



## Novel Method for Synthesis of Schiff Bases Derivatives using Green and Eco-friendly Catalyst as TiO<sub>2</sub> Nanoparticle

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### ABSTRACT

*In this research work an attempt has been made to focus on the new synthetic protocol for new Schiff bases derived from substituted aromatic aldehydes with ethylene diamine and Urea, with a novel method. This method includes the uses of TiO<sub>2</sub> nanoparticle as a green, efficient and new catalyst, which is added to the conventional method of Schiff bases synthesis. From this method new imines are synthesized in high yields within limited time durations under favourable reactions conditions by the use of new catalyst. Further the structural characterization of these newly synthesized compounds are confirmed by physio-chemical and spectral parameters.*

**Keywords:** TiO<sub>2</sub> NPs catalyst, Schiff bases, Aromatic aldehydes, Ethylene diamine/Urea, Eco-friendly method.

### I. INTRODUCTION

Schiff bases are formed from variety of aldehydes and amines either of aliphatic or aromatic nature. The first method was proposed by Hugo Schiff, was reported in 1864<sup>1</sup>. The one spot condensation of amines with aldehydes and ketones has a numerous applications<sup>2</sup>, for preparative, detection, determination and purification uses.<sup>3-4</sup> They also exhibit pharmaceutical and biological activities<sup>5-20</sup>. These applications encourage the workers to prepare these imines for the last 10 decades.

The classical method<sup>1</sup> for synthesis of imines involves mixing of aldehyde or ketone with the primary amines in equimolar quantities. The imine formation reaction is reversible, and therefore, it was advisable to remove the water by distillation or by using an azeotrope – forming solvent<sup>21-22</sup>. Above mentioned method had applied successfully to the synthesis of Schiff bases from reactions of valeraldehyde benzoylacetone and acetylacetone with aromatic amine<sup>23</sup>. With ketones, especially the aromatic ones, higher temperatures, longer reaction times and catalyst are usually required, in addition to the removal of water as it formed. Among the large number of catalyst were used in the synthesis are ZnO<sup>23</sup>, HCl<sup>24</sup>, BF<sub>3</sub><sup>25</sup>. The reported methods have many drawbacks such as use of toxic chemicals, elongated time duration methods, low yields and harsh reactions conditions.



Therefore, it is of valuable importance to deal with alternative method to synthesis these compounds from substituted aromatic aldehydes with amines with the introduction of new and novel TiO<sub>2</sub> NPs catalyst under normal reaction conditions using ethanol as reaction medium (**Scheme 1**). The special properties exhibited by TiO<sub>2</sub> NPs such as eco-friendly, effective, easily recyclable, readily reusable and maintain their catalytic activity accelerated the rate of reaction with high yield of products. A special care is given to the structural elucidation of these new imines by using different parameters namely, melting points, UV and IR spectra.

### Scheme 1: General Reaction scheme for the synthesis of Schiff's base (AJ<sub>4</sub>)

## II. MATERIAL AND METHODS

### Materials:

All chemicals were obtained from Merck, Loba-Chemie and S.D. Fine Chem. Co. and used without further purification. Melting points of new compounds were measured by electrothermal m.p. apparatus model BÜCHI 510 and were uncorrected. The IR spectra were recorded by a computerized FTIR, Bruker model Tensor 27 using KBr pellet. The UV spectra of compounds were also recorded. <sup>1</sup>H and <sup>13</sup>C NMR spectra were also recorded for some compounds using a Bruker instrument (<sup>1</sup>H at 400 MHz and <sup>13</sup>C at 100 MHz) in DMSO-d<sub>6</sub> solvent and TMS as internal standard. The completion of reaction were monitored by thin layer chromatography on 0.2-mm pre-coated plates of silica gel G<sub>60</sub> F<sub>254</sub>.

### Method of Schiff base Synthesis:

#### Preparation of Schiff bases of Substituted aromatic aldehyde with urea catalyzed by TiO<sub>2</sub> Catalyst (AJ<sub>4</sub>) :

Two component condensation reaction of ethylene diamine (0.01 mole) in 5 ml ethanol was slowly added to 0.02 moles of 2-Nitrobenzaldehyde in 5 mL ethanol, the reaction is catalysed by green and efficient catalyst, TiO<sub>2</sub> (3 mol%) taken in ethanol (10 ml) as medium, The mixture was refluxed for 1.5 hours and completion of reaction was monitored by TLC. the light yellow coloured precipitates were collected by filtration. The products were recrystallized from ethanol and are dried in air. Melting point of dry sample has been recorded with good yields from 79-96% (**Scheme 2**).



**Scheme 2: General Reaction scheme for the synthesis of Schiff's base (AJ<sub>4</sub>)**

**III. RESULTS AND DISCUSSION**

During this research work, a new and effected method for the synthesis of Schiff bases from substituted aromatic aldehydes with ethylene diamine and Urea, catalyzed by green Nanoparticle TiO<sub>2</sub> catalyst under optimised reaction conditions is introduced. keeping in view the green chemistry, we report the use of TiO<sub>2</sub> nanoparticle catalyst for the first time during synthesis of Schiff bases under study. This development in the procedure of synthesis by adding TiO<sub>2</sub> as a new catalyst is highly accepted from kinetic<sup>26-27</sup> point of view. The reaction conditions has been optimised to its minimum limit with high yield of products 76-96% as represented in **Figure 1** and the structural elucidation is confirmed by physio-chemical properties such as m.p, colour of Schiff bases prepared, beside their IR and UV spectra summarised in **Table 1**.

**IR Spectral Study of some newly synthesized compounds:**

The IR spectra of Schiff bases under study are shown in **Figure 2** and summarised in **Table 1**, and illustrate the following wavenumbers:-

A broad stretching wavenumbers range between (3285- 3324)cm<sup>-1</sup> Which confirm O-H bond in the carboxyl group of Schiff bases. A strong to medium intensity bands are assigned to carbonyl groups in Schiff bases. They have a stretching frequency ranged between (1623.10-1743.41) cm<sup>-1</sup>. Hence these strong hydrogen bondings stated are accompined by weaken the double bond of carbonyl group in imine . The last results are expected and will shift the frequency of C = O group to lower value<sup>28</sup> of wavenumber. A strong to medium intensities bands are assigned to carbon nitrogen double bond i.e C=N, with stretching frequency range between (1588.10-1616.00)cm<sup>-1</sup>. Schiff bases (**AJ<sub>1</sub>**), shows a medium absorption band a wavenumber of 744.75cm<sup>-1</sup> for carbon Chlorine C-Cl linkage and Stretching bands occur at 3135-3245cm<sup>-1</sup>dueto Hydroxyl groups in Schiff bases. The fundamental frequencies due to C-C have also been observed in the range of 1004- 1051 cm<sup>-1</sup>. An additional band appears in the range 2956-3001 cm<sup>-1</sup> for  $\nu_{C-H}$  (phenylic ring). All compounds exhibit a broad band relatively in theregion of higher frequency between 3403-3232 cm<sup>-1</sup> indicating the presence of coordinated water molecules inthe complexes. The infrared spectral bands of different Schiff's bases are summarized in **Table 1**.

**UV Spectral Study of some newly synthesized compounds:**



The UV spectra of Schiff bases under study are also shown in Figure 3 and are summarized in Table 1. Newly synthesized shows that all UV spectra of Schiff bases have two bands at wavelengths of  $\lambda$  nm values with their molar extinction coefficient values of  $\epsilon_{\max}$  in units of Liter. mole<sup>-1</sup>.cm<sup>-1</sup>. The lower wavelengths bands for all Schiff bases have a range of values between 236-251 nm. They are assigned to the aromatic nature of all Schiff bases observed in Table (1). These bands have a molar extinction coefficient values<sup>29</sup> of greater than one thousand and are attributed to the  $\pi \rightarrow \pi^*$  of the aromatic system. The longer wavelengths bands for the same Schiff bases as in Table (1) also have a range of values between 286-338 nm and are assigned to C = N or C = O linkages or a combination of them. Their  $\epsilon_{\max}$  have either a values<sup>29</sup> greater than a thousand for  $\pi \rightarrow \pi^*$  as in Schiff bases number 2-4 or lower than the value<sup>30</sup> mentioned for  $n \rightarrow \pi^*$  as in Schiff bases numbers 1,3 and 5.

Finally, all IR and UV data besides other physio-chemical constants collected in Table 1 confirms the structure of of Schiff base shown in the same Table 1.

**Table 1: Physio-chemical Properties and UV, IR Data for Schiff bases prepared .**

Entry	R-CHO	Compound Formula	M.P (°C)	Yield %	IR bands cm-1				UV bands $\lambda$ nm( $\epsilon_{\max}$ )
					O-H	C = O	C = N	C-C	
AJ <sub>1</sub>	P-Cl-C <sub>7</sub> H <sub>7</sub> O	C <sub>8</sub> H <sub>7</sub> N <sub>2</sub> O <sub>1</sub> Cl	171 <sup>0</sup> C	82	3285	1681	1616	1004	252(1930), 329(683)
AJ <sub>2</sub>	4-OH-C <sub>7</sub> H <sub>7</sub> O	C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>	181 <sup>0</sup> C	88	3301	1681	1602	1012	243(2936), 329(1952)
AJ <sub>3</sub>	1-OH-C <sub>7</sub> H <sub>7</sub> O	C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	110 <sup>0</sup> C	85	3312	1637	1603	1036	251(2663), 323(1375)
AJ <sub>4</sub>	2- NO <sub>2</sub> -C <sub>7</sub> H <sub>7</sub> O	C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>	112 <sup>0</sup> C	96	3324	1633	1611	1051	255(2473), 329(1110)
AJ <sub>5</sub>	3- NO <sub>2</sub> -C <sub>7</sub> H <sub>7</sub> O	C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	192 <sup>0</sup> C	92	3298	1644	1580	1042	243(1471), 289(910)

Further the confirmation of newly synthesised compounds catalysed by first time used TiO<sub>2</sub> nanoparticles catalyst is proved by the three step mechanism. Mechanism consists of three steps; first step is a fast reversible and is accompanied by the formation of intermediate through a reversible step. The second step is slow rate determining step, which involves the addition intermediate to the positive carbon of carbonyl group. This results to the next formation of second intermediate, it finally leads to formation of Schiff bases by fast dehydration in final step. Our suggested mechanism is having resemblance with mechanism given by Pearson et al<sup>30</sup> and supports our suggestion. Nevertheless these two mechanisms led to the formation of C=N in oxime or in Schiff bases under study.

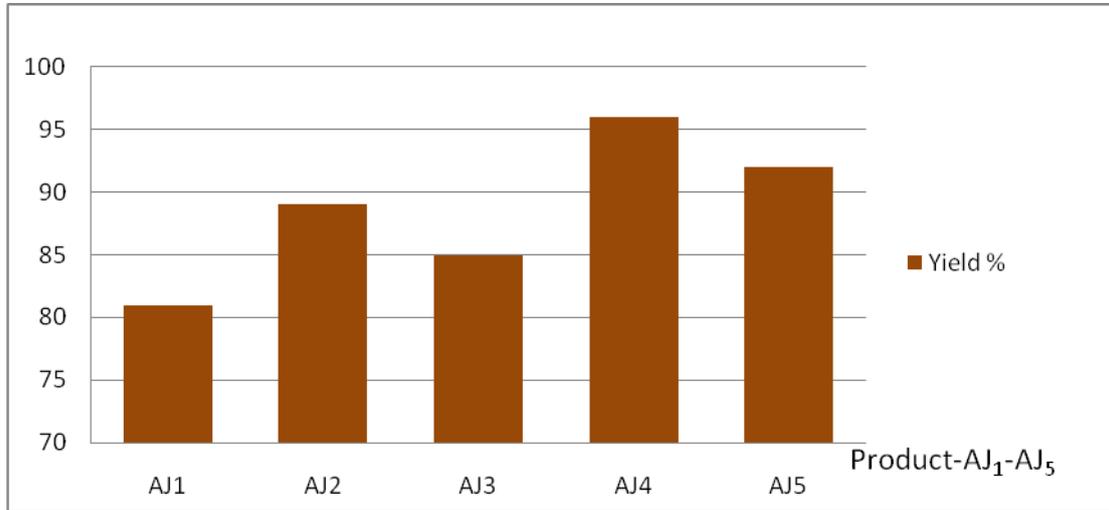


Figure 1. Graphical Representation between Products formed Vs Product Yield%

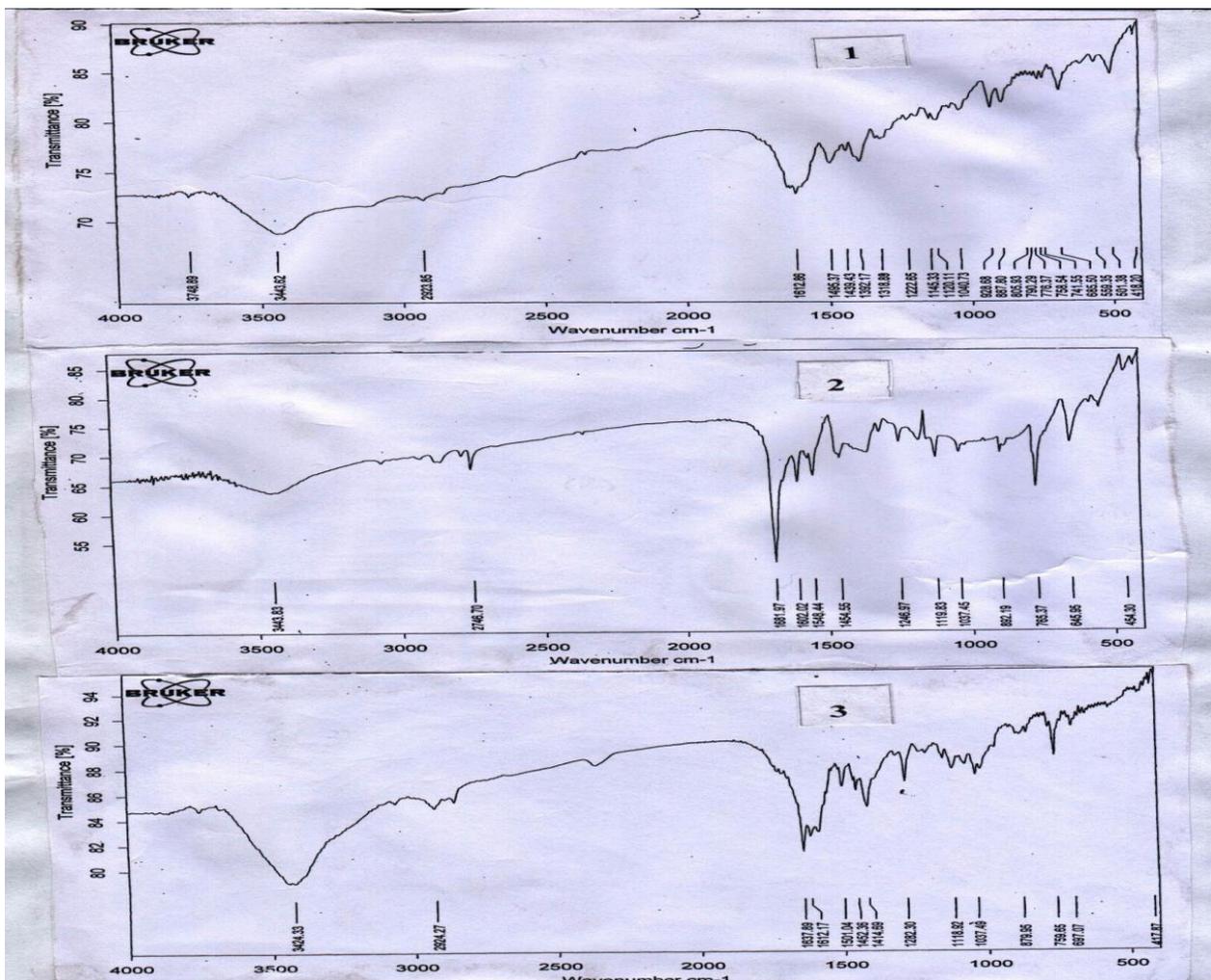


Figure 2: IR Study of Schiff Bases (AJ<sub>1</sub>,AJ<sub>3</sub>,AJ<sub>5</sub>)

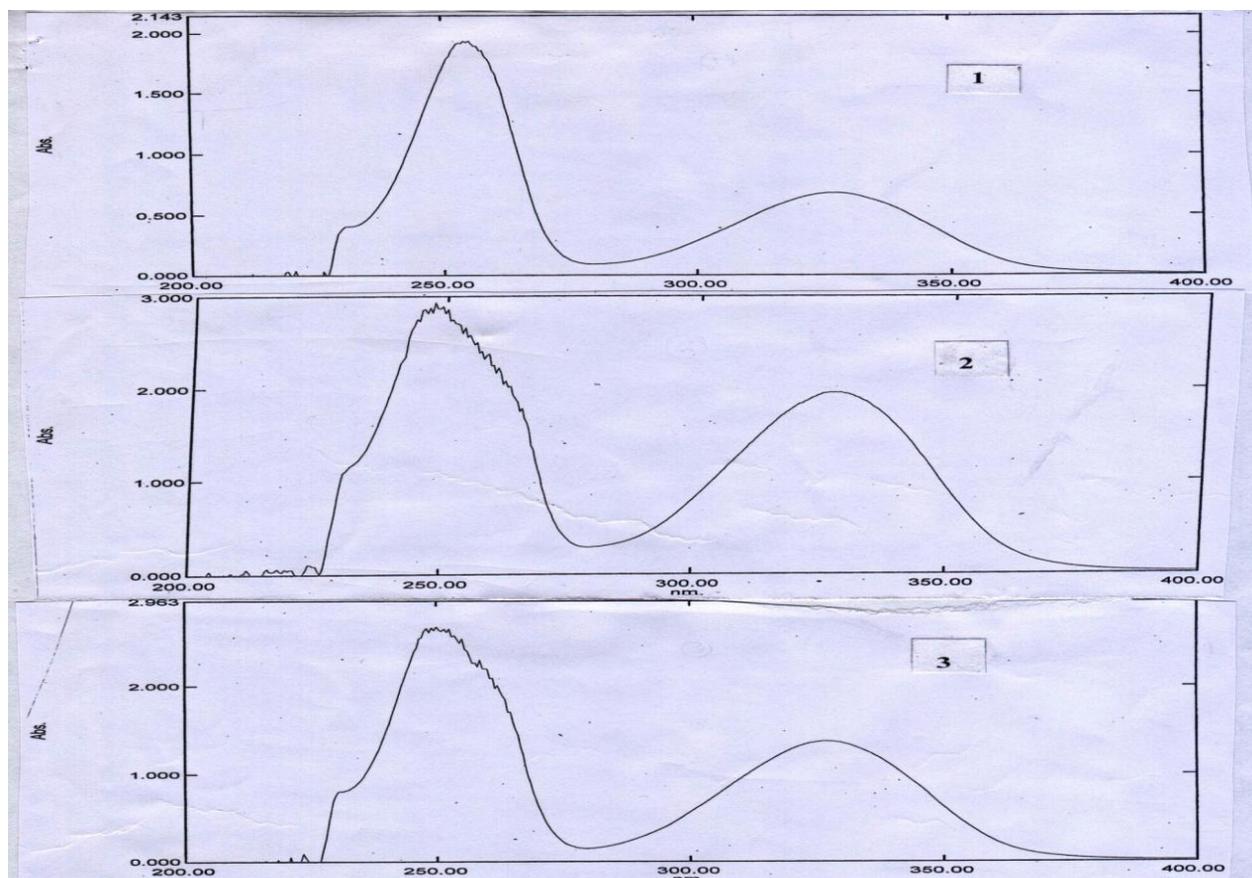


Figure 3: UV Study of Schiff Bases (AJ<sub>1</sub>,AJ<sub>3</sub>,AJ<sub>5</sub>)

#### IV. CONCLUSIONS

A new alternative method for synthesis of some Schiff bases from substituted aromatic aldehydes with ethylene diamine and urea is given. This method used a new and efficient TiO<sub>2</sub> NPs catalyst. TiO<sub>2</sub> NPs can be recycled and reused severally with loss of catalytic activity. The reaction resulted in high yield of newly synthesized compounds within limited times periods under normal reaction conditions as compared to reported methods. A new suggested mechanism for the synthesis of these new Schiff bases is given and confirmed by other study<sup>30</sup>. The chemical structures of Schiff bases were studied by the use of physical methods, namely melting point's or boiling point, IR and UV spectra.

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