

RESEARCH ARTICLE

Reduction of Azomethine Bond of Organic Compound: Part-2. Formation of Aldimine and Ketimine and their Catalytic Hydrogenation[†]

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ABSTRACT

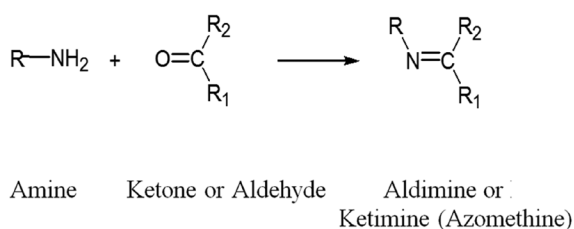
Azomethine compounds were prepared from Benzaldehyde and o-hydroxy-acetophenone with aniline and o-Nitroaniline. The azomethine bond in the compound is reduced using NaBH₄ in 0.1 N sodium hydroxide solution. The reaction is monitored by thin-layer chromatography (TLC) and ultraviolet-visible (UV-Vis) spectral method. Etheral layer is concentrated to get the reduction product. The final products were analyzed by a physical constant, TLC, and spectral techniques such as UV-Vis and Fourier-transform infrared.

Keywords: Azomethine, benzaldehyde, reduction, NaBH₄, reduction and hydrogenation

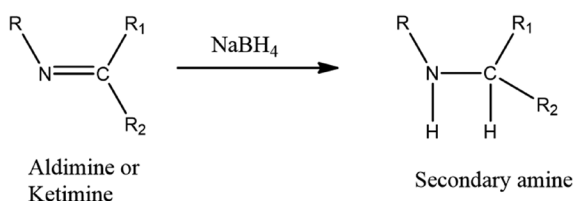
INTRODUCTION

Ketones and aldehydes react with primary amines and other derivatives of ammonia under the specific condition to form imines. An imine is a compound with a carbon-nitrogen double bond (>C=N-),^[1] while the imine obtained from the reaction of carbonyl compound and primary amine is known as azomethines or Schiff base. Azomethine was first prepared by German Chemist Hugo Schiff in 1864, and so it is referred to as Schiff base.^[2]

The general reaction is,



Step-II



Where, R₁ and R₂ may be H, alkyl, aryl, allyl, or heteroaryl, etc. In general, Schiff base with aryl substituent is more stable than alkyl substituent.^[3-5] Literature also shows studies of azomethine containing condensation products by pH-meter as well as electrochemical^[4,6-8] techniques. Recently, we have reported^[9] reduction of C=N- of Schiff base using NaBH₄-CH₃OH system. The azomethine function containing products and their reduction products are useful as an intermediate in varied types of industries and dyes etc. They are useful as antibacterial agent,^[10,11] antifungal agent^[12] and also in the treatment of cancer.^[13] Azomethines and their beta-lactam derivatives have a variety of application in the biological, clinical, analytical, and pharmacological area.^[14,15]

EXPERIMENTAL

In 250 ml reaction flask, the equimolar condensation of the Benzaldehyde (**Bz**) and o-Hydroxy-acetophenone (**2-HOAc**) with aniline (**A**) and o-Nitroaniline (**o-NA**) in the presence of 50 ml alcohol and catalytic glacial acetic acid, on reflux for 4–5 h, indicated absence of amine in the thin-layer chromatography (TLC) analysis, i.e., completion of the reaction. Strip off 20 ml of alcohol, the reaction mass is cooled to get yellow to an orange colored product.

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The melting points reported are uncorrected and were taken on digital melting point apparatus (EQ-730) of Equiptronics make. The ultraviolet-visible (UV-Vis) spectra were recorded in absolute alcohol, on Shimadzu (UV-1800). The Fourier-transform infrared (FTIR) spectra were recorded using KBr pellets on an FTIR Spectrophotometer (Shimadzu, 4000–400 cm^{-1}). Chemicals were purchased from the Sigma-Aldrich and are used as supplied without further purification. The progress of the reaction and purity of the azomethine containing compound were checked by TLC in hexane:ethyl acetate (6:4) silica gel glass plates. The azomethine bond in the compounds synthesized (0.01 mol) is reduced using 0.05 mol of NaBH_4 dissolved in sufficient sodium hydroxide solution, add to it 10 ml glacial acetic acid reagent, stir in an RBF. Withdraw a sample after 1 h and further after each half hour for monitoring the reduction by UV-Vis spectra. Products were isolated and analyzed by physical constants, TLC, UV-Vis, and FTIR spectra.

RESULTS AND DISCUSSION

The azomethine bond-containing compounds were prepared from **Bz** and **2-HOAc** with aniline and **o-NA**, respectively. First, the product of **Bz** with aniline is formed, and 2-Hydroxy-acetophenone reacted with **o-NA** and they were designated as **Bz-A** and **2-HOAc-o-NA**. The products formed above are analyzed by TLC, UV-Vis, and FTIR technique as per earlier reports.^[16-17] The reaction completion is monitored by TLC and the purity of the product is ascertained by TLC in the mobile phase in hexane:ethyl acetate and the R_f value results were recorded in Table 1. Single spot TLC of the product shows the completion of the reaction. The observations are in concurrence with that of previous reports.^[18,19]

One of the Compound **Bz-A** is shown in the close view, immediately after recrystallization in Figure 1. Further, the products were analyzed by UV-Vis; results are depicted in Figure 2.

The representative FTIR spectral output is depicted in Figure 3 for the product of o-hydroxy acetophenone and the o-Nitroaniline.

General procedure for the reduction of $>\text{C}=\text{N}$ -bond using NaBH_4

In a 100 ml conical flask with magnetic needle, add the Schiff base (0.01 mol) to be reduced, homogenize it by dissolving in suitable solvent and put it on magnetic stirrer for mixing and add to this a solution of NaBH_4 (0.05 mol) in NaOH (prepared by mixing 1.89 g NaBH_4 in 18 ml NaOH of 0.1 N strength). After complete addition, stir it for the 45 min and take TLC test to check the completion of the reaction, if not continue till further to completion (if required excess NaBH_4 solution may be added).

The azomethine bond in the compound **Bz-A** is reduced using NaBH_4 in the glacial acetic acid reagent. The reaction is monitored by TLC and UV-Vis spectral method. The UV-Vis spectra obtained after 1 h reduction are depicted in Figure 4. The absorption at 263 nm is diminished to a marked extent indicating the loss in conjugation



Figure 1: Compound **BzA** in close view, immediately after recrystallization

Table 1: Physical properties and spectral data (UV-Vis and FTIR) for azomethine containing compounds **Bz-A** and 2-HOAc-o-NA

S. No.	R_f value	Color of product	m.p. $^{\circ}\text{C}$	UV-Vis λ_{max} in nm	FTIR absorption values, in cm^{-1}
Bz-A	0.52	White with light	51-53	208	1630 $\nu_{\text{C}=\text{N}}$
		Indigo		235	1575, 1451 $\nu_{>\text{C}=\text{C}<}$ (aromatic)
				263	2341 $\nu_{\text{C-H}}$
2-HOAc-o-NA	0.61	Cream	56–57 ⁽⁹⁾	209	1618 $\nu_{\text{C}=\text{N}}$
				222	1558, 1472 $\nu_{>\text{C}=\text{C}<}$ (aromatic)
				231	1550 (asym.) and 1365 (symm.) ν_{NO_2}
				276	2361 $\nu_{\text{C-H}}$
				403	3090 $\nu_{\text{O-H}}$

UV-Vis: Ultraviolet-visible, FTIR: Fourier-transform infrared

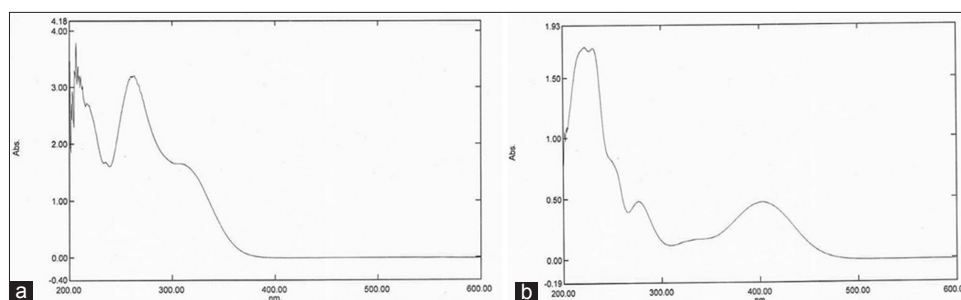


Figure 2: Ultraviolet-visible spectra of the Azomethine containing compound synthesized, (a) **Bz-A** and (b) **2-HOAc-o-NA**, in ethanol

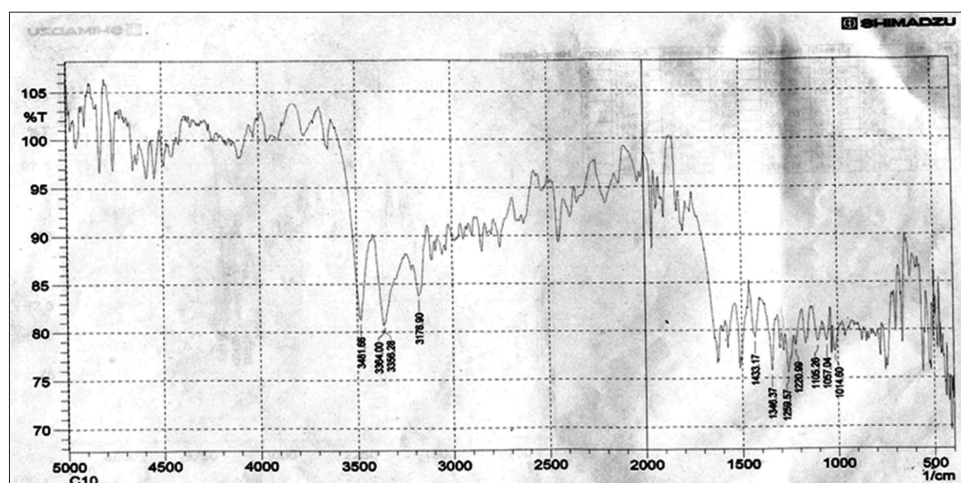


Figure 3: The representative Fourier-transform infrared spectra for the azomethine containing compound, **Bz-A**

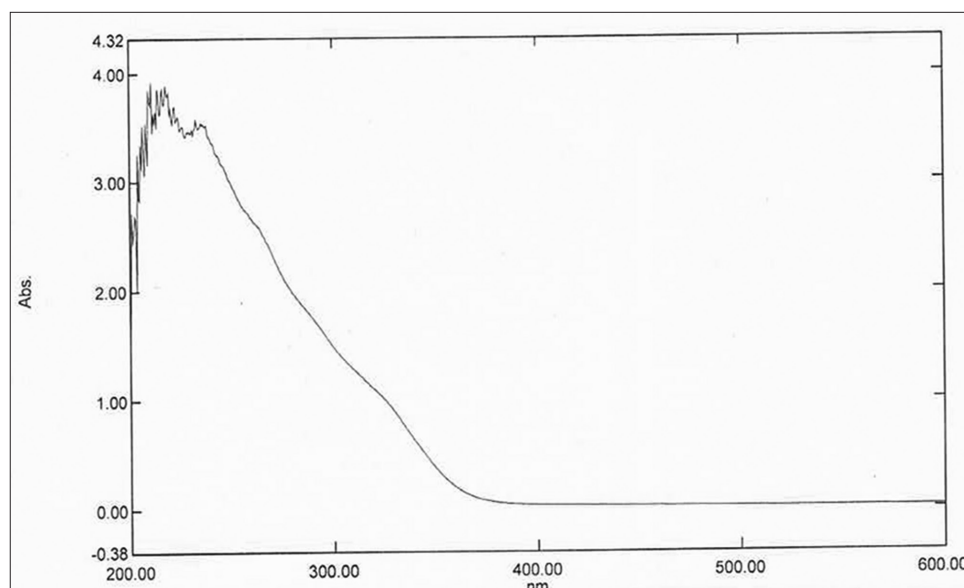


Figure 4: The representative ultraviolet-visible spectra of the azomethine containing compound showing the result after 1 h reduction by NaBH_4 for **Bz-A**

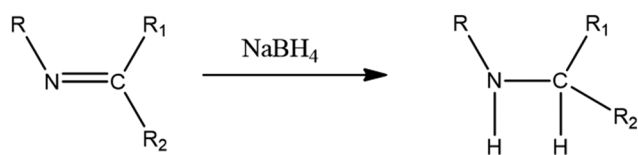
between two aromatic rings, which was present before the reduction process.

Further, the reaction mass is neutralized by NaOH solution and is extracted with ether and the ethereal layer is concentrated to get the reduction product. The final products were analyzed by physical constant (low melting product, 34–37°C), the density of the product is 1.06 g/mL, which

matches with the *N*-phenylbenzylamine in the literature, TLC, and spectral techniques such as UV and FTIR. TLC characteristics, R_f value, is 0.34 in n-Hexane:ethyl acetate (6:4) silica gel glass plates. The FTIR spectra after NaBH_4 reduction indicate the absence of the azomethine frequency band at 1630 cm^{-1} , which was found in the spectra of the compound before reduction.

CONCLUSION

The above study of reduction of the Schiff base using NaBH_4 indicated that the reduction follows the path as shown in the following reaction.



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