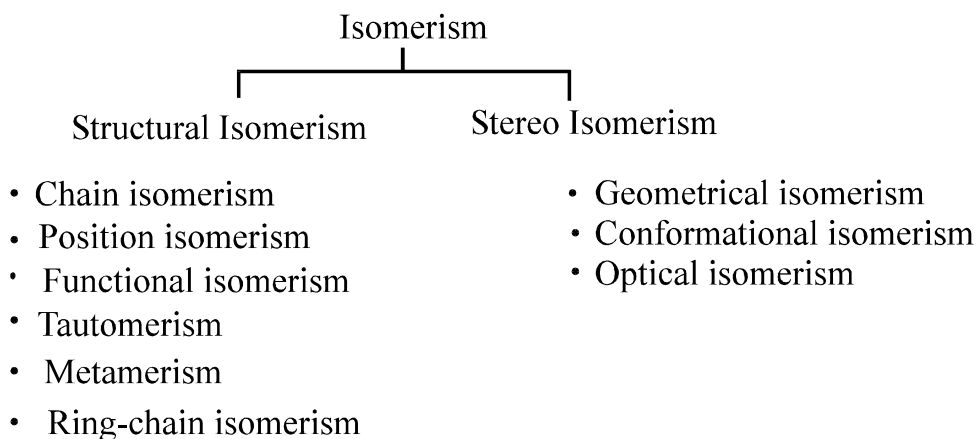


CHAPTER - 10

REACTION MECHANISM

ISOMERISM IN ORGANIC COMPOUNDS

Compounds having same molecular formula but different physical and chemical properties are called isomers and the phenomenon is known as isomerism.



STRUCTURAL ISOMERISM

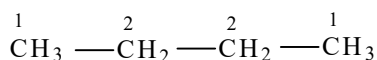
Compounds having same molecular formula, but different structures are called structural isomers

Chain isomerism

This type of isomerism arises due to the difference in the arrangement of carbon chains

* Chain isomerism in alkanes

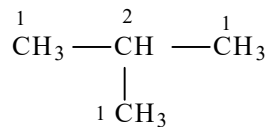
1. Butane (2 isomers)



n-Butane

2 types of hydrogen atoms

(2 types of mono halogenation products)

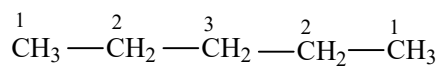


Isobutane

2 types of hydrogen atoms

(2 types of monohalogenation products)

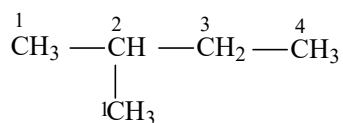
2. Pentane (3 isomers)



n-pentane

3-types of hydrogen atoms

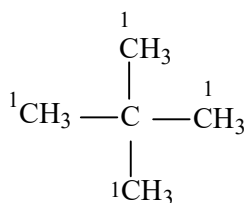
(3-types of monohalogenation products)



Iso pentane

4-types of hydrogen atoms

(4-types of monohalogenation products)



Neopentane

1-types of hydrogen atom

(Only one mono-halogenation product)

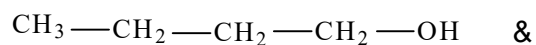
3. Hexane (5 isomers)

4. Heptane (9 isomers)

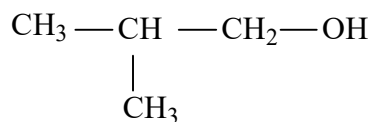
5. Octane (18 isomers)

6. Nonane (35 isomers)

7. Decane (75 isomers)

*** Chain isomerism in alcohols**

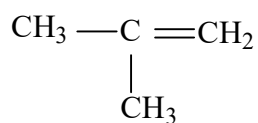
n- butanol



Isobutanol

*** Chain isomerism in alkenes**

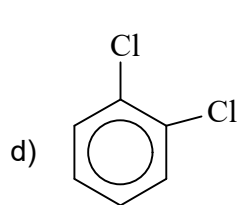
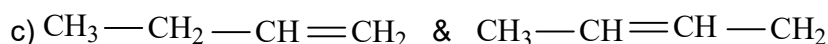
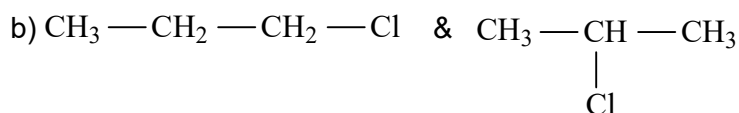
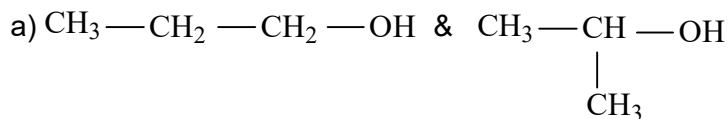
n - butene



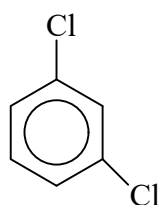
Isobutene

Position isomerism

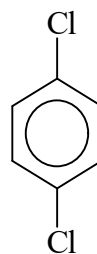
This type of isomerism arises due to the difference in the positions of functional groups, substituents or, unsaturation in the carbon chain.



o-dichloro benzene



m-dichloro benzene



p-dichloro benzene

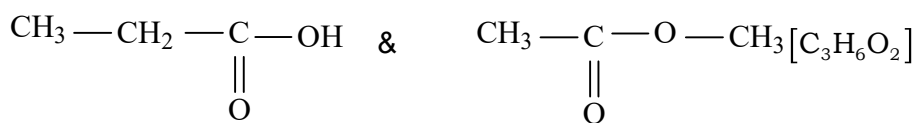
Functional isomerism

Compounds having same molecular formula but different functional groups are called Functional isomers.

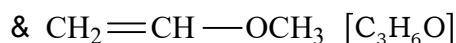
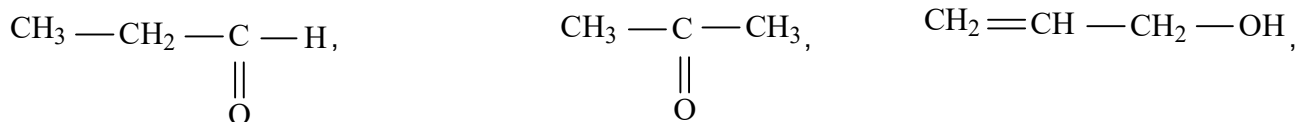
i) Alcohol and ether



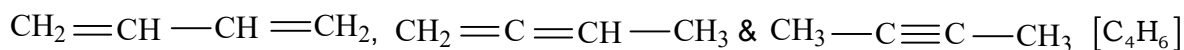
ii) Carboxylic acids and esters



iii) Aldehydes, Ketones, Unsaturated alcohols and Unsaturated ethers



vi) Dienes, Allenes and Alkynes

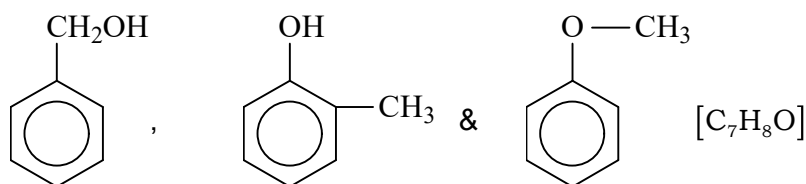


(Diene)

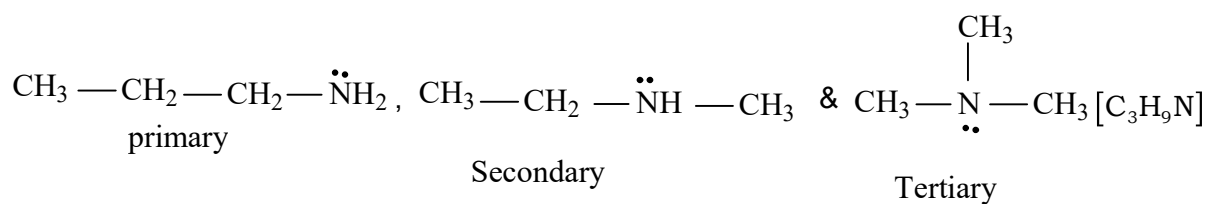
(Allene)

Alkyne

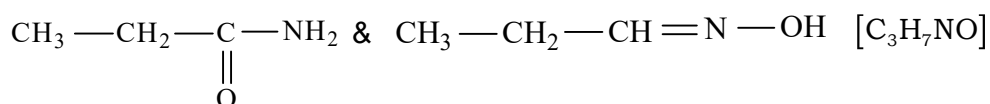
v) Aromatic alcohol, phenols and ethers



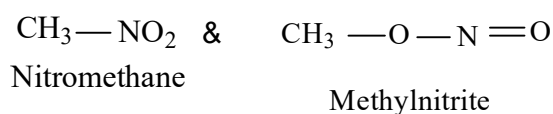
vi) Primary secondary and tertiary amines



vii) Amides and oximes



viii) Nitro alkanes and alkylnitrites

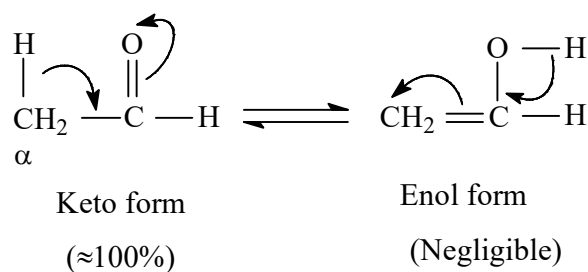


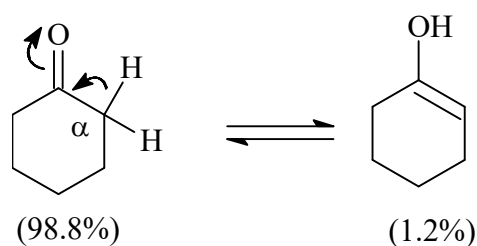
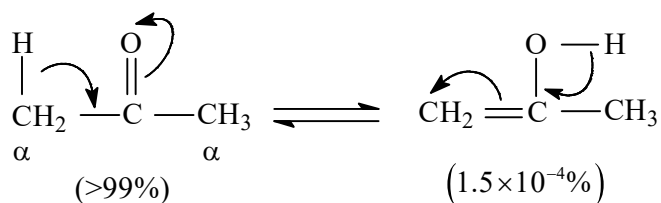
ix) Cyanides (nitriles) and isocyanides (Carbodiimine / Isonitrile)

**Tautomerism**

This is a special type of functional isomerism in which isomers exist in a dynamic equilibrium.

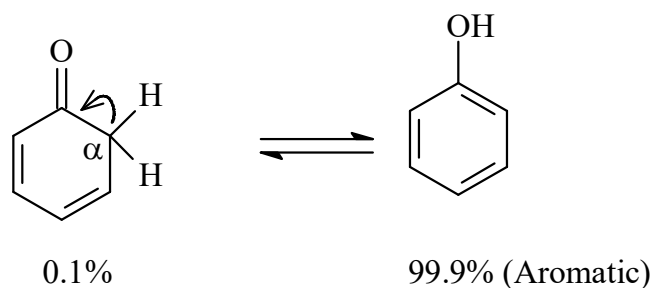
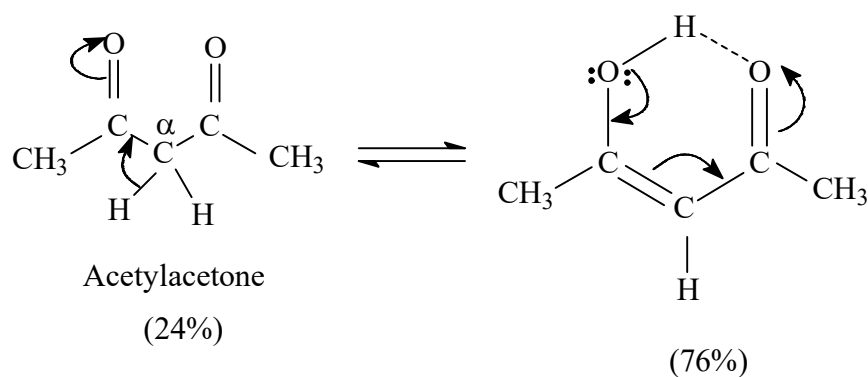
It arises due to the migration of a hydrogen atom from one poly valent atom to the other within the same molecule with necessary rearrangements for linkages.

1) Keto-enol tautomerism



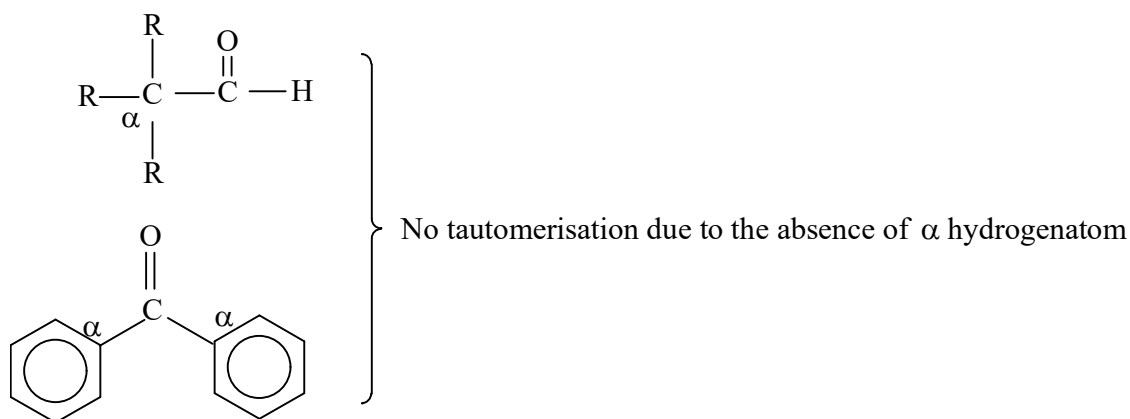
In all the three monocarbonyl compounds listed above, the greater percentage of ketoform is due to the greater strength of $\text{C}=\text{O}$ π bond (364 kJmol^{-1}) as compared to $\text{C}=\text{C}$ π bond (254 kJmol^{-1}).

Note: Hydrogen bonding and resonance increases the percentage of enol form

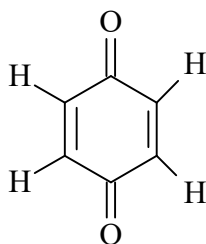


Conditions for tautomerism

1. Presence of atleast one α – hydrogen
2. Presence of electronegative elements such as O, N, S,.... with multiple bonds [$=C=O$, $-N=O$, $=C=S$, $-C\equiv N$, $=C=NH$ ]



Note: Tautomerism is not observed in parabenzoquinone because H-atoms are present on double bonded carbon atoms of the ring.



P-benzoquinone

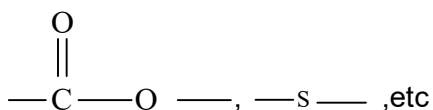
METAMERISM

This type of isomerism is arise due to the unequal distribution of carbon atoms on the either side of the functional group.

Eg: $CH_3CH_2OCH_2CH_3$ & $CH_3OCH_2CH_2CH_3$

Note: Metamerism is not observed in the molecule $CH_3 - CH_2 - O - CH_3$

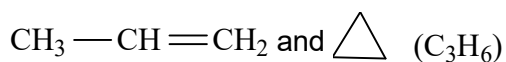
Example for some functional groups showing metamerism are $-O-$, $-NH-$,



Note: $CH_3 - CH_2 - C(=O) - O - CH_3$ and $CH_3 - C(=O) - O - CH_2 - CH_3$ are considered as metamers.

Ring Chain Isomerism

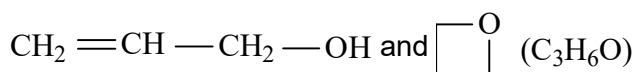
1. Alkenes and cycloalkanes





2. Alkynes and cycloalkenes



3. Unsaturated alcohols and cyclic ethers



Note: Other two cyclic isomers possible for the formula ($\text{C}_3\text{H}_6\text{O}$) are -CH₃ and 

Hybridisation of different types of carbon

1. Carbon with 4- σ bonds \rightarrow sp^3 hybridisation (No unhybridised 'p' orbitals are present)

2. Carbon with 1- π bond \rightarrow sp^2 hybridisation (One unhybridised 'p' orbital is present)

3. Carbon with 2- π bonds \rightarrow sp hybridisation (Two unhybridised 'p' orbitals are present)

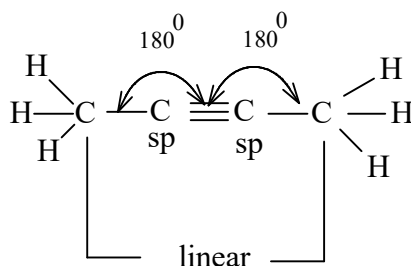
Note:

• Normal sp^3 bond angle $\rightarrow 109^\circ 28'$ (Total 6 tetrahedral angles are present around an sp^3 hybridised 'C')

• Normal sp^2 bond angle $\rightarrow 120^\circ$ (Total 3- 120° angles are present around an sp^2 hybridised 'C')

• Normal sp bond angle $\rightarrow 180^\circ$ (2- 180° angles)

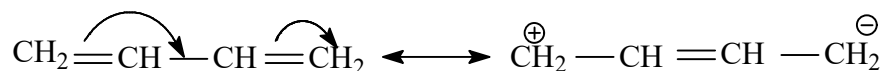
An sp hybridised carbon and carbons bonded to it are linearly arranged.



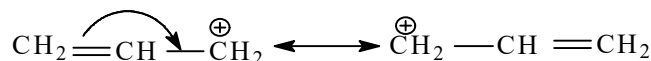
Methods for electron transfer in a covalent bond

1. Resonance

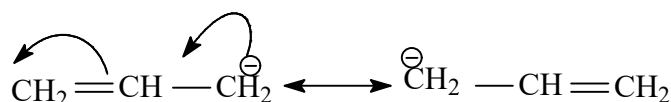
When the actual structure of a molecule is represented by the help of more than one electronic arrangement, the molecule is said to have resonance. i.e., delocalisation of π electrons occurs during resonance.

Resonance in different types of systems1. Resonance involving π – bonds

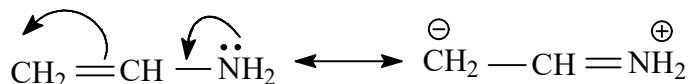
2. Resonance involving +ve charge



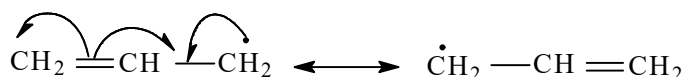
3. Resonance involving -ve charge



4. Resonance involving lone pair



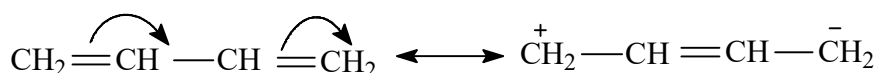
5. Resonance involving free radical



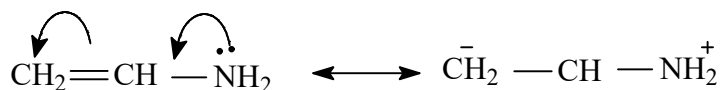
\therefore In the all five cases represented above, resonance involves $\pi - \pi$ conjugation

Resonance effect or Mesomeric effect (R/M - effect)

Polarity produced in a molecule by the interaction between π bonds or between π bond and lone pair of electrons (or non bonding electrons) of an adjacent atom is known as resonance effect or mesomeric effect. There are two types +R or +M and -R or -M.

**+R/+M Effect**

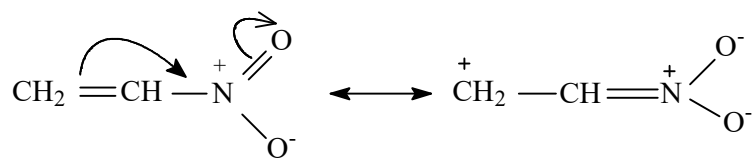
If the group attached to an unsaturated or conjugated system is electron releasing through resonance, the effects called as +R effect.



Examples for some groups showing +R effect : $-\ddot{\text{N}}\text{H}_2$, $-\ddot{\text{N}}\text{HR}$, $-\ddot{\text{N}}\text{R}_2$, $-\ddot{\text{O}}\text{H}$, $-\ddot{\text{O}}\text{R}$, $-\ddot{\text{X}}$:

-R/-M Effect

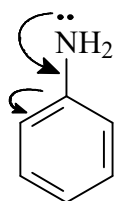
If the group attached to an unsaturated or conjugated system is electron withdrawing through resonance, the effect is called as -R effect.



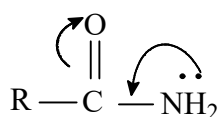
Examples for some groups showing 'R' effect — NO₂, — CN, — SO₃H, — COOH, — CHO etc.

Applications

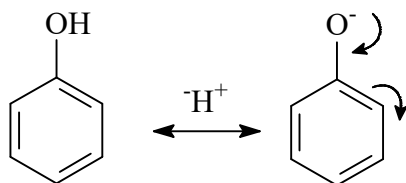
1. Aromatic amines are less basic as compared to aliphatic amines, because due to resonance, the lone pair of electrons on nitrogen is delocalised over the aromatic ring and it is therefore less easily available for protonation.



2. Amides are less basic as compared to amines because due to resonance, the lone pair on N in amides are delocalized over the carbonyl group.



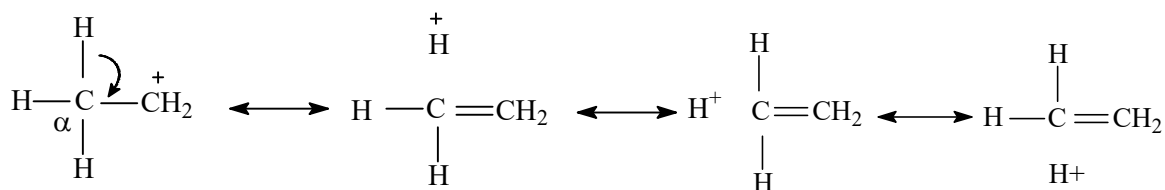
3. Phenols are more acidic as compared to alcohol because the phenoxide ion is stabilized by resonance.

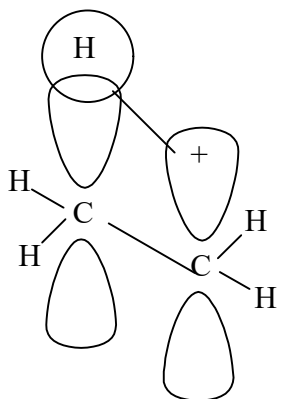


Hyperconjugation (Baker-Nathan effect)

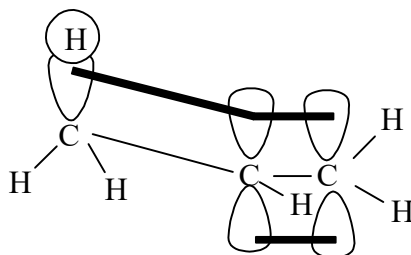
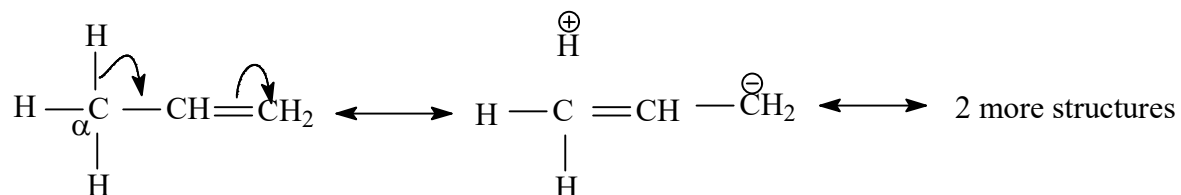
It involves the migration of a C-H σ -electrons of an alkyl group directly attached to an atom of an unsaturated system or to an atom with an unshared 'p' orbital (free radicals or carbocations)

1. Hyperconjugation in carbocation

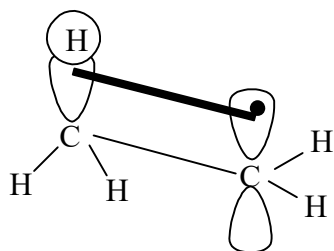
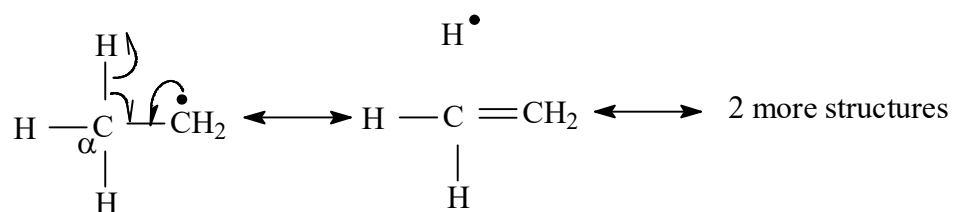




2. Hyper conjugation in unsaturated system

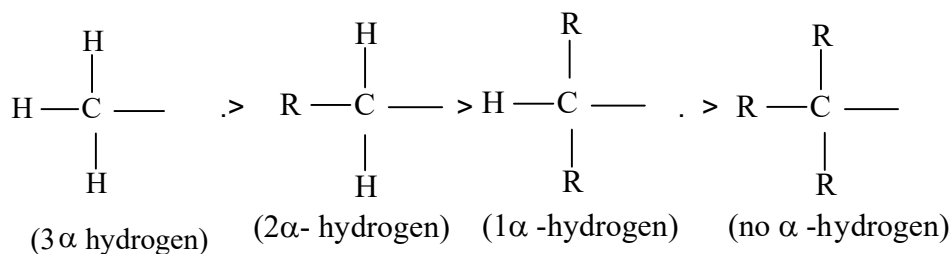


3. Hyper conjugation in free radicals



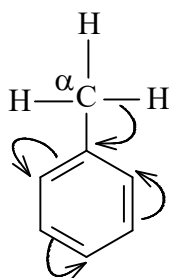
∴ In all the three cases represented above, hyperconjugation involves $\sigma - \pi$ conjugation. Since there is a carbon-hydrogen bond absent in all the hyperconjugative structures, hyperconjugation is also known as no-bond resonance.

The necessary condition for hyperconjugation is the presence of atleast one α -hydrogen atom. As the number of α -hydrogen atom in an alkyl group increases, its hyper conjugative effect also increases. Therefore hyper conjugative effect of some alkyl group follows the order.

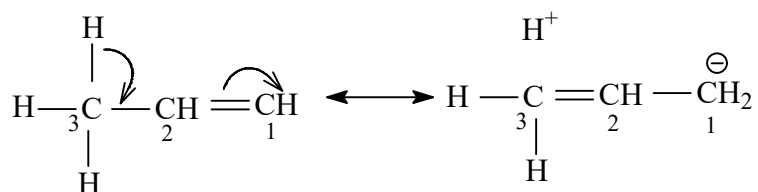


Applications

- Alkyl groups are ortho -para directing groups for electrophiles on aromatic ring due to hyperconjugation



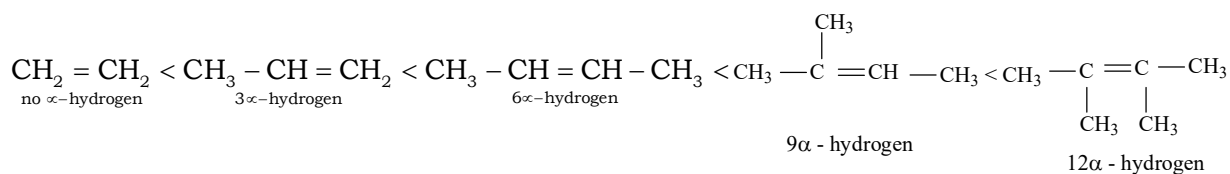
- Shortening of C-C single bond length adjacent to multiple bonds.



Due to hyperconjugation $\text{C}_2\text{-C}_3$ bond in propene have a partial double bond character.

- Relative stabilities of alkene

As the number of α -hydrogen atoms possible for an alkene increases, the number of hyperconjugative structures and stability increases

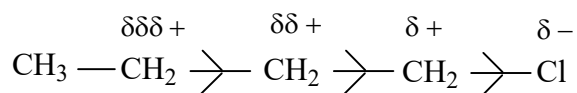


INDUCTIVE EFFECT (I EFFECT)

The polarisation produced in a σ bond due to the polarisation of an adjacent σ bond is called inductive effect.

-I Effect

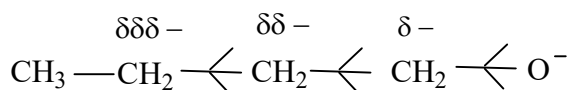
If the group attached to the end of a carbon chain is electron withdrawing through inductive effect, the effect is called as -I effect.



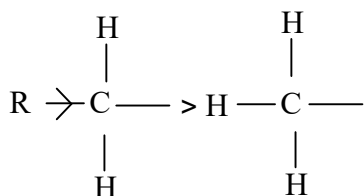
-I effect of some groups follows the order $-\text{NR}_3^+ > -\text{NO}_2 > -\text{CN} > -\text{SO}_3\text{H} > -\text{CHO} > -\text{COOH} > -\text{F} > -\text{Cl} > -\text{Br} > -\text{I}$

+I Effect

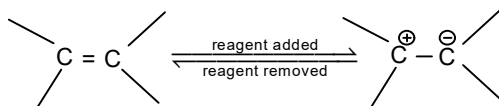
If the group attached to the end of a carbon chain is electron releasing through inductive effect, the effect is called as +I effect.



The +I effect of some groups follows the order $-\text{O}^- > \text{COO}^- > \text{R} \begin{array}{c} \text{R} \\ \downarrow \\ \text{C} \\ \uparrow \\ \text{R} \end{array} > \text{H} \begin{array}{c} \text{R} \\ \downarrow \\ \text{C} \\ \uparrow \\ \text{R} \end{array} >$

**ELECTROMERIC EFFECT (E - EFFECT)**

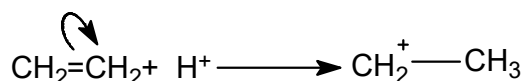
It involves the complete transfer of a π bond to the one of the bonded atom in presence of an attacking reagent



Since the effect operates only in the presence of an attacking reagent, it is a temporary effect

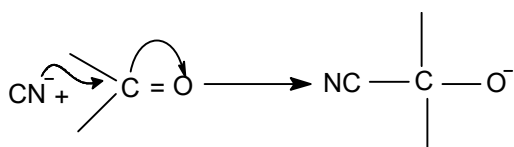
+E effect

If the electrons of the π -bond are transferred to that atom of the π -bond to which the reagent get finally attached is called +E effect



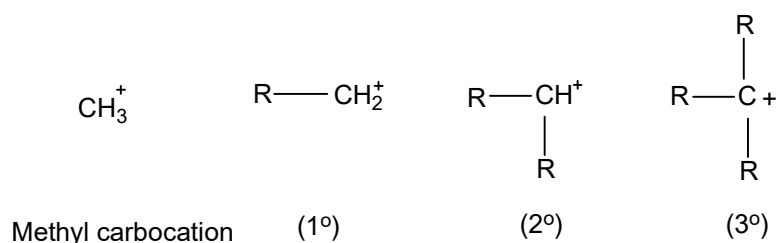
- E effect

If the electrons of the π bond are transferred to that atom of the π -bond other than the one to which the reagent gets finally attached is called -E effect.



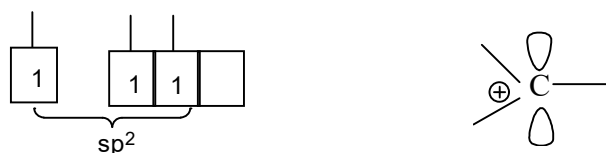
REACTION INTERMEDIATES

- Carbocations (carbonium ions)** : They are intermediate species carrying a positive charge on carbon
Classification



Structure

In carbocation, carbon is in sp^2 hybridised state. The three half filled sp^2 hybridised orbitals form three ' σ ' bonds. The unhybridised 'p' orbital is unoccupied.



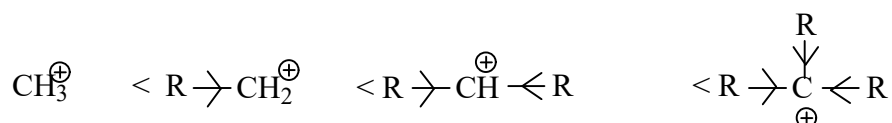
\therefore The carbon in carbocations are associated with 6 electrons in its valence shell

stability

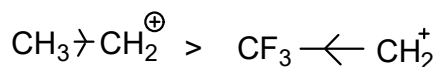
Stability in terms of inductive effect

Electron releasing alkyl groups decrease the magnitude of +ve charge on carbocation through +I effect and therefore such groups increase their stability.

\therefore stability of carbocations follows the order $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

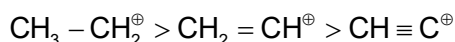


On the other hand electron withdrawing group increases the magnitude of +ve charge on the carbon by - I effect and there for such groups decreases their stability



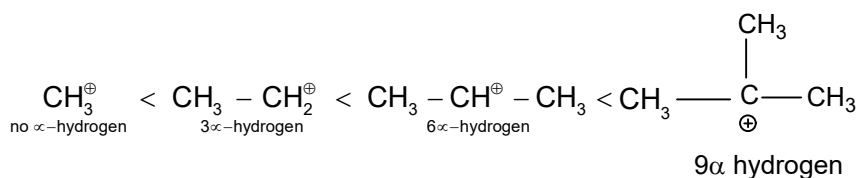
NOTE :

As the 'S' character or electronegativity of carbon bearing the +ve charge increases the stability of carbocation decreases



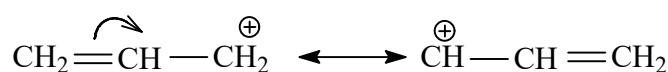
Stability in terms of hyper conjugation

As the number of α - hydrogen possible for a carbocation increases the number of hyper conjugative structures and therefore stability increases

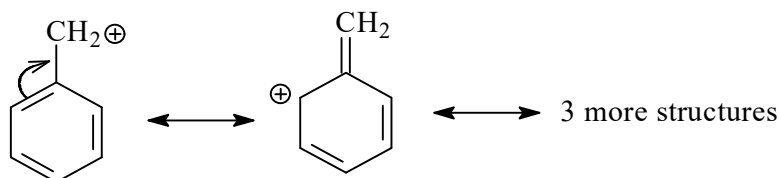


Stability in terms of resonance

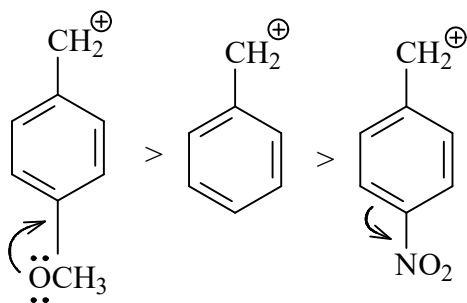
a) Resonance stabilisation of allylic carbocation



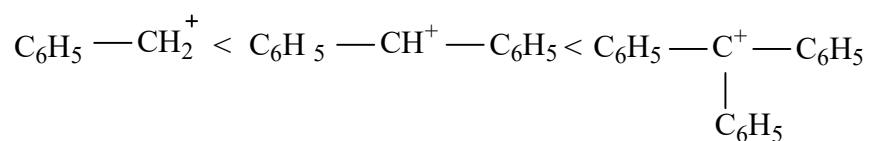
b) Resonance stabilisation of benzylic carbocation



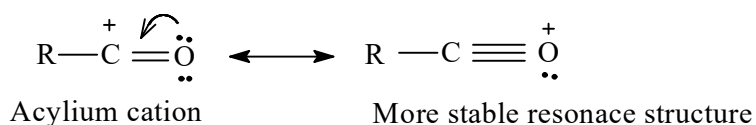
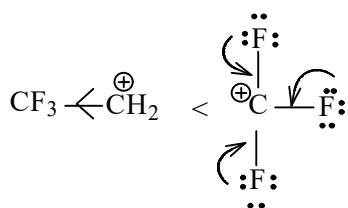
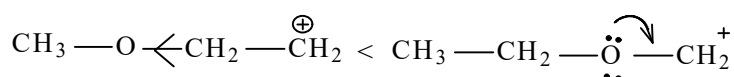
The magnitude of +ve charge is located at ortho- para positions. There fore electron releasing groups at ortho-para positions increases the stability of benzylic carbocation and electron withdrawing groups at ortho-para positions decreases their stability.



As the number of phenyl groups possible for the benzylic carbo cation increases, its resonance stabilisation is also increases.



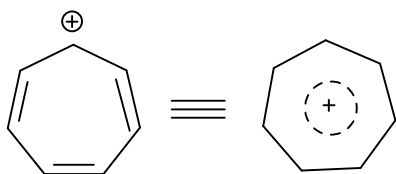
If the positively charged carbon is bonded to a hetero atom carrying lone pair of electrons, the carbocation is stabilised by resonance.



(Octet all atoms are completed)

NOTE :

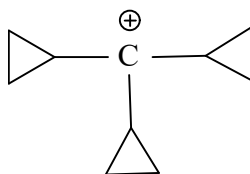
Cycloheptatrienyl cation (Tropylium cation) is more stable than $(\text{C}_6\text{H}_5)_3\text{C}^+$



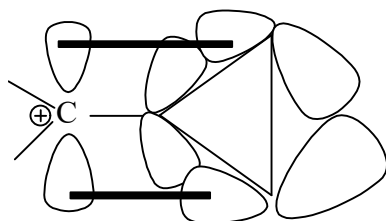
Reason

The carbocation is the resonance hybrid of 7 identical structures and also the cation is aromatic in nature.

The so far discovered most stable carbocation is



Reason:-

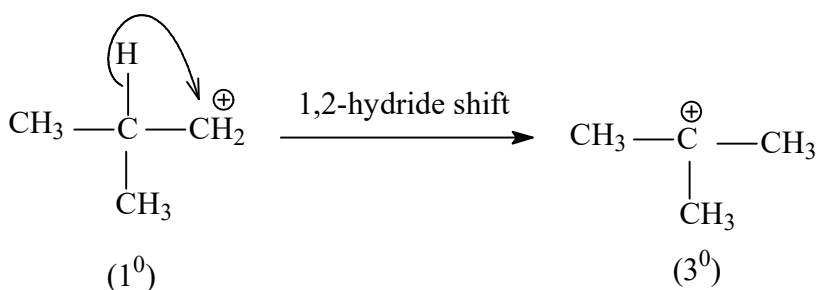
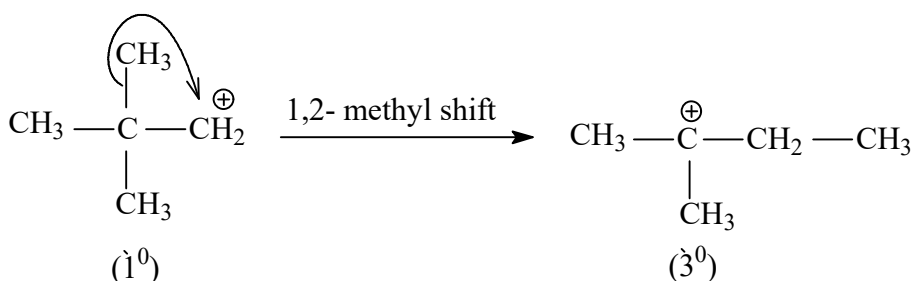


The bent orbitals in cyclopropyl ring release electrons to be vacant 'p'-

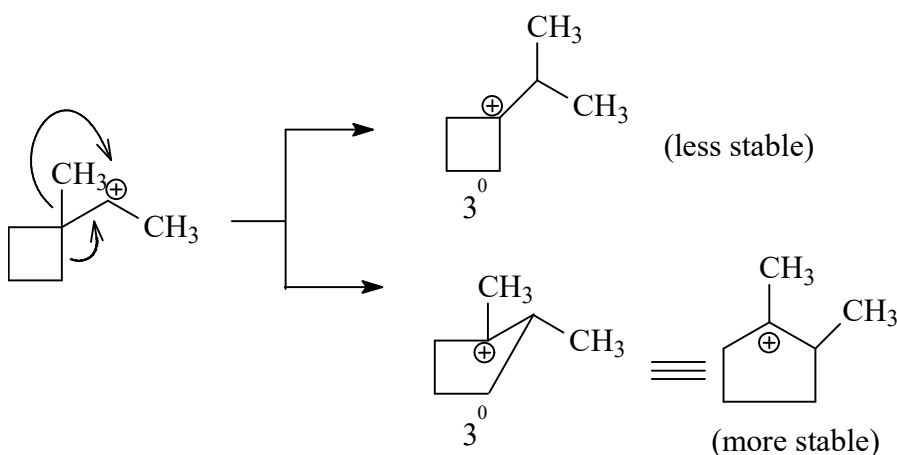
orbital of carbocation (σ - conjugation)

Rearrangement of carbocation

Less stable primary and secondary carbocations rearrange to more stable 3° or 2° carbocations through 1, 2 shifts.



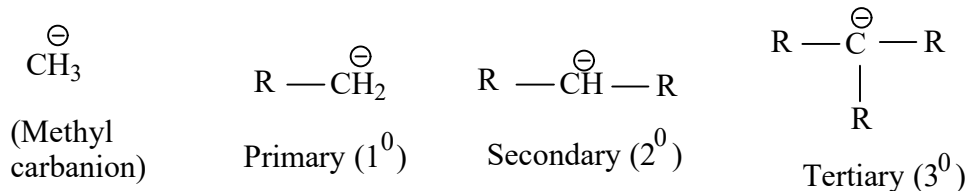
RING EXPANSIONS DURING REARRANGEMENT OF CARBOCATIONS



2. Carbanion

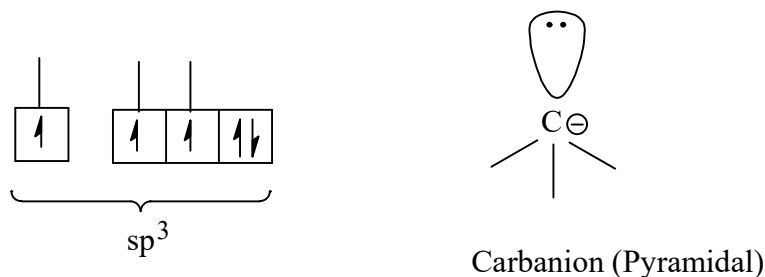
They are intermediate species carrying a negative charge on carbon.

Classification



Structure

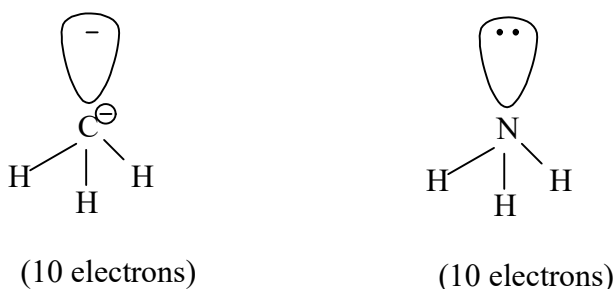
In carbanions, carbon is in sp^3 hybridised state. The three half filled sp^3 hybridised orbitals form 3 σ bonds. 4th sp^3 hybridised orbital contains a pair of electrons. But in resonance stabilised carbanions like, allyl, benzyl etc the negatively charged carbon is sp^2 hybridised.



\therefore The carbon in carbanion are associated with 8 electrons in its valence shell.

NOTE:

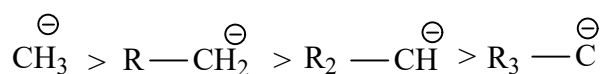
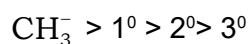
Methyl carbanion and ammonia (NH_3) are iso structural and iso electronic.



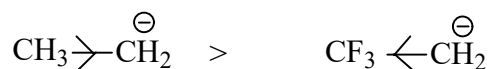
Stability

Stability in terms of inductive effect.

Electron releasing group increases the magnitude of -ve charges on carbanion through +I effect and such groups decreases their stability. \therefore The stability of carbanion is in the order.



On the otherhand electron withdrawing group decreases the magnitude of carbanion through -I effect and such groups increases their stability.

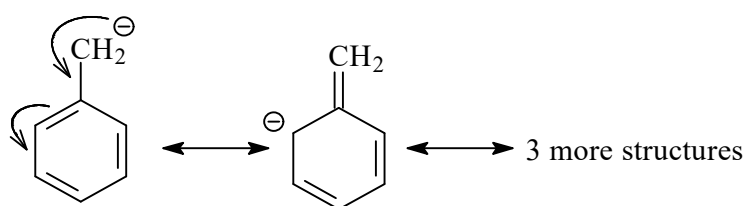


Stability in terms of resonance

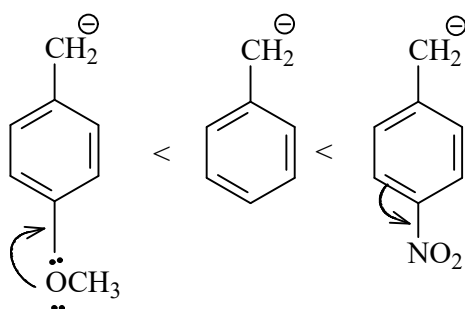
a) Resonance stabilisation of allylic carbanion



b) Resonance stabilisation of benzylic carbanion

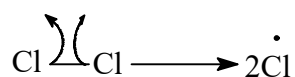


The magnitude of -ve charge is located at ortho-para positions. Therefore electron withdrawing groups at ortho-para positions increase the stability of benzylic carbanion and electron releasing group at ortho- para positions decreases their stability.

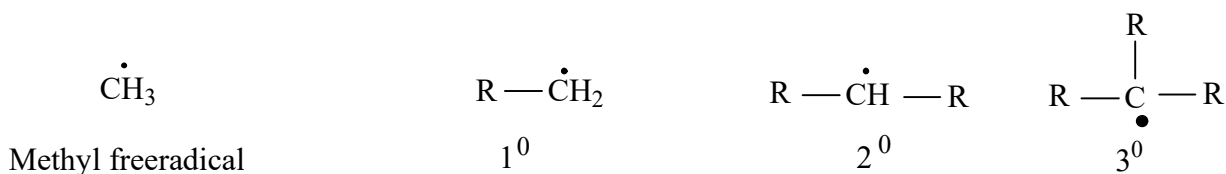


3. Free radicals

They are neutral electron deficient chemical species carrying an unpaired electron. They are generated as a result of homolytic bond cleavage.

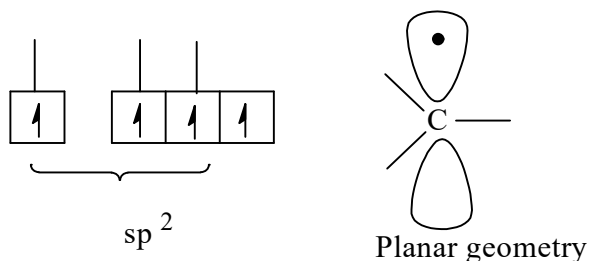


Classification



Structure

In free radicals carbon is in sp^2 hybridisation. The three half filled sp^2 hybridised orbitals form 3 σ bonds. The unshared electron is present in the unhybridised 'p' orbital.

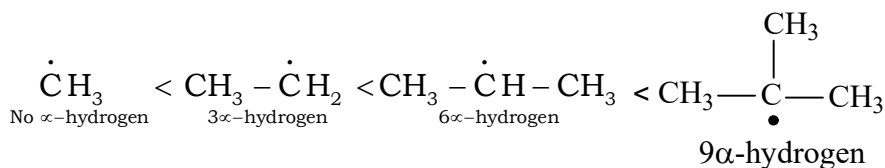


\therefore The carbon in free radicals are associated with $7e^-$ in their valence shell.

Stability

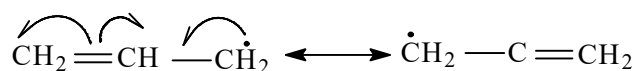
Stability in terms of hyperconjugation

As the number of α – hydrogen atom possible for a free radical increase, the number of hyperconjugative structures and therefore stability increases. Therefore the stability increases in the order $3^\circ > 2^\circ > 1^\circ > CH_3^\bullet$

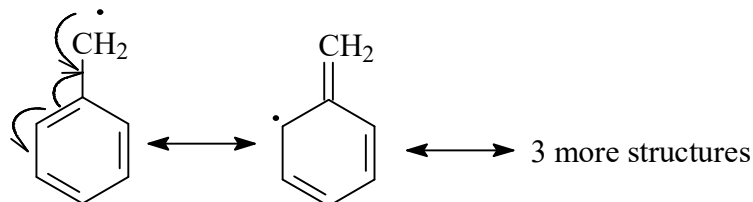


Stability in terms of resonance

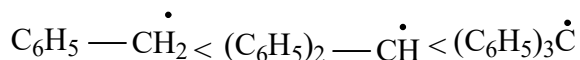
a) Resonance stabilisation of allylic free radical.



b) Resonance stabilization of benzylic free radical.



As the number of phenylic group possible for a benzylic free radical increases the resonance stabilisation is also increases.

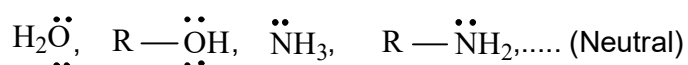
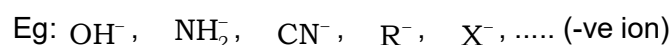


ELECTROPHILES AND NUCLEOPHILES

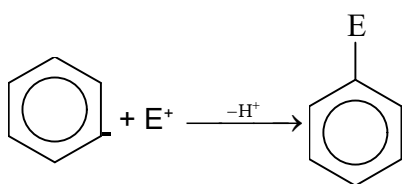
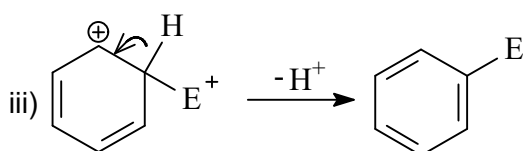
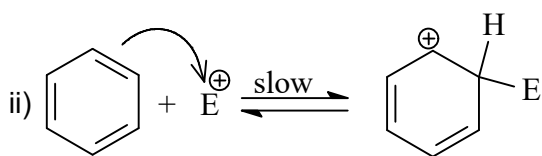
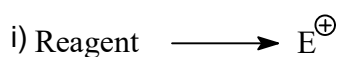
Electrophiles are electron loving chemical species (electron deficient)



Nucleophiles are nucleus loving chemical species (electron rich)

**Different types of organic reactions****1. Substitution reaction****a. Electrophilic substitution reaction (S.E. reaction)**

The substitution reaction is carried out by an electrophile

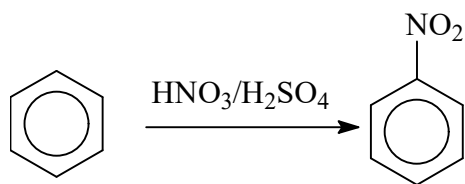
Eg: - Electrophilic substitution reaction in benzene**Mechanism**

The second step is the slowest step and it is therefore the rate determining step

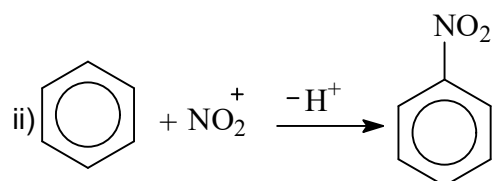
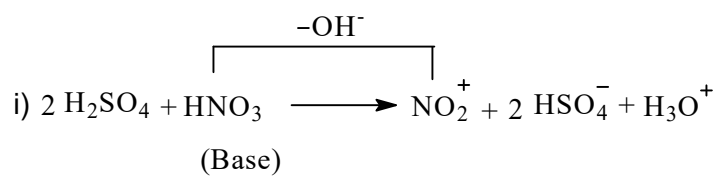
Application

- Benzene and hexadeuteriobenzene gives a particular electrophilic substitution reaction exactly at the same rate, because cleavage of proton is not involved in rate determine step

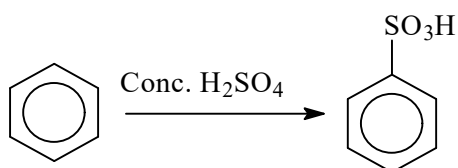
1. Nitration



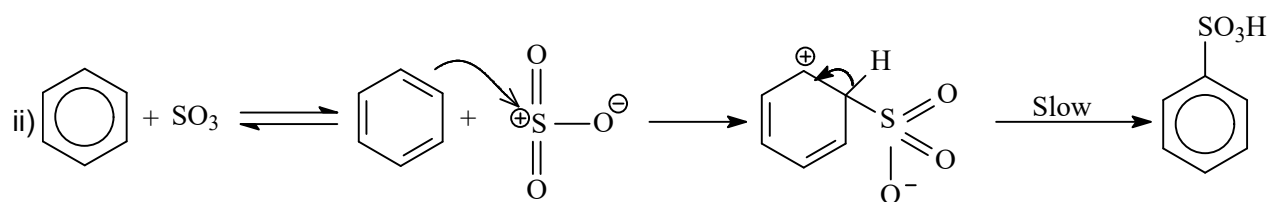
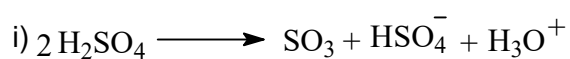
Mechanism



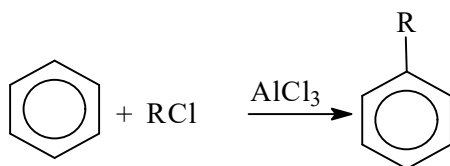
2. Sulphonation

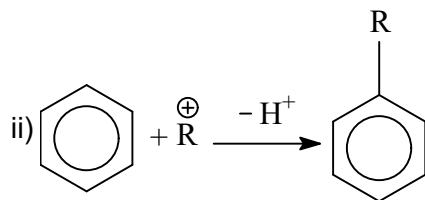
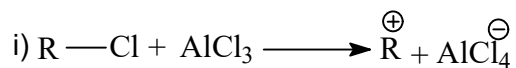


Mechanism:

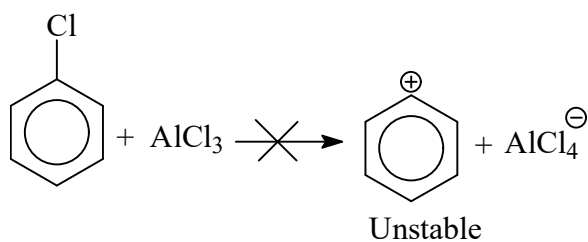
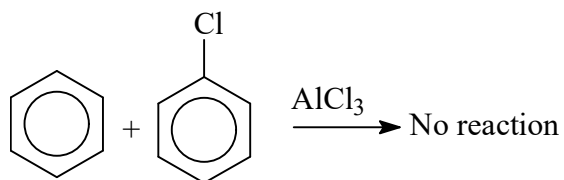
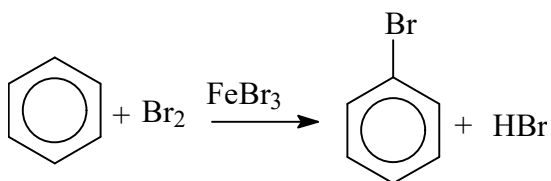
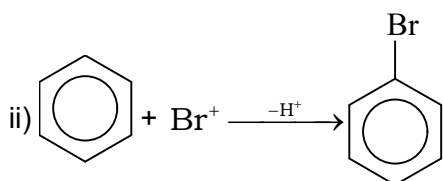
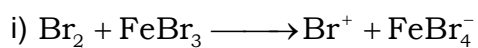


Friedel craft's reaction



Mechanism:**Application:-**

Benzene with chlorobenzene doesn't give Friedel-Craft's reaction because the phenyl carbocation is highly unstable.

**Halogenation****Mechanism:**

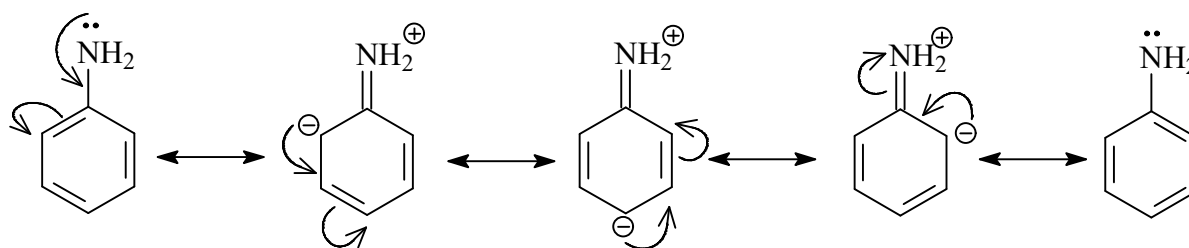
Ring activating groups for electrophilic substitution

Electron releasing groups increases the electron density on benzene ring and therefore such groups activate the benzene ring for electrophilic substitution.

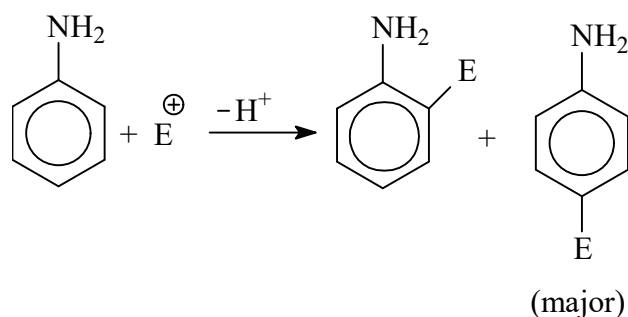
Eg: $-\ddot{\text{N}}\text{H}_2$, $-\ddot{\text{N}}\text{HR}$, $-\ddot{\text{O}}\text{H}$, $-\ddot{\text{O}}\text{R}$ (+R effect)

Alkyl groups (+I and hyperconjugation)

Ring activating effect of $-\ddot{\text{N}}\text{H}_2$ group



The magnitude of -ve charge is located at ortho-para positions. \therefore Ring activating group are ortho-para directing groups or electrophiles



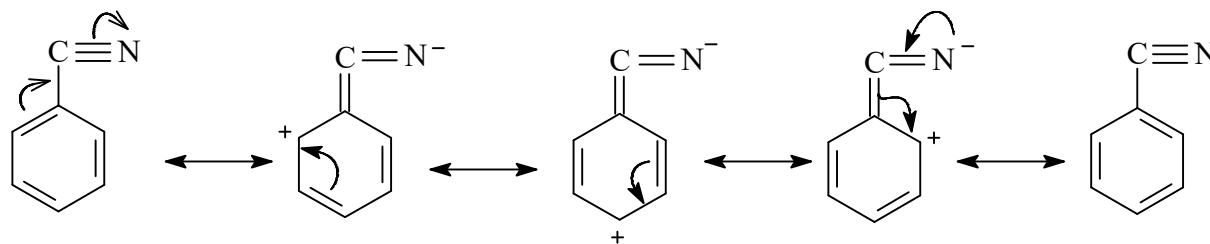
Ring deactivating groups for electrophilic substitution

Electron withdrawing groups decreases the electron density on benzene ring and therefore such groups deactivate benzene ring towards electrophilic substitution.

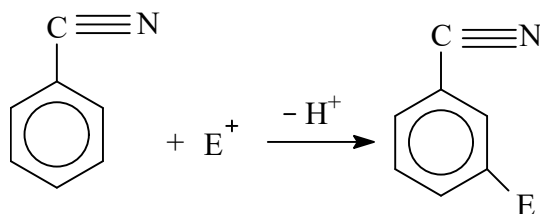
Eg:- NO_2 , $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{CHO}$, $-\text{COOH}$ (-I and -R effect)

Halogens (-I effect)

Ring deactivating effect of cyanide group

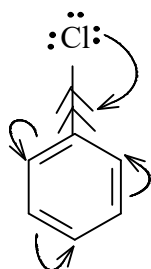


The magnitude of +ve charge is located at ortho-para positions. \therefore Ring deactivating groups are meta directing groups for electrophiles



Anomalous behavior of halogens

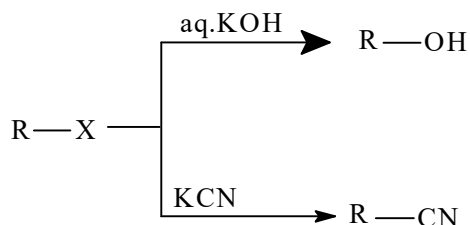
Halogens are ring deactivating groups through their strong -I effect. But orthopara directing groups for electrophiles through their weak +R effect. \therefore Halogens are ortho-para directing deactivators. i.e., the reactivity of the ring is controlled by strong -I effect of halogen and orientation of the electrophile is controlled by its weak +R effect.



b. Nucleophilic substitution reaction

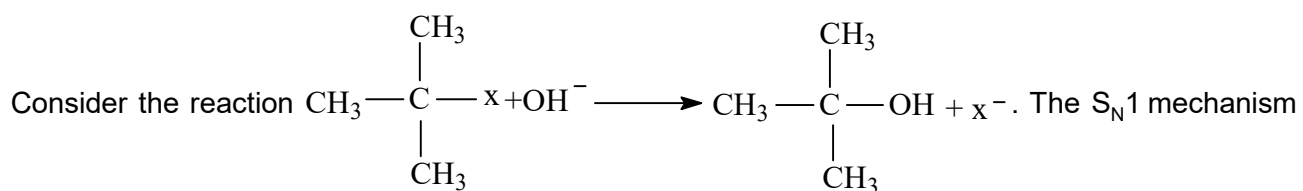
The substitution reaction carried out by nucleophile.

Eg:-

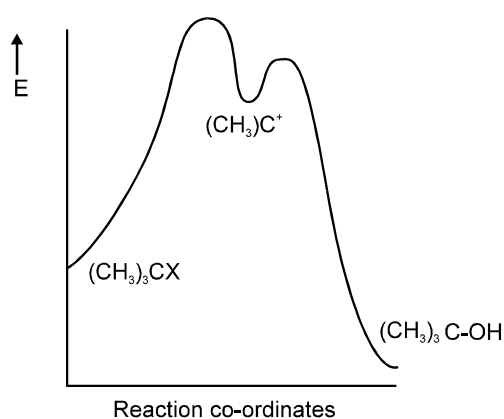
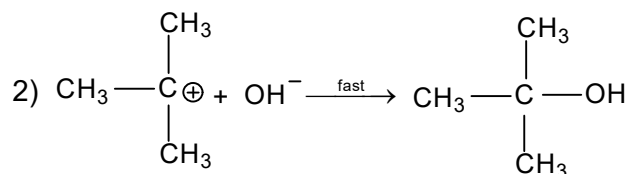
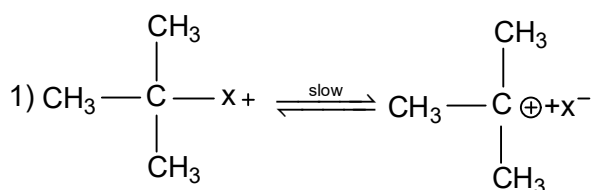


Mechanism of nucleophilic substitution reaction

S_N1 mechanism (substitution nucleophilic unimolecular mechanism)



for this reaction can be explained as

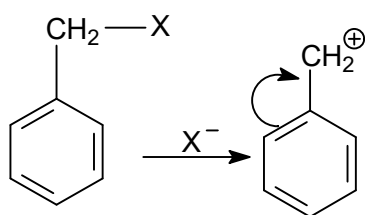
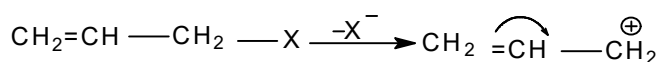


The first step is the slowest step and it is therefore the rate determining step. This step involves only a single reactant molecule. Therefore the mechanism is called as unimolecular.

The rate of S_N1 reaction depends upon the stability of the intermediate carbocation formed in the 1st step. Stability of carbo cation follows the order $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$. \therefore The reactivity of various alkylhalide towards S_N1 reaction follows the order $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{x}$

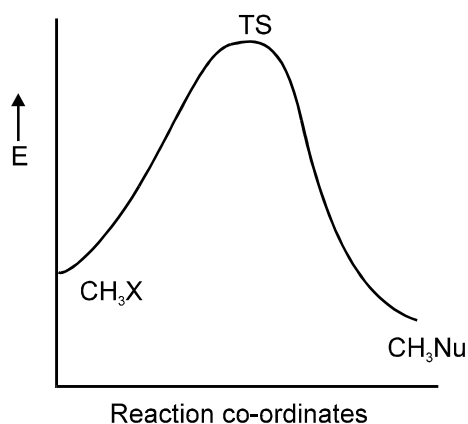
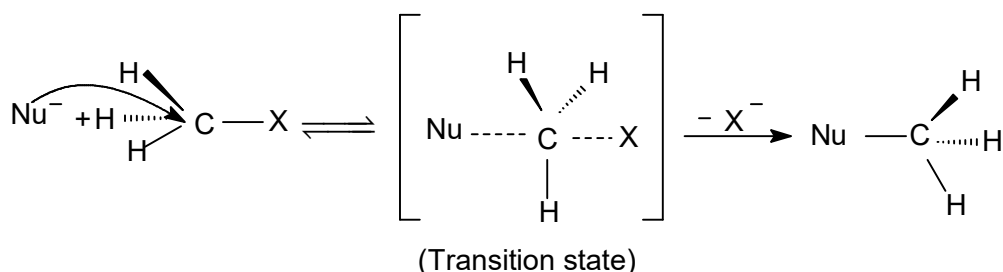
Note:

Allylic and benzylic carbocations are resonance stabilised. Therefore allylic and benzylic halides easily reacts through S_N1 reaction even though they are primary halides



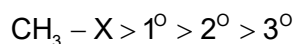
S_N2 Mechanism (Substitution nucleophilic bimolecular mechanism)

S_N2 reaction involves only a single step in which the nucleophile attack from the backside of the leaving group and as a result we get a 100% inversion product and is called Walden inversion



The single step (rate determining step) involves two reactant species. Therefore the mechanism is known as bimolecular.

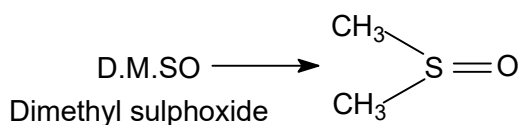
Bulky groups sterically retard the backside attack of the nucleophile. As a result, S_N2 reaction in various alkylhalides follows the order

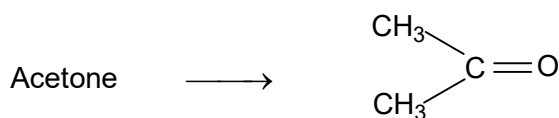
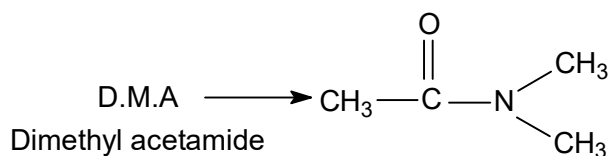
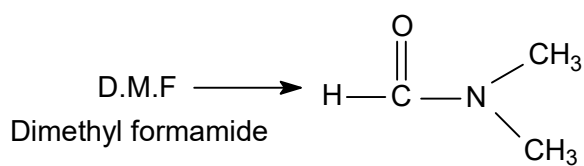
**Note:**

Allylic and benzylic halides are also highly reactive towards S_N2 reaction, because the π electrons in allylic and benzylic group help the cleavage of C–X bonds.

S_N2 reaction at an optically active centre gives a single stereo isomer and its direction of optical activity is unpredictable (may be dextro or laevo)

\therefore S_N2 reactions are slow in polar protic solvents. The commonly used solvents for S_N2 reactions are polar aprotic solvents such as





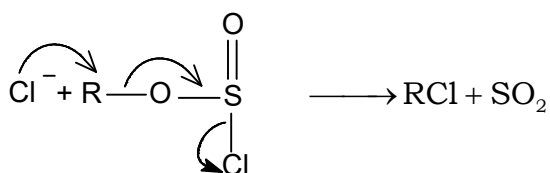
S_N1 Vs S_N2

S_N1

- Nucleophilic strength unimportant
- 3° > 2° > 1° > CH₃-X
- Polar protic solvents
- Rate = k[R-X]
- Rearrangements are possible

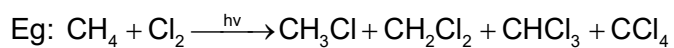
S_N2

- Nucleophiles with high nucleophilicity
- CH₃X > 1° > 2° > 3°
- Weakly polar (aprotic) solvents
- Rate = k[R-X][Nu⁻]
- Rearrangement is not possible

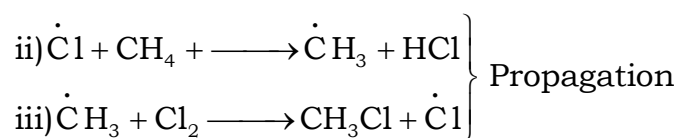
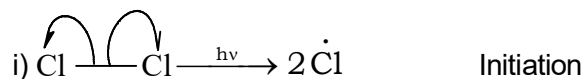


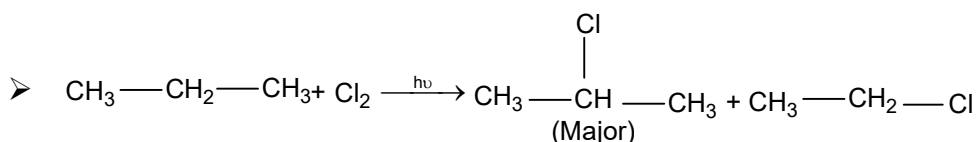
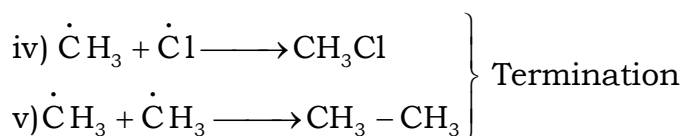
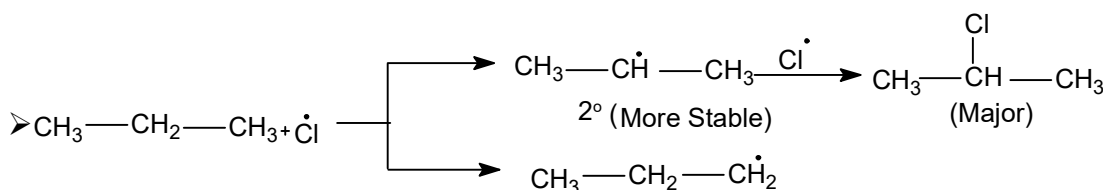
Free radical Substitution Reaction

Substitution reaction is carried out by a free radical

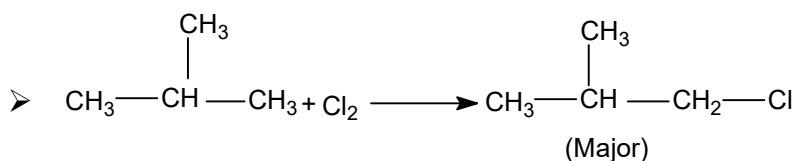


Mechanism

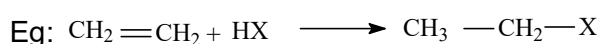
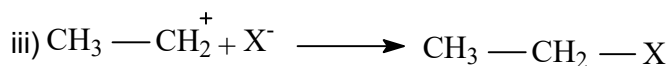
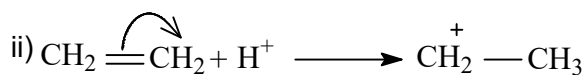
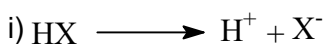
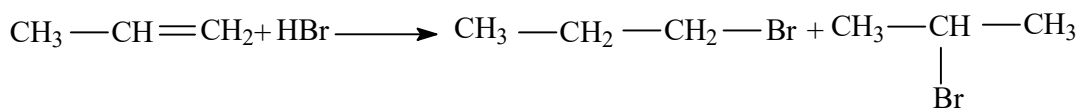


**Mechanism:**

The reactivity of various hydrogen atom towards free radical substitution reaction depends up on the stability of the intermediate free radical generated. The stability of free radical follows the order $3^\circ > 2^\circ > 1^\circ$. \therefore The reactivity of various hydrogen atoms towards free radical substitution reaction follows the order $3^\circ > 2^\circ > 1^\circ$:

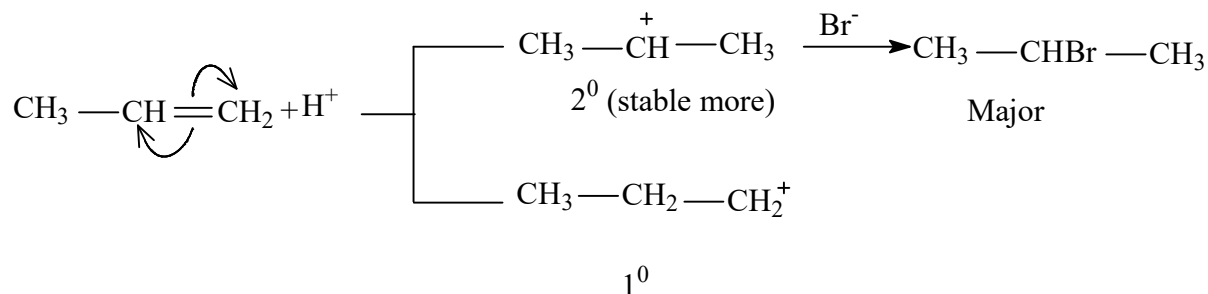
**Addition Reaction****1. Electrophilic addition reaction**

The addition reaction is initiated by an electrophile

**Mechanism:****Application:**

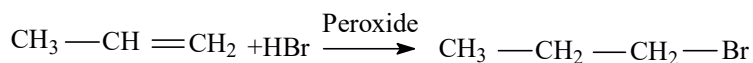
(Major) (Markovnikov's rule)

Mechanism:

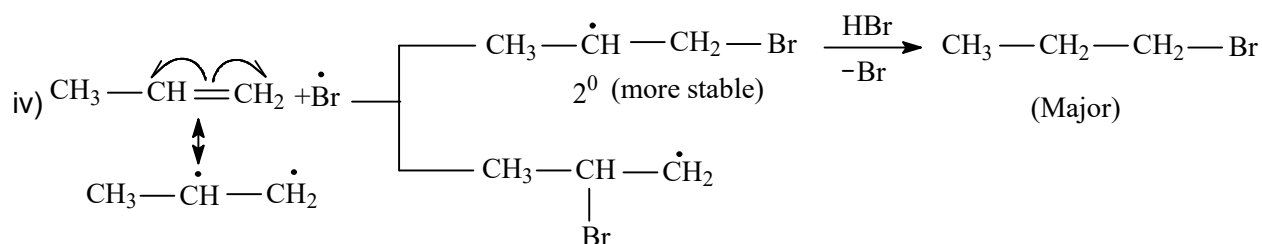
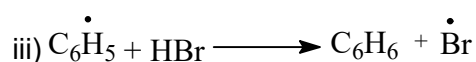
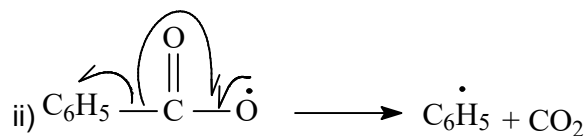
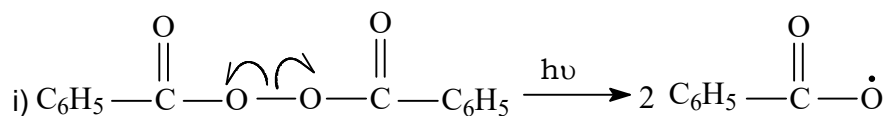


Note:

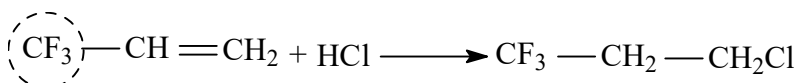
The addition of HBr (not other HX) to an unsymmetrical alkene in presence of a peroxide takes place against Markonikov's rule and is called the anti-Markovnikov's addition or peroxide effect or Kharasch effect.

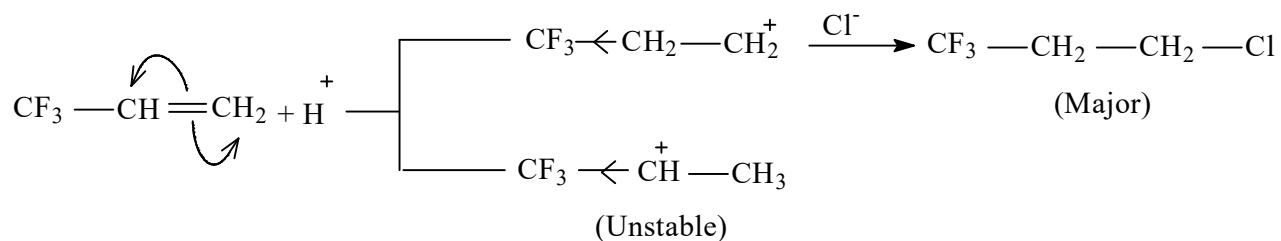


Mechanism:

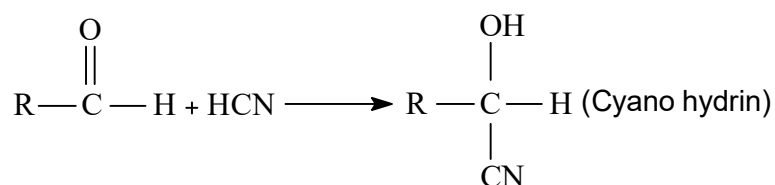
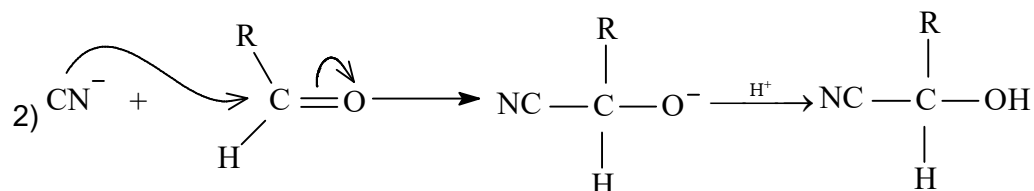
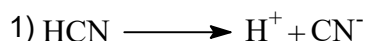


Note: Presence of electron withdrawing groups on unsaturated carbon gives anti-markonikov's addition

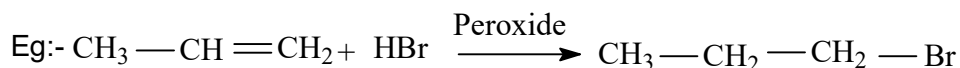


Mechanism:**Nucleophilic addition reaction**

The addition reaction is initiated by a nucleophile

**Mechanism:****Note:****Free radical addition reaction**

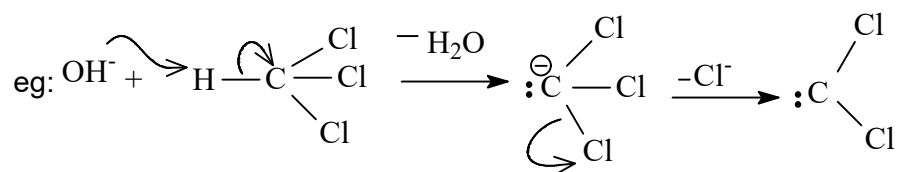
The addition reaction is initiated by a free radical

**ELIMINATION REACTION**

This type of reaction involves the loss of 2 atoms or groups, occurs from the same or adjacent atoms leading to the formation of a multiple bond or its any equivalent.

 α – Elimination reaction;

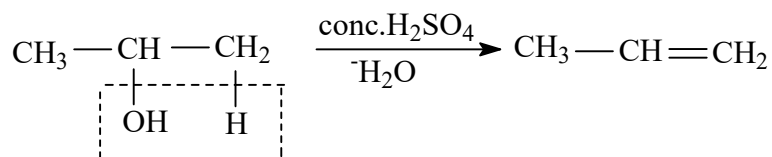
The loss of two atoms or groups occurs from the same atom



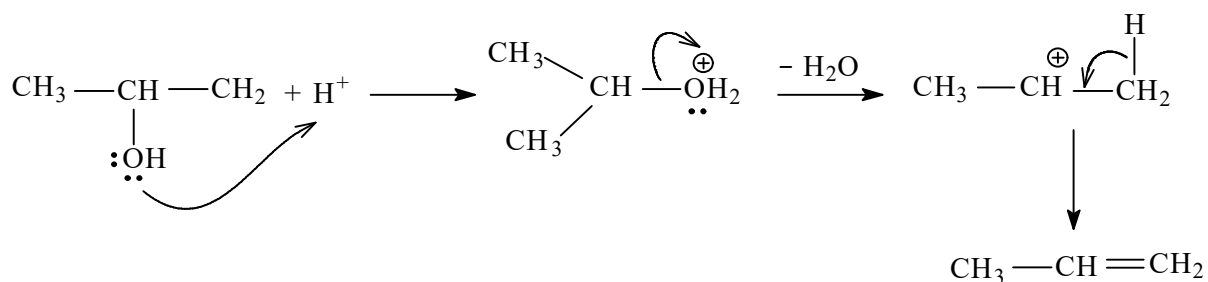
β – Elimination reaction:

The loss of two atoms or groups occurs from two adjacent atoms.

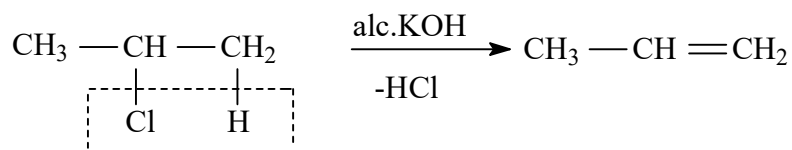
1. Dehydration of alcohols



Mechanism

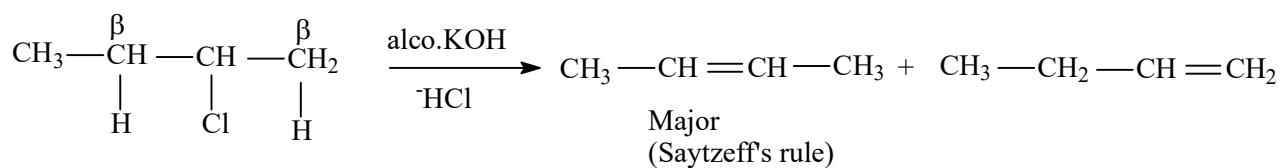


2. Dehydrohalogenation reaction



The reaction involves alkoxide ion (R-O^-) as the reagent. R-O^- is bulkier nucleophile and a strong base. Therefore it prefer to attack the β hydrogen and produce the corresponding elimination product.

Note:



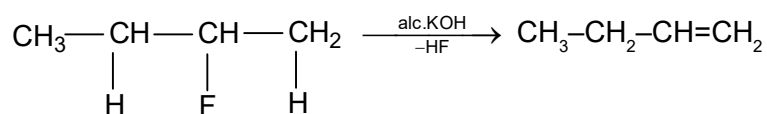
Saytzeff's Rule

In a dehydrohalogenation reaction, the more substituted alkene will be the major product

Reason: More substituted alkenes have a more number of α hydrogen atoms and it is therefore stabilised by hyperconjugation.

Note:

The dehydrofluorination reaction is against Saytzeff's rule and is known as Hofmann's elimination



Reason : The C-F bond strength is greater than C-H bond length. Therefore the more acidic β -hydrogen will be eliminated in the first step

