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## A review on the sustainable chemistry: Preventing wastage, maximizing atom economy

**Snigdha Rani Behera, Anshu Kumar Singh and Suraj Kumar Sharma**

### Abstract

Green chemistry or Sustainable chemistry is defined as the invention, design, development and application of chemical products and processes to reduce or eliminate the use and production of substances harmful to human health and the environment. Experiments should use alternative reagents that are not only environmentally friendly but also readily available nationwide in large quantities at very reasonable prices. Avoid using organic solvents (ether, petroleum ether, ethyl acetate, etc.) if possible. Ethanol and methanol are most preferred.

**Keywords:** Microwave reaction, green synthesis, solvent free Reaction, pollution, hazardous chemical, design, development

### 1. Introduction

Chemistry is going through largest demanding situations in its history. The essential purpose to that is a look for how new assets may be applied within the synthesis of latest compounds. For a lot of the beyond 30 years, inexperienced chemistry has been in large part recognized with principal ideas: the discount or removal of poisonous materials and pollutants prevention.

Fossil assets have supplied the possibility to construct a deliver call for electricity gadget throughout the planet, no matter the scale and geographical role of the population. The transition to renewable electricity assets, specifically to photovoltaics and wind, calls for the improvement of green and reversible electricity garage systems. Although hydrogen fuel line may be used for electricity garage, its low density in addition to unsafe nature limits secure and green packages. Formic acid, formate salts, and alcohols may be appealing options for electricity garage supplied green catalytic strategies are evolved for the facile launch of hydrogen from those molecules, in addition to their regeneration from CO<sub>2</sub> and hydrogen. Laurency, Beller <sup>[1]</sup>, and co-employees reviewed the development in homogeneous catalytic hydrogenation of carbon dioxide to formic acid and methanol and the opposite dehydrogenation reactions. The dehydrogenation of biomass primarily based totally better alcohols turned into additionally discussed. Particular interest turned into given to the sustainability components through specializing in additive unfastened strategies and earth ample metallic catalysts. Detailed mechanistic insights have been additionally given to illustrate the improvement of advanced catalytic systems. The hit substitute of fossil assets within the manufacturing of carbon chemical substances through renewable assets, inclusive of carbon dioxide and biomass, is needed for the improvement of a sustainable. evaluated through Leitner, Bardow <sup>[2]</sup>, and co-employees. The environmental footprints of carbon dioxide and fossil assets-primarily based totally packages have been assessed through reading the artificial methodologies and/or strategies and appearing existence cycle assessments. It turned into proven that the conversion of carbon dioxide to chemical substances does now no longer represent a carbon sink over the existence cycle of the goods due to the fact that carbon dioxide is launched on the cease of existence, however it may result in extra environmentally pleasant manufacturing strategies. Biomass is a globally available, carbon-neutral, renewable feedstock for the manufacturing of carbon chemical substances, that may absolutely update the lately applied fossil-primarily based totally chemical strategies even on this century. Mika and co-workers <sup>[3]</sup> have reviewed the current fame of numerous catalytic alterations of carbohydrates to platform chemical substances consisting of the applicable mechanistic facts in addition to the biochemical manufacturing routes and techniques. Green Chemistry describes pollutants prevention and 0 waste technical ideas on each laboratory and business scales.

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Encourage using budget friendly and environmentally sound technology that now no longer best enhance yield, however additionally lessen the fee of putting off waste on the cease of the chemical system.

## 2. Principle of green chemistry

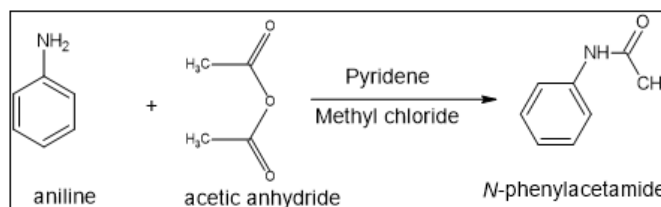
These "12 principles" set the recommendations for designing and growing extra sustainable chemical strategies and products. They goal to lessen the technology of unsafe products, or even use this technology withinside the combat towards pollution [4].

- 1. Prevention:** it's far higher to keep away from the formation of waste than to deal with or easy it after it has formed.
- 2. Economy of atoms:** Synthesis techniques need to be designed to maximize the incorporation of all substances used withinside the very last product.
- 3. Less poisonous chemical intermediates:** Wherever possible, artificial methodologies need to be designed to apply and generate materials with very little toxicity to human fitness and the surroundings.
- 4. Safer cease products:** Chemical need to be designed to hold the effectiveness in their feature whilst lowering their toxicity.
- 5. Reducing using auxiliary materials:** The use of auxiliary materials (inclusive of solvents, isolating agents, etc.) need to be averted as some distance as possible, and be innocent while used.
- 6. Reduction of electricity consumption:** The environmental and financial effect of electricity necessities ought to be diagnosed and minimized. Synthetic techniques need to be carried out at stress and ambient temperature.
- 7. Use of renewable uncooked substances:** Renewable uncooked substances need to be used anyplace technically and economically feasible.
- 8. Reduction of needless drift:** Unnecessary derivatization (blocking off groups, protection/unprotection stages, transient modifications) need to be averted as some distance as possible.
- 9. Use of catalysts:** Catalytic reagents (as selective as possible) are advanced to stoichiometric reagents.
- 10. Design for degradation:** Chemicals ought to be designed in order that on the cease in their feature they do now no longer persist withinside the surroundings and degrade into innocent products.
- 11. Development of analytical technology for real-time tracking:** Analytical methodologies ought to be evolved to allow real-time tracking and manipulate of strategies earlier than unsafe materials are formed.
- 12. Minimizing the chance of chemical accidents:** Chemicals and the approaches wherein they may be utilized in a chemical system need to be selected to limit the capability for chemical accidents, consisting of spills, explosions and fire

## 3. Literature review

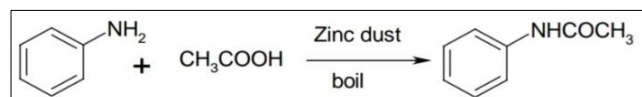
**3.1 Acetylation of primary amine:** Preparation of acetanilide by H. Meshram [5]

## Conventional Procedure



## Non-green Components

- Use of chlorinated solvent like  $\text{CH}_2\text{Cl}_2$
- Pyridine is also not eco-friendly
- Acetic anhydride leaves one molecule of acetic acid unused (not atom-economic)



## Alternative Green Procedure

### Chemicals Required:

- Aniline - 10 ml (10.2 g)
- Glacial acetic acid - 30 ml
- Zinc dust - 0.5 g

A mixture of aniline (10 ml) and zinc dust (0.5 g) in acetic acid (30 ml) in a 100 ml round bottom flask was heated over a gentle flame using water condenser.

Heating was continued for about 2 hrs. The reaction mixture was then carefully poured in cold water (100 ml) in a 250 ml beaker with cooling and vigorous stirring. The shining crystals of acetanilide were separated slowly. After 15 min.

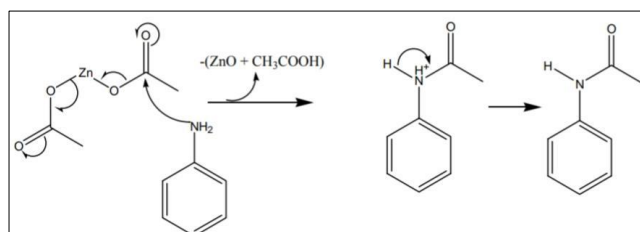
The acetanilide crystals were collected by filtration. The solid crystals were washed over the Buchner funnel with water and the product was dried (yield, 10 gm). It was crystallized in boiling water. (If necessary, decolorizing charcoal may be used),

**Melting point:** 114 °C.

**Yield:** 10 g (91%)

## Green Context

- Avoids use of acetic anhydride (usage banned in some states, due to its
- utility in narcotic business)
- Minimizes waste by-products
- Avoids hazardous solvent



## Mechanism

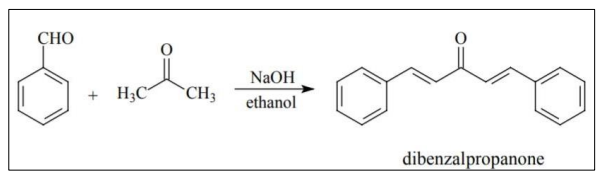
**2. Base catalyzed aldol condensation:** Synthesis of dibenzalpropanone by S. Bhagat, R. Sharma, and A.K. Chakraborti [6]

- **Conventional method**

- **Chemicals Required**

- Acetone – 1 ml (0.83 g)

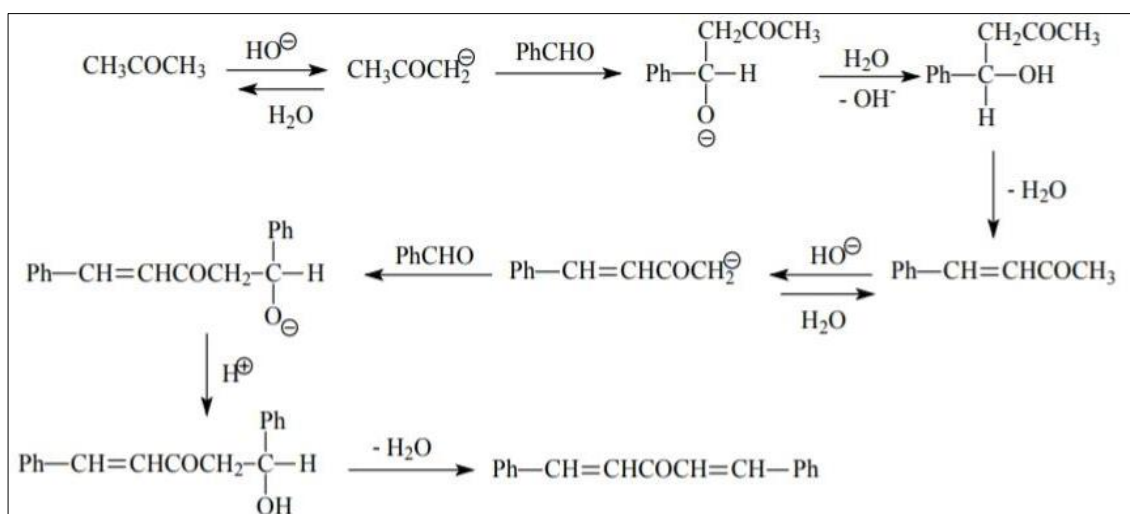
- Benzaldehyde – 3.8 ml (3.9 g) NaOH – 30 ml of 10% solution



**Mechanism**

**Alternative Procedure**

- **Chemicals Required**



Acetone: 0.81 mL (11 mmol)

Benzaldehyde: 2.3 mL (20 mmol)

LiOH.H<sub>2</sub>O: 42 mg (1 mmol, 10 mol %)

In a 25 mL round bottom flask containing a small magnetic bar, the aldehyde and ketone were taken with ethyl alcohol (5 ml) and lithium hydroxide (42 mg) monohydrate was added into it.

The reaction mixture was magnetically stirred vigorously for 8-10 minutes. The pale-yellow solid precipitated out, 5 g of crushed ice was added and the solid was allowed to settle down.

The precipitated pale-yellow solid was filtered, washed with water, air dried and recrystallized with ethanol.

**Yield:** 2.1 g (90%)

**Melting point:** 120 - 121 °C

**Precaution:** The aldehyde should be free from acid.

**Green Context:**

- Hazardous organic solvents are avoided.
- Lithium hydroxide is easy to handle as it is comparatively less hygroscopic than other alkali metal hydroxide.
- Use of catalytic amount of the base

**3. Halogen addition to C=C BOND:** Bromination of trans-stilbene by L. C. McKenzie [6]

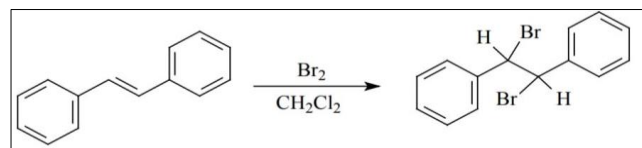
**Conventional Procedure**

In a conical flask fitted with a cork, benzaldehyde (1 ml), acetone (3.8 ml) and methylated spirit (or alcohol) (15 ml) were shaken together for 2 minutes. To it was added 10% sodium hydroxide solution and shaken vigorously for 10 minutes with simultaneous pressure release.

The reaction mixture was cooled in ice and the pale-yellow solid was filtered through a filter paper, washed with water, dried, collected, weighed and recrystallized from ethanol,

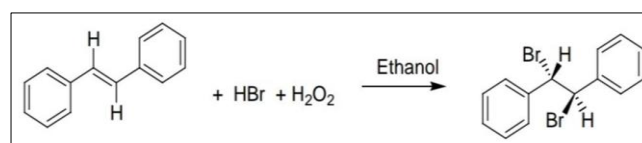
- **Melting point:** 120-122°C

- **Yield:** 3 g (90%)



**Non-green Component**

- Use of liquid bromine
- Chlorinated solvents



**Green Procedure: 1<sup>st</sup>**

**Chemicals Required**

- Trans-Stilbene - 1.8 g
- HBr in water - 5.2 ml
- 30% Hydrogen peroxide - 7 ml
- Ethanol - 10 ml

Trans-stilbene (1.80 g) in ethanol (10 ml) was reflux aqueous solution of HBr (33%) (5.2 ml) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) (7 ml) were added from a dropping funnel sequentially to this refluxing solution of stilbene.

The colorless solution became deep orange in color. Within 15 minutes, the orange color disappeared. This indicates the bromination of stilbene.

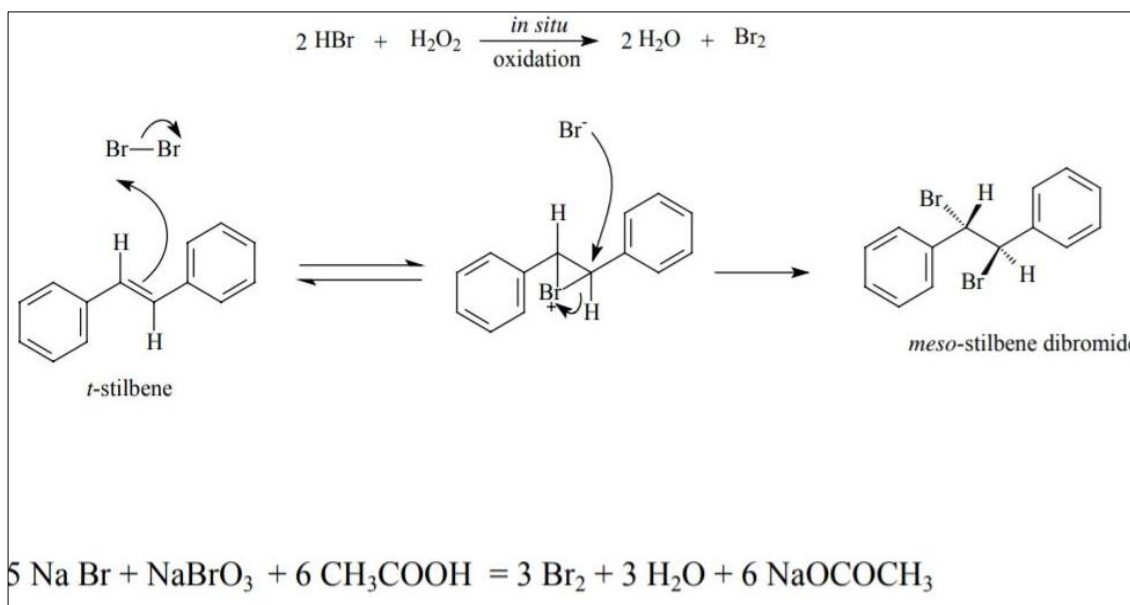
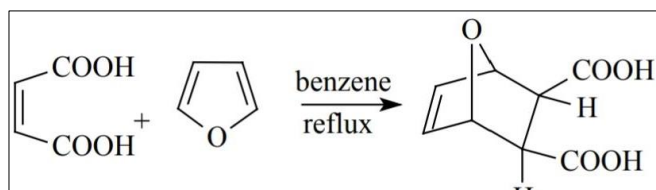
- **Melting point:** 237C
- **Yield:** 2.4 g (70%)

**Green procedure: 2<sup>nd</sup>****Chemicals Required:**

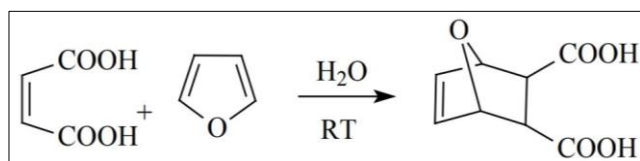
- Trans-Stilbene - 1.8 g
- Glacial Acetic acid - 20 ml
- Sodium bromide - 3 g
- Sodium bromates - 1 g

To a solution of trans-stilbene in acetic acid was added a mixture of sodium bromide and sodium bromate at room temperature with stirring by a glass rod

The reaction mixture was then stirred occasionally with a glass rod for 1 hour. The developed light brown color disappeared.

**Mechanism****4. Cycloaddition reaction:** Diels-Alder reaction between furan and maleic acid by R.B. Woodward and H. Baer <sup>[7]</sup>**Conventional Procedure****Non-green Component**

Use of benzene which is one of the most toxic solvents

**Green Procedure**

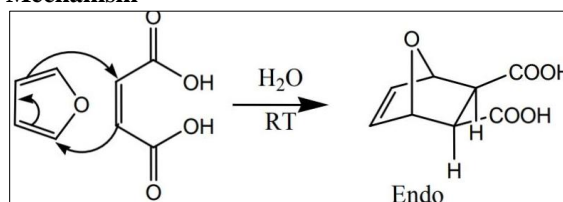
- **Chemicals required:**
- Furan: 1.75 g
- Maleic acid: 1.1 g

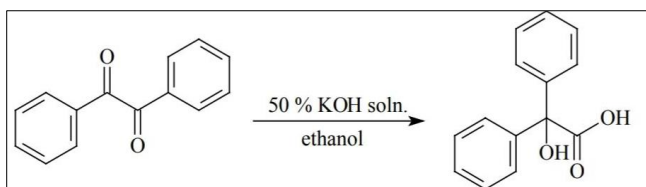
The acetic acid in the reaction mixture was then neutralized by sodium hydroxide solution. The precipitate of stilbene dibromide separated out. This was filtered and dried.

- **Yield:** 2.6 g (80%)
- **Green Context**
- Corrosive liquid bromine is avoided
- Atom efficient
- Water is the only byproduct in HBr- H<sub>2</sub>O<sub>2</sub> method and in NaBr- NaBrO<sub>3</sub> method sodium acetate is formed along with water.
- HBr-H<sub>2</sub>O<sub>2</sub> mixture and bromide-bromate couple offer in situ oxidation of Br<sup>-</sup> to molecular bromine.
- **Caution:** Care must be taken while handling the solution of hydrogen bromide and hydrogen peroxide.

A mixture of furan (1 g), maleic acid (2 g) in water (10 ml) was shaken or stirred for 2-3 hrs at room temperature. The adduct formed, was filtered, washed with water, dried and recrystallized from aqueous ethanol,

- **Melting point:** 138-140 c
- **Yield:** 2.1g (80%)
- **Green Context**
- Reaction carried out in aqueous medium avoiding benzene
- Efficient at room temperature itself 100% atom efficient

**Mechanism****5. Rearrangement reaction:** Benzil-Benzilic acid rearrangement by K. Tanaka and F. Toda <sup>[8]</sup>

**Conventional Procedure**

- **Green Procedure:** Preparation of Benzilic Acid in Solid State under Solvent-free Condition
- **Chemicals Required**
- Benzil: 1 g
- Sodium hydroxide or potassium hydroxide: 1 g
- Conc. Hydrochloric acid

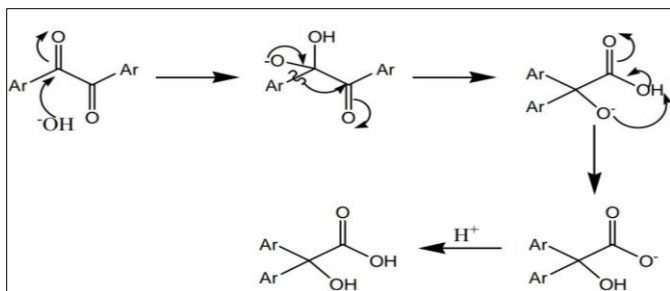
Benzil (1 g) was thoroughly grounded with solid NaOH or KOH (1 g) in a dry mortar with the help of a pestle to make an easy flowing powder.

This material was subsequently taken in a dry conical flask fitted with a piece of cotton at its mouth and heated on a boiling water-bath for 20 minutes.

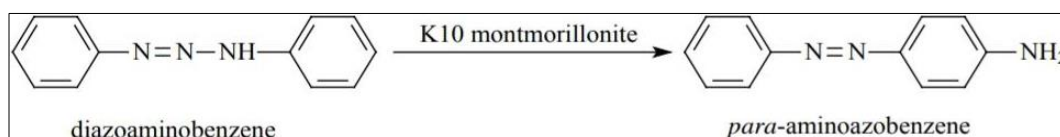
Then it was cooled to room temperature, dissolved in minimum amount of water (unreacted benzil, if any, was removed simply by filtration) and the aqueous solution was acidified with conc. HCl with thorough cooling in ice.

The precipitated benzilic acid was filtered, washed with cold water and crystallized from hot water, if needed.

- **Melting point** 149-151 °C
- **Yield:** 0.86 g (80%.)
- **Green Context**
- Solvent-free procedure
- Atom efficient

**Mechanism****6. Pinacol pinacolone rearrangement reaction-I:** Preparation of benzopinacolone by J. Am. Chem. Soc.<sup>[9]</sup>

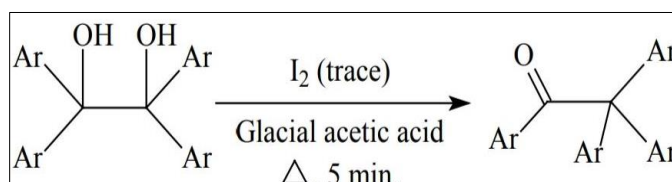
- Benzopinacol obtained in the first experiment is converted to benzopinacolone by heating under reflux (5 minutes) with glacial acetic acid containing trace amount



- **Chemicals Required**
- Diazoaminobenzene – 2 g
- K10 montmorillonite – 2 g

Diazoaminobenzene (2 g) was thoroughly mixed with K10 montmorillonite clay (2 g). The mixture was taken in a round

of iodine dissolved in it. This reaction is known as pinacol- pinacolone rearrangement.

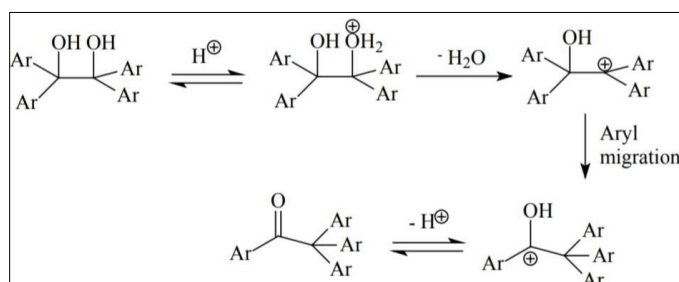
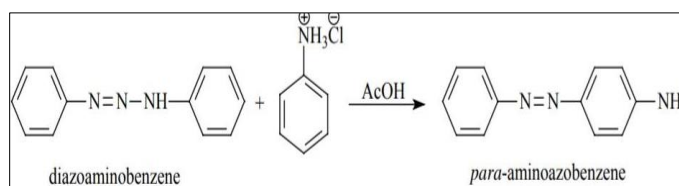


- **Chemicals Required**
- Benzopinacol - 2.0 g
- Glacial Acetic acid - 10 ml
- Iodine – trace amount
- **Procedure**

Benzopinacol (2.0 g) was placed in a round bottomed flask and to it was added a solution of iodine (trace) in glacial acetic acid (10 ml) and the reaction mixture was refluxed on a wire gauze by Bunsen burner for 5-7 minutes.

The reaction mixture was allowed to cool down to room temperature and then kept in the refrigerator overnight. The crystals of benzopinacolone were filtered, dried in air.

**Melting point:** 182 °C

**Mechanism****7. REARRANGEMENT REACTION-II:** Rearrangement of diazoamino-benzene to p-aminoazo-benzene by K. Pitchumani, C<sup>10</sup>**Conventional Procedure**  
**Alternative Green Procedure**

bottom flask and heated in a water bath for 3 hours with periodical shaking after every 15 min.

The mixture was then extracted with ether. The ether layer was evaporated and the residue was recrystallized from aqueous ethanol.

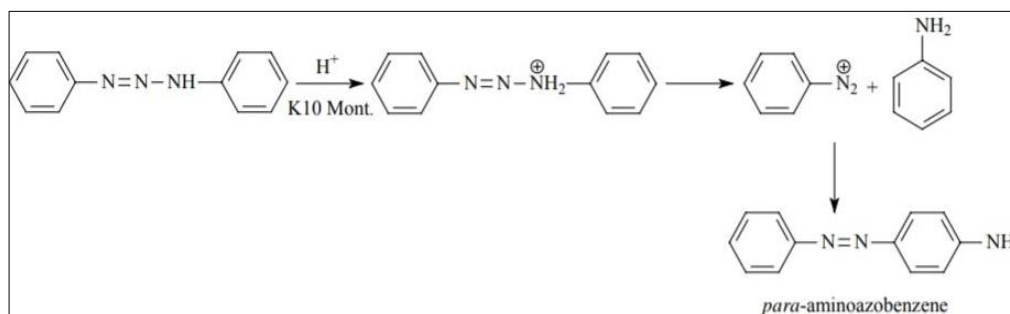
**Melting Point:** 127-128 °C

**Yield:** 1.7 g (85%)

**Green Context:**

- ¾ Eco-friendly method

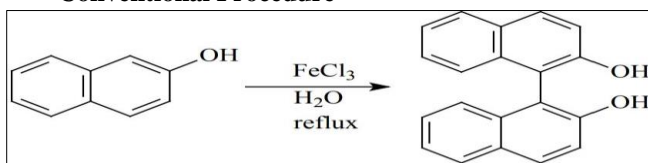
- ¾ Simple reaction procedure.
- ¾ No need for excess aniline and acetic acid



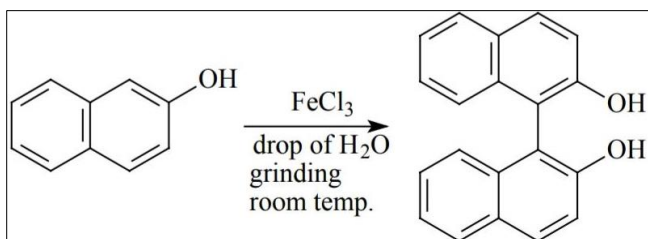
### Mechanism

**8. Radical coupling reaction:** Preparation of 1, 1-bis-2-naphthol by A. I. Vogel

#### Conventional Procedure



- **Non-green Component:** Use of more energy (reflux)



### Green Procedure

#### Chemicals Required

- 2-Naphthol - 2.88 g
- Iron(III) chloride - 0.7 g
- Water - 2 drops
- Toluene (for recrystallization)

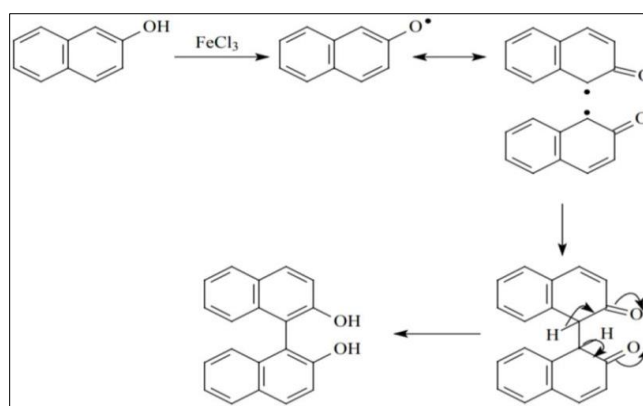
A mixture of 2-naphthol (2.88 g) and iron(III) chloride (0.7 g) with 2 drops of water in an agate (or porcelain) mortar pestle was ground for about 20 minutes.

The mixture was allowed to stand for about 2 hrs with a little grinding now and then. The mixture was transferred with water (40 ml) into a 100 ml beaker and boiled for 10-15 minutes.

The mixture was cooled and the solid was filtered, washed with boiling water (10 ml), dried and recrystallized from toluene.

- **Melting Point:** 214-217 °C
- **Yield** 3.9 g (90%)
- **Green Context**
- Efficient method and easily available catalyst
- Reaction is performed with simple grinding at room temperature without any solvent

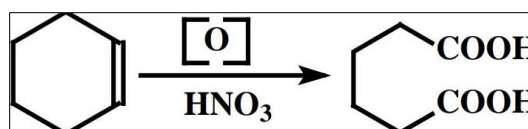
- Work up of the reaction involves aqueous medium This demonstrates the concepts of oxidative coupling, free radical and C-C bond formations.



### Mechanism

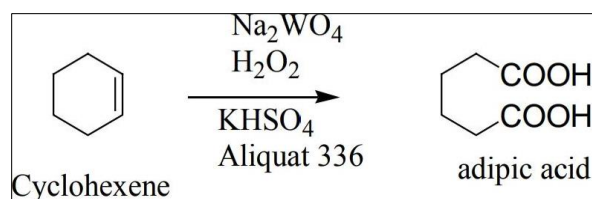
**9. Green oxidation reaction:** Synthesis of adipic acid by S. M. Reed and J. E. Hutchison [11]

#### Conventional Procedure



- **Non-green Component:** This procedure involves corrosive conc. nitric acid. This causes evolution of oxides of nitrogen. The reaction has to be carried out in fume cupboard and oxides of nitrogen need to be absorbed in water.

#### Green Procedure



#### Chemicals Required

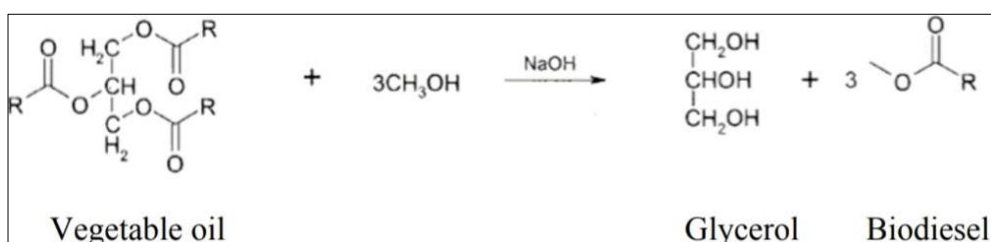
- Cyclohexene - 2 g
- Sodium Tungstate - 0.5 g
- Potassium hydrogen sulphate - 0.37 g

- Aliquat 336 - 0.5 g
- Hydrogen peroxide (30%) - 12 ml
- To a 50 ml round- bottom flask fitted with a condenser sodium tungstate dihydrate (0.50 g) was added. This was followed by addition of aliquat 336 (0.5 g), 30% hydrogen peroxide (12 ml) and potassium hydrogen sulphate (0.37 g).
- The mixture was shaken and then cyclohexene (2 g) was added. The reaction mixture was heated on a sand bath to reflux for 2 hrs. The progress of the reaction was monitored by observing whether the layers are separated.
- As the liquid cyclohexene was converted to the water soluble adipic acid, the organic layer will eventually disappear. After two hours of reflux, the round-bottom flask was removed from the sand bath. Upon cooling, the crude adipic acid was precipitated. The crude sample was recrystallized from water to get pure adipic acid.

- **Melting Point**-153 °C
- **Yield:** 2.5 g (70%)
- **Green Context**
- Eliminates the use of nitric acid
- Atom economy: Waste by-products are minimized, better yield
- Use of hydrogen peroxide as oxidizing agent in place of KMnO<sub>4</sub> or HNO<sub>3</sub>
- Phase transfer catalysis

#### 10. Transesterification reaction: Synthesis of biodiesel by J. E. Thompson <sup>[12]</sup>

This experiment focuses on synthesis of diesel fuel from vegetable oil. The mechanism involves a transesterification reaction, the process of transforming one type of ester into another type of ester.



#### Green Reaction

##### Chemicals Required

Vegetable oil - 100 ml

Methanol - 20 ml

Sodium hydroxide - 3 pellets

- **Green Procedure:** The finely ground anhydrous NaOH was added into pure (99% or higher purity) methanol (20 ml) in a 250 ml Erlenmeyer flask and stirred vigorously until all the NaOH was dissolved. The pure vegetable oil (100 ml) was warmed to about 40°C in a 250 ml beaker. The warmed-up oil was poured into the methoxide solution with continuous stirring. At first the mixture would become cloudy, but should soon two layers would separate. This was stirred for 15-20 minutes. The contents of the flask were transferred into a 250 ml separatory funnel. The mixture will separate into two different layers. The glycerol will fall to the bottom, and the methyl ester (biodiesel) will float to the top. Allow the experiment to sit for an hour. The stopcock of the separatory funnel was opened and the glycerol was allowed to drain into a small beaker.

##### Green Context

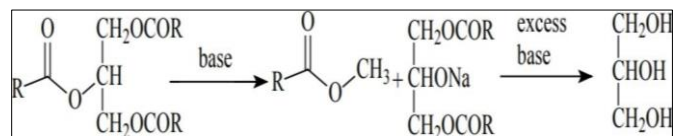
This lab experiment demonstrates three key green principles: the use of renewable feedstock, catalysis and design for degradation. Vegetable oil is a renewable starting material as it is derived from growing plants, rather than irreplaceable material like the earth's petroleum and natural gas supplies. The reaction is catalyzed by NaOH making this process economically viable for the industrial scale production of biodiesel. Biodiesel is an excellent product as it is environmentally friendly.

#### Safety

**Methanol:** Flammable and poisonous. Dispose excess by allowing it to evaporate in the fume hood.

**NaOH:** Very corrosive. Causes severe burns. May cause permanent eye and very harmful by ingestion.

#### Mechanism



#### 11. Solvent-free reaction: Microwave-assisted ammonium formate-mediated Knoevenagel reaction by S. Bhar <sup>[13]</sup>

##### Chemicals Required

- p-Anisaldehyde: 1.32 g
- Ethyl cyanoacetate: 1.13 g
- Ammonium formate: 630 mg
- Domestic Microwave Oven

##### Procedure

p-Anisaldehyde (1.32 g), ethyl cyanoacetate (1.13 g) and ammonium formate (630 mg) were intimately mixed in a round bottomed flask fitted with CaCl<sub>2</sub> drying tube and placed on a bed of alumina taken in a beaker.

This was then subjected to microwave irradiation for 90 seconds (with an installment of 30 sec each at a power level of 300 watts followed by intermittent cooling). After completion of reaction, it was taken out, cooled to room temperature and crushed ice (20 gm) was added to the reaction mixture and shaken well.

The solid product, precipitated in a granular form, was filtered, washed well with water and dried to furnish ethyl 2-

cyano-3-(4'-methoxyphenyl)-propenoate (1.84 g, 80%) in practically pure form. The product can be further purified by recrystallization from ethyl acetate-petroleum ether (60-80 °C)

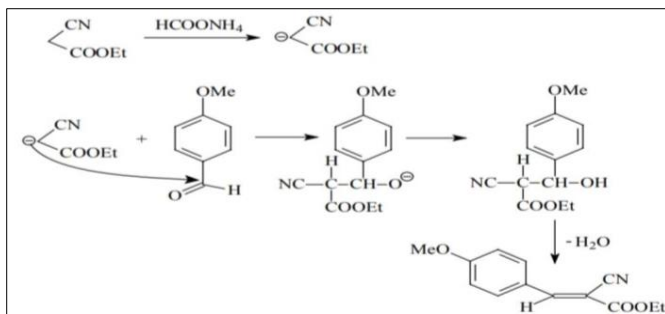
**Melting Point:** 88 °C

**Yield:** 1.8 g (80%)

#### Green Context

- Solvent-free reaction procedure
- Simple workup and rapid conversion (within 90 sec)
- Use of microwave energy for activation

#### Mechanism



#### 4. Result and Discussion

A new approach that combines the application of chemistry with economic growth and environmental protection. Develop a strategy for a sustainable chemical processing industry. It saves limited resources through cost-effectiveness and prevents environmental pollution. Therefore, a fundamental principle of green chemistry is to develop products and processes that reduce or eliminate any waste generation. The most frequently reported green chemical activities were for methanol, zinc and zinc compounds, lead and lead compounds, toluene and ammonia. The chemical manufacturing and metalworking sectors claim to be the greenest chemical operations. Traditional methods should be used whenever possible. It has been replaced with something more eco-friendly to convey the message of this release. The ultimate goal of green chemistry is to completely reduce the flow of chemicals into the environment. Although this goal currently seems unattainable, advances in green chemistry research and their application through a continuous approach will provide the chemical industry with specialized chemicals. safer and more satisfactory processes. there is no doubt.

#### 5. Conclusion

The GREEN chemistry experiments are introduced not to replace the conventional method in any significant way, but they are to be considered as additions to the existing diary. This not only provides a broader view of different techniques, Seeking innovative minds for future growth and development Common themes with a focus on the foundations of green chemistry. Teachers are allowed to conduct regular tests to assess students' understanding of the experiments performed.

#### 6. Reference

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