Research Article

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DOI: 10.4172/2574-0431.100024

Synthesis and Catalysis: Open Access ISSN 2574-0431 **2018** Vol.3 No.3: 6

Solvent-free Knoevenagel Condensation over Amino Acid Amide based Ionic Liquid as an Efficient and Eco-friendly Catalyst

Abstract

Solvent-free Knoevenagel condensation was carried out over 1-((4-chlorophenyl) amino)-1-oxopropan-2-aminium perchlorate based ionic liquid as an eco-friendly catalyst at room temperature. A wide range of aromatic and heteroaromatic aldehydes easily undergo condensation with malononitrile and ethyl cyanoacetate. The reaction proceeds at room temperature without using any organic solvent and is very fast with good to excellent yield. The most significant feature of this methodology is the condensation of aliphatic aldehydes and cyclic ketones, achieved very efficiently at room temperature under solvent-free conditions, which is difficult to achieve by conventional methods. Additionally, the catalyst is easily separable and recyclable without loss of activity.

Keywords: Knoevenagel condensation; Ionic liquids; Solvent-free; Malononitrile; Cyanoacrylate

Received: November 16, 2018; Accepted: November 23, 2018; Published: December 03, 2018

Introduction

Knoevenagel condensation is a versatile C-C bond forming reaction between carbonyl compounds and active methylene compounds to form electrophilic alkenes in organic synthesis [1]. This reaction found many applications such as, in the synthesis of intermediate of fine chemicals [2-4], in the synthesis of intermediates like Quinoline, Imidazopyridines, Coumarin, Benzofuran and Iminocoumarin derivatives of biological important compounds [5-10]. The methods reported so far use harmful organic solvents, long reaction time and is usually catalysed by acid or base at high temperature [11] or it needed other special conditions, such as microwave irradiation [12]. Also in some reactions the catalyst cannot be recycled [13].

Solvent-free organic synthesis has been receiving considerable attention because of growing worldwide concerns over chemical wastes and future resources as well as for the requirements of green chemistry [14]. In such means, scientists are concentrating more on the development of environmentally friendly organic synthesis through the use of metal-free catalysts, eco-friendly solvents, renewable resources, and waste reduction. The utilization of reusable catalysts and solvent-free media for organic synthesis has been recently developed, and relates with

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Citation: Burate PA, Javle BR, Desale PH, Kinage AK (2018) Solvent-free Knoevenagel Condensation over Amino Acid Amide based Ionic Liquid as an Efficient and Eco-friendly Catalyst. Synth Catal Vol.3 No.3:6

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the green chemistry protocols. During last decade ionic liquids (ILs) have emerged as a very potential green alternative to volatile and hazardous organic solvents and are being used as efficient and recyclable reaction media for a variety of important reactions [15,16]. Importantly, they have been introduced as alternative green reaction media due to their unique chemical and physical properties such as low vapour pressure, high thermal, and chemical stability [17-23]. Moreover, they have also been used as catalyst due to its good activity, selectivity, controlled miscibility and ease of recyclability [24,25]. In recent years, many functional ILs have been synthesized and developed further as catalyst, playing a remarkable role in various organic reactions like asymmetric Henry reaction [26]. Mannich reaction [27]. Friedel-Crafts alkylation [28]. A variety of ILs have been employed for Knoevenagel condensation reaction too, such as [C6-mim] PF6 [29]. [bmim]Cl.xAlCl₂, [bpy]Cl.xAlCl₂ [30], [bmim]BF₄ [31]

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[bmIm]OH [32], [MmIm][MSO₄] [33] [MeOEt-MIm]+[CF₃COO]⁻ [34] guanidinium lactate ILs [35] ethylammonium nitrate [36], HMTA-AcOH-H₂O [37], 2-hydroxyethylammonium formate [38], [C₄-choline][Ac] [39], glycine in ILs [40]. Ether- and alcoholfunctionalized ILs [41]. N-methyl morpholine (Nmm) based ILs [42], [Et₃NH][HSO₄] [5], [C₄dabco][BF₄] [43], etc.

To the best of our knowledge, the ILs of N-aryl amino acid amides has not been explored yet for Knoevenagel condensation. On the basis of the above-discussed facts and in extension of our ongoing research program aimed on the development of amino acid amide based IL [44]. We, herein wish to report for the first time, ILs of amino acid amide (1-((4-chlorophenyl) amino)-1oxopropan-2-aminium perchlorate) as an acidic Brønsted IL as an environmentally benign, efficient and recyclable catalyst **Figure 1** for one-pot Knoevenagel condensation in solvent-free media at room temperature.

Results and Discussion

In our preliminary experiments, we investigated the optimum reaction conditions regarding the catalyst and solvent of the reaction. For this purpose, benzaldehyde 1 (0.9 mmol) and malononitrile 2 (0.9 mmol) were chosen as model substrate and 1.0 equiv. of catalyst for the synthesis of representative compound 3a at 80° C.

Initially, we carried out the reaction in the absence of any IL; only trace amounts of product was formed even after 24 h in DMF Table 1 entry 1. Next, we carried out reactions using alanine (amino acid used as precursor for amidation) and amino acid amide without protonation, trace amount of product was formed after 24 h Table 1 Entry 2 & 3. It was then clear that amino acid amide without protonation has no activity in Knoevenagel condensation. Therefore, we used protonated amino acid amide (IL) for Knoevenagel condensation for further studies. Next, to investigate the solvent effect, we performed the reaction in different organic solvents. The desired product was obtained in moderate to good yield within 12 h Table 1 entry 4-10. This is because of poor solubility of IL in organic solvents. When water was used as solvent, the yield of reaction was significantly increased to 71% in 12 h Table 1 entry 11. Further, we carried out solvent-free reaction and observed dramatic increment in the yield of product Table 1 entry 12. Then we carried out same reaction at room temperature and surprisingly, the yield of reaction was increased to 97% in 1 h Table 1 entry 13. Next, we investigated effect of substrate to catalyst ratio Table 1 Entry 14-17 the excellent yield of product was obtained when 0.5 equivalent of IL Table 1 Entry 15 was used. Thus, it is concluded that 0.5 equivalent of IL is an ideal concentration for the best results. Therefore, all further reactions were carried out by using 0.5 equivalent of catalyst at room temperature under solventfree conditions in Figure 2.

Using these optimized reaction conditions, the scope and efficiency of this approach were explored for the synthesis of



Table 1 Optimization of reaction conditions^a.

entry	Solvent	Temp. (°C)	Catalyst (equiv)	Time (h)⁵	Yield (%)C
1 ^d	DMF	80		24	trace
2 ^e	DMF	80	1	24	trace
3 ^f	DMF	80	1	24	trace
4	DMF	80	1	12	43
5	Dioxane	80	1	12	43
6	DMSO	80	1	12	27
7	CH₃CN	80	1	12	24
8	THF	80	1	12	22
9	CH₃OH	80	1	12	42
10	C ₆ H ₅ CH ₃	80	1	12	18
11	H ₂ O	80	1	12	71
12		80	1	6	92
13		RT	1	1	97
14		RT	0.7	1	96
15		RT	0.5	1	97
16		RT	0.3	1	63
17		RT	0.2	1	42

^areaction conditions: benzaldehyde (1) 0.9 mmol and malononitrile (2) 0.9 mmol, ^bReaction progress monitor by TLC. ^cIsolated yield. ^dwithout IL, ^eAlanine, ^famino acid amide was used as catalyst.





other acrylonitrile and cyanoacrylate derivatives **Scheme 1** and the obtained results are summarized in **Table 2**.

As illustrated in **Table 2**, various aromatic aldehydes with electronic donating groups (-Me, - OMe, -Et, -OH, etc.) and electronic withdrawing groups (-Cl, -F, -Br,-CN) at o-, m-, p-positions of aromatic ring, were reacted effectively with active methylene compounds like malononitrile and ethyl cyanoacetate. The good to excellent yields of acrylonitrile and cyanoacrylate derivatives were obtained over IL. From these results it confirms that, the electronic nature of the substituent on the benzene ring does not affect the reaction activity and product yield. Thus, the flexibility of process allows the strategic placement of functional group.

Next, we explored the feasibility of this protocol with various cyclic ketones and aliphatic, heteroaromatic aldehydes **Table 3**, as the condensation of cyclic ketones and aliphatic aldehydes with active methylene compounds is difficult with reported ILs [29-31].

Results show that **Table 3**, cyclic ketones and aliphatic aldehydes can also undergo reaction under optimized reaction conditions to give moderate to good yield with longer reaction time **Table 3** entry 1-4. This may be because of cyclic ketones are less

Table 2Solvent-free Knoevenagel condensation reaction of differentaldehydes with active methylene compounds in presence of IL at RT for 1 h.

Entry	R	Х	Product	Yield % ^a
1	C ₆ H ₅	CN	3a	97
2	4-MeO-C ₆ H ₄	CN	3b	96
3	2-CI-C ₆ H ₄	CN	3c	93
4	4-C ₂ H ₅ -C ₆ H ₄	CN	3d	94
5	3-Br-C ₆ H ₄	CN	3e	77
6	$4-F-C_6H_4$	CN	3f	92
7	$4-CI-C_6H_4$	CN	3g	88
8	2-MeO-C ₆ H ₄	CN	3h	91
9	$4-\text{Me-C}_6\text{H}_4$	CN	3i	98
10	1-C ₁₀ H ₇	CN	3J	84
11	2,5-(Me) ₂ - C ₆ H ₃	CN	3k	86
12	3-CN-C ₆ H ₄	CN	31	72
13	C ₆ H ₅	CO2Et	3m	95
14	4-MeO-C ₆ H ₄	CO2Et	3n	91
15	2-CI-C ₆ H ₄	CO ₂ Et	30	94
16	$4-C_{2}H_{5}-C_{6}H_{4}$	CO ₂ Et	Зр	89
17	$3-Br-C_6H_4$	CO ₂ Et	3q	84
18	$4-F-C_6H_4$	CO ₂ Et	3r	87
19	$4-CI-C_6H_4$	CO ₂ Et	3s	92
20	2-MeO-C ₆ H ₄	CO ₂ Et	3t	96
21	$4-\text{Me-C}_6\text{H}_4$	CO ₂ Et	3u	90
22	2-Me-C ₆ H ₄	CO ₂ Et	3v	93
23	2,5-(Me) ₂ - C ₆ H ₃	CO ₂ Et	3w	83
24	3-CN-C ₆ H ₄	CO ₂ Et	3x	71
25	4-OH-C ₆ H ₄	CN	Зу	71
26	2-Me-C ₆ H ₄	CO2Et	3z	82

^aisolated yield.

reactive than aldehydes, required longer reaction time. Notably, condensation of aliphatic aldehydes with Ethyl cyanoacetate required 4 h reaction time and accomplished with moderate to good yield **Table 3** entry 5 & 6.

Interestingly, heteroaromatic aldehydes such as 2-Thiophenecarboxaldehyde, Furan-2-carboxaldehyde give good yield of corresponding products within 4 h **Table 3** entry 7-10. Surprisingly, α - β -unsaturated aldehyde and di-Substituted aldehyde like 3-hydroxy, 4-methoxy benzaldehyde also easily undergo reaction under optimized reaction condition with ethyl cyanoacetate to afford products in very good yield **Table 3** entry 11 & 12.

The reusability of the catalyst is a significant advantage particularly for commercial applications. Thus, the recovery and reusability of IL were also investigated and results are shown in **Table 4.** After the completion of the reaction, diethyl ether was added to the reaction mixture. The two separate layers were formed diethyl ether layer and aqueous layer (IL containing water generated in the reaction). The aqueous layer was separated by using separating funnel. Aqueous layer was washed with diethyl ether three times. The IL was recovered from aqueous layer by removing water under reduced pressure and was reused for fresh batch. The reaction was repeated six times and results shows that there is no appreciable decrease in yield of Knoevenagel condensation product. These results show that the IL can be easily separable and reuse for Knoevenagel condensation reaction more than six times without loss of activity.

Next, we performed model reaction on 2 g scale and 2.8 g of 3a was prepared in 95% yield. Therefore, it is a simple route to large scale synthesis of substituted electrophilic alkenes using amino acid amide based ILs as catalyst. Moreover, only the E-isomers of cyanoacrylates were detected and confirmed by NOESY NMR analysis of 3 m.

On the basis of the above results and previous related studies a plausible reaction mechanism of Knoevenagel condensation for the synthesis of acrylonitrile and cyanoacrylate using IL as catalyst is shown in **Scheme 1**. As IL used here is a protic Brønsted acidic IL, initially aldehyde was protonated by IL to form reactive intermediate-(I). It facilitated the nucleophilic attack of the active methylene compound for C-C bond formation to form intermediate-(II). The final Knoevenagel condensation product (3a) was formed by the elimination of water molecule from intermediate-(II) and an IL is regenerated, which continue the reaction cycle **Scheme 2 and 3**.

Conclusion

In conclusion, ionic liquid of amino acid amide is successfully developed and used as an environmentally benign, efficient and recyclable Brønsted acidic catalyst for one-pot Knoevenagel

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Entry	1a	Х	Time (h)a	Product (Yield %)b
1	◯ ⊨o	CN	6.0	4a (54)
2	o	CN	6.0	4b (67)
3	O	CO2Et	6.0	4c (53)
4	0	CO2Et	6.0	4d (58)
5	Me	CO2Et	4.0	4e (58)
6	Me O Me H	CO2Et	4.0	4f (53)
7	€ O H	CN	4.0	4g (68)
8	C S H	CN	4.0	4h (62)
9	€	CO2Et	4.0	4i (66)
10	€ S H	CO2Et	4.0	4j (60)
11	O H	CO2Et	2.0	4k (73)
12	MeO OH	CO2Et	2.0	41 (77)

Table 3 IL catalysed Solvent-free Konevenagel, condensation of cyclic ketones, aliphatic heteroaromatics and unsaturated aldehydes.

^areaction monitor by TLC, ^b Isolated yield of product.

 Table 4 Reusability of catalyst for model reaction.

Entry	Run	Time (h)ª	Yield (%)⁵	Entry
1	1	1	97	1
2	2	1	96	2
3	3	1	96	3
4	4	1	95	4
5	5	1	95	5
6	6	1	95	6

^areaction monitor by TLC, ^b Isolated yield of product.

condensation in solvent-free media at room temperature. Present protocol using IL provides a very efficient and convenient method for Knoevenagel condensation of cyclic ketones, aliphatic ketones, aromatic aldehydes and heteroaromatic



aldehydes with different active methylene compounds. With this green procedure excellent yield of condensation products within shorter reaction time was obtained. The attractive feature of this methodology is IL used here can be easily recovered and efficiently reused. Synthesis and Catalysis: Open Access ISSN 2574-0431 2018

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Solvent-free Knoevenagel Condensation over Amino Acid Amide based Ionic Liquid as an Efficient and Eco-friendly catalyst in **Figure 3**.

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Supporting Information

Detail experimental procedure and spectral data proofs are available in supporting information.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

PAB and BJ acknowledges to CSIR, New Delhi, for Junior Research Fellowship.

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