

SYNOPSIS

(ORGANIC CHEMISTRY)

Introduction

Organic chemistry is basically the chemistry of carbon compounds. As we know that carbon forms different types of compounds. This is possible because it forms covalent bonds with itself and with other elements like hydrogen, oxygen, nitrogen, sulphur and halogen in a variety of ways. This result in the formation of large variety of compounds which are widely distributed in nature and play an important role daily lives. Like carbohydrates → source of energy to our body, proteins and enzymes → plays important catalytic function in various bio chemical reactions, nucleic acids (DNA and RNA) → carrying genetic information and helps in protein synthesis

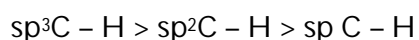
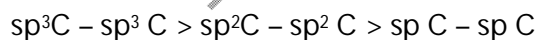
Organic Chemistry deals with these variety of carbon compounds.

Two main reasons for carbon to form such a vast organic compounds are:

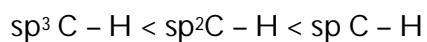
1. **Tetravalency:** Since carbon has four valence electrons, carbon can form a maximum of four covalent bonds. These covalent bonds may be **sigma bonds** and **pi bonds**.

Carbon can use maximum four orbital in the hybridization (one s-orbital and maximum three p orbitals). Hence, carbon can be sp , sp^2 or sp^3 hybridised.

This hybridization influences the bond length and bond enthalpy (or strength) in organic compounds sp hybrid orbital form a stronger and shorter bond than sp^2 or sp^3 due to 50% s-character. The decreasing bond length order is



The increasing bond strength order is

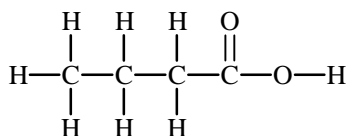


2. **Catenation:** The ability of carbon atom to form a bond with itself. This is responsible for large number of straight chain, branched chain, cyclic compounds of carbon.

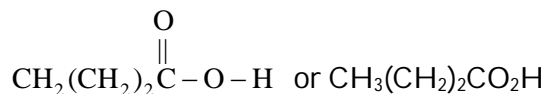
Structure of Organic Compounds

The structures of organic compounds are represented in different ways.

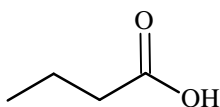
1. **Structural formula** using 'dash' to represent a covalent bond.



2. **Condensed formula** omitting some or all of the covalent bonds and by indicating the number of identical groups attached to an atom by a subscript.



3. **Bond-line structures.** In these structures carbon and hydrogen are not shown and the lines representing carbon-carbon bonds are drawn in zig-zag fashion.



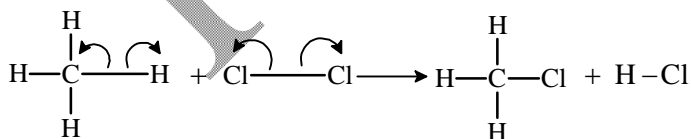
All organic reactions (synthesis as well as properties of organic compound) involves two types of cleavages of covalent bond.

1. Homolytic cleavage

Cleavage of covalent bond in which the electrons of the shared pair are equally divided amongst the bonded atoms. This homolytic cleavage takes place when the electronegativity difference between the two bonded atoms is zero or nearly zero.

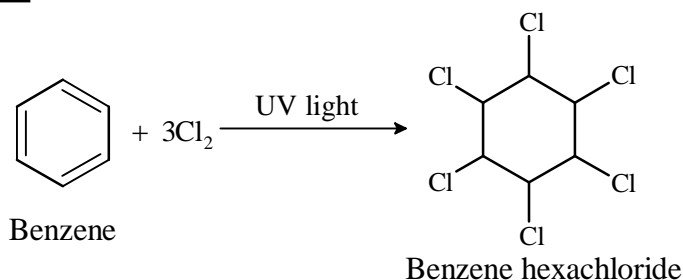


Homolytic cleavage results in the formation of free radicals which are highly reactive. Homolytic cleavage takes place in the presence of light or high temperature.



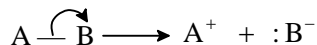
The photochlorination of methane involves free radical formation.

Benzene to benzene hexachloride using Cl_2 in the presence of light also involves free radicals.

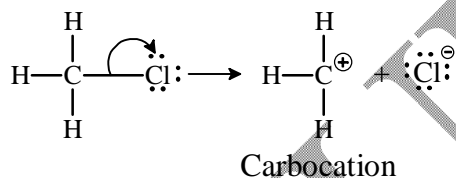


2. Heterolytic cleavage

This type of cleavage takes place when the covalent bond is present between two unlike atoms with large electronegativity difference and the bond is polar. Then, the whole shared pair move towards the more electronegative atom and atom then leaves as anion with lone pair of electrons, the other atom left with positive charge and with an incomplete octet.



Heterolytic cleavage results in the formation of **carbocation** (carbon with positive charge) and **carbanion** (carbon with negative charge).



There are three main reaction intermediates formed during the reactions.

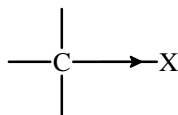
1. Free radicals
2. Carbocations
3. Carbanions

All these reaction intermediates are reactive

The stability of these reaction intermediates can be explained using.

1. Inductive effect
2. Hyperconjugation
3. Electromeric effect
4. Resonance

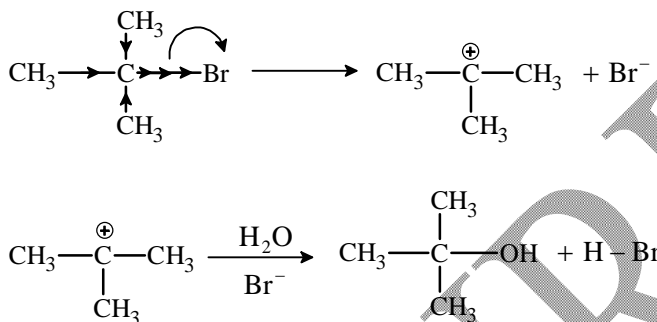
Inductive effect: It is the polarisation of a covalent bond in which the carbon atom of an alkyl group is bonded to hetero atom (atom more electronegative than carbon)



Due to high electronegativity, the hetero atom X exerts an electron withdrawing effect or **-I effect** and the alkyl group pushing electrons towards the hetero atom is electron donating group and exerts

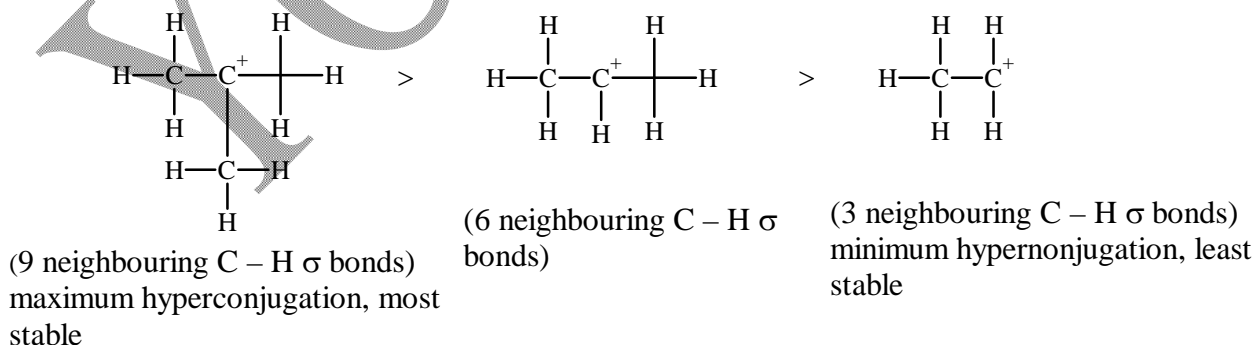
+I effect. All alkyl groups are +I effect. Groups with -I effect are $-\text{NO}_2$, $-\text{OH}$, $-\overset{\text{O}}{\parallel}\text{C}-\text{R}$, etc.

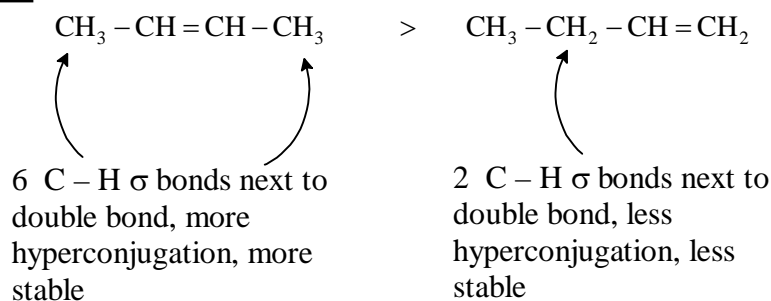
Also, more the number of groups with +I effect, more the polarity of C - X bond, more easily the C - X bond will split up heterolytically.



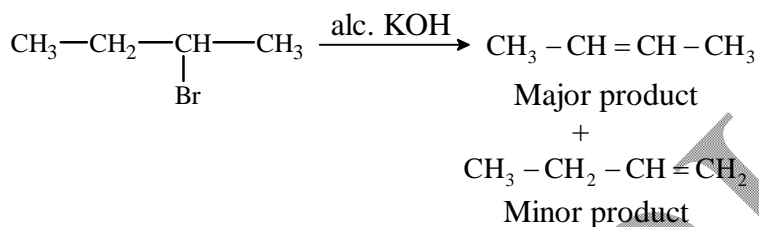
Hyperconjugation: This is defined as the interaction between empty p orbital of an sp^2 carbon atom and adjacent sp^3 -s (C - H bond) σ bond or the interaction between the π system and the adjacent sp^3 -s σ bond.

More the number of adjacent C - H σ bonds, more the hyperconjugation, more the stability of carbocation or the alkenes.



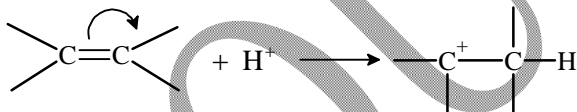


That's why

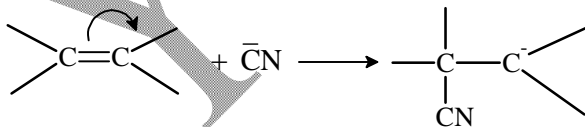


Electromeric effect: It is defined as the polarization of π bond involving some external reagents. It is defined as the complete transfer of a shared pair of π -electrons to one of the atoms joined by a multiple bond on the demand on the attacking reagent. It involves heterolytic cleavage of π -bond. There are two types of electromeric effect.

(i) **+E effect** : In this, the π electrons of the double bond are transferred to that atom to which the reagent gets attached.

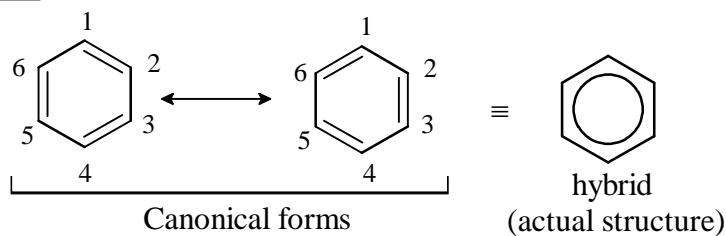


(ii) **-E effect**: In this, the π electron of the double bond are transferred to that atom to which the attacking reagent does not get attached.



When inductive effect and electromeric effects operate in opposite directions, the electromeric effect predominates.

Resonance: It is a phenomenon in which the molecule or ion can be represented by more than one Lewis dot structure. Resonance is a phenomenon which involves delocalization of pi-bonds. For example, benzene can be represented by two resonating energetically identical structures.

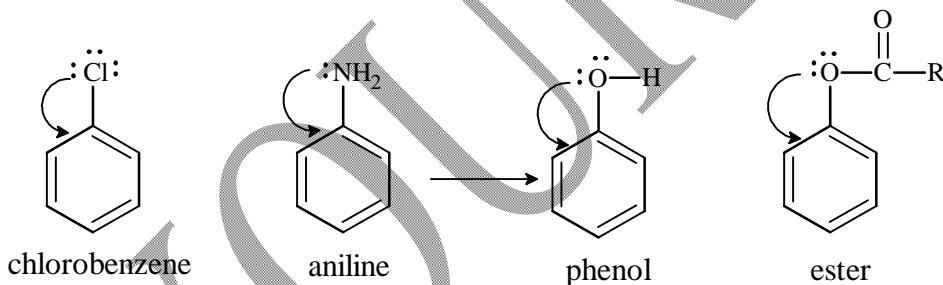


The actual structure is a hybrid of these two and more stable than these two canonical forms called **resonance hybrid** the difference in energy between the actual structure and the lowest energy resonance structure is called the **resonance energy**.

While writing resonating structures:

- (i) Number of atoms and position of atoms remains same
- (ii) Number of electrons remains same, only position of π -bond changes
- (iii) Each and every atom should have a complete octet
- (iv) Negative charge should be on the more electronegative atom and positive charge should be on the less electronegative atom.

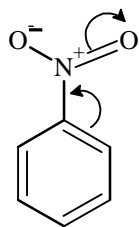
Any group which enhance the resonance by donating electrons exerts **+R effect**.



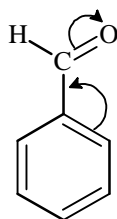
This +R effect is responsible for

- (i) low reactivity of chlorobenzene
- (ii) less basicity of aniline in comparison to alkyl amine
- (iii) high acidic strength of phenol in comparison to alcohols

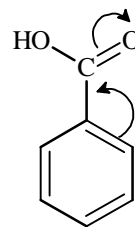
Any group which enhance the resonance by withdrawing electron from the π -system exert **-R effect**.



nitrobenzene



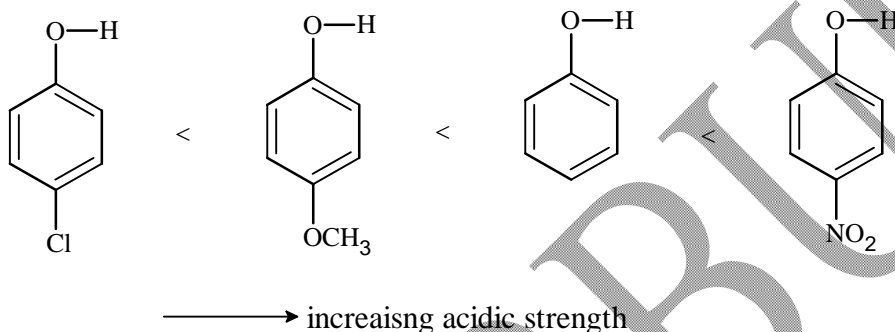
benzaldehyde



benzoic acid

All these effects: Inductive effect, hyperconjugation and resonance effect are used to explain the stability of the reaction intermediates, acidic strength of phenols and carboxylic acids.

Group with +R effect decreases and group with -R effect increases the acidic strength of phenols.



Types of Reagents: There are mainly two types of reagents in organic chemistry:

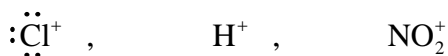
- Nucleophiles (Nu)** → atoms or groups having at least one lone pair of electrons present. These nucleophiles are electron rich, electron pair donor and in reactions involving polar bond, nucleophile attacks at the electron deficient atom (or the electrophilic centre).

Examples of nucleophiles are:

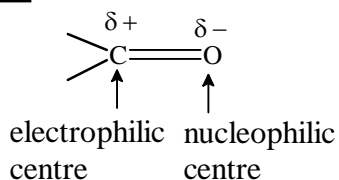


- Electrophiles (E)** → atoms or groups having incomplete octet, having at least one empty atomic orbital available. The electrophiles are electrons deficient species, Lewis acids. The electrophiles attacks at the electron rich atom of a polar bond in reactions.

Examples of electrophiles are:



In $>C=O$, O is due to its high electronegativity is the nucleophilic centre and carbon is the electrophilic centre.



Organic Reactions: Organic reactions are the chemical reactions involving the conversion of organic reactants into organic products using different types of reagents.

For example



All organic reactions involves breaking and making of covalent bonds.

A sequential account of each step in terms of structure and energetics during bond breaking and bond formation that occurs when a reactant is transformed into the product is known as **reaction mechanism**.

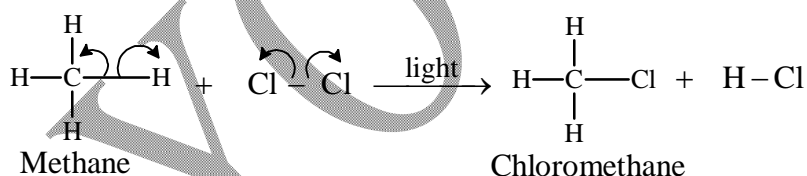
Type of Organic reactions

Organic reactions can be classified into the following main types:

A: Substitution reactions

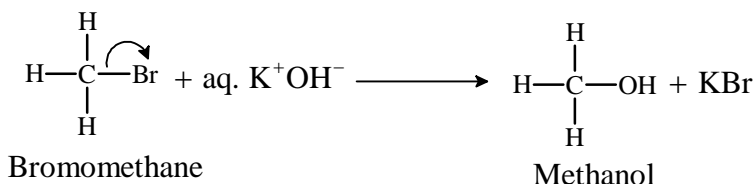
In these reactions, one atom or a group of atom in a molecule is replaced or substituted by another atom or group. The rule of substitution is **like substitutes like mean**.

(i) radical can be replaced by radical, then the reaction is called free radical substitution (S_{FR})



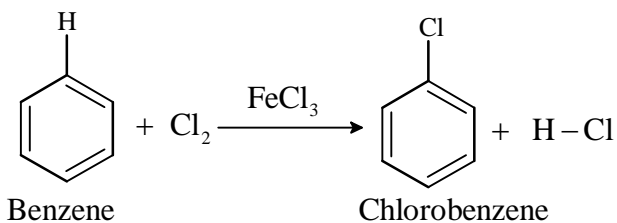
In this reaction H^\bullet has been replaced by Cl^\bullet

(ii) Nucleophile can be replaced by nucleophile, then it is called **nucleophilic substitution reactions. (S_N)**



In this reaction Br⁻ has been replaced by OH⁻.

(iii) Electrophile can be replaced by an electrophile, then it is called **electrophilic substitution reaction** (S_E)

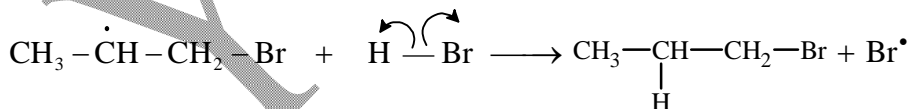
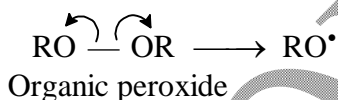
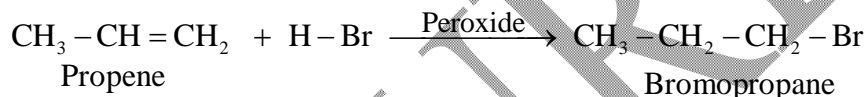


In this reaction, the hydrogen of benzene H⁺ has been replaced by Cl⁺. Reactions involving replacement of H of benzene by any group is called electrophilic substitution reaction.

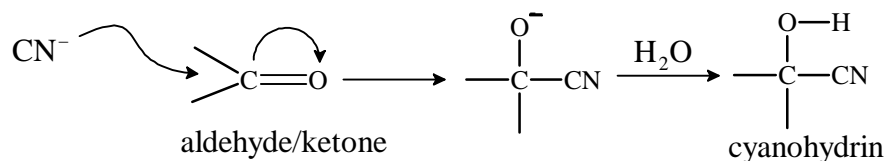
B. Addition reaction

In these reactions, the two or more reactants combine to form a single product having all the atoms of combining units. The addition reactions are given by unsaturated compounds. The addition reactions may be

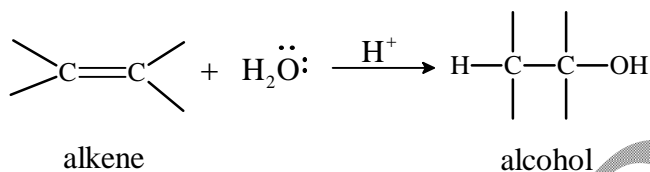
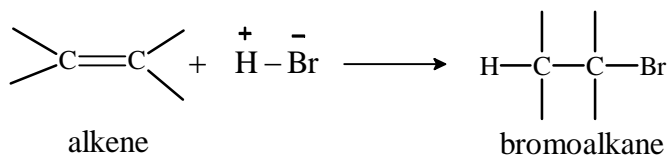
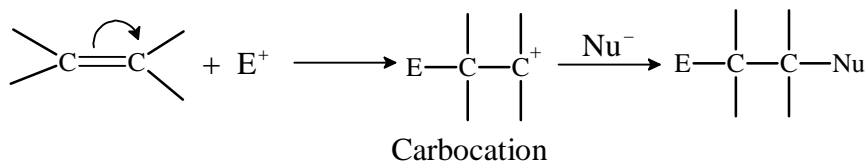
(i) **Free radical addition**, example is Anti-Markovnikov addition of HBr to alkane in the presence of organic peroxide.



(ii) **Nucleophilic addition reactions**, mainly given by aldehydes and ketones, in which the nucleophile adds to the carbonyl carbon and electrophile adds to carbonyl oxygen.



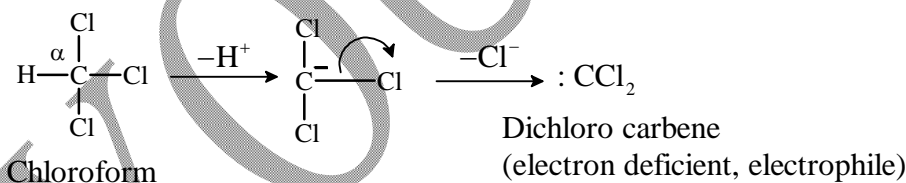
(iii) **Electrophilic addition reactions**, these are mainly given by alkenes like hydrohalogenation, hydration, etc. First step involves the addition of an electrophile to carbon-carbon double bond to form carbocation which then combines with nucleophile to form product.



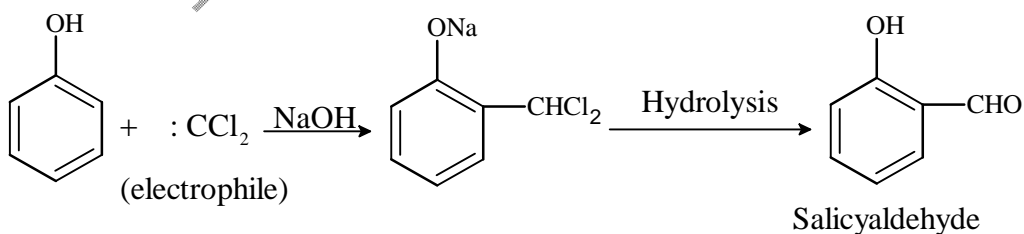
C: Elimination reactions

In an elimination reaction, two atoms or groups of the molecule are eliminated to give the product. Depending upon the relative positions of the atoms or groups eliminated, these reactions are classified as α (alpha), β (beta) or γ (gamma) elimination reactions.

(i) **α -Elimination:** In α -elimination, the two atoms or groups are removed from the α -position giving electron deficient reactive intermediates, which further reacts to give stable product.

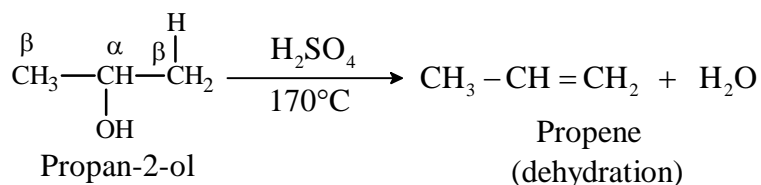
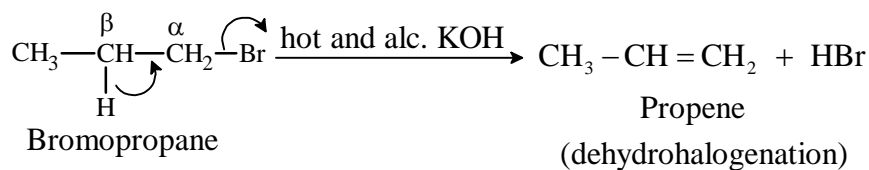


This dichloro carbene is used in the preparation of salicylaldehyde from phenol, (electrophilic substitution)

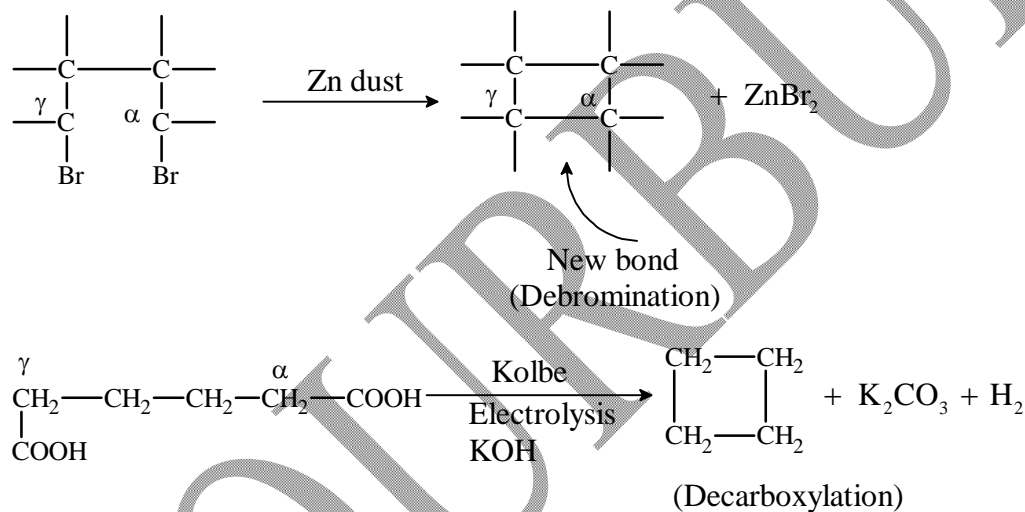


This reaction is known as **Reimer-Tiemann reaction**.

- (ii) **β -elimination:** In this, the two groups are removed from adjacent positions (α and β). As a result double bond is formed between α -and β -carbon atoms.



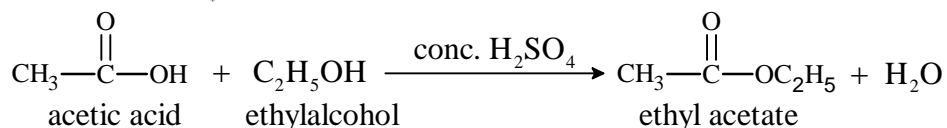
- (iii) **γ -elimination:** In these reactions, the atoms or groups being removed are three bonds away, i.e., at α and γ -position. It involves the formation of a cyclic structure.



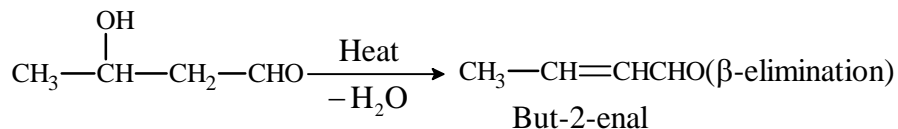
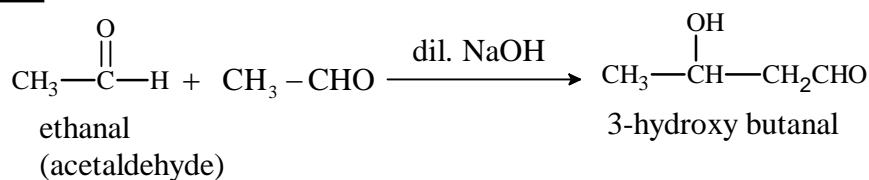
D. Condensation Reactions:

In these reactions, two different or same organic reactants containing functional groups unite to give a product with or without the loss of small and simple molecules.

For example, **esterification reaction** between the carboxylic acid and alcohol in the presence of conc. H_2SO_4 to form ester with the loss of H_2O molecules.



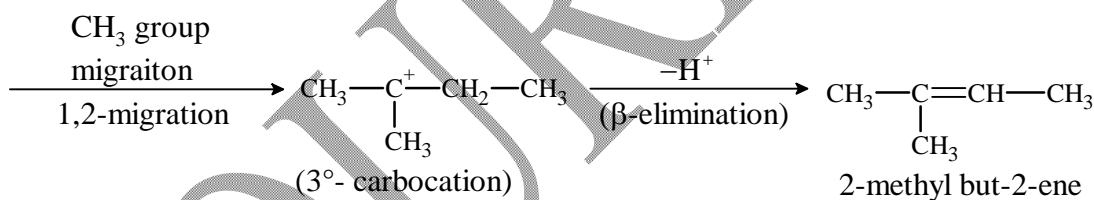
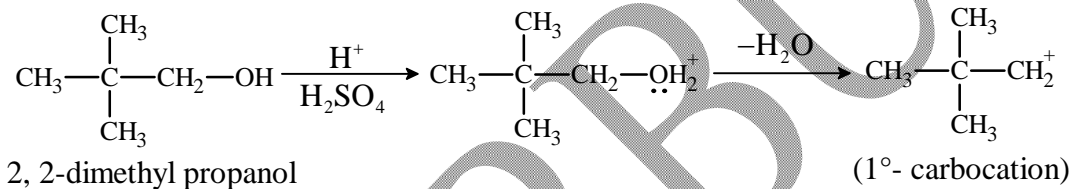
Another example is the **Aldol condensation** in which two molecules of acetaldehyde condense in the presence of dilute alkali to form 3-hydroxy butanal (β -hydroxy aldehyde) which then loses water molecule (just like dehydration of alcohol) to form but-2-enal.



E. Rearrangement reaction:

These reactions involves migration of a group from one atom to another in the same molecule.

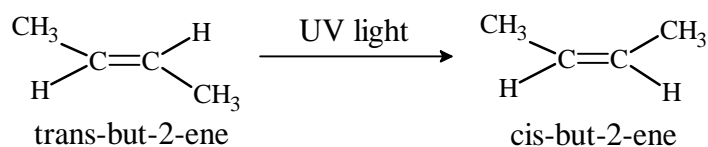
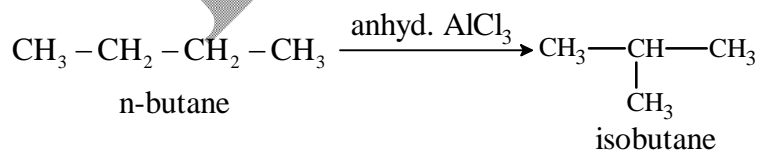
Example: Dehydration of neo pentyl alcohol (2, 2-dimethyl propanol).



F. Isomerisation Reaction:

These reaction involve interconversion of one isomer into another.

For example:



There are some other reactions in organic chemistry which do not involve ionic or free radical intermediates. These reactions occur in single step via a cyclic transition state. The bond breaking and bond formation takes place simultaneously in these reactions. Such reactions are called collectively **pericyclic reactions**.

Example:

