Q What do you understand by solventless processes?

Ans → For a particular reaction, solvents are used due to following reasons:-

1) to dissolve reactants
2) to increase or decrease the rate of reaction
3) to act as heat transfer agent
4) To extract some component etc

For organic solvents we have following drawbacks

1) Organic solvents are expensive
2) Many organic solvents are highly volatile, flammable, toxic and carcinogenic.

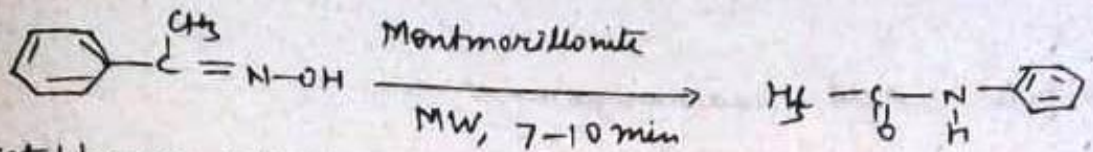
So, if a reaction is performed in absence of organic solvents then it is called solventless process and termed as green method.

A solventless process may have advantages as follows:-

1. It will be cheaper.
2. After completion of reaction, there is no tension of removal of solvent
3. Rate of reaction will be high because concentration of reaction will be high in the reaction mixture
4. It will be environmental friendly process.
5. Fifth principle of Green chemistry will be followed.

There are some examples where Green synthesis is very much successful.

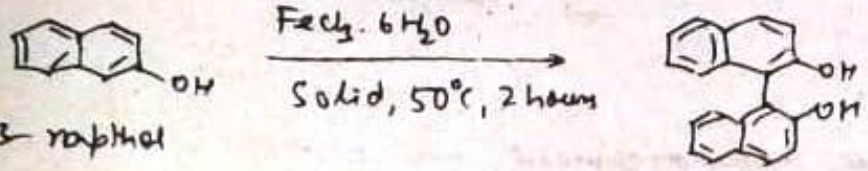
1. Beckmann rearrangent →



Acetophenon oxime

Acetanilide (91%)

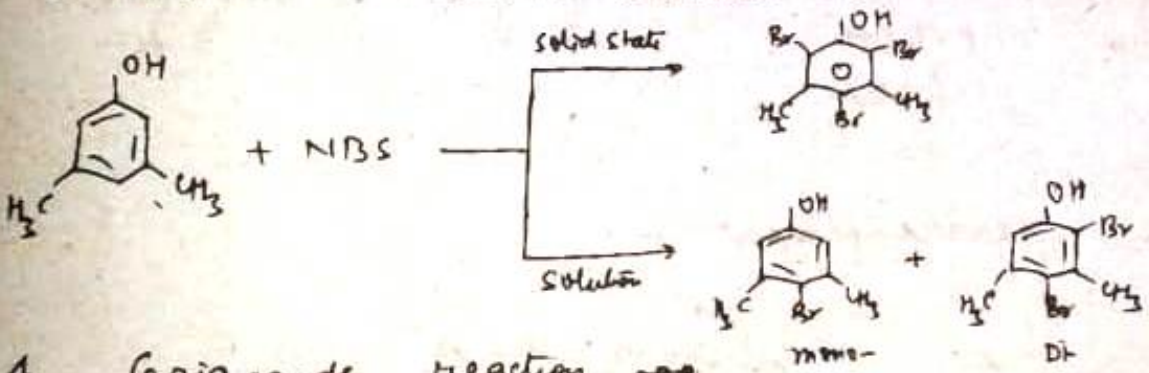
2. Oxidative coupling of Phenols →



β-naphthol

bis-β-naphthol (95%)

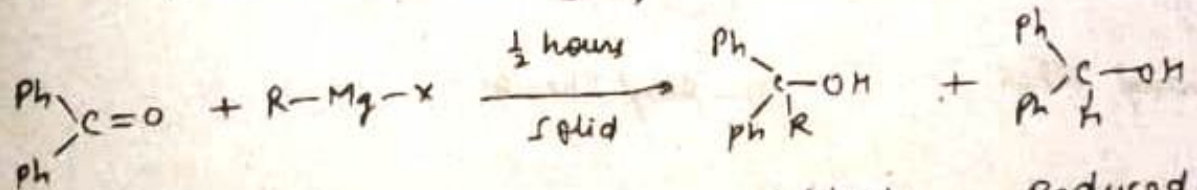
3. Aromatic Substitution reaction →



mono-

Di-

4. Grignards reaction

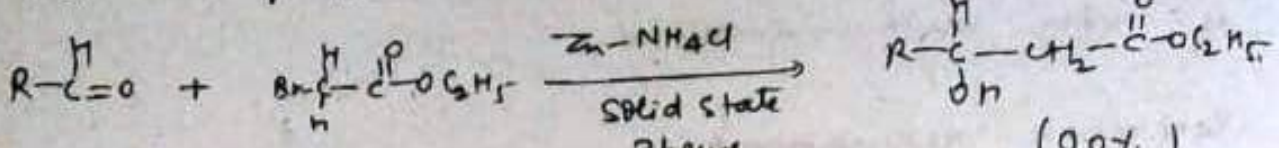


Adduct (A)

Reduced Product (B)

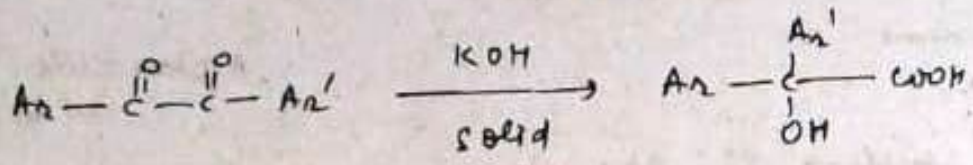
B > A

5. Reformatsky reaction →



(90%)

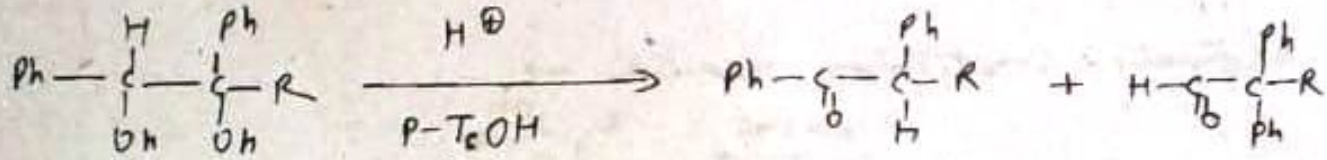
6. Benzilic acid rearrangement →



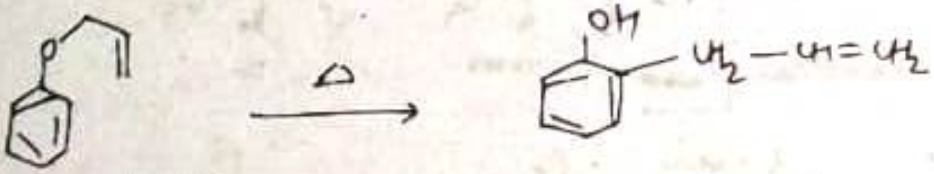
Benzil

Benzilic acid

7. Pinacol – Pinacolone rearrangement →



8. Claisen rearrangement →



Allyl phenyl ether

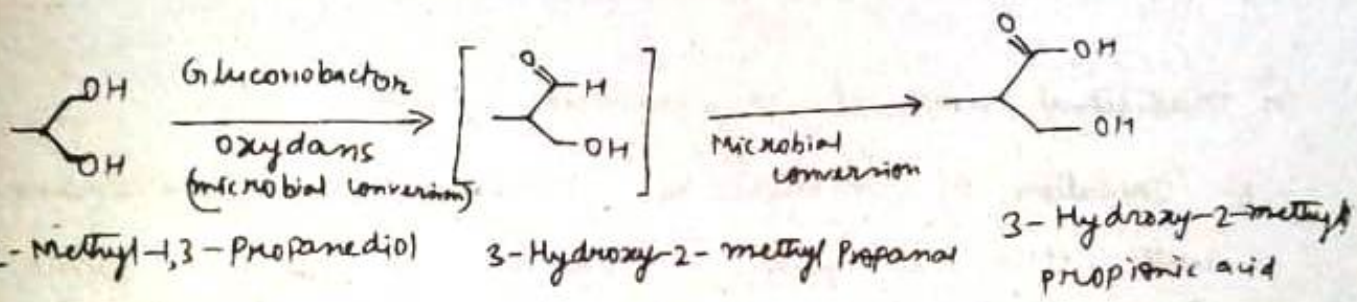
O – Allyl Phenol.

Limitations:—

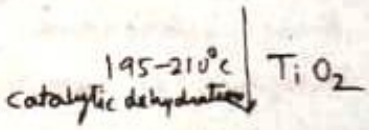
1. After reaction some solvents are required for extraction
2. Homogeneous reactants will mix up
3. Unsuitable for solvent assisted chemical reaction

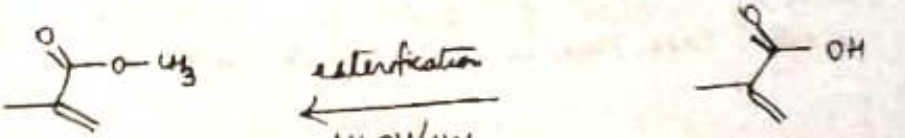
Q Discuss a method for green synthesis of methyl methacrylate.

Ans → Methyl methacrylate green synthesis can be performed by the following method..



2-Methyl-1,3-Propanediol 3-Hydroxy-2-methyl Propanal 3-Hydroxy-2-methyl propionic acid



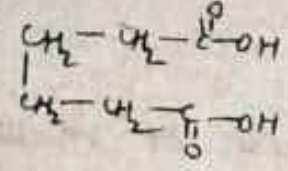


Methyl methacrylate Methacrylic acid

$(CH_2=C(CH_3)-C(=O)-O-CH_3)$

Green synthesis of adipic acid

Adipic acid is a dicarboxylic acid (Hexane-dioic acid)

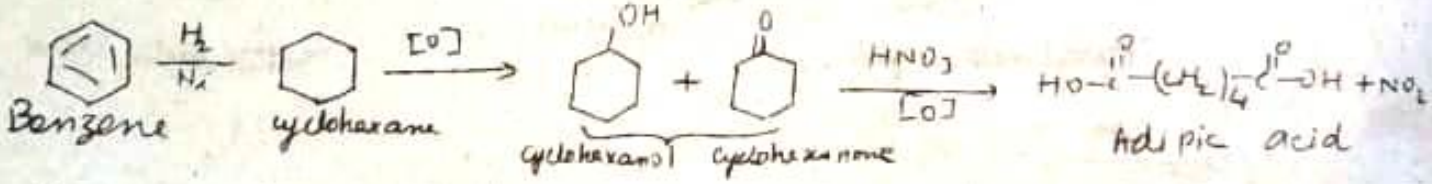


1, 4-butanedicarboxylic acid

It occurs in nature in a very small amount. From industrial point of view, it is most important dicarboxylic acid. It is mainly used for production of nylon. It is white crystalline powder (m.p = 152°C)

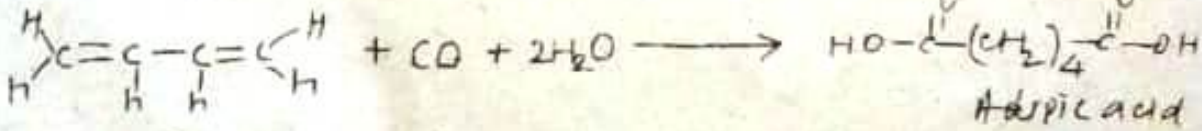
In traditional way, it is prepared by

1) Oxidation of mixture of cyclohexanol and cyclohexanone with HNO_3 to give adipic acid via some intermediate. cyclohexanol and cyclohexanone are obtained from cyclohexane which is a reduction product of benzene. Benzene is carcinogenic substance and HNO_3 is hazardous oxidising agent giving NO_2 (a greenhouse gas)
Oxidation takes place in presence of cupric nitrate and ammonium metavanadate



Here yield is 50-50% and has very less atom economy

2) Adipic acid can also be prepared by carbonylation of Butadiene →



Butadiene

In green method, cyclohexene is directly converted into analytically pure crystalline adipic acid.

Here, cyclohexene is treated with Na_2WO_4, H_2O_2, $KHSO_4$ and finally aliquat 336

Adipic acid may also be synthesised by oxidation of cyclohexanone and cyclohexanol with aqueous 30% H_2O_2 in presence of H_2WO_4 as catalyst

If solvent t-butyl alcohol or dioxane is used then yield is decreased.

cyclohexanone

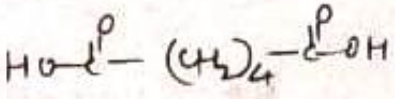
100 g

+ H_2O_2 30%

382 g

3.3 equivalent

$\xrightarrow[\text{20 hours, } 363\ K]{H_2WO_4}$



Adipic acid

135 g. (91%.)

cyclohexanol

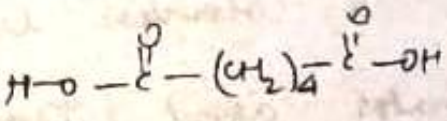
100 g

+ H_2O_2 30%

498 g.

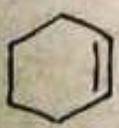
4.4 equiv.

$\xrightarrow[\text{20 hours, } 363\ K]{H_2WO_4}$



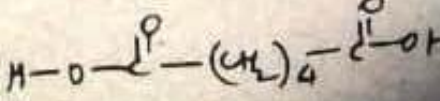
Adipic acid.

127 g. (87.1.)



cyclohexene

$\xrightarrow[KHSO_4,\ \text{aliquat } 336]{Na_2WO_4,\ H_2O_2}$



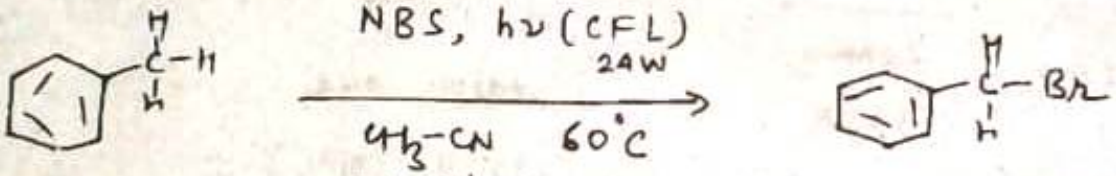
(65%)

Green Synthesis of Benzyl bromide ($C_6H_5-CH_2-Br$)

Benzyl bromide can be synthesised by reaction between Toluene ($C_6H_5-CH_3$) and slight excess of N-bromosuccinimide (NBS) in presence of household compact fluoresent lamp (CFL) using a simple flow reactor design based on transparent fluorinated ethylene polymer tubing.

Reaction is carried in presence of acetonitrile as solvent which is a non-hazardous chemical.

Here CCl_4 is avoided which is a hazardous chlorinated solvent.



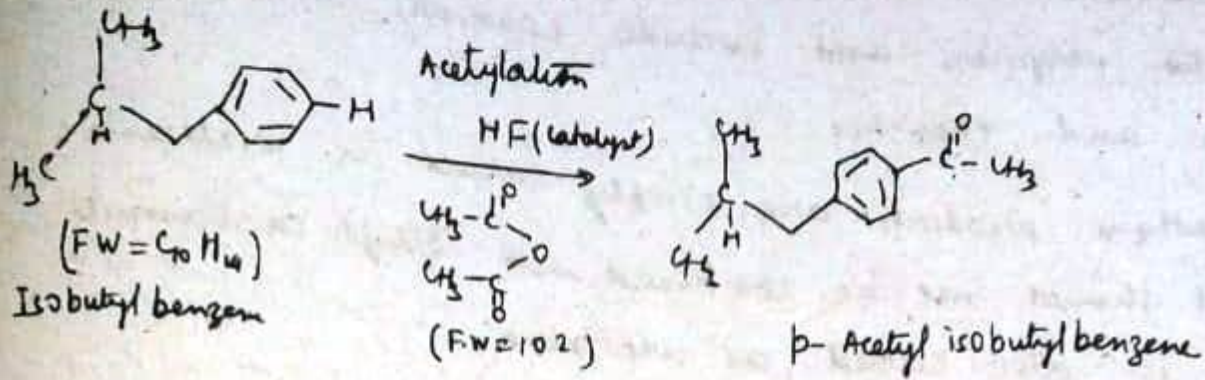
Toluene

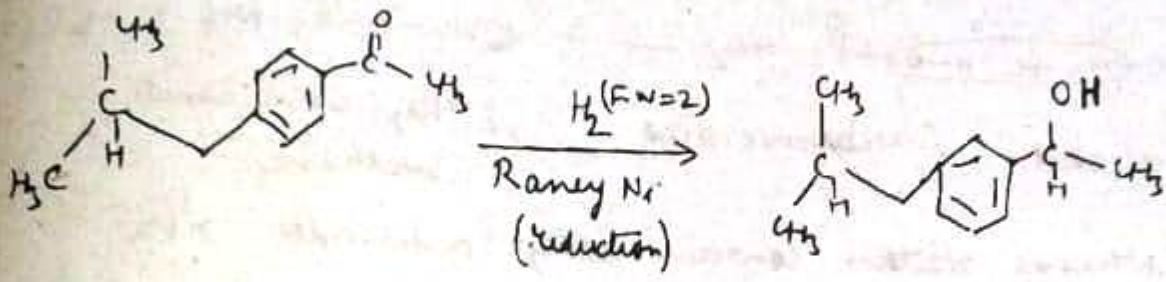
Benzyl bromide.

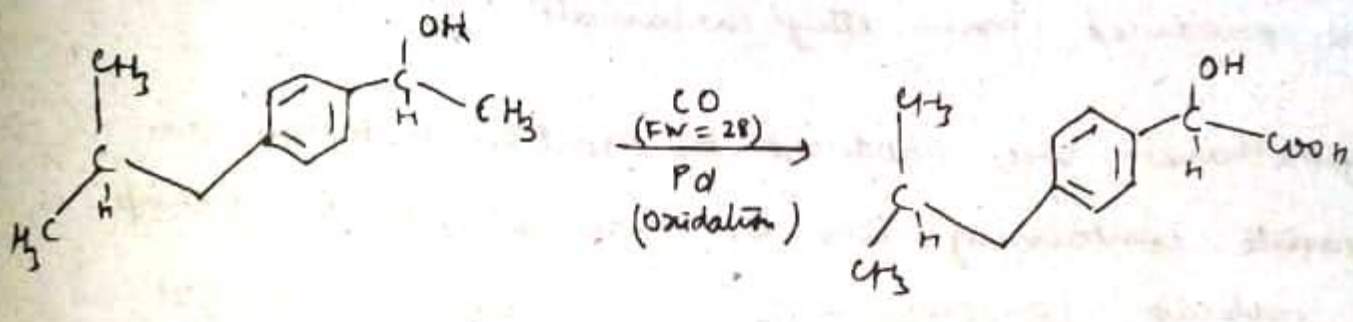
It is a colourless liquid, B.P. 201°C used as lachrymator agent (Tear gas).

The reaction proceeds via free radical mechanism.

Green Synthesis of Ibuprofen







Ibuprofen
(F.w = 206)

Here

$$\% \text{ atom economy} = \frac{\text{F.w. of Ibuprofen}}{\text{F.W. of all reactants}} \times 100$$

$$= \frac{206}{266} \times 100$$

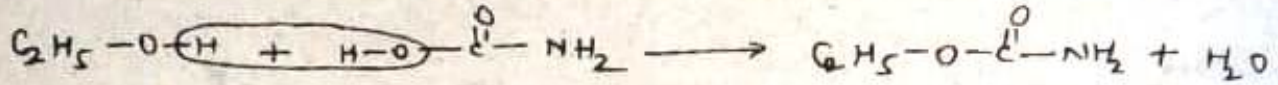
$$= 77\%$$

whereas 40% atom-economy is obtained in traditional method.
Here, all the catalyst used is recovered and can be reused.

Urethane / Polyurethane

Polyurethane (PUR or PU) are reaction polymers not condensation polymers and include epoxides, unsaturated Polyester and Phenolics.

Polyurethane products are simply called as urethanes but it should not be confused with ethyl carbamate which is also called as urethane.



Ethyl alcohol Carbamic acid Ethyl Carbamate (urethane)

Also, polyurethanes neither contain ethyl carbamate nor are produced from ethyl carbamate.

Polyurethanes are produced by reaction between an isocyanate containing two or more isocyanate group per molecule $[R-(N=C=O)_n]$ and a polyol containing an average two or more hydroxyl groups per molecule $[R'-(OH)_n]$ in presence of a catalyst or by activation with UV light.

Two types of catalysts are used

i) Basic catalyst
ii) Acidic catalyst

i) Basic catalyst → Tertiary amine is used for enhancing the nucleophilicity of the diol component
Normally, amines used are triethylenediamine (also called as DABCO 1,4-diazabicyclo [2.2.2] octane or dimethylcyclohexylamine

ii) Acidic catalyst → eg Alkyl tin carboxylate, oxides and mercaptide oxides.

Commonly used acidic catalyst is dibutyltin dilaurate

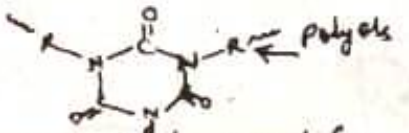
Here, in the formation of urethane three main steps are

i) Urethane formation → This is also called as gellation ie gel formation by combination of polyol with isocyanate

ii) The formation of urea → This is for the formation of cell, also called as 'blow'. This step takes place by the reaction between isocyanate and water.

iii) Formation of isocyanurate rings →

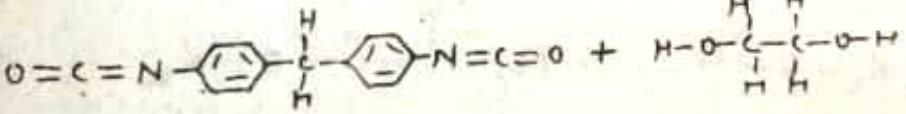
Here potassium acetate is used for isocyanate trimerization reaction



Some surfactants are also used to modify the characteristics of foam and non-foam polyurethane polymer.

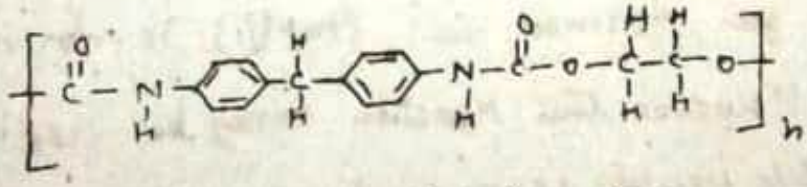
Reactions:-

i)



Di isocyanate

Diol



gel formation

(Polymer)