

Green Synthesis of Schiff Bases by Using Natural Acid Catalysts

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Abstract: The utilization of green chemistry techniques are dramatically reduces chemical wastes and reaction time as recently have been proven in several organic syntheses and chemical transformations. To illustrate these advantages in the synthesis of organic heterocycles, various environmentally benign protocols that involve greener alternatives have been studied. The objective of present research work has also used green methodologies for synthesis of Schiff bases. Conventionally synthesis of Schiff base is carried out with or without acid catalyst and sometimes by refluxing the mixture of aldehyde (or ketone) and amine in organic medium. Present synthesis involves the use of fruit juice of Citrus limetta, Vitis lanata and aqueous extract of Mangifera indica as natural acid catalysts. The synthesized product was identified by its physical properties, melting point, TLC and characterized by Mass spectrometry. Compared with traditional methods, these methods were more convenient and provided higher yield (75-93%), shows maximum efficiency, held without generation of pollution in shorter reaction time, safer to analyst, low cost and simple to run.

Keywords: Green chemistry, Schiff bases, natural acid catalysts, mass spectrometry.

1. Introduction

Green chemistry is the branch of chemistry that involves tools techniques and technologies. It is helpful to chemists and chemical engineers in research, development and production, for development of more ecofriendly and efficient products which may also have significant financial benefits. It is going to now become an essential tool in the synthetic chemistry¹. It is a new way of looking at organic synthesis and the design of drug molecules, offering important environmental and economical advantages over traditional synthetic processes². **The recent interest in green chemistry has posed a new challenge for organic synthesis in that** new reaction conditions need to be found which reduce the emission of volatile organic solvents and the use of hazardous toxic chemicals³. They improve selectivity, reduces reaction time, and simplifies separation and purification of products than the conventional methods.⁴

Schiff bases, known as Imines are compounds containing azomethine group $-(HC=N)-$ and represented by the general formula $R_3R_2C=NR_1$. They are the condensed products of aldehydes or ketones and were first reported by Hugo Schiff in 1864⁵. Originally, the classical synthetic route for synthesis of Schiff bases was reported by Schiff which involves condensation of primary amines with carbonyl compounds⁶ under azeotropic distillation with the simultaneous removal of water. Interests in these compounds are largely due to their structural similarities with natural biological substances and relatively simple procedures of synthesis as well as synthetic flexibility that enable the design of suitable structural properties. They are well known intermediate for the preparation of azetidinone, thiazolidinone, formazone, arylacetamide, metal complexes and many other derivatives⁷. The Schiff bases constitute one of the most active classes of the compounds possessing diversified biological applications such as antitubercular, anticancer, antibacterial, anti-inflammatory, antifungal, antitumor, diuretic, insecticidal, herbicidal, anthelmintic, anti-HIV, antiproliferative, anticonvulsant, antihypertensive

and antiparasitic activities⁸. The Schiff's base derivatives have been extensively investigated for more than a century and employed in different aspects including magneto chemistry, non-linear optics, photo physical studies, catalysis, materials chemistry, chemical analysis, absorption and transport of oxygen⁹.

Due to these beneficial properties, concern for the environmental demands and strong interest in the development of green chemistry, new sustainable catalysts and new environmentally benign processes¹⁰ have been investigated which are both economically and technologically feasible¹¹. Present study also involves some eco-friendly and inexpensive natural catalysts like grapes (*Vitis lanata*) juice, sweet lemon (*Citrus limetta*) juice and aqueous extract of mango (*Mangifera indica*) for the synthesis of Schiff bases.

2. Literature Survey

- 1) **Cimerman et al., (2000)** studied that Schiff bases are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864.
- 2) **Ahluwalia and Kidwai, (2004)** illustrated that Green chemistry is chemistry for the environment. It is really a philosophy and way of thinking that can help chemistry in research and production to develop more eco-friendly solutions.
- 3) **Ibrahim et al., (2006)** synthesized a series of ten Schiff bases by condensation of a variety of aromatic amines with some aniline (or derivative) and aromatic aldehyde derivatives. These Schiff base have been characterized by IR, H NMR in addition to elemental analysis.
- 4) **Chamarthi et al., (2012)** synthesized a library of Schiff base derivatives (12 compounds) under conventional conditions in ethanol as well as ultrasonic conditions in aqueous medium without using any catalyst.
- 5) **Patil et al., (2012)** revealed that the reaction of primary aromatic amines with aryl aldehydes is found to be

catalyzed by lemon juice as natural acid solvent-free conditions to give the corresponding Schiff bases in good yields.

- 6) Pawar *et al.*, (2012) explained about the important and interesting roles of Schiff bases are an intermediate in the biological transmutation reaction.
- 7) Aslam *et al.*, (2013) explained that Schiff bases having azomethine group and their metal complexes are widely used for industrial purposes and also reveal a wide range of biological applications.
- 8) Kajal *et al.*, (2013) summarized information on the diverse biological activities and also highlights the recently synthesized numerous Schiff bases as potential bioactive core.
- 9) Pal, (2013) illustrated about the role of naturally available fruit juice in organic synthesis has attracted the interest of chemists, particularly from the view of green chemistry.

3. Material and Methods

a) Preparation of catalyst: Grapes, sweet lime and unripe mango fruits were procured locally, then grapes were pressed into fruit juicer and filtered with cotton to get liquid juice. While sweet lime fruits was peeled off with knife and fruit slices were pressed into fruit juicer to get semisolid

mass which was then filtered with cotton to get liquid juice to used as catalyst¹².

The upper shell of unripe Mango fruit was removed and the hard fleshy green material (5 g) was boiled with water (100 ml), cooled and filtered with muslin cloth to get clear liquid portion to used as catalyst for the synthesis¹¹.

b) Synthesis of Schiff bases with grapes juice sweet lemon juice and aq. extract of unripe mango under solvent free condition by stirring method: The equimolar amount of benzaldehyde (0.1 mol) with aniline (0.1 mol) was taken in different beakers. In those reaction mixtures natural acid catalyst i.e. grapes juice were added in variable amounts (0.5 ml, 1 ml, 1.5 ml, 2.0 ml, 2.5 ml) and then kept for 5-10 minutes. Further each reaction mixture was stirred for 2 - 4 minutes at room temperature pale yellow solid crude product was appear after completion of reaction which was washed with distilled water and purified by recrystallization with minimum amount of ethanol. The same procedure is repeated with sweet lemon juice and aqueous extract of mango. Melting point of the products were measured by open capillary method which was further identified and purified with the help of TLC and confirmed by using mass spectra.

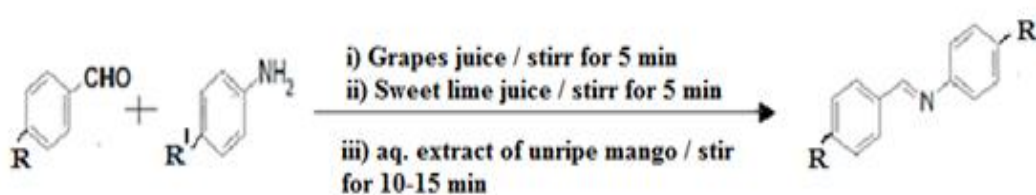


Figure 1: Reaction for Schiff base synthesis in presence of acid catalysts

4. Result and Discussion

If we focus on the mechanism of transformation of aldehydes and amines into Schiff bases, there is nucleophilic attack of primary amine on carbonyl carbon affords hydroxyl compound which on dehydration gives Schiff bases. The formation of Schiff bases in the second step largely depends upon the rate of removal of water from the reaction mixture.

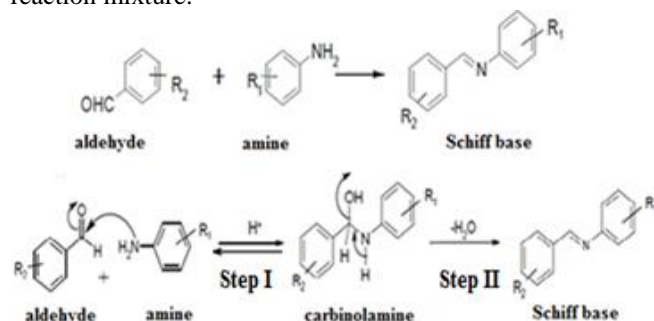


Figure 2: General reaction and mechanism for Schiff base synthesis in acidic solvent media

In the I step of the mechanism the amine reacts with the aldehyde or ketone to give an unstable addition compound called carbinolamine. Then in the II step carbinolamine loses water by either acid or base catalyzed pathways. Since

the carbinolamine is an alcohol, it favors to undergo acid catalyzed dehydration. It is observed that the condensation between a carbonyl compound and an amine leading to the formation of Schiff bases should be a facile reaction due to the good electrophilic and nucleophilic characteristic properties of the carbonyl and amine groups respectively. Formation of carbinolamine and protonation occurs in the same step if the reaction takes place in acidic solvent media while in the acid catalysed mechanism the protonation occurs before the formation carbinolamine.

Logically, in this work the protonation of heteroatom in organic transformation was done with natural acid i.e. fruit juices. All the fruit juices contain many organic acids like citric acid, tartaric acid, malic acid, oxalic acid, succinic acid and amino acids amongst these organic acids, citric acid is the major constituent in many fruit extracts. Thus these organic acids are responsible for acidic nature of fruit juices and provide a desirable pH to catalyze the condensation reaction have used in the synthesis of Schiff bases.

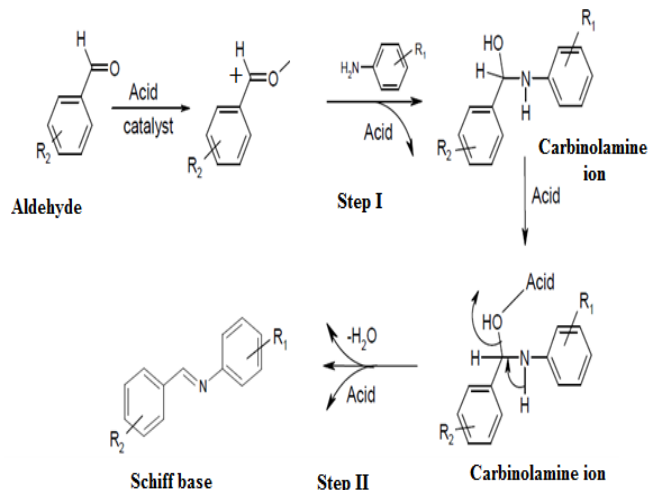


Figure 3: Mechanism for Schiff base synthesis in the presence of acid catalyst

Yields of the N-benzylidene aniline (Sb I) and 4-chloro-N-benzylidene aniline (Sb II) in the presence of different catalysts:

N-benzylidene aniline (Sb I) and 4-chloro-N-benzylidene aniline (Sb II) was successfully synthesized by green catalysts which have been used and good to excellent yield of the product was obtained. The data shows that the acid catalysts are effectively catalyze the synthesis of Schiff bases and even very small amount of natural acids provide quantitative yield of the product.

Table 1: Comparative yields of N-benzylidene aniline (Sb I) and 4-chloro-N-benzylidene aniline (Sb II) in the presence of different catalysts

Title S. No.	Name of catalyst	Amount of catalyst (ml)	Percentage yield (Sb I)	Percentage yield (Sb II)
1	Grape juice	0.5	93.60	88.54
2	Sweet lemon juice	0.5	88.13	79.19
3	Aqueous extract of Mango	0.5	91.11	82.18

The yields of Sb I is always more than Sb II because the electrophilicity of the carbonyl carbon of Sb II reduces due to the presence of the electron-donating substituent group i.e. Cl through resonance and M+ effect (mesomeric effect). From this perspective it has been clear that the yield of the Schiff bases is depend upon the electrophilicity of carbonyl carbon of benzaldehyde and nucleophilicity of aniline¹². Electrophilicity of benzaldehyde increases if any electron attracting substituent group attached to it and decreases if benzaldehyde has any electron donating group in its structure while the nucleophilicity of aniline is increases due to electron donating group and decreases in the presence of electron withdrawing group.

4.4: Effect of catalyst loading on the product yield

Different yields of the product obtained with variable amount of acid catalysts are summarized in Table no. 2 and Table no. 3

Table 2: Yields of the N-benzylidene aniline o(Sb I) obtained with different amount of natural acid catalysts

Title S. No.	Amount of catalyst (ml)	Product yield obtained with grapes juice		Product yield obtained with sweet lemon juice		Product yield obtained with aqueous extract of unripe mango	
		Product Yield (gm)	Percentage yield	Product Yield (gm)	Percentage yield	Product yield (gm)	Percentage yield
1	0.5	2.2468	93.60	2.1345	88.93	2.1868	91.11
2	1	2.1376	89.07	2.0516	85.48	2.0935	87.23
3	1.5	2.0192	84.13	1.9448	81.02	1.9776	82.40
4	2	1.8890	78.71	1.8328	76.37	1.8523	77.18
5	2.5	1.7649	73.54	1.7101	71.25	1.7073	71.14

Table 3: Yields of the 4-chloro-N-benzylidene aniline (Sb II) obtained with different amount of natural acid catalysts

Title S.No	Amount of catalyst (ml)	Product yield obtained with grapes juice		Product yield obtained with sweet lemon juice		Product yield obtained with aqueous extract of unripe mango	
		Product Yield (gm)	Percentage yield	Product Yield (gm)	Percentage yield	Product yield (gm)	Percentage yield
1	0.5	1.8593	88.54	1.6642	79.24	1.7257	82.18
2	1	1.7150	81.67	1.5315	72.93	1.5481	73.72
3	1.5	1.5579	74.19	1.3887	66.13	1.3685	65.17
4	2	1.3983	66.59	1.2816	61.03	1.2306	58.60
5	2.5	1.2553	59.78	1.1862	56.48	1.1258	52.98

The data clearly show that on increasing the amount of acid catalysts product yields were decreasing because of acid

concentration cannot be too high due to the basicity of amines. If the amine is protonated and becomes non-

nucleophilic, equilibrium is pulled to the left and carbinolamine formation cannot occur. Therefore, many Schiff bases synthesis are best carried out at mildly acidic pH¹³.

4.5 Characterization of the products:

Both of the products are stable at room temperature and non hygroscopic. They decompose at high temperature, insoluble in water and soluble in ethanol. Thus Characterization of products was done with its physical properties, melting points, TLC and mass spectra. TLC was performed with chloroform and methanol (1:9) provided a single spot on TLC plate which shows purity of products.

Table 4: Physical characteristics of products

S. No.	Products Name and chemical formula	Product color	Product smell	Physical state	Solubility	Melting point	Rf value
1	N-benzylidene aniline (C ₁₃ H ₁₁ N)	Pale yellow	Disagreeable	Crystalline solid	Both are Insoluble in distilled water, soluble in	54 °C	0.620

2	4-chloro-N-benzylidene aniline (C ₁₃ H ₁₀ NCl)	Pale yellow	Disagreeable	Crystalline solid	methanol, ethanol, and chloroform	62 °C	0.623
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Spectral characterization: It is done with mass spectra of the product. Mass spectrometry is the most accurate method for determining the molecular mass of the compound and its elemental composition. The mass spectrum is a plot representing the m/z values of the various ions (parent as well as fragment ions) against their corresponding relative abundance. In this technique, molecules are bombarded with a beam of energetic electrons. The molecules are ionized and broken up into many fragments, some of which are positive ions. Each kind of ions has a particular ratio of mass to charge, i.e. m/z ratio (value).

Mass spectra of N-benzylidene aniline (Sb I) shows a molecular ion peak at 182.1 with 100 % relative abundance so it is also the base peak of spectra which corresponds to the one additional molecular weight of the synthesized compound because calculated molecular weight of the compound is 181.23 gm/mol. Then with the peak have been described as molecular ion peak another fragment ion peak is clearly visible at 183.1 m/z value which is an isotopic peak for ¹³C with 13 % relative abundance.

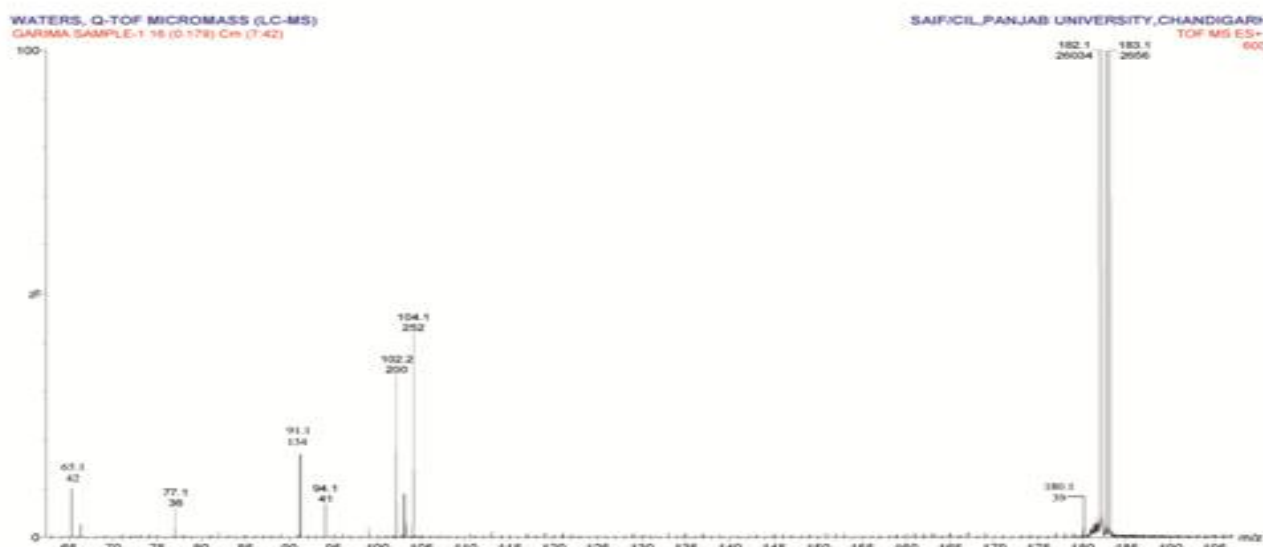


Fig. 4: Mass spectra for N-benzylidene aniline obtained with grapes juice shows fragment ion peaks

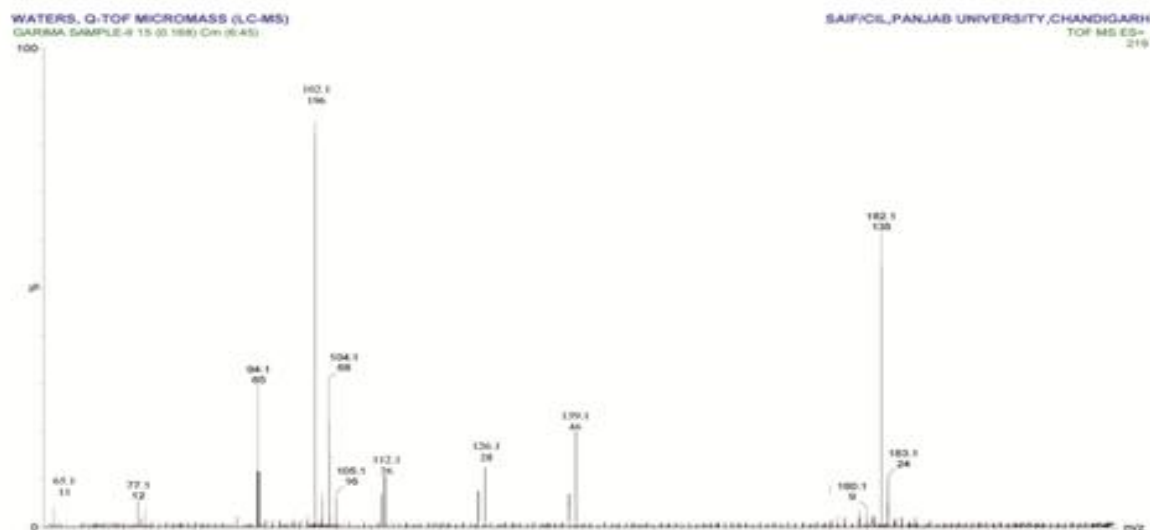


Fig. 6: Mass spectra for 4-chloro-N-benzylidene aniline obtained with grapes juice shows fragment ion peaks



Fig. 5: Mass spectra for N-benzylidene aniline obtained with grapes juice shows molecular ion peak and base peak



Fig. 7: Mass spectra for 4-chloro-N-benzylidene aniline obtained with grapes juice shows molecular ion peak and base peak

In the spectra of 4-chloro-N-benzylidene aniline (Sb II) molecular ion peak observed at the m/z 216.0 with 100 % abundance which correspond to the $(M + H)^+$ ion i.e. one additional molecular weight of the respective compound because calculated molecular weight of the compound is 215.68 gm/mol, it is also the most abundant peak of spectra so the molecular ion peak and base peak both are also same. With this molecular ion peak one extra peak also seen at m/z 218.0 with 24.5 % relative abundance which produced due to the isotopic form of chlorine into it.¹⁴

5. Summary and Conclusion

The present work focuses the importance of fruit juice as natural and biocatalyst in organic transformations. The growing interest of fruit juice in organic synthesis is mainly due to their acidic properties, enzymatic activity, benign environmental character, inexpensive, and commercial availability. The catalytic activity including the application of fruit juices in various organic transformations such as formation of C-C, C-N bonds in different synthetically important organic compounds have been studied. Although many observations have not received by application of fruit juice in synthesis of natural products or complex structured molecules in details, it is believed that in near future the chemistry of natural catalysts will continue to attract significant research activity. Therefore, the present review would serve the need of organic chemists in searching new applications of fruit juice for organic synthesis.

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