

SELECTION OF SOLVENT

2.1. INTRODUCTION

- Solvents which are generally used for organic synthesis are extremely harmful. Most of the organic solvents are known to cause environmental pollution.
- For example a commonly used solvent, benzene is responsible to promote cancer in humans and other animals.
- Halogenated solvents such as chloroform, carbon tetrachloride, methylene chloride and polychloroethylene have been identified as suspected human carcinogens.
- The chlorine free radicals are responsible for depletion of ozone layer. CFCs (chlorofluorocarbons) used for refrigeration are also responsible for the depletion of ozone layer.
- Toluene (an aromatic hydrocarbon) can damage the brain.

2.2. AQUEOUS PHASE REACTIONS (ORGANIC SYNTHESIS IN WATER)

In view of the environmental pollution caused by most of the organic solvents, chemists all over the world are carrying out the experiments in aqueous phase.

2.2.1. Advantages of using water as a solvent

1. Cost effective and economical.
2. Unlike organic solvents, water is a safe solvent.
3. Water-soluble substances can be directly used.
4. The products can be isolated by simple phase separation.
5. It is easier to control the reaction temperature due to largest heat capacity of water.
6. Free from problem of pollution.
7. Water can be readily recycled and can be reused many times.
8. It exists in all the three basic forms - vapour, liquid and solid.
9. The relationship between three forms of water is explained by phase diagram.

2.2.2. Unique physical properties of water

1. Density : The peak density of water is at 3.98°C . It decreases as the temperature decreases to 0°C . Due to this reason ice is lighter than water and floats. *This phenomenon insulates the deeper water from the cold temperature and prevents it from freezing.*

The density of water also decreases when temperature exceeds 3.98°C . It reaches the same density of ice at about 70°C .

2. Specific heat : Water has one of the largest heat capacities of all substances. The high value of specific heat of water is due to the great heat capacity of the water mass. This means that rapid changes of ambient temperatures result in slow changes in water temperature. This effect is used to control the temperature both for endo-as well as exo-thermic reactions in large scale industrial processes.

3. Viscosity : Viscosity of water is inversely proportional to temperature. It decreases with increase to temperature. It is due to the fact that the number of hydrogen bonds (H-bond) decreases with increase in temperature. The movement of solute in water and the sedimentation rate of suspended solids is affected by the viscosity of water.

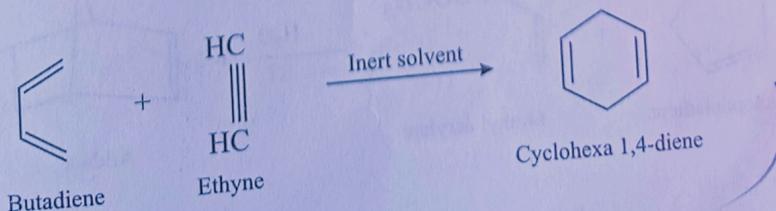
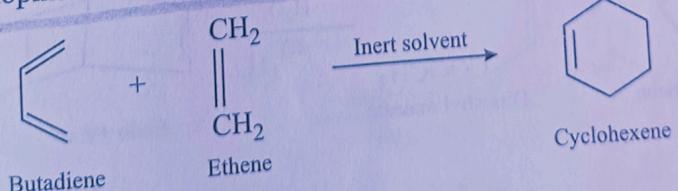
4. Surface tension : Water has one of the highest surface tension of all liquids. The surface tension of water decreases with temperature. The surface tension of water also decreases by the addition of some surface-active agents (surfactants). Examples of surfactants are detergents.

5. Solubility : Many substances are soluble in water. It is dependent on the temperature. The solubility of gases such as O_2 , N_2 and CO_2 in water decreases with rise in temperature, while the solubility of helium gas increases with increase in temperature. For solids, the solubility of silver nitrate (AgNO_3) increases with increase in temperature but for sodium chloride (NaCl), there is only a slight increase in solubility with rise in temperature. The effect of temperature on the solubility is dependent on the heat of solution of a substance. (Heat of solution is the amount of heat emitted or absorbed during the dissolution of one mole of a substance in one litre of water. Polar compounds are called *hydrophilic* in nature because they are highly soluble in water. On the other hand, *hydrophobic* substances are very low soluble in water).

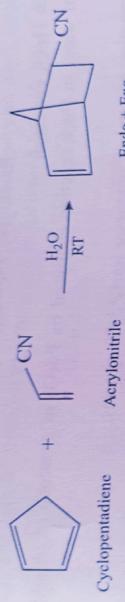
6. Behaviour of water at high pressure and temperature : Ordinary water behaves very differently under high temperature and high pressure. The electrolytic conductance of aqueous solution increases with increase in pressure. This effect is more at lower temperatures. On the other hand, the electrical conductivity of solutions decreases with increase in pressure, for all other solvents. (This unusual behaviour of water is due to its associative properties).

2.2.3. Reactions in water

Diels-Alder reaction : It is a [4+2] cycloaddition reaction. It consists of two reactants, one conjugated diene (4π -electron system) and a *dienophile* (2π -electron system). Conjugated diene on combination with dienophile forms an adduct. For example

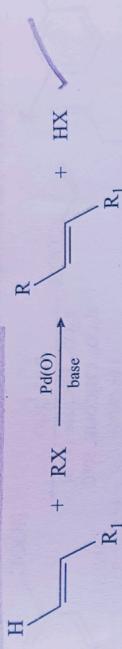


Quantitative yield of the adduct is obtained in the reaction of cyclopentadiene and acrylonitrile.



Lewis acids are used for the activation of substrate in Diels-Alder reaction. Most of the Lewis acids are deactivated or decomposed in water. Water stable catalysts for Diels-Alder reaction are :

- (i) $[\text{Ti}(\text{Cp}^*)(\text{H}_2\text{O})_2]^{2+}$
 - (ii) Scandium triflate $[\text{Sc}(\text{OTf})_3]$
 - (iii) Lanthanide triflate $[\text{Ln}(\text{OTf})_3]$
- 2. Heck reaction :** The coupling of an alkene with a halide or triflate in the presence of Pd(O) catalyst to give a new alkene is known as **Heck reaction**.



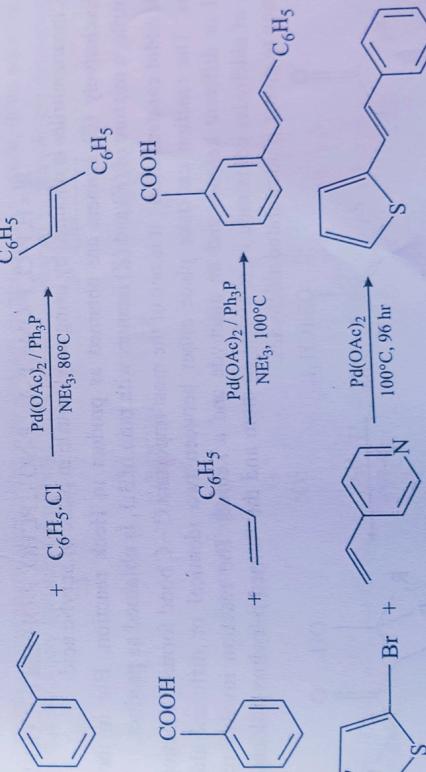
where $R =$ aryl, vinyl (or alkyl) group without β -hydrogens on a sp^3 hybridised carbon atom.

$X =$ halide (or triflate)

Mild base such as $(\text{C}_2\text{H}_5)_3\text{N}$ or anions like OH^- , CH_3COO^- , CO_3^{2-} etc. are used in Heck reaction.

Anhydrous polar solvents (e.g. DMF and CH_3CN) and tertiary amines as bases are traditionally used in Heck reactions.)

Other examples



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where
 $\text{Ac} = \text{CH}_3\text{COO}$
 $\text{Et} = \text{C}_2\text{H}_5, \text{Ph} = \text{C}_6\text{H}_5$

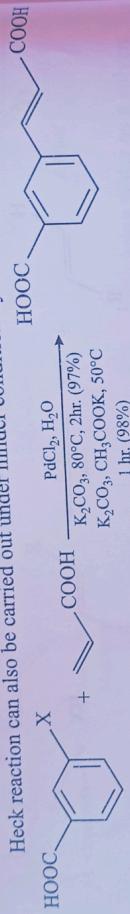
Role of water in Heck reaction

The role of water in Heck reaction catalysed by Pd(O) in presence of phosphine ligands is as follows :

- (i) Transformation of catalyst precursor into Pd(O) species.
- (ii) Generation of zero-valent palladium species capable of oxidative addition by oxidation of salts in presence of inorganic bases like KOH , K_2CO_3 , Na_2CO_3 and NaHCO_3 etc.

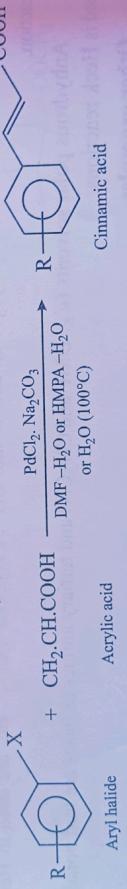
Heck reaction can also be carried out under mild conditions using phase-transfer catalyst (PTC) conditions with inorganic carbonates as bases at room temperature.

Heck reaction can also be carried out under milder condition by addition of acetate ion.



Application of Heck reaction

Synthesis of cinnamic acid from aryl halide and acrylic acid



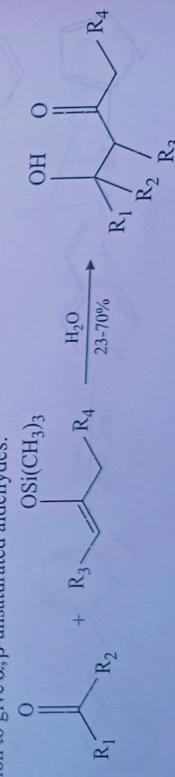
X = I, Br

R = H, P-Cl , P-OMe , P-Ac , P-NO_2 , PCHO , P-OH and $m\text{-COOH}$ etc.

Cinnamonnitriles is obtained by using acrylonitrile in place of acrylic acid.

Exclusively (E) isomers are obtained as product in Heck reaction. But in the reaction of acrylonitrile, a mixture of (E) and (Z) isomers with ratio of 3:1, is obtained as product.

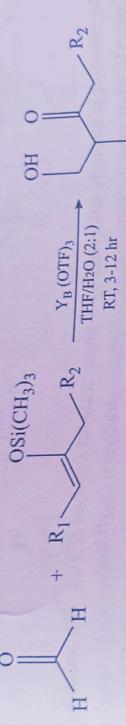
3. Aldo condensation : It is one of the most important C–C bond forming reactions in organic synthesis. The reaction can take place either between two identical or different aldehydes, two identical or different ketones and an aldehyde and a ketone. The reaction involve reversible self addition of aldehydes containing an α -hydrogen atom and the formed β -hydroxy aldehydes undergo dehydration to give α, β -unsaturated aldehydes.



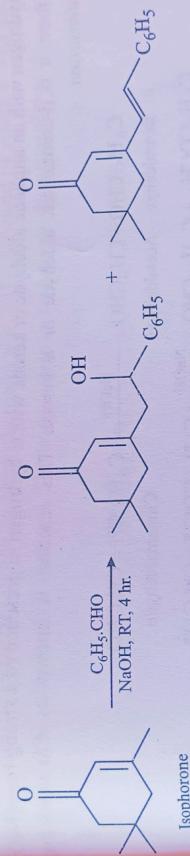
Mechanism

Reaction between silyl enol ethers and aldehydes in presence of water.

The reaction takes place at a slow rate and complete in several days, because water acts as a weak lewis acid. The rate of reaction and the yield is increased by addition of a stronger lewis acid such as lanthanide triflate.



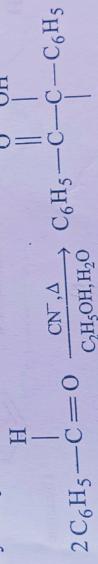
Isophorone when reacts with benzaldehyde in water, gives only vinyllogous aldol product (low yield). However, in presence of CTACl, the condensation product, (E)-benzylideneisophorone is obtained in 80% yield. While in presence of tetrabutyl ammonium chloride (TBACl), a mixture of addition and condensation products is obtained.



in presence of
Water only 24%
CTACl — 80%
TBACl 27% 58%

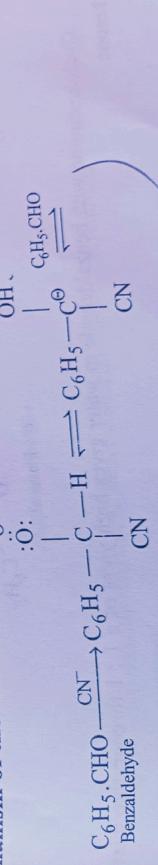
4. Benzoin condensation

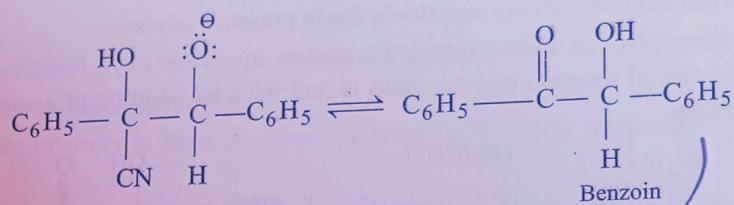
The reaction of aromatic aldehydes with sodium or potassium cyanide, in an aqueous ethanolic solution give α -hydroxy ketones (benzoins). This reaction is known as benzoin condensation.



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Benzoin
Benzaldehyde
Mechanism of the reaction



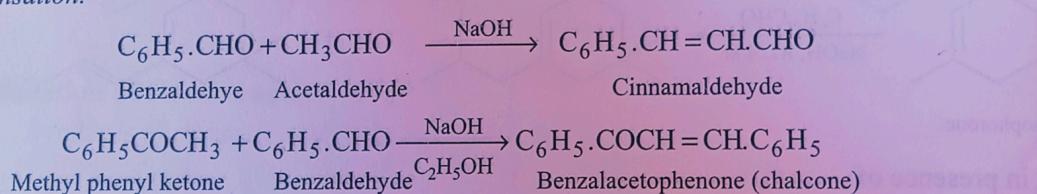


The reaction is strongly catalysed by a phase transfer catalyst (PTC). The aromatic aldehydes required lesser (5 min) time in comparison to aliphatic aldehydes (5-10 hrs).

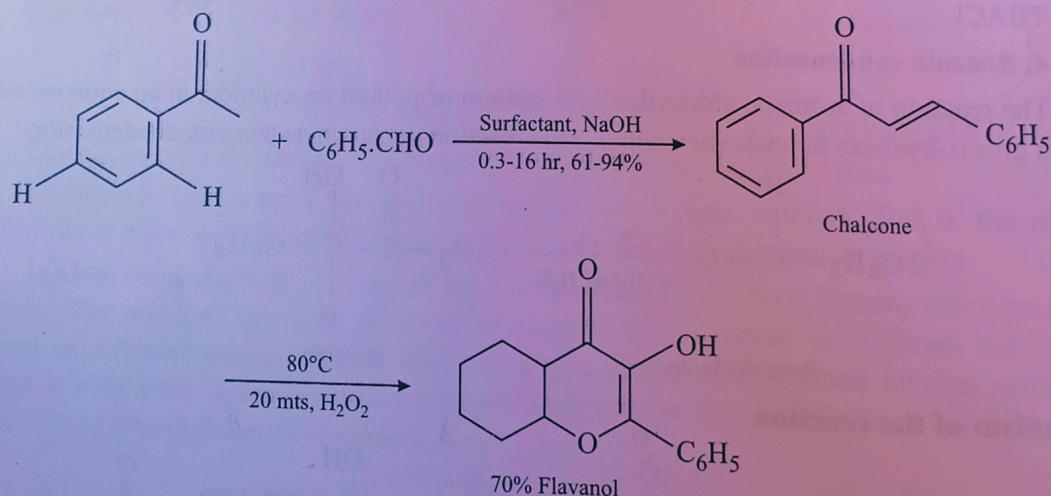
Mixed α -hydroxyketones are obtained by the condensation of aromatic and aliphatic aldehydes. Breslow found that the rate of benzoin condensation is **200 times faster in aqueous media** than in organic salts such as LiCl than in ethanol without any inorganic salts.

γ -cyclodextrin increases the rate of reaction, whereas β -cyclodextrin decreases (inhibits) the rate of condensation.

5. Claisen-Schmidt condensation : The condensation of aromatic aldehydes without α -hydrogen with an aliphatic aldehyde or ketone with α -hydrogen in presence of a strong base (NaOH) to form a α,β -unsaturated aldehyde or a ketone. This reaction is known as *Claisen-Schmidt condensation*.



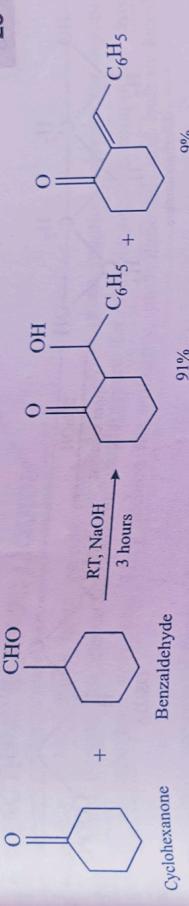
Reaction of acetophenone with benzaldehyde in presence of surfactants (cetylammonium compounds) in mild alkaline conditions give chalcones, which on cyclisation give flavanols.



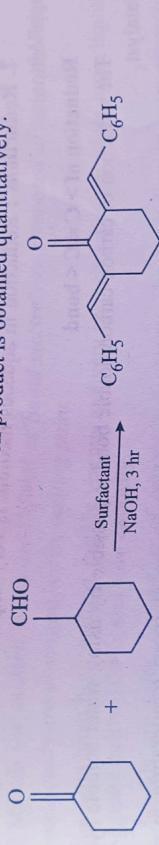
Cyclohexanone with benzaldehyde in water gives high yield of a 1 : 1 threoerythro mixture of the ketone.

Selection of Solvent

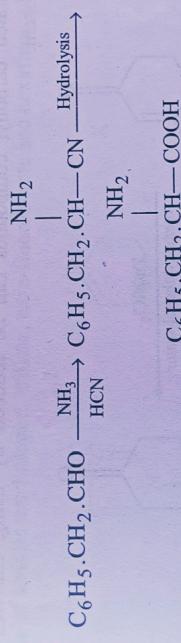
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In presence of surfactant, the bis-condensation product is obtained quantitatively.



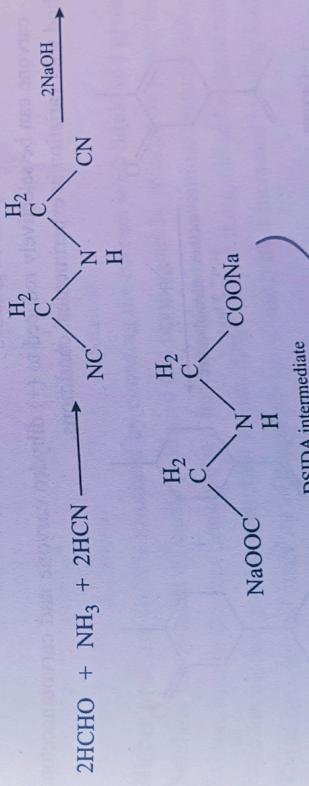
6. Strecker synthesis : When an aldehyde reacts with NH_3 , followed by reaction with HCN, α -aminonitrile (intermediate) is obtained. The intermediate on hydrolysis gives α -amino acid.



The intermediate α -aminonitrile can be obtained by Erlenmeyer modification.

It can also be obtained by Zelinsky-Stadnikoff modification.

Strecker synthesis is useful in synthesising an intermediate disodium iminodiacetate (DSIDA). This is an example of green synthesis required for the synthesis of a herbicide Monsantos' Roundup. This is an example of green synthesis.



Since HCN is a hazardous chemical, hence a special handling is required to minimise the risk to workers and the environment.

Alternative synthesis of DSIDA (By Monsanto)

2.3. REACTIONS IN IONIC LIQUIDS



Recently, ionic liquids have gained much attention as green reaction solvents for organic synthesis. Ionic liquids are emerging as novel replacement for volatile organic compounds used traditionally as industrial solvents. They reduce the volatility, environmental, and human health hazards.

Ionic liquids are one of those odd species in chemistry, they are molten salts, colourless, fluidic and easily handled even at low temperatures (-96°C).)

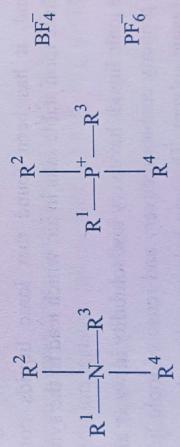
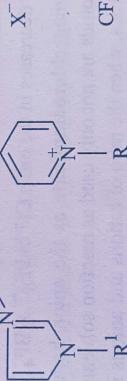
Liquid Electrolytes - Ionic liquids (or molten salts) are defined as liquid electrolytes composed of anions. Molten salts and ionic liquids are distinguished by melting point.

Molten salts have high melting, highly viscous and very corrosive medium while ionic liquids have melting point below 100°C and low viscosity.

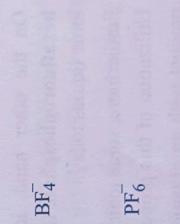
Ionic liquids are salts, consisting of cations and anions. The Ionic liquids have attractive properties for a solvent.

Examples of cations are Imidazolium, pyridinium, quaternary ammonium and quaternary phosphonium.

Examples of anions are halogen triflate, tetra-fluoroborate and hexa-fluorophosphate.



B-Anions
A-Cations



Higher product yield is obtained by choosing the correct ionic liquid in a given reaction.

- Similarly the amount of waste produced in a reaction can be reduced by proper ionic liquids.
 - In ionic liquids the reactions are at a faster rate than in conventional organic solvents.
 - Ionic liquids are good solvents for a wide range of both inorganic and organic materials.
 - The selectivity and stability of transition metal catalysis is increased by using ionic liquids.

2.3.1. Characteristics of ionic liquids

Chemical properties Ionic liquids exhibit many properties which make them potentially attractive

- room temperature ionic liquids are media for a large number of organic reactions.

 1. They have no *vapour pressure*, *i.e.*, they do not evaporate and are easy to contain.
 2. They are able to dissolve a wide range of inorganic, organic and organometallic compounds.

3. They possess good thermal stability.
4. They do not decompose over a large range of temperature, thereby making it feasible to carry out reaction requiring high temperature conveniently in ionic liquids.
5. The solubility of ionic liquids depends upon the nature of cations and counter-cations.
6. When an ionic liquid is used as a reaction solvent, the solute is solvated by ions only.
7. Ionic liquids act as good medium to solubilise gases such as O_2 , CO , CO_2 and H_2 .
8. Many organic syntheses are now being performed using ionic liquids and super critical CO_2 .
9. Ionic liquids generally do not coordinate to enzymes, metal complexes and different organic substrates.

10. They can be stored without decomposition for a long period of time.

11. They possess relatively low viscosity.
12. They also have high ionic conductivity.
13. Due to their polar and non-coordinating properties, ionic liquids show a high degree of potential for enantioselective reactions.

14. *Chiral ionic liquids* have been used to control the stereoselectivity.

15. Highly branched and compact alkyl chain are used to decrease the viscosity of 1-alkyl-3-methyl imidazolium salts. The viscosity is also decreased by changing the nature of anion. The viscosity decreases in the order $Cl^- > PF_6^- > BF_4^- \approx NO_3^- > NTF_2^-$.

- Ionic liquids containing chloroaluminate as the anion have been investigated for many years. These ionic liquids are not only used as reaction solvents, but also exhibit Lewis acids or Lewis base properties, when the ratio of cations and anions is changed. However, they can only be used under an inert atmosphere or vacuum, due to their high moisture sensitivity.
- On the other hand, it has been found that ionic liquids containing anions such as hexafluorophosphate form stable salts in air, which lead to the synthesis of numerous stable ionic liquids today.

• Furthermore, some ionic liquids have very low solubility in water and polar organic solvents. Utilization of this property enables recovery and reuse of ionic liquids, after extracting the product with an organic solvent. This can help to reduce the waste of traditional solvents which are rarely reused.

- Moreover, ionic liquids have attracted much attention as safe solvents, due to their low volatility.

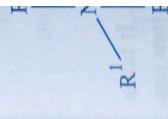
2.3.2. Types of ionic liquids

Ionic liquids consist of a salt where one or both (cation and anion) are large, and the cation has a low degree of symmetry. The lattice energy of the crystalline form of the salt is reduced by these factors. It results in the lowering of melting point. Ionic liquids are grouped in two categories as follows :

1. Simple salts
2. Binary ionic liquid

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Tetraalkyl
SbF6-, ZnC

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Al3Cl10-, A

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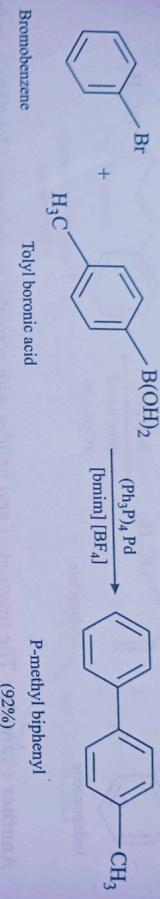
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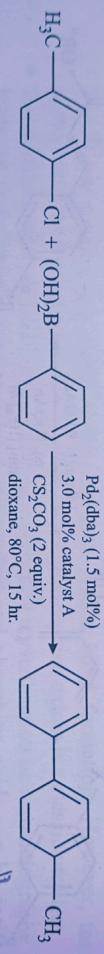
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The active catalyst in Heck reaction is a palladium nanoparticles. They are generated *in situ* from palladium-carbene species. The solution of ammonium stabilised Palladium clusters are also used as catalyst for the Heck reaction.

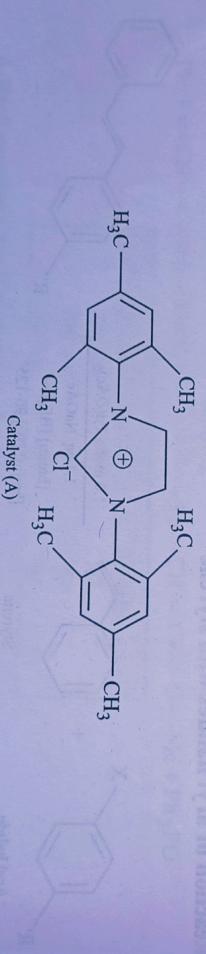
Suzuki coupling reaction : Reaction between aryl-halides or aryl triflates and aryl boronic acids in presence of palladium catalyst in an ionic liquid as the solvent is known as *Suzuki coupling reaction*. The product is biaryls. The yield is excellent. For example,



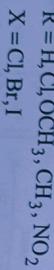
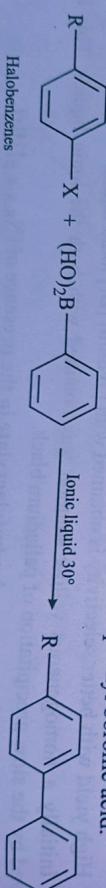
Another example is the reaction between *P*-chlorotoluene and phenylboronic acid in dioxane at 80°.



The reaction is catalysed by 1, 3-bis-(2, 4, 6-trimethylphenyl) imidazol-2-ylidene (A). Since the imidazol-2-ylidene carbenes are not very stable to air and moisture, the carbene liquid was generated *in situ* from the salt (A) using CS_2CO_3 as the base.



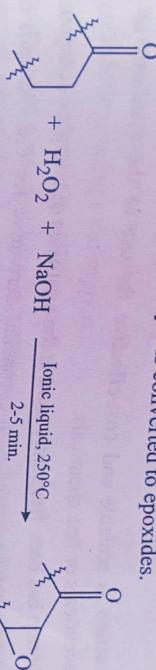
This reaction has also been carried out under mild conditions in an ionic liquid with methanol as a cosolvent using ultrasound. The methanol is required to solubilise the phenyl boronic acid.



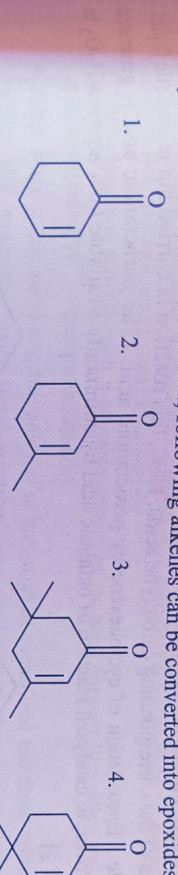
8. Epoxidation :- Epoxidation is the chemical reaction which converts the carbon-carbon double bond into oxiranes (epoxides), using a variety of reagents.

Epoxidation of electrophilic alkenes in ionic liquids

Electrophilic alkenes in ionic liquids, [bmim] $\text{[PF}_6]$ [bmim] $\text{[PF}_4]$ as solvent by using aqueous solution of H_2O_2 in the presence of basic catalyst is converted to epoxides.

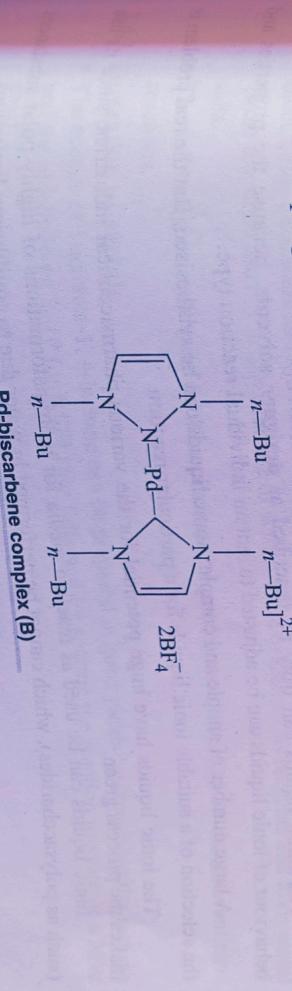


By using ionic liquids as solvent, following alkenes can be converted into epoxides (oxiranes). 80-90% yields



Synthesis of epoxides

- Peroxy carboxylic acids are generally used for the preparation of epoxides (oxiranes).
- Handling, transport and storage are certain prohibitive factors for the use of peroxy carboxylic acids as inactive Pd-black is formed during the above reaction, which prevents the recycling of the catalyst.
- This problem is overcome by synthesising a Pd-biscarbene complex (B); The Pd-biscarbene complex (B) is used as a catalyst with methanol as solvent under sonchemical conditions for Suzuki coupling reaction.



Performing organic reactions in solid state (or solventless reactions) are the best alternative in the context of green chemistry.

These reactions can be conducted in three ways as follows :

1. Solid state reactions at room temperature,
2. Solid state reactions on heating, and
3. Solid state reactions using solid support.

2.4.1. Solid state reactions using solid support

In chemistry, solid phase synthesis is a method in which molecules are covalently bound on a solid support material and synthesised step by step in a single reaction vessel utilising selective protecting group chemistry.

- In solid state reactions using solid support, the reactants are dissolved in a suitable solvent like water, alcohol, methylene chloride etc.
- The solution is stirred with a suitable adsorbent or solid support like silica gel, alumina or phyllosilicate (M^{n+} —montmorillonite).
- After stirring the solution, the solvent is removed in *vacuo* and the dried solid support on which the reactants have been adsorbed are used for performing the reaction under microwave irradiation.
- Most of the reactions in solid state are carried out in open glass containers (test tubes, beakers and round bottom flasks (RBFs) using neat reactants under the solvent free conditions in an unmodified household MW oven.

Some of the important supporting reagents are as follows :

(i) Clay supported iron (II) nitrate (Clayfen),

(ii) Clay supported copper (II) nitrate (Claytop)

Benefits compared with normal synthesis in a liquid state are :

- High efficiency and throughput
- Increased simplicity and speed.

2.4.2. Protection and deprotection reactions :

- Protection and deprotection are important steps for the preparation of monomer building blocks, fine chemicals and synthesis of various pharmaceuticals.

- These reactions usually involve the use of acidic, basic or hazardous reagents and toxic metal salts.

- The solid support synthesis (MW-accelerated) provides an alternative to the conventional reactions.

2.4.3. Formation of acetals

- The acetals of 1-galacto-1, 4-lactone can be prepared in good yields by absorbing the lactone and the aldehyde on K-10 (or KSF) clay followed by heating the reaction mixture in a MW oven.

3

SUPERCRITICAL CARBON DIOXIDE (CO_2)

3.1. INTRODUCTION

- Scarf*
- Supercritical CO_2 is a fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure.
 - CO_2 generally behaves as a gas in air at standard temperature and pressure (STP) or as a solid called dry ice when frozen.
 - If the temperature and pressure are both increased from STP to be at or above the critical point for carbon dioxide, it can adopt properties midway between a gas and a liquid.
 - At 31°C and 73 atm. CO_2 exists as supercritical fluid.
 - CO_2 behaves as a supercritical fluid above its critical temperature and critical pressure expanding to fill its container like a gas but with a density like that of a liquid.

3.2. PHASE DIAGRAM FOR CO_2

A phase diagram provides a graphic representation to the states of CO_2 under various conditions of temperatures and pressures (fig. 3.1)

CO_2 can exist in different states depending on the temperature and pressure of its surroundings.

However, on increasing the pressure, CO_2 becomes liquid; at this point A (-56°C and 5.1 atm.), CO_2 exists as gas, liquid and solid simultaneously.

At point B (31°C and 73 atm) carbon dioxide exists as supercritical fluid.

In the supercritical state, CO_2 has a viscosity similar to that of a gas and density similar to that of a liquid.

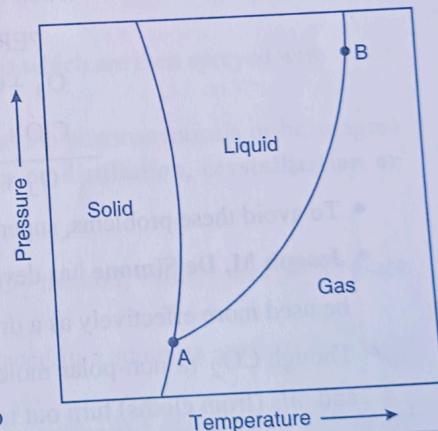


Fig. 3.1 : Phase diagram of CO_2

3.3. PROPERTIES OF SUPERCRITICAL CO_2

Supercritical CO_2 is simply carbon dioxide that is pressurized and heated above its critical point (31.1°C and 73 atm).

The fluid has many useful properties including low viscosity, high density, very low cost and leaves no residual solvents.

Green Chemistry and Nanotechnology

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The solvent properties of supercritical CO_2 (e.g. dielectric constant, solubility parameters, viscosity and density) can be altered or changed in a manner not possible with conventional solvents via manipulation of temperature and pressure.

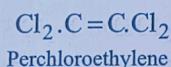
The properties of SC- CO_2 are intermediate between those of a liquid and a gas.

3.4. APPLICATIONS

1. Supercritical CO_2 is becoming an important commercial and industrial solvent due to its role in chemical extraction in addition to its relatively low toxicity and environmental impact.
2. The relatively low temperature of the process and the stability of CO_2 also allows most compounds to be extracted with little damage (or denaturing)

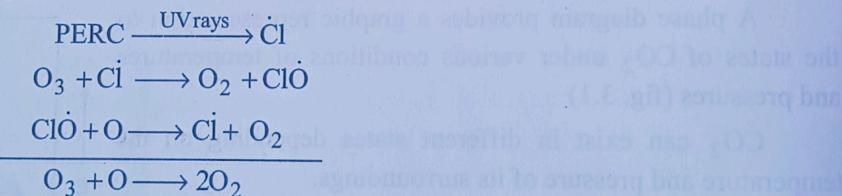
3. Use of supercritical CO_2 for dry cleaning :

- Supercritical CO_2 is used as a more environmentally friendly solvent for dry cleaning over traditional solvents such as chlorocarbons, including perchloroethylene or PERC.
- Most of the drycleaners use the solvent Perchloroethylene or PERC



Disadvantages of Perchloroethylene or PERC :

- Disposable of Perchloroethylene (a suspected carcinogen) can contaminate ground water.
- PERC when released into atmosphere rises to stratosphere region, where it gets decomposed into chlorine radical by the action of UV rays of the sun. (The chlorine radicals are responsible for the depletion of ozone layer)



- To avoid these problems, supercritical CO_2 is used as drycleaning solvent.
- **Joseph M. De Simone** has developed polymers that act as surfactants so that liquid CO_2 can be used more effectively as a drycleaning solvent.
- Though CO_2 (a non-polar molecule) dissolves nonpolar substances but most of the greases and oils (from cloths) turn out to be very insoluble in CO_2 .
- However the new surfactants (developed by De Simone) increase the solubility of oils and grease in CO_2 , in the same way that soaps increase the solubility of non-polar substances in water. This makes CO_2 a more effective drycleaning solvent.
- The surfactant (Polymer) has 'CO₂-Phobic' and 'CO₂-Philic' segments.

Conversion o

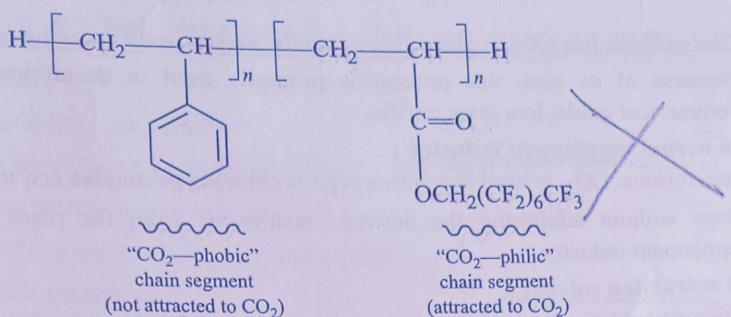
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Supercritical Carbon Dioxide (CO_2)

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Conversion of ' CO_2 -phobic' segment to lipophilic or hydrophilic :

- When De Simon's polymer is placed in a medium of supercritical or liquid CO_2 , it assembles into a micelle structure.
- The ' CO_2 -philic' segment surrounds the ' CO_2 -phobic' segments.
- The micelle structure can surround materials such as oils and grease in the inner ' CO_2 -phobic' area of the micelle structure and allow them to be washed away by the CO_2 solvent.
- The micelle technologies** have produced **dry cleaning machines** that use liquid CO_2 and surfactant to dryclean clothes, potentially replacing the environmentally harmful PERC ($\text{CCl}_2 = \text{CCl}_2$).

4. Decaffeination :

- Supercritical CO_2 is gaining popularity among coffee manufactures looking to move away from classic decaffeinating solvents.
- Supercritical CO_2 is forced through the green coffee beans which are then sprayed with water at high pressure to remove the caffeine.
- The caffeine can then isolated for other purposes (e.g., to the pharmaceuticals or beverages) by passing the water through **activated charcoal filters or distillation, crystallisation or reverse osmosis**.

Process of decaffeination :

- The most recent of the decaffeination processes is the CO_2 method, which uses CO_2 in place of any chemicals.
- First, the coffee beans are soaked in water, and then placed in a stainless steel container (or extraction vessel).
- The container is sealed, and liquid CO_2 is forced into the coffee at 1,000 pounds of pressure per square inch to extract the caffeine.
- The CO_2 solvent dissolves and draws only the caffeine out of the coffee, leaving behind all of the flavor molecules.
- The caffeine packed CO_2 is then moved to another container, known as the **absorption chamber**, where the pressure is released and the CO_2 returns to a gaseous state and only the caffeine remains.

- The caffeine free CO_2 is placed back into the pressurized tank to be used again.
- Because of its cost, this process is primarily used to decaffeinate large quantities of commercial grade, less toxic coffee.

5. In herbal supplement industry :

- Supercritical CO_2 is used to remove organochloride pesticides and metals from agricultural crops without adulterating the desired constituents from the plant matter in the herbal supplement industry.

6. As extraction solvent :

- Supercritical CO_2 is used as the extraction solvent for the extraction of essential oils and other herbal distillates.
- Due to its ability to selectively dissolve organic compounds and assist the functioning of enzymes, SCO_2 has been suggested as a potential solvent to support biological activity on Venus or superearth type planets.

7. As chemical reagent : Environmentally beneficial, low cost substitutes for rigid thermoplastic and fired ceramic are made using supercritical CO_2 as a chemical reagent.

8. Supercritical CO_2 is used in the forming of polymers.

9. Supercritical CO_2 is used as the working fluid in high efficiency domestic water heat pumps.

10. The unique properties of CO_2 present advantages for close-loop power generation and can be applied to various power generation applications.

11. Allam power cycle uses CO_2 as the working fluid in combination with fuel and pure oxygen.

12. Aerogel production : SCO_2 is used in the production of silica, carbon and metal based aerogels.

13. Sterilization of biomedical materials : Supercritical CO_2 is used for sterilization of biological materials and medical devices with combination of the additive peracetic acid (PAA).

14. Other important applications on the use of SCO_2 as solvent for organic reactions are as follows :

- Supercritical polymerisations
- Free radical bromination
- Hydrocarbon functionalisation
- Diels-Alder reaction
- Kolbe-Schmidt synthesis
- Bromination
- Polymerisations
- Freidel-Crafts reaction
- Hydrogenation in $\text{Sc}-\text{CO}_2$

4.3. TYPES OF GREEN ENERGY

The main sources of green energy are wind energy, solar power and hydroelectric power (including tidal energy, which uses ocean energy from the tides in the sea).

Some most common forms of green energy are as follows :

1. **Solar power** : Solar energy may be directly used either by active solar systems or passive solar systems.

India has been one of the major producers of photovoltaic (PV) systems.

PV systems currently used include street lighting systems (SLS), domestic lighting systems (DLS), community lighting systems and TV (CD_5 and TV), water pumping systems and small power plants.

2. **Wind Power** : Wind energy uses the power of the flow of air around the world to push turbines that then generate electricity. It suited to offshore and higher altitude sites.

3. **Hydropower** : This type of green energy uses the flow of water in rivers, streams, dams or elsewhere to produce electricity.

4. **Tidal power** : Tidal power projects harness the energy of the tides as the mass of water moves in and out. Dams built across the mouths of river confluence with oceans, permit the flows through small opening fitted with propellers connected to electric turbines.

5. **Geothermal energy** : This type of green power uses thermal energy that has been stored just under the earth's crust. Based on geologic criteria, several geothermal systems may be defined e.g., hydrothermal convention systems, hot igneous systems and geopressured systems.

4.4. IMPORTANCE OF GREEN ENERGY

- Green energy is important for the environment as it replaces the negative effects of fossil fuels with more environmentally friendly alternatives.
- Derived from natural resources, green energy is also often renewable and clean, (emit no or few green house gases and are often readily available).
- Green energy release for less green house gases than fossil fuels, as well as few or low levels of air pollutants.
- Green energy also represents a low cost solution for the energy needs of many parts of the world.

4.5. GREEN ENERGY IN THE CONTEXT OF SUSTAINABLE DEVELOPMENT

Though the term sustainable development is difficult to define, as concept, it is very popular throughout the world.

One of the most widely held definitions is provided by the Brundtland report in 1987; defined as "sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs".

- Another often-quoted definition by caring provides for the Earth : "improving the quality of human life while living within the carrying capacity of supporting ecosystems" (Munro 1995).