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REGULAR ARTICLE

STUDIES ON SYNTHESIS OF ALDIMINES: PART-I. SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF ALDIMINES FROM BENZALDEHYDE WITH VARIEDLY SUBSTITUTED ANILINES

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ABSTRACT

A conventional condensation reaction of an aromatic aldehyde, Benzaldehyde with seven different aromatic amines viz. Aniline, 2-Choro-aniline, 3-Choro-aniline, 4-Choro-aniline, 2-Nitro-aniline, 3-Nitro-aniline and 4-Nitro-aniline and reacted efficiently to synthesize a series of Aldmines, I to VII, in moderate to high yield and high purity. The reaction was monitored and the products were analyzed by employing the TLC technique. All the products obtained were characterized by their colour, physical constant, TLC, elemental analysis and spectral (UV-Vis and FTIR) method. The synthesized Aldimines were subjected to *in vitro* biological activity.

Keywords: Aldimines or Schiff bases, Benzaldehyde, Conventional, TLC, UV-Vis, FTIR and biological activity

INTRODUCTION

From this laboratory, the synthesis of aldimines viz. of Schiff bases from Benzaldehyde and Anisaldehyde reacted with aniline, p-bromo-aniline and p-methoxy-aniline by Conventional and Grindstone method, which is environmental friendly reaction also, green sustainable chemistry (GSC) were reported with their biological activity [1,2]. We have reported the evaluation of biological properties of schiff bases from 2-aminobenzothiazoles and 4-chorobenzaldehyde [3]. Further, we have also communicated studies on TLC of closely related organic compounds [4]. Review of the literature, shows that many researchers have used this method to synthesize the varied aldimines of salicyladehyde and varied anilines and heteroaromatic amines [5]. A solvent free condensation of different aldehydes with two different piperazine based amines, gave a series of imines [6-7]. The rapid synthesis of Schiff bases without solvent under irradiation. Recently, we have communicated conventional synthesis of schiff bases from ketones like o-hydroxy-acetophenone [8] and benzophenone [9]. N-Substituted benzylidene-aniline derivatives were synthesized by conventional and their antibacterial activity are studied [7] at 200 to 800 mg/ml concentration with ciprofloxacin as standard drug and 10% DMSO as control sample.

In the present study we have putforth a conventional condensation reaction of an aromatic aldehyde viz. benzaldehyde with each separately seven different aromatic amines viz. Aniline, 2-Choro-aniline, 3-Choro-aniline, 4-Choro-aniline, 2-Nitro-aniline, 3-Nitro-aniline and 4-Nitro-aniline to yield Aldimines of high purity (Scheme-1). Also, an account of study of their antifungal potential and comparison with a standards drug, Fluconazole, is described herein.

MATERIALS AND METHODS

The raw materials Benzaldehyde and the Anilines viz. Aniline, 2-Choro-aniline, 3-Choro-aniline, 4-Choro-aniline, 2-Nitro-aniline, 3-Nitro-aniline and 4-Nitro-aniline used were of synthesis grades(Sigma-Aldrich). The solvents toluene, ethyl acetate and ethanol used for TLC and UV-Vis spectra purpose were of synthesis and spectroscopic grade. The reaction was monitored by employing the technique such as TLC on aluminum plates coated with silica gel G-TLC 60 F 254 (Merck make).

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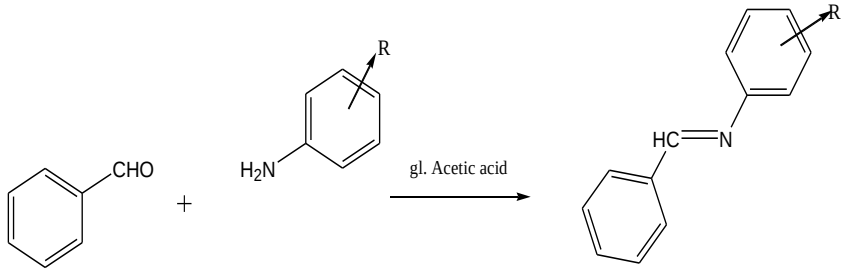
Scheme-1:



R = -H(1); 2-Cl(2); 3-Cl(3); 4-Cl(4); 2-NO_2(5); 3-NO_2(6); 4-NO_2(7);

Experimental

General Procedure for the synthesis of aldmines

The condensation reaction of aromatic aldehyde, Benzaldehyde with each separately seven different aromatic amines viz. Aniline, 2-Choro-aniline, 3-Choro-aniline, 4-Choro-aniline, 2-Nitro-aniline, 3-Nitro-aniline and 4-Nitro-aniline, each of 15 mm by conventional method were reacted [10] and gave formation of Aldimines or Schiff bases. The reaction process and completion is monitored by employing by technique of TLC, on aluminum plates coated with silica gel. The obtained products were recrystallized in absolute solvent.

The UV-Vis spectra were recorded on Schimadzu-1800 spectrophotometer in alcohol. Stock solutions prepared in absolute ethanol and were of 0.01 M concentration. These solutions were diluted serially and were used for the UV-Vis Spectral determination. The FTIR spectra were recorded on a Shimadzu FTIR 8400 spectrophotometer (Model-IR Affinity-1) using sample mixed in powder form with KBr powder, the frequency values, '□' are in the range of 4000-400 cm^{-1}. The structural assignment of the products was based respectively on the elemental (CHN), TLC and Spectral analysis.

After confirming the desired molecular studies, these Aldimines were studied for their anti-fungal activity by subjecting to *in vitro* antifungal activity against fungi using disc diffusion method [1, 10].

RESULTS AND DISCUSSION

The condensation reaction products of an aldehyde and amines called as Aldmines or Schiff base. In the present study reports the synthesis of aldimines from Benzaldehyde with Aniline, 2-Choro-aniline, 3-Choro-aniline, 4-Choro-aniline, 2-Nitro-aniline, 3-Nitro-aniline and 4-Nitro-aniline, and abbreviated respectively as I to VII. The progress of reaction was monitored by Silica Gel TLC 60 F 254 plates of (Merck), visualized by iodine vapour or in UV at short and long wavelength. These products were yellow to brown in colour. The purity of compounds was ascertaining by melting point range determination. Their TLCs were recorded on aluminum plates coated with thin layers of silica gel. The analytical results of synthesized aldimines are shown in table 1. The analytical results and % yields are in the range 80.3 % to 67.6 %.

All compounds gave satisfactory elemental analysis. Values are in the close agreement with the values calculated for expected molecular formula assigned to these compounds and are in 5 % in statistics. The physical constant and their purity confirmed by TLC. The TLC of amine and the final product is monitored, indicated the single spots and obtained data is as.

Anal. Data for Schiff bases(ID; m. p.(°K); % CHN(Obs./Cal.): I 321.8-322.1, 86.12/86.13, 6.07/6.07, 7.69/7.73; II, 372.3-376.3, 72.40/72.36, 4.61/4.64, 6.46/6.49; III, 72.34/72.36, 4.66/4.64, 6.42/6.49; IV, 334.2-334.1, 72.34/72.36, 4.63/4.64, 6.42/4.49; V, 344.1-346.2, 68.89/68.99, 4.39/4.42, 6.21/6.19; VI, 367.7-370.6, 68.96/68.99, 4.41/4.42, 6.16/6.19; VII, 389.7-390.1, 68.92/68.99, 4.41/4.42, 6.15/6.19.

In addition, in this the compounds, I to VII were also characterized by spectral viz. UV-Vis and FTIR and the results obtained were depicted in Table 2.

All the studied Aldimines or Schiff base compounds are soluble in ethanol and their UV-Vis spectra in ethanol were n the studied range 450 nm to 200 nm. The UV-V is spectral analysis of Aldimine shows the two to three peaks in the studied range. These are attributed to n→*π and n→*π transition respectively due to the presence of varied auxochrom group (auxochrom) and>C=N-group transition and aromatic phenyl ring transition of moderate energy. The spectral data are in close agreement with the structure of the synthesized compounds, as reported earlier [11]. Table 2 also indicates the assigned structure for the spectral results.

Table 1: Analytical results for synthesized N-benzylidene-anilines, I to VII derived from Benzaldehyde

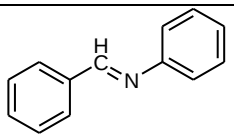
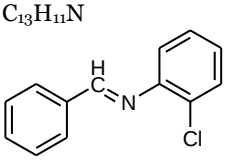
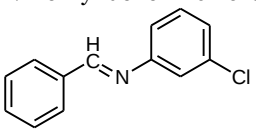
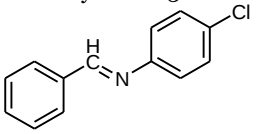
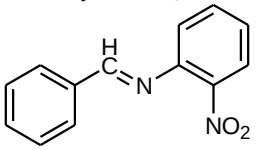
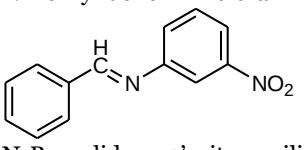
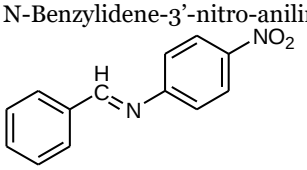
Product ID	Aniline	Mol. Wt. of aniline	Mol Wt of product,	Wt of product, gm	% Yield*
I	Aniline	93.13	181	8.8	72.3
II	2-Choro-aniline	127.63	215	5.21	69.5
III	3-Choro-aniline	127.63	215	3.10	67.6
IV	4-Choro-aniline	127.63	215	11	78.2
V	2-Nitro-aniline	138.13	226	10.74	75.3
VI	3-Nitro-aniline	138.13	226	1.91	69.1
VII	4-Nitro-aniline	138.13	226	10.11	80.3

*isolated yield

The FTIR spectra of the synthesized aldimines, 1 to 7 indicated, medium intensity band observed in the frequency range 2885-3310 cm^{-1} in all compounds are attributed to–C-H stretching vibrations viz. Symmetric and Asymmetric of the aromatic ring. All these compounds showed a characteristic band in the region 1620-1628 cm^{-1}, which is attributed to–CH=N-group(stretching). These values are close in agreement with values reported for the similar Schiff bases [12-14]. The three band in the frequency range 1500-1595 cm^{-1}. Indicate aromatic nature of the compound. A sharp band in the range 1192-1178 cm^{-1}. In all synthesized Schiff base may be assigned to the aryl–C-N stretching vibration [15] additional band at 785-780 cm^{-1} for Schiff base II, III and IV may be attributed to aryl C-Cl group on comparison with that of the varied FTIR frequency of compound, I. The Schiff base V, VI and VII have displayed strong band at 1487-1440 cm^{-1}, 1356-1338 cm^{-1} which may be assigned to stretching vibration of conjugated nitro group according to Hassan [15] and Bellamy [16].

On the basis of the foregoing discussion and based on TLC spectral observation, the structure of the synthesized compound is assigned. The Table 3 also indicated the assigned structure from the spectral results.

Table 2: The spectral data for synthesized aldimines, I to VII, derived from benzaldehyde

ID	UV-Vis (nm)	FTIR (cm^{-1})	Assigned structure, name and Mol. formula
I	312.0(4,400) 244.0(15,740) 203.0 (33,780)	$\nu_{Ar-C=C}$-1595, 1582, 1510 ν_{Ar-C-H} 2890, 3310 $\nu_{>C=N-}$1625 s ν_{-C-N} 1192	 N-Benzylidene-aniline, $C_{13}H_{11}N$
II	412.5(1,486) 334.5(35,280) 260.0(47,911)	$\nu_{Ar-C=C}$-1590, 1572, 1534 ν_{Ar-C-H} 2890, 3305 $\nu_{>C=N-}$1620 s ν_{-C-Cl} 818 and 780 ν_{-C-N} 1192	 N-Benzylidene-2'-chloro-aniline, $C_{13}H_{10}NCl$
III	337.0(2,800) 291.0(16,723) 229.0(14,234)	$\nu_{Ar-C=C}$-1595, 1565, 1510 ν_{Ar-C-H} 2885,3310 $\nu_{>C=N-}$1620 s ν_{-C-Cl} 825 and 785 ν_{-C-N} 1170	 N-Benzylidene-3'-chloro-aniline, $C_{13}H_{10}NCl$
IV	318.0(4,200) 246.0(18,940) 203.0(34,440)	$\nu_{Ar-C=C}$-1590, 1576, 1500 V_{Ar-C-H} 2925, 2915 $\nu_{>C=N-}$1623 ν_{-C-Cl} 820 and 780 ν_{-C-N} 1185	 N-Benzylidene-4'-chloro-aniline, $C_{13}H_{10}NCl$
V	414.0(2,215) 338.0(13,562)	$\nu_{Ar-C=C}$-1595, 1575, 1500 ν_{Ar-C-H} 2925, 2910 $\nu_{>C=N-}$1623 s ν_{-NO_2} 1456,and 1338 ν_{-C-N} 1180	 N-Benzylidene-2'-nitro-aniline, $C_{13}H_{10}N_2O_2$
VI	332.5(18,976) 253.0(35,199)	$\nu_{Ar-C=C}$-1595, 1585, 1500 ν_{Ar-C-H} 2925, 2980 $\nu_{>C=N-}$1628 s ν_{-NO_2} 1487 and 1356 ν_{-C-N} 1185	 N-Benzylidene-3'-nitro-aniline, $C_{13}H_{10}N_2O_2$
VII	380.0(26,960) 228.0(12,240) 201.0(18,940)	$\nu_{Ar-C=C}$-1590,1582, 1510 ν_{Ar-C-H} 3035,2980 $\nu_{>C=N-}$1622 s ν_{-NO_2} 1440 and 1355 ν_{-C-N} 1178	 N-Benzylidene-2'-nitro-aniline, $C_{13}H_{10}N_2O_2$

s = strong

Table 3: The data showing the antifungal activity (MIC) of Aldimines, I-VII for different strains after 48 h

Comp. ID	*C. albicans*,(NCIM 3471)		*A. niger*, (NCIM 1196)	
	50 g/ml	100 g/ml	50 g/ml	100 g/ml
I	10	11	12	13
II	09	11	11	11
III	10	12	09	12
IV	09	10	10	10
V	12	12	11	14
VI	13	12	12	11
VII	10	10	12	11
DMSO (-ve control)	-	-	-	-
Fluconazole (Std,+ve control	18	21	16	18

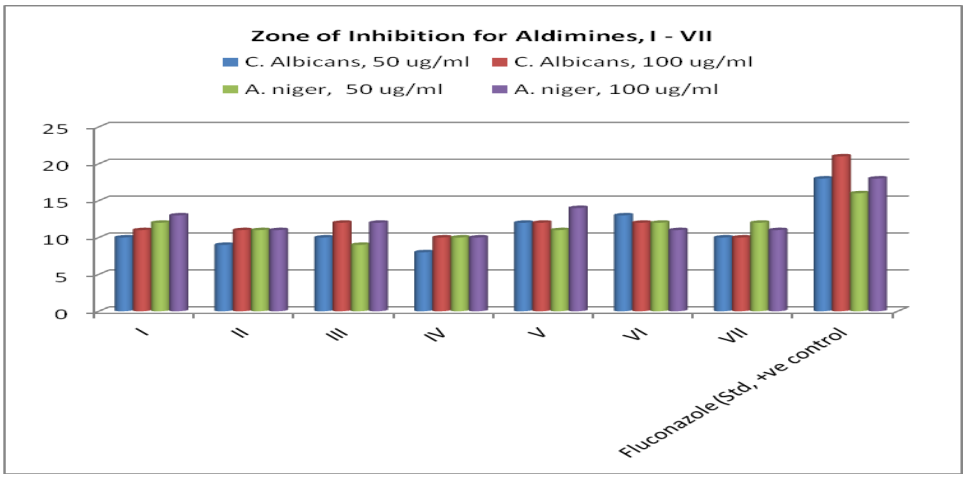


Fig. 1: The graphical representation of the zone of inhibition for the synthesized Aldimine, I–VII

Antifungal activity

After confirming the desired molecular studied, these Aldimine, I to VII were studied for their fungal activity using disc diffusion method [1, 9-10], using strains like *C. albicans* (NCIM 3471) and *A. Niger* (NCIM 1196). The results of zone of inhibition are depicted in Table 3.

The observed antifungal activity of all the compounds have been studied which may be due to the>C=N-linkage of the Schiff bases. The zone of inhibition is directly proportional to the degree of sensitivity of the bacterial strain and the concentration of the compound under test. The systematic data of antifungal activity reveals that with the increase in concentration of the test sample or the drug there is increase in the zone of inhibition is marked in the petri-dish. The results of antibacterial activity against *C. albican* and *A. niger* are compare with that of the standard drug, Fluconazole. Solvent DMSO is used as negative control. All the marked activity coefficients for the studied compounds are moderate to less than the standard drug, Fluconazole.

The graphical representation of the result of zone of inhibition (in mm) is depicted in Fig. 1.

Glimpses of antifungal study

✓ Schiff base I to VII are active against both strains.

✓ Schiff base IV is least active against *C. albican*(50 µg/ml).

✓ Schiff base V is most active of all (100 µg/ml) against *A. niger* than *C. albican*.

✓ All the marked Zone of Inhibition for the studied compounds are moderate to less than the standard drug, Fluconazole.

CONCLUSION

Seven Schiff bases were synthesized and characterized on the basis of analytical and spectral data. These compounds will be useful as building block by organic researchers in the near future. Screening of these compounds against pathogenic microorganism reveals that these compounds have the capacity of inhibiting metabolic growth of some microorganisms to different extent. The antifungal activity of the compounds is also dependent on the nature of substituent present on the aromatic ring.

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