was synthesised, acting as a homogeneous "green" catalyst with both the Brønsted acidic and Lewis basic sites. *IL1* was used effectively for one-pot three-component condensations of aldehydes, malononitrile and cyclic ketones to synthesise pyranopyrazoles and benzopyrans at ambient temperature and for the synthesis of amino-2-chromenes and 3,4-dihyropyrano[*c*]chromenes via the reaction of aldehydes, malononitrile and α-naphthol/β-naphthol or 4-hydroxycoumarin under solvent-free conditions. The reactions are clean, the catalyst is readily synthesised and reusable and the products are easily separated.

In addition, several acidic catalysts such as *IL2*, *III*, and *IV* were synthesised, with *IL2* exhibiting an efficiency comparable to *IL1* because of its double Brønsted acidic sites.

These methods not only afford excellent yields in very short reaction times, but also avoid the problems associated with catalysts including high cost, difficulty in handling, and poor safety and pollution.

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