J IRAN CHEM SOC (2013) 10:695–699
DOI 10.1007/s13738-012-0202-4

ORIGINAL PAPER

Solvent-free synthesis of polyfunctional tetrahydropyrimidines promoted by recyclable ionic liquid

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Received: 26 March 2012 / Accepted: 30 November 2012 / Published online: 9 January 2013

Abstract The synthesis of nitrogen containing heterocyclic compounds from diethyl ester, formaldehyde, and various aromatic/aliphatic amines via a simple and efficient one-pot multicomponent reaction in ionic liquid is described. The catalyst can be recycled at least three times without obvious loss in catalytic activity.

Keywords Multicomponent reaction · Tetrahydropyrimidines · Heterocyclic compounds · Ionic liquid · Recyclability

Introduction

The search for novel compounds with beneficial therapeutic effects is at the forefront of medicinal chemistry research. With this in mind, developing procedures for the efficient generation of small heterocyclic organic molecules is of paramount importance in identifying the next generation of drug candidates. In this context, multicomponent reactions have emerged as powerful and bond-forming efficient tools that allow the preparation of polycyclic targets by connecting several components in a one-pot sequential and efficient manner [1–5]. Due to their high versatility, small heterocycles [6–8] were particularly attractive in multicomponent reaction for pharmaceutical development.

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Furthermore, the discovery of novel multicomponent reactions [9–12] can be considered as an interesting topic for academic research. Therefore, considerable effort has been dedicated to the development of synthesis and mechanism of the multicomponent reaction.

Among nitrogen containing heterocycles [13–17], pyrimidine and their derivatives such as pyrazolopyrimidines, isooxazolopyrimidines, pyrimidopyrimidines, and tetrahydropyrimidines have generated a widespread interest owing to the vast range of biological activities [18, 19] that these compounds possess. They have been used as preventative and prophylactic drugs in the treatment of male erectile dysfunction [20]. Specifically, tetrahydropyrimidines containing an amino acid unit have attracted much attention due to their potential biological activities [21] such as M_1 muscarinic receptor agonists for treatment of Alzheimer's disease [22, 23], human immunodeficiency virus (HIV) protease inhibitors [24], and other inhibitors against mycobacterium tuberculosis [25]. Literature methods for the synthesis of fused pyrimidines [26–29] generally involve either cyclization of substituted pyrimidines or condensation of specific moieties with pyrimidine [30–33]. The synthesis of tetrahydropyrimidines relies on three as well as four-component system and both route provided excellent yields of products. In our knowledge only few versions for the synthesis of multifunctional tetrahydropyrimidines have been presently developed [33, 34]. Although, entirely these methods have not been satisfactory and are associated with drawbacks such as toxic reagents/solvents, stoichiometric amounts of catalysts, long reaction times, unsatisfactory yields, complex procedure, and mostly there is no recovery of the catalyst.

During the past few years, ionic liquids [35–39] have been demonstrated as efficient and practical alternatives of green reaction medium for many important organic

transformations [6–8, 40–42]. In recent times, ionic liquids have been marched for beyond showing its significant role in controlling the reaction as catalyst [43, 44]. A number of ionic liquid with unique properties [45–48] have been successfully applied in many types of reactions such as Friedel–Craft acylations [49], alkylations [50], and Mannich-type reaction [51, 52]. Considering these elegant discoveries of addition activity of ionic liquid, we envisage that other types of multicomponent reaction could also be catalyzed by ionic liquid. Thus keeping in mind a more efficient and economical methodology for the synthesis of bioactive tetrahydropyrimidines, we report herein an environmentally benign route for the synthesis of polyfunctional tetrahydropyrimidine derivatives using ionic liquid as a recyclable catalyst.

Experimental

Chemicals and apparatus

General

The materials were purchased from Sigma-Aldrich and Merk, and used without any purification. The ionic liquids were prepared by reported procedures [53]. All reactions and purity of tetrahydropyrimidines were monitored by thin layer chromatography (TLC) using aluminum plates coated with silica gel (merk) using hexane-ethylacetate (90:10) as an eluent. The isolated products were further purified by preparative TLC using silica gel G (particle size 10–40 microns, 300 mesh) purchased from Spectrochem Pvt. Ltd. Mumbai, India. ^{1}H NMR and ^{13}C NMR (300 and 75 MHz, respectively) spectra were recorded on Bruker Avance Spectrospin 300 (300 MHz). All NMR samples were run in $CDCl_3$ and chemical shifts are expressed as δ relative to internal Me_4Si. IR spectra were obtained on Perkin Elmer FT-IR spectrometer spectrum-2000 using potassium bromide pellets or as liquid films between two sodium chloride pellets. ESI–MS mass spectra were recorded on a Waters LCT Micromass. The temperature of the reaction mixture was measured through a non-contact infrared thermometer (AZ, Mini Gun Type, Model 8868). All of the obtained products are known compounds.

General procedure for the synthesis of tetrahydropyrimidines

General procedure for the synthesis of polysubstituted tetrahydropyrimidine derivatives via three-component reaction

Method (A) In a 50 ml round bottom flask a stirred mixture containing but-2-ynedioic acid diethyl ester (1 mmol), aniline (2.0 mmol), 2 mL ionic liquid, and formaldehyde (3 mmol) was heated at 80–90 °C for 60 min. The progress of reaction mixture was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature. The product was extracted with diethyl ether (3 × 10 mL) (ionic liquid being insoluble in ether). Ether layer was decanted, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. After the solvent was removed *vacuo*, the crude product was purified by preparative TLC with petether/ethylacetate (90:10) as the eluent to afford the desired product in 89 % yield. The rest of viscous ionic liquid was thoroughly washed with ethyl acetate and recycled in subsequent reactions.

General procedure for the synthesis of polysubstituted tetrahydropyrimidine derivatives via four-component reaction

Method (B) In a 50 ml round bottom flask, but-2-ynedioic acid diethyl ester **1** (1 mmol) and aniline **2** (R^1NH_2) (1 mmol) in 2 mL ionic liquid were mixed very slowly and stirred at room temperature for 5–10 min. To this, other different amines (R^2NH_2)/benzylamine **4** (1.1 mmol) and formaldehyde **3** (3 mmol) was added with stirring at 80–90 °C for 40 min. The progress of reaction mixture was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature. The product was extracted with diethyl ether (3 × 10 mL) (ionic liquid being insoluble in ether). Ether layer was decanted, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. After the solvent was removed *vacuo*, the crude product was purified by preparative TLC with petether/ethylacetate (90:10) as the eluent to afford the desired product in 93 % yield. The rest of viscous ionic liquid was thoroughly washed with ethyl acetate and recycled in subsequent reactions.

Spectral data for the selected compounds: 1,3-diphenyl-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylic acid diethyl ester (**5a**): Yellowish oil[15]; IR (Film): ν_{max} = 3,248, 2,984, 1,752, 1,696, 1,544, 1,486, 1,370, 1,243, 1,188, 1,107, 1,035, 745 cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 10H), 4.86 (s, 2H), 4.28 (s, 2H), 4.17 (q, J = 7.2 Hz, 2H), 3.96 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 6.9 Hz, 3H), 0.99 (t, J = 7.6 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$): δ = 165.3, 164.2, 148.6, 146.1, 143.5, 129.8, 129.3, 128.7, 126.7, 125.6, 122.8, 118.3, 117.4, 101.5, 69.3, 62.5, 60.0, 47.3, 14.3, 13.8, 13.1 *m/z* (ESI–MS) 380.01 (M + 1, requires 380.17).

1,3-Dibutyl-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylic acid diethyl ester (**5b**): Yellowish oil[15]; IR (Film): ν_{max} = 3,436, 2,981, 1,728, 1,685, 1,572, 1,490, 1,332, 1,265, 1,228, 1,140, 1,035 cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$): 4.35 (q, J = 7.2 Hz, 2H), 4.26 (q, J = 7.2 Hz,

Scheme 1 One-pot synthesis of polysubstituted tetrahydropyrimidines via MCRs

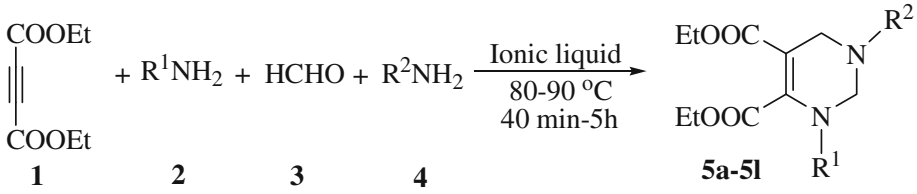

Table 1 Optimization of the reaction conditions for teytrahydropyrimidines in different ionic liquids

Entry	Ionic liquid	Time (min)	Yield (%)[a]
1	[bmim]PF_6	60	30
2	[bmim]Cl	60	32
3	[bmim]BF_4	60	89
4	[bmim]Br	60	80

Reaction conditions: 1.0 equivalent of but-2-ynedioic acid diethyl ester, 2.0 equivalent of aniline, 3.0 equivalent of formaldehyde; different ionic liquids (2 mL); temperature 80–90 °C

[a] Isolated yields

Table 2 Recycling of ionic liquid

No. of cycles[a]	Fresh	Run 1	Run 2	Run 3
Yield (%)[b]	89	89	88	86
Time (min)	60	60	60	60

[a] Reaction conditions: 1.0 equivalent of but-2-ynedioic acid diethyl ester, 2.0 equivalent of aniline, 3.0 equivalent of formaldehyde; ionic liquid [bmim]Br; temperature 80–90 °C

[b] Isolated yields

Table 3 Ionic liquid ([bmim]BF_4) mediated one-pot synthesis of teytrahydropyrimidines via MCRs

Entry	R^1NH_2	R^2NH_2	Product	Time (min)	Yield (%)[a]
1	$PhNH_2$	$PhNH_2$	**5a**	60	89
2	n-$BuNH_2$	n-$BuNH_2$	**5b**	40	95
3	$BnNH_2$	$BnNH_2$	**5c**	40	93
4	4-$MeC_6H_4NH_2$	4-$MeC_6H_4NH_2$	**5d**	60	86
5	$PhNH_2$	$BnNH_2$	**5e**	40	93
6	$PhNH_2$	n-$BuNH_2$	**5f**	50	91
7	$BnNH_2$	$PhNH_2$	**5g**	40	86
8	$PhNH_2$	4-$MeC_6H_4NH_2$	**5h**	120	84
9	$PhNH_2$	4-$ClC_6H_4NH_2$	**5i**	120	80
10	$PhNH_2$	3-$MeC_6H_4NH_2$	**5j**	120	82
11	$PhNH_2$	2-$MeC_6H_4NH_2$	**5k**	360	62
12	$PhNH_2$	4-$NO_2C_6H_4NH_2$	**5l**	360	70

Reaction conditions: 1.0 equivalent of but-2-ynedioic acid diethyl ester, 2.0 equivalent of aniline, 3.0 equivalent of formaldehyde; ionic liquid [bmim]Br (2 mL); temperature 80–90 °C

[a] Isolated yields

2H), 3.69 (s, 2H), 3.38 (s, 2H), 2.77 (t, $J = 7.4$ Hz, 2H), 2.26 (t, $J = 7.4$ Hz, 2H) 1.63 (m, 4H), 1.30 (m, 4H), 1.11 (m, 6H), 0.93 (m, 6H); ^{13}CNMR (75 MHz, $CDCl_3$): $\delta = 166.0, 164.1, 147.6, 91.5, 67.4, 59.3, 51.8, 50.1, 48.4, 31.6, 30.2, 20.9, 19.7, 14.3, 13.8, 13.4$ *m/z* (ESI–MS) 340.09 (M + 1, requires 340.45).

3-Benzyl-1-phenyl-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylic acid diethyl ester (**5g**): Yellowish oil[15]; IR (Film): $\nu_{max} = 3{,}440, 2{,}974, 1{,}722, 1{,}672, 1{,}558, 1{,}465, 1{,}388, 1{,}261, 1{,}206, 1{,}105, 1{,}028, 752$ cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$): $\delta = 7.46$–7.27 (m, 7H), 6.92–6.87 (m, 3H), 4.41 (s, 2H), 4.28 (q, $J = 7.6$ Hz, 2H), 4.22 (s, 2H), 4.18 (q, $J = 7.5$ Hz, 2H), 4.05 (s, 2H), 1.06 (m, 6H); ^{13}CNMR (75 MHz, $CDCl_3$): $\delta = 165.3, 164.4, 148.0, 137.2, 130.5, 128.3, 127.6, 120.8, 117.5, 95.1, 65.2, 62.3, 59.8, 54.6, 45.8, 14.7, 13.2$ *m/z* (ESI–MS) 393.68 (M + 1, requires 394.18).

Results and discussion

On the basis of this consideration, we assumed that the MCRs [51, 52] would proceed smoothly in the presence of ionic liquid as well. Recently, as a part of our ongoing research program for the synthesis of nitrogenous heterocyclic compounds, here we became interested to develop a more efficient and recyclable catalytic method by the use of ionic liquid ([bmim]BF_4) for the synthesis of potentially biologically active polysubstituted 1,2,3,6-tetrahydropyrimidines via a three- and four-component condensation reaction in order to conduct a new architecture of heterocyclic compounds containing α- and β-amino acid unit.

Initially, we first allowed but-2-ynedioic acid diethyl ester (1 mmol), aniline (2 mmol), and formaldehyde (3 mmol) in the presence of ionic liquid ([bmim]BF_4) (2 mL) at 80–90 °C. The reaction completed almost instantly (determined by TLC) and afforded the corresponding product 1,3-diphenyl-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylic acid diethyl ester with 89 % yield (Scheme 1).

We then turned our attention to investigate the effect of different ionic liquids on the rate of reaction and the yield of products. During this process, [bmim]BF_4 was found to be more appropriate ionic liquid (Table 1, entry 3). But the reaction was found to be slow and a complex mixture of

compound was observed when the reaction was carried out in the presence of [bmim]Br, [bmim]Cl, and [bmim]PF_6. Therefore, we chose [bmim]BF_4 as a catalyst for the synthesis of tetrahydropyrimidines.

The ionic liquid could be recycled and reused for three times without obvious loss in activity. Since ionic liquid ([bmim]BF_4) is immiscible in ether, the desired product may be extracted with it and the retained ionic liquid phase may be reused. The second and third runs using recovered ionic liquid afforded almost similar yields to those obtained in the first run (Table 2).

Having established the optimal reaction conditions for the multicomponent reaction, we explored the scope and limitations of the reaction using but-2-ynedioate, different aromatic/aliphatic amines and formaldehyde. All the substituted aryl, alkyl, and benzyl amines perform well and the corresponding products were obtained in good to excellent yields. Meaningfully, the substituted group at the 1- or 3-position on the tetrahydropyrimidine ring could be selectively induced by changing the addition order of the two different amines as mentioned in the general procedure for method B. Aniline (Table 3, entry 1) was dripped first resulting in product **5a** in 89 % yield. On the contrary, 1-phenyl-3-benzyl-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylic acid diethyl ester **5g** was obtained in 86 % yield (Table 3, entry 7). The results indicated that the substituted group decreased the reactivity of MCRs with much longer reaction time (Table 3, entries 8–12) and were mainly depend on the structure of NH_2R^2. In addition, the steric hindrance effect associated with methyl group on the *ortho*-position of the aromatic ring resulted in a low yield (Table 3, entry 11). The activity of substituted aromatic amines was obviously lower than that of aliphatic ones, which indicates that the activity of the aliphatic amines is higher. In case of aliphatic amines, delocalisation of lone pair of electrons on the nitrogen is not possible. Furthermore, in aliphatic amines, the electron density on the nitrogen atom is increased by electron donating inductive effect. Therefore, lone pair on nitrogen atom is easily available to make them react as a good nucleophile in comparison to aromatic amines. As in case of aromatic amines, due to resonance, the lone pair of electrons on the nitrogen atom gets delocalised in the π-system of the benzene ring and thus there is less electron density on nitrogen available for making it a weak nucleophile.

Conclusions

In summary, a convenient and ecofriendly one-pot multicomponent synthesis of polyfunctional tetrahydropyrimidines have been developed in solvent-free conditions using ionic liquid as a recyclable mild acid catalyst. In addition, the products obtained are interesting nitrogen containing heterocyclic molecules containing α- and β-amino acid blocks.

Acknowledgments Authors Neeraj Kumar Mishra and Saurav Bhardwaj thank to Council of Scientific and Industrial Research (CSIR), New Delhi, India for the grant of Research Associateship and Senior Research Fellowship.

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