Microwave Induced Green synthesis

Microwaves have wavelength bet^n 1 cm and 1 m

Frequencies → 300 GHz to 300 MHz.

These are similar to significant frequencies of radar and telecommunications devices.

House hold and industrial microwave oven → 2.45 GHz (Freq.) absorbed

In microwave induced organic reactions carried out — solvent medium
— Solid support in which no solvent is used.

⇒ An excellent solvent in domestic microwave oven is N,N-dimethylformamide (DMF)

(ε → dielectric const. → 11.1)

B.p. → 216°C

⇒ Hydrocarbon solvents for ex. hexane, benzene, toluene, xylene are unsuitable solvent due to less D.M. (these absorb microwave radiations poorly).

⇒ liquid CCl_4 do not have a D.M. → cannot be heated by microwave

Reactions in microwave energy instead of conventional heating can manifest in —

1. Highly accelerated reaction rates.
2. Improved yield
3. Stereo or regioselectivity in some cases
4. reduction of side product
5. limited amount of solvent needed.

Reactions conducted in Microwave: — Microwave heats polar molecules due to selective absorption of microwave radiation. Non polar molecules are inert.

Homonuclear diatomic molecules such Cl_2, H_2, etc. & Linear polyatomic molecules CO_2 → do not show microwave spectra.

Microwave spectra occurs in (1–100 cm^{-1}) spectral range of 1–100 cm^{-1}

Microwave region :-

→ Lies betn IR and radio frequency region i.e 1cm to 1m in electromagnetic spectrum.

→ Frequency 300GHz to 300MHz.

→ only wavelength 12.2 cm used carring out reactions (2450MHz).

→ only polar molecules absorbed the microwaves.

→ Non-polar molecules are inactive.

→ very selective as it depends only on the dielectric properties of molecules.

→ Heating under microwave can be explained by dipolar ~~poly~~ polarization.

Microwave oven :→ In recent years, the M.O. has became a very familiar and useful device in Kitchen. Its mode of operation depends upon the absorption by the food of the microwave radiation in which it is placed.

The water molecules in the food absorb the M.W. radiation and are thereby raised to the higher rotational states. and water molecules are excited and the excess rotational energy is re-emitted as heat with the help of which food get cooked.

Conventional oven → external heating

M.W. oven → Internal.

M.W. radiation also affect the human body. Hence, the door seal of the mw. oven must be in good condition to ensure that no radiation leaks out.

Microwave spectra (Rotational) → These spectra result from transitions between the rotational energy levels of a gaseous molecules on the absorption of radiations falling in M.W. region.

~~rotational~~ These spectra shown by molecules which possess a per. D.M. Hcl, CO

Microwave assisted Reactions

Reactions in microwave energy instead of conventional heating can manifest in —

1. Highly accelerated reaction rates.
2. Improved yield
3. Stereo or regioselectivity in some cases.
4. Reduction of side product
5. Limited amount of solvent needed.

Types :-

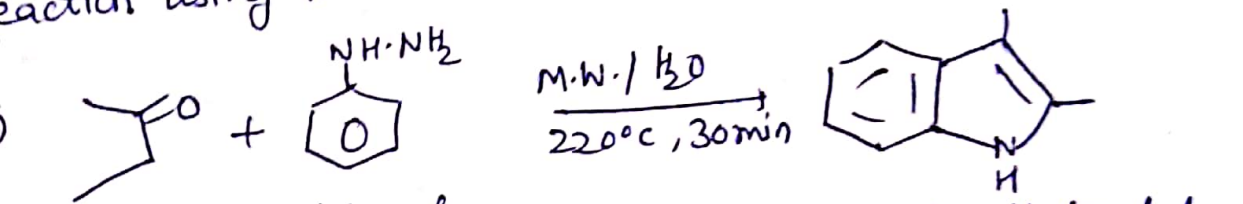
(A) Reaction using polar solvent :-

Drawbacks :-

1. Evaporation of solvent is not perfectly controlled.
2. High vapour pressure is generated due to volatility of solvent.
3. Removal of High Boiling solvents is a difficult process.

Reaction using solvent :-

(1)



Butane-2-one + phenyl hydrazine → 2,3-dimethyl Indole (67%)

(2) $C_6H_5CH_2Cl + H_2O \xrightarrow[3\,min]{M.W} C_6H_5CH_2OH$ (97%)

Conventional method taked 35 min.

(3) Oxidation

$C_6H_5CH_3 \xrightarrow[\text{aq. KOH}]{[O]\ \text{aq. } KMnO_4 +} C_6H_5COOH$ (5 min.) (40%)

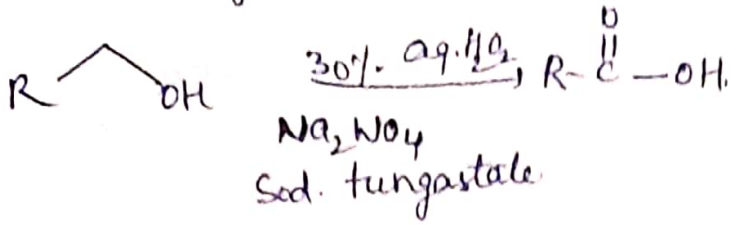
Conv. heating → 12 hrs.

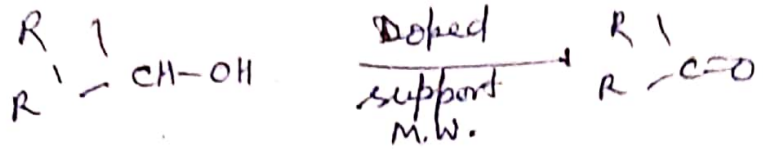
(4) Esterification.

$C_6H_5COOH + n\text{-}CH_3CH_2CH_2OH \xrightarrow[MW,\,6\,min]{Conc.\ H_2SO_4} C_6H_5COOC_3H_7$ (70%)

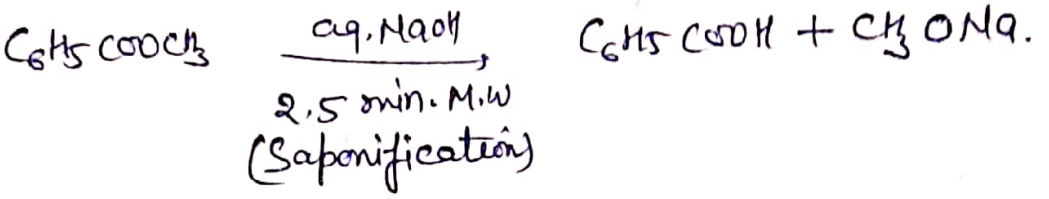
Propyl benzoate.

(5) Oxidation of alcohols

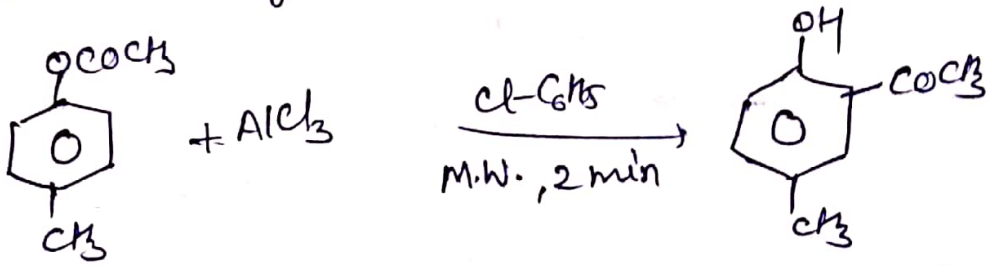




(6) Hydrolysis of Methyl benzoate to benzoic acid



(7) Fries rearrangement :-



2-hydroxy-4-methyl acetophenone (85%)

(B) Reactions in Solvent-free Conditions :→

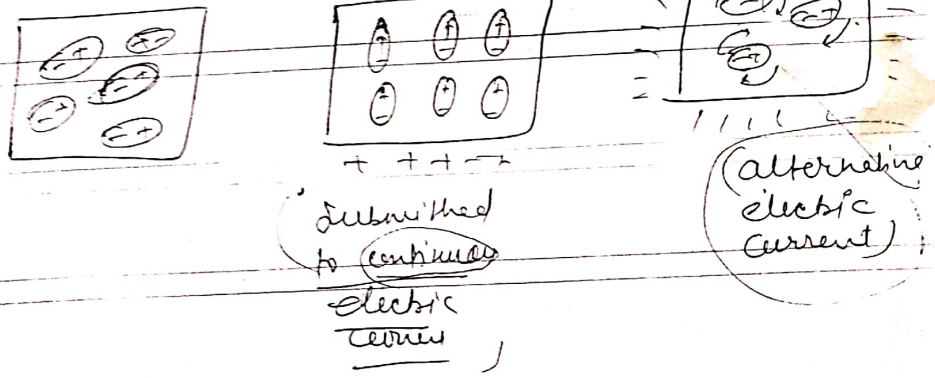
Neat reactions (No solvent)

- Dry media reactions using inorganic solid supports
- Solvent-free techniques represent a clean, economical, efficient and safe ecofriendly procedure and rxn carried out in open vessel without any explosion.

Microwave Induced green synthesis :→

Microwave region
- first used in organic rxn 1970
- 1cm–1m (30GHz – 300MHz)
- region b/w IR and radio frequency region
  - Similar to freq. of radar and telecommunication
- only 12.2 cm (now light) used in rxn
- Solvent to be used must have a dipole moment so as to absorb microwave and b.p. at least 20°–30°
  - Hexane, benzene & toluene
  - Xylene unsuitable because of less dipole moment
- only polar molecule absorb microwave

Microwave heating
- explained by dipolar polarisation



MI A R

Microwave assisted reaction :-

- fast, safe, ecofriendly, simple technique
- Yield ↑
- waste ↓
- Side products ↓
- Limited amount of solvent needed

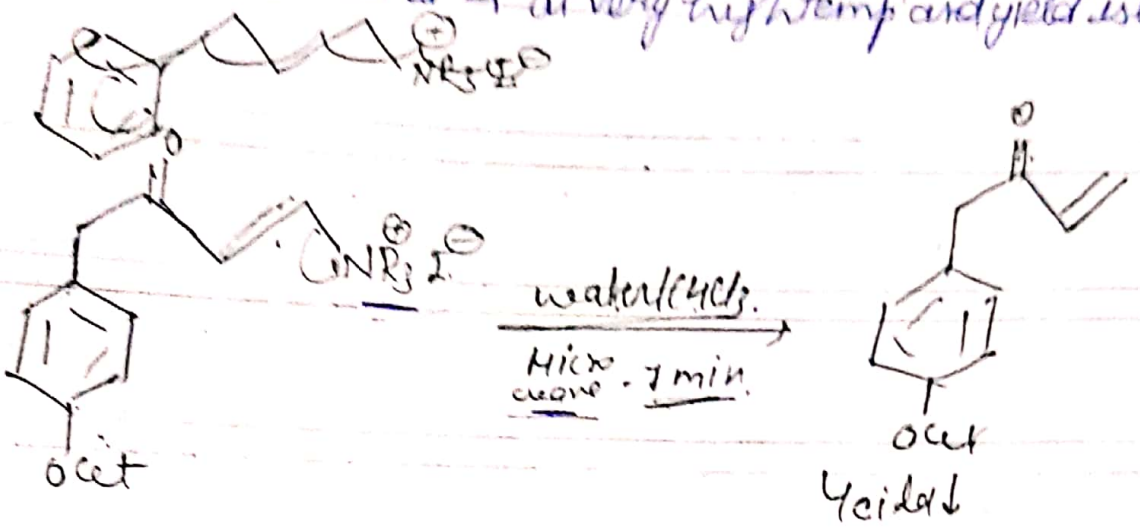
Categories of Microwave assisted reaction

1. Microwave assisted reaction in water
2. Microwave assisted reaction in Organic Solv
3. Microwave Solvent free rxn or (Solid State rxn)
   - Solvent free rxn are → economic efficient
     - safe
     - ecofriendly
     - clean

(1) Microwave assisted rxn in water :-

(a) Hoffmann elimination :-

Normal method → at very high temp and yield is less.



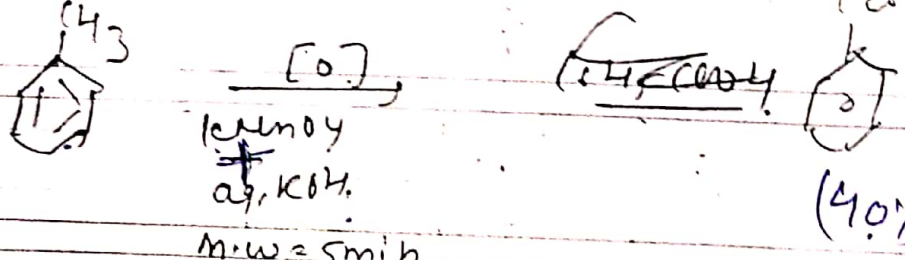
(b) Hydrolysis :- The usual hydrolysis in normal way takes 35 min.

(1) $C_6H_5-CH_2Cl + H_2O \xrightarrow[3\,min]{M.W} C_6H_5-CH_2OH$ (Benzyl alcohol 97%)
(Benzyl chloride, −HCl)

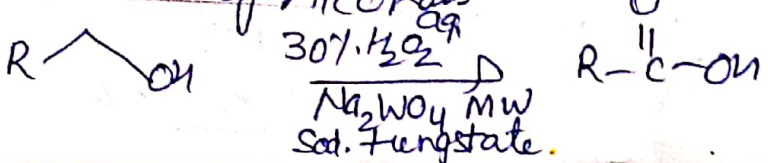
(2) $C_6H_5CONH_2$ (Benzamide) $\xrightarrow[M.W\ 7\,min]{20\%\ H_2SO_4} C_6H_5COOH$ (99%)

(3) $C_6H_5CONHC_6H_5$ (N-phenyl benzamide) $\xrightarrow{20\%\ H_2SO_4}$ C_6H_5COOH (74%)

(c) Oxidation of Toluene Normal condition it takes 10-12 hrs



(D) Oxidation of Alcohols



② Microwave reaction using solvent

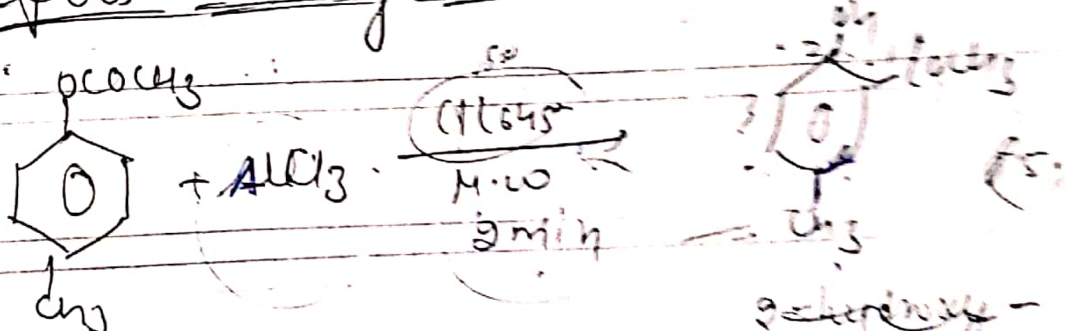
i) Oxidation
[illegible]

① Esterification

$C_6H_5COOH + n\text{-}CH_3CH_2CH_2OH \xrightarrow[M.W\ =\ 6\ min]{conc.\ H_2SO_4} C_6H_5COOC_3H_7$ (Propyl Benzoate) 7?%

propyl alcohol

② Fries rearrangement :→

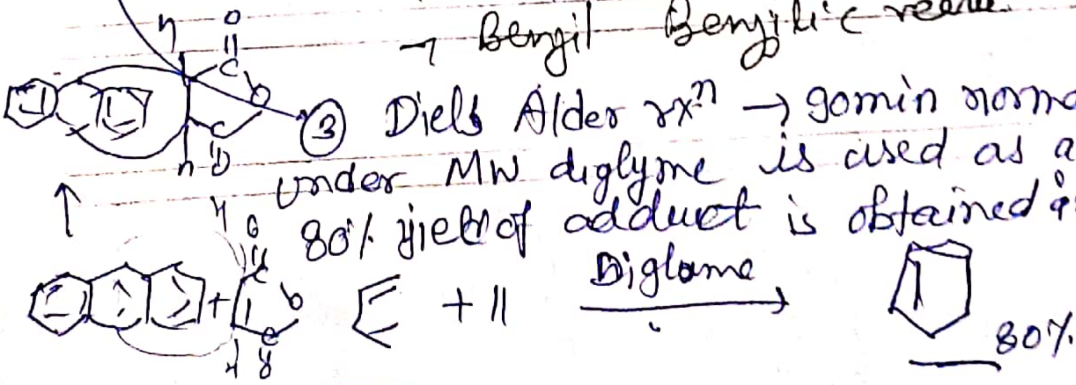


2-hydroxy-5-methyl acetophenone (85%)

③ Microwave solvent free rxⁿ

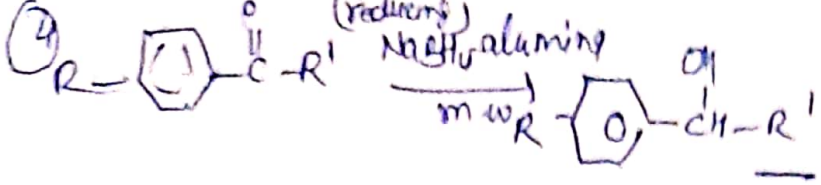
eg) → Claison rearrangement
→ Pinacol - Pinacolone
→ Benzil Benzilic rearr.

③ Diels Alder rxⁿ → 90 min normal condition under MW diglyme is used as a solvent and 80% yield of adduct is obtained in 90 sec.

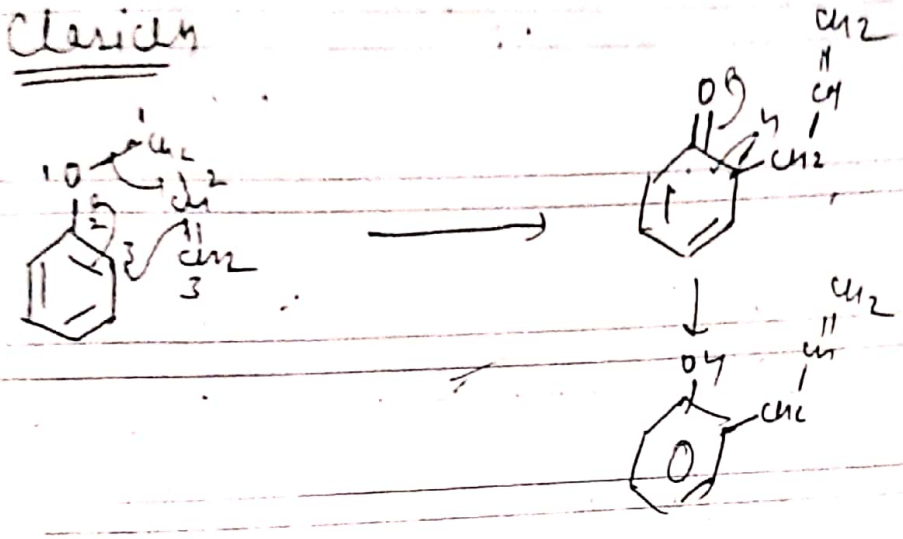


80%

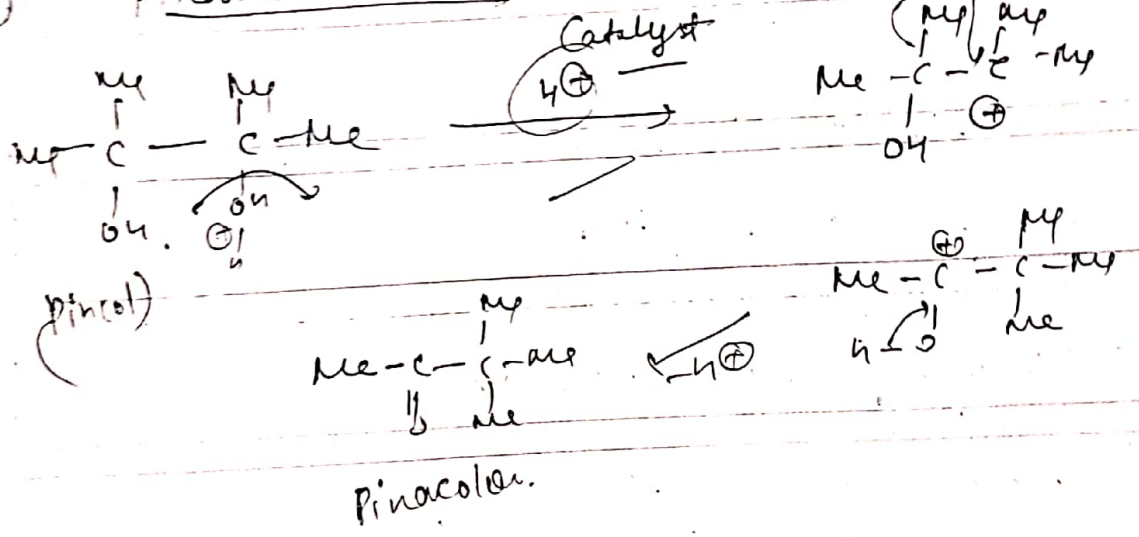
Reduction :-



(1) Claisen



(2) Pinacol- Pinacolone :-



(3) Benzil-Benzilic rearrangement :-