

Solvent Free Condensation Reactions between Diketone, Aromatic Aldehydes and A Nitrogen Source- A Green Chemical Approach - One Pot and Three Component Synthesis

A. Rajendran^{1,*}, C. Karthikeyan², S. Ramu², D. Ragupathy³

¹Department of chemistry, Sir Theagaraya College, Chennai – 600 021, TN, India.

²Research and Development Centre, Bharathiar University, Coimbatore – 641 046, TN, India.

³Department of Chemistry, National Institute of Technology, Puducherry – 609 605, India.

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ABSTRACT

The parameters like selectivity and overall yield, raw material, time, human resources, energy requirements, as well as the toxicity and hazard of the chemicals and the protocols involved are considered to be very important yard sticks for a neat and efficient organic synthesis. The development of multicomponent reactions (MCRs) in the presence of task-specific ionic liquids (ILs), used not only as environmentally benign reaction media, but also as catalysts, is a new approach that meet with the requirements of sustainable chemistry. Here, we propose the multicomponent condensation reaction of dimedone, aromatic aldehydes, and an aromatic amine under solvent-free conditions using the ionic liquid $[\text{Et}_3\text{NH}]^+ [\text{BF}_4]^-$. Short reaction time (40-55 min), good to high yields (90-95 %), not using the organic solvents and simple work-up procedure and the recyclability of the ionic liquid are some of the advantages of this method. The same reaction was carried out in other ionic liquids in order to prove that the proposed ionic liquid is more efficient than them.

1. Introduction

In the context of sustainable chemistry [1] the design and development of sequences allowing highly selective access to elaborated molecular scaffolds while combining structural diversity [2], with eco-compatibility [3], are great challenges for organic chemists. Thanks to their ability to build one product in a single operation from three or more reactant molecules with good to high atom-economy[4] and multiple-bond-forming efficiency [5], multicomponent reactions (MCRs)[6], are now well-established approaches to reach this near ideal goal. Developing the cheap and best synthetic routes for Nitrogen containing heterocyclic systems is an important task in organic Chemistry. Multi-component reactions (MCRs) [7-9] are significant tools for the rapid and efficient synthesis of a wide variety of organic compounds. These reactions have been investigated extensively in organic and diversity oriented syntheses, primarily due to their ability to complex molecular functionality from simple starting materials *via* one-pot reactions. In recent years, extensive research on the synthesis of tricycle compounds containing acridine derivatives, has been reported. Acridine derivatives have been found to possess useful biological activities such as antitumor properties, carcinogenic activity [10], anti-malarial activity [10] and heart defibrillation [10]. Due to its planar structure, acridine chromophore moiety sometimes has excellent DNA binding properties. Recently, the synthesis of polyacridinic compounds, as potential *bis*-intercalating agents [11] has been extensively studied. Moreover, new acridine (naphthalene-quinolines) skeleton fused with a five or six-membered ring yields polycyclic derivatives, which also play important roles as some DNA-intercalating anticancer drugs [12]. Thus, the synthesis of acridine derivatives is an important and principal task in organic chemistry. Some methods are available in the literature for the synthesis of acridine derivatives from dimedone, aldehydes and different nitrogen sources like urea [13], methyl amine [14], ammonium acetate [15] and etc. It can be synthesized also under microwave irradiation [16], using ionic liquids [17-19] and some nano materials [20]. A very few reports are available in the literature on the synthesis of acridine derivatives mediated by ionic liquids with respect to different aldehydes. In continuation of our interest

we are going to use the ionic liquid, $[\text{Et}_3\text{NH}]^+ [\text{BF}_4]^-$ having solvent cum catalytic activity to synthesize the acridine derivatives with different aldehydes. To the best of our knowledge, the acridine derivatives were not prepared still using this ionic liquid.

2. Experimental Methods

2.1 Materials, Chemicals

All chemicals were obtained from Merck, Aldrich and SD fine chemicals. IR spectra were recorded from KBr disk using an FT-IR Bruker Tensor 27 instrument. ^1H NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer using TMS (Tetramethyl silane) as an internal standard. Chemical shift values are given in ppm (δ). Mass spectral measurements were performed by E1 method on a Jeol JMC-300 Spectrometer at 70 eV. Melting points were measured by using the capillary tube method with an electro thermal 9200 apparatus.

2.2 Synthesis of Ionic Liquid

The ionic liquid, $[\text{Et}_3\text{NH}]^+ [\text{BF}_4]^-$ was prepared according to the reference [21].

2.2.1 General Method for the Preparation of Acridine Derivatives

A mixture of dimedone **1** (2 mmol), aromatic aldehyde **2** (1 mmol), and aromatic amine **3** (1 mmol) was taken in a 100 mL RB. To this 3 mL of ionic liquid was added and the mixture was heated at 70 °C for a particular time (40-55 min). The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and copious amount of water was added. A mixture of products containing water soluble catalyst and water insoluble products. The product (maximum of yellow in colour) was then collected by simple filtration, dried and recrystallized from methanol to give pure compounds scheme 1.

2.2.2 Procedure for Recycling and Reusing of the Ionic Liquid

Due to the fact that the catalyst was soluble in water, it could therefore be recycled by simply evaporating the filtrate. The separated catalyst was washed with ethyl acetate and dried at 60 °C under vacuum for 2 h and was reused in subsequent reaction. The catalyst could be used at least four times without significant loss of activity.

*Corresponding Author

Email Address: annamalai_rajendran2000@yahoo.com (A. Rajendran)

2.3 Spectral Data

4a: Yellow solid, mp – 235-238 °C

IR (KBr): 1652 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H and m, 5H)

MASS: m/z 425 [M⁺]; C₂₉O₂NH₃₁

4b: Yellow solid, mp – 212-214 °C

IR (KBr): 1631 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H and m, 4H); 3.73-3.74 (s, 3H, OCH₃)

MASS: m/z 455 [M⁺]; C₃₀O₃NH₃₃

4c: yellow solid, mp – 255-257 °C

IR (KBr): 1672 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 7.62-8.2 (m, 4H, NO₂-H)

MASS: m/z 470 [M⁺]; C₂₉O₄N₂H₃₀

4d: yellow solid, mp – 242-245 °C

IR (KBr): 1611 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 7.65-8.27 (m, 4H, NO₂-H)

MASS: m/z 470 [M⁺]; C₂₉O₄N₂H₃₀

4e: yellow solid, mp – 201-202 °C

IR (KBr): 1644 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 7.61-8.18 (m, 4H, OH-H); 5.31-5.39 (s, 1H, OH)

MASS: m/z 441 [M⁺]; C₂₉O₃NH₃₁

4f: Brown solid, mp – 208-210 °C

IR (KBr): 1642 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 7.63-8.22 (m, 4H, OH-H); 5.32-5.42 (s, 1H, OH)

MASS: m/z 441 [M⁺]; C₂₉O₃NH₃₁

4g: Orange solid, mp – 182-184 °C

IR (KBr): 1663 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 7.14 -7.43 (m, 4H, Cl-H)

MASS: m/z 459.45 [M⁺]; C₂₉O₂NH₃₀Cl

4h: Orange solid, mp – 188-189 °C

IR (KBr): 1638 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 7.11 -7.49 (m, 4H, Cl-H)

MASS: m/z 459.45 [M⁺]; C₂₉O₂NH₃₀Cl

4i: Brown solid, mp – 162-164 °C

IR (KBr): 1654 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 2.81-2.89 (s, 6H, N-2CH₃); 6.61-7.25 (m, 4H, N-H)

MASS: m/z 468 [M⁺]; C₃₁O₂N₂H₃₆

4j: Yellow solid, mp – 188-189 °C

IR (KBr): 1661 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 3.66-3.73 (s, 9H, OCH₃-H); 6.12-6.82 (s, 2H)

MASS: m/z 515 [M⁺]; C₃₂O₅NH₃₇

4k: Yellow solid, mp – 172-174 °C

IR (KBr): 1647 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 5.21-5.38 (m, 1H, OH); 3.66-3.73 (m, 3H, OCH₃-H); 7.39-8.04 (m, 2H)

MASS: m/z 516 [M⁺]; C₃₀O₆N₂H₃₂

4l: Yellow solid, mp – 177-178 °C

IR (KBr): 1673 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 5.25-5.42 (s, 1H, OH); 3.57-6.82 (m, 5H)

MASS: m/z 485 [M⁺]; C₃₁O₄NH₃₅

4m: Grey solid, mp – 154-156 °C

IR (KBr): 1655 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 8.25-8.42 (s, 1H); 7.55-7.87 (s, 4H); 7.28-7.49 (s, 4H)

MASS: m/z 525 [M⁺]; C₃₇O₂NH₃₅

4n: Brown solid, mp – 168-169 °C

IR (KBr): 1642 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.2-7.4 (m, 5H, Ar-H); 7.59-7.88 (s, 3H); 7.33-7.47 (s, 4H)

MASS: m/z 475 [M⁺]; C₃₃O₂NH₃₃

4o: Dark green solid, mp – 88-89 °C

IR (KBr): 1686 (C=O) cm⁻¹

¹HNMR (300 MHz, CDCl₃) : δ 0.7(s, 6H, 2CH₃), 1.2 (s, 6H, 2CH₃), 1.8-2.0 (m, 4H, 2C⁴H₂ and 2C⁵H₂), 2.1-2.2 (m, 4H, 2C²H₂ and 2C⁷H₂), 4.9 (s, 1H, CH); 7.16-7.37 (m, 3H)

MASS: m/z 415 [M⁺]; C₂₇O₃NH₂₉

3. Results and Discussion

3.1 Selection of Ionic Liquid

The chosen ionic liquids such as [Et₃NH]⁺[BF₄]⁻; [Et₃NH]⁺[HSO₄]⁻; and [TBA][AMPS] were prepared as per the available literature[21]. Using these ionic liquids, the condensation reaction was conducted between the dimedone **1**, Benzaldehyde **2**, and aniline **3**. The results vividly demonstrates that [Et₃NH]⁺[BF₄]⁻ is more efficient than the other two ionic liquids chosen for the study Table 1.

Table 1 Selection of ionic liquid.

Entry	Ionic liquid	Conditions	Yield (%) ^a
1	[Et ₃ NH] ⁺ [HSO ₄] ⁻	80 °C, 2 hrs	91
2	[TBA][AMPS]	80 °C, 2 hrs	88
3	[Et ₃ NH] ⁺ [BF ₄] ⁻	80 °C, 2 hrs	94

3.2 Optimization of Volume of Ionic Liquid, [Et₃NH]⁺[BF₄]⁻

After the selection of the ionic liquid, the same condensation reaction for at least half a dozen time was performed with, [Et₃NH]⁺[BF₄]⁻ to ascertain the optimal volume of the chosen ionic liquid for the best results. The results show that 3 mL of the ionic liquid is suitable and ideal volume to carry out this condensation reaction Table 2.

Table 2 Optimization of volume of ionic liquid ([Et₃NH]⁺[BF₄]⁻)

Entry	volume of ionic liquid in mL	Yield (%) ^a
1	0	-
2	1	74
3	2	85
4	3	94
5	4	95
6	5	94

Aldehyde-Benzaldehyde; Temp- 70 °C; Time- 40 min.

Table 3 Recycling and Reusing of the Ionic liquid.

Entry	Yield (%) ^a
1	-
2	74
3	85
4	94

Aldehyde-Benzaldehyde; Temp- 70 °C; Time- 40 min.

The one pot three component condensation reaction of dimedone **1**, Aromatic aldehydes **2**, and a nitrogen source (aromatic amine) **3** in an ionic liquid, [Et₃NH]⁺[BF₄]⁻ at 70 °C for a period of time (40-55 min) resulted in the formation of yellow to pale yellow solid of acridine diones **4 a-o** in good to high yields (90-95%). The product was collected by filtration using 10 mL of distilled water. The filtrate containing the ionic liquid was then recovered for reuse after drying at 60 °C in a vacuum for 2 h. The ionic liquid was recovered and reused for four times. Even in the fourth run the yield of the product is fairly good (Table 3).

In the scope of this one-pot three component condensation reaction for the synthesis of phenyl polyhydroacridinedione derivatives is illustrated by conducting the reaction with aromatic aldehydes having electron donating as well as electron withdrawing substituents on

benzene ring. It appears that the reactions were independent regarding the substituents on the benzene ring as well as the positions of the substituents (Table 4).

Table 4 One-pot three component synthesis of phenyl polyhydro acridine diones in an ionic liquid $[\text{Et}_3\text{NH}]^+[\text{BF}_4]^-$ medium.

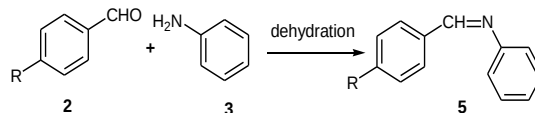
Entry	Aldehyde(s)	Product	Reaction Time (min)	Yield(%) ^a
1	Benzaldehyde		45	91
2	<i>p</i> -Methoxy benzaldehyde		40	93
3	2-Nitro benzaldehyde		50	91
4	4-Nitro benzaldehyde		50	92
5	2-Hydroxy benzaldehyde		40	90
6	4-Hydroxy benzaldehyde		45	94
7	2-Chloro benzaldehyde		40	90
8	4-Chloro benzaldehyde		45	91
9	<i>p</i> -Dimethylamino benzaldehyde		50	95
10	3,4,5-trimethoxy benzaldehyde		45	91
11	4-Hydroxy-3-Methoxy-5-Nitro benzaldehyde		50	92
12	3-Ethoxy-4-hydroxy benzaldehyde		45	91
13	Anthraldehyde		50	93
14	Naphthaldehyde		55	92
15	Furfuraldehyde		55	90

^a - isolated yield.

The structures of all the products have been established on the basis of analytical and spectroscopic data (UV-Vis, IR, ^1H NMR and Mass). This ionic-liquid mediated reaction has advantages of easier work-up, favourable reaction conditions, high yields and an environmentally benign procedure and the ionic liquid (catalyst) is reusable.

3.3 Plausible Mechanism for This Condensation Reaction:

Initial formation of imine from aldehyde and amine:



Further steps involved in the mechanism:

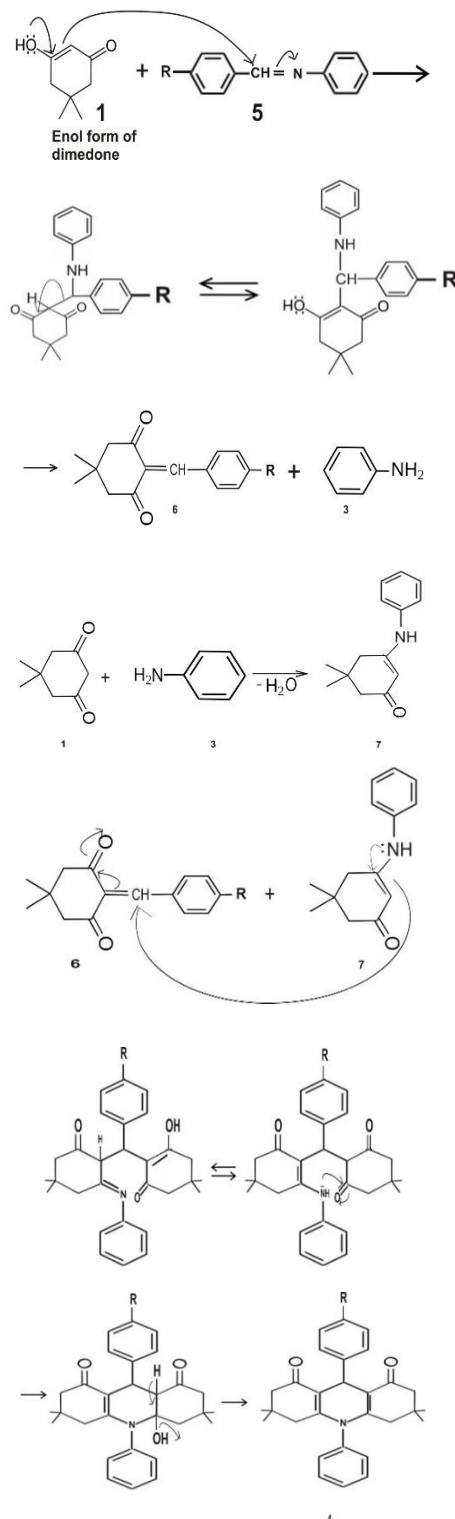


Fig. 1 Acridine derivatives

The formation of **4** could be explained by the proposed plausible mechanism. The reaction occurs via an initial formation of the imine **5** from the condensation of aromatic aldehyde **2** and aniline **3**, which suffers nucleophilic attack by dimedone **1** and loses amine to give the intermediate **6**. Condensation of another molecule of dimedone **1** with aniline **3** gives another intermediate enamine **7**. Then, the Michael

addition, cyclization and dehydration between intermediates **6** and **7** will take place to give the final product **4**, Fig. 1.

4. Conclusion

In conclusion, we have developed a method for the condensation reaction between the dimedone, aldehydes, and a nitrogen source using $[\text{Et}_3\text{N}^+\text{BF}_4^-]$ as an efficient catalyst cum reaction media in the synthesis of acridine derivatives under solvent free conditions. Shorter reaction times, very good to high yields, simple workup procedure, and eco-friendly conditions are the main merits of this method. Further, the ionic liquid (catalyst) was recycled and reused for the same reactions for four times without significant loss in its activity. The wide scope of this three-component ionic liquid mediated reaction is that it tolerates the presence of electron withdrawing as well as electron releasing groups on benzene ring. Thus, we believe that this simple and green methodology will be a practical alternative to the existing procedures.

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