FACILE AND CONVENIENT SYNTHESIS AND CHARACTERIZATION OF NOVEL SCHIFF BASES INVOLVING HETEROCYCLIC RING THROUGH ONE POT MULTICOMPONENT REACTIONS UNDER MILD CONDITIONS

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Abstract: A convenient and efficient procedure for one pot preparation of novel Schiff bases through three component reactions of heterocyclic aldehyde, ammonium hydroxide and other aldehyde is described. In this reaction, the desired products were easily obtained in excellent yields and in short reaction time under mild conditions.

Keywords: Schiff base, heterocyclic aldehyde, aliphatic aldehyde, ammonium hydroxide

Introduction

Schiff base ligands have been extensively studied over past few decades of the various classes of Schiff bases which can be prepared by condensation of different types of amines and carbonyl compounds salicylaldimines, potential O, N-donors are very popular due to divers chelating ability [1]. Schiff bases that have solvent dependent Uv-Vis spectra (solvatochromicity) can be suitable NLO (non linear optical active) materials [2]. These ligands offer a versatile and flexible series of compounds having properties for practical applications [3]. Tetradentate Schiff bases with N_2O_2 donor atom set are well known to coordinate various metal ions, and this has attracted the interest of many authors [4-7].

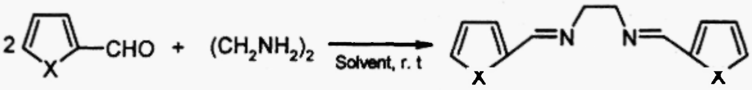
Schiff base complexes find many applications such as a model compounds for the study of the active sits of metallo-enzymes [8], solid phase extraction of metal ions[9] and etc. With attention to the importance of these ligands, each year many papers instead literature have been published regarding the synthesis and their application in different fields for various purposes.

Recently multi-component reactions constitute an especially attractive synthetic strategy for rapid and efficient generation due to the fact that the products are formed in a single step and the diversity can be achieved simply by varying the reacting components [10]. The importance of these one-pot three component reactions in such synthesis has been demonstrated in the Mannich, Ugi, Biginell and aza-Baylish-Hillman reactions [11-14]

In continuation of our current efforts on research, we are focused on the development of the multicomponent reaction and the utilization of these processes toward the synthesis of novel Schiff bases. In this study, we report a practical and efficient three component reactions by reacting heterocyclic aldehydes with other aldehydes and ammonium hydroxide at room temperature.

Results and discussions

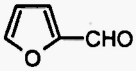
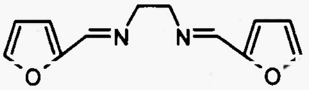
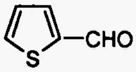
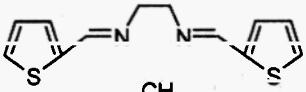
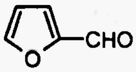
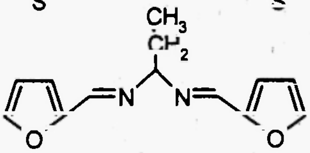
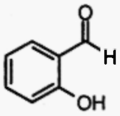
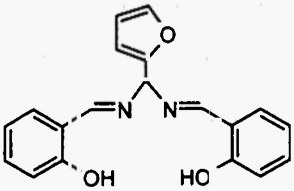
As shown in scheme 1, when 2 mols heterocyclic aldehyde were treated with 1 mol ethylenediamine at room temperature the pail yellow substance obtained with high yield. In this reaction, heterocyclic aldehydes have been applied and corresponding products was obtained. The conditions of the reactions are presented in Table 1.



X =O and S

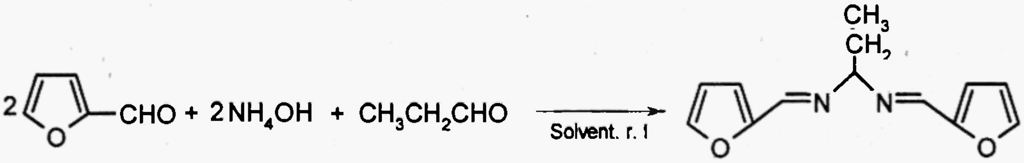
Scheme 1

Table 1 Preparation of Schiff base containing heterocyclic rings through two and three component reaction

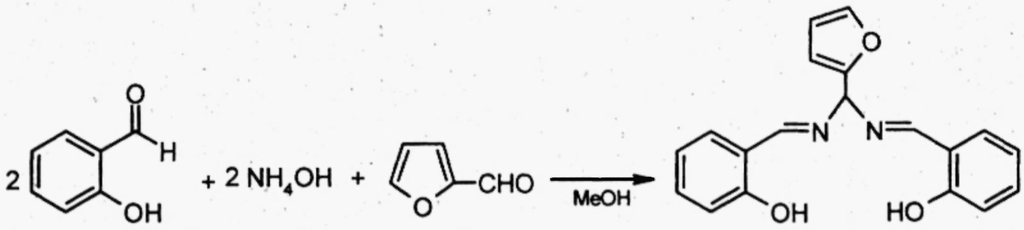
Entry	Substrate(1)	Substrate(2)	Product	Time (h)	M.P (°C)	Yield[a] (%)
1		Ethylendiamine		3.4	78-80	85
2		Ethylendiamine		4.5	90-92	85
3		Propanal		4	84-86	95
4		Fourfural		3	88-90	95

a) Isolated product yields

With attention to the importance of the multicomponent reaction, in continuation of this study, the preparation of Schiff base ligands have been investigated via one pot three component reactions. When 1 mol of propanal, 2 mols of ammonium hydroxide and 2 mols of furfural were reacted together at one step reaction, the yellow product was produced with excellent yield at short reaction time(Scheme 2).



Scheme 2



Scheme 3

When the above mentioned reaction was performed in the presence of salicylaldehyde, furfural and ammonium hydroxide, corresponding product, N, N'-bis (2-hydroxybenzilidene)-1,1- furylmethane-diamine was obtained with excellent yield and short time(Scheme 3). The results of these investigations were summarized in Table 1.

The structures of the products were confirmed by spectroscopic methods. In the IR spectra, the characteristic Schiff base C=N stretching frequency is formed in the region between υ=1600-1700 Cm^{-1} as a signal strong band. The OH stretching frequency is found at υ–3400 cm^{-1} with particular width. The stretching vibration of C-H in the alkyl groups appear at region between υ= 2700-2800 Cm^{-1} with sharp absorptions. In the ^1H NMR spectra, the broad signal with δ=12.4 p.p.m is assigned to the OH groups. Two protons of CH=N have the same chemical shifts in δ=8.30-8.46 ppm and the signal around the δ= 4-6 ppm is assigned to the protons of the NCHN.

In conclusion, in this study we have been reported an efficient, convenient, and mild two and three component method for synthesis of some novel Schiff base ligands containing heterocyclic ring. The products have been afforded in excellent yields and short reaction time.

Experimental

Materials

All the materials were of commercial reagent grade. The salicylaldehyde and other aldehyde compounds were purified by standard procedures. The purity of them was determined by thin layer chromatography (TLC) and gas chromatography (GC).

Apparatus

Chemicals were purchased from the Merck Chemical Company in high purity. IR spectra were recorded as KBr pellet on a Perkin-Elmer 781 Spectrophotometer and an Impact 400 Nickolet FTIR Spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ with (400 MHz) Spectrometer using of TMS as an internal reference. Melting points were obtained with a Yanagimoto micro melting point apparatus are uncorrected. The purity determination of the substrates and the reactions monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates.

General procedure

General Procedure for Synthesis of 2, 2'-[1,2-ethanediylbis-(nitrilomethylidene)]bis-furane

To the stirred solution of furfural (4 mmol) in 5 ml MeOH ethylendiamine (2 mmol) at room temperature was added. The reaction was continued for 3.4 h. The progress of the reaction was monitored by TLC. After the reaction was completed of the reaction, the brown oil was collected and dissolved in hot petroleum ether. After cooling pail yellow solid product was obtained, this was filtered off and washed with cold MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, 2,2'-[1,2-ethanediylbis-(nitrilomethylidene)]bis-furane was obtained in 85% yield, m.p=78-80 °C. The structure of the Schiff base was confirmed by spectroscopic methods.

General Procedure for Synthesis of N,N'-bis(2-hydroxybenzylidene)-1,1-furanmethanediamine

To the stirred mixture of salicylaldehyde (0.4 g, 3.27 mmol) and furfural (1.64 mmol) in MeOH was added NH_4OH (0.25 g, 3.27 mmol) was added. The reaction was continued to 3 h at room temperature. The progress of the reaction was monitored by TLC. After the reaction was completed the reaction mixture turned yellow. After cooling the solid product was formed and then this product was filtered off and washed with cold MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, N,N'-bis(2-hydroxybenzylidene)-1,1-furanmethanediamine was obtained in 95% yield, m.p=88-90 °C. The Schiff base products were identified by spectroscopic methods.

2, 2'-[1,2-ethanediylbis-(nitrilomethylidene)]bis-furane: mp 78-80 °C; IR (KBr)/ υ (cm^{-1}) 3050, 2900, 1627 (s, C=N), 1450, 1540 (Ar); ^1H NMR/$CDCl_3$/ δ p.p.m 3.96 (s, 4 H, 2 CH_2N), 6.5-7.2 (m, 6 H, Ar), 8.2 (s, 2 H). C NMR /$CDCl_3$ / δ p.p.m; 170, 148, 142, 120, 110, 43; MS: m/z= 217 (M^++1, 6%), 216 (M^+, 10), 108 (55), 39(90), 29 (97), Anal. Calcd. For C. H. N.: C, 66.70, H, 5.6; N, 12.96; Found; C, 68.2; H, 6.1; N, 12.96.

2,2'-[1,2-ethanediylbis-(nitrilomethylidene)]bis-thiophene: mp 90-92 °C; IR (KBr)/ υ (cm^{-1}) 3050, 2900, 1623 (s, C=N), 1450, 1540 (Ar); ^1H NMR/$CDCl_3$/ δ p.p.m 3.6 (s, 4 H, 2 CH_2N), 6.6-7.3 (m, 6 H, Ar), 8.3 (s, 2 H): C NMR /$CDCl_3$ / δ p.p.m; 171, 149, 144, 123, 118, 45. MS: m/z= 249 (M^++1, 5%), 248 (M^+, 10), 123 (42), 58(85), 45 (87), 39 (92); Anal. Calcd. For C. H. N.: C, 58.06; H, 4.84; N, 11.29; Found; C, 59.11; H, 5.04; N, 11.29.

2,2'-[1,1-propanediylbis-(nitrilomethylidene)]bis-furane: mp 84-86°C; 3050, 2900, 1625 (s, C=N), 1450, 1550 (Ar); ^1H NMR/$CDCl_3$/ δ p.p.m 0.9 (t, 3 H, CH_3), 1.8 (qu, 2 H, CH_2), 4 (t, 1 H, NCHN), 6.9-7.4 (m, 6 H), 8.2 (s, 2 H, HC=N): C NMR /$CDCl_3$ / δ p.p.m; 171, 147, 143, 120, 114, 82, 25, 20;

MS: m/z= 231 (M^++1, 4%), 230 (M^+, 8), 136 (78), 41(66), 39 (88), 29 (95); Anal. Calcd. For C. H. N.: C, 67.83; H, 6.09; N, 12.17; Found; C, 67.98; H, 7.02; N, 12.17.

N,N'-bis(2-hydroxybenzylidene)-1,1-fouranmethanediamine: mp 88-90°C; IR (KBr)/ υ (cm^{-1}) 3400-3700 (br, OH), 3100, 2900, 1625 (s, C=N), 1485, 1576 (Ar); ^1H NMR/DMSO/ δ p.p.m 6 (s, 1 H, NCHN), 6.2-7.8 (m, 11 H, Ar), 8.3 (s, 2 H, HC=N), 12.4 (s, 2 H, OH); C NMR /$CDCl_3$ / δ p.p.m; 174, 156, 148, 137, 130, 128, 122, 120, 118, 113, 92;

MS: m/z= 321 (M^++1, 3%), 320 (M^+, 8), 91 (85), 79 (80), 77(60), 39 (85), 29 (90); Anal. Calcd. For C. H. N.: C, 71.25; H, 5.00; N, 8.75; Found; C, 72.01; H, 5.91; N, 8.75.

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