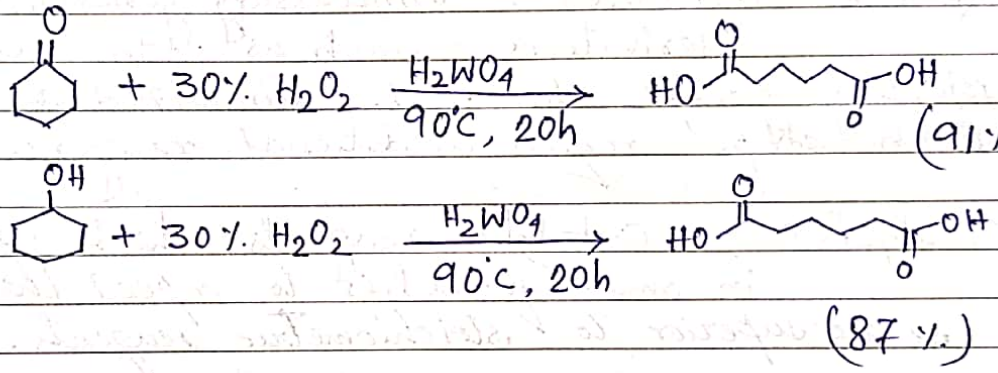
Green Chemistry

Designing a green synthesis

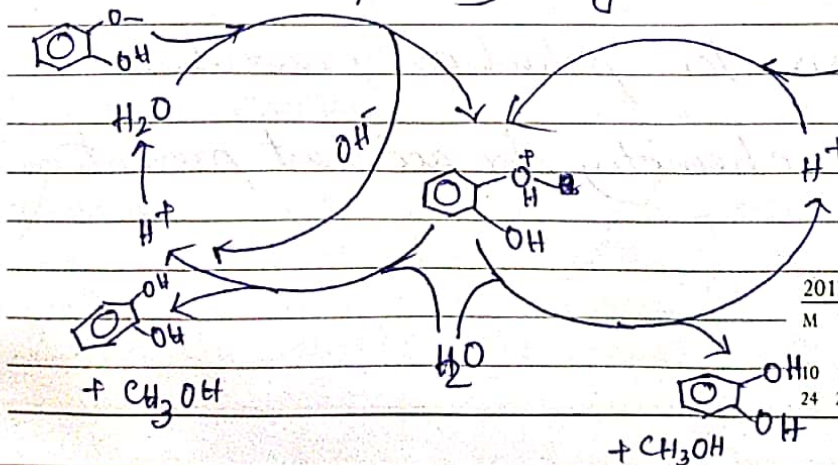
Synthesis of adipic acid ⇒

Cyclohexanone and cyclohexanol are oxidized to adipic acid with aq. 30% H_2O_2 in the presence of H_2WO_4 as a catalyst under organic solvent and halide-free conditions.



Synthesis of catechol ⇒

Guaiacol (a monomer present in lignin) is converted to ~~cate col~~ catechol in organic solvents and water, specially high temperature water.



(*) Effect of pH ⇒ The presence of hydrogen enhances the reaction.
At lower pH, the yield is maximum as it is an acid catalyzed reaction.

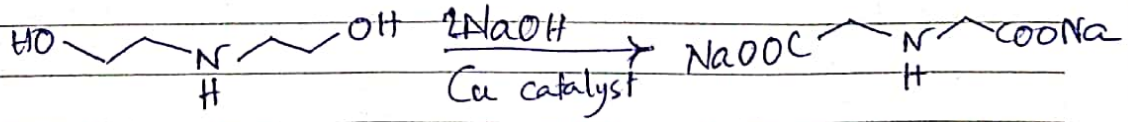
(*) Effect of presence of chlorides : Here $FeCl_3$, $CuCl_2$ are used as catalysts in low pH ≈ 2.6 and 3.8 respectively.

(*) The relative selectivity of phenol and catechol :-
With increasing in pH, the alcohol/catechol ratio increases.

(*) Effect of NaOH in reaction ⇒
The reaction can also be base catalyzed but base catalyst increases the percentage of side products thus decreases the yield.

Synthesis of disodium iminodiacetate ⇒

Catalytic Dehydrogenation ⇒



It is an alternative pathway of traditional Strecker process.

05 28th Week • 186-179 2017
Wednesday • July

Microwave induced Green Synthesis :=

Normally microwaves have wavelengths between 1cm to 1m.

Microwave induced organic reactions, the reactions can be carried out in a solvent medium or on a solid support in which no solvent is used. for reactions in a solvent medium, the choice of solvent is very important.

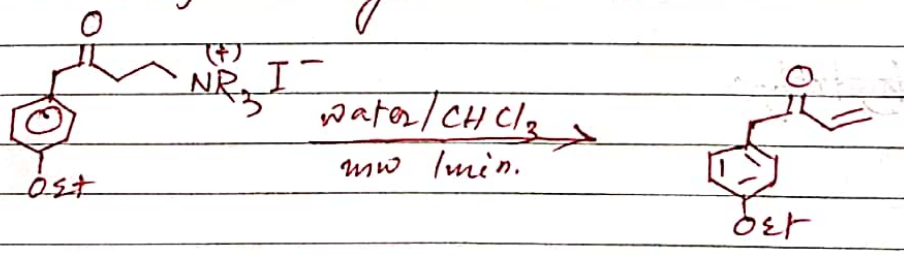
The solvent to be used must have a dipole moment so as to absorb microwaves and a boiling point at least 20-30°C higher than the desired reaction temperature. An excellent solvent in a domestic microwave oven is N,N-dimethylformamide. The solvent can retain water formed in a reaction, thus obviating the need for water separation.

Hydrocarbon solvents cannot be used in microwaves due to lower dipole moment and they absorb microwave radiation very poorly. By adding some polar liquid to a miscible non-dipolar liquid, the mixture will rapidly achieve a uniform temperature under irradiation.

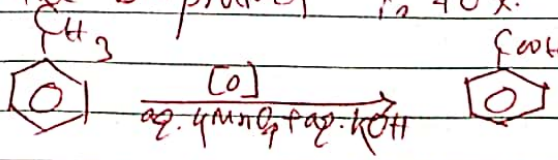
Applications :- Microwave can be used for organic synthesis.
They are divided into three catagories :
i) Microwave-assisted reactions in water
ii) Microwave-assisted reactions in organic solvent
iii). Microwave solvent-free reactions (solid state reactions)

i) Microwave-assisted reactions in water :

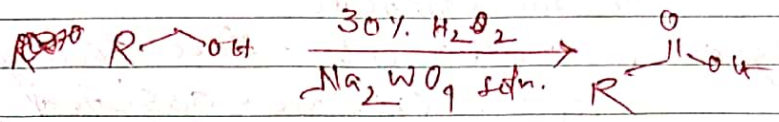
a) Hoffmann Elimination :
Quaternary ammonium salts are heated at high temperature and the yield of the product is low. Microwave irradiation has led to high-yielding synthesis of a thermally unstable Hoffmann elimination product. Here water-chloroform system is used.



b) Oxidation of toluene : Oxidation of toluene with KMnO4 under normal conditions of refluxing takes 10-12 hr compared to rx in microwave conditions it take only 5 min and the product is 40%.

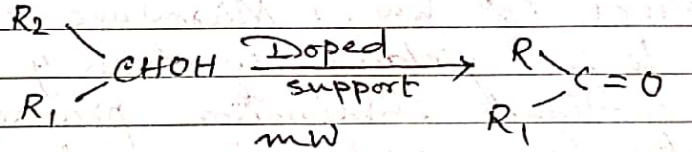


c) Oxidation of ~~ester~~ alcohols ⇒



Primary alcohols can be oxidised to the corresponding carboxylic acid using sodium tungstate as catalyst in 30% aqueous hydrogen peroxide.

Secondary alcohols have been oxidised under microwave irradiation by using doped supports like clayfen, silica manganese dioxide, claycop-H_2O_2, CrO_3-wet alumina, iodobenzenediacetate-alumina etc.



~~d) hydrolysis~~

d) Hydrolysis of methylbenzoate to Benzoic Acid

Saponification of methyl benzoate in aq. NaOH under microwave gives ≈ 81% yield of the benzoic acid.

$$C_6H_5COOCH_3 \xrightarrow[2.5\ min,\ in\ mW]{aq.\ NaOH} C_6H_5COOH$$

ii) Microwave assisted reactions in organic solvents:

This section includes those microwave induced reactions in which one or both the reactants (if liquid) act as a solvent and also those reactions in which organic solvent is used to assist the reaction.

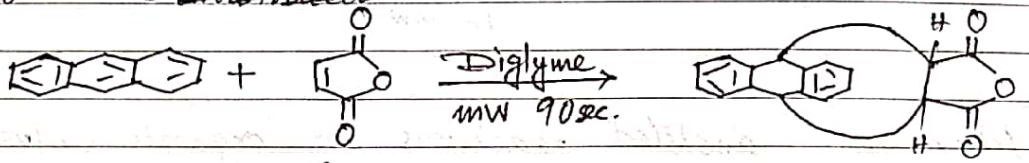
a) Diels-Alder Reaction:

The reaction involves 1,4-addition of an alkene to a conjugated diene to form an adduct of six membered ring. Sunday 09
Under usual condition it requires a reflux period of 90 min. However, under microwave condition, diglyme is used as a solvent and 80% yield of the adduct is obtained in 90 sec.

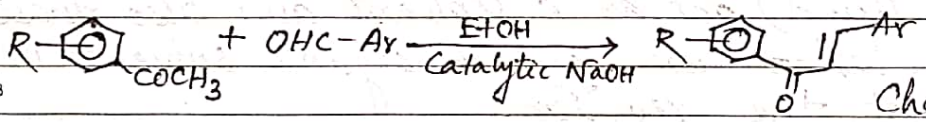
b) Decarboxylation :

Conventional decarboxylation of carboxylic acids involve refluxing in quinoline in presence of copper chromite and the yields are low. However in presence of microwaves, decarboxylation takes place in much shorter time.

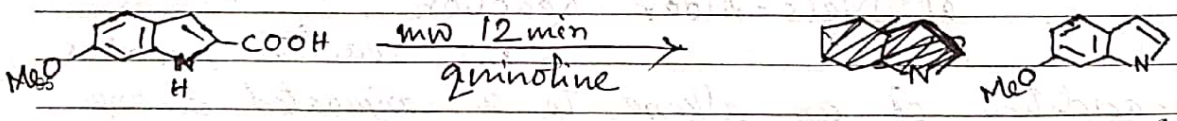
~~Illustrated~~



Anthracene Maleic anhydride (Adduct) 80%.



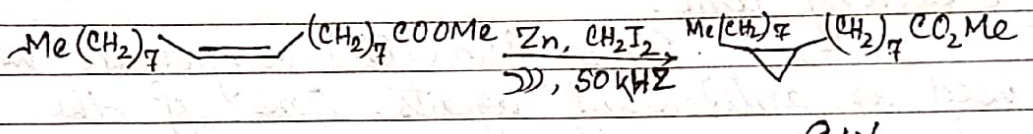
Chalcone
90-100 %.



6-Methoxy indole (99%.)

Ultrasound Assisted green synthesis :-

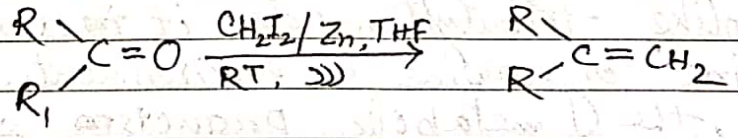
Simmons-Smith reaction → Here sonochemically activated zinc and methylene iodide are used. The generated carbene adds on to an olefinic bond to give 91% yield of the cyclopropane derivative compared to 51% yield by the normal route.



91%.

The reagent Zn/CH_2I_2 is known as Simmons-Smith reagent.

Ketones on reaction with Simmons-Smith reagent results in methylenation of carbonyl group. Sonication or ultrasound replaces many complex reagents used in such ~~methylation~~ methylenation of carbonyl group.



$R = R_1$ = alkyl

R = alkyl $R_1 = H$.

12 | 29th Week • 193-172 | 2017

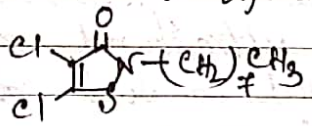
Wednesday • July

Synthesis of an environmentally safe Marine Antifoulant ⇒

The ~~antifouling~~ antifouling agents are used on boat hulls to reduce the build up of marine organisms like algae, plants, diatoms. A build up of these organisms cause additional cost involved in increased fuel consumption and cleaning time.

Tributyltin (TBT) compounds were earlier used as antifoulant agents. One of the main drawbacks was their persistence in the environment and bioaccumulation in various nontarget marine organisms.

Rohm and Haas has developed the use of 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI) as an antifouling agent.



Unlike tributyltinoxide it does not persist in marine organisms or environments. Also in case of DCOI, the metabolic products are non-toxic.