Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Der Pharmacia Lettre, 2015, 7 (12):109-113
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-5071
USA CODEN: DPLEB4

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

C. J. Patil*, Manisha C. Patil and Mrunmayee C. Patil†**

**Dept. of Chemistry, Smt. G. G. Khadse College, Muktainagar, Dist-Jalgaon, M.S., India*
***Dept. of Zoology, Dr. A. G. D. Bendale Mahila College, Jalgaon, Dist-Jalgaon, M.S., India*
†Dept. of Pharma. Sci. and Techn., Institute of Chemical Technology, Matunga, Mumbai, M.S., India

---

ABSTRACT

Schiff bases(Ketimines) were prepared from Methyl-1-naphthyl-ketone with 2-Hydroxy-aniline, 3-Hydroxy-aniline, 4-Hydroxy-aniline, 3-Nitroanilines and 4-Bromo-aniline using toluene as solvent by azeotropic(reflux) method using Dean and Stark. The synthesized ketimines were characterized by colour, physical constants, TLC and FTIR spectra. The purity of the synthesized compounds was confirmed from the information gathered from TLC, elemental and FTIR spectral analysis.

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

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.

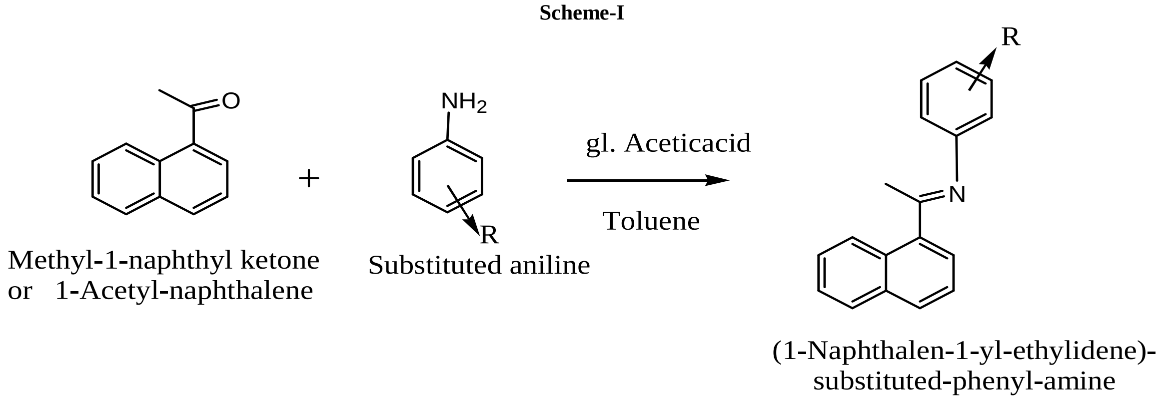
Ketimines are the compounds containing imine or azomethine(>C=N-) as a functional group. These compounds were initially discovered by Hugo(Ugo) Schiff [1] in 1864 and studied by several others[2-3]. Schiff bases soon became the research theme of other synthetic chemists, biologists, pharmacists and even the physicists. Schiff bases or Ketimines are 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 compound. 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 synthesis and the 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 employees 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 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], P_2O_5[16] and acetic acid[9], by using materials like Hydrocalcite[17] and also the dehydrating solvents such as tetramethyl orthosilicate [18] and trimethyl orthoformate[19]. Hossein et. al.[20] have reported solvent less method using P_2O_5/Al_2O_3. Recently, environinental friendly synthetic processes have received much more attention using a mortar grinding without solvent [7]. Varma et. al.[17] 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[21-22]. Imine or azomethine groups are present in various natural, natural-derived, and non-natural compounds. Recently[23], varied ketimines are reported from our laboratory. Further these ketimines were used to synthesize thiazolidinone as per the reports[24].

Looking to the importance as discussed in the literature survey pertaining to Methyl-1-naphthyl ketone in the M.Sc. dissertation[25] from our laboratory. Here we have putforth the study of synthesis of ketimines from Methyl-1-naphthyl ketone and derivatives of aniline. The proposed reactions are shown in the following **Scheme-I**.

Scheme-I



2NE2PA, R =2-HO; 3NEAP, R =3-OH; 4NEAP, R =4-OH; NE3NPA, R =3-NO_2; 4BPNEA, R =4-Br

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. and b. p. apparatus, Model EQ-730. All the melting points where determined in centigrade scale in one end open capillary. The FTIR 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 2-Hydroxy-aniline (2.70 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 oil bath. After about 12 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 recrystallization to give single spot TLC (product). Record the weight (4.20 gm), physical constant (m.p =169-175°C) of product, colour of product (light brown) and calculated % yield of the product is to 64.07 %, it is designated as 2NEAP.

While the product NE3AP is synthesized by following the same procedure but as no solids obtained on cooling at room temperature, the product nature must be liquid (form) so it is purified by distillation. For this liquid we have determine first density is evaluated by using gravity bottle. Thus calculated mass is used to calculate the % yield.
Similarly, the remaining products 4NEAP, NE3NPA and 4BPNEA were prepared by using different substituted anilines and employing above general method and the obtained details are recorded in **Table-1**.

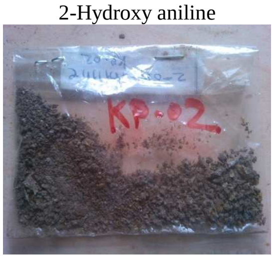
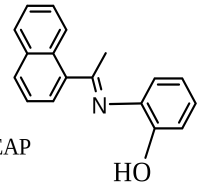
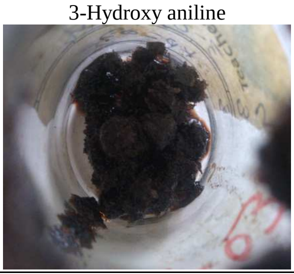
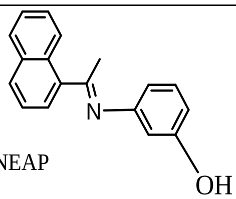
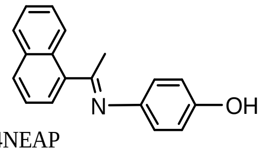
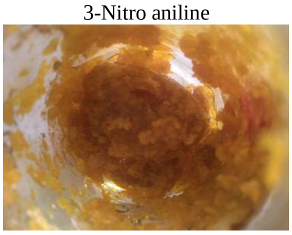
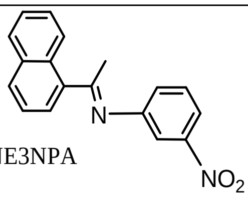
Results and Discussions: In this reaction Methyl-1-naphthylketone is react with aniline and substituted aniline where converted into their respective Ketimines or Schiff bases. The experimental yields are in the range 76.43 to 26.64 %. The results of elemental analysis are in close agreement (5 % variation) to the calculated values. The physical constant are determined and given in the **Table-1.**

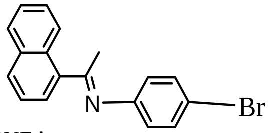
Table-1. Physical and Analytical Data for Synthesized Ketimines from Methyl-1-naphthyl ketone

Compound ID	Aniline Used	Mol. Wt. of Product	Colour of product	m.p/ (b.p) °C	Wt. in gm / (ml)	% Yield
2NEAP	2-Hydroxy aniline	261	Light Brown	169-171	4.20	64.07
3NEAP	3-Hydroxy aniline	261	Dark Brown	119-121	5.01	76.43
4NEAP	4-Hydroxy aniline	261	Brown	114-117	3.60	54.91
NE3NPA	3-Nitro aniline	290	Yellow	(110)	1.94	26.64
4BPNEA	4-Bromo aniline	323	Gray-green	158-159	3.10	38.22

The FTIR 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	2-Hydroxy aniline 	$\nu_{>C=N-}$ = 1598 $\nu_{Ar-C=C<}$ = 1498 ν_{-C-N} = 1140 ν_{-C-CH3} = 1460 $\nu_{-Ar-C-H}$ = 3051 ν_{-C-OH} = 600	 2NEAP 2-(1-Naphthalen-1-yl-ethylidene- -amino)-phenol
2	3-Hydroxy aniline 	$\nu_{>C=N-}$ = 1597 $\nu_{Ar-C=C<}$ = 1597 ν_{-C-N} = 1300 ν_{-C-CH3} = 2848 $\nu_{-Ar-C-H}$ = 3049 ν_{-C-OH} = 692	 3NEAP 3-(1-Naphthalen-1-yl-ethylidene- -amino)-phenol
3	4-Hydroxy aniline 	$\nu_{>C=N-}$ = 1697 $\nu_{Ar-C=C<}$ = 1479 ν_{-C-N} = 1166 ν_{-C-CH3} = 2848 $\nu_{-Ar-C-H}$ = 3035 ν_{-C-OH} = 707	 4NEAP 4-(1-Naphthalen-1-yl-ethylidene- -amino)-phenol
4	3-Nitro aniline 	$\nu_{>C=N-}$ = 1678 $\nu_{Ar-C=C<}$ = 1525 ν_{-C-N} = 1242 ν_{-C-CH3} = 2929 $\nu_{-Ar-C-H}$ = 3093 ν_{-C-NO2} = 1525 and = 1348 $\nu_{-N=O}$ = 1525	 NE3NPA (1-Naphthalen-1-yl-ethylidene)- -(3-nitro-phenyl)-amine

5	4-Bromo aniline 	$\nu_{>C=N-}$ = 1622 $\nu_{Ar-C=C<}$ = 1494 ν_{-C-N} = 1193 ν_{-C-CH3} = 2850 $\nu_{-Ar-C-H}$ = 3053 ν_{-C-Br} = 800	 4BPNEA (4-Bromo-phenyl)-(1-naphthalen-1-yl-ethylidene)-amine

In continuation of this series we are working [12] and 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 wish to continue the some more work in the same direction in our lab and further work[12] 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.

Acknowledgement
We are thankful to Central Lab, M. J. College, Jalgaon for recording the FTIR spectral analysis. We are also very grateful to the Management and the Principal, Smt. G. G. Khadse College, Muktainagar and Dr. A. G. D. Bendale Mahila College, Jalgaon for availing the required facilities for this work. One of us (Mrunmaye C. Patil) is thankful to the Director, Inst. of Chemical Technology, Matunga, Mumbai.

REFERENCES

[1] a) Hugo Schiff, Mitteilungen aus dem universitatslaboratorium in Pisa: Eineneue reihe organischer basen. (in German). Justus Liebigs Ann. Chem., 131 (**1864**) 118; b) H. Schiff, Annals, 131 (**1895**) 480.
[2] C. J. Patil, A. S. Madhava, G. Ramachandriah and D. N. Vyas, *Bull. Electrochem*., (**1991**) 7 (6), 283-285,
[3] G. Y. Yeap, S. T. Ha, P. L. Lim, P. L. Boey and W. A. K. Mahmood, *Mol. Cryst. Liq. Cryst*., 423 (**2004**) 73,
[4] G. Y. Yeap, S. T. Ha, P. L. Lim, P. L. Boey, M. M. Ito, S. Sanehisa and Y. Youhei, *Liq. Cryst*., 33 (**2006**) 205,
[5] D. N. Dhar and C. L. Taploo, J. Sci. Ind. Res., 41 (**1982**) 501,
[6] P. Przybylski, A. Huczynski, K. Pyta and B. Bart, *Curr. Org. Chem*., 13 (**2009**) 124, http://dx.doi.org/10.2174/138527209787193774
[7] C. J. Patil, A. S. Madhava, G. Ramachandriah and D. N. Vyas, *Bull. Electrochem*., 9 (**1993**) 95,
[8] C. J. Patil, A. S. Madhava, G. Ramachandriah and D. N. Vyas, *Bull. Electrochem*., 13 (**1997**) 370,
[9] A. S. Madhav, C. J. Patil, G. Ramachandriah and D. N. Vyas, *Bull. Electrochem*., 12 (**1996**) 355,
[10] C. J. Patil, C. A. Nehete and Hemant A. Mahajan, *International Journal of Green and Herbal Chemistry*, 2(2) (**2013**) 226.
[11] B. P. Branchaud, J. Org. Chem., 48 (**1983**) 3531, Studies on the preparation and reactions of tritylsulfenimines.
[12] C. J. Patil, Manisha C. Patil, Mrunmayee C. Patil and R. G. Mahale, (commun. to *J. Chem. Biol. Phy. Sci*., Dec. **2015**) Studies on Aromatic Schiff bases from Methyl-1-Naphthyl Ketone. Part-II: Synthesis and Characterization of Ketimines from 1-Acetylnaphthalene with Derivatives of Aniline.
[13] R. S. Vaas, J. Dudas, R. S. Varma, *Tetrahedron Lett*., 40(27) (**1999**) 4951,
[14] G. Reddelien, Berichte der deutschen chemischen Gesellschaft, 46(3) (**1913**) 2712-2717, DOI: 10.1002/cber.19130460340, Über Selbstkondensation bei Anilen. (Studien über Zinkchlorid als Kondensationsmittel III); Eng version: About autocondensation at Anilen. (Studies of zinc chloride as condensing agent III.
[15] A. K. Chakraborti, S. Bagat, S. Rudrawar, *Tetrahedron Lett.*, 45(41) (**2004**) 7641-7644,
[16] H. Naeimi, F. Salimi, K. Rabiei, *J. Mol. Catal. A Chem.* **2006**, *260*, 100–104,
[17] Li. Lingjun, Zhu Lizhi, Zhang Xinying, Zhang Guisheng, Qu Guirong, *Can. J. Chem*., 83 (**2005**) 1120.
[18] R. S. Varma, R. Dahiya, S. Kumar, *Tetrahedron Lett*., 38 (**1997**) 2039.
[19] (a) J. D. Armstrong, C. N. Wolfe, J. L. Keller, J. Lynch, M. Bhupathy, R. P. Volante, *Tetrahedron Lett*., 36 (**1997**) 1531; (b) G. Liu, D. A. Cogan, T. D. Owens, T. P. Tang, J. A. Ellman, *J. Org. Chem*., 64 (**1999**) 1278.
[20] a) K. Taguchi and F. H. Westheimer, *J. Org. Chem*., 36 (1971) 1570; b) B. E. Love and J. Ren, *J. Org. Chem*. 58 (1993) 5556.
[21] R. B. Moffett and N. Rabjohn, Editor, Organic Synthesis, John Wiley & Sons, Inc., New York, 4 (**1963**) 605.
[22] Hossein Naeimi and Mohsen Moradian, *Journal of Chemistry*, 2013, Article ID 701826, 8 pages, DOI: 10.1155/2013/701826 R. S. Varma, R. Dahiya, S. Kumar, *Tetrahedron Lett*., 38 (1997) 2039.

[23] a) C. J. Patil, Manisha C. Patil and Mrunmayee C. Patil, (Accepted *J. Chem. Biol. Phy. Sci*., 28th Nov. **2015**) Studies on Synthesis of Aromatic Schiff Bases: Part-I. Synthesis and Characterization of Ketimines from o-Hydroxy-acetophenone with Substituted-anilines; b) C. J. Patil, Manisha C. Patil and Mrunmayee C. Patil, (commun. to J. Chem. Biol. Phy. Sci., Dec. **2015**) Studies on Synthesis of Aromatic Schiff Bases: Part-II. Synthesis and Characterization of Ketimines from Benzophenone with Substituted-anilines; c) C. J. Patil, Manisha C. Patil and Mrunmayee C. Patil, (commun. to Int. J. Green Herbal Chem., Nov. **2015**) Studies on Synthesis of Aromatic Schiff Bases. Part-III. Synthesis and Characterization of Ketimines from 5-Chloro-4-methyl-2-hydroxy-acetophenone with disubstituted anilines; d) C. J. Patil and C. A. Nehete, *Der. Chemica Sinica*, 6(10) (**2015**) 1-6, Part-IV.

[24] C. J. Patil and C. A. Nehete, *Der. Chemica Sinica*, 6(10) (**2015**) 7-12,

[25] G. K. Patil and V. G. Kinge, M.Sc. Dissertation, Smt. G. G. Khadse College, Muktainagar (**2014-15**).