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AN EFFICIENT ONE POT SYNTHESIS OF SUBSTITUTED BENZYLIDENYL AMINO NAPHTHALENE AND STUDY OF ANTIMICROBIAL ACTIVITY

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ABSTRACT

In this study, six new imine compounds (3a-f) were synthesized from 1-naphthyl amine with substituted aromatic aldehydes in EtOH and The catalyst Bronstd acid such as Methanesulphonic acid used as a catalyst and their chemical structures were defined by 1H/13C NMR, IR and elemental analysis studies. Besides, the antimicrobial activity was evaluated by these compounds.

KEYWORDS

Schiff bases, Imines, 2-naphthylamine and Aromatic aldehyde.

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INTRODUCTON

Generally, Schiff bases (imines) occur from primary amines and carbonyl compounds (aldehydes or ketones, in Scheme No.1) and were first synthesized in 1869 by the German chemist Hugo Schiff[1,2]. The bond formed by reaction with aldehyde is called azomethine or Azoschiff bases compounds derived from the reaction between the Schiff base and azo compounds. Schiff base derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represented in important series of widely studies organic ligands[1]. Schiff bases and azo Schiff bases important intermediates for the synthesis of some application such asbiologicalactivity[2-4], clinical[5,6], analytical[7,8], Anticancer[9,10] and catalystical[11,12]. Azo Schiff base compounds are highly important well known and widely used substances in textile, paper and coloring agents for foods and cosmetics industries[13,14]. Azo Schiff base

and their complexes with transition metal ions are also of importance due to their complexing, catalytically, biological properties[15,16] and corrosion inhabitation in acid media[17,18] aldimine, while the bond formed by reaction with ketone is called imine or ketamine.

In this study, nine new imine compounds (3a-h) were synthesized from 1- naphthyl amine with aromatic aldehydes in ethanol and their chemical structures were defined by 1H and 13C NMR, IR, and elemental analysis studies. The evaluation of the analysis results had proved the accuracy of the synthesized structures.

MATERIAL AND METHODS

Experimental

All starting materials and reagents were commercially available procured from Merck chemicals and used without further purification except where indicated. Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F255) and spots were visualized with ultraviolet (UV) light. The melting points were determined on a Yanagimoto micro-melting point apparatus and were uncorrected. IR spectra were measured on a SHIMADZU Prestige-21 (200 VCE) spectrometer.^{1}H and ^{13}C NMR spectra were measured on spectrometer at VARIAN Infinity plus 400 and at 100MHz, respectively. 1H/13C chemical shifts are referenced to the internal deuterated solvent. Chemical shift values (δ) are given in ppm. The elemental analysis was carried out with a LecoCHNS-932 instrument.

General procedure for the synthesis of substituted benzylidenyl amino naphthalene (3a-f)

The mixture of 1-naphthylamine (1) (1.0mmol) and substituted aromatic aldehydes derivatives (2) (1.0mmol) were stirred and refluxed for 3 hours in ethanol (15ml). The methane Sulphonic acid slowly added in the reaction and after completion of the reaction, the mixture was left cooling to room temperature and poured on cold water (50ml). The product (3) was filtered and dried. The reaction was continuing for two hours. The progress of the reaction was checked with help of TLC (EtOAc: n-Hexane- 4:6) and after which the reaction mixture was cooled to room temperature (25^{o}C) to afford ethanol insoluble solid products. The products were recrystallized from ethanol to afford highly pure products.

N-(benzylidenyl) napthy-amine (3a)

Yellow compound, M.P. 167-169^{o}C; Yield-91%, IR (KBr, cm-1): 3044 (aromatic C-H), 2965 (azomethine C-H), 1602 (Ar-CH=N-Ar), 1567 (-C=C-).^{1}H NMR (400 MHz, CDCl3) δ ppm: 7.278-8.027 (12H, m, Ar-H), 8.878 (1H, s, Ar-CH=N-). 13CNMR (100 MHz, $CDCl_3$) δ ppm: 161.21, 145.53, 138.75, 130.21 and 119.3. LCMS (m/z); 231.44 (M+); Molecular formulae: $C_{17}H_{13}N$: Elemental analysis; Calculated: C- 88.28, H- 5.66, N -6.06; Obtained: C-88.30, H- 5.20, N- 6.09.

N-(3, 4-dihydroxybenzylidene) napthylamine(3b)

Yellow compound, M.P. 167-169^{o}C; Yield-91; IR (KBr, cm -1): 3400-3320, 3028, 2960, 1610, 1560. 1H NMR (400 MHz, CDCl3) δ ppm: 4.73 (s, 2H,–OH), 6.90-7.80 (10H, m, Ar-H), 8.56 (1H, s, Ar-CH=N-Ar). 13C NMR (100 MHz, CDCl3) δ ppm: 160.82, 142.53, 139.73, 136.79, 130.21, 120.63. LCMS (m/z); 264.11(M+); Molecular formulae: $C_{17}H_{13}NO_2$: Elemental analysis; Calculated: C-77.55, H- 4.98, N- 5.32; Obtained: C 77.63, H-5.00, N- 5.20.

N-(4-methoxybenzylidene) napthylamine (3c)

Yellow compound, M.P - 187-189^{o}C; Yield-94; IR (KBr, cm -1): 3066, 2987, 1658, 1577, 1136.1H NMR (400 MHz, CDCl3) δ ppm: 3.714 (s, 3H,–OCH3), 7.152-7.950 (11H, m, Ar-H), 8.887 (1H, s, Ar-CH=N-Ar). 13CNMR (100 MHz, CDCl3) δ ppm: 162.54, 160.08, 142.53, 131.51, 119.73, and 56.57. LCMS (m/z); 262.38 (M+H); Molecular formulae: $C_{18}H_{15}NO$: Elemental analysis; Calculated: C -82.73, H -5.50, N- 5.36; Obtained: C- 82.80, H -5.49, N- 5.20.

N-(4-methylbenzylidene) Napthyl-amine (3d)

Yellow compound, M.P. 167-169^{o}C; Yield-91%; IR (KBr, cm^{-1}): 3048, 2959, 1603, 1564, 1354; ^{1}HNMR (400MHz, $CDCl_3$) δ ppm: 2.345 (s, 3H, -CH_3), 7.254-8.254 (11H, m, Ar-H), 8.578 (1H, s, Ar-CH=N-Ar); ^{13}CNMR (100 MHz, $CDCl_3$) δ ppm: 161.25, 144.63, 141.45, 132.41, 120.53; LCMS (m/z); 246.77(M+H); Molecular formulae:

$C_{18}H_{15}N$: Elemental analysis; Calculated: C- 88.13, H- 6.16, N- 5.71; Obtained: C -88.20, H- 6.20, N - 5.80.

N-(4-Chlorobenzylidene) naphthalene-1-amine (3e)

Yellow compound, M.P. 184-186^{o}C; Yield-89%; IR (KBr, cm^{-1}): 3057, 2971, 1621 and 1554, 1109, 1039. ^{1}HNMR (400 MHz, $CDCl_3$) δppm: 7.283-8.472 (11H, m, Ar-H), 8.759 (1H, s, Ar-CH=N-Ar). 13CNMR (100 MHz, $CDCl_3$) δ ppm: 161.72, 143.83, 136.38, 129.55, and 119.95. LCMS (m/z); 267.55(M+2); Molecular formulae: $C_{17}H_{12}NCl$: Elemental analysis; Calculated: C-77.84, H- 4.55, N- 5.30; Obtained: C-76.99, H -4.49, N- 5.26.

N-(4-Nitrobenzylidene) naphthalene-1-amine (3f)

Yellow compound, M.P. 169-171^{o}C; Yield-88%; IR (KBr, cm-1): 3058, 2984, 1602, 1569, 1335; 1H NMR (400 MHz, CDCl3) δ ppm: 7.347-8.557 (11H, m, Ar-H), 8.841 (1H, s, -Ar-CH=N-Ar). 13CNMR (100 MHz, $CDCl_3$) δ ppm: 159.02, 143.54, 143.55, and 130.51-120.47. LCMS (m/z); 277.25(M+H); Molecular formulae: $C_{17}H_{12}N_2O_2$: Elemental analysis; Calculated: C-73.90, H- 4.38, N -10.14; Obtained: C -73.92, H- 4.25, N- 10.07.

RESULTS AND DISCUSSION

In our research, the Schiff base benzylidenyl aminonaphthalenes (3a-h) were prepared by refluxing an appropriate amount of 1-naphthylamine with the different aromatic aldehydes in methanol under mild experimental conditions. For purification, the products obtained were poured on cold water and filtered. The efficiency of the products obtained was between 85-92% conversions. In addition, the reaction mechanism of the Schiff bases obtained was considered to be as outlined in Scheme No.1.

According to the literature research, all spectral evidences of the titled product were showed and Schiff Bases were identified to be consistent with the expected results. In the IR spectra showed characteristic absorption bands at around 3058, 2984, 1602, 1569 and 1335cm-1 regions was confirming the presence of (-OH), aromatic (C-H), azomethine (C-H), (C=N), (C=C) respectively. A strong absorption band at 1557-1665cm-1 was due to (C=N) vibration. The absorption bands at 3025-3075cm^{-1} and 1584-1547cm−1 belonged to the stretching frequency of the aromatic ring.

Further, we observed a singlet of integration intensity equivalent to one hydrogen at 8.547–8.886ppm in the 1H NMR spectra of the Schiff bases, indicating the presence of the zomethineproton (–CH=N–). The peaks of naphthalene aromatic and phenyl group protons appeared as multiple signal at 7.145-8.417ppm. Also compounds 3e and 3f (–O-CH3) protons were found 3.728ppm as singlet signal. The peak at 2.135ppm was due to three methyl protons (s,-CH_3) in 3b. Finally, signal of (-OH) groups protons in compounds 3g and 3h were observed nearly at 4.00 ppm. The 1H NMR spectroscopies provided an additional support for the formation of Schiff base derivatives and total 1H NMR results were showed evidences above characterization.

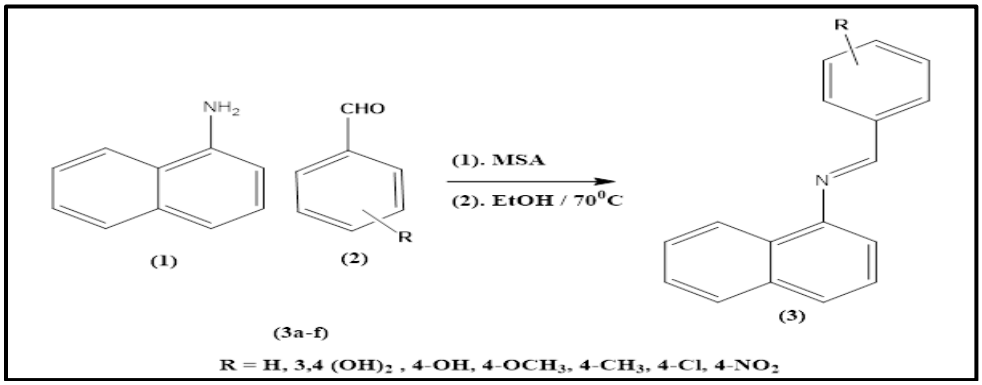
For compound 3(a-f), characteristic 13C-NMR signal of the azomethine group (-C=NH) was observed at 162.42-160.74ppm. This characteristic peak has been found for the others at 162.4 (4-OMe-Ar-), 143.5(-Ar-NO2), 142.3(-Ar-N=), 136.63(-Ar-Cl), 139.3(4-OH-Ar), 136.09(3-OH-Ar) and 56.82(-O-CH3), respectively. Furthermore, signal of aromatic carbons (compound 3) were observed at 132.41-120.55ppm. The purity of all imine compounds was confirmed by mass analysis.

Biological Activity

All the desired compounds were evaluated by anti-bacterial activity as well as antifungal. Activity the electron withdrawing group of compounds and electron releasing group compounds exhibited different potent activities against bacterial as well as fungal strains. Therefore, electron withdrawing group of compounds showed low biological potent activity compared with electron releasing groups. All halogen compounds exhibit well to excellent activity. The compound which possess electron donating group showed moderate activity as shown in Table No.1.

Table No.1: Antimicrobial activity screening activity Titled compounds scaffold

S.No	Compound Code	*Zone of inhibition in (mm)					
		Bacteria				Fungi	
		S.aureus	***E.coli***	***S. typhi***	***B.substill***	***A. Niger***	***C. albicans***
1	3a	04	06	08	06	05	05
2	3b	14	15	13	15	06	07
3	3c	20	19	15	18	14	12
4	3d	18	20	20	19	15	16
5	3e	12	11	13	11	10	09
6	3f	10	12	09	10	08	06
7	streptomycin	25	25	22	22	NA	NA
8	Ketoconazole	NA	NA	NA	NA	20	20
9	DMSO	---	----	---	---	---	---



Scheme No.1

CONCLUSION

The structure of the newly synthesized derivatives was elucidated on the basis of elemental analysis and spectral data. When all analysis results of the synthesized compounds were examined, the presence of characteristic peaks proving the formation of imine was observed and the synthesis of the compounds was successful. Also, this synthesis has quite environmentally friendly synthesis method because ethanol and methane Sulphonic acid as a catalyst was used as solvent.

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CONFLICT OF INTEREST

The author declares no conflict of interest.

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