Chapter –II
Mechanism of Organic Reactions

Contents:

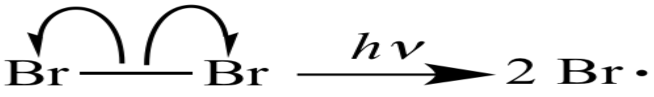
Chapter –II
Mechanism of Organic Reactions

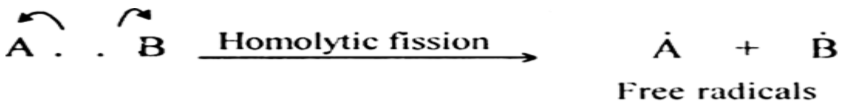
Introduction: In chemistry, a reaction mechanism is the step by step sequence of elementary reactions. Reaction mechanism, or reaction pathway, describes the successive steps at the molecular level that take place in a chemical reaction. In each step, molecular bonds are either created or broken. The study of the detailed processes of reaction mechanisms is important for many reasons; including the help it gives in understanding and controlling chemical reactions. The ability to draw such analogies frequently makes it possible to predict the course of untried reactions. Mechanisms explain how things work. This makes them important in their own right, but also means that they are often used when designing clinical studies. A chemical mechanism is a theoretical conjecture that tries to describe in detail what takes place at each stage of an overall chemical reaction. The conjectured mechanism is chosen because it is thermodynamically feasible, and has experimental support in isolated intermediates or other quantitative and qualitative characteristics of the reaction. It also describes each reactive intermediate, activated complex, and transition state, and which bonds are broken (and in what order), and which bonds are formed (and in what order). A complete mechanism must also explains the reason for the reactants and catalyst used, the stereochemistry observed in reactants and products, all products formed and the amount of each.

Types of bond breaking:

1) **Homolytic bond cleavage (breaking) or Homolysis:** The term homolysis generally means breakdown (-lysis) to equal pieces (homo = same).

   Symmetrical fission (cleavage) of a covalent bond between two atoms or group in such a way that each atom or group acquires one electron from the bonding electron pair is called as Homolytic fission (Homolysis).





$$:\ddot{Cl}\ -:\ddot{Cl}: \xrightarrow[523\ K]{u.v.\ light} :\ddot{Cl}\quad -\cdot\ddot{Cl}:$$

Free radicals

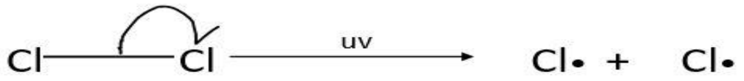
$$Cl_2 \xrightarrow{uv} 2Cl\bullet$$

One chlorine molecule two chlorine radicals

OR

$$Cl{-}Cl \xrightarrow{uv} Cl\bullet + Cl\bullet$$

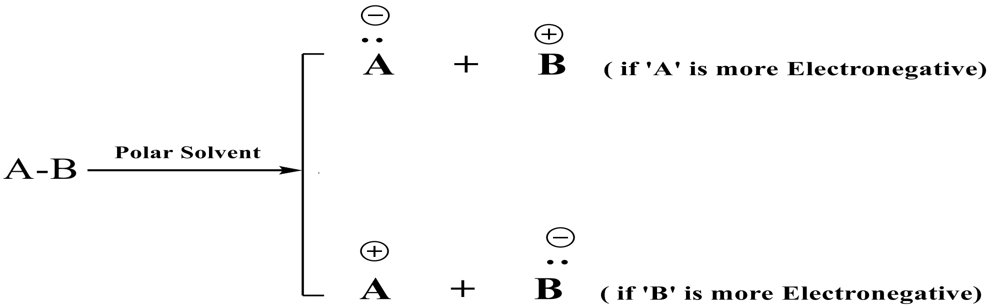
Sometimes, homolytic fission is represented with a curly half-arrow as below.



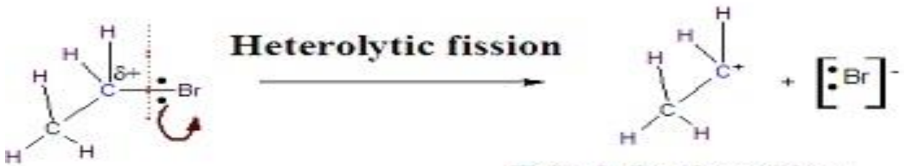
$$CH_3\text{-}CH_3 \longrightarrow \overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3$$

2) **Heterolytic bond cleavage (breaking) or Heterolysis:** The term heterolysis generally means breakdown (-lysis) to unequal pieces (hetero = dissimilar).

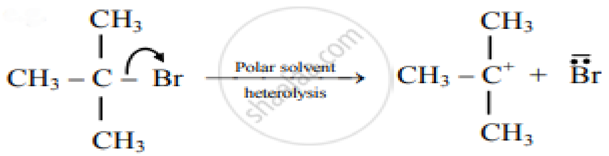
Unsymmetrical fission (cleavage) of a covalent bond between two atoms or group in such a way that shared bonding electron pair retains with more electronegative, is called as Heterolytic fission (Heterolysis).



Organic species having positively charged and triply bonded carbon atoms which is formed by heterocyclic fission is called as carbocations or Carbonium ion.



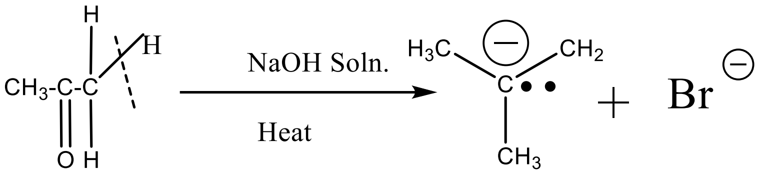
Ethyl Carbocation



(Carbon is less electronegative than bromine atom)

Organic species having negatively charged and triply bonded carbon atoms which is formed by heterocyclic fission is called as carbanions ion.

In this type of carbon retains both unshared bonding electrons to get negative charge.



Carbanions ion

(Carbon atom is more electronegative than hydrogen)

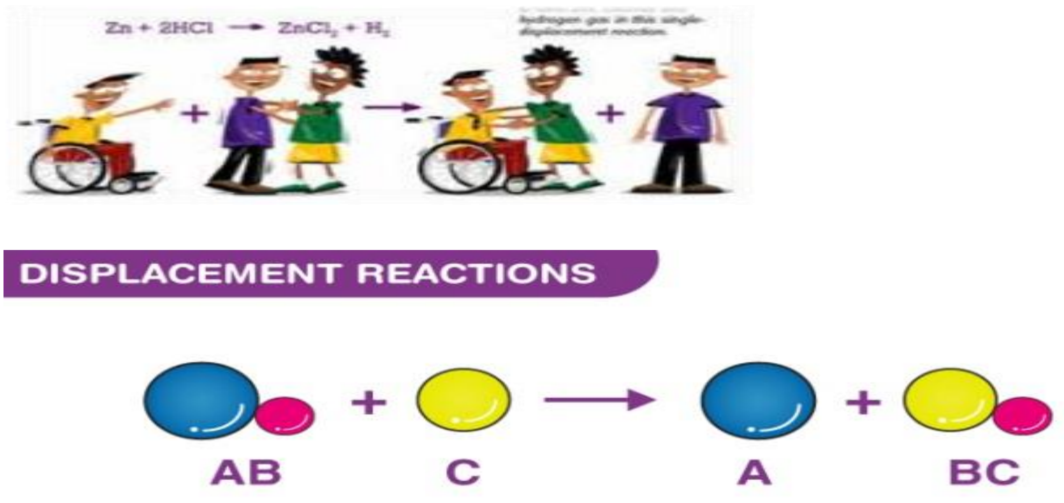
Types of organic Reagents:

1) **Electrophilic reagents**: Positively charged species like H^+,NO_2^+,NO^+,CH_3^+ or electron deficient neutral molecules (Lewis acids) like $AlCl_3$,BF_3 are called as electrophiles.

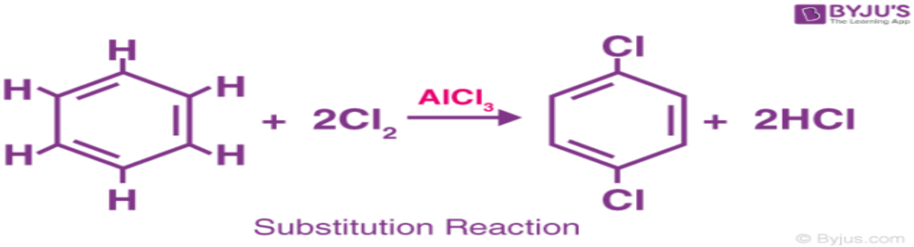
   They attack on negatively charged electron rich species.
2) **Electrophilic reagents**: Negatively charged species like OH^-,CN^-,OR^-,$RCOO^-$ and neutral molecules with unshared pair of electrons (Lewis bases) like R-O-R,R-OH,$R\text{-}NH_2$ etc. are called as Nucleophiles. They can donate a pair of electrons for bond formation with another electron deficient molecule.

Types of organic Reactions:

A) Substitution or displacement reactions: A substitution reaction (also known single displacement reaction or single substitution reaction) is a chemical reaction during which one functional group in a chemical compound is replaced by another functional group. Substitution reactions are of prime importance in organic chemistry. Substitution reactions in organic chemistry are classified either electrophilic or nucleophile depending upon the reagent involved, whether a reactive intermediate involved in the reaction is a carbocations, a carbanions or a free radical, and whether the substrate is aliphatic or aromatic. Detailed understanding of a reaction type helps to predict the product outcome in a reaction.



In electrophilic substitution, hydrogen atom attached to carbon atom of an organic compound is substituted by electrophile.



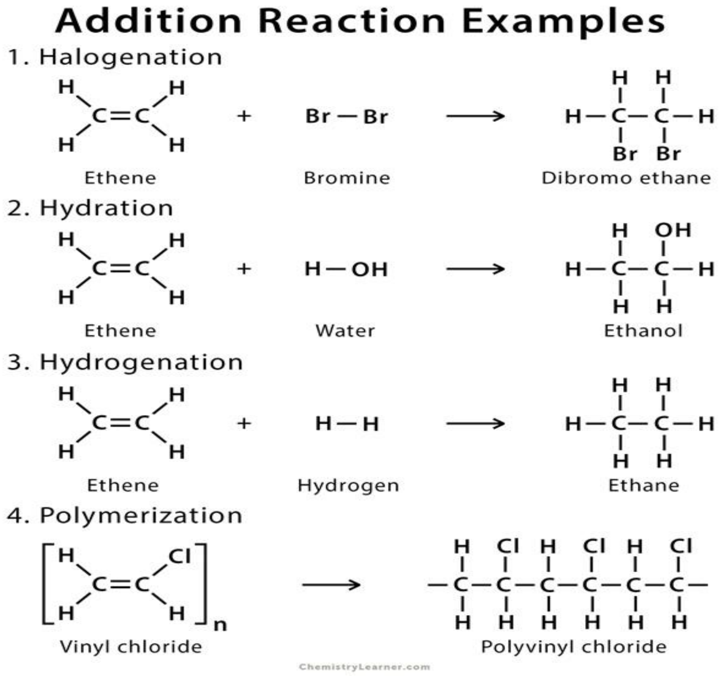
In Nucleophilic substitution, it is an atom other than hydrogen atom is substituted by nucleophile.

$$CH_3\text{-}Br + CN^{-} \longrightarrow CH_3\text{-}CN + Br^{-}$$

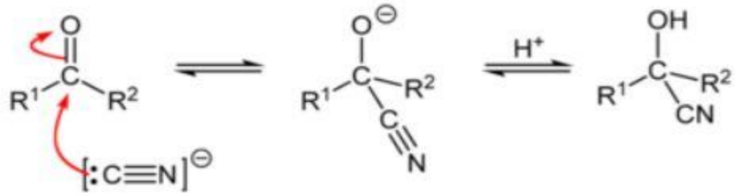
B) Addition reactions: Addition reaction occurs when two or more reactants combine to form a product without the loss of any atoms present in the reactants.

Addition reaction is common in compounds that have unsaturated C-C bond, like double (alkenes) and triple (alkynes) bonds. The weaker π bond is converted into two new stronger σ bonds. This product will contain all the atoms that were present in the reactants.

An addition reaction is initiated by electrophile is called as electrophilic addition reaction.



An addition reaction initiated by nucleophile is called as Nucleophilic addition reaction.

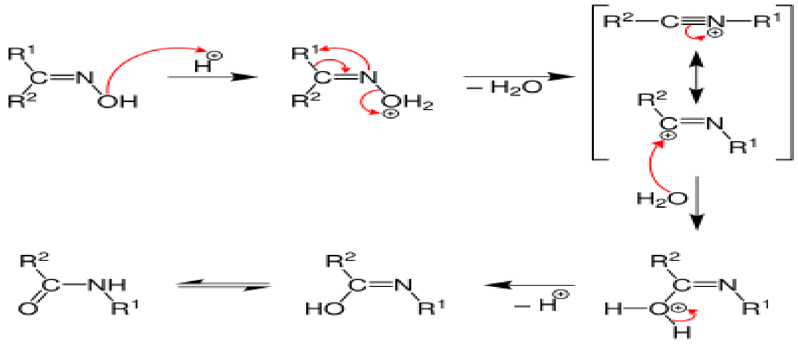


(CN$^-$ as nucleophile)

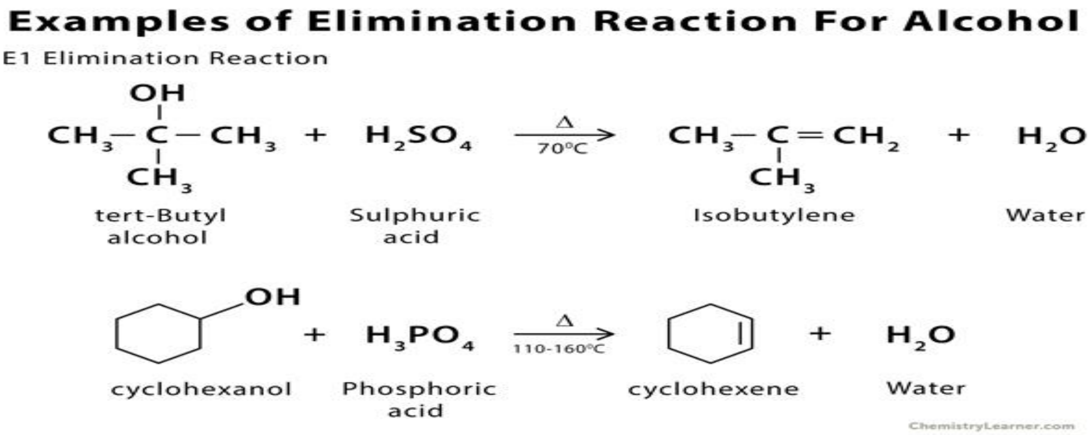
C) Elimination Reaction: A reaction in which two atoms or groups from a molecule are removed without replacement by another atom or group is called as elimination reaction. There are two types of elimination reactions.

1,1 or α, α-elimination reaction: If two atoms from same carbon atom are removed called as 1,1 or α, α elimination reaction.

$$CHCl_3 \xrightarrow[\text{Heat}]{\text{NaOH}} \underset{\text{Carbene}}{:C\text{-}Cl_2} + HCl$$

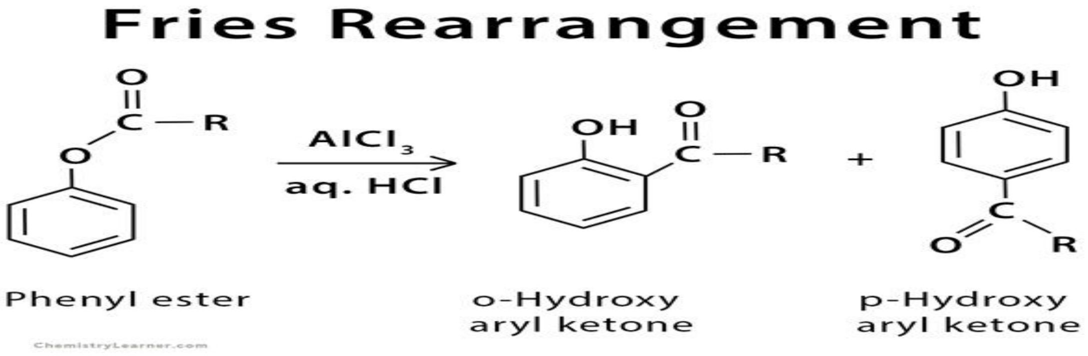


1,2 or α, β elimination reaction: A reaction in which two atoms or groups attached to adjacent carbon atom (α, β) in a molecule are removed without being replaced by another atom or group, resulting in the formation of alkenes, is called as 1,2 or α, β elimination reaction.



d) Rearrangement reaction: It involves the migration of an atom or group from one position to another position within the molecule to form structural isomer of the original compound.In this type, molecule undergoes a reorganization of its constituent parts.

Example 1) Phenyl acetate in presence of anhydrous $AlCl_3$ undergoes rearrangement to form ortho and Para hydroxy acetophenone (Fries Reaction).



2) Ketoximes with PCl_5 or $SOCl_2$ or acid gives anilides.(Beckmann rearrangement)

Reactive Intermediates:

Introduction: In chemistry, a reactive intermediate or an intermediate is a short-lived, high-energy, highly reactive molecule. When generated in a chemical reaction, it will quickly convert into a more stable molecule. Only in exceptional cases can these compounds be isolated and stored, e.g. low temperatures, matrix isolation. When their existence is indicated, reactive intermediates can help explain how a chemical reaction takes place.

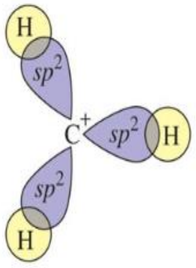
The series of steps together make a reaction mechanism. A reactive intermediate differs from a reactant or product or a simple reaction intermediate only in that it cannot usually be isolated but is sometimes observable only through fast spectroscopic methods. In certain cases, they are separated and stored. For example, Matrix isolation and Low temperatures.

Common features of reactive intermediates:

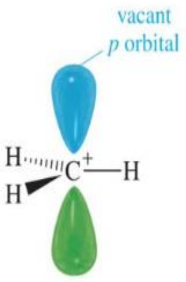
1) Low concentration.
2) Dot not obey the Lewis octet rule with the exception of carbanions, hence the high reactivity.
3) Often generated on chemical decomposition.

4) It is often possible to prove the existence of this species by spectroscopy.
5) Cage effects have to be taken into account
6) Often stabilization by conjugation or resonance.
7) Often difficult to distinguish from a transition state.
8) Prove existence by means of chemical trapping.
1) **Carbocations (Carbonium ion): Structure:**

Structure of Carbocations: Generally, in the carbocations the positively charged carbon atom is bonded to three other atoms and has no nonbonding electrons. It is sp^2 hybridized with a planar structure and bond angles of about 120°. There is a vacant unhybridized p orbital which in the case of CH_3^+ lies perpendicular to the plane of C-H bonds.



top view

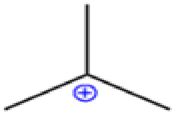


side view

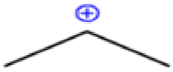
Carbocations has only six electrons in its valence shell. Carbocations bears positive charge hence electron deficient and thus strong electrophile and reacts with negatively charged Nucleophiles.

Classification of carbocations: on the basis of the number of carbon groups bonded to the carbon. The carbocations can be termed as methyl, primary, secondary or tertiary.

- Methyl carbocations: If no carbon is attached to the carbon with the positive charge it is simply called as **methyl carbocations**.
- If one, two or three carbon is attached to the carbon with the positive charge it is called the **primary carbocations, secondary carbocations, and tertiary carbocations** respectively.



tertiary carbocation



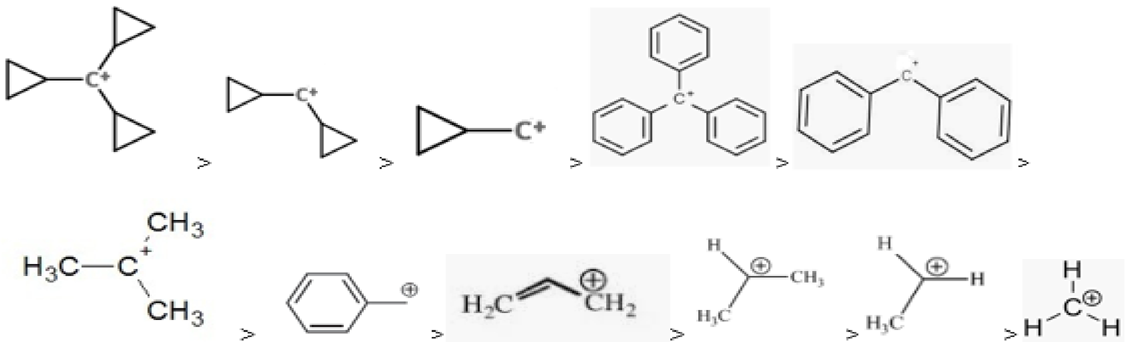
secondary carbocation

primary carbocation

methyl carbocation

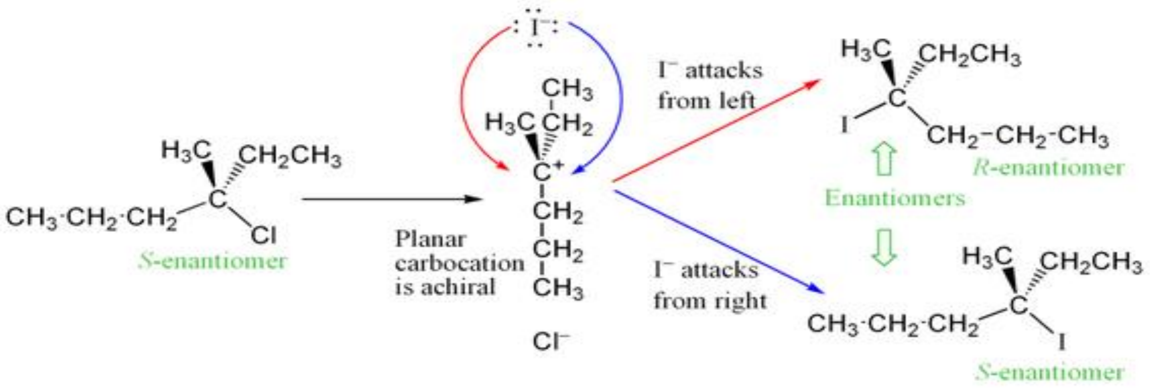
- If there is a carbon-carbon double bond next to the carbon with the positive charge it is termed as **allylic carbocations**.
- In the same way, if the carbon with the positive charge is attached to a double bond, the carbocations is termed as **vinylic carbocations**. Here, hybridization of the carbon having the positive charge is ‘sp’ and geometry is linear.
- Whenever the carbon which consists of the positive charge is part of a benzene ring, then the carbocations an **aryl carbocations**.
- If the carbon having a positive charge is immediately next to a benzene ring, it is termed as a **benzylic carbocations**.

Stability of carbocations : The stability order of carbocations is as follows:



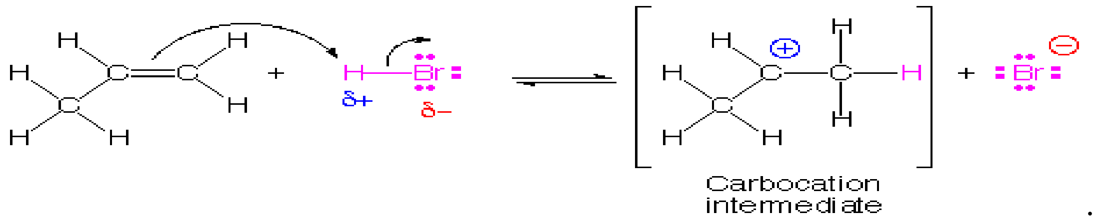
Tertiary carbocations is more stable due to inductive and hyper conjugation effects.

Methods of formation of carbocation:1)When tertiary butyl chloride on heating with aqueous iodine solution forms tert.butyl carbocations as an intermediate.(i.e.SN^1 reaction).

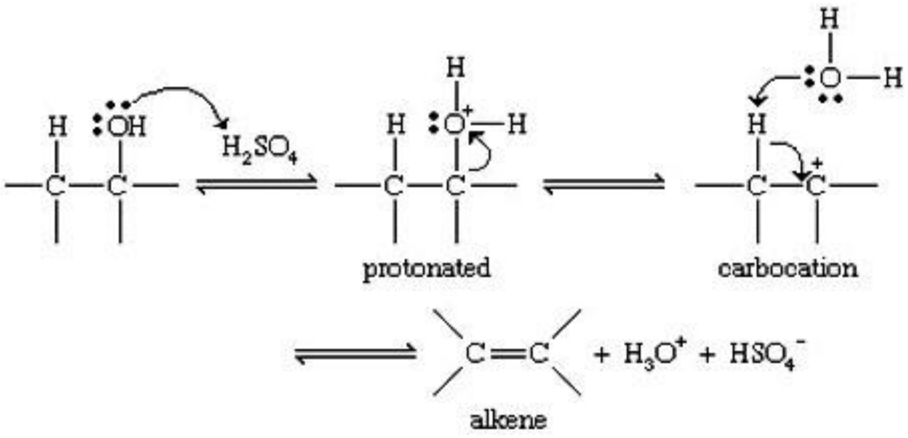


2) Alkene in the presence of strong acids undergoes protonation to form carbocations.

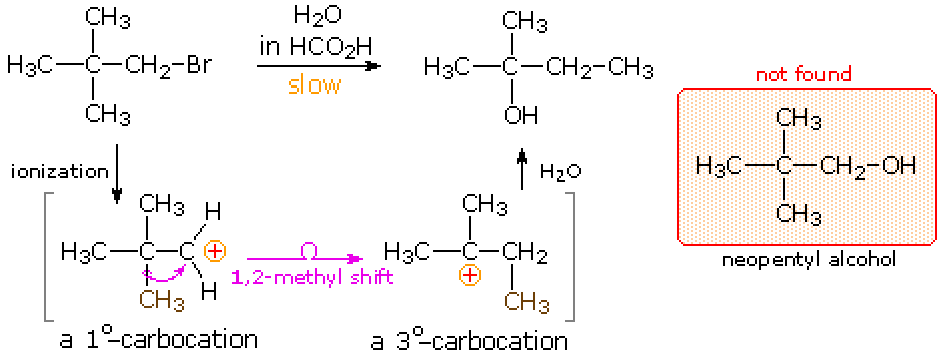
Step 1 : Carbocation Formation



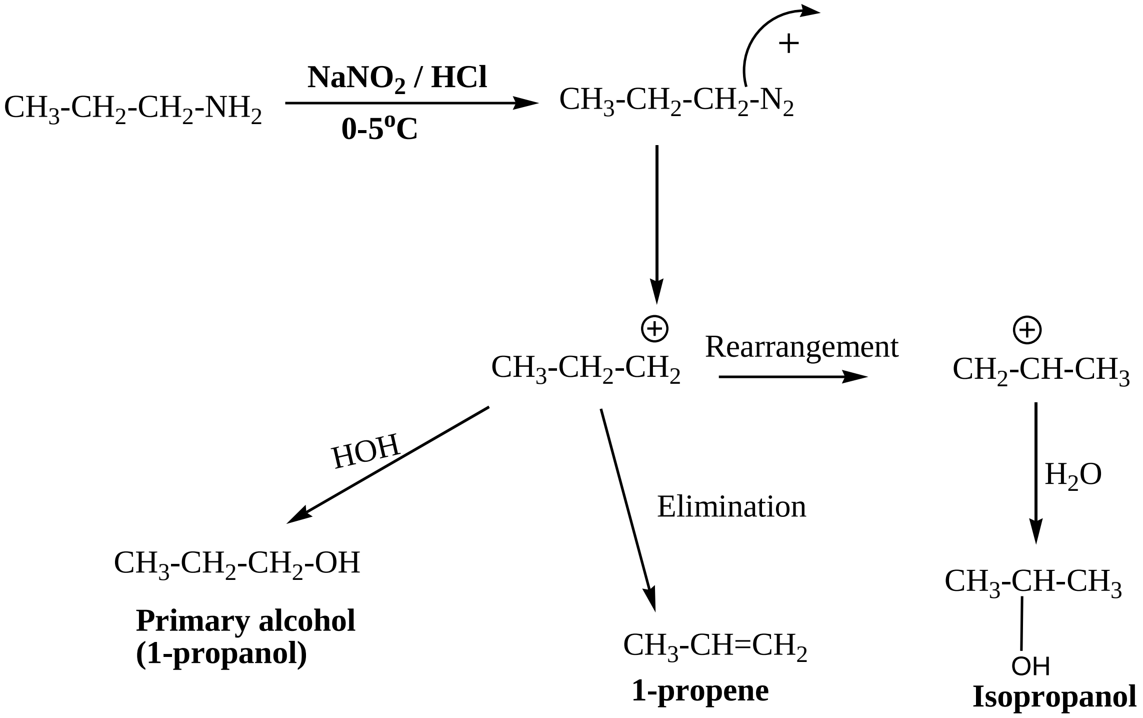
3) Alcohol in the presence of strong acids undergoes protonation to form carbocations.



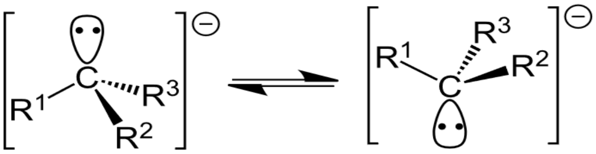
Reactions of carbocation:1)**Rearrangement reaction**: Neo-pentyl bromide on hydrolysis undergoes SN^1 reaction to give 2-methyl-2 -butanol and not 2,2 dimethyl -1-propanol (neo pentyl alcohol) i.e. expected product. Here, less stable primary carbocations undergoes rearrangement to form more stable tertiary carbocations to give 2-methyl-2-butanol as substituted product**.**



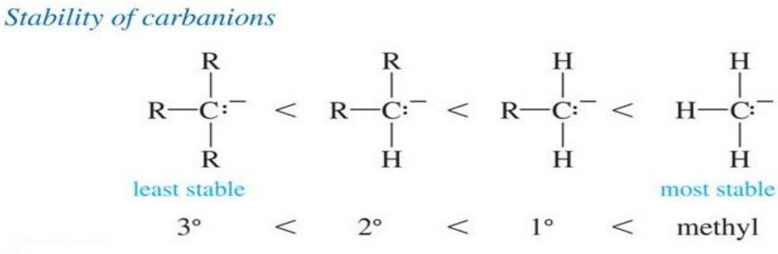
4) **Combination with Nucleophiles:** When carbocations combines with Nucleophiles undergoes elimination and rearrangement to give different products.



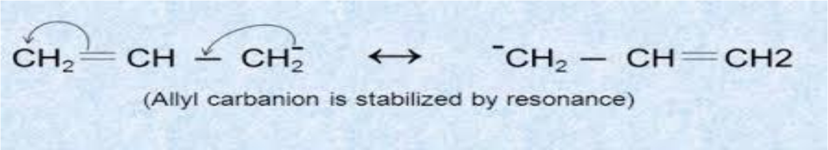
Carbanions (Carbanions): A carbanions can be defined as triply bonded, negatively charged, electron rich, highly reactive species in which a carbon atom exhibits trivalence (implying it forms a total of three bonds) and holds a formal negative charge whose magnitude is at least -1. When pi delocalization does not occur in the organic molecule (as it does in the case of aromatic compounds). It is important to note that all carbanions are conjugate bases of some carbon acids. There are eight electrons around the carbon atom (Three bonding electron pair and one nonbonding lone pair in valence shell).In all carbanions, the electron density is highly concentrated at the negatively charged carbon atom. Therefore, this carbon becomes an ideal point of attack for many Eletrophiles and other electron-deficient species. Furthermore, this carbon atom is also the site at which the molecule reacts with proton donors and halogenating reagents such as di iodine.



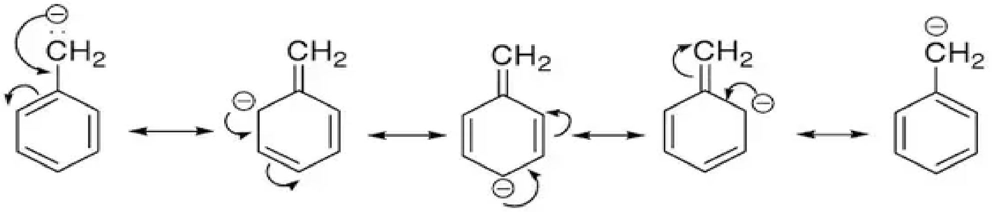
Stability of carbanions) : An inductive effect, via which highly electronegative substituent groups (like -NO_2,-CN,-COOR,-Cl,-CO-,-CHO etc.) attached to the carbanions help subdue the negative charge on it and make the molecule more stable. On the other hand, highly electropositive substituent groups (like -CH_3,-OCH_3-OH, -NH_2 etc.) can increase the negative charge on the carbanions and, therefore, decrease the overall stability of the molecule. More the number of alkyl group on the carbon atom carrying the negative charge, more would be the intensity of the negative charge on the carbon atom and hence less stable is the carbanions.



B) The resonance effect, via which the delocalization of the electrons distributes the negative charge all over the carbanions, adding stability in the process. Aromatic systems add a great deal of stability to carbanions when they are present as a substituent group as a result of the resonance effect (and the greater extent of delocalization of electrons over the aromatic system).For example in allyl and benzyl carbanions,

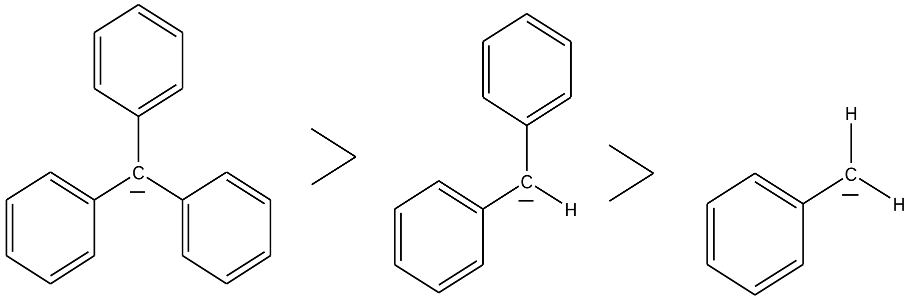


(Allyl carbanion is stabilized by resonance)

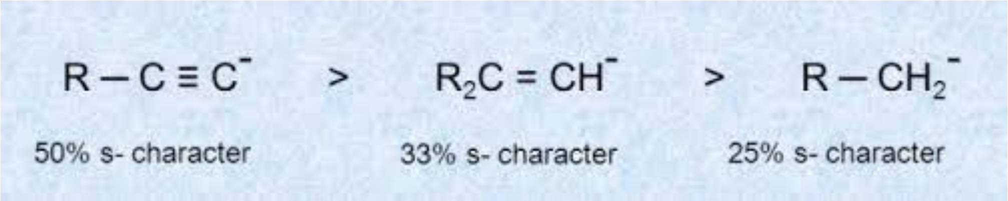


Canonical forms of benzyl carbanion

C) More the number of phenyl group,greater is the stability.

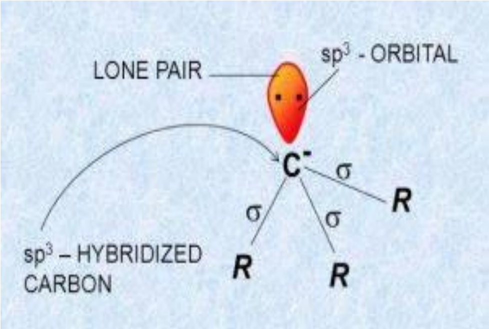


D) Stability of carbanions increases with the increase in s-character of the carbon carrying negative charge.

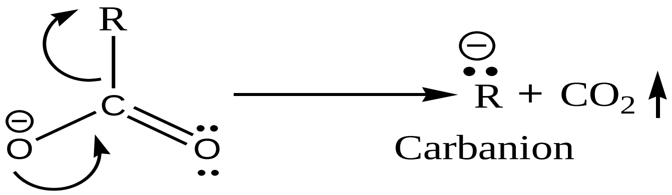


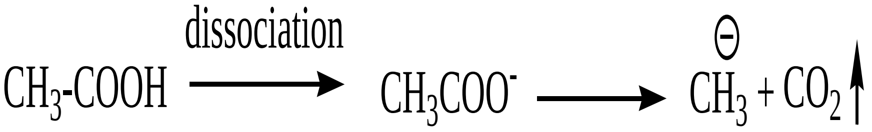
$R-C\equiv C^-$	>	$R_2C=CH^-$	>	$R-CH_2^-$
50% s- character		33% s- character		25% s- character

Structure:1. The valence shell of negatively charged Carbon-atom contains 8-electrons. Thus its octet is complete & it contains a lone pair of electrons. Carbanions typically assume a bent, linear, or a trigonal pyramidal molecular geometry.2. The negatively charged carbon is in a state of sp^3 hybridization and have bond angle 107^0.The hybrid orbital's are directed towards the corners of a tetrahedron. Three of the hybrid orbital's are involved in the formation of single covalent bonds with other atoms while the IVth hybrid orbital contains a lone pair of electron. Thus it has a pyramidal structure similar to NH_3 molecule.



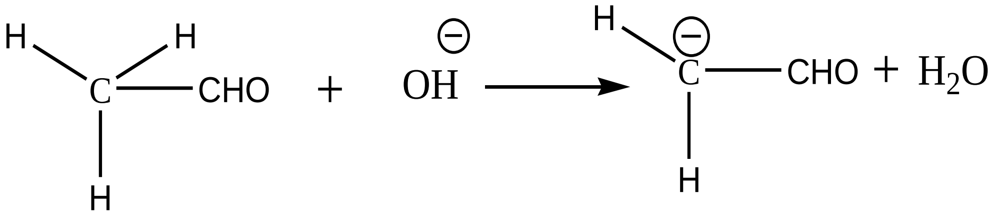
Methods of generation of carbanions:1) By the decomposition of carboxylate anions: When carboxylate anions undergoes dehydration it produces carbanions with elimination of carbon dioxide gas.

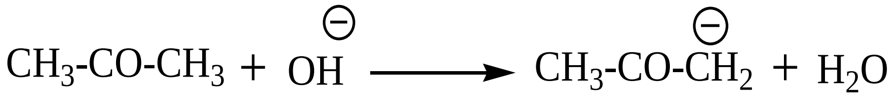




$$CH_3\text{-}COOH \xrightarrow{\text{dissociation}} CH_3COO^- \longrightarrow \overset{\ominus}{C}H_3 + CO_2\uparrow$$

2) **Reaction of carbonyl group with alkali**: By heating the aldehyde and ketone with base such as NaOH or KOH, α-hydrogen atom is to be loosed and forms carbanions.

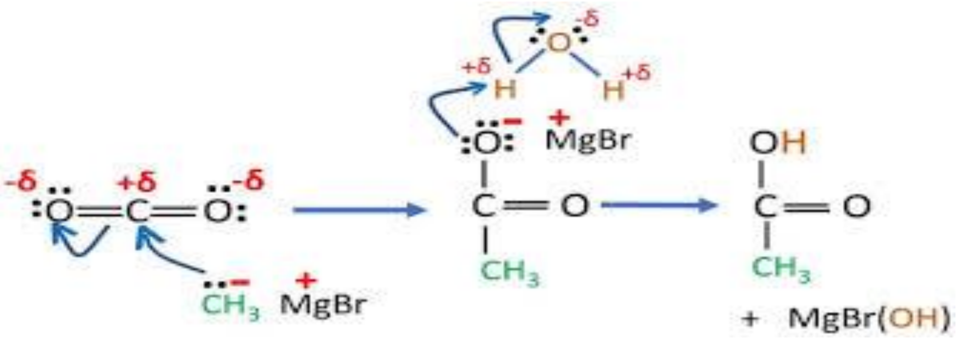




$$CH_3\text{-}CO\text{-}CH_3 + \overset{\ominus}{OH} \longrightarrow CH_3\text{-}CO\text{-}\overset{\ominus}{C}H_2 + H_2O$$

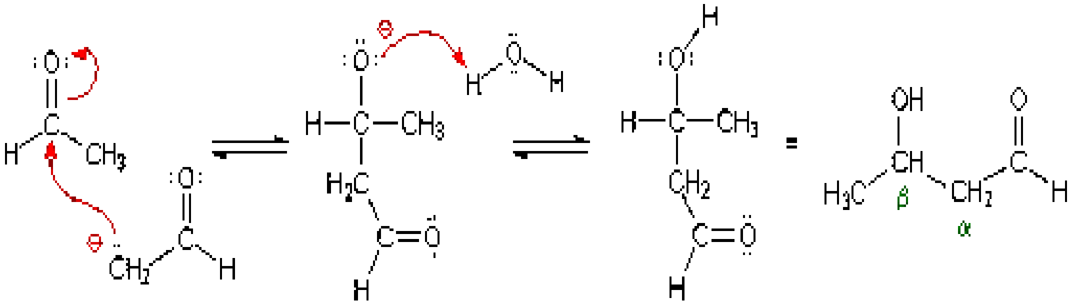
Reactions of carbanions:

1) Addition reaction: When carbanions generated from Grignard reagent adds to CO_2 to form respective carboxylic acid.

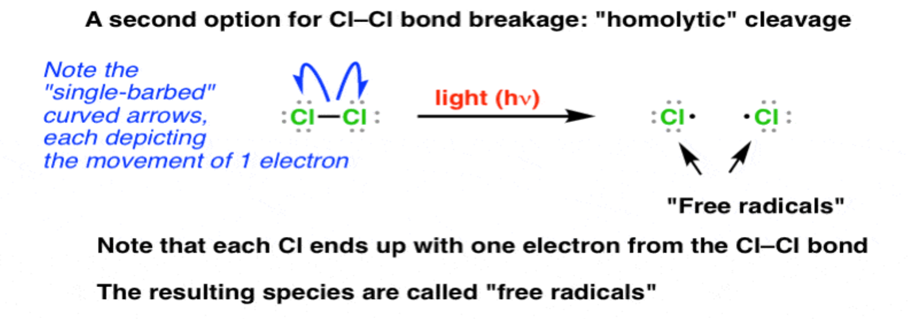


2) Aldol reaction: When aldehyde or ketone which having α-hydrogen atoms, on treatment with alkali solution undergoes condensation reaction to form β-hydroxy aldehyde or β-hydroxy ketone called as Aldol or Ketol.

$$NaOH \longrightarrow Na + OH$$



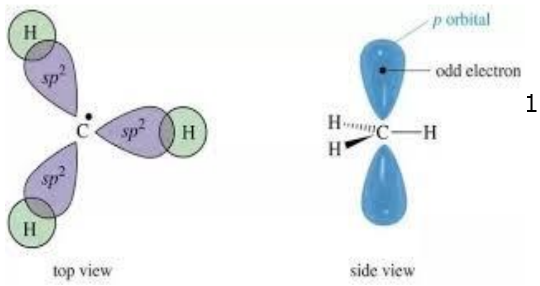
Free radicals: Free radicals are **reaction intermediates** formed due to the Homolytic cleavage of a covalent bond containing carbon such that carbon gets an unpaired electron. **Free radicals** actively take part in chemical reactions and are highly **reactive**, short-lived, high-energy, when generated in a chemical reaction, it will quickly convert into a more stable molecule. Only in exceptional cases can these compounds be isolated and stored, e.g. low temperatures, matrix isolation. Free radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes, including human physiology.

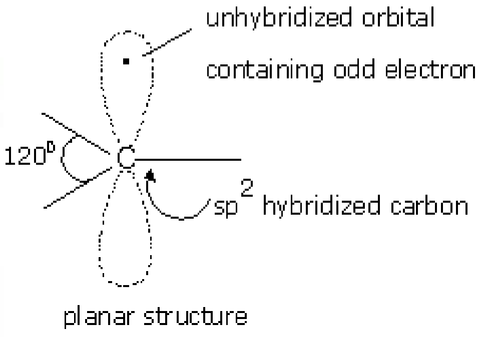

A second option for Cl–Cl bond breakage: "homolytic" cleavage

Note that each Cl ends up with one electron from the Cl–Cl bond

The resulting species are called "free radicals"

In CH_3 free radicals, there are seven electrons. It needs one electron to get stable octet state. Hence carbocations and free radicals are electron deficient and acts as Eletrophiles. **Structure of Free radicals:** In carbon radicals e.g. methyl radical carbon atom is sp^2hybridizedPz orbital lies perpendicular to the plane of three C-H bonds and possesses an odd electron. Hybridization is SP^2 and bond angle is 120^0





Characteristics of free radicals: 1) Free radicals are generally electrically neutral species.

2) They are highly unstable.

3) They are short lived and highly reactive on account of the presence of odd electrons.

4) They readily try to pair up the odd electrons.

5) Free radicals are paramagnetic in nature.

6) Free radicals are generally formed either in presence of UV/ visible light or in presence of peroxides.

Stability of free radicals:

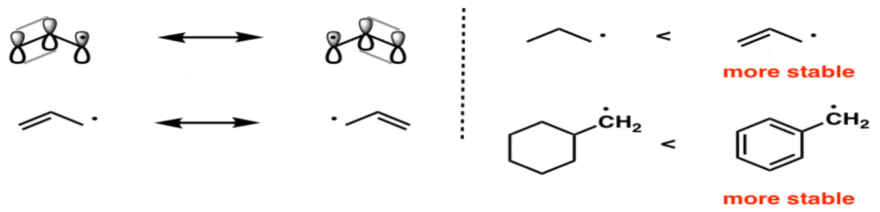
The increasing order for this stability order is,

Benzylic carbon > allylic carbon > Tertiary carbon > Secondary carbon > Primary carbon.

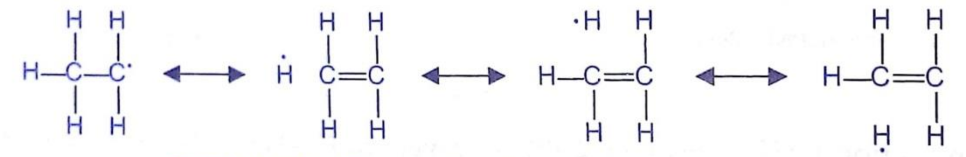
Radicals are most stabilized by following things:

1. Electron density from substituent: Like carbocations, free radicals are electron-deficient species. They can be stabilized through donation of electron density by neighbors; for this reason, radical stability increases in the order methyl < primary < secondary < tertiary. Thus free radicals adjacent to an electron-withdrawing group are less stable, since in effect, electron-density is being taken away from what is already an electron deficient species.

2. Resonance: A second important factor which stabilizes free radicals is "delocalization" – that is, if the radical can be spread out over two or more carbons. A more familiar way of saying this is that free radicals are stabilized by resonance.



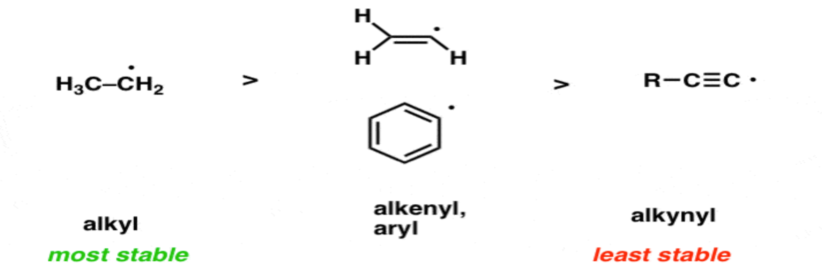
3. Hyper conjugation: The more alkyl substituent's a radical carbon atom possesses, the more stabilized it becomes from hyperconjugation.The interaction of the double-occupied C-H σ bonding orbital with the single-occupied, non-bonding p orbital of the radical carbon atom is comparable to the stabilization by hyper conjugation in carbenium ions.



The ethyl radical (hyperconjugation in an alkyl free radical)

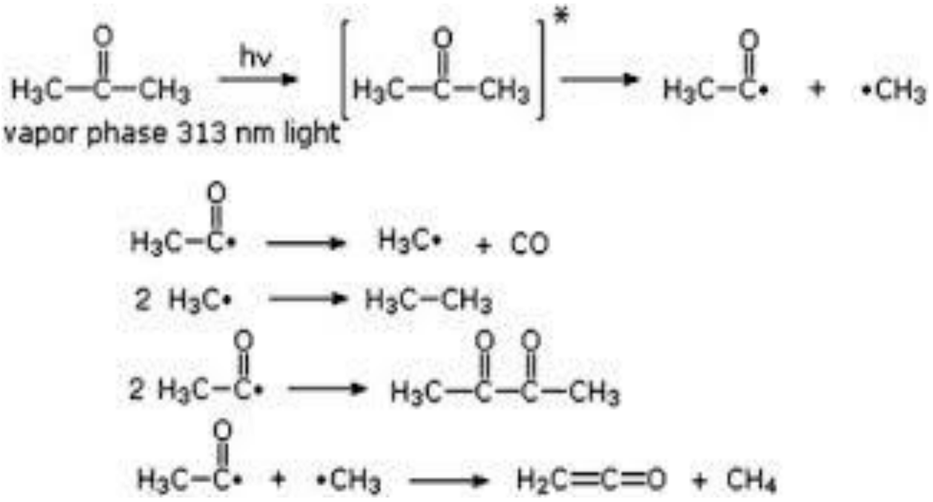
4.Electronegativity of attached substituent on free radicals: Across a row of the periodic table, free radicals decrease in stability as the electronegativity increases. Free radicals increase in stability going down a column of the periodic table, F• <Cl• < Br• < I• since the electron-deficient orbital is spread out over a greater volume.

5. Percentage of s-character: Free radicals decrease in stability as the % of s-character in the orbital increases [i.e. as the half-empty orbital becomes closer to the nucleus]. For that reason, free radical stability decreases as the atom goes from alkyl to alkenyl to alkynyl.

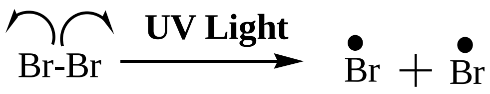


Methods of generation of free radicals:1) By photolysis:

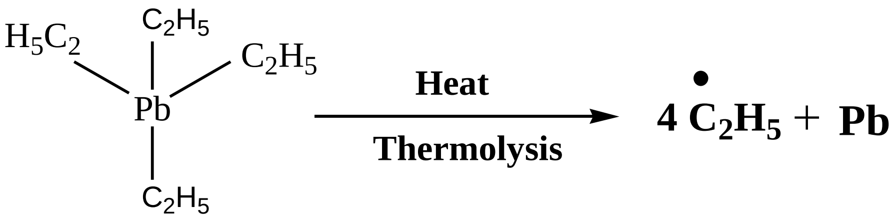
A) Acetone in vapor phase gets decomposed by UV rays to give methyl radical.



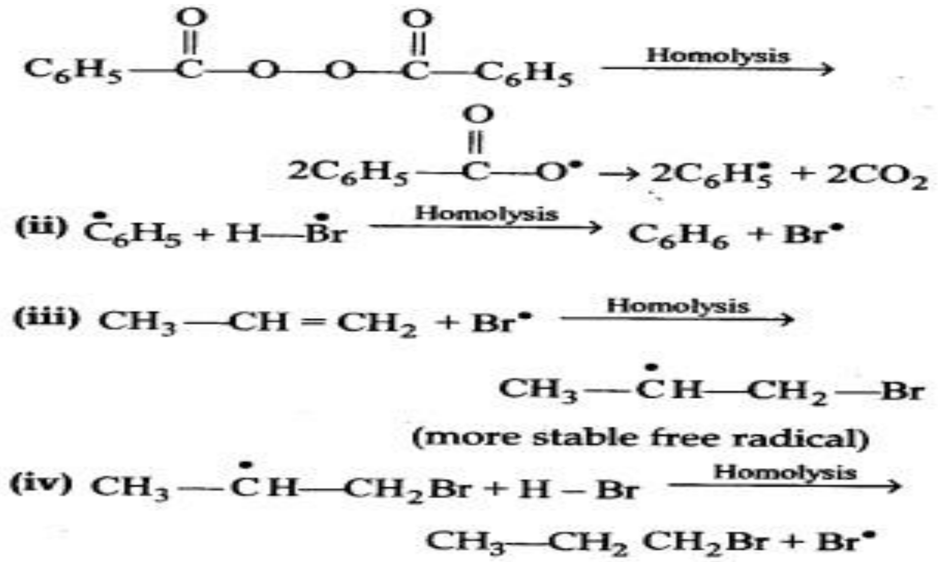
B) Photolysis of molecular bromine produces bromide free radicals.



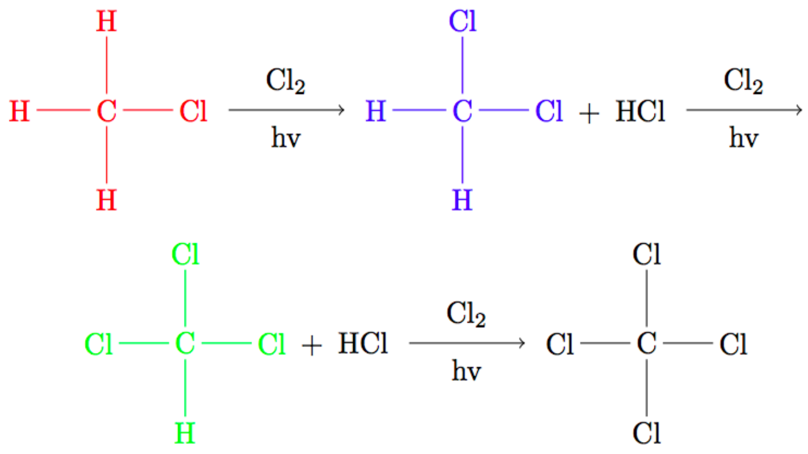
1) By thermolysis: When tetraethyl lead in vapor phase generates ethyl free radicals.



Reactions of free radicals:1) Addition of HBr: In the presence of benzoyl peroxide, the addition of HBr to an unsymmetrical alkene takes place according to antimarkovnikov rule.It is called as **Peroxide effect or Kharash effect.**



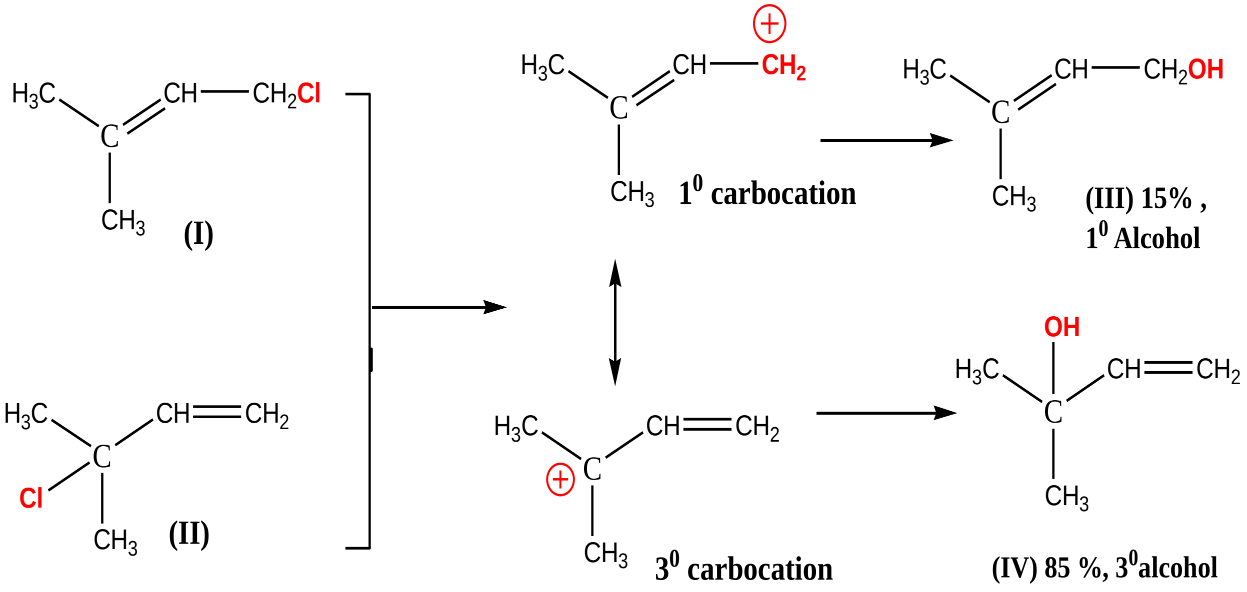
2) Halogenations: Chlorination of alkanes takes place either thermally or photo chemically to give a mixture of respective chloro derivatives.



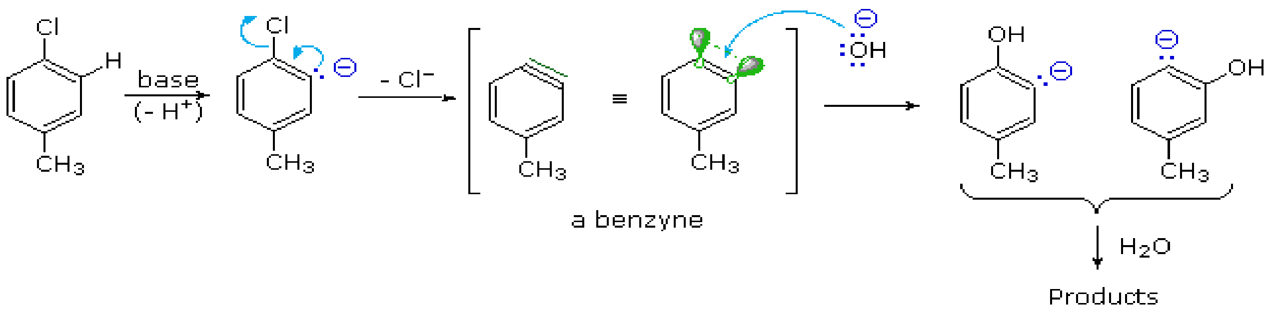
Methods of determination of reaction mechanism: In a chemical reaction a reactant molecule is converted into product molecule. An organic reaction mechanism is detailed study of the transformation which gives information regarding number of steps involved and sequence of breaking and making of bonds. Following are commonly used methods for determination of reaction.

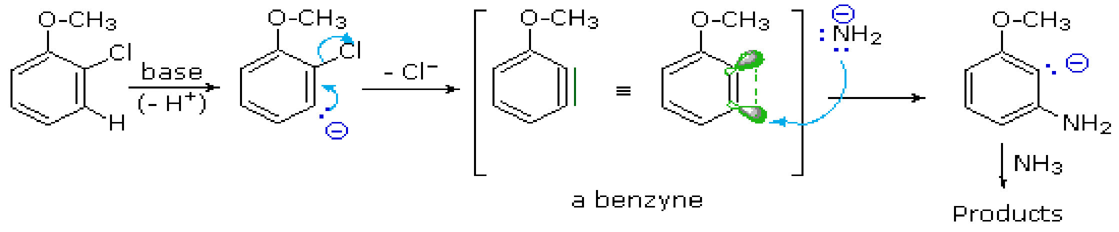
1.Product analysis: Fundamental information about the reaction mechanism is provided by establishing the structure of product, biproducts and their quantities.

A) Two isomeric allyl chlorides that is 1-chloro-3-methyl-2-butene (I) and 3-chloro-3-methyl-1-butene on hydrolysis gives different products.



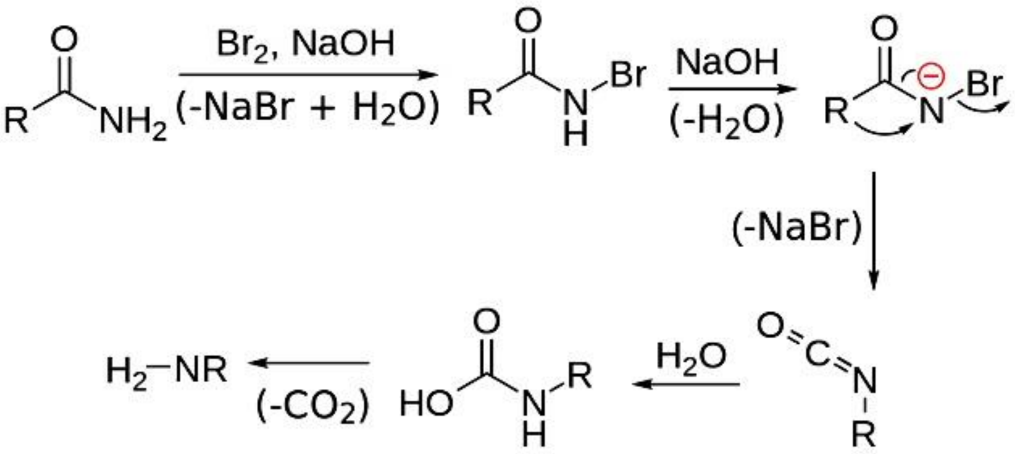
2)When p-chloro toluene on treatment with sodamide and liquid ammonia at -33°C gives mixture of p-toluidine as expected product and m-toluidine as unexpected product, reaction does not follow normal direct substitution reaction, reaction must take place through the formation of intermediate which should give meta and para toluidine as products. It is possible due to only benzyne intermediate; this may be confirmed by isotopic labeling and spectroscopic methods. Mechanism is as follows,



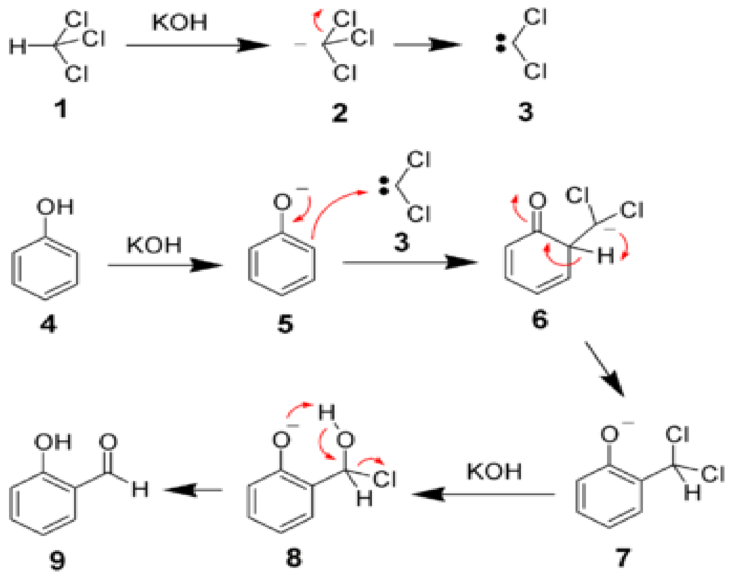


Determination of the presence of intermediates: Many organic reactions take place through the formation of intermediates which can be isolated, detected by spectroscopic methods and entrapment method, with an added compound. We can propose the correct mechanism by establishing the structure of intermediate.

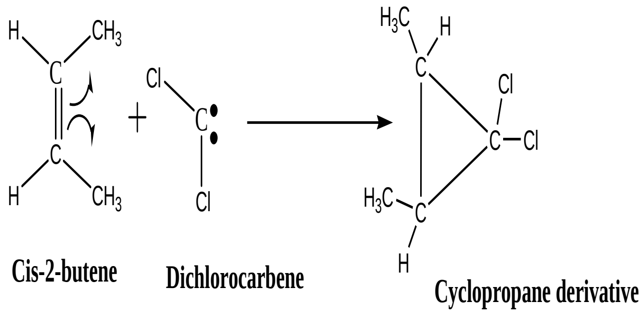
1) In **Hoffmann rearrangement**, i.e. amide with Br2/KOH solution gives a primary amine, before completion of reaction, intermediates formed in this reaction like N-bromo amide and its anion RCONBr and isocyanate (RNCO) have been isolated and mechanism is proposed.



2) **In Reimer –Tiemann reaction**, phenol on treatment with chloroform and NaOH solution gives o-hydroxy benzaldehyde; proposed mechanism involves formation of dichlorocarbene which is confirmed by carrying same reaction in presence of cis-2-butene gives cyclopropane derivatives. Mechanism can be proposed as,

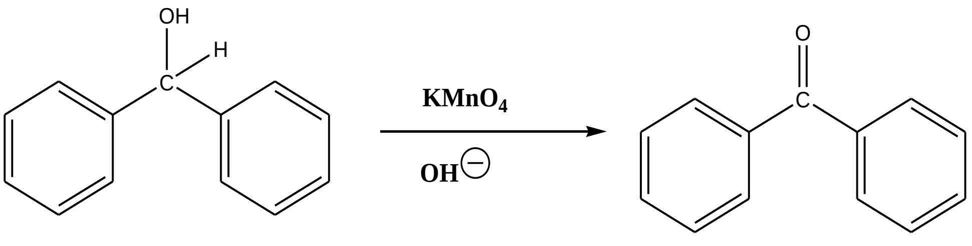


Existence or appearance of dichlorocarbene has been confirmed by formation of cyclopropane derivatives by dichlorocarbene (CCl_2).



Isotope effect: C-D bond breaks at a slower rate than C-H bond due to isotope, the greater mass of the isotope makes the bond stronger and hence breaks more slowly. By comparing the rate of original bond breaking with that of heavier isotope substituted bond. We can determine whether a particular bond breaks in rate determining step or not. The effect of heavier isotope substitution on rate of the bond breaking is said to be primary kinetic isotope effect.Examples

1) **Oxidation of secondary alcohol.**



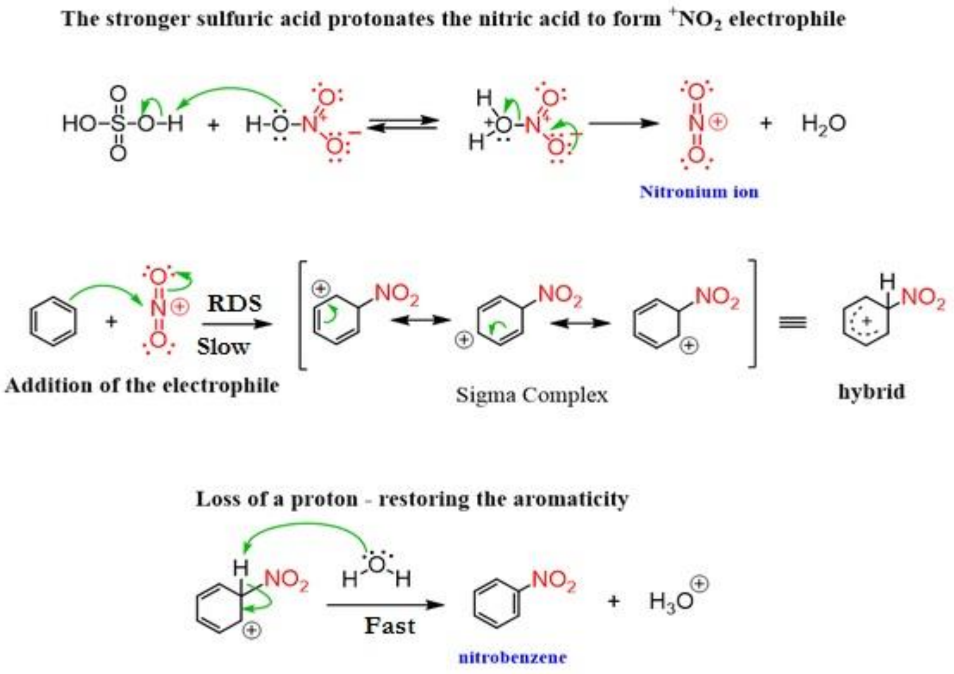
Diphenyl ethanol (Secondary alcohol)

Benzophenone (Ketone)

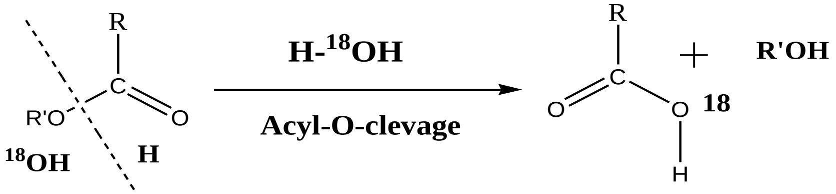
It is found that, **secondary alcohol is oxidized 6-7 times rapidly** as $C_6H_5C\text{-}DOH$, reaction is said to be exhibit a **primary kinetic isotope effect** and breaking of C-H bond must clearly be involved in rate limiting step of reaction.

2) **Nitration of benzene:** Benzene (C_6H_6) and hexadeutero benzene (C_6D_6) are found to undergo nitration at the same rate. i.e. There is no primary kinetic isotope effect. It shows that C-H bond

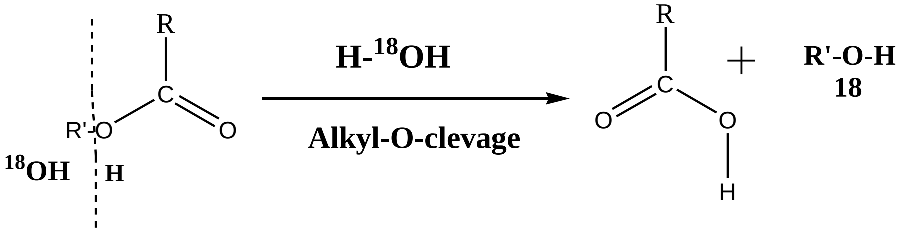
breaking is not involved in rate determining step but C-NO_2 bond formation is involved in rate determining step.



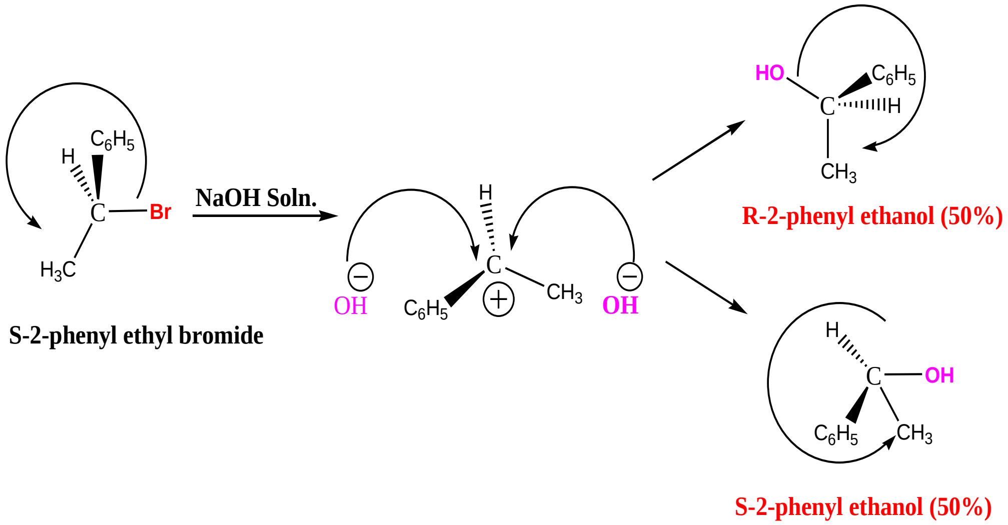
3) Hydrolysis of ester: In ester molecule there are C-O sigma bonds, one is acyl-O and other is alkyl-O (-O-R') .Ester is hydrolyzed using water solvent enriched with H-^{18}O-H. If ester undergoes hydrolysis with acyl-O cleavage,^{18}O atom will found in the acid.



If ester undergoes hydrolysis with alkyl-O cleavage the alcohol contains ^{18}O atom.



Acid and alcohol are isolated and they are subjected to mass spectroscopic study to detect the presence of ^{18}O.If we get ^{18}O atom in isolated acids indicates that ester hydrolysis with acyl-O cleavage. But if we get ^{18}O in isolated alcohol, it proves ester undergoes hydrolysis with alkyl-O cleavage.**4) Stereo chemical evidence:** Mechanism of organic reaction also confirmed by stereochemistry. **Example**: Nucleophilic substitution reactions weather it is SN^2 or SN^1 can be investigated by performing experiments with optically active compounds and then checking the optical activity of the products. If Nucleophilic substitution reaction with optically active reactant takes place with the formation of racemic mixture (optically inactive) product that is reaction follows SN^1 pathway and thus formation of planar carbocations in which nucleophile attacks equally on either side that is possibility of backside attack or front side attack producing a mixture of equal number of optical isomers.

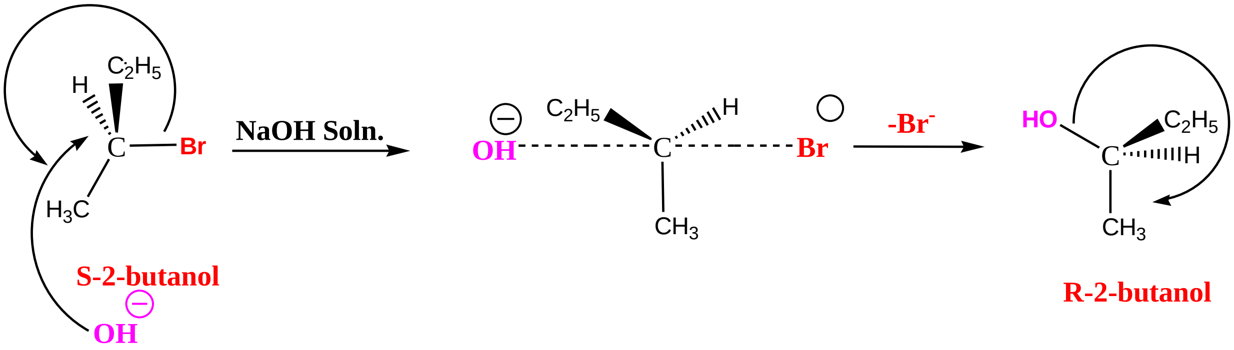


S-2-phenyl ethyl bromide

R-2-phenyl ethanol (50%)

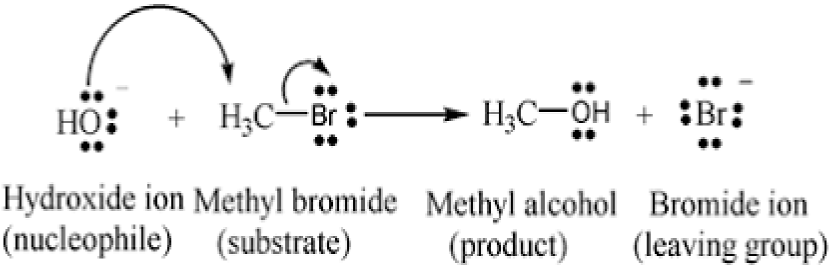
S-2-phenyl ethanol (50%)

If Nucleophilic substitution takes place with an optically active reactant with formation of product which having opposite configuration .In this one reaction follows SN^2 pathways, thus mechanism must involve the attack of nucleophile OH^- on carbon atom of reactant from a opposite side to leaving group which gives the opposite configuration. i.e. Inversion of configuration.



5) Kinetic evidence: As we know that rate of reaction depends upon the concentration of reactants, the greater the concentration, the more often the reactant colloid and greater the chance of reaction. Order of reaction is number of atoms or molecules whose concentration determines the reaction velocity, that is first, second and third order, depending on whether concentration of one, two and three reactants determines reaction velocity. According to the law of mass action, velocity of chemical reaction is proportional to the product of active masses of interacting reactants at that moment. The expression (equation) that relates the rate of reaction and concentration of reactants is called the kinetic expression for the reactants.

For example:1) Hydrolysis of methyl bromide with aq. NaOH.(SN^2 reaction)



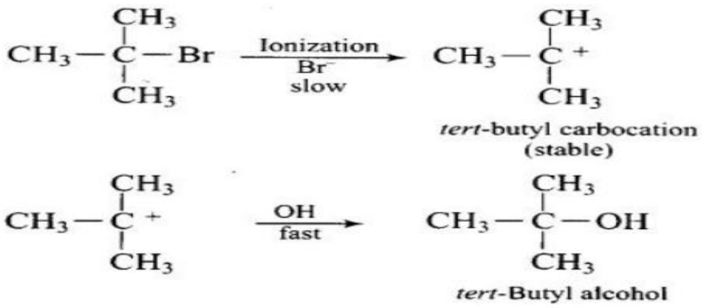
The reaction is carried out at a specific temperature because rate of reaction is temperature dependent. Several experiments are to be carried out by keeping the temperature the same but varying the initial concentration of the reactants. It shows that rate of reaction depends on concentration of both methyl bromide and OH^- ions thus,

Rate α (CH_3Br) (OH^-)

Rate = K (CH_3Br) (OH^-) where K= rate constant

Hence hydrolysis of primary alkyl halide is said to be second order and bimolecular because two reactants are involved in rate determining step.

Example: 2) Hydrolysis of tertiary butyl bromide with aqueous NaOH.



Conclusion of above reaction/experiment is that rate of product formation is dependent on the concentration of tertiary butyl bromide but it is independent on concentration of hydroxide ions. That is doubling the concentration of tertiary butyl bromide the rate of reaction doubles, but has no effect of NaOH solution.

Rate α $[(CH_3)_3Br]$

Rate = K $[(CH_3)_3Br]$ where K= rate constant.

Hence hydrolysis of tertiary butyl bromide with alkali solution is unimolecular and first order and designated as SN^1.

Bharat Shikshan Sanstha's
Shri Chhatrapati Shivaji College, Omerga
Tq. Omerga Dist. Osmanabad - 413606 (MS), India
(Affiliated to Dr. Babasaheb Ambedkar Marathwada University, Aurangabad) | NAAC Reaccredited 'B' Grade
DEPARTMENT OF CHEMISTRY

Question Bank

Class: B.Sc. Semester –I

Name of Paper: Organic Chemistry (Paper –II) CHE-102

Title of Chapter: Mechanism of Organic Reactions.

Questions

Q.1. Define and give an example of each of the following terms.

1) Homolytic cleavage 2) Heterolytic cleavage 3) Carbocations 4) Carbanions
5) Free radicals

Q.2. Describe the structure and two methods of preparation of carbocations. Explain why tertiary butyl carbocations is more stable than ethyl carbocations.

Q.3. Comment on structure of carbanions. Explain why tertiary butyl carbanions are less stable than ethyl carbanions?

Q.4. Explain the structure, two methods of generation and two reactions of carbanions?

Q.5. Explain the structure, two methods of generation and two reactions of free radicals?

Q.6.Eplain how product analysis helps in establishing the mechanism of reaction?

Q.7.What is primary kinetic isotopic effect? Explain how to use isotope effect to determine whether a C-H bond is being broken in the rate determining step of reaction?

Q.8. Explain how isotope effect is useful in ester hydrolysis reaction to decide acyl-O and alkyl-O cleavage?

Q.9. Explain with suitable examples how presence of reactive intermediates helps in establishing the mechanism of reaction?

Q.10. Comment on the use of Stereochemical and kinetic evidence in deciding the mechanism pathway of reaction?

Q.11. Offer explanation for the following?

A) Tertiary butyl carbocations is more stable than iso-propyl and ethyl carbocations.

B) Methyl carbanions are more stable than iso-propyl and ethyl radicals.

C) Tertiary butyl free radicals are more stable than iso-propyl and ethyl radicals.

D) P-chloro toluene on treatment with sodamide and liquid ammonia at -33^{0}C yields a mixture of expected p-toludine and unexpected m-toludine.

E) SN^1 reaction takes place with racemization.

F) SN^2 reaction takes place with inversion of configuration.

G) SN^2 reaction is bimolecular and it is second order reaction.

H) SN^1 reaction is unimolecular and it is first order reaction.

Q.12. Write short notes on following.

1) Homolytic and Heterolytic fissions
2) Stereochemical criterion
3) Kinetic evidences
4) Stability of carbocations
5) Stability of carbanions
6) Reactions of free radicals.

Multiple choice Questions

1. Compound undergoing homolytic bond cleavage will lead to formation of which chemical species?

   a) Anion

   b) Cation

   c) Free radical

   d) Atoms

2. In which form energy is stored in chemical bonds?

   a) Kinetic energy

   b) Chemical energy

   c) **Potential energy**

   d) Thermal energy

3. Which energy is required for homolytic cleavage?

   a) **Singlet**

   b) Doublet

   c) Triplet

   d) Quadruplet

4. A covalent bond between two atoms may be broken in different ways depending upon

   a) Nature of given organic compound

   b) Nature of attacking reagent

   c) Reaction conditions

   d) All of the mentioned

5. Select the incorrect statement from the following option.

   a) Fission of covalent bond leads to the generation of intermediate organic species

   b) They are stable and long-lived

   c) The presence of reactive intermediates is confirmed by their detection by spectroscopic methods

   d) None of the mentioned

6. The breaking of a covalent bond in such a way that each atom separates with one electron of the shared pair is called ___________

   a) Homolytic fission

   b) Heterolytic fission

   c) Monolytic fission

   d) Morpholytic fission

7. The breaking of a covalent bond in such a way that both the electrons of shared pair are carried away by one of atom is called ___________

   a) Morpholytic fission

   b) Monolytic fission

c) Heterolytic fission

d) Homolytic fission

8. Heterolytic fission takes place between two atoms of widely different __________

a) Conductivity

b) Viscosity

c) Electronegativity

d) All of the mentioned

9. Select the incorrect statement from the following option.

a) Heterolytic fission takes place generally in a polar solvent

b) Heterolytic fission takes place usually at higher temperatures

c) Cations and anions formed are generally carbon-based

d) None of the mentioned

10. Which of the following is intermediate organic species based on carbon formed by homolytic fission?

a) Carbenes

b) Carbocations

c) Carbanions

d) Free radicals

11. Which of the following is intermediate organic species based on carbon formed by photolysis?

a) Carbenes

b) Carbocations

c) Carbanions

d) Free radicals

12. The shape of carbanions is __________

a) Linear

b) Trigonal planar

c) Pyramidal

d) Bent

13. In Heterolytic fission, _____ are formed. In homolytic fission, _____ are formed

a. One free radical and one Cation; One free radical and one anion:

b. Free radicals; a Cation and anion
c. One free radical and one anion; One free radical and one cation
d. A Cation and anion; free radicals.

14. Which condition will most likely favor homolytic fission of a covalent bond?
    a) Presence of a polar solvent at low temperature.
    b) Presence of a non-polar solvent at low temperature.
    c) Presence of a polar solvent at high temperature.
    d) Presence of a non-polar solvent at high temperature.

15. Which of the following bonds is most likely to be first broken down heterolytically during a chemical reaction?
    a) Carbon-Hydrogen bond
    b) Carbon-Carbon bond
    c) Carbon-Halogen bond
    d) Carbon=Carbon bond (C=C)

16. The bond breaking in which the atoms at each end of bond is left with one electron (e-) from the pair forming covalent bond is
    a) Homolytic fission
    b) Heterolytic fission
    c) Homolytic fusion
    d) Heterolytic fusion

17. Carbanions has ________
    a) Trigonal structure
    b) Trigonal planar structure
    c) Pyramidal structure
    d) Trigonal pyramidal structure

18. Homolytic cleavage is ……..

a) One of electrons from shared pair goes with each of atom.

b) Shared pair goes with one atom only.

c) Compound breaks into identical atoms

d) None of these

19. Homolytic fission is also known as…..

a) Free radical reactions

b) Homopolar reactions

c) Nonpolar reactions

d) All of these

20. Carbocations are highly _______ and _______.

a) Stable and reactive

b) Unstable and reactive

c) Stable and nonreactive

d) Unstable and non reactive

21. In heterolysis, one atom has _______ while other has _______.

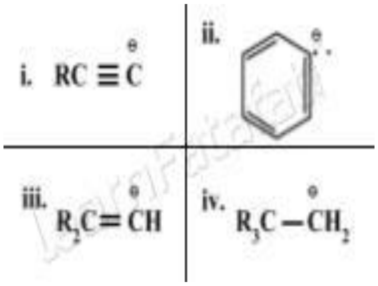
a) 6 electrons and positive charge, at least one lone pair and negative charge.

b) 6 electrons and positive charge, at least one lone pair and neutral charge.

c) 6 electrons and negative charge, at least one lone pair and positive charge.

d) None of these

22. The order of stability of given carbanions is



a) i > ii > iii > iv

b) ii > iii > iv > I

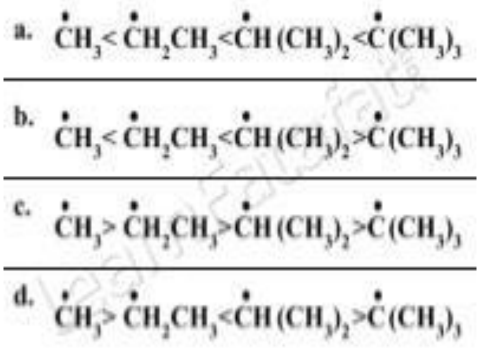
c) iv > ii > iii > I

d) i > iii > ii > iv

23. Carbocations have _______.

- a) Tetrahedral structure
- b) Planar structure
- c) Trigonal planar structure
- d) Tetrahedral planar structure

24. Identify correct order of stability of alkyl radical



a. $\dot{C}H_3 < \dot{C}H_2CH_3 < \dot{C}H(CH_3)_2 < \dot{C}(CH_3)_3$

b. $\dot{C}H_3 < \dot{C}H_2CH_3 < \dot{C}H(CH_3)_2 > \dot{C}(CH_3)_3$

c. $\dot{C}H_3 > \dot{C}H_2CH_3 > \dot{C}H(CH_3)_2 > \dot{C}(CH_3)_3$

d. $\dot{C}H_3 > \dot{C}H_2CH_3 < \dot{C}H(CH_3)_2 > \dot{C}(CH_3)_3$

- a)
- b)
- c)
- d)

25. Heterolytic cleavage is also known as _______.

- a) Ionic reactions
- b) Heteropolar reactions
- c) Polar reactions
- d) All of these

26. Reaction mechanism is ________.

- a) Transformation of reactant to products by showing movement electron movement
- b) Transformation of reactant to products by showing movement electron movement
- c) Both a and b
- d) None of these

27. Base strength of

i) $H_3CC^{\ominus}H_2$

ii) $H_2C{=}C^{\ominus}H$

iii) $H{-}C{\equiv}C^{\ominus}$

a) ii > i > iii

b) iii > ii > I

c) i > iii > ii

d) i > ii > iii

28. Identify given reaction $CH_3Br \longrightarrow H_3C^+ + Br^-$

a) Homolytic cleavage

b) Heterolytic cleavage

c) Bond formation

d) None of these

29. Choose correct order of stability of carbocations….

a) $C^+H_3 < CH_3C^+H_2 > (CH_3)_2C^+H < (CH_3)_3C^+$

b) $C^+H_3 > CH_3C^+H_2 > (CH_3)_2C^+H > (CH_3)_3C^+$

c) $C^+H_3 < CH_3C^+H_2 < (CH_3)_2C^+H < (CH_3)_3C^+$

d) $C^+H_3 > CH_3C^+H_2 < (CH_3)_2C^+H > (CH_3)_3C^+$

30. Identify the one which does not come under the organic addition reaction?

a) Hydration

b) Dehydration

c) Halogenation

d) Hydrohalogenation.

31. **Find the incorrect statement for a nucleophile**s

a) Nucleophile is a Lewis acid

b) Nucleophiles do not seek electron.

c) Ammonia is a nucleophile

d) Nucleophiles attacks low electron density sites

32. **The correct order of increasing nucleophilicity is**

    a) $Cl^- < Br^- < I^-$

    b) $Br^- < Cl^- < I^-$

    c) $I^- < Br^- < Cl^-$

    d) $I^- < Cl^- < Br^-$

33. Which of the following cannot react as a nucleophile?

    a) CH_3NH_2

    b) $(CH_3)_2NH$

    c) $(CH_3)_3N$

    d) $(CH_3)_4N^+$

34. Which of the following cannot react as a nucleophile?

    a) $H_2C=CH_2$

    b) BH_3

    c) $H_2C=NH$

    d) CH_3CH_2SH

35. Which of the following is not a typical electrophile?

    a) Cl_2

    b) HBr.

    c) Br_2

    d) $(CH_3)_4N^+$

36. Which of the following reactions is elimination?

1. $(CH_3)_3CCl \longrightarrow (CH_3)_2C=CH_2 + HCl$

2. 

$CH_3\overset{O}{\overset{\|}{C}}OH + NH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}O^- + NH_4^+$

3. $H_2C=O + H_2O \longrightarrow H_2C(OH)_2$

4. 

$CH_3\overset{O}{\overset{\|}{C}}OH + CH_3OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OCH_3 + H_2O$

37. Which of the following reactions is a substitution?

1) $(CH_3)_3CCl \longrightarrow (CH_3)_2C{=}CH_2 + HCl$

2)

$CH_3\overset{O}{\overset{\|}{C}}OH + NH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}O^- + NH_4^+$

3) $H_2C{=}O + H_2O \longrightarrow H_2C(OH)_2$

4)

$CH_3\overset{O}{\overset{\|}{C}}OH + CH_3OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OCH_3 + H_2O$

38. Which of the following reactions is an addition?

1 $(CH_3)_3CCl \longrightarrow (CH_3)_2C{=}CH_2 + HCl$

2.

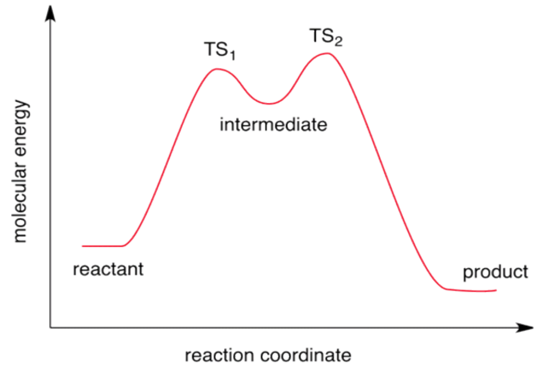
$CH_3\overset{O}{\overset{\|}{C}}OH + NH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}O^- + NH_4^+$

3. $H_2C{=}O + H_2O \longrightarrow H_2C(OH)_2$

4.

$CH_3\overset{O}{\overset{\|}{C}}OH + CH_3OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OCH_3 + H_2O$

39. Which of the statements (a)-(d) about the reaction profile below is false?



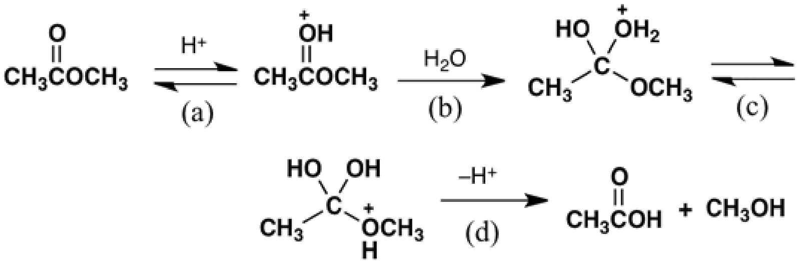
a) The product is more stable than the reactant.

b) The first step is rate determining

c) The reaction is exothermic.

d) The equilibrium constant is > 1 if the molar entropy change is negligible.

40. The following stepwise reactions comprise a mechanism for the acid-catalyzed hydrolysis of an ester. Which step of (a)-(d) is an addition?



a) Step ‘a’

b) Step ‘b’

c) Step ‘c’

d) Step‘d’

41. The following stepwise reactions comprise a mechanism for the acid-catalysed hydrolysis of an ester. Which step of (a)-(d) is an elimination?

a) Step ‘a’

b) Step ‘b’

c) Step ‘c’

d) Step‘d’

42. Which of the following can react as a nucleophile?

a) $(CH_3)_3B$

b) $CH_3)_3CH$

c) $(CH_3)_3N$

d) $(CH_3)_3O^+$

43. Which of the following does not normally react as a nucleophile?

a) $CH_3)_2O$

b) $(CH_3)_2OH^+$

c) CH_3CH_2OH

d) $CH_3CH_2O^-$

44. Which of the following reacts most readily as an electrophile?

a) HBr

b) CH_3Br

c) CH_3OH

d) $(CH_3)_4N$

45. Which of the following normally reacts as an electrophile?

a) $CH_3)_3CH$

b) $H_2C{=}CH_2$

c) $(CH_3)_2O$

e) CH_3Cl

46. Which of the following statements is wrong?

It is not necessary for a nucleophile to have an unshared electron pair

a) A species can react as an electrophile if it contains an atom (other than hydrogen) with an incomplete valence octet.

b) A species can react as an electrophile, even if it has one or more unshared electron pairs.

c) Any species bearing a lone pair can normally react as a nucleophile.

47. The formation of single product from two reactant molecules is known as…..

a) Addition reaction

b) Elimination reaction

c) Substitution reaction

d) Oxidation reaction

48.The reaction in which replacement of one atom /group of atoms is involved is termed as…

a) Addition reaction

b) Elimination reaction

c) Substitution reaction

d) Oxidation reaction

49. Breakdown of any molecule with water (H_2O) in any reaction is…..

a) Addition reaction

b) Elimination reaction

c) Substitution reaction

d) Hydrolysis.

50. Which compound could be involved in an addition reaction?

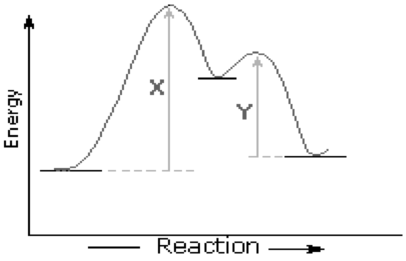
e) Methylbenzene

b) Hex-2-ene

c) Benzene

d) Hexane

51. Which of the descriptions (A to D) correctly describe the following energy diagram?



a) Two-step exothermic reaction having an activation energy = X

b) Two-step endothermic reaction having an activation energy = Y

c) Two-step exothermic reaction having an activation energy = Y

d) Two-step endothermic reaction having an activation energy = X

52. Which of the following series contain a free radical, a nucleophile and an electrophile?

a) $Br\cdot$, BF_3, NH_3

b) NH_3,NO_2^+ , Br_2

c) H_2O,$Cl\cdot$,NH_3

d) Cl_2, CH_4, NH_3

53. Which of the following is not an electrophile?

a) $C_2H_5OC_2H_5$

b) BF_3

c) $[CH_3]_3C^{(+)}$

d) HOCl

54. Which of the following is not a nucleophile?

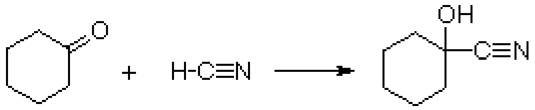
a) H_2O

b) CH_3NH_2

c) C_2H_5SH

d) C_6H_{12} (Cyclohexane)

55. Classify the following reaction.



- a) Substitution
- b) Addition
- c) Elimination
- d) Rearrangement

56. Which of the following compounds would be considered an electrophilic reagent?

- a) NH_3
- b) Br_2
- c) CH_3OH
- d) NH_2OH

57. Which of the following intermediates is pyramidal in shape?

- a) $H_3C(+)$
- b) $H_2C:$
- c) $H_3C:(-)$
- d) $HC\equiv C:(-)$

58. Carbanions are formed by treating an organic compound with a strong _____.

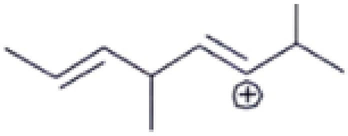
- a) Acid
- b) Base
- c) Buffer
- d) Solution

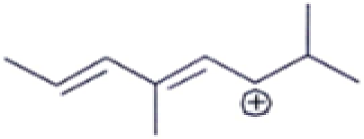
59. If you needed a reaction intermediate that contained a single electron, which intermediate would you need to try and make?

- a) Free radicals
- b) Carbanions
- c) Carbocations
- d) Nitrenium ion

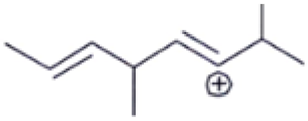
60. Which carbocation is the most stable?

a)

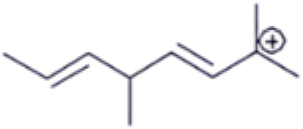




b)



c)



d)

61. The order of decreasing stability of the following cations is?

(I) $CH_3C^+HCH_3$ **(II) $CH_3C^+HOCH_3$** **(III) $CH_3C^+HCOCH_3$**

a) III > II > I

b) I > II > III

c) II > I > III

d) I > III > II