5

MICROWAVE AND ULTRASOUND ASSISTED GREEN SYNTHESIS

5.1. MICROWAVES ASSISTED ORGANIC SYNTHESIS (MAOS)

- Microwave assisted synthesis is considered as an important approach toward green chemistry, because this technique is more eco-friendly.
- Due to its ability to couple directly with the reaction molecule and by passing thermal conductivity leading to a rapid rise in the temperature, microwave irradiation has been used to improve many organic synthesis.
- **Microwave chemistry** is the science of applying microwave radiation to chemical reactions.
- Microwave synthesis represents a major breakthrough in synthetic chemistry methodology.
- **Microwaves** may be considered as a more efficient source of heating than **conventional heating** (Steam or oil heating), since the energy is directly imparted to the reaction medium rather than through the walls of a reaction vessel.
- The rapid heating capacity of the microwave leads to a considerable saving in dissolution of the reaction time.
- The problem associated with waste disposal of solvents has been overcome by performing reactions without a solvent under microwave irradiation.
- Microwave radiations are electromagnetic waves.

5.2. MICROWAVE SYNTHESIS APPARATUS

- The reaction-vessel for microwave induced organic reaction, is a tall beaker, loosely covered.
- The capacity of the beaker should be much greater than the volume of the reaction mixture.
- Alternatively, teflon and polystyrene container can be used. These materials are transparent to microwaves.

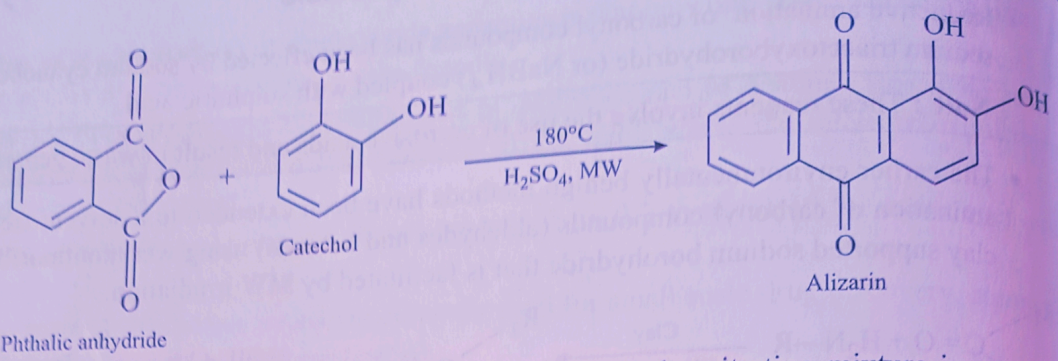
> **Note :** Metallic containers should not be used as reaction vessels, as it gets heated soon due to preferential absorption and reflection of rays.

The apparatus for MAOS include :

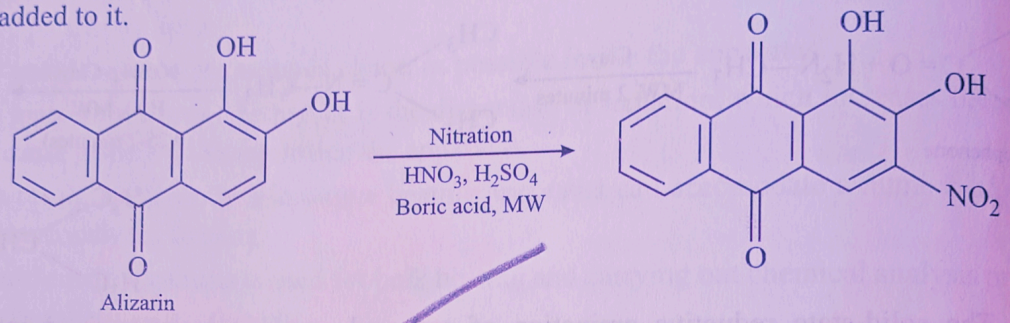
1. Single-mode microwave ovens, and
2. Multi-mode microwave ovens.

1. Single-mode microwave apparatus

- The differentiating feature of a single-mode apparatus is its ability to create a standing wave pattern. This interface generates an array of nodes where microwave energy intensity is zero, and an array of antinodes where the magnitude of microwave energy is at its highest.



2. Compound (II) is prepared by the nitration of alizarin by nitrating mixture in presence of boric acid in a vessel and is irradiated in a microwave oven. The product is cooled and water is added to it.



5.4. ADVANTAGES OF MAOS

Microwave assisted synthesis has become highly relevant in the field of green synthesis. This is due to the reduction of the number of synthetic steps.

This technique has some other advantages over conventional methods. These are :

- Shortening the reaction times,
- Increasing the reaction yields,
- Increasing the homogeneity of the heating,
- Avoid or decrease the surge of by-product,
- No selective heating of the surface,
- Energy savings process,
- Lower processing cost,
- Small narrow particle size distribution, and
- High purity over other conventional approaches.

The main advantages of microwave assisted organic synthesis are :

Faster reaction

- The microwave-enhanced chemical reaction rate can be faster than those of conventional heating methods by as much as 1,000 times.
- The microwave can use higher temepratures than conventional heating system, and consequently the reactions are completed in few minutes instead of hours. *e.g.*, synthesis of fluorescein takes only 35 minutes by microwave heating as compared to 10 hours of conventional heating.

Better yield and higher purity : Higher yield of product is obtained due to formation of less side product in microwave heating.

e.g., 85% to 97% yield of aspirin is obtained by microwave synthesis.

Energy saving : Heating by microwave radiation is a highly efficient process and results in significant energy saving.

Uniform and selective heating

In case of microwave heating, only the solvent and the solute particles are excited, resulting in uniform heating of the solvent.

Selective heating is based on the principle that different materials respond differently to microwaves. Some materials are transparent whereas others absorb microwaves.

Green synthesis

Reactions conducted using microwaves are cleaner and more ecofriendly than conventional heating methods.

- Microwaves heat the compounds directly, therefore usage of solvents in the chemical reaction can be reduced or eliminated.
- The use of microwaves has also reduced the amount of purification required for the end products of chemical reactions involving toxic reagents.

5.5. DISADVANTAGES (OR LIMITATIONS OF MAOS)

- One of the limitations of microwave scale-up technology is the restricted depth of microwave irradiation into absorbing materials. This means that solvent or reagents in the centre of large reaction vessel are heated by convection and not by direct 'in core' microwave dielectric heating.
- Microwaves can not heat materials such as sulphur, which are transparent to their radiation.
- Improper use of microwave heating for rate enhancement of chemical reactions involving radioisotopes may result in uncontrolled radioactive decay.
- Conducting microwave reactions at high-pressure conditions may result in uncontrolled reactions and cause explosions.
- Health hazards related to microwaves are caused by the penetration of microwaves.

5.6. ULTRASOUND ASSISTED ORGANIC SYNTHESIS

- Ultrasound refers to sound waves having frequencies higher than those to which the human ear can respond (> 16 kHz) (Hz = Hertz = cycles per second).
- **'Power ultrasound'** (between 20 and 100 kHz), provides a form of energy for the modification of chemical reactivity which is different from the normally used *i.e.*, light and pressure.
- Under ultrasound irradiation, organic transformations occur in high yield, short reaction times, or milder conditions.
- Ultrasound-assisted technique is increasingly used for the acceleration of organic reactions and it is an environment-friendly synthetic protocol.

5.7 INSTRUMENTATION

- The instrumentation for the generation of ultrasound requires an ultrasonic transducer (a device by which electrical or mechanical energy can be converted into sound energy).
- The most commonly used are the electromechanical transducers which convert energy into sound (these are based on Piezo-electric effect).
- The Piezo-electric effect is the production of a potential difference across opposite faces of a crystal of a material when it is subjected to sudden compression and is found in some crystalline materials like quartz.
- The inverse effect is produced when a rapidly alternating potential is placed across the faces of Piezoelectric crystal.
- This will induce dimensional changes in the crystal and thus generate vibrational (sound) energy.
- Two commonly used ultrasound instruments are as follows :

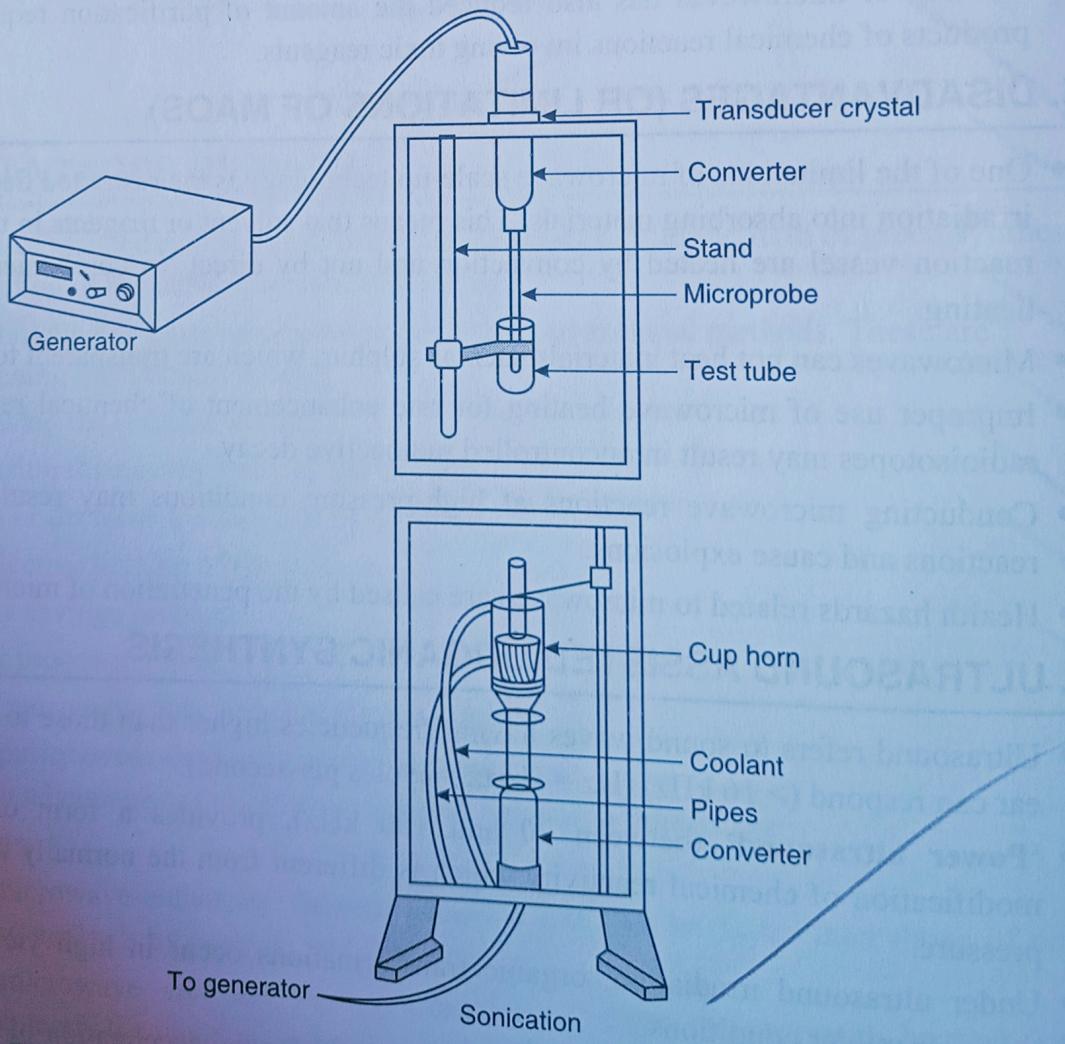


Fig. 5.1 : Ultrasound instruments

- However, ultrasound is much more effective in these reactions because ultrasonic waves generate extremely fine emulsions which result in very large interfacial contact areas between the liquids—the result is a dramatic increase in the reactivity between species dissolved in the separate liquids and therefore, should react much faster than the conventional phase-transfer conditions.
- In some cases, it has been found that a combination of sonication and PTC has a better overall effect than either of the two techniques alone.

3. Heterogeneous solid-liquid reactions

These are of two types :

Type I—those in which the solid serves as one of the reagents, and is consumed during the reaction.

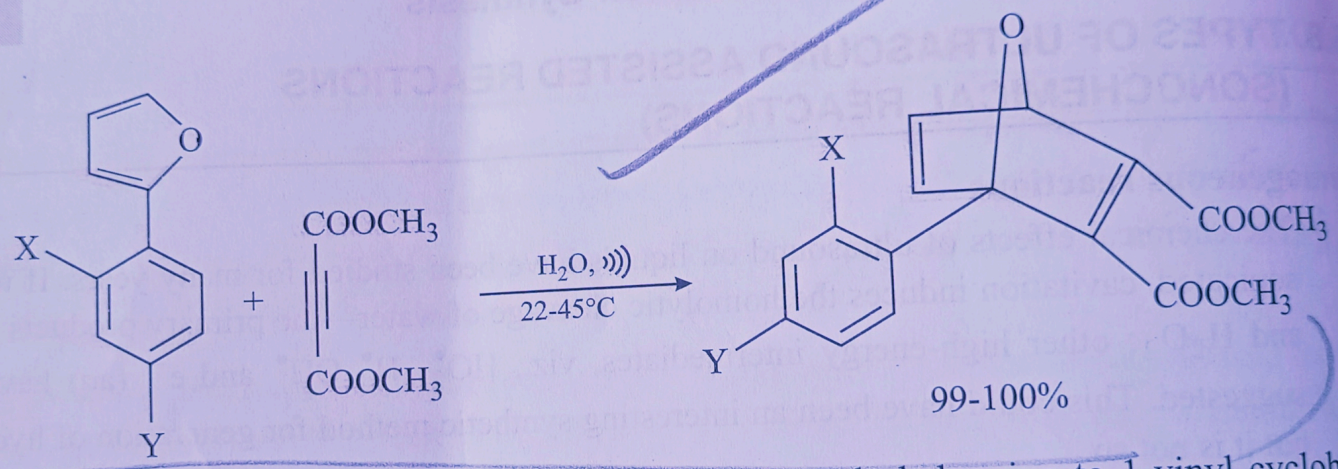
The type II are those in which the solid often a metal functions either as a catalyst or is consumed.

The type I reactions have been used with success to improve yields—this is due to the dispersing and microstreaming effects of ultrasound.

In type II reactions, the cavitational erosion is the major effect which is observed when ultrasonic waves propagate towards, or in the vicinity of a solid. The erosion of the metal follows the sequence Pb > Mg > Zn > Cu. Alkali metals have been submitted to sonochemical conditions is a variety of reactions.

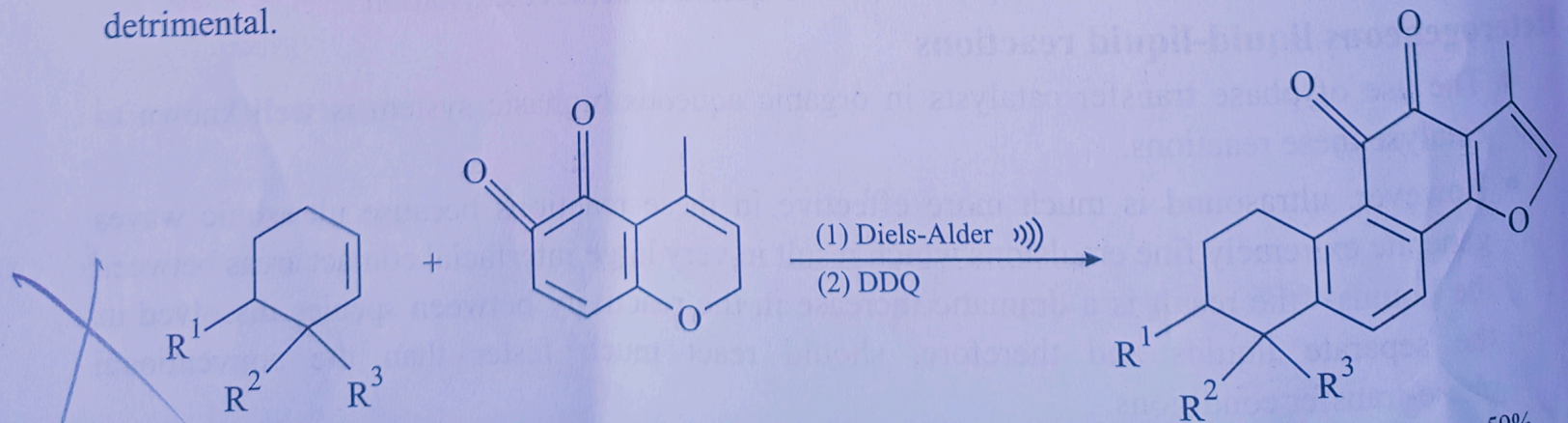
5.9. DIELS-ALDER REACTION

- Diels-Alder reaction is facilitated by sonication.
- The addition of dimethylacetylene dicarboxylate to furan derivatives in water at 22-45°C gives quantitative yield of adduct.



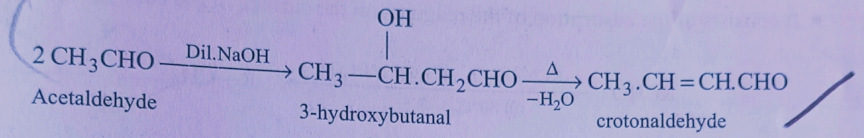
The Diels-Alder cycloaddition of various dienes (mostly belonging to 1-vinyl cyclohexenes) with *o*-quinone proceeds very well under ultrasound conditions to give the expected adducts in 59% yield compared to 30% under normal reaction conditions.

Better results are obtained by sonication of the neat mixture, and the presence of solvent is detrimental.

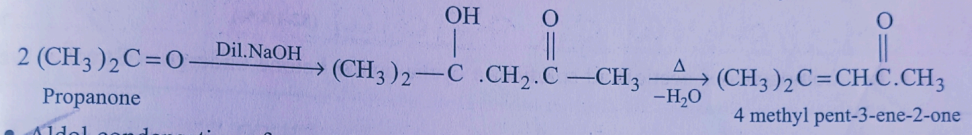


5.10. ALDOL CONDENSATION

- The aldol condensation is one of the most important C – C bond forming reactions in organic synthesis.
- The conventional aldol condensation involves reversible self-addition of aldehydes containing α-hydrogen atoms; the formed β-hydroxy aldehydes undergo dehydration to give α, β-unsaturated aldehydes.
- The reaction can occur either between 2 identical or different aldehydes, two identical or different ketones and an aldehyde and a ketone.



Acetaldehyde — 3-hydroxybutanal — crotonaldehyde



Propanone — 4 methyl pent-3-ene-2-one

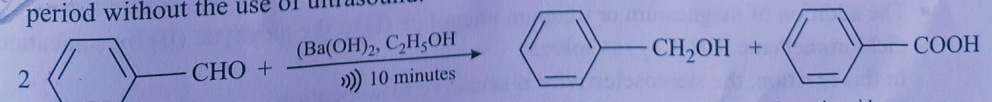
- Aldol condensation of acetyl ferrocene with aldelydes afforded ferrocenylenones in 76-92% yields under ultrasound at room temperature.
- High intensity ultrasound (HIU) promoted the aldol type condensation as an alternative mean of synthesizing pyrazines in a **Maillard reaction (MR) model**.
- The HIU would generate an extremely high temperature and pressure environment that is favored by the aldol-type condensation as a high-pressure favored reaction.

The Aldol reaction under high intensity ultrasound (HIU)

- A number of aldols that under usual conditions would undergo elimination were isolated in good yields.
- Within 15-30 minutes, acetophenone reacted with non-enolizable aldehydes to afford the aldol exclusively, while under conventional conditions (stirring or heating under reflux) the same compounds either failed to react or gave, after several hours, the enone often in complex product mixtures.
- Benzaldehyde reacted with a series of 1, 3 dicarbonyl compounds to afford the corresponding bis (benzylidene) adducts.

5.11. CANNIZZARO REACTION

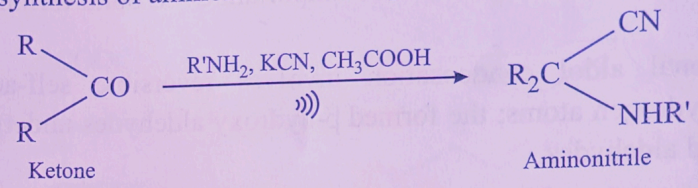
- The cannizzaro reaction under heterogeneous conditions catalysed by barium hydroxide is considerably accelerated by **low intensity ultrasound** (cleaning bath).
- The product yields are 100% after the minutes, whereas no reaction is observed during this period without the use of ultrasound.



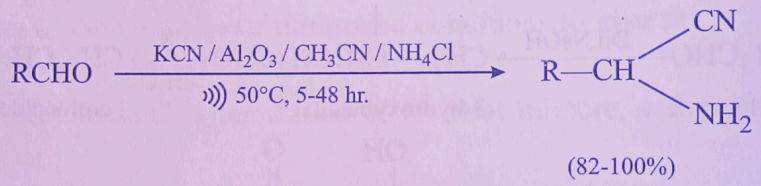
Benzaldehyde — Benzylalcohol — Benzoic acid

5.12. STRECKER REACTION

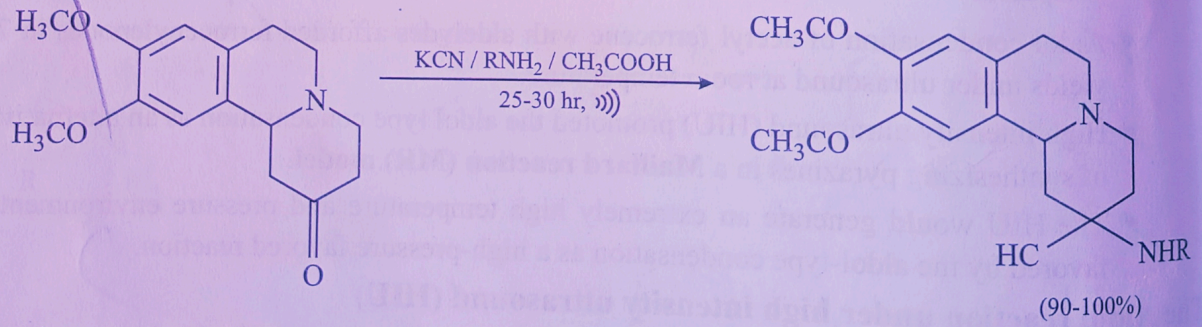
- The Strecker synthesis of aminonitriles takes place by sonication.



- α-amino nitriles in excellent yield (82-100%) is prepared by modified Strecker synthesis.
- It consists of the adsorption of the reagents on the surface of the catalyst before the reaction.



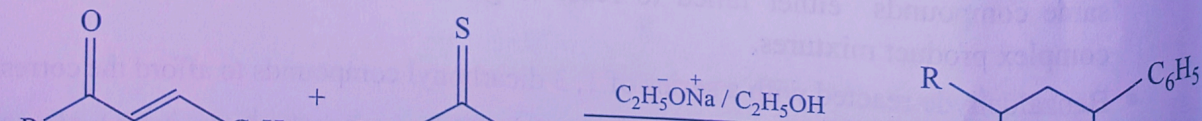
- In a homogeneous acetic acid solution, a cyclic amine ketone undergoes Strecker synthesis easily.



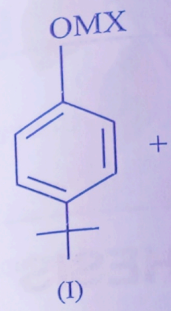
where $R = H, -C_6H_5, -C_6H_5.CH.CH_2$

- Under sonication, basic catalysed addition of thiourea to ferrocenyl chalcones (I) give excellent yield (58-79%) of the product (II).

While thermal process gives mixtures which cannot be separated due to instability of the compounds.



Microwave and Ultra



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MgBr
MgBr
Ti (OPr-i)3

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