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Short Communication

Green synthesis of Azomethines in natural solvents

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Abstract

Azomethines are frequently used for industrial purposes, also known as Schiff base, shows a broad range of biological activities. A rapid synthesis of series of biologically active azomethines in natural solvents has been carried out. The percentage yield of the product in various solvents has been determined. The goal of this study was to investigate the percentage yields and time required for the completion of reaction for Schiff bases in green solvents. A comparative analysis of the yield is presented.

Keywords: Azomethines, Schiff base, fruit extract, green solvent.

Introduction

The condensation reaction of an aldehyde or ketone with primary amine leads to the formation of azomethines. RHC=N-R^1 is the azomethine group, where R and R^1 are either alkyl, aryl groups, which corresponds to the structural feature of these compounds, also referred to as Schiff bases and imines. The term azomethine is often synonymous with Schiff base after the name of its discoverer Hugo Schiff[1]. This possess good biological and medicinal properties.

The pharmacological applications and complexometric properties of azomethines and their derivatives has been the subject of research[2,3]. Because of these properties it exhibits biological activities[4], like antibacterial[5,6], antiviral[7], antifungal[8,9], anticancer[10], antitubercular[11], anticonvulsant[12], anti-HIV[13], anthelmintic[14], antiamoebic[15], antiinflammatry[16], antinociceptive[17], anti-MHV[18], anti-HSV-1[19], anti-AD-5, antimalarial[20], pesticidal[21] and herbicidal[22] activities. Environmental chemistry[23], metallic deactivators, electrochemistry, bioinorganic catalysis, separation processes are the areas where azomethines have shown great potential. This leads to great interest in the development of efficient methods for the preparation of Schiff bases, in view of their numerous applications in various fields of chemistry.

Green Chemistry approach is an eco-friendly approach and has tremendous applications for the preparation of various compounds and key intermediates in recent past. This technique involves an alternative reaction media to replace hazardous and expensive solvents routinely used in organic synthesis[24]. Shorter reaction time, simple and better efficient workup procedures, highly improved selectivity's and easy purification and separation than organic solvents[25] are the merits of solvent free reactions.

Recently fruit juices are known to be potential organic solvents for the synthesis of compounds of pharmaceutical importance[26]. The wide spread applications of different natural acid catalyst like fruit juices[27] are due to their non-toxic, safe, inexpensive and environmental benign nature.

The principles of Green chemistry are applicable to most of the synthetic routes with microwave irradiation. Microwave assisted reactions are cleaner with lesser reaction time, have maximum yield and formation of negligible waste. Synthesis of Schiff bases by employing fruit juice's as catalyst is an advantageous green approach method.

Our present work focuses the green route for synthesis of Schiff base from aromatic aldehydes and aromatic primary amines using green catalysts like fruit juices of lemon, orange, amla[28] and a comparative study of the formed Schiff base via condensation reaction and green methods.

Materials and Methods

Chemicals and solvents manufactured by Merck, Spectorchem and SD fine meck were used. The melting points of the products are uncorrected, were taken by open capillary method. i. Conventional method: The Schiff bases were prepared (Figure-1) by refluxing equimolar quantities of aromatic primary amine (0.01M) and substituted benzaldehyde (0.01M), using ethanol as solvent in presence of catalytic amount of glacial acetic acid. Monitoring of reaction progress was done by TLC. After completion of the reaction, mixture was dropped onto ice cooled water and pale-yellow solid which get separated, was filtered and then washed with cold ethanol and ether. The product was recrystallized from hot ethanol. All compounds have a well-known structures Table-1. ii. Synthesis in Aqueous medium[29]:

To a solution of aromatic primary amines (0.01M) in 10ml of water, substituted benzaldehyde (0.01M) was added.
The reaction was carried out at room temperature with stirring. Monitoring of reaction progress was done by TLC. The workup of the yellow coloured product was performed. The remaining series of the compounds were prepared by said procedure. iii. Synthesis of Schiff base with lemon, orange and aqueous extract of amla[30]: Equimolar amounts of aromatic amines (0.01M) and substituted benzaldehyde (0.01M) were taken in 100ml beaker. 2ml of natural acid i.e., lemon juice/orange juice/aq. Extract of amla was dropped into the reaction and kept for stirring for 2 mins and microwaved for 4-6mins. Reaction progress was observed by TLC method. Melting point of the product was checked by open capillary tube. The process is repeated with orange and amla juice.

The results are tabulated in Table-5. iv. Synthesis of Schiff base with mango water[31]: Preparation of mango water: The green mango fruit was pilled off and the seed was eliminated. The pulp (10gm) was boiled with 50ml of water, cooled and filtered. The extracted water solution of green mango was utilized in the synthesis of azomethines.

Procedure: A mixture of equimolar amount of substituted benzaldehyde (0.01M), aromatic amines (0.01M) and 2ml mango water were taken in a mortar and it was ground by pastel at room temperature. The progress of reaction was monitored by TLC. After completion of the reaction, the content in the mortar was poured on cooled water. Product formed was recrystallized using ethanol.

Results and discussion

Schiff's bases were prepared by conventional method of refluxing in organic solvents like ethanol, the mixture of amine and aldehyde using acetic acid as catalyst (Table-1).
Our process describes a mild, efficient, high yielding reaction for the condensation of aromatic aldehydes and aromatic primary amines in aqueous medium at room temperature. This process was selected as green, benign, clean, and safe to promote the synthesis of various Schiff's bases (Table-1). It was observed that water as solvent leads to fast reaction and easy work-up of water insoluble products. The crude reaction products show adequate purity.

The present work highlights the utility of fruit juice in organic transformations as natural biocatalyst, Non-hazardous character, acidic nature, enzymatic activity, cost effective, and ample availability of fruit juice is the cause of growing interest of its use in organic synthesis.

Here we have used juice of lemon, orange, aqueous extract of amla and green mango water. Microwave and grinding methods were applied to obtain products. The results are revealed in the Table-2. Using these methodologies, the reactions were completed in considerable time with better yields. Thus, the green reactions require simple procedures to isolate the products being mostly water insoluble and the desired products were obtained with good purity.

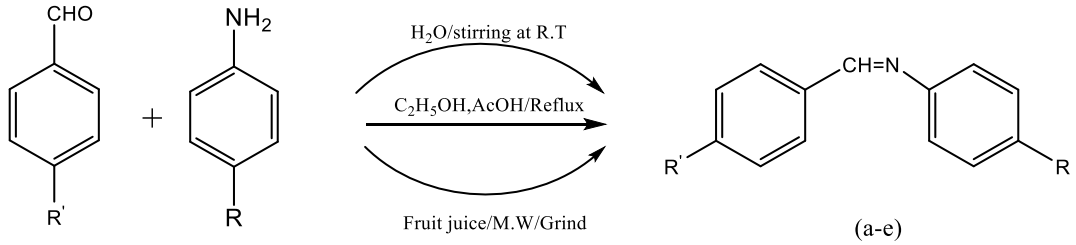

Fig 1: Representing three different routs for synthesis of Azomethines

Table-1: Comparative yield by conventional route and in aqueous medium.

Product	R	R'	Time (min)	% yield		M.P* ^{0}C
				Conventional route	Aqueous medium	
a	H	p-OCH_3	45	88	86	67-70
b	H	H	45	79	75	49-51
c	H	p-CH_3	45	62	61	51-55
d	H	p-OH	45	75	74	155-160

e	H	p-Cl	45	78	72	48-52

Table-2: Comparative yields in various fruit juice media.

Product	Time (min)	% Yield				M.P* ^{0}C
		Lemon juice	Orange juice	Amala extract	Mango water	
a	45	87	78	75	88	67-70
b	45	80	75	73	81	49-51
c	45	64	61	60	65	51-55
d	45	74	69	65	77	155-160
e	45	75	66	63	74	48-52

* The melting points are in good agreement with respect to literature as the products are known compounds.

Conclusion

This study unfolds that the synthesis of Schiff bases can be achieved by using fruit extract as well as in aqueous medium. This environmentally clean method is easily accessible, do not need organic solvent and can be performed without refluxing. The comparative study reveals that high-quality products were obtained, with excellent yields and shorter reaction time.

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