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Green Synthesis Methods of Schiff Base Compounds: A Review

Hiba Shihab Ahmed[1], Zainab Esmail Sadeq[2], Noor Sabah Al-Obaidi[3*], Mostefe Khalid Mohammed[4], Anfal Salam Al-Mahdawi[5]

[1,2]University of diyala, Iraq.

[3,5]Department of Chemistry, College of Science, Unversity of Diyala , Iraq.

[4]Department of Chemistry, College of Education for Pure Science, Unversity of Diyala , Iraq .

*Corresponding author: noorsabah@uodiyala.edu.iq

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Abstract

Synthesis of Schiff bases using the principles of green chemistry is an environmentally friendly approach to obtain these important organic compounds. Schiff bases are widely utilized in various applications, but traditional synthesis methods often involve the use of toxic reagents and solvents. This review highlights a sustainable and ecological strategy for the preparation of the Schiff base. The green chemistry method emphasizes the selection of non-toxic and readily available starting materials, such as primary amines and carbonyl compounds, while minimizing waste generation and energy consumption. Environmentally benign solvents, like water or ethanol, are favored over toxic organic solvents. The use of green catalysts, including solid or bio-derived catalysts, enhances reaction rates and selectivity, reducing the need for excess reagents. The synthesis is conducted under mild reaction conditions, such as ambient or slightly elevated temperatures, to avoid the formation of hazardous byproducts. The work-up and purification processes are optimized to minimize waste production, employing simple techniques like filtration or recrystallization. The schiff bases that are synthesized are categorized utilizing spectroscopic techniques, such as NMR, IR, or mass spectrometry, to confirm their structures and purities. By employing green chemistry principles, the preparation of Schiff bases becomes more sustainable and environmentally conscious, contributing to the overall goal of a greener chemical synthesis. This abstract serves as an introduction to the green chemistry method for preparing Schiff bases, providing a concise overview of the approach's key principles and highlighting its potential to reduce environmental impact while obtaining high-quality organic compounds.

Introduction

Schiff bases are organic substances with an imine or azomethine (-C=N-) functional group. They are frequently utilized in several industries [1], including organic synthesis, medicinal chemistry, and coordination

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chemistry. The traditional methods of preparing Schiff bases often involve the use of toxic and environmentally harmful reagents and solvents [2]. However, with the growing emphasis on sustainability and environmental consciousness, the field of green chemistry has emerged, aiming to develop more environmentally friendly synthetic methodologies. The preparation of Schiff bases using green chemistry principles focuses on reducing or eliminating the use of hazardous reagents and solvents [3], minimizing waste generation, and improving overall process efficiency. Here, the researchers are going to give general procedures by using the green chemistry approach in order to prepare Schiff bases [4]. Schiff bases have been produced using green chemistry principles focuses on reducing or eliminating the use of hazardous reagents and solvents, minimizing waste generation, and improving overall process efficiency. Selection of Starting Materials: Choose starting materials that are non-toxic, readily available, and easily handled. These can include primary amines (aliphatic or aromatic) and carbonyl compounds such as aldehydes or ketones [5,6]. Solvent Selection: Opt for environmentally benign solvents whenever possible, such as water or ethanol, instead of toxic organic solvents like chloroform or benzene. Catalysts: Employ green catalysts, such as solid catalysts or bio-derived catalysts, to promote the between an amine and a carbonyl molecule in condensation [7]. These catalysts can enhance the reaction rate and selectivity while minimizing the need for excess reagents. Reaction Conditions: Conduct the reaction at ambient temperature or slightly elevated temperatures[8], avoiding harsh reaction conditions that might generate toxic byproducts. Additionally, optimize the reaction time to achieve maximum yield while minimizing energy consumption[9]. Work-Up and Purification: Implement efficient work-up procedures that minimize waste generation. Utilize simple purification techniques such as filtration or recrystallization, which require fewer chemicals and generate less waste compared to traditional methods[10]. Characterization: Employ multiple spectroscopic methods, including Nuclear Magnetic Resonance (NMR), Infrared (IR), or Mass Spectrometry, to validate the synthesized Schiff base's structure and purity by analyzing it [11]. By following these green chemistry principles, the preparation of Schiff bases can be made more sustainable and environmentally friendly. The use of non-toxic starting materials, benign solvents, and green catalysts[12], combined with efficient work-up and purification methods, contributes to reducing the environmental impact of the synthesis process while maintaining high product quality[13]. Please consult relevant literature or specific experimental procedures for the synthesis of the desired Schiff base using the green chemistry approach, as the specific reaction conditions and experimental details may vary depending on the choice of starting materials and desired product [14].

1- Synthesis Schiff bases by using cerium(III) as catalyzed [15] :

A equimolar combination of aldehydes (10 mmol.) as well as amines (10 mmol.) was positioned in a ceramic container as well as completely blended. Cerium (III) chloride heptahydrate (1mmol.) has included and the blend was dynamically blended. The reaction advancements were observed through tthin-layers

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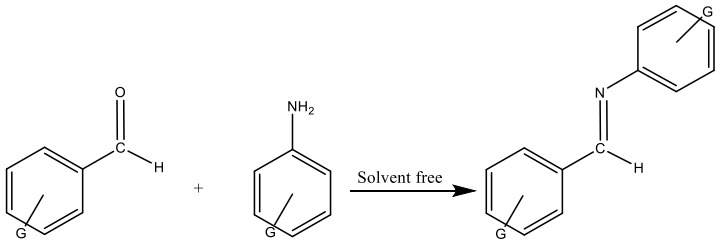
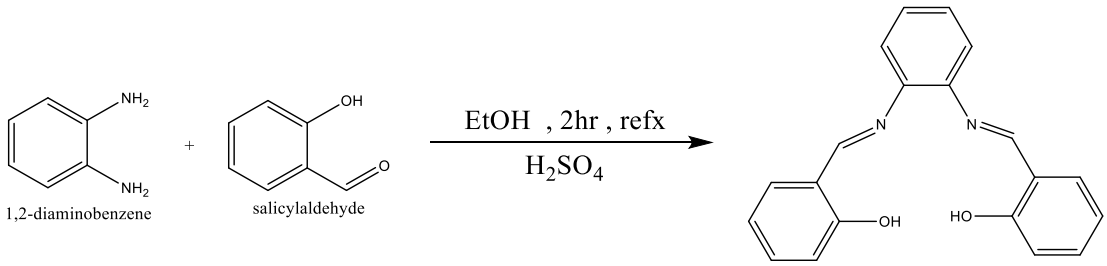
chromatographyy (iTLC). At first, the blend liquified and then hardened, suggesting the development of the imine. The product was further cleansed through recrystallization utilizing absolute ethanol. The reaction procedure in the absence of cerium (III) chloride heptahydrate was the same as before. As in the schemes below.



Scheme 1. Formation of imine using cerium(III) as catalyzed

2- Synthesis Schiff bases of 1,2-diaminobenzene in aqueous medium [16] :

A mixture containing 1.08 grams of 1,2-diaminobenzene (0.01 mol) in 10 milliliters of water was combined with 1.22 grams of salicylaldehyde (0.01 mol) at ambient temperature for 10 minutes. The resulting golden solid was separated by filtration, rinsed with water, and dried to produce golden crystals. As in the schemes below.



Scheme 2. Formation of imine in aqueous medium

3- Synthesis Schiff base by unconventional route [17]:

0.1 mole of p-toludine dissolved in 5 ml of methanol, and in another container, 0.1 mole of p-toludine was dissolved in 5 ml of methanol. Both solutions were combined in a beaker; a small amount of acetic acid was added as a catalyst, and the beaker was placed in a sonicator at a temperature of 45 degrees Celsius for a period of 9-10 minutes. As in the schemes below. A light yellow product was formed, indicating the successful formation of the desired product. The synthesized product was then recrystallized using the shock cooling method, using ethanol as the solvent, resulting in the formation of fine crystals of 2-methoxy-6-[(4-methylphenyl) imino] methylphenol.

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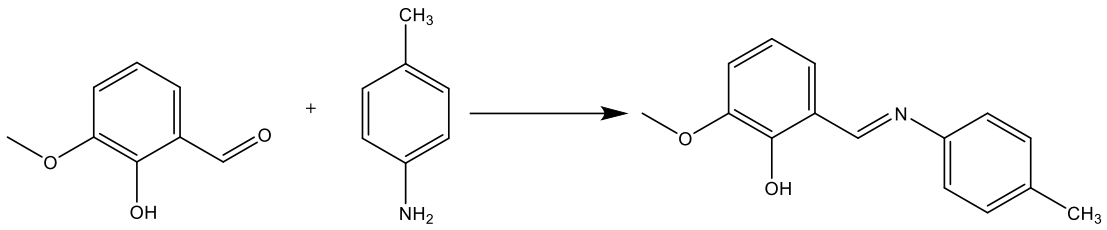
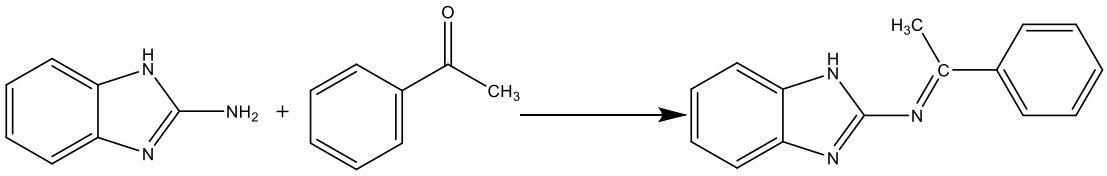


Scheme 3. Formation of imine by unconventional route

4- Synthesis Schiff bases by One-pot microwave assisted under green chemistry conditions [18] :

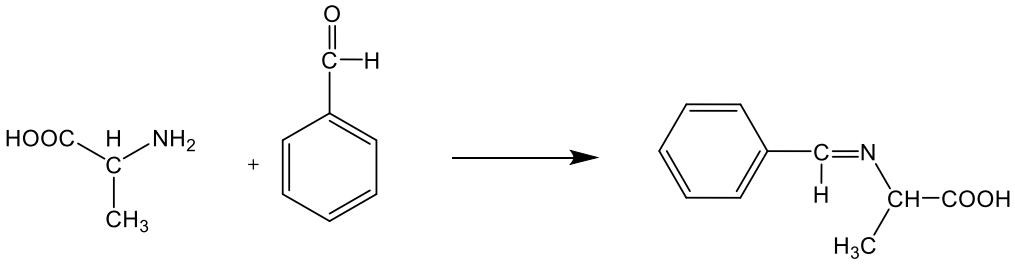
Simple mixing of the 2- aminobenzimidazole(1 mmol) and the acetophenone outgrowth(2.1 mmol) in the presence of catalytic quantities of acetic acid(one drop,0.2 mmol) and irradiation in a Biotage generator2.0 were each that was needed to complete the conflation, which redounded in the product of the benzimidazole derivations in excellent yields. With the exception of the 1- naphthyl secondary 3i, which was produced at 250 C, only the Schiff bases could be separated at a temperature of 160C. As in the schemes below.



Scheme 4. One-pot microwave-assisted imine synthesis in a green chemistry environment

5- Synthesis using the chemistry of grinding, construct Schiff bases. [19] :

A minimum volume of water (0.5 ml) was used to dissolve an equimolar combination of DL- alanine amino acid(0.01 spook) and substituted sweet aldehyde(0.01 spook). The admixture was also pounded using an applicable- sized mortar and pestle for 5 to 10 twinkles. The original thick response admixture solidified in 20 to 25 twinkles after being permitted to stand for eight hours. The solid residue was also suction filtered, washed with water, dried, and formed from the ethanol to produce the product. After being distilled off, the ethanol used forpost-processing was employed formerly again. As in the schemes below.



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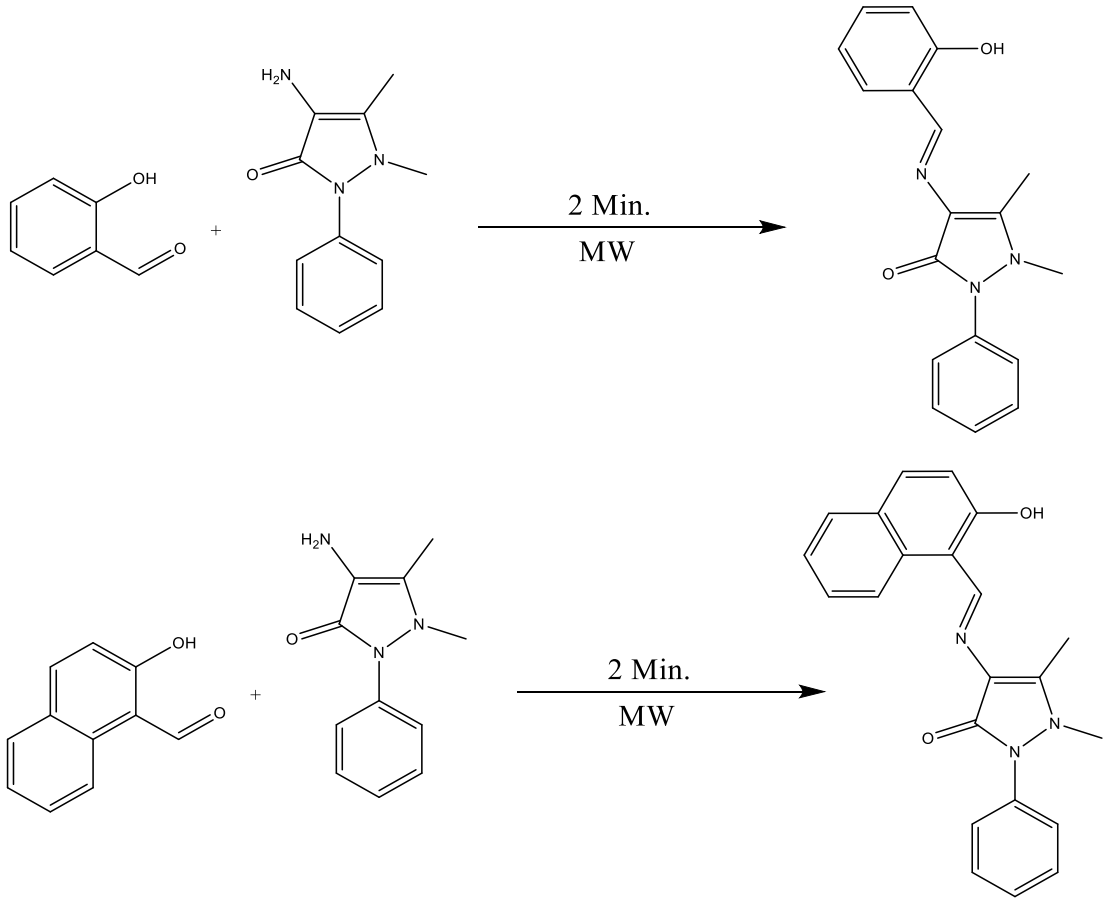
Scheme 5. Formation of imine by using grinding chemistry technique

6- Synthesis Novel Schiff Base Dyes [20] :

Salicylaldehyde (2.6 mmol), 4-aminophenazone (0.5 g, 29.6 mmol), and a few drops of biperidine were diluted in DMF (3 ml) using a flask. MW oven radiation was applied to the reaction mixture for 2 minutes. As in the schemes below. The mixture was added to ice-cold water when the reaction (as determined by TLC) had finished. A good yield (85%) of dye was produced after filtering, washing with very cold water, and drying the separated solid at room temperature. The dye was then recrystallized from chloroform and ethanol (8: 2), yielding crystals that were pale yellow in color.

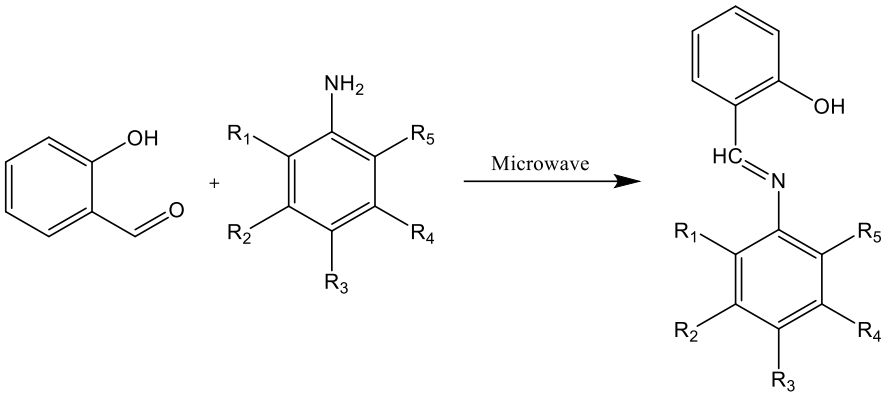


Scheme 6. Formation of imine by MW oven

7- Synthesis Schiff bases in aqueous media [21] :

In the microwave oven tube, a result of salicylaldehyde(0.004 spook) and substituted sweet amines(0.004 spook) in water(1 mL) was introduced. As in the schemes below. The accoutrements were exposed to microwave oven radiation at 200 W for roughly 30 seconds to two twinkles. TLC kept track of the response's

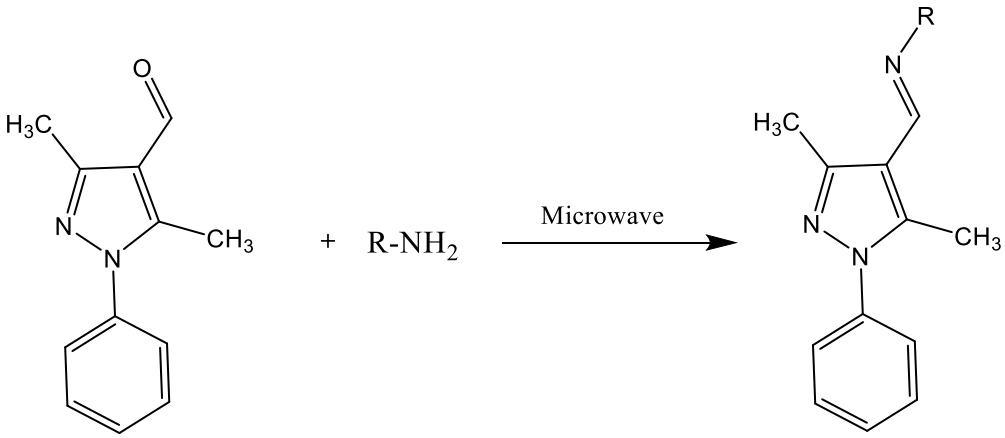
development. After the response was finished, the response admixture included a solid product, which was filtered and also recrystallized with methanol. The title composites are attained as solid chargers by recrystallization.



Scheme 7. Formation of imine in aqueous media

8- Synthesis novel Schiff base derivatives of pyrazole [22] :

Anhydrous methanol(15 mL), heterocyclic amines(5.8 mmol), 3,5- dimethyl-1-phenyl pyrazole-4-carboxaldehyde(5.8 mmol), and a many drops of acetic acid were combined, and the response admixture was hotted in a microwave oven for 2 to 5 twinkles(210 Watts, or 30 microwave oven power). TLC kept track of the response's development. After the response was finished and cooled, the product was attained and formed again using the applicable detergent. As in the schemes below.

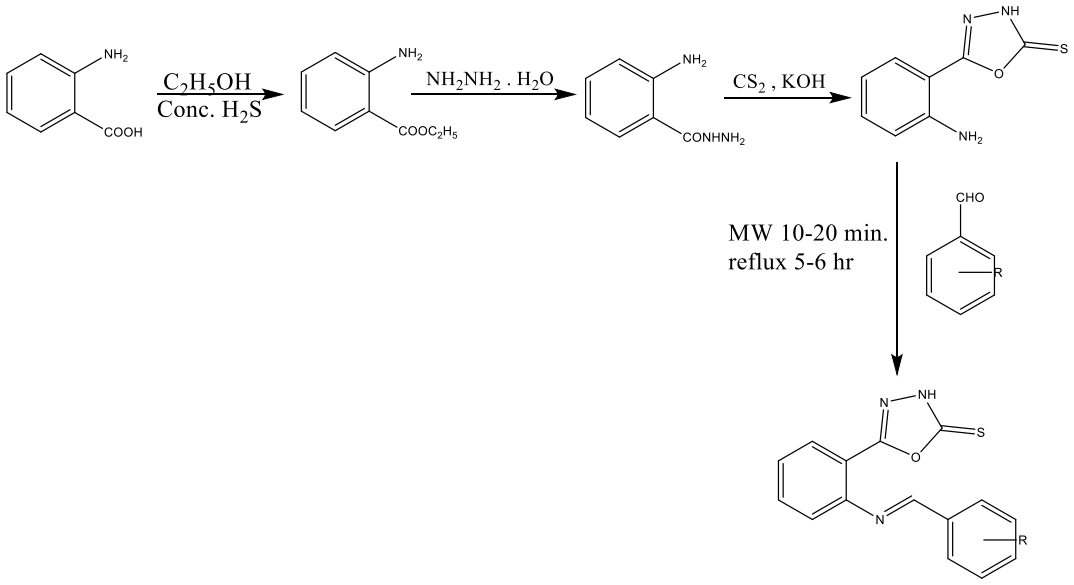


Scheme 8. Formation of novel Schiff base derivatives of pyrazole

9- Synthesis Schiff Base of 1,3,4-oxadiazole Analogues [23] :

The solution of 5-(2-aminophenyl)-1,3,4-oxadiazole-2-thione was subjected to 210 W of radiation for 10 to 15 minutes with the presence of substituted benzaldehyde and a small amount of GAA (0.01 mole, 1.93g) in 5ml

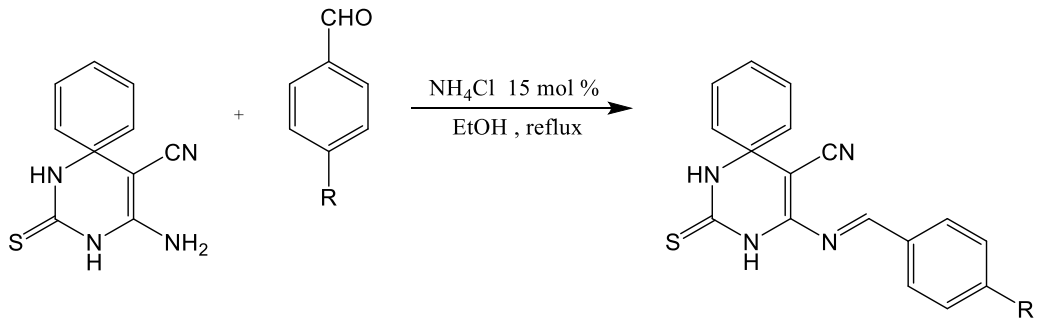
of ethanol. As in the schemes below. TLC was periodically monitored to ensure completion of the reaction. To obtain the solid outcome, the reaction mixture was cooled and placed in ice-cold water. The product was then filtered, washed with cold water, dried, and recrystallized using ethanol.



Scheme 9. Formation Schiff Base of 1,3,4-oxadiazole Analogues

10- Synthesis of Schiff Bases from 4Amino2Thioxo1,3Diazaspiro[5.5]undec4Ene5 Carbonitrile as Potential AntiInflammatory Agents [24] :

A matching quantity of the corresponding fragrant aldehyde (10 millimoles) was included in a solution of (2.22 grams, 1 millimole) in pure ethanol (10 milliliters). After NH_4Cl (15 percent molar) was added, the mixture was heated to boiling for the necessary duration while being monitored by thin layer chromatography. Once the reaction was complete, the mixture was treated with cold water (15-25 milliliters). The solid product was purified, washed with cold water, dehydrated, and crystallized again using the appropriate solvents. As in the schemes below.



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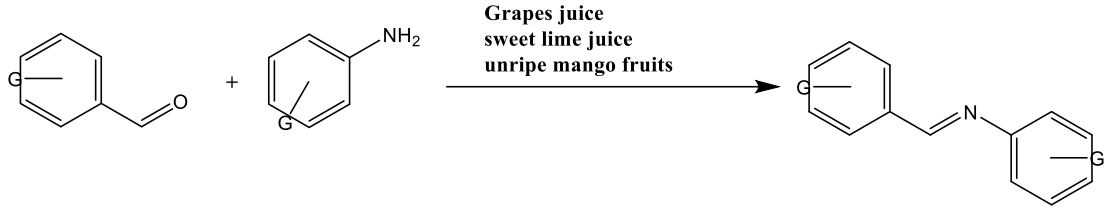
Scheme 10. Formation of imine by using NH_4Cl as catalyst

11- Synthesis Schiff Bases by using natural acid catalysts [25] :

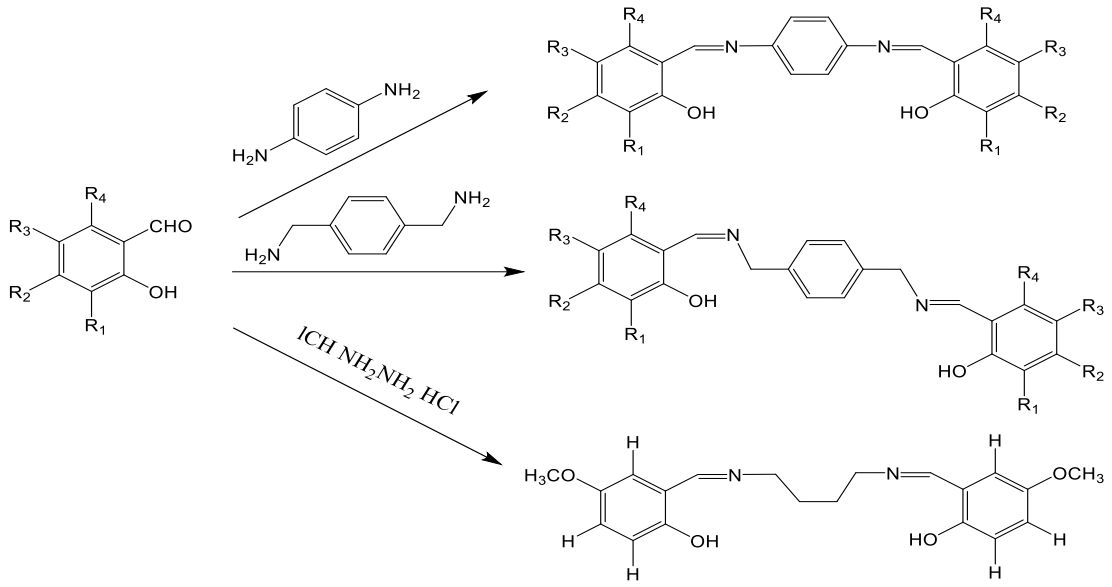
In different containers, equal amounts of aniline and benzaldehyde (0.1 mol each) were combined. Grape juice, a naturally present acid catalyst, was introduced to these mixtures in different quantities (0.5 ml, 1 ml, 1.5 ml, 2.0 ml, and 2.5 ml), and the mixtures were subsequently allowed to sit for 5 to 10 minutes. As in the schemes below. Once the reaction was finished, each mixture was stirred for an additional 2 to 4 minutes at ambient temperature. The resulting light yellow solid crude product was then cleaned by recrystallization with a small quantity of ethanol. The identical process is carried out using mango aqueous extract and sweet lemon juice. The products' melting points were determined using the open capillary technique, which was followed by identification and purification using TLC and confirmation by using mass spectra.



Scheme 11. Formation of imine by using natural acid catalysts

12- Synthesis utilizing ultrasound to create bis-Schiff bases as opposed to using a microwave or a traditional technique without a catalyst [26] :

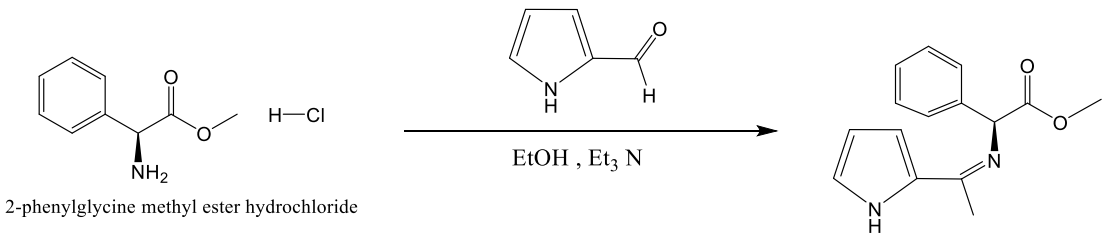
Diamines (1 mmol) and salicylaldehyde derivatives (2 mmol) were fully combined before being exposed to 450 W radiation at room temperature (25 ^{o}C) for 6–10 minutes. The reaction mixture was placed in 20 mL of dichloromethane (DCM) and rinsed with 3–5 mL of water. Anhydrous magnesium sulfate was placed on top of the dried DCM layer. Pure chemical was produced when DCM was removed under low pressure. As in the schemes below.



Scheme 12. Formation of imine by using ultrasound versus microwave and conventional method

13- Synthesis new amino acid Schiff bases [27] :

After mixing thoroughly in a grinder with Et3N for 30 minutes, the appropriate ratio (1:1 or 1:2) of aromatic aldehydes and 2-phenylglycine methyl ester hydrochloride were added. At 850 watts and 100 °C, the microwave reactor irradiated the reaction mixture. With higher yields, the reaction was finished quickly (5.5–8.5 min). As soon as the reaction was finished, the mixture was cooled, and the separated solid was filtered before being washed with ice-cold ethanol. The end result was then made again by recrystallizing ethanol. As in the schemes below.



2-phenylglycine methyl ester hydrochloride

Scheme 13. Formation of imine by using new amino acid

14- Synthesis Schiff base based (Gr@ NiO_2/Cu_2O NCs) nanocomposite [28] :

“A combination of Gr@NiO2/Cu2O nanoparticles, the suitable aldehyde (1.1 mmol), and 2-amino-benzo [de]isoquinolin-1, 3-dione or 2-aminoisoindoline-1, 3-dione (1 mmol) was added to 15 mL of DMF along with a few drops of glacial acetic acid. As in the schemes below. The reaction mixture was stirred and thin layer

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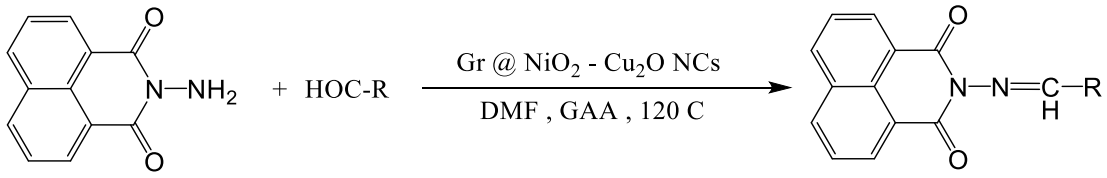
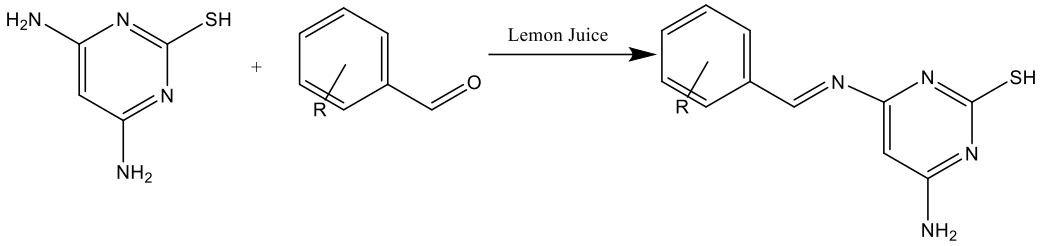
chromatography (TLC) was used to monitor the progress of the reaction at 120°C. After the reaction was complete, the insoluble catalyst was collected, filtered, and then rinsed with cold dichloromethane".



Scheme 14. Formation of imine by using Gr@ NiO_2/Cu_2O NCs) nanocomposite

15- Synthesis of Shiff's base Lemon Juice as a Natural Catalyse [29] :

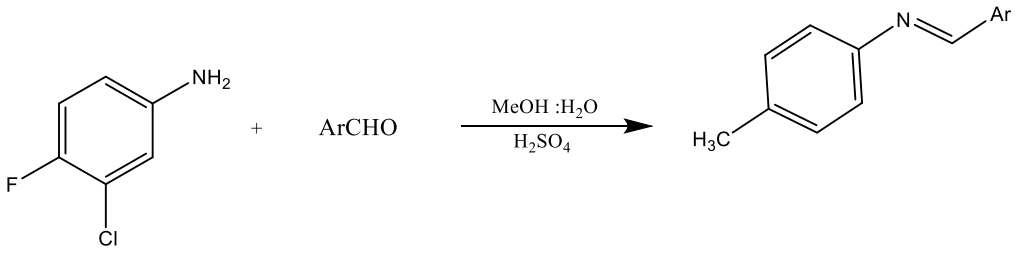
The chosen aldehyde (0.1 mmol), 4,6-diamino-2-thiol pyrimidine (0.1 mmol), catalyst juice (10 ml), and the necessary time were added and agitated at 55 °C. TLC kept track of the reaction's development. To get the pure product, the substance was dried and recrystallized from hot alcohol. Melting point was a feature of the product. As in the schemes below.



Scheme 15. Formation of imine by using Lemon Juice as a Natural Catalyse

16- Synthesis of novel Schiff bases using green chemistry techniques [30] :

The progress of the reaction was observed using thin layer chromatography (TLC) as the mixture of correctly substituted benzaldehyde (10 mmol) and amine compound (10 mmol) in methanol: water (3:1) (10 mL) and concentrated sulfuric acid (3-4 drops) was subjected to ultrasound at 50 degrees Celsius for 20 minutes. A precipitate formed when the solvent evaporated under decreased pressure. In order to obtain the desired product, the obtained compound was purified by recrystallization using an appropriate solvent. As in the schemes below.



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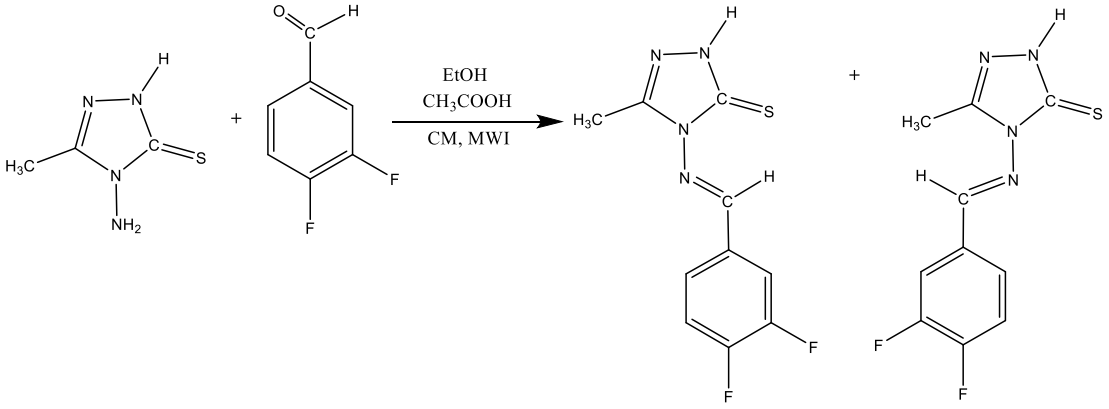
Scheme 16. Formation of imine by using green chemistry techniques

17- Synthesis of thione ⇔thiol Schiff base with triazole-thione moiety: Green synthesis [31] :

In a sealed borosilicate tube "that had been subjected to microwave radiation for five minutes, one millimole of 4-amino-5-methyl-2,4-dihydro-1,2,4-triazole-3-thione, one millimole of 3,4-difluorobenzaldehyde, 50 milliliters of ethanol, and 0.1 milliliters of acetic acid were added. (E)-4-((3,4-difluorobenzylidene) amino)-2,4-dihydro-5-methyl-3H-1,2,4- triazole-3-thione was obtained through the process of filtration and recrystallization". As in the schemes below.



Scheme 17. Formation of imine by thione ⇔thiol Schiff base with triazole-thione moiety

18- Synthesis of Nitro-Schiff Base Catalyzed by Gold Nanoparticle [32] :

Gradually, a methanolic solution of 4-amino phenol (218 mg, 2 mmol) was introduced to a solution of 5-nitro salicylaldehyde (334 mg, 2 mmol) in methanol. The mixture of chemicals was then heated and stirred for a complete hour. The Schiff base formed as a light-yellow solid. The mixture of chemicals was strained, cooled to ambient temperature, and then rinsed with chilled methanol before being dehydrated under vacuum. As in the schemes below.

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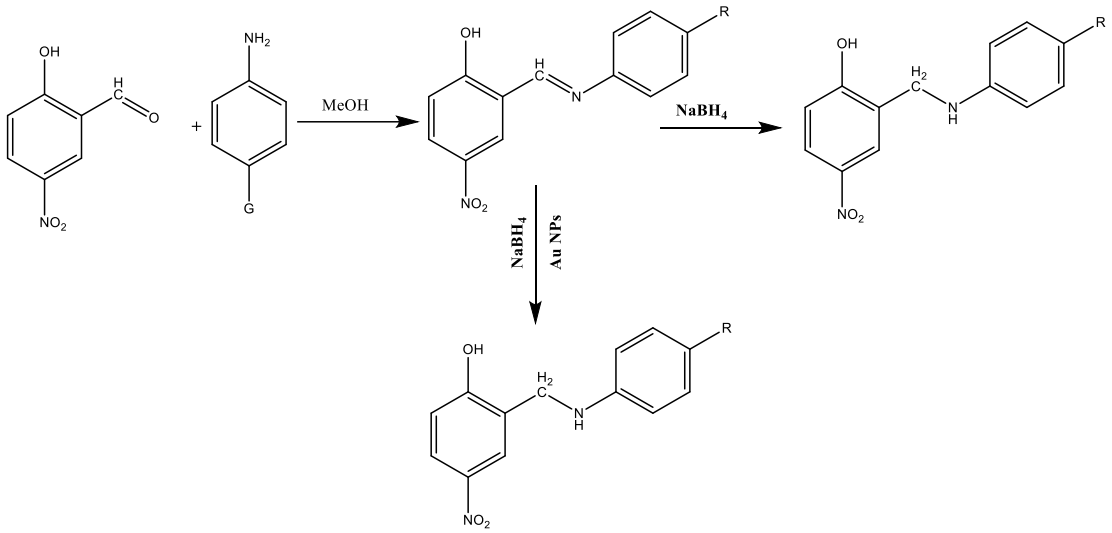
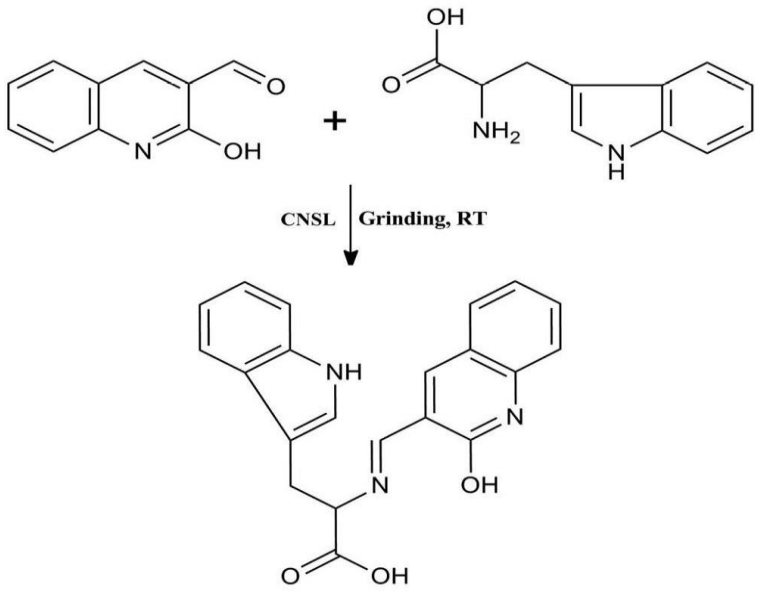


Scheme 18. Formation of imine by Gold Nanoparticles Catalysed Reduction

19- Synthesis Schiff base by Cashew nutshell liquid as catalyzed [33] :

A mixture containing equal amounts of 2-hydroxyquinoline-3-carbaldehyde (0.012 mol) and L-tryptophan (0.012 mol) was prepared. The catalyst CNSL (2 mL) was added and the mixture was ground at room temperature for 2-10 minutes, resulting in a jelly-like blend. To dissolve the waxy or jelly-like substances, 3-4 mL of 95% ethanol was added to the reaction mixture. As in the schemes below. The catalyst was separated from the mixture and washed thoroughly with petroleum ether (3-5 mL) before being dried in the air. The raw material was purified using a simple recrystallization process with ethanol.



Scheme 19. Formation of imine by Cashew nutshell liquid as catalyzed

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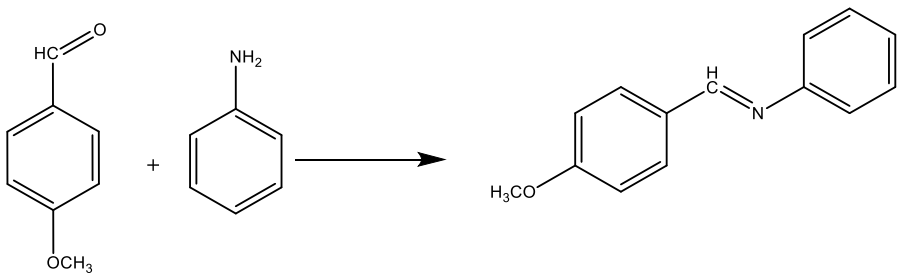
20- Synthesis of Schiff base foundation from freeze-dried fruit juice and berry juice [34]:

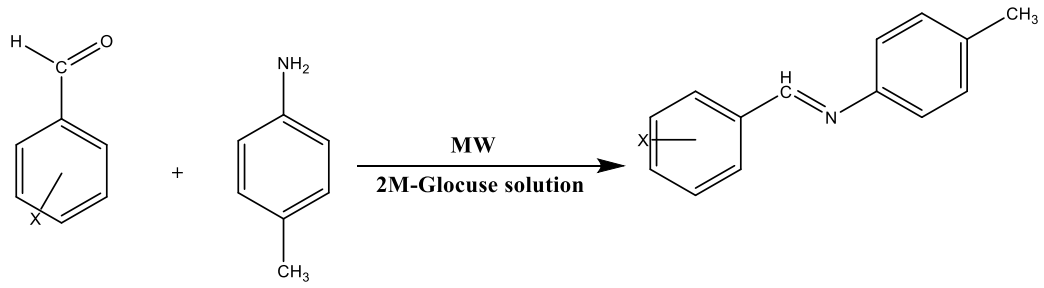
5.0 mL of freeze-dried blackberry fruit juice extract was added to equimolar volumes of aldehyde and aniline in a beaker. The combination was then allowed to sit for two minutes. The mixture was then held at room temperature for a further 20 minutes while being agitated at 400 to 600 rpm, and it was also kept there until a solid crystal product had formed. After the reaction was finished, the product was purified and recrystallized using the least amount of ethyl acetate possible. As in the schemes below.



Scheme 20. Formation of imine by berry fruit juice freezedried extract

21- Studying the use of glucose as an environmentally benign catalyst for microwave-assisted green synthesis of Schiff base [35] :

In a 100 ml "borosilicate conical flask, 0.0025 mole of p-toluidine and 0.0025 mole of desired aldehyde were combined to form Schiff bases. The reaction mixture was then given 10 ml of the necessary glucose solution. The reaction mixture was subjected to MW irradiation (240 W) for the specified duration. As in the schemes below. The reaction mixture was taken out from the microwave and cooled before being stirred at room temperature after every 1 minute of exposure under microwave irradiation. The progress of the reaction was continuously monitored by testing TLC. After the reaction was finished (as determined by TLC), the reaction mixture was placed into ice cold water".



Scheme 21. Formation of imine by using glucose as ecofriendly catalyst for microwave

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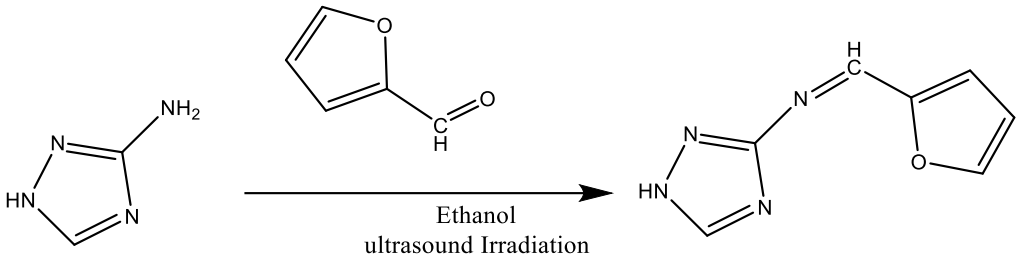
22- Green synthesis, electrochemical, and DFT tests on certain new triazole Schiff base derivatives' ability to prevent steel from corroding in a solution of hydrochloric acid [36] :

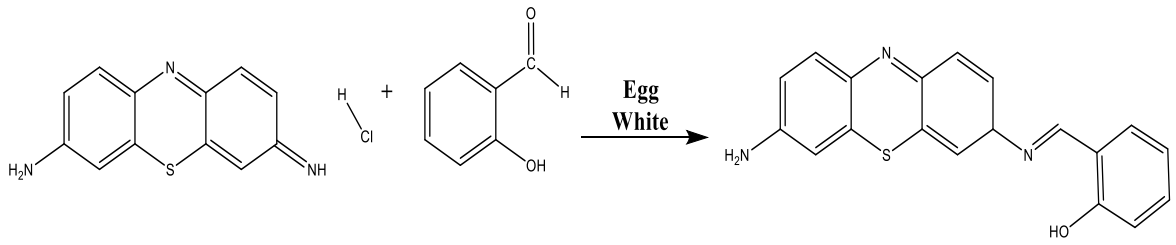
"A mixture of 3-amino-1,2,4-triazole (2.44 g, 0.029 mol) with three different aldehydes 2-hydroxy-1-naphthaldehyde (5.00 g, 0.029 mol), furfural (2.4 mL, 0.029 mol), and thiophene-2-carboxaldehyde (2.7 mL, 0.029 mol) in 5 mL ethanol or distilled water/acetic acid was placed in 50 mL erlenmeyer flask and exposed to ultrasound irradiation waves at room temperature for the necessary time until completion of the reaction (monitored by TLC)". As in the schemes below.



Scheme 22. Formation of imine by using ultrasound irradiation waves

23- Synthesis of phenothiazine Schiff base [37]:

For a period of 45 minutes, a mixture containing Salicylic aldehyde (11.6 millimoles), Thionine (which known as Lauth's violet (12 millimoles), as well as 0.5 mL of albumeni were stirredi at room itemperature. Following the 45-minute duration, the resulting pale yellow solid was separated by filtration, and the pristine crystallized substance was obtained via water crystallization. As in the schemes below.



Scheme 23. Formation of imine by using egg white

24- Cashew shell extract is used in the Schiff bases syntheses as a natural acid catalyst. [38] :

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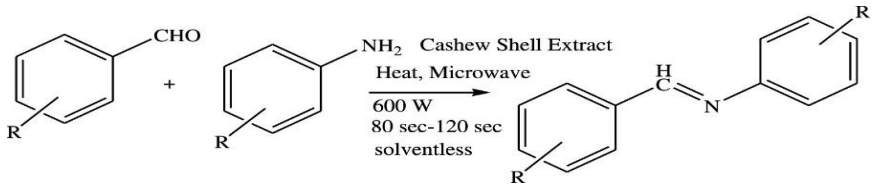
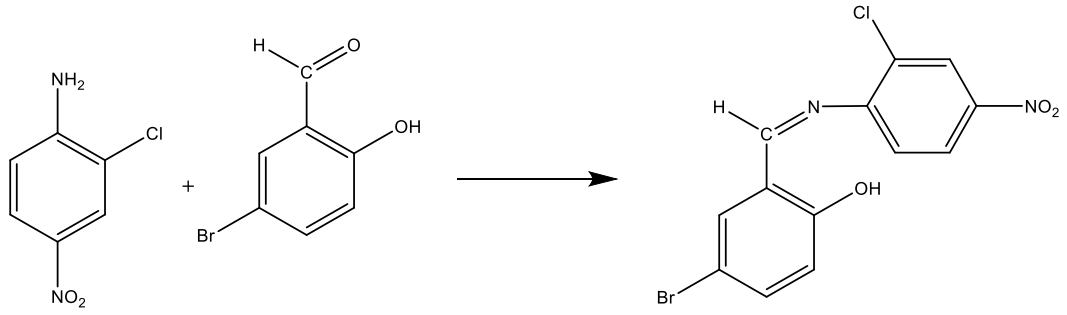
A 100 mL cone-shaped bottle was filled with Aldehyde fragrance (millimole), fragrant amine (millimole), and Cashew Nut Shell Liquid (CNSL) (mL). Aluminum foil was used to cover this cone-shaped bottle. At 600 W, the mixture of chemicals was kept in the microwave. It takes between 80 and 120 seconds to create Schiff bases through microwave exposure. This reaction was carried out without the use of a solvent, and TLC was used to monitor the results. As in the schemes below.



Scheme 24. Formation of imine by utilizing a natural acid catalyst made from cashew shell extract.

25- Synthesis of 4-iBromo-2-(((2'-iChloro-4'-initrophenyl) iimino) imethyl) iphenol iSchiff iBase: iGreen iSynthesis, iUrease iInhibitory iActivity, andi Antioxidanti Potentiali

Two millimeters of 2-chloro-4-nitroaniline (0.345 g) and two millimeters of 5-bromo-2-hydroxybenzaldehyde (0.402 g) were combined in a mortar. "Glacial acetic acid" that is water-free (anhydrous) acetic acid (0.5 mL) has been added to this mix in order to serve as a catalyst. Without using any solvent, As in the schemes below. The mixture has been mashed by using a pestle for three hours at room temperature. To monitor the reaction development, thin layer chromatography was used (the mobile phase was made up of a 4:1 mixture of ihexane as well as ethyli ethanoatei). The final creation has diluted in imethanol and gravity-filteredi utilizing No. 1 Whatmani filters papers. The filtrates were put iin a porcelain dishes for collection. The product is recrystallized from ethyl acetate after the solvent evaporated at room temperature in a fume hood. Consequently, vivid red crystals were produced.



Scheme 25. Formation of imine by using Thin layer chromatography

Table 1. Show some properties of different synthetic methods

No.	Type of reaction	Temperature	Catalyst	Time	Yield%	Ref.
1-	Stirred	Room Temp.	$CeCl_3.7H_2O$	2 hr	41-91	15
2-	Stirred	Room Temp.	---------	10 min	97	16
3-	Stirred	45°C	---------	9-10 min	95.8-98.3	17
4-	Microwave oven and irradiated	160-250°C	---------	20-60 min	70-93	18
5-	Grindstone friction-activated synthesis	---------	---------	30-35 min	72-78	19
6-	Microwave reactor and irradiated	Room Temp.	---------	2 min	85	20
7-	Microwave reactor and irradiated	50-80°C	---------	30sec-2 min	30-96	21
8-	Microwave irradiation	---------	---------	2-5 min	82.2-90.2	22
9-	Microwave irradiation	---------	---------	10-15 min	89	23
10-	Refluxed	---------	---------	15-60 min	75-91	24
11-	Stirred	54°C	Natural acid	5-10 min	73-93	25
12-	Microwave irradiation	Room Temp.	DCM	6-10 min	70-88	26
13-	Microwave irradiation	100°C	Et_3N	5.5-8.5 min	96	27
14-	Stirred	120 °C	DMF	30 min	90	28
15-	Stirred	55°C	Lemon juice	appropriate time	70-80	29
16-	Refluxed	50 °C	---------	20 min	82-89	30
17-	Microwave irradiation	---------	---------	5 min	96	31
18-	Stirred with Reflux	---------	---------	1 hr	89	32

19-	Refluxed	Ambient Temp.	CNSL	2-10 min	84	33
20-	Stirred	Room Temp.	Blackberry fruit juice	20 min	90-93	34
21-	Microwave irradiation	Room Temp.	---------	1 min	76-94	35
22-	Ultrasound irradiation	Room Temp.	---------	30 min	95	36
23-	Stirred	Room Temp.	Egg white	45 min		37
24-	Microwave irradiation	---------	Cashew shell	80-120 sec	65-88	38
25-	Thin layer chromatography	Room Temp.	glacial acetic acid	3 hr	96	39

Conclusion

Green chemistry outperforms conventional synthetic techniques in terms of both environmental and monetary advantages. In comparison to conventional procedures, green synthetic techniques must increase selectivity, speed up reaction times, and simplify product purification. All of the working methods listed in the above table are green ways of synthesizing Schiff bases. The authors recommend adopting the method used by Pooja, B., & Tanay, P. (2019). to accomplish the fundamentals of green chemistry.

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