

# SYNTHESIS OF NEW ALDIMINES VIA ENVIRONMENTALLY OBLIGING AND ENERGY-PROFICIENT GREENER APPROACHES

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## Abstract

Aldimines constitute a class of pharmaceutical and medicinally important molecules. The conventional methods for the synthesis of aldimines require long reaction times but non classical methods (water based reaction, microwave and grindstone chemistry) were used for the preparation of Schiff bases. We report a novel and eco-friendly condensation reaction method permitting the "green synthesis" of various aldimines from amines with various aromatic aldehydes. These methodologies constitute an energy-efficient and environmentally benign greener chemistry version of the classical condensation reactions for aldimines formation.

**Keywords:** Aldimines, Microwave irradiation, Grinding, Greener chemistry.

## Introduction

Aldimines are important intermediates in organic synthesis, which have been used in various areas such as peptide synthesis<sup>1</sup>, medicinal chemistry<sup>2-3</sup>, as chiral sources<sup>4-5</sup> and polymer materials<sup>6</sup>. The concept of green chemistry and its applications in synthetic organic chemistry have emerged as major solutions for the development of clean and more benign chemical processes. Various methodologies and routes have been developed for this purpose. As a green chemistry approach, microwave-assisted synthesis has been highly intriguing since last few decades by the chemists. Microwave irradiation methods used for carrying out chemical transformations are pollution free, eco-friendly, low cost, and offer high yields together with simplicity in processing and handling. The important area of green chemistry is to use non-conventional approaches of synthesis because of less or no solvent requirements, easy isolation, eco-friendly nature, less reaction time with good yield and purity of target molecules<sup>7-9</sup>. Considering the numerous applications of aldimines in various fields of chemistry, there has been tremendous interest in developing efficient methods for their preparation. In the present work, we report our results for the preparation of aldimines by conventional as well as some non conventional methods under the aspect of environmentally benign processes with high yields, which are superior to conventional methods.

## Experimental

Sigma-Aldrich and Merck chemicals were used as such without further purification. Solvents used for spectroscopic and other physical studies were reagent grade and were further purified by literature methods. Melting points are determined by open capillary electro thermal melting point apparatus and are uncorrected. IR spectra were obtained in on a Bruker spectrophotometer and expressed in wave numbers (cm<sup>-1</sup>). <sup>1</sup>H-NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer operating at 500 MHz for <sup>1</sup>H-. The <sup>1</sup>H-chemical shifts were expressed in ppm with reference to tetramethylsilane. Elemental analyses were performed at IISER Bhopal. Microwave irradiations are carried out in an unmodified IFB microwave.

## General Procedure for Synthesis

The three different methods include conventional as well as greener methods were adopted for preparing aldimines are as follow:

### *Method I: Conventional Method*

To a solution of 4-Hydroxy-3-Methoxybenzaldehyde and substituted new primary amine (0.01 mole) in ethanol (10 ml) was refluxed in presence of 1-2 drops of conc. H<sub>2</sub>SO<sub>4</sub> for 2 hours. The contents were cooled and transferred over the

crushed ice; the solid separated was filtered under suction and recrystallized from ethanol to get crystallize solid.

### Method II: Microwave Based Non Conventional Method

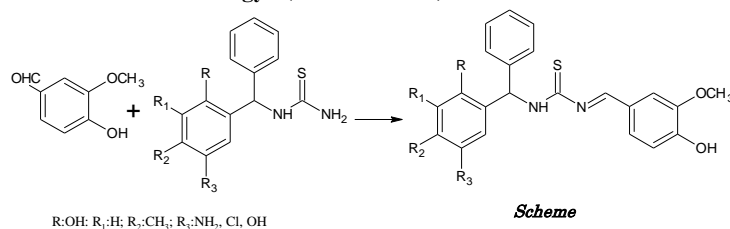
A mixture of 4-hydroxy-3-methoxybenzaldehyde and substituted new primary amine (0.01 mole) in just 2ml ethanol was taken in RBF and irradiated over microwave for 3-5 min. on cooling the mixture aldimines was obtained over crushed ice.

### Method III: Grind Stone synthesis

A mixture of 4-hydroxy-3-methoxybenzaldehyde and substituted new primary amine (0.01 mole) was grinded in a mortar with a pestle made up of porcelain for 15 min than the mixture turns pasty after few min of grinding. Leave the reaction mixture overnight and the solid obtained was recrystallised from ethanol.

## Result and Discussion

Conventional and greener methods for the synthesis of new aldimine i.e Substituted phenyl methyl]-3-[(E)-(4-hydroxy-3-methoxyphenyl)methylidene]thiourea involves probably nucleophilic addition followed by elimination in which Primary amines, R-NH<sub>2</sub> or ArNH<sub>2</sub>, undergo nucleophilic addition with aldehydes to give carbinolamines which then dehydrate to give substituted aldimines. In comparison of conventional and two greener methods, the second method was most efficient. Conventional method involve heating of reaction mixture and use of much amount of solvent while The grinding method is much greener as it not consumes any type of energy.e neither electrical nor thermal and yields good but it consume much time for reaction to complete but The simple microwave technique affords aldimines with short reaction times and excellent yields in comparison to rest two methods. The microwave irradiation technique led to improvement in the yield of all the target compounds with reduction in their reaction byproducts. The microwave process also substantially reduced the overall process time as expected, by reduction in reaction time against the described conventional method. The formulas of the synthesized compounds were confirmed by the elemental analysis and their structures were determined by IR, 1 H-NMR, and mass spectral data. The reaction time and the yield of products by conventional and both greener methods are listed in table.



Reaction time and percent yield of compounds by conventional and nonconventional methods						
Compound	Conventional Method		Nonconventional Methods			
	Reaction time	Yield %	Grinding stone method		Microwave irradiation	
Reaction time			Yield %	Reaction time	Yield %	
I	2hrs	56%	24hrs	65%	3-5 min	85%
II	2hrs	42%	24hrs	52%	3-5 min	83%
III	2hrs	73%	24hrs	85%	3-5 min	98%
IV	2hrs	68%	24hrs	83%	3-5 min	94%

## Spectral Data of Compounds

**1-[(5-amino-2-hydroxyphenyl) (phenyl) methyl]-3-[(E)-(4-hydroxy-3-methoxyphenyl) methylidene] thiourea:** color: brick red, mp: 172<sup>o</sup>C; IR (ν<sub>max</sub> cm<sup>-1</sup>) 3739.10, 3018.90, 1659.35, 1145.49, 724.32; <sup>1</sup>HNMR (CDCl<sub>3</sub>) 8.13(1H, S), 7.29 (2H, d), 7.49 (1H, m), 2.43 (s, 2H, NH<sub>2</sub>), 1.31(d, H, NH); MS:m/z: 413.3

**1-[(5-chloro-2-hydroxyphenyl) (phenyl) methyl]-3-[(E)-(4-hydroxy-3-methoxyphenyl) methylidene] thiourea:** color: yellow, mp: 163<sup>o</sup>C; IR (ν<sub>max</sub> cm<sup>-1</sup>) 3654.12, 3022.13, 1645.85, 1142.91, 728.16; <sup>1</sup>HNMR (CDCl<sub>3</sub>) 8.06(1H, S), 7.34 (2H, d), 7.53 (1H, m), 2.36 (s, 2H, NH<sub>2</sub>), 1.24(d, H, NH); MS:m/z: 410.6

**1-[(2-hydroxy-4-methylphenyl) (phenyl) methyl]-3-[(E)-(4-hydroxy-3-methoxyphenyl) methylidene] thiourea:** color: brown, mp: 128<sup>o</sup>C; IR (ν<sub>max</sub> cm<sup>-1</sup>) 3698.12, 3016.78, 1652.52, 1135.25, 719.25; <sup>1</sup>HNMR (CDCl<sub>3</sub>) 8.22(1H, S), 7.21 (2H, d), 7.38 (1H, m), 2.44 (s, 2H, NH<sub>2</sub>), 1.42(d, H, NH); MS:m/z: 399.2

**1-[(2, 4-dihydroxyphenyl) (phenyl) methyl]-3-[(E)-(4-hydroxy-3-methoxyphenyl) methylidene] thiourea:** color: Dark Brown, mp: 132<sup>o</sup>C; IR (ν<sub>max</sub> cm<sup>-1</sup>) 3712.25, 3011.04, 1651.47, 1148.93, 719.65; <sup>1</sup>HNMR (CDCl<sub>3</sub>)

8.08(1H, S), 7.36 (2H, d), 7.49 (1H, m), 2.35 (s, 2H, NH<sub>2</sub>), 1.29(d, H, NH); MS:m/z: 406.5.

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