3. MICROWAVE & ULTRASOUND ASSISTED GREEN SYNTHESIS

3.1 INTRODUCTION OF MAOS

Electromagnetic waves with wavelength between **30 cm to 0.03 cm** (frequencies of **1 GHz to 1000 GHz**) are called as microwaves. Generally **micro wave ovens** and microwave appliances operate at a fixed frequency of **2.45 GHz** (wavelength of **12.2 cm**). The microwave radiations are used in Radio Detection and Ranging (RADAR).

The frequency of molecular rotation falls under the frequency of the microwave region. The molecules with a **permanent dipole moment** undergo dipolar rotation and ionic conduction upon irradiation of microwaves. In dipolar rotation, the molecules rotate back and forth to align its dipole in the direction of electric field. It is called as dipolar rotation and it causes friction between the molecules and generates heat. The ionic species move translationally in presence of electric field and the friction between the moving free ions generates heat.

The classical heating involves transfer of heat by preheated molecules. The microwave heating associates with core and **homogeneous heating**.

A solvent that is more polar has stronger dipole and absorb more microwave energy and a solvent with less polar has weaker dipole and absorb less microwave energy. The solvents can be divided into three different levels based on absorption of microwave energy. These are: low, medium, and high absorber. Generally, low absorbers are low polar hydrocarbons while the high absorbers are more polar compounds.

Microwave Absorbance Levels

S.No.	Absorbance Level	Solvents
1	High	DMSO, ethanol, methanol, propanol, nitrobenzene, formic acid, ethylene glycol.
2	Medium	Water, DMF, butanol, acetonitrile, HMPA, acetone, nitromethane, acetic acid, trifluoroacetic acid.
3	Low	Chloroform, DCM, pentane, hexane, benzene, carbon tetrachloride, ethyl acetate, pyridine, triethyl amine, toluene.

3.2 APPARATUS OF MAOS

Microwave ovens are used to perform microwave assisted organic synthesis. The apparatus comprises of two types of ovens: 1. Single mode microwave oven 2. Multi-mode microwave oven.

Microwave ovens consist of four main components, which are: 1. High power source, 2. Waveguide feed, 3. Oven cavity and 4. Reaction vessel.

1. ***High power source:*** The high-power source of microwaves is magnetron. It is a thermionic diode vacuum tube consists of cathode and anode.
2. ***Waveguide feed:*** It is a rectangular channel made with metal sheet. The reflective walls of waveguide feed are made with microwave transparent materials such as teflon or polystyrene. It transmits microwaves from the magnetron to the microwave cavity.
3. ***Oven cavity:*** It is the place where material is placed to heat. It is generally made of glass or fiber materialwith reflective surfaces which increase the oven efficiency and prevent the hazardous leakage. The fans in microwave oven remove hot air and vapors and prevent oven from getting heated up to higher temperatures.
4. ***Reaction vessel:*** It is made with microwave transparent materials such as teflon, polystyrene, pyrex or borosilicate glass. These materials are poor absorbers of heat and withstand at higher temperatures.

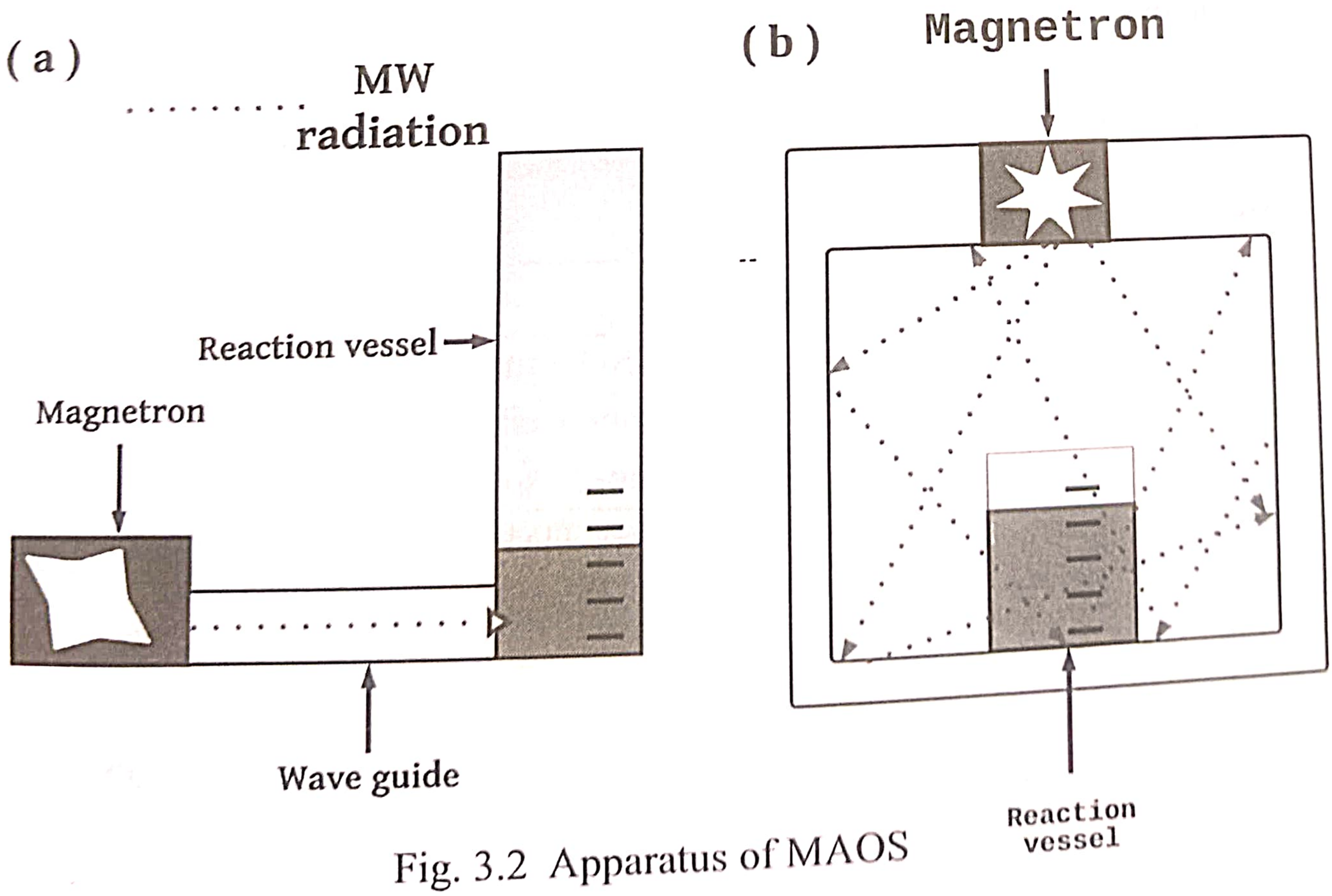


Fig. 3.2 Apparatus of MAOS

3.3 ADVANTAGES & DISADVANTAGES OF MAOS

Advantages

- Microwave radiation transmits through the walls of the vessel and heats only the reactant and solvent, not the reaction vessel.
- Uniform heating takes place throughout the material.
- Handling of MAOS is very easy.
- Microwave irradiation accelerates rate of the reaction, decreases reaction time and increases yield of the reaction.
- MAOS offers improved reproducibility, rapid synthesis and rapid optimization.
- Desirable chemical and physical effects are produced.
- Microwave heating facilitates the solvent-free and solid-supported reactions (dry reactions).
- Better and rapid process control is achieved.
- Low operating cost.
- Microwave irradiation activates catalysts.
- MAOS reduces production of waste by reducing unwanted side reaction and formation of by-products.
- MAOS forms high purity products.
- Low energy input.
- MAOS involves usage of green or eco-friendly solvents.
- Reduction in heat loss from the reaction vessel and environmental heat loss can be avoided.
- MAOS is a regioselective and chemo selective.
- Evaporation of solvent is reduced.
- Flexibility in reaction conditions.

Disadvantages

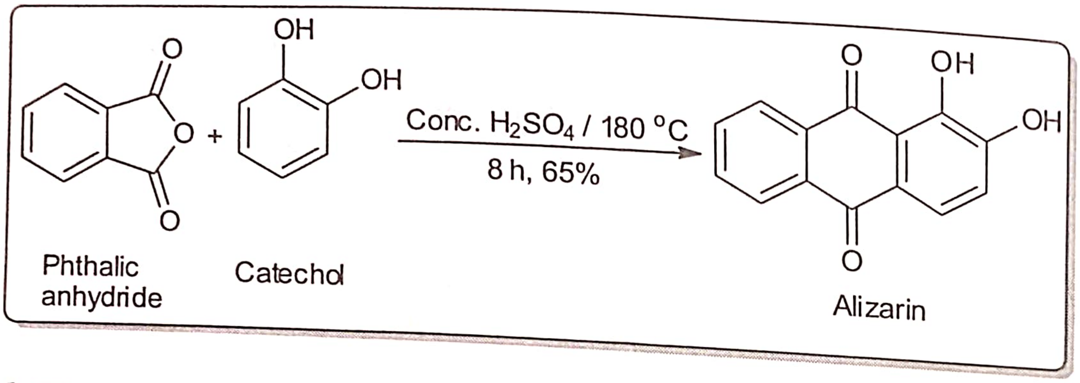
- Equipment is expensive.
- Heat force control is difficult.
- MAOS is not suitable for thermally unstable compounds.
- The closed container is dangerous because it may explode.
- In situ monitoring.
- Water evaporation.
- Expensive setup.
- More maintenance cost.
- Every solvent and reagent absorb microwave energy differently.

3.4 EXAMPLES OF MAOS

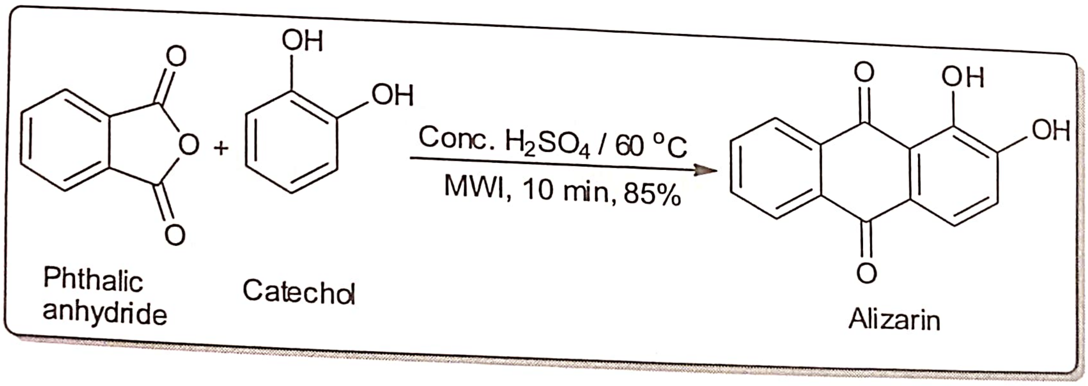
3.4.1 Synthesis of Fused Anthraquinones

Anthraquinones (AQ) and its derivatives are widely used in the production of liquid crystals, dyes, pesticides and medicines.

Conventional Method: The reaction of phthalic anhydride with catechol in presence of dilute H_2SO_4 at 180 °C forms derivative of anthraquinone, alizarin. The reaction requires 8 hours, and the yield of the reaction is 65%.



Green Method: The reaction of phthalic anhydride with catechol in a microwave oven in presence of dilute H_2SO_4 at 60 °C forms alizarin. The reaction requires only 10 minutes, and the yield of the reaction is 85%.

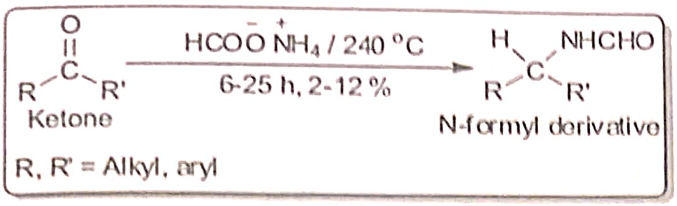


The microwave assisted organic synthesis of alizarin has showed greater reduction of reaction time, temperature and significant increase in the yield.

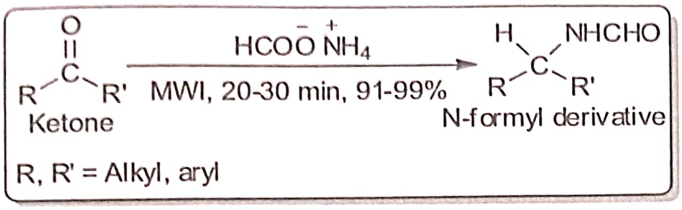
3.4.2 Leuckart Reductive Amination of Ketones

The reductive amination of carbonyl compounds (aldehydes or ketones) with ammonium formate or combination of formic acid and formamide forms N-formyl derivative.The hydrolysis of N-formyl derivative forms amines. It is known as Leuckart reaction.

Conventional Method: The conventional Leuckart reaction needs high temperature (240 °C) and takes long reaction times (6 to 25 hours). The prolonged exposure to high heat for long time leads to thermal decomposition of products and lower yields (2-12%).



Green Method: When the reaction is carried out using microwave irradiation under solvent free conditions, it takes place in short time (20-30 minutes) with high yields (91 to 99%).

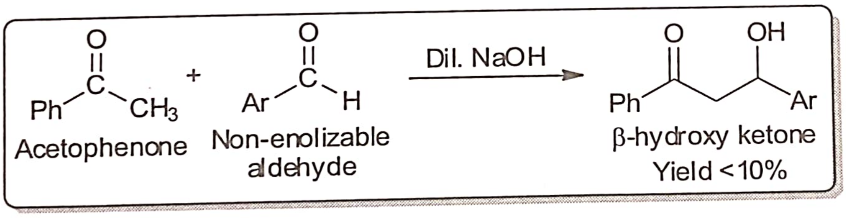


3.5 EXAMPLES OF ULTRASOUND ASSISTED SYNTHESIS

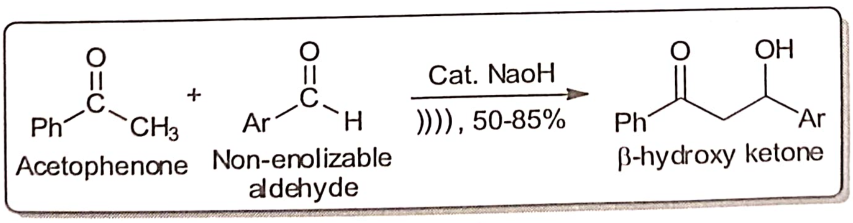
3.5.1 Aldol Condensation

The condensation reaction between aldehyde or ketone containing at least one alpha hydrogen with a carbonyl compound forms β-hydroxy aldehyde or β-hydroxyketone, followed by dehydration to give α, β-unsaturated carbonyl compounds. It is known as aldol condensation. Aldol condensations are important in formation of carbon–carbon bonds in organic synthesis.

Conventional Method: Aldol condensation reactions are generally catalyzed by strong acids or bases. The presence strong acid or base promotes the reverse reaction and self-condensation of the reacting molecules lead to low yields and formation byproducts.

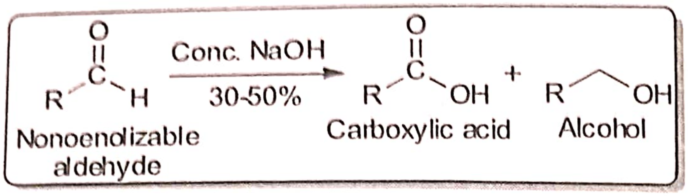


Green Method: High intensity ultrasound assisted aldol condensation reaction under water takes place in short time with good yields (50-85%). It eliminates many byproducts formed in conventional method.

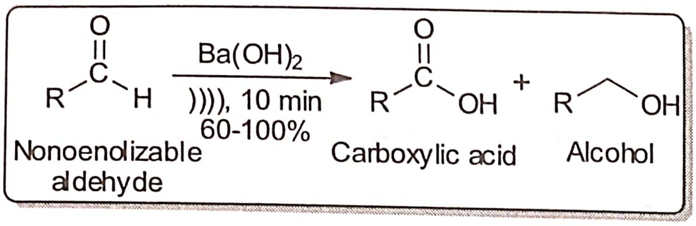


3.5.2 Cannizzaro Reaction

The redox disproportionation reaction of non-enolizable aldehydes into carboxylic acids and alcohols in presence of strong bases is known as Cannizzaro reaction.



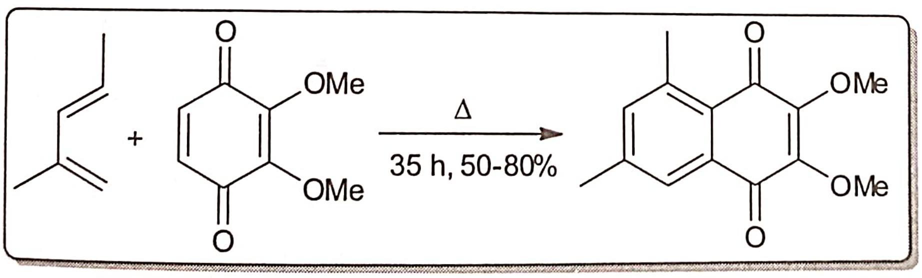
Green Method: The ultrasound assisted Cannizzaro reaction has exhibited short reaction time (10 min) with increase in yields (60-100%). No reaction is observed in absence of ultrasound during 10 min time.



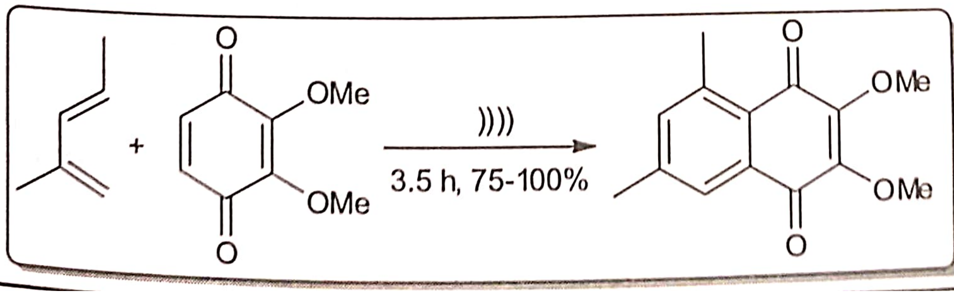
3.5.3 Diels-Alder Reaction

The Diels-Alder reaction is a thermal [4+2] π cycloaddition reaction between conjugated diene and reactive alkene or alkyne (dienophile) which forms cyclohexene derivative.

Conventional Method: The reaction between substituted 1,3-butadiene with substituted 1,4-benzoquinone forms substituted 1,4-naphthoquinone. The solvents used in conventional method are benzene, toluene and dichloromethane. This method has several disadvantages such as long reaction period (35 h) and the solvents employed are toxic. It is unsuitable for some dienes which have carboxy or methyl substituents.

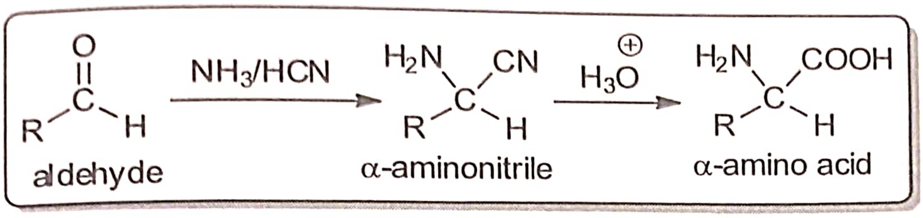


Green Method: Ultrasound enhanced the yield (75-100%) of the Diels-Alder reaction with shortening of reaction period (3.5 h).

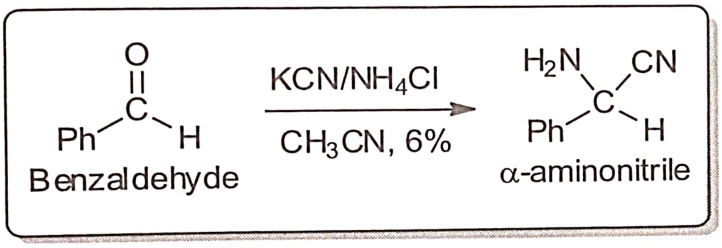


3.5.4 Strecker's Synthesis

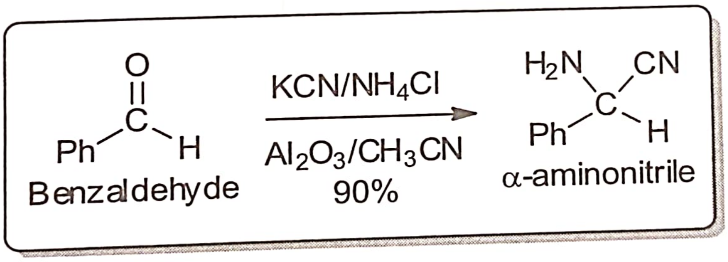
The Strecker's synthesis is a two-step procedure used to synthesize α-amino acids from aldehyde. The condensation reaction of an aldehyde with ammonia in presence of cyanide forms α-aminonitrile, which upon hydrolysis produces α-amino acid.



Conventional Method: The direct reaction between aldehyde, ammonia and cyanide forms mixture of products along with α-aminonitrile with poor yield (6%).



Green Method: The sonochemical reaction between aldehyde, ammonia and cyanide in presence of alumina suspended in acetonitrile mainly forms α-aminonitrile with good yield (90%).



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