

The Eco-Friendly Synthesis Of N-[2-Pyridinylmethylidene]Aniline

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Abstract: *N*-[2-pyridinylmethylidene]aniline was obtained from the reaction between aniline and 2-formylpyridine using three (3) techniques; refluxing in ethanol, stirring in ethanol and an ethanol-water (1:1) mixture at ambient temperature. This research ascertains two (2) novel eco-friendly procedures both taking place at ambient temperature for an hour in ethanol and an ethanol-water (1:1) mixture. The synthesis of *N*-[2-pyridinylmethylidene]aniline gave a light brown solid product with melting point range of 98-100°C. The room temperature reaction with the solvent mixture gave the highest yield of 95.2% while the conventional method and the reaction in ethanol at room temperature gave 54.4% and 82.3% yield of the compound respectively. The IR spectrum showed the following bands; 1625cm⁻¹ (C=N), 1591cm⁻¹ (aromatic C=C stretch), 3056cm⁻¹ (aromatic C-H stretch), 1435cm⁻¹ (aromatic C=N stretch). The ¹³C NMR spectrum showed the following chemical shifts (δppm); 163.06 (C=N, imino), 149.29 and 163.06 for C-N of aromatic pyridine moiety and 114.92 – 147.24 for ring carbon atoms. The ¹H NMR spectral data (δppm) for the compound gave the following results; 7.40-7.01, m (4H), 7.66-6.51, m (5H) and 8.45, s (1H) portraying the chemical environments for the pyridine protons, phenyl protons and imino proton respectively. The spectral data was in correlation to that reported in literature.

Keywords: Green solvents, Schiff bases, aniline, 2-pyridinecarboxaldehyde.

I. INTRODUCTION

Schiff bases are classified under the group of organic compounds called imines. Imines are characterized with a carbon-nitrogen double bond (-C=N-) called the imino group.[1] Schiff bases have been synthesized using different routes and techniques with varying solvents ranging from ecofriendly to toxic.[2] The conventional method for the synthesis of these compounds involves refluxing an amine and an aldehyde in the presence of a solvent and acidic or basic catalyst.[3,4] Other methods that have been used for the synthesis of Schiff bases include the use of microwave irradiation, sonication, stirring at room temperature [4] and grinding method.[5] The solvents that have been used range

from green solvents like water and ethanol, to toxic solvents like benzene.

These compounds have found application in the manufacture of dyes, drug with different pharmaceutical importance owing to their biological activities which span from antimalarial to antifungal and antitubercular.[6,7] They are also used to produce agrochemicals such as herbicides, insecticides and plant growth regulators. [8]

The synthesis of Schiff bases with the pyridine moiety has been through the use of solvents like ethanol [9-14], dichloromethane [15], methanol [16], ethanol-chloroform (2:1) [17], methanol-water (1:1) [18], ethanol-water (1:1) [19], acetone-ethanol (2:1) [20], ethanol-methanol (1:1) [21]. Furthermore, the techniques that have been used for the synthesis of pyridine-derived Schiff bases include; stirring

under reflux temperature [9], [10], [13], stirring at room temperature [22-24], microwave irradiation [25] and sonication [16].

This paper focuses on the use of three green solvents for the synthesis of N-[2-pyridinylmethylidene]aniline with the aim of determining the best method for its synthesis considering reaction time and yield.

II. EXPERIMENTAL

A. MATERIALS

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 .

B. METHODS

a. SYNTHESIS OF N-[2-PYRIDINYLMETHYLIDENE]ANILINE USING ETHANOL AT REFLUX TEMPERATURE

2-Formylpyridine (0.94g, 0.01mol) was dissolved in 20ml ethanol in a 150ml flat bottom flask followed by aniline (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. A brown viscous oil was obtained after extraction from the reaction solvent using water and dichloromethane. This gave a light brown solid overnight after trituration with diethyl ether. The solid product was washed with ethanol, filtered and air-dried. Rf: 0.61, m.p: 98-100°C, yield: 54.4%, IR: 1625 cm^{-1} (C=N), 1591 cm^{-1} (aromatic C=C stretch), 3056 cm^{-1} (aromatic C-H stretch), 1435 cm^{-1} (aromatic C=N stretch), ^{13}C NMR (δppm); 163.06 (C=N, imino), 149.29 and 163.06 for C-N of aromatic pyridine moiety and 114.92 – 147.49 for all aromatic carbons, ^1H (δppm) 7.40-7.01, m (4H) pyridine moiety, 7.66-6.51, m (5H) phenyl moiety and 8.45, s (1H) imino proton.

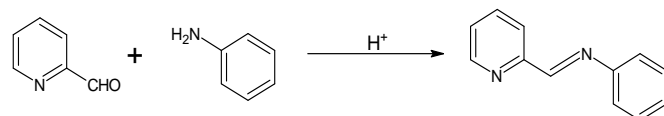
b. SYNTHESIS OF N-[2-PYRIDINYLMETHYLIDENE]ANILINE USING ETHANOL AT ROOM TEMPERATURE

2-Formylpyridine (0.94g, 0.01mol) was dissolved in 20ml ethanol in a 150ml flat bottom flask followed by aniline (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. A brown viscous oil was obtained after extraction from the reaction solvent using water and dichloromethane. This gave a light brown solid overnight after trituration with diethyl ether. The solid product was washed with ethanol, filtered and air-dried. Rf: 0.61, m.p: 98-100°C, yield: 82.3%, IR (KBr): 1625 cm^{-1} (C=N), 1591 cm^{-1} (aromatic C=C stretch), 3056 cm^{-1} (aromatic C-H stretch), 1435 cm^{-1} (aromatic C=N stretch), ^{13}C NMR (δppm); 163.06 (C=N, imino), 149.29 and 163.06 for C-N of aromatic pyridine moiety and 114.92 – 147.49 for all aromatic carbons, ^1H (δppm) 7.40-7.01, m (4H) pyridine moiety, 7.66-6.51, m (5H) phenyl moiety and 8.45, s (1H) imino proton.

c. SYNTHESIS OF N-[2-PYRIDINYLMETHYLIDENE]ANILINE USING ETHANOL-WATER (1:1) AT ROOM TEMPERATURE

2-formylpyridine (0.94g, 0.01mol) was dissolved in 20 ml ethanol-water (1:1 v/v) in a 150ml flat bottom flask followed by aniline (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. A brown viscous oil was obtained after extraction from the reaction solvent using water and dichloromethane. This gave a light brown solid overnight after trituration with diethyl ether. The solid product was washed with ethanol, filtered and air-dried. Rf: 0.61, m.p: 98-100°C, yield: 95.2%, IR (KBr): 1625 cm^{-1} (C=N), 1591 cm^{-1} (aromatic C=C stretch), 3056 cm^{-1} (aromatic C-H stretch), 1435 cm^{-1} (aromatic C=N stretch), ^{13}C NMR (δppm); 163.06 (C=N, imino), 149.29 and 163.06 for C-N of aromatic pyridine moiety and 114.92 – 147.49 for all aromatic carbons, ^1H (δppm) 7.40-7.01, m (4H) pyridine moiety, 7.66-6.51, m (5H) phenyl moiety and 8.45, s (1H) imino proton. The general reaction equation for the synthesis of N-[2-pyridinylmethylidene]aniline is illustrated in fig. 1 below.



2-Formylpyridine + Aniline $\xrightarrow{\text{H}^+}$ N-[2-pyridinylmethylidene]aniline
Figure 1: General reaction equation for the synthesis of N-[2-pyridinylmethylidene]aniline

III. RESULTS AND DISCUSSION

The synthesis of N-[2-pyridinylmethylidene]aniline was carried out using three (3) different methods; the conventional method (stirring the reactants in ethanol under reflux for 2 hours) and two (2) novel routes (stirring the reactants in ethanol at room temperature for an hour and stirring the

reactants in an ethanol-water (1:1 v/v) at room temperature for an hour). The work-up procedure for the extraction of N-[2-pyridinylmethylidene]aniline from the reaction solvent was tedious and time-consuming for all procedures, however, this was necessary to ensure purity of the compound.

The syntheses at ambient temperature were preferred because the title compound was formed at half the reaction time when compared to the conventional method. Also, and most importantly, these novel methods gave higher yields (82.3% and 95.2%) 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 anticipated. The presence of a peak at 1625cm^{-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, proved the formation of the Schiff base. In addition, the proton NMR result showed the presence of the imino proton, with a single peak at 8.45 ppm and the ^{13}C NMR showed the imino (C=N) peak at 163.06 ppm due to the inductive effect of nitrogen on the doubly bonded carbon as a result of electronegativity difference between them.

IV. CONCLUSION

This research proves that the synthesis of pyridine-based Schiff bases can be achieved by the use of green solvents and methods. This research has led to the discovery that the title compound N-[2-pyridinylmethylidene]aniline can be synthesized at a very high yield using only green solvents at ambient temperature.

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