• Microwave Assisted Reactions in Water:

1. Hofmann elimination:

In this method, quarternary ammonium salts are heated at high temperature and the yield of the product is low. However, use of microwave irradiation in water-chloroform system gives high yielding synthesis of a thermally unstable Hofmann elimination product.

2. Oxidation of alcohol:

Magnetically nano Fe₃O₄ efficiently catalyzes green oxidation of primary and secondary benzylic and aliphatic alcohols to give the corresponding carbonyl products in good yields. The reactions were carried out in an aqueous medium in the presence of hydrogen peroxide as an oxidant at 50°C.

3. Oxidation of toluene:

Oxidation of toluene with KMnO₄ under normal condition of refluxing takes 10-12 hr. compared to reaction in microwave conditions, which takes only 5 min and the yield is 40%.

4. Hydrolysis of Methyl Benzoate to Benzoic Acid (Saponification):

Saponification of methyl benzoate in aqueous sodium hydroxide under microwave irradiation takes only 2.4 min and gives 84% yield of benzoic acid.

• Microwave Assisted Reactions in Organic Solvents:

1. Diels-Alder Reaction:

The reaction involves 1,4-addition of an alkene (e.g. maleic anhydride) to a conjugated diene (e.g. anthracene) to form an adduct of six membered ring. Under usual condition, the reaction requires a refluxing time of 90 min. Under microwave irradiation diglyme is used as a solvent and 80% yield of the adduct is obtained in 90 sec.

In a similar way anthracene reacts with dimethyl fumarate within 10 min in p-xylene to afford yield where as conventional heating conditions give only 67% yield in 5 hr.

2. Decarboxylation:

Microwave irradiation simplifies the decarboxylation reaction in presence of phase transfer catalyst which afford 90% yield.

Diethyl 2-phenylmalonate

Ethyl-2-phenylacetate

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Conventional decarboxylation of carboxylic acid involves refluxing in quinolone in presence of copper chromite and the yields are low. However, in presence of microwaves, decarboxylation takes place in much shorter time.

• Organic Synthesis in Supercritical Carbon Dioxide:

Use of Supercritical Carbon Dioxide (SC-CO₂) for Dry Cleaning:

Articles of clothing made from fabric cannot be washed in water and require a dry cleaning process. The term dry cleaning is somewhat misleading because a liquid solvent is actually used for removing dirt and stains. Most of the drycleaners use the solvent perchloroethylene or PERC.

Perchloroethylene

Disposal of perchloroethylene, a suspected carcinogen, can contaminate ground water. Besides this, PERC when released into the atmosphere rises to the stratosphere region, where it gets decomposed into chlorine radical by the action of UV rays of the sun. The Cl radicals are responsible for depleting of ozone layer.

PERC
$$\xrightarrow{\text{UV rays}}$$
 $\overset{\cdot}{\text{Cl}}$

$$O_3 + \overset{\cdot}{\text{Cl}} \longrightarrow O_2 + \overset{\cdot}{\text{ClO}}$$

$$Cl\overset{\cdot}{\text{O}} + O \longrightarrow \overset{\cdot}{\text{Cl}} + O_2$$
Net result $O_3 + O \longrightarrow 2O_2$

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The environmental problems associated with dry cleaning clothes and rising costs of complying with environmental laws have encouraged search for alternative methods. One such approach uses liquid or super critical carbon dioxide as the cleaning solvent.

Though carbon dioxide dissolves non-planar substances, most greases and oils (from cloths) turn out to be very insoluble in CO₂. However, the new surfactants increase the solubility of oils and grease in CO₂, in much the same way that soaps increase the solubility of non-polar substances in water. This makes CO₂ a more effective cleaning agent.

The surfactant developed by De Simone is a polymer composed of 'CO₂-philic' segments (which are attracted to CO₂) and 'CO₂-phobic' segments (which are not attracted to CO₂).

$$H = H_2C - \frac{H}{C}$$

$$H_2C - \frac{H}{C}$$

$$C = 0$$

$$OCH_2(CF_2)_6CF_3$$

$$"CO_2-phobic"$$

$$chain segment$$

$$"CO_2-philic"$$

$$chain segment$$

The 'CO₂-phobic' segment can be made lipophilic (attracted to fats, oils and grease) or hydrophilic (attracts to water). When this polymer is placed in a medium of supercritical or liquid CO₂, it assembles into a micelle structure. The 'CO₂-philic' segment surrounds or encase the 'CO₂-phobic' segments.

The micelle structure can encase materials such as greases and oils in the inner 'CO₂-phobic' area of the micelle structure and allow them to be washed away by the CO₂ solvent.

The micellization technologies have produced dry cleaning machines that use liquid CO₂ and a surfactant to dry clean clothes, potentially replacing the environmentally harmful PERC.

• <u>Ultrasound Assisted Organic Synthesis:</u>

Simon-Smith Reaction: (Sonochemical methylenation of alkenes and carbonyl compounds)

Methylenation of alkenes with CH_2I_2 in presence of zinc is referred as Simmon Smith Cyclopropanation. It is possible to carry out the reaction on a large scale in specially designed apparatus. This method has been slightly modified to be run with dibromo methane, much cheaper than the diiodo analogue.

In case of cyclopropanation of dimethyl maleate, the reaction catalyzed with cobalt chloride is stereoselective, which is not the case with nickel chloride.

Methylenation of carbonyl group which frequently requires complex reagents, can be easily accomplished by Simmon-Smith reagent (Zn/CH_2I_2) with sonication.