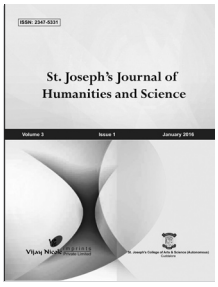
St. Joseph's Journal of Humanities and Science
ISSN: 2347 - 5331
http://sjctnc.edu.in/6107-2/



Ultrasound Mediated Synthesis of Schiff Base

S. Richard Rajkumar[a]*
V. Periyanayagasamy[a]

ABSTRACT

Imines are synthesised using aldehydes and amines (various combinations) by conventional method and in ultrasound condition and compared the yield and time taken for the completion of the reaction. The compounds synthesised were characterised by IR spectra, UV-visible spectra, and melting point determination.

Keywords: Schiff base, ultrasound condensation reaction, aldehyde

1.0 INTRODUCTION

The nitrogen atom is present in most natural products, biologically important molecules, pharmaceuticals, and dyes. [1] Imines and their derivatives are useful intermediates in organic synthesis, [2] in particular for the preparation of hectrocycles and non-natural aminoacids. [3] Several methods for the synthesis of imines are described in the literature; they can be obtained from aldehydes, [4] gem-dibromomethylaryl derivates, [5] formamide, [6] palladium catalyzed amination as well as by polymer supported. [8] However these methodologies often require complex procedure, long reaction time, and large quantities of aromatic solvents. This conventional phase solution chemistry typically involves distillation under reduced pressure or azeotropic removal of water by a Dean-Stark apparatus. Solvent-free synthesis of imines and enamines under microwave irradiation has been described.[9]. However this method was applied for a limited number of compounds and the possibility of scaling up the synthesis was not evaluated. We have synthesised Schiff bases using aldehydes and amines by both conventional method and ultra sound method.

2.0 RESULTS AND DISCUSSION

This thesis deals with the synthesis of twelve Schiff's bases from aromatic aldehyde and aromatic monoamines, aliphatic diamines and aromatic heterocyclic aldehydes. Thermo method involving ethanol as the medium and sonication method using power ultrasound of 42 KHz are employed in the preparation of these compounds. The main aim of the present work is to compare the two methods for the synthesis of Schiff base and to find out the advantage of one method over the other. These compounds are characterized by melting point determination, FT-IR and visible spectral studies.

2.1 SYNTHESIS OF SCHIFF BASES

2.1.1 Conventional Method

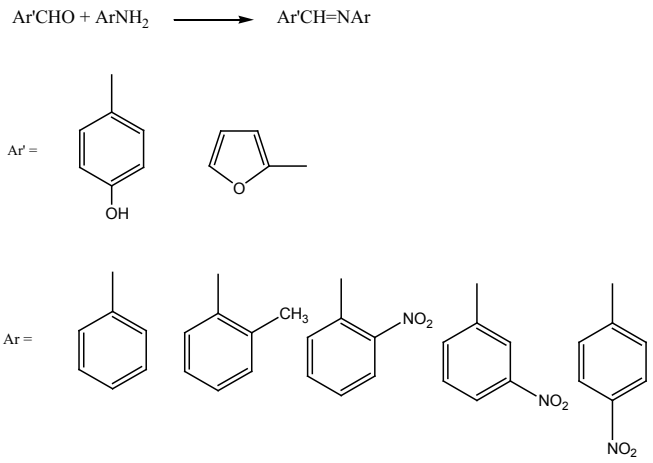
The Schiff bases were prepared by refluxing aromatic monoamines, 1:1 mole ratio, heterocyclic aldehydes and diamines in 2:1 mole ratio. Ethanol was used as solvent. The contents were refluxed over a hot water bath for 6-8 hours and the crude product formed was filtered and dried. [11]

[a]Department of Chemistry, St. Joseph's College of Arts and Science, Cuddalore -1.
*E-Mail: richardrajkumar@gmail.com, Mobile: +91 94887 24557.

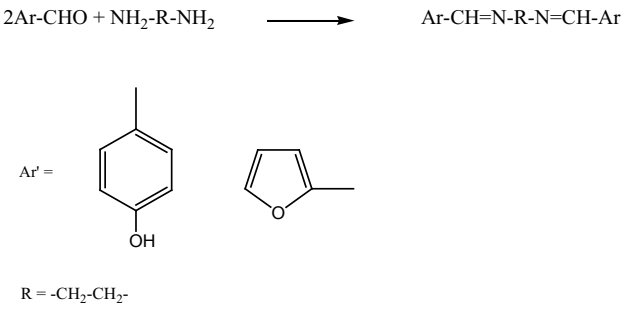
2.1.2 SONICATION METHOD

In sonication method the Schiff base were prepared by exposing aldehyde and amine in ethanol for a period of 2 to 3 hours to power ultrasound with 42 KHz frequency. The temperature of the system increased up to 65°C during exposure. The crude product was obtained, filtered and washed with water. The scheme adopted for synthesis of Schiff base using monoamine and diamine is given below. Scheme I and II.

Scheme I

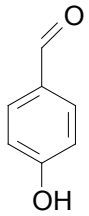
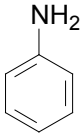
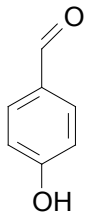
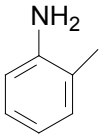
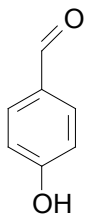
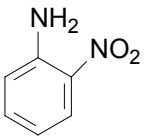


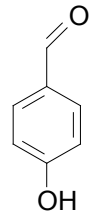
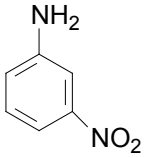
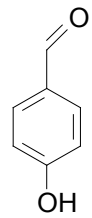
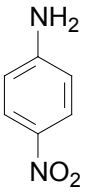
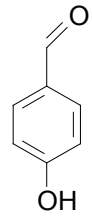
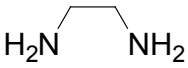
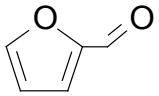
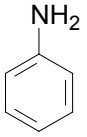
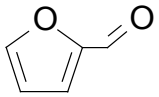
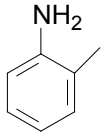
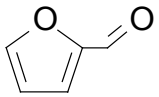
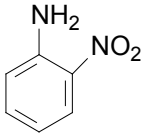
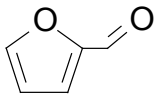
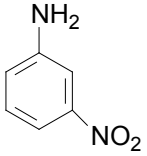
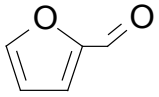
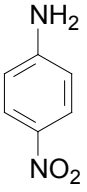
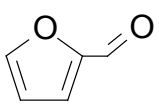
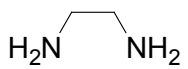
Scheme II



The aldehydes, amines used, reaction time, % yield are tabulated as follows:

Table 1: Compounds of Methods Employed in Synthesis of Certain Schiff Base

S. No.	Aldehyde	Amine	Conventional Condition		Ultrasound Condition	
			Time/h (Hours)	Yield %	Time/h (Hours)	Yield %
1			4:10	82	2	89
2			2:30	65	1:15	76
3			5	33.3	1:45	87

4			1:30	66.6	5	89
5			5	48	2	54
6			6:30	33	3:30	45
7			5	86	2:30	91
8			8	82	2	87
9			8	30	2:30	48
10			5:45	45	2:15	77
11			9	56	2:30	67
12			9	19	3	40

The results obtained shows that the sonication method has more advantage over conventional method with respect to the reaction time and percentage yield.

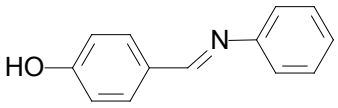
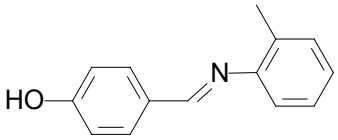
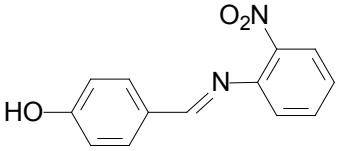
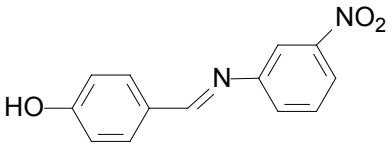
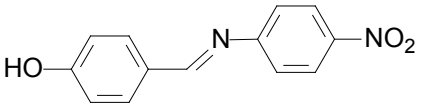
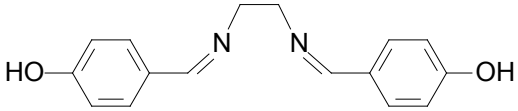
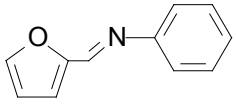
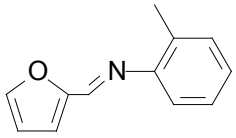
2.2 CHARACTERIZATION OF SCHIFF BASE

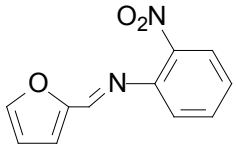
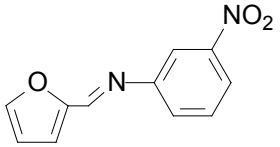
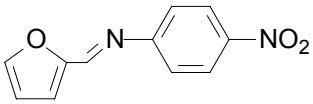
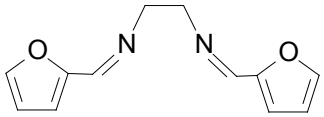
The Schiff base synthesized by both the methods was characterized by determining the melting point and by studying their spectral characteristics. [12,13].

2.3 Physical Propertied of Schiff Bases

The structure of 12 Schiff's bases is prepared in the work, their molecular formula and their colors are given in Table 2.

Table 2: Characterization of Schiff Bases

S. No	Structure of Formula	Molecular Formula	Melting Point °C	Colour
1.		$C_{13}H_{11}ON$	216-218	Rose
2.		$C_{14}H_{13}ON$	202-205	Rose
3.		$C_{13}H_{10}O_3N$	97	Yellow
4.		$C_{13}H_{10}O_3N$	210	Yellow
5.		$C_{13}H_{10}O_3N$	170	Dark yellow
6.		$C_{16}H_{16}O_2N_2$	>240	Dark red
7.		$C_{11}H_9ON$	163-165	Brown
8.		$C_{12}H_{11}ON$	215	Black

9.		$C_{11}H_8O_2N$	110	Yellow
10.		$C_{11}H_8O_2N$	210	Yellow
11.		$C_{11}H_8O_2N$	225	Dark green
12.		$C_{12}H_{12}O_2N_2$	>240	Brown

It is found that the melting points are influenced by the substituent present in the aromatic rings. The Schiff base obtained from p-hydroxy benzaldehyde and o-nitro aniline has the lowest melting point. The presence of substituent in the aromatic ring invariably increases the melting point. The higher melting points in some of the Schiff bases are due to intermolecular H-bonding.

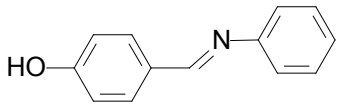
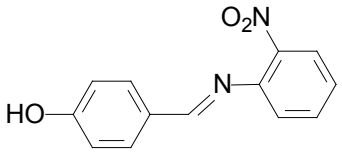
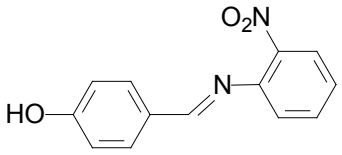
The melting point obtained for 12 Schiff bases are influenced by molecular weight, resonance of polar group, steric effect, and H- bonding. These compounds are almost insoluble in water, but relatively soluble in ethanol.

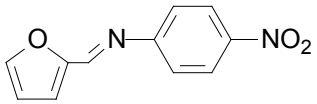
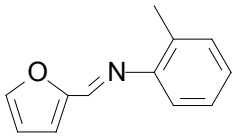
2.4 SPECTRAL PROPERTIES

The structure of Schiff base prepared in the work is determined by IR spectra. IR spectra were recorded by incorporating the compound in KBr. The assignments of absorption frequencies are given in Table 3.

The strong absorption at 1620-1640 cm^{-1} in the spectra is due to C=N stretching. This confirms that condensation has occurred. The assignments for other group frequencies are indicated in table III. The spectra confirm the Schiff bases.

Table 3: Characterization of Schiff Bases

S. No.	Schiff bases	IR Absorption Frequency (cm^{-1})
1.		3433 (OH) vibration, 1603 (C=N) vibration 690-monosubstituted, (C-H) out of plane bending. 841-p-substituted phenyl, (C-H) out of plane bending
2.		3468 (OH) vibration 1630 (C=N) vibration 742-o-Substituted phenyl, (C-H) out of plane bending.
3.		1635 (C=N) vibration 3481 (O-H) vibration 841- 1,4 disubstituted benzene (C-H) out of plane bending 1308- NO_2 symmetric stretching 1473- NO_2 Asymmetric stretching

4.		1606-(C=N) vibration 835-p-substituted benzene (C-H) bending 3447-furan (C-H) bending
5.		1636 (C=N) vibration 745 (C-H) bending 3448- Furan (C-H) bending.

2.5 UV VISIBLE SPECTRA

All the 12 Schiff bases are colored and hence they absorb only in the visible region. Therefore visible spectra were recorded for these compounds in the wavelength range 320-450 nm. Ethanol was used as solvent. These parameters are for π- π* transition as suggested by high values of ϵ_{max}. The data indicate that max values influenced the presence of substituent in the aromatic rings. It is found that when –OH or NO_2 group is introduced into the ring there is bathochromic shift. It may be pointed out that when methylene groups are introduced between benzylic carbon there is Ipsochromic Schiff.

The presence of heterocyclic ring in the Schiff base causes bathochromic shift, but when nitrogen group is present in aromatic amine in the o-position there is ipsochromic shift.

3.0 SUMMARY AND CONCLUSION

In the present investigation 12 Schiff base compounds were synthesized from structurally different aromatic aldehydes and aromatic monoamine and aliphatic diamine. Two different subject one is conventional thermal method and the other is sonication method with power ultrasound of frequency 42 KHz. Ethanol was used medium in both the methods. All the 12 compounds were obtained in pure state, the melting point of these compounds were determined accurately. It is found that the melting point of Schiff base compounds are influenced by the nature of the substituent and as well as the position of substituent in the aromatic ring. These compounds were almost insoluble in water but soluble in ethanol. IR spectra were recorded for these compounds in order to identify the groups present in these molecules. Satisfactory assignments were made for the adsorption frequencies obtained in the IR spectra of these compounds.

These compounds are colored and hence only visible spectra were taken for these compounds. The wavelength of maximum absorption and molar extension coefficient value for all 12 Schiff base compounds are reported. It is found that the λ_{max} values are affected by the type of substituent and their position in the aromatic ring. It is found that the sonication method has more advantages over the typical conventional method. Sonication procedure does not require drastic conditions and long heating. Good Yield of the products was isolated by sonication method.

REFERENCES

1. G.Thoma, International Medicinal Chemistry, Wiley, New York, (2000).
2. X.L. Hou, J.Wu,R.H. Fan, C.H. Ding, Z.B. Luo, L.X. Dai, Synthetic letters , 181 (2006). b. R.W. Layer, Chemical. Review, 63 (1963) 483.
3. Z.R. Xu, X.Y.J. Lu, Organic Chemistry, 63, (1998) 5031.
4. A .Simion, C. Simion, T. Kanda,S. Negashima, Y. Hitoma, T. Yamada,T. Journal of Chemical Society, Perkin Trans.1 (2001) 2071
5. N. Wibel, L.J. R.F Charbonniere, Ziessel ,Journal of Organic Chemistry, 67 (2002) 7876.
6. B.L. Feringa,Jansen, Journal of Synthesis184 (1988).
7. J. Barluenga, C. Valdas, C.Chemistry Communication (2005) 4891.
8. R. Annuziata, M. Benaglia, M.Cinguini, F.Cozzi, F. Journal of Organic Chemistry (2002), 1184.
9. R.S. Varma, R. Dahiya, S. Kumar, Tetrahedron Letters, 38(1997) 2039.

10. A.K. Chakraborti,S. Bagat, S. Rudrawar, Tetrahedran letters, 45 (2004) 7641.
11. B.S. Furniss, A.J. Hannaford, V. Roger, P.W.G. Smith, A.W. Tatchell, Vogel's Textbook of practical Organic Chemistry; 5th ed.; Pearson Education: Delhi, (2004).
12. Jag Mohan, Organic Spectroscopy; 2nd ed.; Narosa Publication: New Delhi, 2005.
13. R.M. Silver, G.C. Bassler, C.M. Terence, Spectrometric Identification of Organic Compounds; 5th ed.; John Wiley and sons: Canada (1991).
14. M.D.R.S. Luisa Martins, Susanta Hazra, M. Fatima, C. Guedes da silvaa, J.L. Pomberio, RSC Advances, 00, (2016) 1-3.