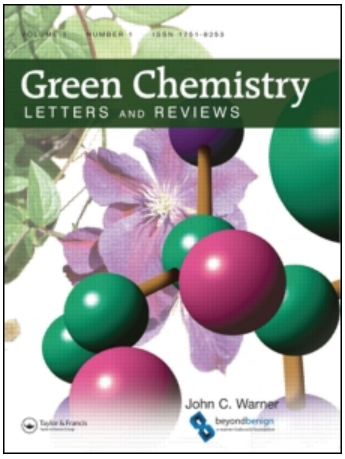

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Simple ammonium ionic liquid catalyses the 1,5-benzodiazepine derivatives under mild conditions

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RESEARCH LETTER

Simple ammonium ionic liquid catalyses the 1,5-benzodiazepine derivatives under mild conditions

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An incredibly elementary procedure for the effective synthesis of 1,5-benzodiazepine derivatives using triethyl ammonium acetate (TEAA) $[Et_3NH][CH_3COO]$ ionic liquid has been developed. TEAA was found to be practical, inexpensive, reusable and has a simple work-up procedure, which is absent in other catalyst. The role of TEAA as the reaction medium as well as the catalyst has shown the benefits of the use of TEAA in organic synthesis. The effect of $[Et_3NH][CH_3COO]$ on the synthesis of 1,5-benzodiazepine derivatives has been studied and results are provided herein.

Keywords: benzodiazepines; triethyl ammonium acetate (TEAA); ionic liquid; o-phenylenediamines; green chemistry

Introduction

Benzodiazepines are an important class of pharmacologically active compounds, having applications as tranquilizers, anticonvulsants, and even anti-anxiety and hypnotic agents (*1–3*). Besides this, benzodiazepines are valuable synthons used for the preparation of fused ring compounds, such as triazolo (*4*), oxazino, or furanobenzodiazepine (*5*) have commercial uses in photography (*6*) (as dyes for acrylic fibres) and act as anti-inflammatory agents (*7*). The classical methods for the synthesis of benzodiazepines involves the condensation reaction of o-phenylenediamines with α,β-unsaturated carbonyl compounds like β-haloketones (*8,9*) or ketones in the presence of a catalyst, such as BF_3-etherate (*10*), $NaBH_4$ (*11*), polyphosphoric acid (*12*), $MgO/POCl_3$ (*13*), $(OTf)_3$ (*14*), Al_2O_3/P_2O_5 (*15*), or HOAc under microwave (*16*) were employed for the transformation. Recent papers reported the use of other catalysts using stoichiometric amounts of zinc {(L) proline} (*17*), I_2 (*18,19*), ferric perchlorate (*20*), magnesium perchlorate (*21*), $InCl_3$ (*22*), $InBr_3$ (*23*), $H_{14}[NaP_5W_{30}O_{110}]$ (*24*), polyanilinesulphate (*25*), and NBS (*26*) for the reaction. However, many of these processes suffer from one to another limitations, such as the use of expensive reagents, harsh conditions, relatively long reaction times, high catalyst loading, low selectivity, the requirement of special apparatus, the presence of side reactions, and the creation of effluent pollution. Almost all of them make use of an acid catalyst, giving rise to tedious work-up procedures for their separation. Hence, there is a need to develop a convenient, efficient, and practical method for the synthesis of 1,5-benzodiazepine derivatives.

Ionic liquids as new reaction media and catalysts have been experimentally and theoretically recognized, and accepted (*27–32*). The application of ionic liquids as novel media may provide convenient solutions to both solvent emission and catalyst reuse problems (*33–36*). A great deal of attention has been given to imidazolium ionic liquids in the past several years (*37*). Jarikote et al. had synthesised 1,5-benzodiazepine using ionic liquids such as [bbim] Br and [bbim] BF_4 (*38*) at room temperature. They had used a stoichiometric amount of ionic liquids and this has been shown to have serious drawbacks, especially imidazolium systems with BF_4 anions, which are as toxic as benzene to certain aquatic ecosystems, and also liberate hazardous HF during recycling (*39*). Apart from this, the high cost and disposability of these solvents also limit their utility (*40,41*). Therefore, low-cost ionic liquids, such as ammonium ionic liquids have drawn much attention. Herein, we describe an operationally simple, highly efficient, eco-friendly, and straightforward method for the synthesis of 1,5-benzodiazepine derivatives.

Results and discussion

A main goal of our research group is to germinate catalyst and reaction medium that can be utilized as a green chemistry tool. Our previous experimental

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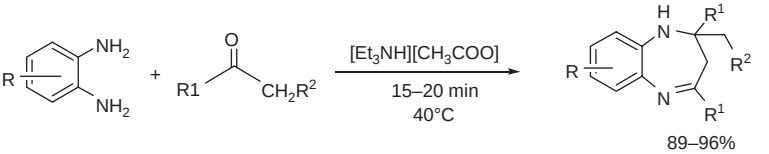
studies have shown the preparation of the 1,5-benzodiazepine derivative by using green chemistry methods (*42*). Recently our group has shown the utility of the simple ammonium ionic liquid (triethyl ammonium acetate – TEAA) in aza/thia Michael reactions (*43*). In order to further explore the synthesis of potential biologically active heterocyclic compounds using eco-friendly method, we investigated the synthesis of 1,5-benzodiazepine derivatives by using TEAA ionic liquid (Scheme 1).

It is noteworthy that the preparation of ammonium ionic liquids is direct, simple, high-yielding, and eco-friendly, eliminating the need for volatile organic solvents such as dichloromethane and acetonitrile used in the preparation of some reported ionic liquids (*44,45*). TEAA is air and water stable, easy to synthesize from triethyl amine and acetic acid, and relatively cheap as compared to other ionic liquids. The thermal stability of TEAA is very high, remaining stable up to 150°C. These properties can provide a more detailed understanding of TEAA and how it can be used in organic synthesis. At first, o-phenylenediamine and acetone were chosen as model systems and we found that TEAA catalyzed the synthesis of 1,5-benzodiazapenes giving a yield of 96% (Table 1). To establish these optimal conditions, studies were carried out by using various conditions with the reaction mixture of o-phenylenediamine and acetone (12.1 molar ratio); TEAA (1 mL) was added and stirred at 25°C for 0.5–10 h, giving only 45% product yield. When the same reactants were treated at 40°C for 15 min, the yield of product was found to be 96%. An increase in reaction time (up to 1 h) showed no increase in the yield of product (entries 4 and 5, Table 1). There are no significant changes in the yield with increase in temperature from 40 to 50°C (entry 6, Table 1). The optimal conditions were obtained when the reaction was conducted at 40°C for 15 min giving a 96% yield for 1,5-benzadiazapens derivatives. The completion of the reaction was monitored by thin layer chromatography (TLC) and GC analysis. It should be noted that the reaction does not proceed in the absence of TEAA. This demonstrates the ability of TEAA to act as a catalyst and reaction medium. To demonstrate the reusability of TEAA, we carried out subsequent reactions and found that TEAA could be recycled and reused for the subsequent 10 times without considerable loss of reactivity and yield (Table 2).

An exhaustive survey of the literature reveals that in comparison with the other catalysts used previously for the preparation of 1,5-benzodiazepines, TEAA is inexpensive and has operational simplicity with decreased reaction time (Table 3) (*20,24–26,33–36*). In comparison to the heteropolyacids, TEAA is more time recyclable and gives a better yield in a shorter time frame. The increase in the yield through the use of TEAA for the preparation of 1,5-benzodiazepine derivatives, shows its catalytic efficiency (Table 3). Traditional catalysts do not have the reclaimable tendency exhibited with TEAA and yields were remarkable lower, along with the possibility of side reactions. It is also notable that the procedure for the preparation of catalysts (entries 1–6, Table 2) reported in the literature are difficult to follow, whereas, TEAA can be easily prepared by using simple acids and bases. In addition to this, TEAA is very easy to separate from the reaction mixture and can be reused further. The efficacy of this method is due to its operational simplicity, which only requires stirring the reaction mixture at ambient temperature without the need for high temperatures, the use of external catalyst, solvent systems, or sonication. Through these results we have explicitly found that TEAA has significant potential in organic synthesis.

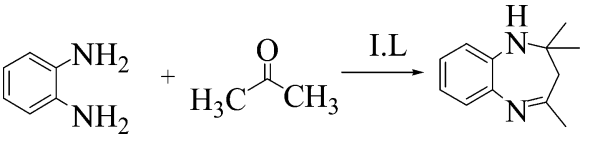
In order to understand the wide utility of TEAA, the optimized system was used for the synthesis of a variety of 1,5-benzodiazepines (Table 4). Having established reaction conditions, various ketones, such as 2-butanone, cyclopentanone, acetophenone, and 4-iodo-acetophenone reacted smoothly with o-phenylenediamine or with substituted phenylenediamine under similar reaction conditions to afford the corresponding 1,5-benzodiazepine derivatives in good to excellent yields in relatively short reaction times (entries 1–12, Table 3). It should be noted that this method is suitable for the preparation of 1,5-benzodiazepine derivatives with both electron rich as well as electron deficient ketones and o-phenylenediamine derivatives with fine results.



R=H, Me, NO_2; R^1, R^2=H, alkyl, aryl

Scheme 1. Synthesis of 1,5-benzodiazepines derivatives.

Table 1. Model reaction of o-phenylendiamine with acetone at 40°C.



Entry	IL	Temperature (°C)	Time	Yield[a] (%)
1.	TEAA	25	30 min	20
2.	TEAA	25	06 h	45
3.	TEAA	25	10 h	45
4.	**TEAA**	**40**	**15 min**	**96**
5.	TEAA	40	1 h	96
6.	TEAA	50	15 min	96

[a]Isolated yield.

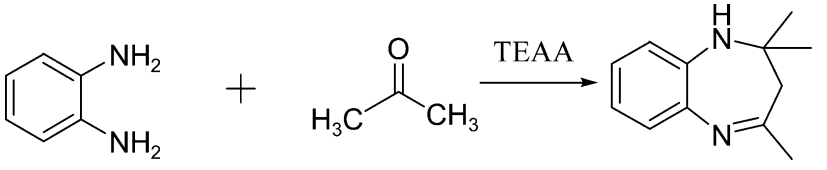
The mechanism of the reaction most likely involves an intramolecular imine–enamine cyclization promoted by triethyl ammonium ionic liquid which may be attributed to the inherent Bronsted and Lewis acids of [Et_3NH] cation which makes the N–H bond weaker, enhancing the nucleophilicity of nitrogen as shown in Scheme 2. Amino groups of o-phenylene-diamine attack the carbonyl group of the ketone giving the intermediate diimine **2**. 1,3-Hydrogen shift attached to methyl group then occurs to form an isomeric enamine **3**, which cyclizes to afford the seven-member ring **5** (Scheme 2).

Experimental

General methods

All reagents used were AR grade. Melting points were determined by using a Thomas Hoover melting point apparatus and are uncorrected. ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker 300 NMR spectrometer in $CDCl_3$ (with TMS for ^1H and chloroform-*d* for ^{13}C as internal references) unless otherwise stated. Mass Spectrum was recorded on Hybrid Quadrupole-TOF LC\MS\MS mass spectrometer (Q. Star XL). Microanalyses were obtained with an Elementar Analysensysteme GmbH VarioEL

Table 2. Catalytic cycle for the reuse of ionic liquid TEAA ([Et_3NH][CH_3COO]) for model reaction.



Number of recyclable turns	Yield (%)
1	96
2	96
3	96
4	96
5	96
6	93
7	93
8	92
9	92
10	90
11	80

Table 3. Showing various catalytic systems for the reaction of o-phenylendiamine with acetone.

Entry	Catalyst	Time	No. of recyclable	Yield[a] (%)	References
1.	[bibm][BF_4]	50 min	6	93	(*33–36*)
2.	[$EtNH_3$][NO_2]	50 min	6	53	(*33–36*)
3.	Polyanilinesulphate	3 h	6	82	(*25*)
4.	NBS	2 h	4	95	(*26*)
5.	H_{14} [$NaP_5W_{30}O_{10}$]	75 min	3	92	(*24*)
6.	Fe (ClO_4)	15 min	2	85	(*20*)
7.	**TEAA**	**15 min**	**10**	**96**	

[a]Isolated yield.

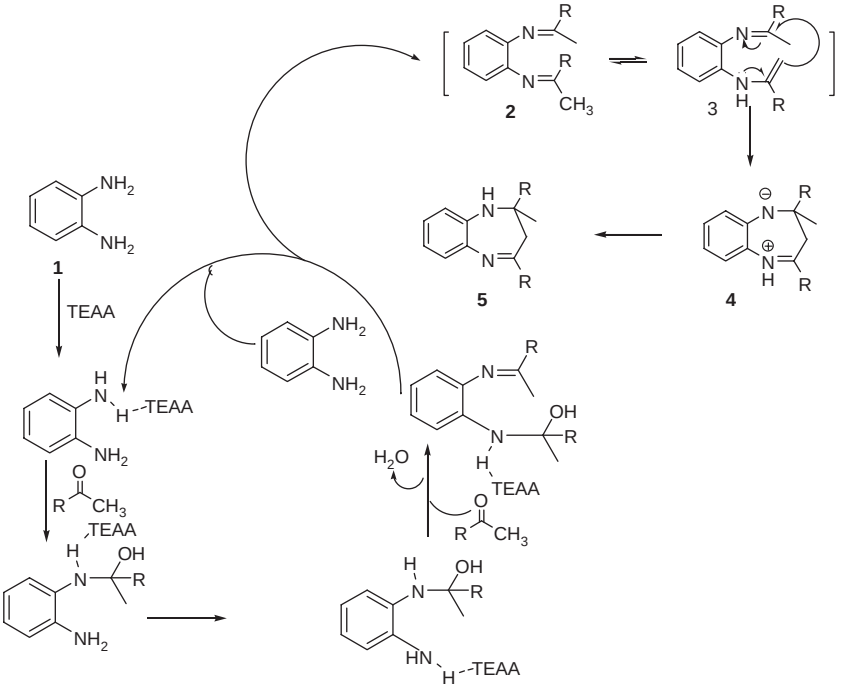
V3.00 element analyzer. The reactions were monitored by TLC using aluminium sheets with silica gel 60 F_{254} (Merck). The density of pure compounds and mixture were measured by means of an Anton Paar DMA 4500 M with accuracy of $\pm 0.00005\ g\ cm^{-3}$. The calibration of the apparatus was checked by the standard procedure, i.e. by measuring the density of pure water and air at 298.15 K and at atmospheric pressure.

Modified general procedure of triethyl ammonium acetate [Et3NH][CH3COO] (TEAA) synthesis (46–48)

The synthesis of the ionic liquid was carried out in a 250 mL round-bottomed flask, which was immersed in a water-bath and fitted with a reflux condenser. Acetic acid (1.5 mole, 90.1 g, 86.03 mL) was dropped into the triethyl amine (1 mole, 101.2 g, 139.4 mL) at 70°C in 1 h. After the addition, the reaction mixture was stirred for 2 h at 80°C to ensure that the reaction had proceeded to completion. The reaction mixture was then dried at 80°C until the weight of the residue remained constant. The samples were analyzed by Karl Fisher titration and revealed very low levels of water (below 70 ppm). The yield of TEAA was 98%. ^{1}H NMR (DMSO-d_6): Δ (ppm) 1.18 (t, 9H), 2.10 (s, 3H), 3.10 (m, 6H), 9.0 (s, 1H). Density: 1.01586 g/cm^3, specific gravity: 1.018880 at temperature: 25°C.

General procedure for synthesis of 1,5-benzodiazepines derivatives

A solution of o-phenylenediamine (1 mmol) and the corresponding ketone (2.1 mmol) in TEAA (1 mL) was stirred at 40°C for 15–20 min. The completion of the reaction was monitored by TLC. The resultant product formed in one-phase system was diluted with water (3 mL) and extracted with diethyl ether (5 mL × 3).



Scheme 2. Proposed mechanism for the TEAA catalyzed reaction.

Table 4. Condensation of o-phenylenediamine with various ketones catalyzed by TEAA.

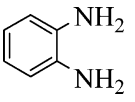
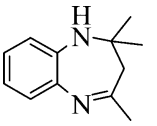
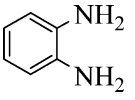
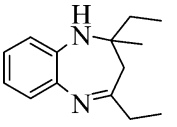
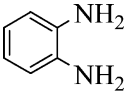
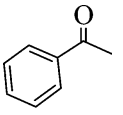
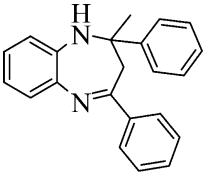
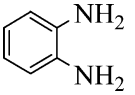
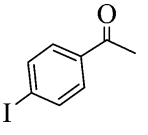
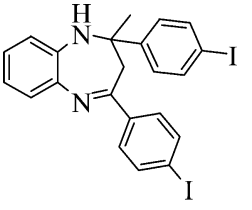
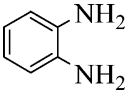
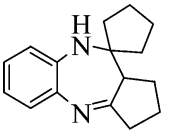
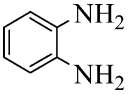
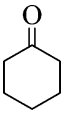
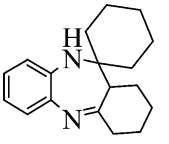
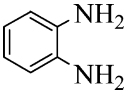
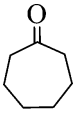
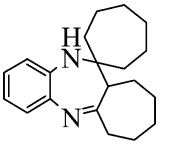
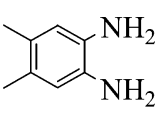
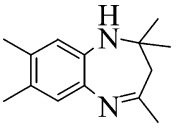
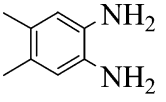
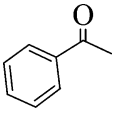
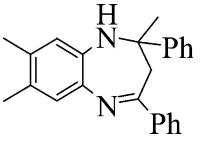
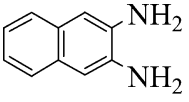
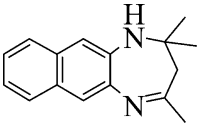
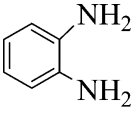
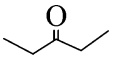
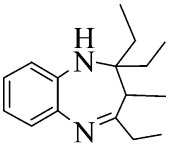
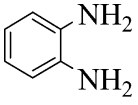
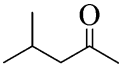
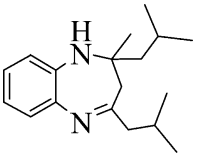
Entry	Substrates	Ketone	Product	Time (min)	Yield (%)[a]	MP (°C) found reported[b]
1				15	96, 94[c]	137–138 136–138 (*42*)
2				18	92	137–138 137–139 (*22,23*)
3				18	94	148–150 150–152 (*42*)
4				18	95	145–147 New compound
5				18	93	136–138 137–138 (*42*)
6				16	92	134–136 136–137 (*22,23*)
7				16	93	134–136 135–137 (*22,23*)

Table 4 (*Continued*)

Entry	Substrates	Ketone	Product	Time (min)	Yield (%)[a]	MP (°C) found reported[b]
8				15	95	110–112 112–114 (*24*)
9				18	91	114–115 115–116 (*24*)
10				20	89	213–214 212–214 (*42*)
11				15	95	141–143 143–144 (*22,23*)
12				18	93	118–120 118–120 (*22,23*)

[a]Isolated yield.
[b]All results reported in references (*22–24,42*) unless otherwise noted.
[c]Yield on a 5 g scale.

The combined organic layer was separated, dried over anhydrous sodium sulphate, and evaporated under reduced pressure to afford the 1,5-benzodiazepine derivatives. The aqueous layer consisting of the TEAA was subjected to distillation (80°C) for 2 h to remove water, leaving behind the TEAA, which was further used and recycled. The conversion and the yield were not reduced significantly after being reused subsequently for 10 times. The entire isolated product was re-crystalized from EtOAc/petroleum ether (single spot on TLC). All the compounds were compared with authentic samples and their structure were also assigned on the basis of IR, ^{1}H, ^{13}C NMR, and LC-MS spectroscopic data.

Spectral and analytical data of new compound (entry 4, Table 3).

Compound characterization

2,4-di (4′-iodo-phenyl)-2-methyl-2,3-dihydro-1H-1,5-benzodiazepine: yellow solid; mp 145–147°C; IR (cm^{-1}) 3261 (NH), 1660 (C = N); ^1H NMR ($CDCl_3$, 300 MHz) Δ 7.57 (t, 4H, $J = 8.1$ Hz), 7.33–7.25 (m, 5H), 7.11–7.02 (m, 2H), 6.82 (d, 1H, $J = 6.9$Hz), 3.43 (s, NH), 3.05 (d, 1Hm, $J = 13.2$ Hz), 2.87 (d, 1H, $J = 13.2$ Hz), 1.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz), Δ 166.2, 147.1, 139.8, 137.2, 128.7, 128.6, 126.7, 122.0, 121.4, 96.7, 92.8, 73.4, 42.8, 29.8; LCMS m/z 564.9 (M + 1).

Conclusion

We have described that the use of TEAA as a catalyst/reaction medium for the synthesis of 1,5-benzodiazepines under solvent-free conditions. This procedure offers several advantages, such as (a) TEAA is a cost effective and environmentally benign reagent, (b) green synthesis (avoiding hazardous and toxic organic solvents for work up), (c) applicability to a wide range of substituted ketones (d) room temperature reaction condition, and (e) it is recyclable for at least 10 times without appreciable loss in yield. Furthermore, better yields, simple reaction conditions, shorter reaction times, and easy work up make this a green, facile and superior method for the synthesis of 1,5-benzodiazepine derivatives.

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