Preparation and Identification of Some New Pyridinium Salts

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Abstract

In this work the pyridinium salts were prepared by two stage. The first step was preparation of Schiff bases compounds (A1-A5), The second step is preparation of pyridinium salts (B1-B5) by N-alkylation reaction between Schiff bases compounds and a proper alkyl halide(1,2-Chloroethane, 1-bromopropane, benzyl chloride, benzyl chloride andbromoethane). All the compounds were confirmed their structures by using spectroscopic techniques (FTIR and ^{1}HNMR).

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Keywords: Schiff base compounds, Pyridinium Salt, FTIR, HNMR.

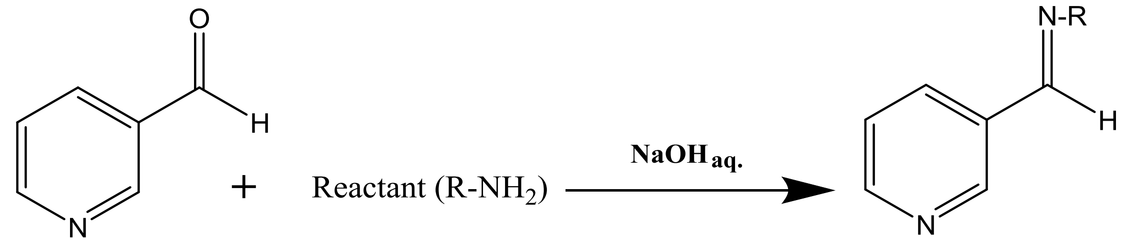
1. Introduction

Pyridine and its synthesized derivatives are important chemical compounds with huge direction of applications in the various fields.3-nicotinaldehyde is a pyridine derivative found in the liquid phase, it is useful starting material to obtain a precursor and followed steps to obtain target molecules. Enormous reports on synthesis of heterocyclic derivatives containing S, O and Natoms have been listed to have abroad spectrum of biological activity. Numerous data concerning synthesis of heterocyclic have been reported [1−3]. Pyridinium salts have a kind of positively charged surfactants that have a hydrophilic fragment, polar chemical environment, and a hydrophobic side that can be interred into nonpolar chemical molecular mass. Aromatic ring heterocyclic derivatives in addition to different groups of function can be presented either on N atom or on the pyridine rings. A considerable attention pay for pyridinium compounds that tested with their pharmacological and biological activities. They have importance in their antimicrobials [4–9] antivirals [10–12] anti-hypertension and immune stimulate activities [13]. Some of pyridinium derivatives of aldoximehaveeffectiveness antidote against poisoning of organophosphate [14]. In the present work, we prepared some pyridinium salts by preparation of Schiff base compounds and N-alkylation reaction with alkyl halides. All the compounds were confirmed their structures by using spectroscopic techniques (FTIR and ^{1}HNMR).

2. Experimental part.

2.1. Synthesis of Schiff base compounds (A1-A5).

The Schiff base compounds was prepared according to the following procedure: An ethanolic solution of nicotinaldehyde (0.005mol) was added to an ethanolic solution of a proper amine (0.005 mol). Then (10% NaOH, 0.3mL) was added to the solution and refluxed for 4-6 hrs. After concentration of the solution, the precipitate was separated, filtered, washed with ethanol. Finally, the yield was recrystallized from ethanol. The physical properties of compounds (A1-A5) are shown in Table (1).



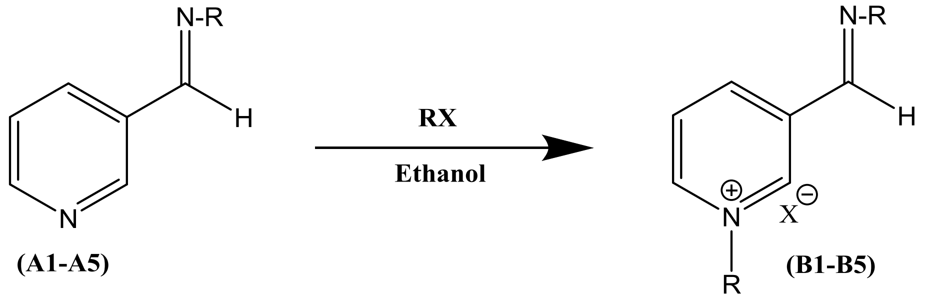
nicotinaldehyde **(A1-A5)**

R-NH$_2$: O-Tulodin . 2-Chloroaniline . Benzylamine . 4-Aminoacetophenone .
4-Bromo-2-methylaniline

Table (1)
Physical properties of compounds (A1-A5).

	Name of compound	Chemical Formula	Color	M.P. °C	Yield (%)
A1	1-(pyridin-3-yl)-N-(o-tolyl)methanimine (A1)	$C_{13}H_{10}N_2$	Pale brown	150-153	79
A2	N-(2-chlorophenyl)-1-(pyridin-3-yl) methanimine(A2)	$C_{12}H_9ClN_2$	Black	135-138	70
A3	N-benzyl-1-(pyridin-3-yl)methanimine (A3)	$C_{13}H_{12}N_2$	Yellow	116-120	76
A4	1-(4-((pyridin-3-ylmethylene)amino) phenyl)ethan-1-one (A4)	$C_{14}H_{12}N_2O$	Yellow	129-133	87
A5	N-(4-bromo-2-methylphenyl)-1-(pyridin-3-yl)methanimine (A5)	$C_{13}H_{11}BrN_2$	Gray	145-149	76

2.2. Synthesis of Pyridinium salts (B1-B5):



(A1-A5) **(B1-B5)**

RX: Benzyl chloride. 1-Bromopropane . 1,2-dichloroethane .
. Bromoethane

A mixture of (0.01 mol) Schiff base product(A1-A5) and (0.01 mol) of a proper alkyl halide (1,2-Chloroethane, 1-bromopropane, benzyl chloride, benzyl chloride and bromoethane) in 10 mL of acetonitrile was allowed to stand 12 hours at room temperature. Then, the mixture was refluxed for 6 hrs. The final product (B1-B5) was filtered, washed with acetonitrile and dried. The physical properties of compounds (B1-B5) are shown in Table (2).

Table (2)
Physical properties of compounds (B1-B5).

	Name of compound	Chemical Formula	Color	M.P. °C	Yield (%)
B1	1-propyl-3-((o-tolylimino)methyl)pyridiniumbromide	$C_{16}H_{19}BrN_2$	Off white	300dec.	80
B2	1-benzyl-3-((benzylimino)methyl)pyridinium chloride	$C_{20}H_{19}ClN_2$	Orange	223-228	71
B3	3-(((4-acetylphenyl)imino)methyl)-1-(2-chloroethyl)pyridinium chloride	$C_{16}H_{16}Cl_2N_2O$	Brown	230dec.	79
B4	3-(((4-bromo-2-methylphenyl)imino)methyl)-1-ethylpyridinium bromide	$C_{15}H_{16}Br_2N_2$	White	120-124	75
B5	3-(((2-chlorophenyl)imino)methyl)-1-ethylpyridinium bromide	$C_{14}H_{14}BrClN_2$	White	165-169	64

3. Results and Discussion.

The present work was included new pyridinium salt derivatives (B1-B5) Through usual preparation methods by converting nicotinaldehyde to Schiff base compounds (A1-A5), and followed by preparing pyridinium salts (B1-B5) by reaction the Schiff base compounds with a proper alkyl halide (1,2-chloroethane, 1-bromopropane, benzyl chloride, benzyl chloride and bromoethane). All the compounds were confirmed their structures by using spectroscopic techniques. In general, the characteristic stretching bonds of FTIR spectra to Schiff base compounds (A1-A5) are (C=N) bonds. The stretching (C=N) bonds of the compounds (A1-A5) within the range (1650-1620 cm^{-1}) with disappearing (C=O) bond of nicotinaldehyde. There are others characteristic stretching bonds, as (C-H) aromatic bond at (3100-3000 cm^{-1})[15]. Table(3) show the spectral data of IR for compounds (A1-A5). In general, the characteristic stretching bonds of FTIR spectra data of pyridinium salts (B1-B5) are (C-H) aromatic bond at (3100-3000 cm^{-1})and (C-H) aliphatic bond at (3000-2850 cm^{-1})[15]. Table(4) is show FTIR spectral data for prepared compounds (B1-B5). The ^{1}HNMR spectra of the pyridinium salt derivatives (B1-B5) show that aliphatic and aromatic hydrogen (C-H) in different chemical shift positions [15] and that's confirmed structure of derivatives (B1- B5) (solvent (D_2O)) Table (5) and Figure (1) are shown^{1}H-NMR spectral data of derivatives (B1- B5).

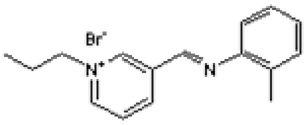
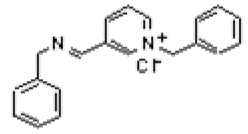
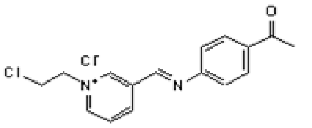
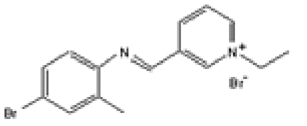
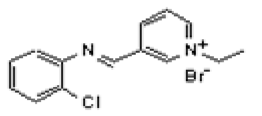
Table (3)
FTIR spectral data for prepared compounds (A1-A5).

Comp. No.	ν C-H aromatic	ν C-H aliphatic	ν C=C aromatic	ν C=O	ν C=N
A1	3021	2916	1575 1483	-	1628
A2	3059	-	1581 1477	-	1631
A3	3055	2950	1582 1478	-	1641
A4	3035	2885	1589 1475	1724(C=O)	1631
A5	3032	2949	1564 1475	-	1625

Table (4)
FTIR spectral data for prepared compounds (B1-B5).

Comp.No.	ν C-H aromatic	ν C-H aliphatic	ν C=C aromatic	ν C=O	ν C=N
B1	3078	2978	1593	**-**	1635
B2	3032	2924	1612	**-**	1635
B3	3047	2985	1612	1743	1630
B4	3025	2924	1579	**-**	1631
B5	3020	2978	1616	**-**	1639

Table (5)
^{1}H-NMR spectral data of derivatives (B1- B5) in ppm.

Comp.No.	Compound structure	^{1}H-NMR data of (δ-H) in ppm
B1		4H of pyridine-ring (8.7-9.2); 4H of phenyl- rings (7.2-8.7), 2H of $-CH_2-N^+$group (5.0); 1H of imine (8.3); 1.0-2.5 of 5H of aliphatic; 3H of methyl group (2.2)
B2		4H of pyridine-ring (8.7-9.5); 10H of phenyl- rings (7.3-8.7) ,2H of $-CH_2$-ph (5.9); 1H of imine (8.3); 4.3 of 2H of aliphatic amine
B3		4H of pyridine-ring (8.7-9.0); 4H of phenyl- rings (6.9-8.7) ,2H of $-CH_2-N^+$(4.7); 1H of imine (8.3); 2.5 of 3H of aliphatic; 1.7 of 2H of aliphatic-halide
B4		1H of CH=N- (8.3);4H of pyridine-ring (8.7-9.4); 3H of phenyl- rings (6.8-7.6), 2H of $-CH_2$ group (4.7); 1.0-1.53H of aliphatic; 2.5 of 3H of methyl-ph
B5		1H of CH=N- (8.3);4H of pyridine-ring (8.7-9.4); 4H of phenyl- rings (6.8-7.6), 2H of $-CH_2$ group (4.7); 1.0-1.53H of aliphatic

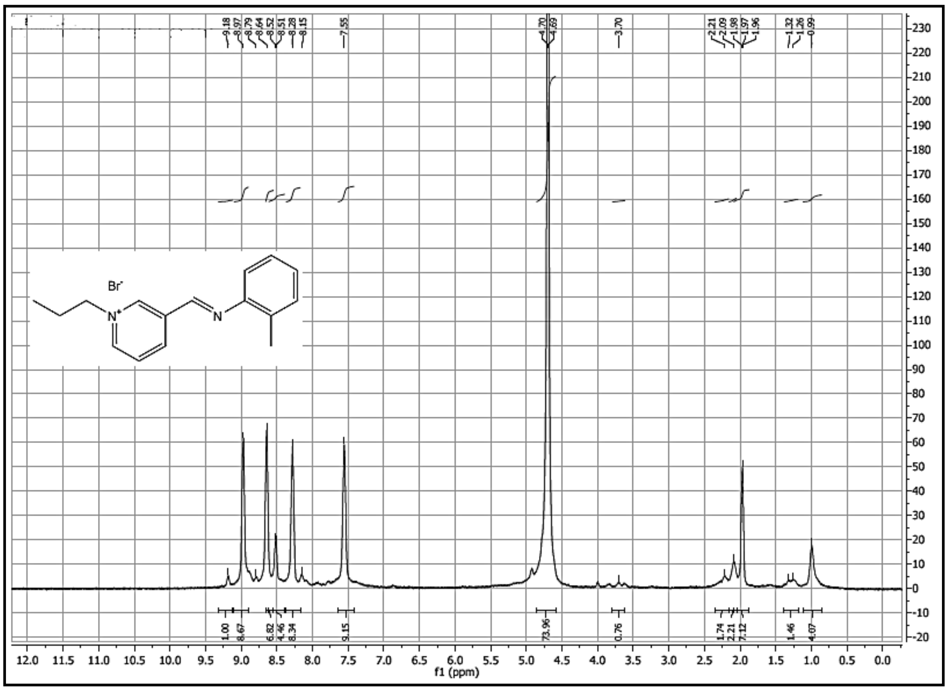


Fig.(1): ^{1}HNMR for compound (B1).

4. Conclusion:

Some pyridinium salts derivatives (B1-B5) were prepared by known chemical steps included imine formation then formation of pyridinium salt by Menschutkin reaction. The chemical structure of prepared compounds was confirmed using spectroscopic techniques and determined their physical properties.

Acknowledgements:

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