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Graphical Abstract

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An unprecedented imidazolium based ionic liquid tuned selective aminolysis of ester-carbonyl and cyclization catalysis involving carbonyl group of acetoacetates is demonstrated to achieve acetoacetas, their chiral analogues and benzimidazoles.

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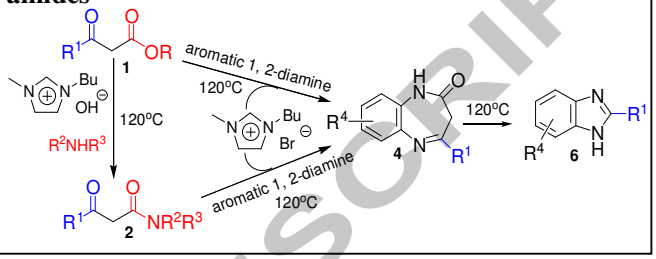

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Selective exploitation of acetoacetate carbonyl groups using imidazolium based ionic liquids: Synthesis of 3-oxo-amides and substituted benzimidazoles

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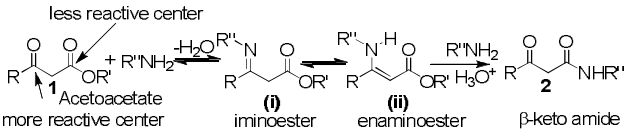
ABSTRACT

An unprecedented Brønsted base ionic liquid tuned selective aminolysis of ester carbonyl of acetoacetates is demonstrated to achieve acetoacetamide derivatives. Other imidazolium ionic liquid performs an efficient cyclization catalysis involving acetoacetate-carbonyl groups and o-phenylenediamine at elevated temperature to produce benzimidazoles via C-C bond cleavage of intermediate 1,5-benzodiazepinones under solvent-free conditions.

β-Ketoamides (3-oxo-amides) are recognized as highly versatile synthons in organic synthesis because of the presence of several reactive sites in one molecule diversifies its application in various synthetic strategies[1] to multifunctional entities. Synthesis of a wide variety of such multi-functionalized molecules through development of a new domino reaction[2] is an important addition to the existing synthetic approaches in organic chemistry. A large number of heterocyclic compounds having different pharmacological activities[3] have been synthesized involving multiple bond-forming transformations[4] using substituted acetoacetamides. For these reason, it is always of current interest to find new and simple procedures for the synthesis of *N*-substituted acetoacetamides. Usually two protocols for the synthesis of *N*-substituted acetoacetamides (**2**) are commonly followed: (i) acylation of amide enolates or their synthetic equivalents[5a] and (ii) two components coupling of amines with β-ketoacids or their synthetic analogues such as β-ketoesters,[5b] β-ketothioesters,[5c,d] ketene dimer,[5e,f] and acylketens[5g-j] obtained from thermal decomposition of 2,2,6 trimethyl-4*H*-1,3-dioxin-4-one. Apparently, the direct aminolysis of inexpensive β-ketoester (**1**) would be a straightforward pathway to β-ketoamides (**2**) but this synthesis generally involves low yields of the product due to the presence of more reactive keto-carbonyl group leading to co-occurrence of side product enamino esters[2b,6] (**3**, Scheme 1).



Scheme 1: Synthetic strategy for the amidation of acetoacetate

Moreover huge quantity of xylene is required for such transformation, which is objectionable in respect to green chemistry principles. Other methods for the synthesis of β-ketoamides from acylated Meldrum's acids,[7] lipase catalysis[8] and enamine-based[9] domino strategy of acetoacetamides are also known. Although some of the methods are very effective in terms of yield but synthesis of starting materials are cumbersome and many of them are posed to serious negative impact to health and environment. Thus, the development of a method that can suppress the formation of intermediate iminoester (**i**) or eneminoester (**ii**) thereby shield the keto-carbonyl from the nucleophilic attack of amine (Scheme 1), which would be more viable and attractive to achieve desired β-ketoamide (**2**). As a part of our ongoing program to design and develop solvent and metal-free strategies in organic synthesis,[10] we were interested to observe the effect of imidazolium-based basic ionic liquid as catalyst in the direct amidation of alkyl acetoacetate and synthesis of benzimidazoles by C-C bond cleavage of acetoacetate. It is expected that basic

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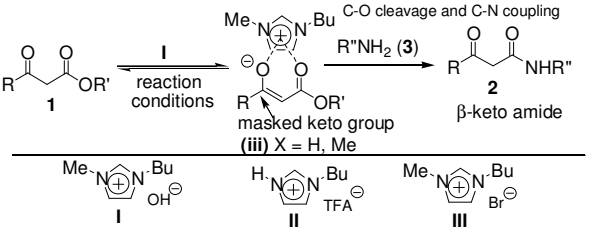
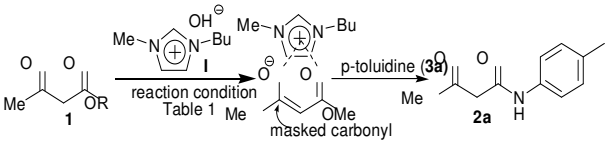
ionic liquid **I** ([BMIm]OH)[11] will facilitate enolization of **1** that can be stabilized by imidazolium cation and simultaneously the ester group also activated. Thus it will favor the amidation reaction (Scheme 2). We also screened two more ionic liquids namely 1-butyl imidazolium trifluoroacetate (**II**) and 1-butyl-3-methyl imidazolium bromide (**III**) in the present study(Scheme 2).



Scheme 2: Basic ionic liquid catalyzed synthesis of **2**

In our initial experiments, the amidation of methyl acetoacetate with *p*-toluidine (**3a**) was chosen as a model reaction to optimize the reaction conditions (Table 1). Few drops toluene were used for smooth stirring of the mixture at 80 °C and the reaction was unsuccessful in the absence of basic ionic liquid. Whereas in the presence of 50mol% of basic ionic liquid (**I**) it provided a mixture of products (Table 1, entry 2). Although the expected β-ketoamide (**2a**) was found at 120 °C, but ^{1}H NMR spectra of the crude products indicated the presence of very small amount of enemine of the β-ketoamide. Acidic hydrolysis of the mixture with 10% aqueous HCl followed by purification over silica-gel column chromatography afforded 82% of the desired product (**2a**, Table 1, entry 3). Increased amount of amines did not significantly improve the yield; however using 100 mol% of ionic liquid afforded the desired product in excellent yield (90%, Table 4, entry 4) after 4hrs. Without solvent or changing solvents from nonpolar to polar the yield was drastically dropped (Table 1, entries 5-7) and the reaction was arrested in protic solvent glycerol (Table 1, entry 8). To ascertain the role of ionic liquid we have carried out the same reaction without basic ionic liquid, and with KOH and 18-crown-6 under similar reaction conditions. Our observed essentiality of ionic liquid for the reaction to occur because only a trace amount of the desired acetoacetanilide was detected (not included in Table 1). For further improvement of yield we were curious about the effect of alkyl group present in acetoacetate. However, only a little difference was observed between methyl or ethyl acetoacetate (Table 1, entries 4 vs 9). However considerable discrimination was observed in the case of isopropyl acetoacetate that produced only 70% of the corresponding product (Table 1, entry 10). After isolation of products by solvent extraction, the aqueous layer containing ionic liquid can be collected (concentrated and vacuum dried) and recycled at least 4 times without significant loss of catalytic activity (Table 1, entry 11). It is noteworthy to mention that protic ionic liquid *N*-butylimidazolium trifluoroacetate (**II**) and neutral ionic liquid 1-butyl-3-methyl imidazolium bromide (**III**) are favoring the formation of imine (**i**) - enamine (**ii**) tautomeric form of β-ketoester (**1**) and only a little amount of desired acetoacetanilides (**2a**) was detected in both the reactions (not shown in the Table 1). On the basis of successful results shown in Table 1 (entry 4) we decided to perform subsequent reactions with varieties of amines and β-ketoesters for establishing it as general strategy. As listed in Figure 1, different kinds of amines were acetoacetylated using methyl or ethyl acetoacetate in good to excellent yields. Aromatic amines followed slower reaction

Table 1: Optimization of amidation of acetoacetate by the catalysis of ionic liquid



Entry	R	BIL (mol%)	Temp (°C)	Solvent	Yield (%)[a,b]
1	Me (**1a**)	no	80	Toluene	mixture
2	Me	50	80	Toluene	mixture
3	Me	50	120	Toluene	82
4	**Me**	**100**	**120**	**toluene**	**90**
5	Me	100	120	-	50
6	Me	100	100	Dioxane	75
7	Me	100	90	CH_3CN	40
8	Me	100	120	Glycerol	NR
9	Et (**1b**)	100	120	Toluene	88
10	^{i}Pr (**1c**)	100	120	Toluene	70
11[c]	Me	100	120	toluene	88, 87, 87, 85

*[a] yields refer to purified yield; [b] 0.5 mL toluene was used in each entry; [c] using recycled basic ionic liquid (**I**)*

rate with respect to aliphatic amines with better yield. Aniline, o-toluidine, naphthylamine and 4-methoxyaniline all undergo smooth amidation with β-ketoester to form β-ketoamide (**2b-e**, Fig. 1) in good to excellent yield. Among the aromatic amines, the electron releasing aromatic amine proceeded faster reaction than the aromatic amines containing electron withdrawing substituents such as nitro, fluoro- and pyridine (amide **2f-i**, Fig. 1). Aliphatic amines like morpholine, piperidine, benzylamine and *tert*-butyl amine also produced corresponding amides (**2j-m**, Fig. 1) in high yield without any difficulty. Ethyl benzoylacetate[12] produced corresponding β-ketoamides **2n-q** in excellent yield with shorter reaction time as compared to the

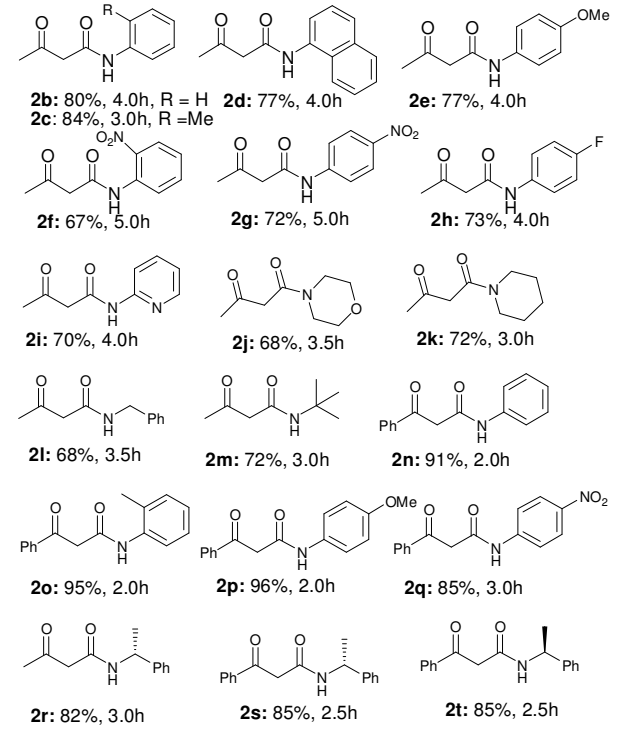
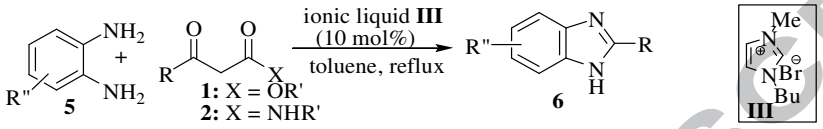
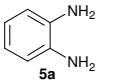
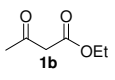
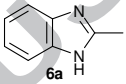
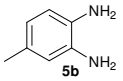
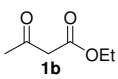
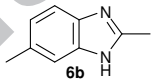
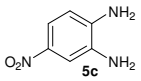
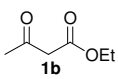
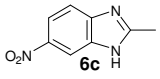
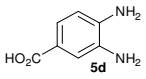
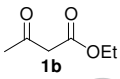
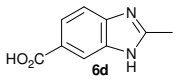
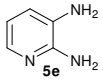
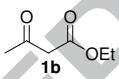
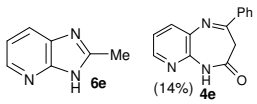
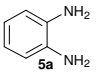
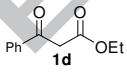
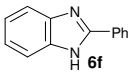
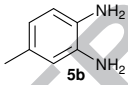
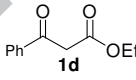
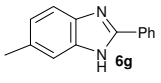
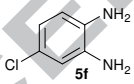
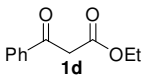
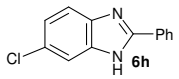
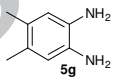
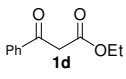
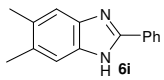
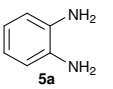
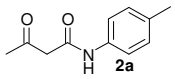
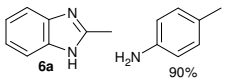
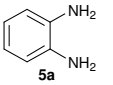
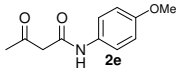
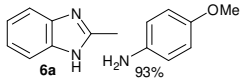
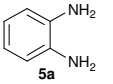
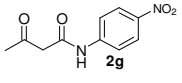
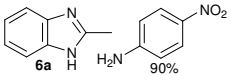
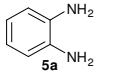
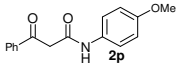
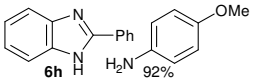


Figure 1: Description of various synthesized acetoacetamides

methyl or ethyl acetoacetate. Versatility of the strategy is examined by synthesizing valuable chiral acetoacetamides (**2r-t**, Fig. 1) under the same reaction conditions. It was known for a long time that o-phenylenediamine reacts with ethyl acetoacetate (EAA) under acidic conditions[13] or microwave irradiation[14] to affords 1,5-benzodiazepinone derivatives (**4**). Since under basic condition ketone carbonyl of β-ketoester becomes masked, we reasoned that o-phenylenediamine may react with two molecules of ethyl acetoacetate to produce bis-acetoacetamide, which could be a potential ligand for the detection/sensing of metal ions or other interesting application. Accordingly o-phenylenediamine (**5a**) was allowed to reacts with EAA under the catalysis using basic ionic liquid **I** in toluene under refluxing conditions. This reaction results mainly 2-methyl benzimidazole (**6a**) as one of the products with small amount of unidentified other by-products. However a very clean reaction occurs in the presence of 10 mol% of ionic liquid 1-butyl-3-methyl-imidazolium bromide (**III**) under solvent-free conditions affording 2-methyl benzimidazole (**6a**) in 95% isolated yield (Table 2, entry 1). To the best of our knowledge there is no report for such transformation performed under neutral conditions. This interesting observation prompted us to explore the synthetic utility and mechanism of the benzimidazole formation under solvent-free protocol. To this end, we have utilized series of aromatic diamines (**5**)

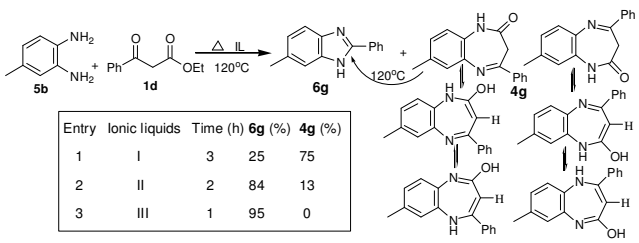
Table 2: Ionic liquid **III** promoted synthesis of substituted benzimidazole



Entry	Diamine (5)[a]	Ketoester/amides	Time (min)	Product (6)	Yield (%)[b]
1			90		95
2			60		95
3			180		90
4			180		91
5			120		75
6			45		92
7			60		95
8			60		84
9			45		88
10			120		95
11			60		95
12			60		92
13			90		97
14			120		93[c]

[a] reaction carried out in one mmol scale; [b] yield refers to purified yield of benzimidazoles; [c] reaction was conducted using 2-methyl-1,3-dibutyl imidazolium bromide as activator

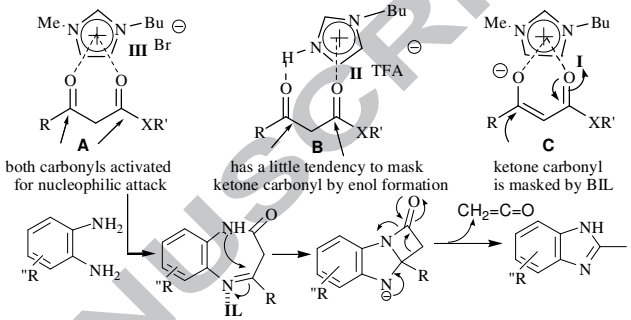
and several β-ketoesters for the synthesis of multi substituted benzimidazoles (**6**, Table 2). When ethyl acetoacetate (**1b**) was allowed to react with aromatic amine **5b-e** in the presence of ionic liquid **III** under solvent-free conditions at 120 ºC smooth transformation to highly substituted benzimidazole **6b-e** were observed in high yield of 75-95% (Table 2, entries 2-5). No 1,5-benzodiazepinoe was detected except in the case 2,3-diamino pyridine (Table 2, entry 5). In this case 1,5-benzodiazepinone was isolated in small quantity (14% yield), which showed the presence of amide carbonyl in its FTIR spectrum, but in NMR it exists as four tautomeric forms (ESI). Ethyl benzoylacetate (**1d**) also reacted with aromatic diamine **5a-b**, **5f**, **5g** (Table 2, entries 6-9) to afforded **6f-i** in excellent yield. All the synthesized products (**6a-i)** were characterized by spectral analyses and the data were compared with reported compounds (ESI). Similar trends were observed in the cases of *N*-aryl acetoacetamides (**2a, e, g, p,** Table 2, entries 10-13) and 2-methyl benzimidazole (Table 2, entries 10-12) and 2-phenyl benzimidazole (Table 2, entry 13) were obtained with concomitant formation of the parent amines. Formation of free amine ($ArNH_2$) is strongly suggested that 1,5 benzodiazepinone forms as initial intermediate in these reactions. Although we were unable to isolate intermediate 1,5-benzo-diazepinones from the reaction of diamines with acetoacetic ester or amides (Table 2) even quenching of reaction mixture after short time (except entry 5), however the reaction of ethyl benzoylacetate (**1d**) with 4-methyl-1,2-diaminobenzene (**5b**) with catalyst ionic liquid **I** and **II** a variable mixture of 2-phenyl-5(6)-methyl benzimidazole (**6g**) and 4-phenyl-8-methyl-2,3-dihydro-1*H*-1,5-benzodiaze-pin-2-one (**4g**) were obtained (Scheme 3). With the use of basic ionic liquid **I** reaction yields a mixture benzimidazole (**6g**) and benzodiazepinone (**4g**) in a ratio of 1:3 whereas reverse effect was observed in the case of protic ionic liquid **II** (**6g**:**4g =** 6:1). In contrast to the previous result exclusive formation of **6g** (95%) was observed in a shorter reaction time on employing ionic liquid 1-butyl-3-methyl imidazolium bromide (**III)** (Table 2, entry 7). Appearance of infrared stretching frequency at 1677cm^{-1} indicated the presence of -NHCO- group in **4g** whereas NMR spectra in $CDCl_3$ (^1H, ^{13}C) of **4g** showed the existence of four tautomeric forms (Scheme 3). Thus with these experimental results in hand we proposed that at high temperature in the presence of ionic liquid 1,2-diaminobenzene or its derivative reacts with β-ketoester or amide to produce substituted 1,5-benzodiazepinone, which than undergo facile thermolysis to benzimidazoles and ketene (Scheme 4). Involvement of thermolytic decomposition in the formation of benzimidazole (**6**) from benzodiazepinone was also further confirmed by heating of 4-phenyl benzodiazepinone (**4g**) in the presence of ionic liquid **III** at 120 ºC (Scheme 3). These results



Entry	Ionic liquids	Time (h)	**6g** (%)	**4g** (%)
1	I	3	25	75
2	II	2	84	13
3	III	1	95	0

Scheme 3: Effect of IL in the formation of benzodiazepinone

indicated that basic ionic liquid mask the carbonyl of β-ketoesters as well benzidiazepinone through enolization thereby retard the reaction to complete, whereas other ionic liquids facilitate nucleophilic attack through simultaneous activation of carbonyls of β-ketoesters or amides to form benzodiazepinone **4** followed by activation of other nitrogen that helps for ring closure followed by C-C bond cleavage to form benzimidazole **6** (Scheme 4). Involvement of activated hydrogen at C-2 of ionic liquid may be ruled out because on use of 2-methyl-1,3-dibutyl imidazolium bromide as activator also produced the desired product 2-methyl benzimidazoles (**6a**) in 93% yield (Table 2, entry 14).



Scheme 4: Proposed mechanism of benzimidazole formation

In conclusion, this article described[15] a very fast, simple and efficient method to synthesize functionalized synthons β-ketoamides and their chiral analogues, and substituted benzimidazoles from β-ketoesters through selective aminolysis of less reactive ester carbonyl by masking of more active carbonyl group with powerful basic ionic liquid. On treatment of 1,2-diaminobenzenes with β-ketoesters or amides benzimidazoles were formed by exploiting both carbonyls of *via* formation of 1,5-benzodiazepinone intermediate under the influence of a neutral ionic liquid. Details mechanistic investigation, trapping of intermediate ketene and other substrate scope is underway and results will be communicated in due course.

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15 Representative experimental procedure: (a) **For aceto-acetamide derivatives**- A mixture of methyl/ethyl acetoacetate (0.58g, 5.0 mmol), basic ionic liquid (0.78g, 5.0 mmol) and an *p*-toluidine (0.64g, 6.0 mmol) in toluene (1 mL) was refluxed for 4 hrs. The mixture was diluted with water (30 mL) and extracted with ethylacetate or ether (3 x 10mL). The aqueous layer containing basic ionic liquid was recycled. The organic layer was stirred with 10% HCl (10 mL) at room temperature for 2hrs. The organic layer was collected, washed with water (3 x 10 mL), dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The crude product was purified over silica-gel (60–120 mesh) using ethyl acetate-hexane (3:7) as eluent to afford **2a** as colourless needles. Similar procedure was followed for other esters. (b) **For benzimidazole derivatives**- A stirred mixture of aromatic diamine (1 mmol) and β-ketoester or β-ketoamide (1 mmol) was heated under inert condition at 120 ºC in the presence of 10mol% of ionic liquid **III**. After completion of reaction as revealed by TLC, product was crystallized from ethyl acetate–hexane or passes through short pad silica-gel to remove any colour impurities from the product to obtain analytically pure benzimidazoles.

HIGHLIGHTS

- Basic ionic liquid [BMIm]OH catalyzed amidation of 3-oxo esters were developed.
- [BMIm]OH acts as masking agent of ketone carbonyl and activator of ester carbonyl.
- Benzimidazole was formed via 1,5-benzodiazepinone followed by C-C bond cleavage.