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$[BPy]HSO_4$ Acidic Ionic Liquid as a Novel, Efficient, and Environmentally Benign Catalyst for Synthesis of 1,5-Benzodiazepines under Mild Conditions

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Abstract: A novel and simple ionic liquid methodology for the synthesis of 1,5-benzodiazepines is described. 1-Butylpyridinium hydrogen sulphate ($[BPy]HSO_4$), an acidic room-temperature ionic liquid, as a novel and efficient catalyst, was synthesized and used in the preparation of a series of 1,5-benzodiazepine derivatives by the reaction of *o*-phenylenediamine with chalcones under mild conditions. This method is easy, efficient, environmentally friendly, economical, free of toxic catalysts, and has good yields for the formation of 1,5-benzodiazepines

Keywords: Acidic counterion, 1,5-benzodiazepines, 1-butylpyridinium hydrogen sulpates, room-temperature ionic liquid

INTRODUCTION

The synthesis of 1,5-benzodiazepines and their derivatives have attracted considerable attention from researchers, including pharmaceutical and organic synthetic chemists, in recent years because their medicinal properties as anti-anxiety, hypnotic, antidepressive, tranquilizing, anti-inflammatory, anticonvulsant, antifeedant, antibacterial, and analgesic agents.[1,2] In addition, benzodiazepines derivatives are also used in industry as dyes for acrylic

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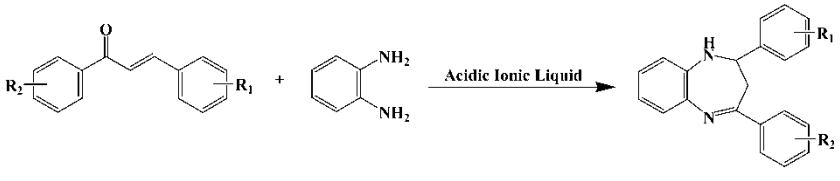
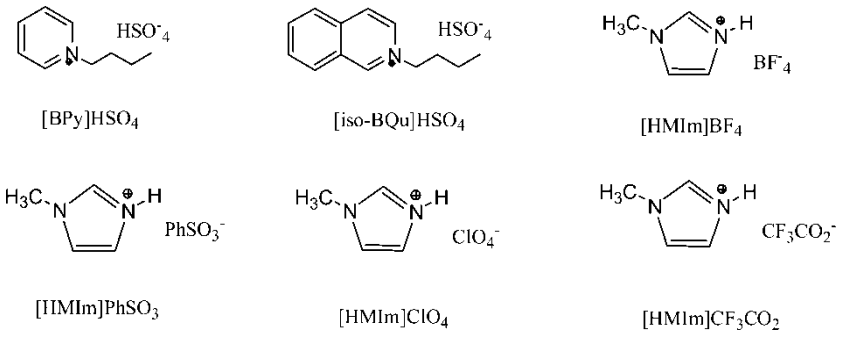
fibers[3] in photography. Moreover, 1,5-benzodiazepines are valuable synthons used for the preparation of other fused ring compounds such as triazolo, oxazino, and furano-benzodiazepines.[4] Thus, the synthesis of these heterocyclic nuclei is still of much interest.

1,5-Benzodiazepines have commonly been synthesized by the reaction of *o*-phenylenediamine with α,β-unsaturated carbonyl compounds, β-halo ketones, or ketones. There are many methods for the preparation of 1,5-benzodiazepines in the literature, including BF_3–etherate,[5] $NaBH_4$,[6] polyphosphoric acid or SiO_2,[7] Amberlyst-15[8], $Yb(Otf)_3$,[9] $MgO/POCl_3$,[10] Al_2O_3/P_2O_5 or acetic acid under microwave irradiation,[11] $TiCl_4/Sm/THF$ system,[12] [bbim]Br ionic liquid,[13] sulfated zirconia,[14] silica gel,[15] and $CeCl_3/NaI/$silica gel.[16] Many of these processes suffer from limitations such as requiring harsh conditions, expensive reagents, high catalyst loading, corrosive reagent, or toxic ions; low to moderate yields; and occurrence of several side reactions. It is also necessary to find a milder, selective, nonhazardous, and inexpensive reagent.

Room-temperature ionic liquids (RTILs) have increasingly attracted attention as the green, high-tech reaction media of the future.[17,18] ILs are used as green solvents and have unique properties such as wide liquid range, good solvating ability, tunable polarity, and high thermal stability. As a result of their green credentials and potential to enhance rates and selectivity, ILs based on imidazolium salts are finding increasing applications in organic synthesis,[19] but there are no examples of synthesis and application of ILs based on pyridinium and iso-quinolinium salts in the area of functionalized acidic ILs, especially with hydrogen sulphate counteranion. However, ILs based on imidazolium salts with HSO_4^- counteranion as catalyst have been investigated many acid-catalyzed reactions.[20–22] To extend the scope and decrease the cost of ILs, we synthesized and explored the utility of two novel acidic ILs 1-butylpyridinium hydrogen sulphate ([BPy]HSO_4) and 1-butyl-iso-quinolinium hydrogen sulphate ([iso-BQu]HSO_4), as efficient catalysts to promote the formation of 1,5-benzodiazepines. Herein, we report a facile, efficient, and environmentally benign method for the preparation of 1,5-benzodiazepine derivatives by condensation of *o*-phenylenediamine with ketones using a catalytic amount of [BPy]HSO_4 and [iso-BQu]HSO_4 acidic ILs under mild conditions (Schemes 1 and 2).



Scheme 1. Synthesis of 1,5-benzodiazepines from *o*-phenylenediamine and chalcones.



Scheme 2. Acidic ionic liquids used in the present work.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a Shimadzu 8600 FT spectrometer in KBr with absorptions in cm^{-1}. ^1H NMR spectra were recorded on a Bruker AV400 spectrometer and TMS was used as internal standard. Mass spectra were taken on a Bruker BiFlexIII mass spectrometer. Elemental analyses were carried out on an EA 1110 instrument. Products were characterized by comparison of their spectroscopic data (^1H NMR, IR, and mass) and meltine points with those reported in the literature.

Preparation of Ionic Liquids as Catalyst for 1,5-Benzodiazepines

[BPy]HSO_4 and [iso-BQu]HSO_4 derived from chloride salts were obtained by a dropwise addition of 1 equiv of concentrated sulphuric acid (98%) to a cooled solution of the corresponding 1-butylpyridinium or iso-quinolinium chloride (1 equiv) in anhydrous methylene chloride. The mixture was refluxed for 48 h, and the HCl by-product formed in the reaction was distilled out of the condenser and dissolved in 10% NaOH solution. When the formed HCl had been completely removed, the solution was cooled to room temperature, and methylene chloride was evaporated with a rotary evaporator. The ionic liquid was dried under high vacuum at 80°C for 2 h. After elimination of water, it is recommended that it be handled under an inert atmosphere.

[BPy]HSO_4: viscous oil, ^1H NMR (400 MHz, d_6-DMSO) δ_H (ppm): 0.86 (t, 3H), 1.25 (m, 2H), 1.87 (m, 2H), 4.63 (m, 2H), 7.61 (1H, br s, OH), 8.61 (m, 1H), 8.13 (m, 2H), 9.16 (m, 2H).

[iso-BQu]HSO_4: viscous oil, ^1H NMR (400 MHz, d_6-DMSO) δ_H (ppm): 0.87 (t, 3H), 1.26 (m, 2H), 1.95 (m, 2H), 4.74 (m, 2H), 8.00–8.85 (m, 7H), 10.20 (1H, s).

Other protic acidic ionic liquids (Table 1) were synthesized and purified according to the literature.[20]

Table 1. Comparison of the effect of catalysts in the synthesis of 1,5-benzodiazepine (a) from *o*-phenylenediamine and chalcone

Entry	Catalyst	Catalyst loading (mol%)[a]	Ratio of substrate[b]	Time (h)	Yield (%)
1	[Bpy][HSO_4]	5	1.0	3	69
2	[iso-Bqu]HSO_4	5	1.5	3	84
3	[HMIm]BF_4	5	1.5	3	43
4	[HMIm]$PhSO_3$	5	1.5	3	59
5	[HMIm]$CF_3CO_2^-$	5	1.5	3	57
6	[HMIm]ClO_4	5	1.5	3	44
7	[Bpy][HSO_4]	5	1.5	3	87
8	[Bpy][HSO_4]	10	1.5	3	88

[a]Calculated based on chalcone (M/M).
[b]Ratio of *o*-phenylenediamine to chalcone.

General Procedure for the Synthesis of 1,5-Benzodiazepines

In a typical experiment, ionic liquid (0.05 mmol) was dissolved into the mixture of chalcone (1.0 mmol) and *o*-phenylenediamine (1.5 mmol) in ethyl acetate (3 mL) in a 25-mL round-bottom flask equipped with a distillation condenser. The reaction mixture was stirred vigorously at 80°C for the desired time under atmosphere. The completion of reaction was followed by TLC using 20% EtOAc in petroleum ether as eluent. After completion, methanol or ethanol was added to the reaction mixture, and the content was filtered to afford the 1,5-benzodiazepines. The products, thus isolated, were pure (single spot on TLC). They were subjected to further purification by chromatography through a column of silica gel using *n*-hexane/ethyl acetate (1:4) as eluent.

After reaction, it was possible to reuse the IL catalyst in another run after washing twice with EtOAc or Et_2O and eventually drying under high vacuum at 70 °C for 0.5 h (for elimination of the unreacted starting products because of their immiscibility with the ionic liquid).

SPECTROSCOPIC DATA FOR SELECTED PRODUCTS

2,3-Dihydro-2,4-diphenyl-1H-1,5-benzodiazpine ***(a)***: yellow solid, mp 129–130 °C (lit.[23] 129–129.5°C). ^{1}H NMR (400 MHz, d_6-DMSO), δ_H (ppm) 3.06 (dd, 1H, $J = 9.2$ Hz, $J = 7.2$ Hz), 3.38 (dd, 1H, $J = 8.4$ Hz, $J = 6.8$ Hz), 3.66 (s, 1H), 5.88 (s, 1H), 6.83 (m, 1H), 7.00–7.42 (m, 11H), 7.77 (d, 2H, $J = 1.6$ Hz, $J = 3.6$ Hz). ν/cm^{-1} 1609 (C=N), 3366 (N-H); MS: $m/z = 298$ (M^+), 283, 221, 194, 119, 103, 91, 77, 65, 51; $C_{21}H_{18}N_2$ (298.387): calcd. C, 84.53; H, 6.08; N, 9.39; found C, 84.76; H, 6.22; N, 9.01.

2,3-Dihydro-2-phenyl-4-(4′-methylphenyl)-1H-1,5-benzodiazpine ***(b)***: yellow solid, mp 126–127°C (lit.[23] 127°C). ^{1}H NMR (400 MHz, d_6-DMSO), δ_H (ppm) 2.30 (s, 3H), 2.53 (m, 2H), 3.04 (m, 1H), 5.16 (s, 1H), 6.83-7.84 (m, 13H). ν/cm^{-1} 1607 (C═N), 3360 (N-H); MS: $m/z = 312$ (M^+), 297, 246, 221, 208, 119, 103, 91, 77, 65, 51; $C_{22}H_{20}N_2$ (312.413): calcd. C, 84.58; H, 6.45; N, 8.97; found C, 84.69; H, 6.28; N, 9.02.

2,3-Dihydro-2-phenyl-4-(4′-nitrophenyl)-1H-1,5-benzodiazpine ***(e)***: yellow solid, mp 104–105°C (lit.[23] 104–105°C). ^{1}H NMR (400 MHz, d_6-DMSO), δ_H (ppm) 2.59 (m, 2H), 3.08 (m, 1H), 5.41 (s, 1H), 7.46–8.28 (m, 13H). ν/cm^{-1} 1600 (C═N), 3346 (N-H); MS: $m/z = 343$ (M^+), 328, 266, 240, 221, 194, 119, 103, 91, 77, 65, 51; $C_{21}H_{17}N_3O_2$ (343.385): calcd. C, 73.45; H, 4.99; N, 12.24; found C, 73.29; H, 5.16; N, 12.01.

2,3-Dihydro-2-(3′,4′-dichloropheny)l-4-phenyl-1H-1,5-benzodiazpine ***(d)***: yellow solid, mp 150–151°C. ^{1}H NMR (400 MHz, d_6-DMSO), δ_H (ppm) 2.49 (m, 2H), 3.02–3.18 (m, 1H), 5.26 (s, 1H), 6.97–7.77 (m, 13H). ν/cm^{-1} 1612 (C═N), 3341 (N-H); MS: $m/z = 366$ (M^+), 351, 289, 263, 221, 119, 103, 91, 77, 65; $C_{21}H_{16}N_2Cl_2$ (367.277): calcd. C, 68.68; H, 4.39; N, 7.63; found C, 68.79; H, 4.44; N, 7.80.

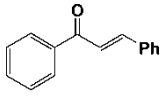
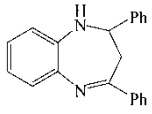
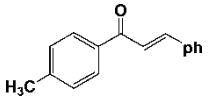
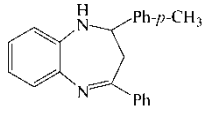
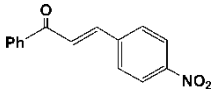
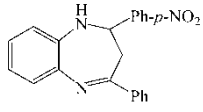
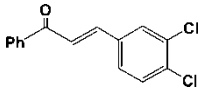
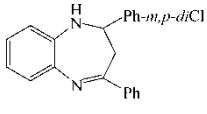
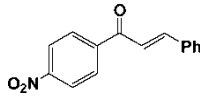
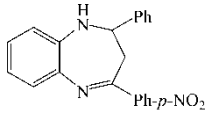
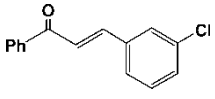
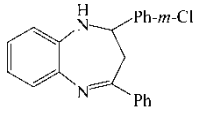
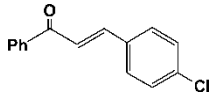
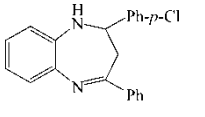
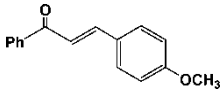
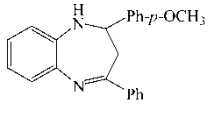
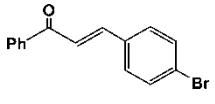
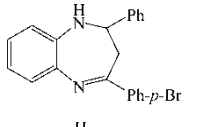
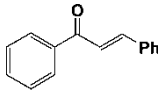
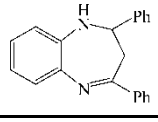
2,3-Dihydro-2-(4′-methoxyphenyl)-4-phenyl-1H-1,5-benzodiazepine ***(h)***: yellow solid, mp 145–146°C (lit.[23] 146–147°C). ^{1}H NMR (400 MHz, d_6-DMSO), δ_H (ppm) 3.05 (d, 2H, $J = 3.8$ Hz), 3.63 (s, 3H), 3.77 (br s, 1H), 5.03 (dd, 1H, $J = 4.7$, 4.6 Hz), 6.71–7.94 (m, 13H). ν/cm^{-1} 1610 (C═N), 3362 (N-H); MS: $m/z = 328$ (M^+), 297, 221, 194, 119, 103, 91, 77, 65, 51; $C_{22}H_{20}N_2O$ (328.413): calcd. C, 80.46; H, 6.14; N, 8.53; found C, 80.37; H, 6.22; N, 8.58.

RESULTS AND DISCUSSION

We initially tested the reaction of *o*-phenylenediamine with chalcone at 80 °C in the presence of [BPy]HSO_4 ionic liquid. The conversion was only 69% when using equimolar amounts of chalcone and *o*-phenylenediamine (Table 1, entry 1). Fortunately, the desired reaction was efficiently accomplished when the reaction was carried out using 1.5 equiv. of *o*-phenylenediamine (Table 1, entry 2). When the catalytic amount of ILs was increased, the conversion reached 88% (Table 1, entry 8) with only a marginal increase in the reaction rate. The subsequent condition optimization experiments revealed that the 5 mol% of catalyst amount was necessary to complete the reaction (Table 1, entry 7).

The result of synthesis of 1,5-benzodiazepines from *o*-phenylenediamine with chalcone suggested that the catalytic performance of the [BPy]HSO_4 and [iso-BQu]HSO_4 could be much better than that of the other protic acidic ILs under the same reaction conditions. However, it should be noted that the

Table 2. Synthesis of 1,5-benzodiazepines over $[BPy]HSO_4$[a]

Entry	Chalcone	Product (num.)	Time (h)	Yield (%)
1		 **a**	3.0	87
2		 **b**	2.5	89
3		 **c**	1.5	95
4		 **d**	3.0	80
5		 **e**	1.5	93
6		 **f**	3.0	91
7		 **g**	2.5	90
8		 **h**	2.5	88
9		 **i**	2.0	92
10[b]		 **a**	3.0	84

[a]Reaction conditions: *o*-phenylenediamine, 1.5 mmol; chalcone, 1.0 mmol; ionic liquid, 5 mmol%; temperature: 80°C.

[b]Reused four times.

reaction rate in ILs is dependent upon the IL chosen, and in this case, [HMIm]BF_4, [HMIm]$PhSO_3$, [HMIm]CF_3COO, and [HMIm]ClO_4 give a lower rate enhancement (Table 1, entries 3–6) than the [BPy]HSO_4 and [iso-BQu]HSO_4 ILs as catalysts (Table 1, entries 1, 2). Probably this is due to the higher Brønsted acidity of the hydrogen sulphate counteranion. [iso-BQu]HSO_4 also has good activities for this reaction, but [BPy]HSO_4 seems to be slightly better compared with [iso-BQu]HSO_4 (Table 1, entries 2, 7).

To investigate the scope and limitation of [BPy]HSO_4 as a catalyst for the synthesis of 1,5-benzodiazepines, other chalcones as a substrate were also tested, and the results are summarized in Table 2. Various chalcones and *o*-phenylenediamine were efficiently converted to the corresponding 1,5-benzodiazepines in the presence of 5 mol% [BPy]HSO_4 acidic IL. Yields of these reactions are almost quantitative in most cases. The presence of electron-donating and electron-withdrawing groups on the aromatic ring of chalcones reacted with *o*-phenylenediamine without any significant difference to give the corresponding 1,5-benzodiazepines in good yields (Table 2, entries 1–9). It is noteworthy that [BPy]HSO_4 acidic IL could be recycled and used in the next run. In the reaction of chalcones, [BPy]HSO_4 could be easily reused for four cycles with little decrease in activity.

CONCLUSION

In summary, [BPy]HSO_4 acidic IL was found to be a novel, environmentally benign, and highly efficient acid catalyst for the synthesis of 1,5-benzodiazepines under mild conditions. The advantages of the present protocol are air stability of the catalyst, ready availability, environmental friendliness, low cost, mild conditions, and easy workup, which make the procedure an attractive alternative to the existing methods for the synthesis of 1,5-benzodiazepines.

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