

INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN
CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213; e-ISSN: 2348-5221)

www.ijrcrps.com

DOI: 10.22192/ijrcrps

Coden: IJCROO(USA)

Volume 5, Issue 8 - 2018

Research Article

DOI: <http://dx.doi.org/10.22192/ijrcrps.2018.05.08.004>

Novel green techniques for the synthesis of N-Benzylidenepyridine-2-Amine

Umofia Eno, Abayeh Ovire J., Omuaru Victor O.T., *Achugasim Ozioma.

University of Port Harcourt, Choba, Rivers State, Nigeria.

*E- mail: ozzioma.achugasim@uniport.edu.ng

Abstract

Pyridine-derived Schiff bases have been synthesized using a variety of solvents and most of these solvents and solvent mixtures are not ecofriendly. N-benzylidenepyridine-2-amine, obtained from the condensation reaction between benzaldehyde and 2-aminopyridine, has only previously been synthesized using the conventional method (refluxing in ethanol). This study develops and discovers two (2) new green techniques both occurring at room temperature with ethanol and an ethanol-water (1:1) mixture for a reaction time of 1 hour. The synthesis of N-benzylidenepyridine-2-amine gave a cream-colored solid product with melting point range of 67-69°C. The synthesis at ambient temperature with the solvent mixture gave the highest yield of 95.6% while the conventional method and synthesis with ethanol at ambient temperature gave 54.4% and 86.3% yield of the product respectively. The IR result showed the following bands; 1662cm^{-1} (C=N), 1554cm^{-1} (aromatic C=C stretch), 2944cm^{-1} (aromatic C-H stretch), 1449cm^{-1} (aromatic C=N stretch). The ^{13}C NMR spectrum showed the following chemical shifts (ppm); 163.21 (C=N, imine), 149.43 and 160.31 for C-N of aromatic pyridine moiety and 119.99–137.49 for all aromatic carbons. The ^1H NMR spectral data (ppm) for the compound gave the following results; 8.50-7.33, m (4H), 8.02-6.98, m (5H) and 9.16, s (1H) depicting the chemical shift for the pyridine moiety protons, benzaldehyde moiety protons and imino proton respectively. The spectral data obtained was in good correlation to that reported in literature.

Keywords: Green solvents, 2-aminopyridine, benzaldehyde, Schiff bases, ethanol-water, ethanol.

Introduction

Schiff bases are organic compounds that possess a functional group called the imino group composed of a carbon-nitrogen double bond (-C=N-) (da Silva *et al.*, 2011). They are obtained conventionally by the condensation reaction of an amine and an aldehyde using a reflux system (Savalia *et al.*, 2013). A variety of solvents and routes have been used for their synthesis ranging from toxic solvents to green solvents and the reaction has been carried out under ambient and reflux temperature (Umofia *et al.*, 2016; Cimerman *et al.*, 2000). Their syntheses have also been via microwave irradiation, sonication and even solvent-free grinding method (Qin *et al.*, 2013). These compounds possess a variety of pharmaceutical, agrochemical, and industrial importance ranging from

the antimicrobial activities to their antimalarial, insecticidal and herbicidal importance (Mhaske *et al.*, 2014). In addition, they possess anticorrosion properties; they have been used as plant growth regulators, dyes, electrochemical sensors, electroluminescent materials, to mention but a few of their applications. (Anis *et al.*, 2013)

Pyridine-based Schiff bases have become very common over the years due to their various agrochemical and pharmaceutical applications (Bendale *et al.*, 2011). Their syntheses have been through a variety of methods and solvents (Devidas *et al.*, 2011). Pyridine-based Schiff bases have been synthesized using; ethanol (Arun and Gowramma,

2014; Gupta and Barhate, 2012; Shaibu and Watkin, 2015; Shamky, 2016; Yoshida *et al.*, 2000) methanol (Yoshida *et al.*, 2000), ethanol-chloroform (2:1) (Zhou *et al.*, 2012), methanol-water (1:1) (Mishra *et al.*, 2012), ethanol-water (1:1) (Li Kam Wah and Bangarigadu-Sanasy, 2013), acetone-ethanol (2:1) (Singh and Dhakarey, 2009), ethanol-methanol (1:1) (Prasad and Rao, 2014). Furthermore, the techniques that have been used for the synthesis of pyridine-derived Schiff bases include; stirring under reflux temperature (Devidas *et al.*, 2011; Arun and Gowramma, 2014; Shamky, 2016), stirring at room temperature (Dnyaneshwar and Arvind, 2015; Omya *et al.*, 2014; Khan *et al.*, 2014), microwave irradiation (Jha and Kumar, 2013; Malakyan *et al.*, 2016) and sonication (Mishra *et al.*, 2012).

This paper focuses on the use of three (3) methods for the synthesis of N-benzylidenepyridine-2-amine with the aim of determining the best method for its synthesis considering reaction time and yield.

Experimental

Materials and Methods

The chemicals used for this research were synthesis grade chemicals purchased from Sigma-Aldrich. The melting point was determined with a melting point apparatus and was uncorrected while the Thin Layer Chromatography (TLC) was carried out using a Merck pre-coated silica gel plate (10x10 cm), the Rf value obtained using ethyl acetate as the mobile phase and the spot located and visualized using an ultraviolet lamp at 256 nm. The IR spectrum of the sample was recorded on a Fourier Transform Infra Red spectrometer, Carry 630 Agilent Technologies in the range of 650-4000 cm^{-1} . ^1H NMR and ^{13}C NMR spectrum of the sample was recorded on a JEOL Eclipse 400 NMR spectrophotometer by JEOL (Pleasanton, USA) using DMSO-d_6 .

Synthesis of N-benzylidenepyridine-2-amine using ethanol at reflux temperature.

2-aminopyridine (0.94g, 0.01mol) was dissolved in 20ml ethanol in a 150ml flat bottom flask followed by benzaldehyde (1.06g, 0.01mol) in 20ml ethanol. The reaction mixture was stirred under reflux at 80°C for 1 hr followed by the addition of a few drops of concentrated hydrochloric acid. The reaction was then stirred for one more hour and its progress monitored by thin layer chromatography (TLC) using ethyl acetate as the mobile phase. An oily product was extracted from the solvent using water and dichloromethane which formed a cream-colored solid after 24 hours. The solid product was filtered, recrystallized using ethanol and air-dried. Rf: 0.57, m.p: $67-69^\circ\text{C}$, yield: 54.4%, IR: 1662cm^{-1} (C=N),

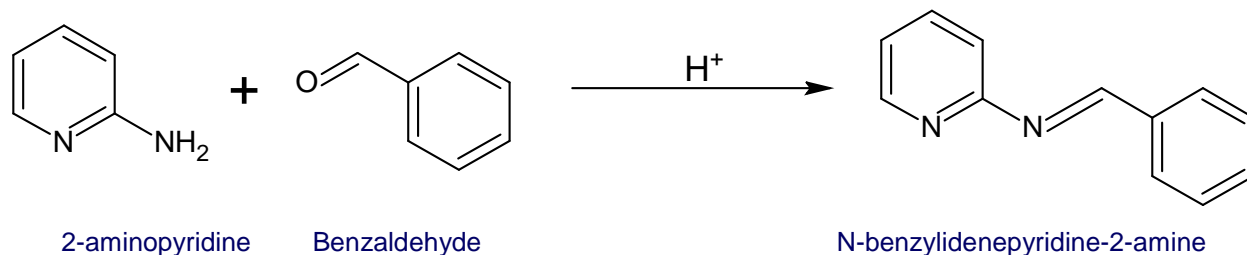
1554cm^{-1} (aromatic C=C stretch), 2944cm^{-1} (aromatic C-H stretch), 1449cm^{-1} (aromatic C=N stretch), ^{13}C NMR (ppm); 163.21 (C=N, imine), 149.43 and 160.31 for C-N of aromatic pyridine moiety and 119.99 – 137.49 for all aromatic carbons, ^1H (ppm) 8.50-7.33, m (4H) pyridine moiety , 8.02-6.98, m (5H) benzaldehyde moiety and 9.16, s (1H) imino proton.

Synthesis of N-benzylidenepyridine-2-amine using ethanol at room temperature.

2-aminopyridine (0.94g, 0.01mol) was dissolved in 20ml ethanol in a 150ml flat bottom flask followed by benzaldehyde (1.06g, 0.01mol) in 20ml ethanol. The reaction mixture was stirred at room temperature for 30 mins followed by the addition of a few drops of concentrated hydrochloric acid. The reaction was then stirred for another 30 mins and its progress monitored by thin layer chromatography (TLC) using ethyl acetate as the mobile phase. An oily product was extracted from the solvent using water and dichloromethane which formed a cream-colored solid after complete evaporation of the DCM within 24 hours. The solid product was filtered, recrystallized using ethanol and air-dried. Rf: 0.57, m.p: $67-69^\circ\text{C}$, yield: 86.3%, IR: 1662cm^{-1} (C=N), 1554cm^{-1} (aromatic C=C stretch), 2944cm^{-1} (aromatic C-H stretch), 1449cm^{-1} (aromatic C=N stretch), ^{13}C NMR (ppm); 163.21 (C=N, imine), 149.43 and 160.31 for C-N of aromatic pyridine moiety and 119.99 – 137.49 for all aromatic carbons, ^1H (ppm) 8.50-7.33, m (4H) pyridine moiety , 8.02-6.98, m (5H) benzaldehyde moiety and 9.16, s (1H) imino proton.

Synthesis of N-benzylidenepyridine-2-amine using ethanol-water (1:1) at room temperature.

2-aminopyridine (0.94g, 0.01mol) was dissolved in 20 ml ethanol-water (1:1 v/v) in a 150ml flat bottom flask followed by benzaldehyde (1.06g, 0.01mol) in 20 ml ethanol-water (1:1 v/v). The reaction mixture was stirred at ambient temperature for 30 mins followed by the addition of a few drops of concentrated hydrochloric acid. The reaction was then stirred for another 30 mins and its progress monitored by thin layer chromatography (TLC) using ethyl acetate as the mobile phase. An oily product was extracted from the solvent using water and dichloromethane which formed a cream-colored solid overnight. The solid product was filtered, recrystallized using ethanol and air-dried. Rf: 0.57, m.p: $67-69^\circ\text{C}$, yield: 95.6%, IR: 1662cm^{-1} (C=N), 1554cm^{-1} (aromatic C=C stretch), 2944cm^{-1} (aromatic C-H stretch), 1449cm^{-1} (aromatic C=N stretch), ^{13}C NMR (ppm): 163.21 (C=N, imine), 149.43 and 160.31 for C-N of aromatic pyridine moiety and 119.99 – 137.49 for all aromatic carbons, ^1H (ppm): 8.50-7.33, m (4H) pyridine moiety , 8.02-6.98, m (5H) benzaldehyde moiety and 9.16, s (1H) imino proton.



Results and Discussion

The synthesis of this pyridine-derived Schiff base was carried out using three (3) different methods; stirring the reactants in ethanol under reflux for 2 hours, stirring the reactants in ethanol at room temperature for 1 hour and stirring the reactants in an ethanol-water (1:1 v/v) at room temperature for 1 hour. The first method is the conventional method for the synthesis of Schiff bases. The work-up procedure for N-benzylidenepyridine-2-amine was quite tedious for all methods.

The syntheses carried out at ambient temperature was preferred because of two (2) main factors; the compound formed faster (in the absence of heat) and they gave higher yields (86.3% and 95.6%) when compared with the conventional method (54.4%). The physicochemical and spectral studies proved that all the methods gave the same compound.

The results obtained from the spectral analysis proved that the structures of the compounds were as expected. The presence of a peak at 1662cm^{-1} , depicting the presence of the imino group (C=N) and the absence of the amino and carbonyl group peaks at $3400\text{-}3250\text{cm}^{-1}$ and $1740\text{-}1720\text{cm}^{-1}$ respectively suggested the complete formation of the Schiff base. In addition, the ^{13}C NMR showed the imino peak at 163.21 ppm due to the deshielded nature of the imino carbon (C=N) as a result of the electronegativity difference between carbon and nitrogen. Moreover, the ^1H NMR result showed the presence of the imino proton, with a single peak at 9.16 ppm and this was in correlation to data from literature (Dalelio, 1969).

Conclusion

The synthesis of Schiff bases can be achieved by the use of eco-friendly solvents and techniques. The use of toxic solvents is gradually becoming a thing of the past as a result of the discovery of novel methods. This research has led to the discovery that the title compound N-benzylidenepyridine-2-amine can be synthesized at a very high yield using only green solvents at ambient temperature.

Acknowledgments


The authors would like to thank the Department of Pure and Industrial Chemistry, University of Port

Harcourt, for making available their postgraduate research laboratory for the purpose of this research. In addition, the analysts and technologists at Ahmadu Bello University, Zaria are highly appreciated for their assistance in carrying out spectral analyses of the Schiff bases.

References

- Anis, I., Aslam, M., Noreen, Z., Afza, N., Hussain, A., Safder, M., and Chaudhry, A.H. 2013. "General Applications of Schiff Base Transition Metal Complexes" *Int. J. Cur. Pharma. Res.* 5(2): 21-24.
- Arun, N.T. and Gowramma, B. 2014. "Synthesis and Biological Evaluation of Some Novel Schiff Bases of Cephalexin" *Int. J. Pharm. Sci. Res.*, 5(3): 1008-1014.
- Bendale, A.R., Bhatt, R., Nagar, A., Jadhav, A.G. and Vidyasagar, G. 2011. "Schiff Base Synthesis by Unconventional Route An innovative Green Approach" *Pharma Chem.* 3(2): 34 – 38.
- Cimerman, Z., Miljanic, S. and Galic, N. 2000. "Schiff Bases Derived from Aminopyridines as Spectrofluorimetric Analytical Reagents" *Croat. Chem. Acta*, 73(1): 81-95.
- Dalelio, G. 1969. "Exploratory Polymer Synthesis Quarterly Status Report, 1 Aug.- 31 Oct. 1969 (Heterocyclic Schiff Base Type Monomer Prepared by Reaction of Carbon Compounds with Amino Compounds)" 31-33.
- da Silva, C.M., da Silva, D.L., Modolo, L.V., Alves, R.B., de Resende, M.A., Martins, C.V.B. and de Fatima, A. 2011. "Schiff Bases: A Short Review of their Antimicrobial Activities" *J. Adv. Res.* 2: 1-8.
- Devidas, S.M., Quadri, S., Pathan, A., Kamble, S.A., Farooqui, M., Nuzaat, D.A., Shaikh, J.D, Farooqui, M. and Syed, F.M. 2011. "Pharmaceutically Fine Synthesis and their Study of Antimicrobial Activity of Metal Complexes with some Schiff Bases" *Pharma Chem.* 3(4): 486-490.
- Dnyaneshwar, P.G. and Arvind, K.A. 2015. "Synthesis and Characterization of Schiff Base Ligands Derived from 2-aminopyridine and 3-aminophenol by using Green Approach" *Pelagia Res. Lib. Der Chemica Sinica*, 6 (10): 34-37.
- Gupta, A.K.S. and Barhate, V.D. 2012. "Synthesis, Characterization and Study of Microbiological Activity of Some Transition Metal Ion Complexes with [N-(o-hydroxybenzylidene)-Pyridine-2-Amine]

- (NOHBPA)" Res. J. Pharm. Bio. Chem. Sc. 3(3): 1013-1026.
- Jha, Y.S., and Kumar, D.N. 2013. "An Innovative Green Synthesis of Some Schiff Bases and their Antimicrobial Activity" Int. J. Pharm. and Bio Sci. 4(4): 197 – 204.
- Khan, A.N., Patil, A., Tajane, S., Kadam, J.J., Lokhande, M.V. 2014. "Antibacterial Activity of 2-[(2-Chloro-4-Methylbenzylidene)Amino]Pyridin-4-ol and its Some Transitional Metal Ion Complexes" J. Appl. Chem. 7 (8): 14-20.
- Li Kam Wah, H.T.Y. and Bangarigadu-Sanasy, S. 2013. "Synthesis and Antibacterial Activity of New Schiff Bases Derived from 2,3-Diaminopyridine and Their Copper(II), Iron(III), Nickel(II) and Zinc(II) Complexes" Asian J. Chem. 25 (16): 9221-9225.
- Malakyan, M., Babayan, N., Grigoryan, R., Sarkisyan, N., Tonoyan, V., Tadevosyan, D., Matosyan, V., Aroutiounian, R., Arakelyan, A. 2016. "Synthesis, Characterization and Toxicity Studies of Pyridinecarboxaldehydes and L-tryptophan Derived Schiff bases and Corresponding Copper (II) Complexes" F1000Research 5 (1921): 1-12.
- Mhaske, G., Nilkantha, P., Auti, A., Davange, S. and Shelke, S. 2014. "Aqua-Medicated Microwave Assisted, Synthesis of Schiff Bases and Their biological Evaluation" Int. J. Inn. Res. Sci. Eng. Technol. 3(1): 8156 – 8162.
- Mishra, A.P., Mishra, R., Jain, R. and Gupta, S. 2012. "Synthesis of New VO(II), Co(II), Ni(II) and Cu(II) Complexes with Isatin-3-Chloro-4-Floroaniline and 2-Pyridinecarboxylidene-4-Aminoantipyrine and their Antimicrobial Studies" Kor. Soc. Mycol.: Mycobiology 40 (1): 20-26.
- Omya, A.M.A., Samir, M.E., Ahmed, D.A. and Nassar, D.A. 2015. "Synthesis, Characterization, Fluorescence and Catalytic Activity of some New Complexes of Unsymmetrical Schiff Base of 2-Pyridinecarboxaldehyde with 2,6-Diaminopyridine" Spectrochimica Acta Part A: Mol. Biomol. Spec. 144: 99–106.
- Prasad, A.V.G.S. and Rao, P.V. 2014. "One-Pot Synthesis of Schiff Base Compounds Derived from 2-Nitro Benzoic Acid with Aldehydes" J. Chem. Env. Sci. and its Appl. 1(1): 7–14.
- Qin, W., Long, S., Panunzio, M. and Biondi, S. 2013. "Schiff Bases: A Short Survey on an Evergreen Chemistry Tool" Molecules. 18: 12264-12269.
- Savalia, R.V., Patel, A.P., Trivedi, P.T., Gohel, H.R and Khetani, D.B. 2013. "Rapid and Economic Synthesis of Schiff Base of Salicylaldehyde by Microwave Irradiation" Res. J. Chem. Sci. 3(10): 97-99.
- Shaibu, R.O. and Watkins, G.M. 2015. "Synthesis and Spectroscopic Studies of Schiff Bases from Variously Substituted Benzaldehydes and 2-Aminomethylpyridine". Ife J. Sc. 17(1): 31-39.
- Shamkhy, E.T. 2016. "Preparation and Characterization of New Schiff Base Derived from Pyridine and its Metal Complexes" Int. J. Cur. Res. Chem. Pharm. Sc. 3(4): 118-123.
- Singh, P. and Dhakarey, R.K.S. 2009. "Synthesis, Characterization and Antimicrobial Studies of Metal Complexes with Schiff Bases Derived From 2-Thienyl Glyoxal" Rasayan J. Chem. 2 (4): 869-874.
- Umofia, E., Omuaru, V. O. T., Achugasim, O. 2016. "Green solvents for the synthesis of some toluidine-derived Schiff bases" J. Chem. Soc. Nig. 41(1): 15-18.
- Yoshida, N., Ichikawa, K. and Shiro, M. 2000. "Supramolecular Motifs in Metal Complexes of Schiff Bases. Part 5. Zinc (II)-Assisted Self-Assembly of Some Bis-*N,N*- and *N,O*-Bidentate Schiff Bases and Chiral Packing Modes in Solid State" J. Chem. Soc. Perkin Trans. 2: 17–26.
- Zhou, W., Fan, R., Wang, P. and Yang, Y. 2012. "N,N-Bis[1-(pyridin-2-yl)ethylidene]-benzene-1,4-diamine" Acta Cryst. E68: 1-5.

Access this Article in Online	
	Website: www.ijcrpps.com
	Subject: Chemistry
Quick Response Code	
DOI: 10.22192/ijcrpps.2018.05.08.004	

How to cite this article:

Umofia Eno, Abayah Oviere J., Omuaru Victor O.T., Achugasim Ozioma. (2018). Novel green techniques for the synthesis of N-Benzylidenepyridine-2-Amine. Int. J. Curr. Res. Chem. Pharm. Sci. 5(8): 20-23.
DOI: <http://dx.doi.org/10.22192/ijcrpps.2018.05.08.004>