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Studies on schiff bases from methyl-1-naphthyl ketone. Part-II: Synthesis and characterization of ketimines from 1-acetylnaphthalene with derivatives of aniline

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ABSTRACT

The Ketimines (Schiff bases) were prepared from Methyl-1-naphthyl-ketone with Aniline, 2-Chloro-aniline, 3-Chloro-aniline, 4-Chloro-aniline and 2-Nitroaniline using toluene as solvent by azeotropic(reflux) method using Dean and Stark. The synthesized ketimines were characterized and confirmed by colour, physical constant, TLC and spectral(UV-Vis and FTIR) information.

Key words: Methyl-1-naphthyl-ketone, 1-Acetylnaphthalene, Ketimines (Schiff Bases), azeotropic method and Dean Stark Apparatus.

INTRODUCTION

There are many classes of compounds in Organic Chemistry like aldehyde, ketone, nitrile, ester, lactone, anhydride, ketimine, azo and diazonium compounds etc. From this simplest ketimine class of compounds is selected for the present study which also plays an important role in the synthetic chemistry.

Ketimines are the compounds containing imine or azomethine(>C=N-) as a functional group. These compounds were initially discovered by Hugo(Ugo) Schiff [1] in 1864 and studied by several others[2-3]. Schiff bases soon became the research theme of other synthetic chemists, biologists, pharmacists and even the physicists. They are the compounds containing azomethine group (-HC=N-). Schiff bases were represented by the general formula $(R_1R_2)C=N-R_3$, where R_3 group is a alkyl or phenyl which makes the Schiff base a very stable imine. The chemistry of heteropolar unsaturated functions are very well explored [4-5] and imines in particular are of special interest in literature due to their numerous practical applications. [6-8]. In the recent years, ester derivatives of aromatic schiff bases have been reported to have liquid crystalline properties [5-6]. Previously we have reported the synthesis, electrochemical characterization of some aldimines[7-8] and their complexes[9].

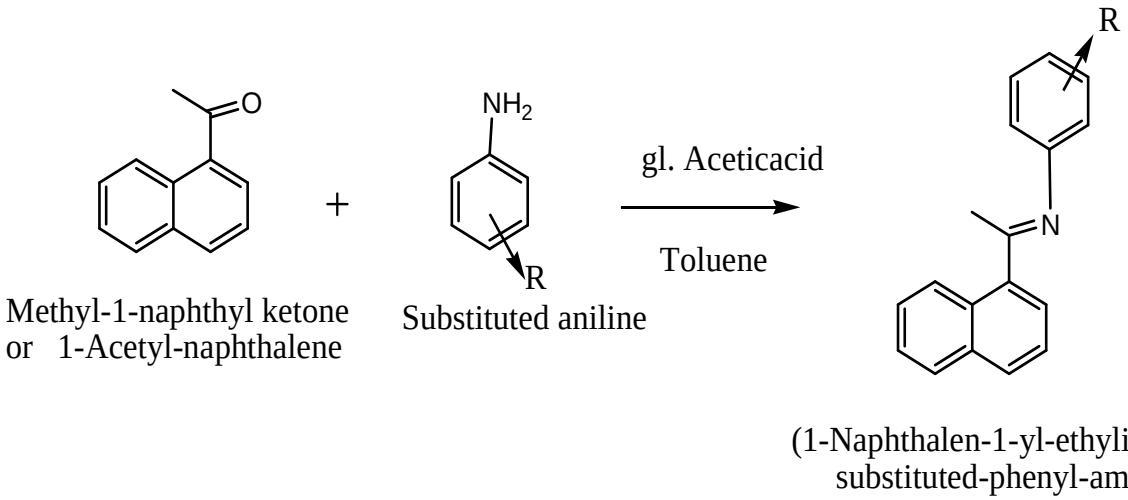
The classical way of synthesis of Schiff base was shown to chemist by H. Schiff [1] The classical synthesis reported by Schiff involves the condensation of a carbonyl compound with an amine under azeotropic distillation [10-11]. These are the condensation products of primary amines with carbonyl compounds such as an aldehyde or

a ketone and an amine by a nucleophilic addition reaction resulting in a hemi-aminal, which generates an aldimine[10] or ketimines[12] after dehydration. From aldehyde or ketonic compound method of forming Schiff bases employing different techniques or methods. The de-hydration during this condensation also conventionally facilitated by using a Dean-Stark apparatus or molecular sieves [13]. To overcome the difficulties in the removal of water, alternative method II has been employed in which Lewis acid is used as catalyst which accelerates nucleophilic attack of amines on carbonyl carbon as well as serving as dehydrating agent for removal of the water in the second step. Several modified methods have been reported in the literature in which Lewis acids were used as catalysts such as $ZnCl_2$[14], $TiCl_4$[15], alumina[16], P_2O_5[17] and acetic acid[7], by using materials like Hydrocalcite[18] and also the dehydrating solvents such as tetramethyl orthosilicate [19] and trimethyl orthoformate[20]. Hossein et. al.[21] have reported solvent less method using P_2O_5/AI_2O_3. Recently, environinental friendly synthetic processes have received much more attention using a mortar grinding without solvent [7]. Varma et. al.[19] have reported the synthesis of Schiff base under microwave conditions using montmorillonite K-10 as a solid support.

Schiff bases have been the subject of extensive interest due to versatility of their applications in various fields. The nitro and halo derivatives of Schiff bases have antimicrobial and antitumor activities [4]. Furthermore, Schiff bases possess a variety of interesting results. Schiff bases have also been shown to exhibit a broad range of biological activities[10], including anti-microbial (antifungal and antibacterial), antimalarial, anti-inflammatory, antipyretic, antiviral and anti-proliferative properties[22-23]. Imine or azomethine groups are present in various natural, natural-derived, and non-natural compounds. Recently, varied aromatic[24] and heteroaromatic[25]ketimines are reported from our laboratory. Further these ketimines were used to synthesize thiazolidinone as per the reports[26].

Looking to the importance as discussed and the literature survey pertaining to Methyl-1-naphthyl ketone here we have continued[12] to study the synthesis of ketimines from Methyl-1-naphthyl ketone and derivatives of aniline. The proposed reactions are shown in the following **Scheme-I**.

Scheme-I



NEPA, R = -H**; NE3HPA,** R = 2-NO_2**; NE2CPA,** R = 2-Cl**; NE3CPA,** R = 3-Cl**; NE4CPA,** R = 4-Cl

MATERIALS AND METHODS

All the materials used viz. Methyl-1-naphthylketone or 1-Acetyl-naphthalene, Aniline derivatives, Toluene and glacial aceticacid are of the synthesis grade. The apparatus used consist of a R.B. flask with reflux condenser in a bath containing oil. TLC plates of aluminium coated with silica gel made by Merck Co. The physical constant viz. (m.p. and b.p.) was determined by Equiptronics Digital m.p. apparatus, Model EQ-730. All the boiling point range were determined in centigrade scale in one end open capillary. IR spectra were recorded on a affinity-1 FTIR 8400 spectrophotometer using KBr pellet the frequency values**, '**ν' are in cm^{-1}.

General Method for the Synthesis of Schiff bases using Dean and Stark Apparatus: Charge Methyl-1-naphthyl ketone or 1-Acetyl-naphthalene (4.27 gm, 0.025 mole) of and equimolar aniline (2.33 gm, 0.025 mole) in 250 ml round bottom flask. Add to this 40 ml toluene as a solvent, connect the round bottom flask to water condenser and use Dean and Stark apparatus and start heating on water bath. After some hours a crude product is formed, monitor the reaction by TLC of reactant consumed, for completion of reaction, the reaction is completed. Purify the product by vaccum distillation to give single spot TLC (product). Record the weight (4.52 gm), physical constant (b.p =140°C) of product, colour of product (light red) and calculated % yield of the product is to 70.57 %, it is designated as NEPA.

Similarly, the remaining products **NE2NPA, NE2CPA, NE3CPA** and **NE4CPA** are in liquid form so they are purified by distillation. They are in the purified liquid state. For this liquid we have determine first density is evaluated by using specific gravity bottle. Thus calculated mass is used to calculate the % yield.

Results and Discussions: In this reaction Methyl-1-naphthylketone is react with aniline and substituted aniline where converted into their respective Ketimines or Schiff bases. The physical constant are determined and given in the **Table-1**.

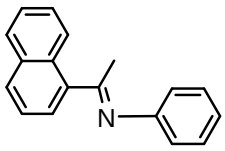
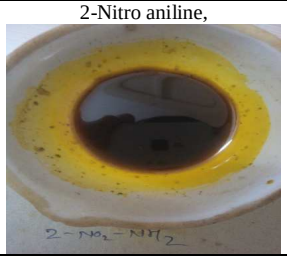
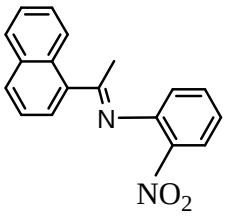
Table: 1. The Physical and Analytical Data for the Synthesized Ketimines from Methyl-1-naphthyl ketone.

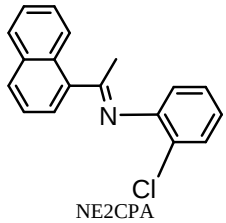
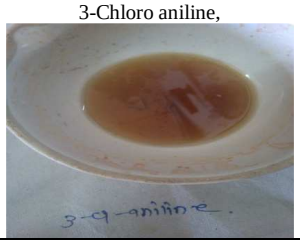
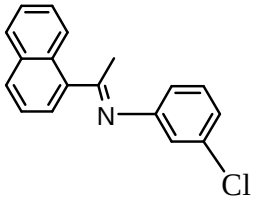
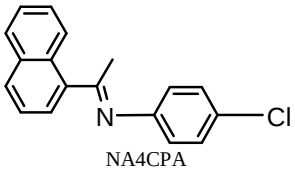
Compound ID	Aniline Used	Mol. Wt. of Product	Colour of product	m.p/ (b.p) °C	Wt. in gm/ (ml)	% Yield
NEPA	Aniline	255	Light yellow Red	(148-140)	(4.52)	70.57
NE2NPA	2-Nitro aniline	290	Dark yellow	(153-155)	(6.50)	89.28
NE2CPA	2-Chloro aniline	279	Light Red	(142-151)	(6.05)	86.42
NE3CPA	3-Chloro aniline	279	Yellow Red	(168-170)	(6.97)	97.57
NE4CPA	4-Chloro aniline	279	Yellow Red	(179-180)	(6.45)	92.14

The experimental yields are in the range 97.57 to 70.57 %, similar to our earlier reports[ ].

The FT-IR spectra of the studied compounds were recorded and their assigned frequencies are depicted in **Table-2.** On the basis of the foregoing spectral(FTIR) and chromatographic analysis and single spot TLC, the structure of final compounds are as shown in below **Table-2**.

Table-2: The Photographic Representation and FTIR Spectral Frequencies of Ketimines from Methyl-1-naphthyl ketone

Sr.No.	Aniline used, Photograph of Purified Product	IR Frequencies in (cm^{-1})	Structure of Schiff bases ID with Name
1	Aniline, 	$\nu_{>C=N-}$ = 1600 $\nu_{Ar-C=C<}$ = 1508 ν_{-C-N} = 1240 ν_{-C-CH3} = 1433 $\nu_{-Ar-C-H}$ = 3049	 NEPA
5	2-Nitro aniline, 	$\nu_{>C=N-}$ = 1693 $\nu_{Ar-C=C<}$ = 1571 ν_{-C-N} = 1280 ν_{-C-CH3} = 3003 $\nu_{-Ar-C-H}$ = 3050 ν_{-C-NO2} = 1508 and = 1344 $\nu_{-N=O}$ = 1508	 NE2NPA

7	2-Chloro aniline, 	$\nu_{>C=N-}$ = 1672 $\nu_{Ar-C=C<}$ = 1485 ν_{-C-N} = 1251 ν_{-C-CH3} = 2935 $\nu_{-Ar-C-H}$ = 3051 ν_{-C-Cl} = 775	 NE2CPA
8	3-Chloro aniline, 	$\nu_{>C=N-}$ = 1672 $\nu_{Ar-C=C<}$ = 1604 ν_{-C-N} = 1259 ν_{-C-CH3} = 2931 $\nu_{-Ar-C-H}$ = 3059 ν_{-C-Cl} = 887	 NE3CPA
9	4-Chloro aniline, 	$\nu_{>C=N-}$ = 1674 $\nu_{Ar-C=C<}$ = 1494 ν_{-C-N} = 1242 ν_{-C-CH3} = 3003 $\nu_{-Ar-C-H}$ = 3086 ν_{-C-Cl} = 775	 NA4CPA

In continuation of this series we have communicated earlier work[12b] and also we are working on the corrosion, UV-Vis spectral and antimicrobial studies of these compounds.

CONCLUSION

These synthesized ketimines will be useful as building block for future target molecules by young budding researchers. Looking to the skeleton of the product it look like these products may have good potential in medicine and chemistry we have continue the same work in the same direction and communicated the previous article report[12b] also. In future we may go for the applications of these products in various fields such as anti-microbial activity, antioxidant activity, dying properties and corrosion etc.

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