

Vol III Issue VII Jan 2014

Impact Factor : 1. 9508(UIF)

ISSN No :2231-5063

International Multidisciplinary Research Journal

Golden Research Thoughts

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RNI MAHMUL/2011/38595

ISSN No.2231-5063

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GREEN PROTOCOL FOR THE SYNTHESIS OF β -ENAMINOKETONES

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Abstract:-An environmentally benign and clean synthesis of β -Enamino ketones has been achieved using aqueous extract of Acacia concinna pods as a natural surfactant type biocatalyst. We found for the first time that the aqueous extract of Acacia concinna pods could be effectively used for the synthesis of β -Enamino ketones. This efficient process proceeds smoothly in aqueous medium at room temperature. The low cost, easy availability of the catalyst and simple reaction conditions suggest the possible use of present method for the large scale preparations of β -Enamino ketones.

Keywords: β -Enamino ketones, Dimedone, Substituted amines, Biocatalyst.

1. INTRODUCTION:

The enaminones are an important class of organic synthetic intermediates. They have a very high impact as synthons for the synthesis of various heterocyclic and biologically active analogues [1], including anticonvulsant [2], anti-inflammatory [3] and antitumor agents [4]. Due to their wide range of activity and importance, a simple and high yielding one-pot approach for the synthesis of β -Enaminone is highly desirable. The conventional method for the synthesis of enaminone is the azeotropic removal of water by refluxing an amine with 1,3-diketone in an aromatic solvent [5]. Various modified synthetic pathways have been reported in literature such as the addition of metallic esters or amide enolates to nitriles [6], tosyl imines [7] or imidoyl halides [8]. Apart from these, the enamination of 1,3-dicarbonyl compounds has been carried out using catalyst systems such as silica/micro-wave [9], clay K10/ultrasound [10], NaAuAl₄ [11], and PEG-Water [12]. More recently, Bi(TFA)₃ [13] as well as Zn(ClO₄)₂·6H₂O [14] have also been reported as effective catalysts. All above reported methods require solvents for the extraction and purification of compounds and these methods could not achieve better yields. Thus with environmental concern, development of environmentally benign organic reaction is a demand in modern organic chemical research. As a part of ongoing programme on the development of novel methodologies in organic synthesis under mild condition [15] here we describe new biocatalysed synthesis of β -Enaminones in aqueous medium at room temperature as a new, rapid and environmentally friendly practical route for the synthesis of β -Enaminones. (Scheme 1)

Acacia is a medicinal plant (commonly known as Shikakai, Leguminosae family) grows in a tropical rainforest of southern Asia. The fruit is known as "fruit for hair" in its use as a traditional shampoo. Various properties of Acacia fruit are due to the presence of saponins in it, which are foaming agent. These saponins have surfactant properties similar to dodecyl benzene sulphonates [15]. Surfactants are best known to us as detergents which have ability to solubilize non polar materials. This ability to solubilize non polar materials has made aqueous surfactant systems increasingly popular alternatives to organic solvents in various applications. The fruit is known to contain 10-11.5 % saponins. The structures of different saponins present in the fruit have been recently established [16]. The pods of Acacia have been found to contain the saponin of acacic acid. Acacic acid was found to be a trihydroxy monocarboxylic triterpenic acid of either tetracyclic or α -amyrin group [17]. The aqueous extract of these pods of Acacia shows acidic pH that is due to the presence of an acacic acid [18]. Thus, these interesting properties of aqueous extract of Acacia fruit inspired us to use it as an eco-friendly acidic surfactant type catalyst for the synthesis of various enaminones. Our approach reduces the use of hazardous organic solvents and uses simple and mild conditions, with inherently lower costs.

RESULT AND DISCUSSION

In our initial studies, a test reaction using Dimedone (2 mmol) and Aniline (2 mmol) in 5 ml 10% (W/V) aqueous extract of Acacia pods at room temperature was performed in order to establish the real effectiveness of the catalyst. And we are fortunate to get the excellent yield of the product in very short reaction time (90%, 10 min). In order to optimize the reaction conditions same reaction was carried out using different concentrations of catalyst. It was found that 20% of catalyst shows maximum yield (90%). Higher concentration of the catalyst (30%, 50%) neither increases the yield nor lowers the conversion time. Thus, 20% (W/V), 5 ml aqueous extract was found to be the optimal quantity and sufficient to push the reaction forward. The purity of product obtained was high enough for spectroscopic analysis without any further purification. The identical reaction when performed in water without any catalyst, starting material was recovered. To learn scope and limitations of this reaction with the use of electron donating and electron withdrawing groups containing amines. As usual aromatic amines bearing electron withdrawing groups are slightly less reactive. Thus electron donating group containing amines reacts faster giving excellent yields as compared to electron withdrawing group containing amines.

The rate enhancement in aqueous extract of Acacia concinnapods might be attributed due to its surfactant property and acidic pH. The probability of enzyme catalyzed reaction is ruled out because the plant extraction is carried out at 100°C. The saponins which are highly acidic solubilize the reactant species strongly by hydrogen bond formation in aqueous medium. This increases number of favorable collisions between the reactant species. Further encapsulation of reactants in micellar cages may drives the equilibrium towards product side by expelling the water molecule out of its hydrophobic interior which increases the speed as well as yields of products [19]. [Image-1]

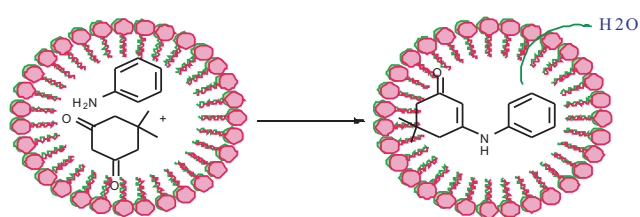
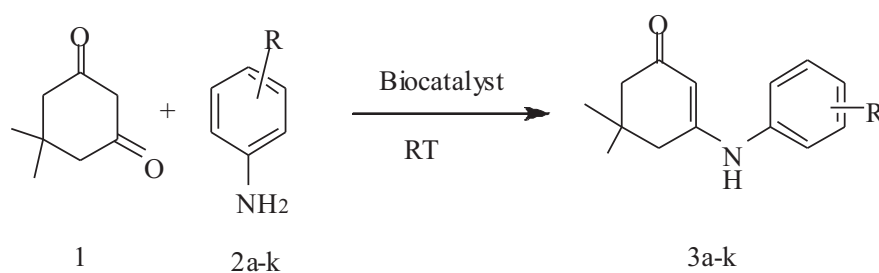

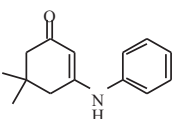
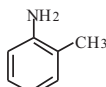
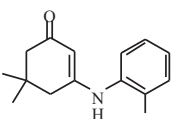
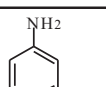
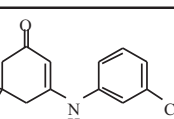

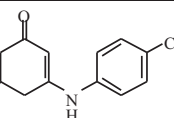
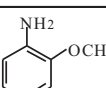
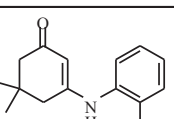

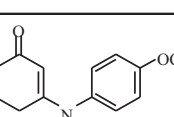

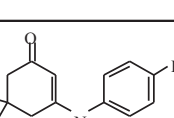
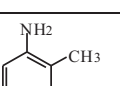
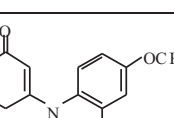
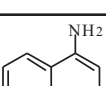
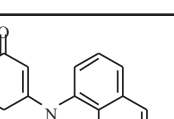
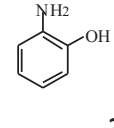
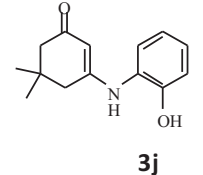
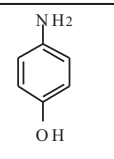
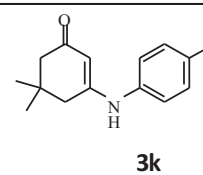
Image-1: Micelle-cages of β -Enamino ketones**Reaction Scheme****Scheme-1: Biocatalysed synthesis of β -Enamino ketones**

Table-1-Synthesis of pyrano β -Enamino ketones from Dimedone and Substituted Amines

Sr.No.	Aromatic Amines	Product	Time in Hours	% Yield ^a
1	 2a	 3a	5.5	90
2	 2b	 3b	4.5	88
3	 2c	 3c	6.5	87
4	 2d	 3d	5.5	88
5	 2e	 3e	4.5	86
6	 2f	 3f	4.0	89
7	 2g	 3g	5.5	88
8	 2h	 3h	7.5	85
9	 2i	 3i	7.5	87

10	 2j	 3j	8.0	85
11	 2k	 3k	8.0	86

a Isolated yields**Materials and Methods****Experimental****General procedure for the preparation of catalyst**

Powdered pods of Acacia fruit (20 g) and water (100 ml) in a 250 ml conical flask was boiled for 15 min. The material was then filtered off and the aqueous extract was employed as a catalyst (20%, w/v) for the synthesis of β -Enaminone.

General procedure for the synthesis of β -Enaminones

A mixture of substituted amines (2 mmol)(2a-k), Dimedone (2 mmol) and catalyst (20%, 5 ml) were taken in a round-bottomed flask and stirred at room temperature for specified time period. After completion of reaction (Monitored by TLC), separated solid product was filtered-off, washed with water, dried to obtain the product in pure form(3a-k)

Spectral Data of Selected Compound

5,5-dimethyl-3-(2-Methyl-phenylamino)-cyclohex-2-enone (3b)

M. P. 190-192°C, yield 88%; IR (cm⁻¹): ν_{max} 3223,3024, 2940, 1695, 1595, 1246, 1184, 666. ¹H NMR (CDCl₃, 300 MHz): δ 12.05 (s, 1H), 7.15 (d, 1H), 7.01(t, 1H), 6.65(t, 1H), 6.12 (d, 1H), 5.54 (s, 1H), 2.45(s, 2H), 2.20(s, 2H), 2.12(s, 3H), 1.1(s, 6H). ¹³C NMR (CDCl₃, 75 MHz): δ 196.9, 162.2, 136.6, 135.6, 131.3, 127.6, 126.5, 123.7, 99.8, 49.5, 42.8, 32.4, 27.2, 27.2, 17.7

CONCLUSION

In summary, the aqueous extract of Acacia pods was successfully employed as a natural surfactant type catalyst for the synthesis of wide variety of β -Enamino ketones by condensing variety of substituted amines with dimedone at room temperature. Simple and mild reaction conditions, cheap, readily available and biodegradable catalyst are the important features of this protocol.

ACKNOWLEDGEMENT

The author is thankful to Department of Chemistry, RatnagiriSub-Centre, University of Mumbai,Ratnagirifor providing research facilities. Also author is grateful to Instrument centre, Solapur University Solapur for providing the spectral analysis.

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