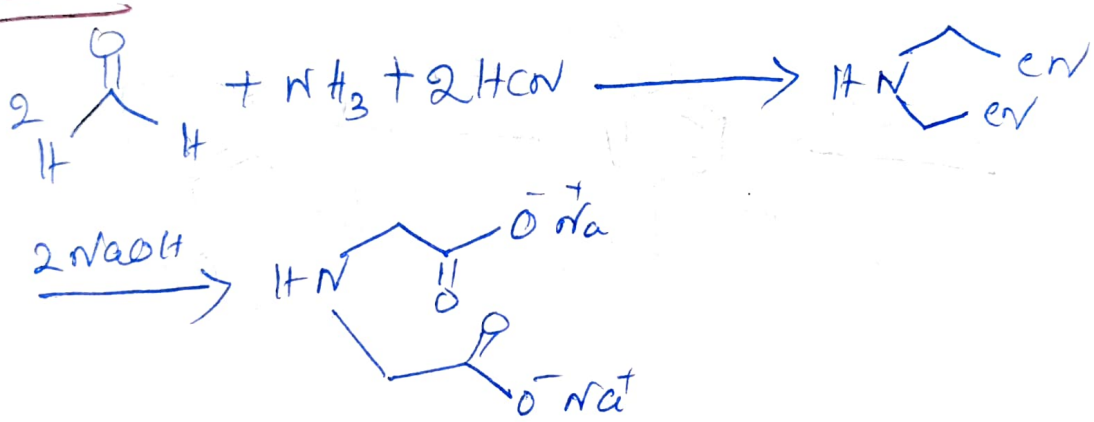
Green Synthesis of Disodium Iminodiacetate (DSIDA)

Disodium iminodiacetate (DSIDA) is a key intermediate for the production of Monsantos Roundur herbicide. DSIDA was synthesized by Monsanto and others by using Strecker process, which requires formaldehyde, ammonia, HCN & HCl.

Reaction

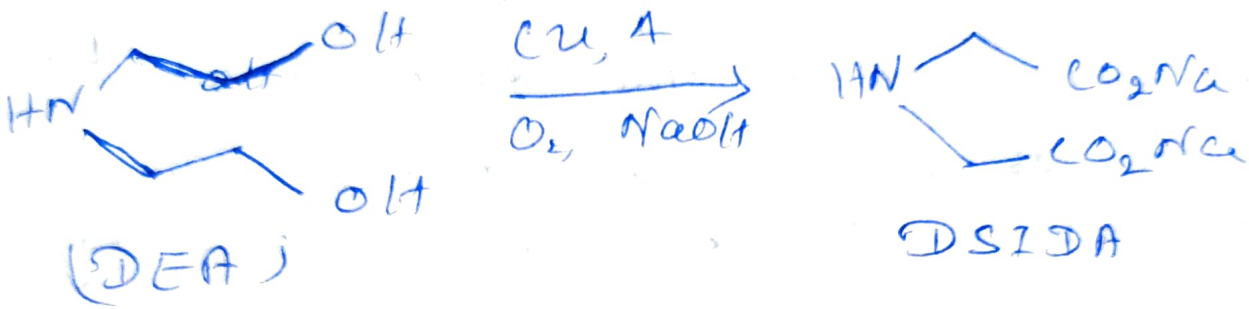


Disodium iminodiacetate.

Drawbacks:

* HCN is extremely toxic and requires special expertise in handling.
* The reaction is highly exothermic with potential unstable intermediate.
* The over all process generate lots of wastes i.e 1kg of waste for ~~every~~ every 1 kg of product, which is contaminated with HCN and formaldehyd
* This has to be treated ~~pure~~ before disposal.

An alternative green synthesis of ~~DSS~~ DSIDA was developed by Monsanto. The process involved copper-catalyzed dehydrogenation of diethanolamine (DEA)



(DEA) DSIDA

Advantage!

→ This is endothermic reaction and safer.
→ It avoid use of HCN & formaldehyde
→ Cu-catalyst can be recycled.
→ It has higher overall yield.

Microwave Assisted Reaction

Conventionally reactions are carried out by heating with different ways such as oil bath, heating mantle, sand bath etc. As compared to the conventional heating which is inefficient and time consuming. Microwave Synthesis can be effectively applied to faster reaction, improving yields and producing clean chemistry.

The advantage of microwave chemistry has proved to be highly effective for chemical reactions due the facts:

→ Faster rate of reaction.
→ Efficient source of heating
→ Uniform heating throughout the reaction mixture.
→ Selective heating of microwave absorbing materials
→ Better yields & higher purity.

Microwave assisted organic Synthesis are grouped into following three categories

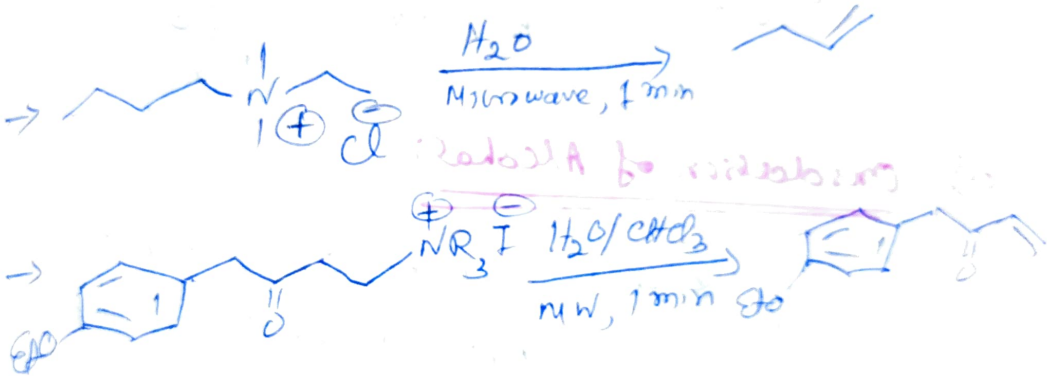
→ Microwave assisted reaction in water
→ " " " in organic Solvent
→ " " " in Solvent free

Examples of Microwave assisted Reaction in Water:

a) Hoffmann Elimination:

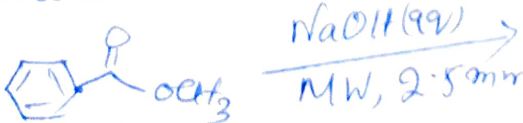
Pyrolysis of quarternary ammonium salt give the least substituted olefin as the major product is known as Hoffmann elimination. In this reaction the yield is very low.

Use of microwave irradiation in water as a solvent has led to high yield.



b) Hydrolysis of Methyl Benzoate to Benzoic acid (Saponification)

Saponification of methyl benzoate in aq. NaOH under microwave condition gives benzoic acid with 84% of yield within 2.5 min.

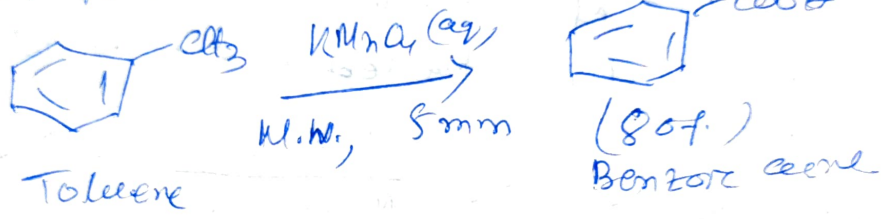


Methyl benzoate. Benzoic acid

c) Oxidation of Toluene ~~to Alcohol~~

Conventionally oxidation of toluene with $KMnO_4$ under reflux condition takes above 10–12 hour with low yield.

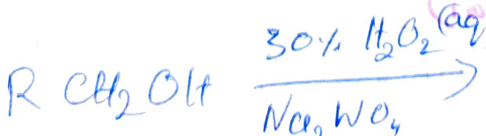
The same reaction in microwave condition takes place in 5 min only with better yield i.e 80%.



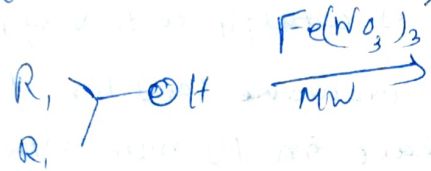
Toluene (80%) Benzoic acid

d) Oxidation of Alcohol:

Primary alcohols can be oxidized to the corresponding carboxylic acid using Sodium tungstate (Na_2WO_4) as catalyst in 30% aq. H_2O_2



Similarly 2° alcohols can be oxidized under microwave conditions in clayfen (iron immobilized on clay surface) giving very good yield.

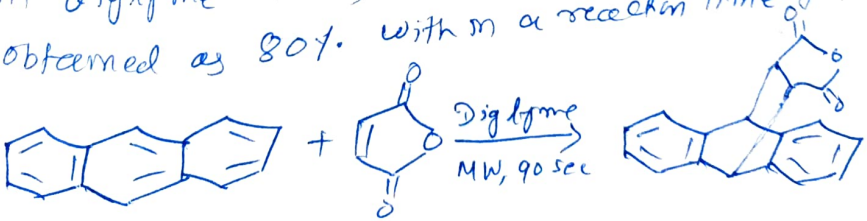


where R_1 & R_2 are aliphatic, aromatic & hetero aromatic groups.

Examples of Microwave assisted reaction in Organic Solvents:

a) Diels-Alder Reaction:

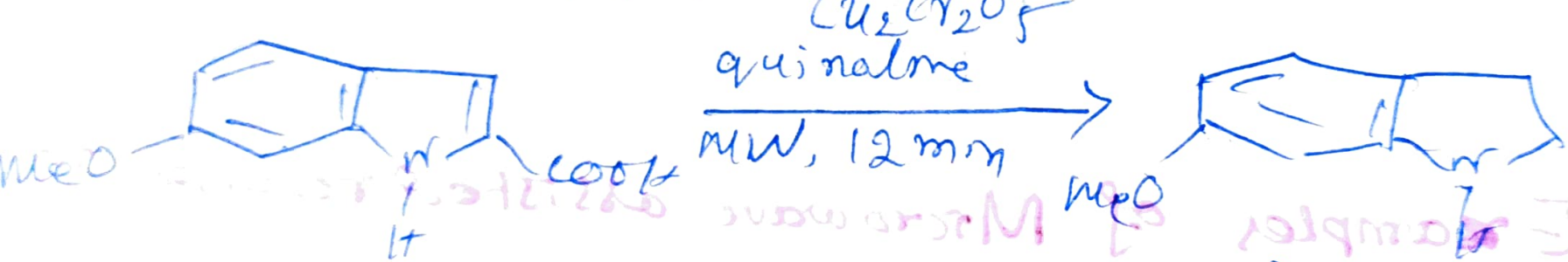
Under normal condition, the reaction between anthracene and maleic anhydride in reflux condition gives the addition product after 30 min. However in microwave condition in diglyme solvent, the desired product is obtained as 80% with in a reaction time of 90 sec.



Diglyme:

b) Decarboxylation:

The conventional method for decarboxylation of carboxylic acid involves refluxing in quinoline in presence of copper chromite as catalyst with very low yield. However, under microwave condition the reaction takes place in 12 min with a yield of 99 %.



6-Methoxy indole
2-carboxylic acid.

(99 %.)

6-Methoxy indole