CHAPTER - 00
REACTION MECHANISM

ISOMERISM IN ORGANIC COMPOUNDS

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

Isomerism

Structural Isomerism

- Chain isomerism
- Position isomerism
- Functional isomerism
- Tautomerism
- Metamerism
- Ring-chain isomerism

Stereo Isomerism

- Geometrical isomerism
- Conformational isomerism
- Optical isomerism

STRUCTURAL ISOMERISM

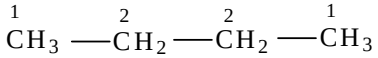
Compounds having same molecular formula, but different structures are called structural isomers

Chain isomerism

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

*** Chain isomerism in alkanes**

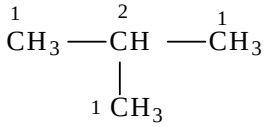
1. Butane (2 isomers)



n-Butane

2 types of hydrogen atoms

(2 types of mono halogenation products)

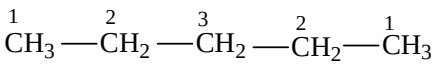


Isobutane

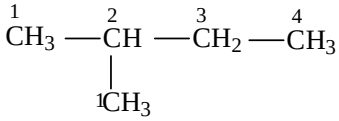
2 types of hydrogen atoms

(2 types of monohalogenation products)

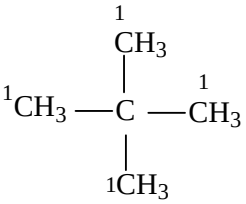
2. Pentane (3 isomers)



n-pentane
3-types of hydrogen atoms
(3-types of monohalogenation products)



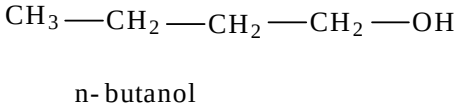
Iso pentane
4-types of hydrogen atoms
(4-types of monohalogenation products)



Neopentane
1-types of hydrogen atom
(Only one mono-halogenation product)

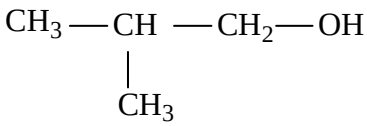
3. Hexane (5 isomers)
4. Heptane (9 isomers)
5. Octane (18 isomers)
6. Nonane (35 isomers)
7. Decane (75 isomers)

* **Chain isomerism in alcohols**



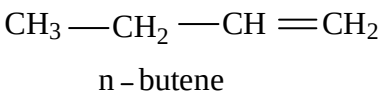
n-butanol

&



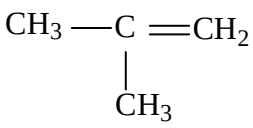
Isobutanol

* **Chain isomerism in alkenes**



n – butene

&



Isobutene

Position isomerism

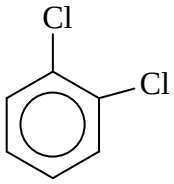
This type of isomerism is arise due to the difference in the positions of functional groups, substituents or, unsaturation in the carbon chain.

a) $CH_3-CH_2-CH_2-OH$ & $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$

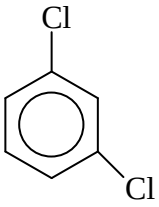
b) $CH_3-CH_2-CH_2-Cl$ & $CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$

c) $CH_3-CH_2-CH=CH_2$ & $CH_3-CH=CH-CH_2$

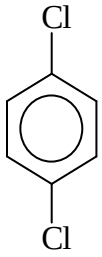
d)



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

CH_3-CH_2-OH & CH_3-O-CH_3 $[C_2H_6O]$

ii) Carboxylic acids and esters

$CH_3-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-OH$ & $CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-O-CH_3$ $[C_3H_6O_2]$

iii) Aldehydes , Ketones, Unsaturated alcohols and Unsaturated ethers

$CH_3-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-H$, $CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$, $CH_2=CH-CH_2-OH$,

& $CH_2=CH-OCH_3$ $[C_3H_6O]$

vi) Dienes, Allenes and Alkynes

$CH_2=CH-CH=CH_2$, $CH_2=C=CH-CH_3$ & $CH_3-C\equiv C-CH_3$ $[C_4H_6]$

(Diene) (Allene) Alkyne

Note:

Number of double bond equivalents possible for an organic compound

$$\left[\sum \frac{n(V-2)}{2}\right]+1$$

n: Number of atoms of a particular element

v: Valency of the corresponding atom

2 double bonds are equivalent to one triple bond. One double bond is equivalent to one cyclic compound.

1. Number of double bond equivalents possible for C_4H_6

$$C_4H_6 \rightarrow \frac{4(4-2)}{2}+\frac{6(1-2)}{2}+1$$

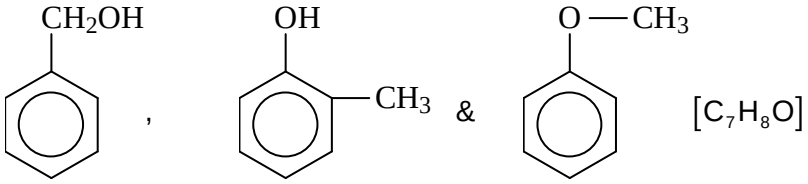
$$= 4-3+1=2$$

2. Number of double bond equivalents for C_3H_6O

$$C_3H_6O \rightarrow \frac{3(4-2)}{2}+\frac{6(1-2)}{2}+\frac{1(2-2)}{2}+1$$

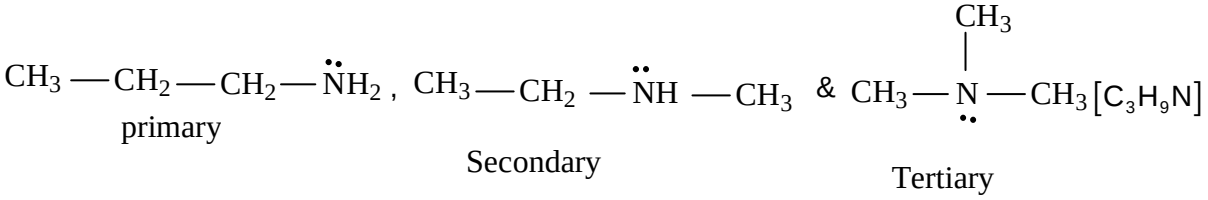
$$= 3-3+0+1=1$$

v) Aromatic alcohol, phenols and ethers



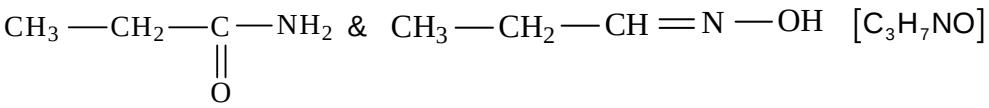
, & $[C_7H_8O]$

vi) Primary secondary and tertiary amines



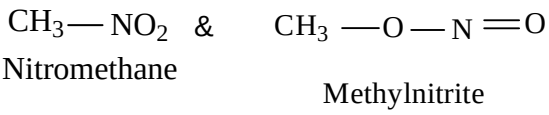
& $[C_3H_9N]$

vii) Amides and oximes



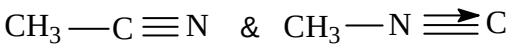
$[C_3H_7NO]$

viii) Nitro alkanes and alkylnitrites



Nitromethane Methylnitrite

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

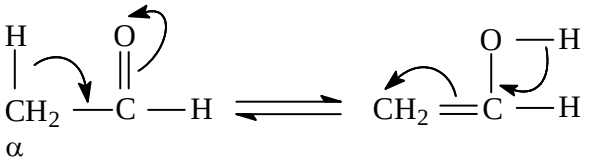


Tautomerism

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

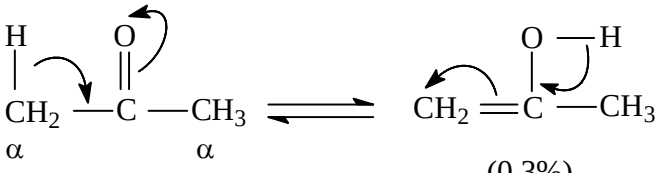
It arises due to the migration of a hydrogen atom from one poly valent atom to the other within the same molecule with necessary rearrangements for linkages.

1) Keto-enol tautomerism

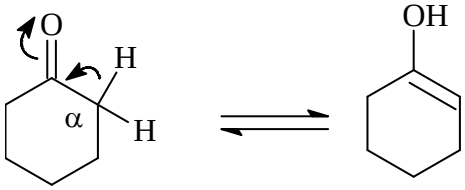


Keto form Enol form

(99.99%) (Negligible)



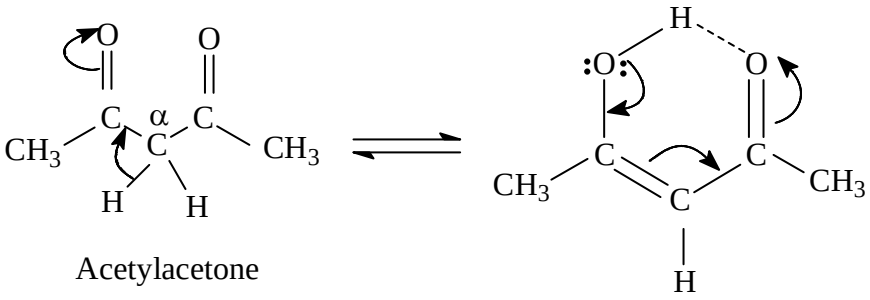
(99.7%) (0.3%)



(98.8%) (1.2%)

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

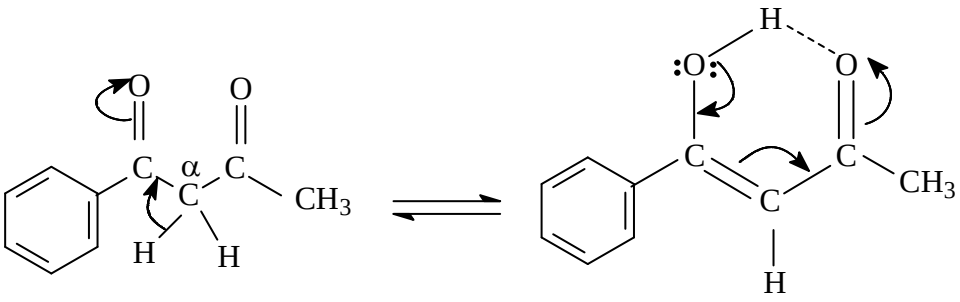
Note: Hydrogen bonding and resonance increases the percentage of enol form



Acetylacetone

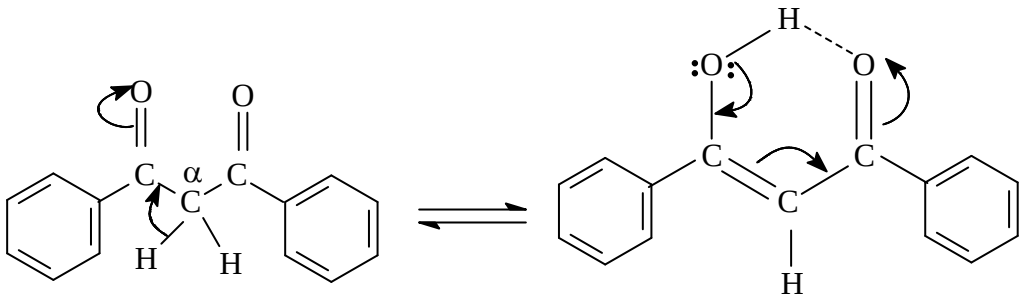
(24%)

(76%)



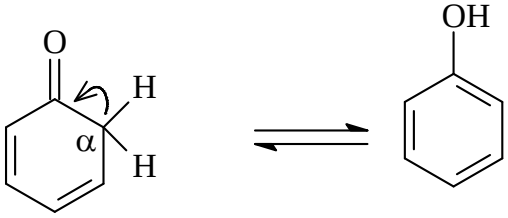
(11%)

(89%)



(4%)

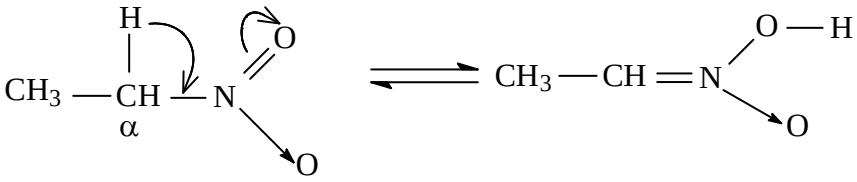
(96%)



0.1%

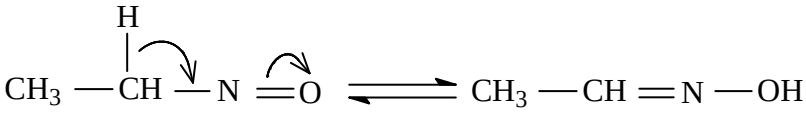
99.9% (Aromatic)

2) Nitro-acinitro tautomerism



Nitroform Acinitroform

3.Nitroso oximino tautomerism

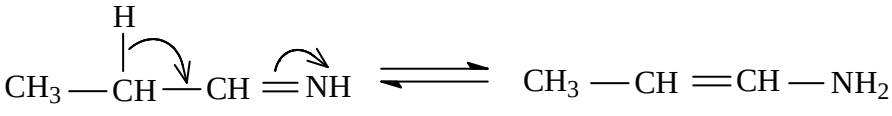


Nitrosoform Oximinoform

Note:

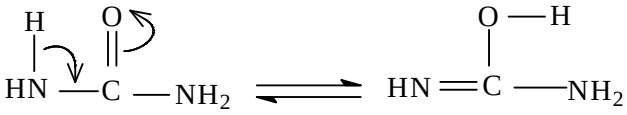
Oximes are functional isomers of amides and they are tautomers of nitroso compounds.

4) Imine -Enamine tautomerism



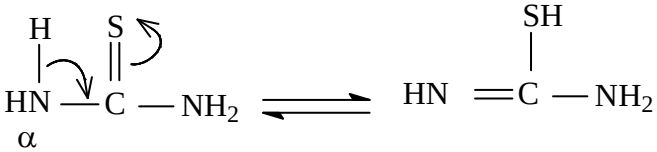
Imine form enamine form

5) Amido - Imidol tautomerism



Amido form Imidol form

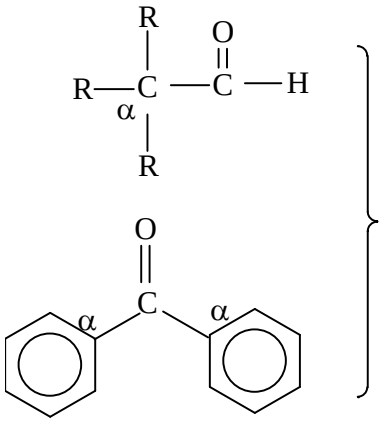
6) Thioamido - Imithiol tautomerism



Thioamido form Imithiol form

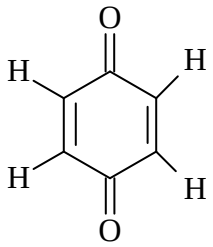
Conditions for tautomerism

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



No tautomerisation due to the absence of α hydrogenatom

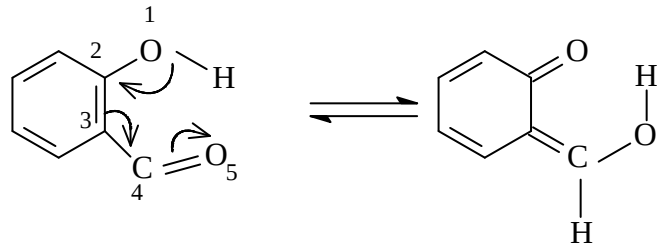
Note: Tautomerism is not observed in parabenzoquinone because H-atoms are present on double bonded carbon atoms of the ring.

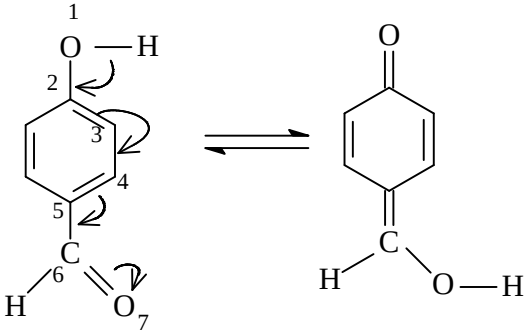


P-benzoquinone

Note:

In addition to 1,3- migration, 1, 5 and 1,7-migrations are also observed in tautomerisation.





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 $-O-$, $-NH-$, $-\overset{\overset{O}{\|}}{C}-O-$, $-S-$,etc

Note: $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3$ and $CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$ are considered as metamers.

Ring Chain Isomerism

1. Alkenes and cycloalkanes

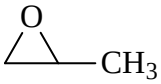
$CH_3-CH=CH_2$ and  (C_3H_6)

2. Alkynes and cycloalkenes

$CH_3-C\equiv CH$ and  (C_3H_4)

3. Unsaturated alcohols and cyclic ethers

$CH_2=CH-CH_2-OH$ and  (C_3H_6O)

Note: Other two cyclic isomers possible for the formula (C_3H_6O) are  and 

Hybridisation of different types of carbon

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

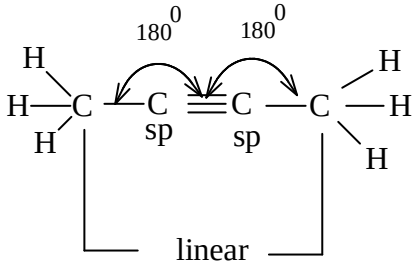
2. Carbon with $1-\pi$ bond $\rightarrow$ sp^2 hybridisation (One unhybridised 'p' orbital is present)

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

Note:

- Normal sp^3 bond angle $\rightarrow 109^0 28'$ (Total 6 tetrahedral angles are present around an sp^3 hybridised 'C')
- Normal sp^2 bond angle $\rightarrow 120^0$ (Total 3-120^0 angles are present around an sp^2 hybridised 'C')
- Normal sp bond angle $\rightarrow 180^0$ (2-180^0 angles)

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



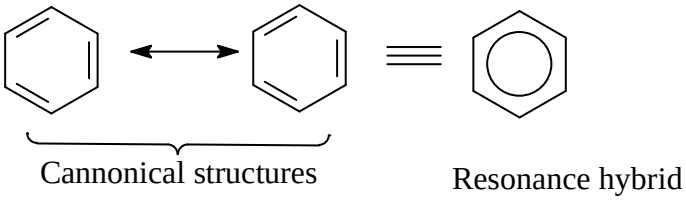
Methods for electron transfer in a covalent bond

1. Resonance

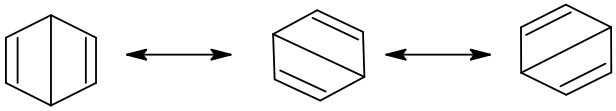
When the actual structure of a molecule is represented by the help of more than one electronic arrangement, the molecule said to have resonance.i.e.,delocalisation of π electrons occurs during resonance.

eg: **Resonance in benzene**

i) Kekule structures



ii) Dewar structures



Each Kekule structure give around 39% and each Dewar structures give around 7% to the total resonance hybrid of benzene.

Note:

Total number of resonance structures possible for a benzoid aromatic compound $= \frac{n!}{\left(n/2\right)!\left(n/2+1\right)!}$

where 'n' is the number of π electrons involved in resonance

Eg: Number of resonance structures possible for benzene $= \frac{6!}{3!\,4!} = 5$

Evidences for resonance in benzene

1. Difference in the expected bond length

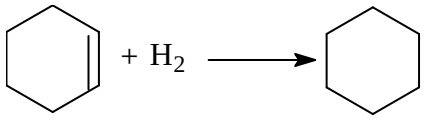
C-C single bond length = $1.54\,\overset{0}{A}$

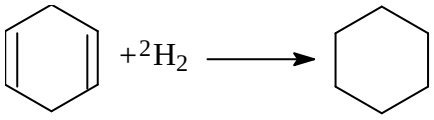
C=C double bond length = $1.34\,\overset{0}{A}$

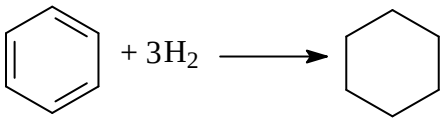
$\therefore$ We can expect three $1.54\,\overset{0}{A}$ length bonds and three $1.34\,\overset{0}{A}$ length bonds in benzene. But in benzene all the carbon-carbon bond lengths are identical $\left(1.39\,\overset{0}{A}\right)$

2. Benzene doesn't gives addition reaction under normal condition because the double bonds in benzene are stabilized by resonance

3. Calculation of resonance energy in benzene

i)  $\Delta H = -28.6$ k cal mol^{-1}

ii)  $\Delta H = 2 \times -28.6$ k cal mol^{-1}

iii)  ΔH expected = 3×-28.6

= -85.8 k cal mol^{-1}

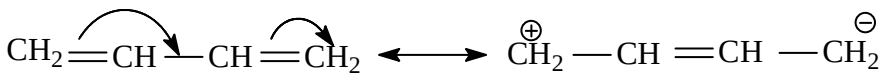
ΔH observed = -49.8 K cal mol^{-1}

$\therefore$ Resonance energy in benzene = 85.8-49.8 = 36 K cal mol^{-1}

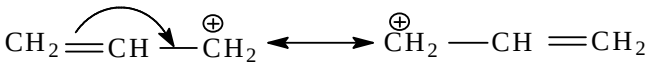
$\therefore$ Each double bonds in benzene are stabilised by around 12 K cal mol^{-1}

Resonance in different types of systems

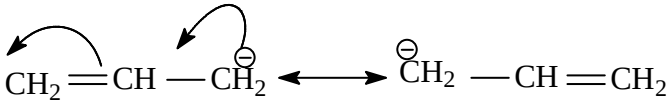
1. Resonance involving $\pi -$ bonds



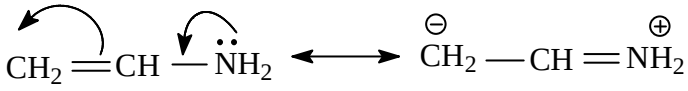
2. Resonance involving +ve charge



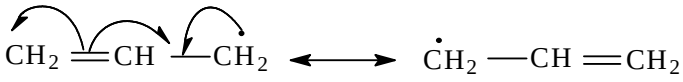
3. Resonance involving -ve charge



4. Resonance involving lone pair



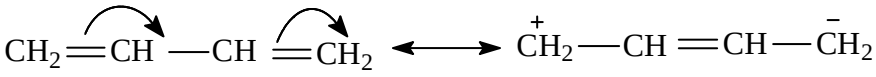
5. Resonance involving free radical



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

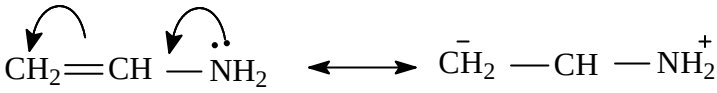
Resonance effect or Mesomeric effect (R/M - effect)

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

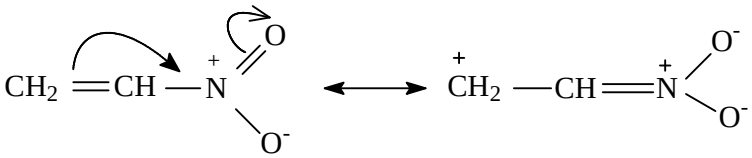
If the group attached to an unsaturated or conjugated system is electron releasing through resonance., the effects called as +R effect.



Examples for some groups showing +R effect : $-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$, $-\ddot{O}H$, $-\ddot{O}R$, $-\ddot{X}:$

-R/-M Effect

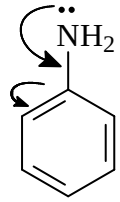
If the group attached to an unsaturated or conjugated system is electron withdrawing through resonance, the effect is called as -R effect.



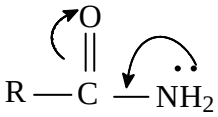
Examples for some groups showing '-R' effect $-NO_2$, $-CN$, $-SO_3H$, $-COOH$, $-CHO$ etc.

Applications

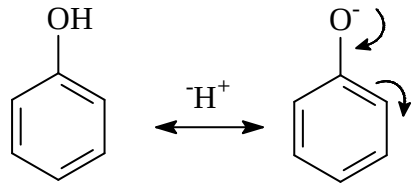
1. Aromatic amines are less basic as compared to aliphatic amines, because due to resonance, the lone pair of electrons on nitrogen is delocalised over the aromatic ring and it is therefore less easily available for protonation.



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.



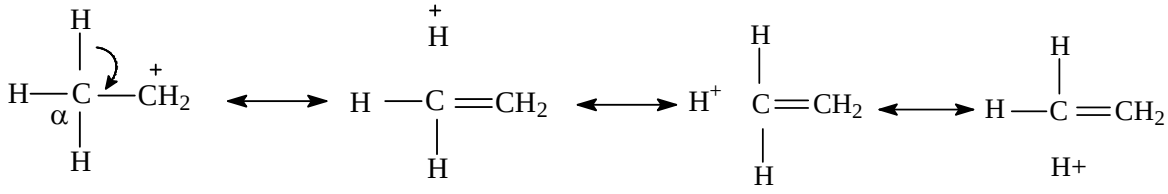
3. Phenols are more acidic as compared to alcohol because the phenoxide ion is stabilized by resonance.

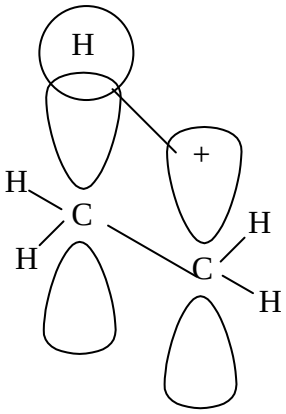


Hyperconjugation (Baker-Nathan effect)

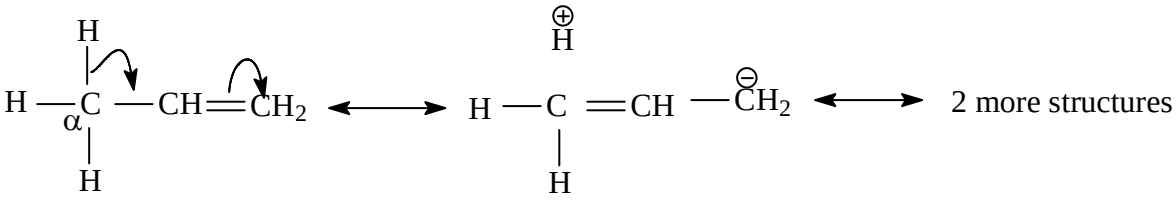
It involves the migration of a C-H σ-electrons of an alkyl group directly attached to an atom of an unsaturated system or to an atom with an unshared 'p' orbital (free radicles or carbocations)

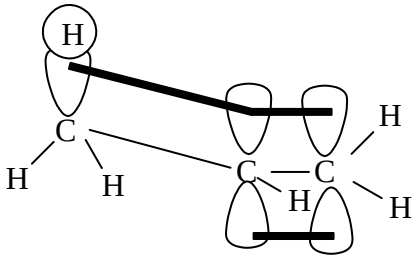
1. Hyperconjugation in carbocation



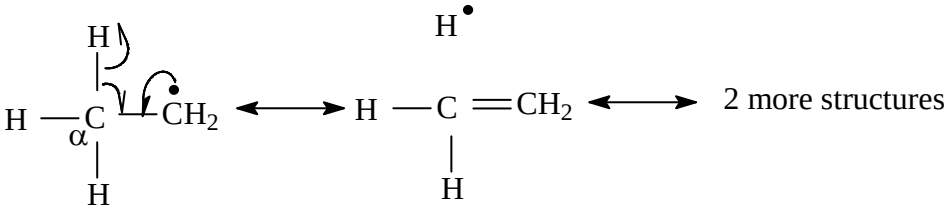


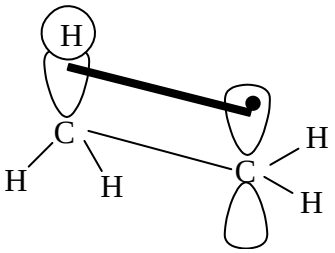
2. Hyper conjugation in unsaturated system





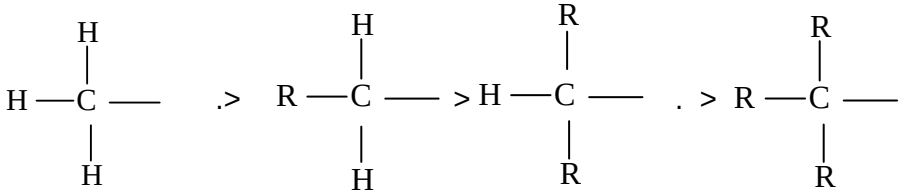
3. Hyper conjugation in free radicals





$\therefore$ 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.

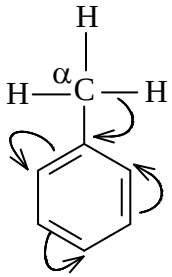
The necessary condition for hyperconjugation is the presence of atleast one $\alpha -$ hydrogen atom. As the number of $\alpha -$ hydrogen atom in an alkyl group increases, its hyper conjugative effect also increases. Therefore hyper conjugative effect of some alkyl group follows the order.



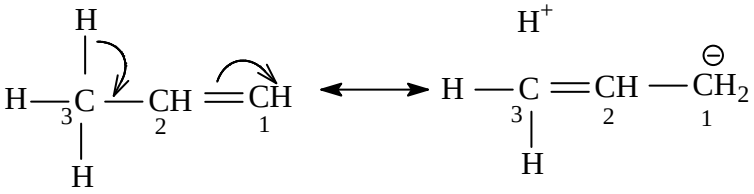
(3α hydrogen) (2α- hydrogen) (1α -hydrogen) (no α -hydrogen)

Applications

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



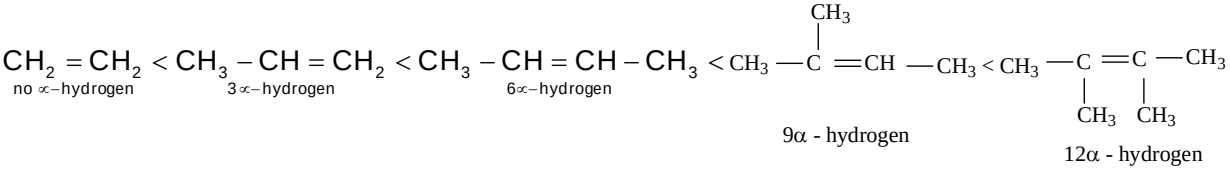
2. Shortening of C-C single bond length adjacent to multiple bonds.



Due to hyperconjugation C_2-C_3 bond in propene have a partial double bond character.

3. Relative stabilities of alkene

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

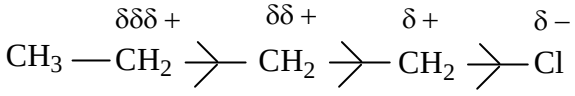


INDUCTIVE EFFECT (I EFFECT)

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

-I Effect

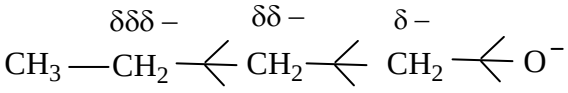
If the group attached to the end of a carbon chain is electron withdrawing through inductive effect, the effect is called as -I effect.



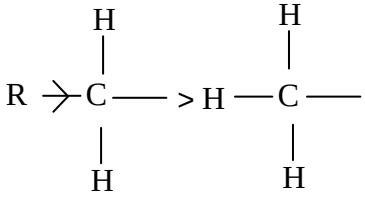
-I effect of some groups follows the order $-\overset{+}{N}R_3 > -NO_2 > -CN > -SO_3H > -CHO > -COOH > -F > -Cl > -Br > -I$

+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.



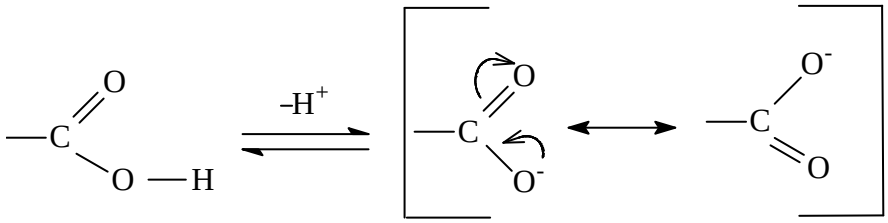
The +I effect of some groups follows the order $-O^- > COO^- > R > H > $



Applications

1. Acidity of carboxylic acid

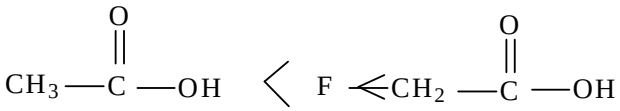
The carboxylate anion generated from carboxylic acid after the removal of a proton is stabilized by resonance. This is responsible for the acidity of carboxylic acids.



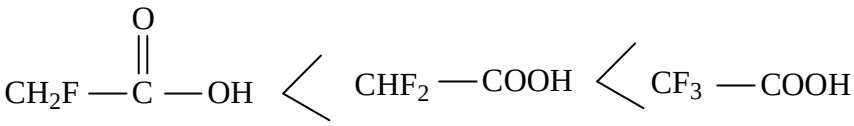
Presence of electron withdrawing groups on carbonyl carbon increases the stability of carboxylate anion and therefore such groups increases the acidity of carboxylic acid. On the other hand electron releasing group on carbonyl carbon decreases the stability of carboxylate anion and therefore such groups decreases the acidity of carboxylic acid.

a) Effect of electron withdrawing substituents (halogens)

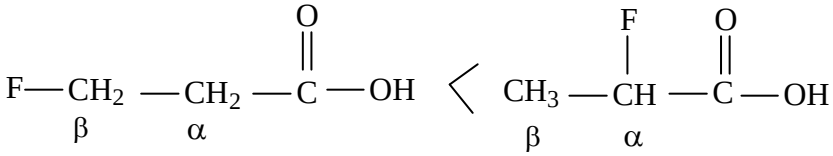
• Presence of electron withdrawing halogens increases the acidity of carboxylic acids through -I effect.



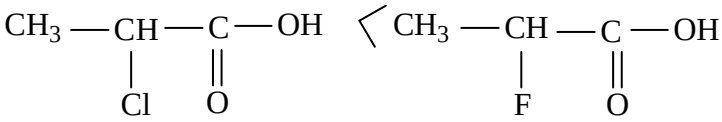
• The acidity of carboxylic acids increases with increase in number of halogen atom



• As the distance of halogen from the carbonyl group increases, the acidity of haloacids decreases.

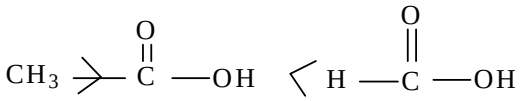


• The electronegativity of halogen decreases from F → I ∴ The acidity of α – halo acids decreases from F → I



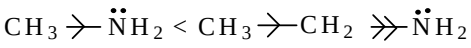
<u>b) Effect of electron releasing substituents (Alkyl groups)</u>

Electron releasing alkyl groups decreases the acidity of carboxylic acids through +I effect

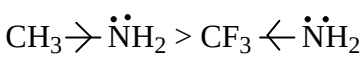


Basicity of amines

Presence of electron releasing groups on nitrogen increases its electron density through their +I effect and therefore such groups increases the basicity of amines.

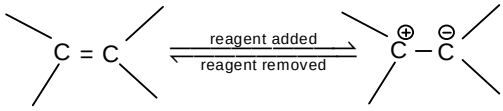


On the other hand electron with drawing groups decreases the basicity of amines through - I effect



<u>ELECTROMERIC EFFECT (E - EFFECT)</u>

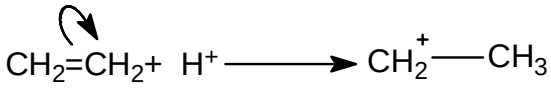
It involves the complete transfer of a π bond to the one of the bonded atom in presence of an attacking reagent



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

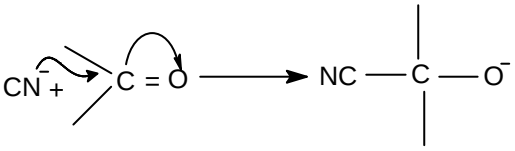
+E effect

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



- E effect

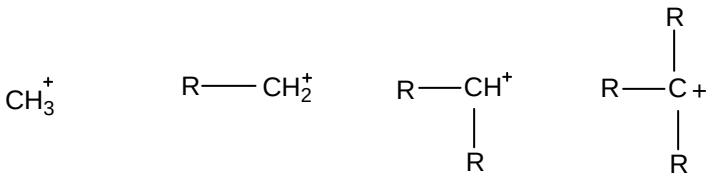
If the electrons of the π bond are transferred to that atom of the π-bond other than the one to which the reagent get finally attached is called -E effect.



REACTION INTERMEDIATES

1. Carbocations (carbonium ions) : They are intermediate species carrying a positive charge on carbon

Classification



Methyl carbocation (1^o) (2^o) (3^o)

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.

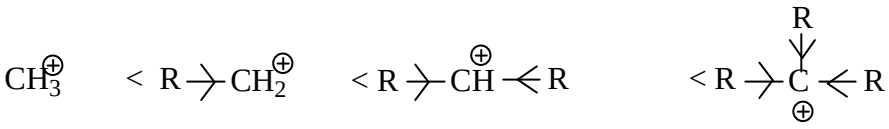
$\therefore$ The carbon in carbocations are associated with 6 electrons in its valence shell

stability

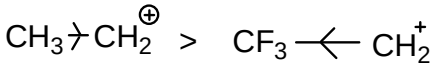
Stability in terms of inductive effect

Electron releasing alkyl groups decreases the magnitude of +ve charge on carbocation through +1 effect and there fore such groups increases their stability.

$\therefore$ stability of carbocations follows the order $3° > 2° > 1° > CH_3^+$



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



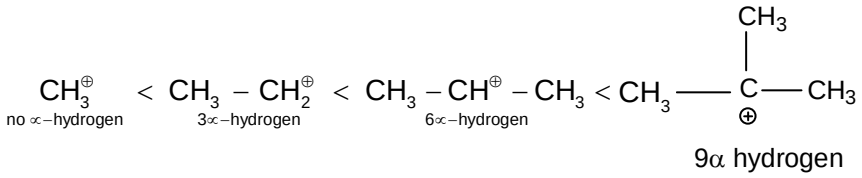
NOTE :

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

$$CH_3 - CH_2^{\oplus} > CH_2 = CH^{\oplus} > CH \equiv C^{\oplus}$$

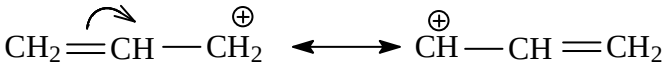
Stability in terms of hyper conjugation

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

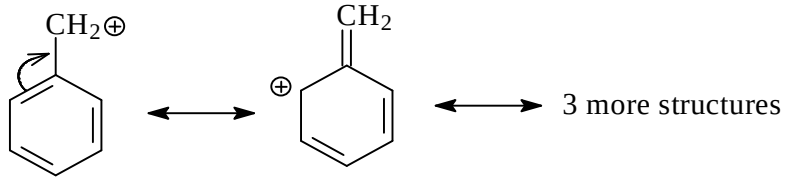


Stability in terms of resonance

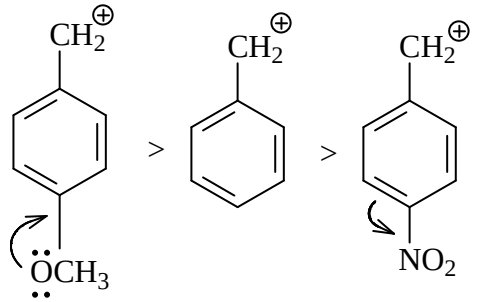
a) Resonance stabilisation of allylic carbocation



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.

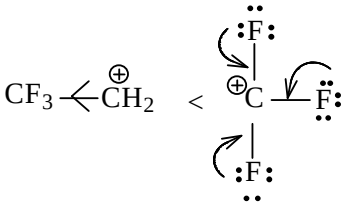


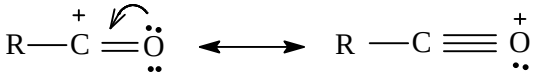
As the number of phenyl groups possible for the benzylic carbo cation increases, its resonance stabilisation is also increases.

$$C_6H_5-\overset{+}{C}H_2 < C_6H_5-\overset{+}{C}H-C_6H_5 < C_6H_5-\underset{C_6H_5}{\overset{+}{C}}-C_6H_5$$

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

$$CH_3-O-CH_2-\overset{+}{C}H_2 < CH_3-CH_2-\ddot{O}-\overset{+}{C}H_2$$



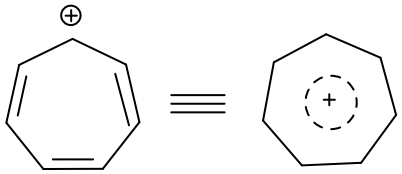


Acylium cation — More stable resonace structure

(Octect all atoms are completed)

NOTE :

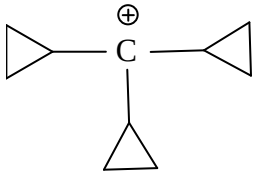
Cycloheptatrienyl cation (Tropylium cation) is more stable than $(C_6H_5)_3C^+$



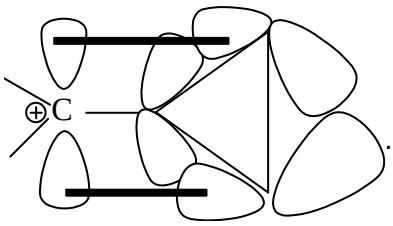
Reason

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



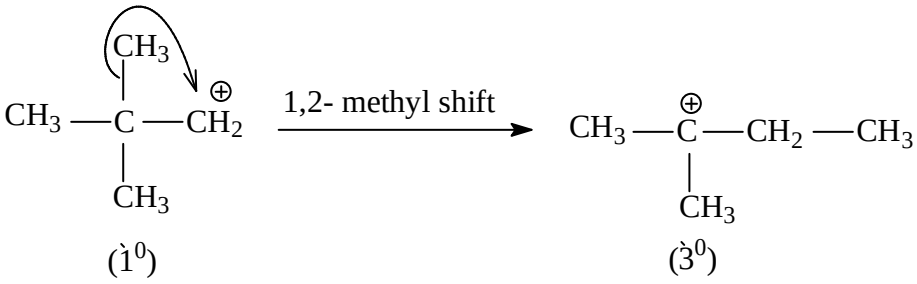
Reason:-



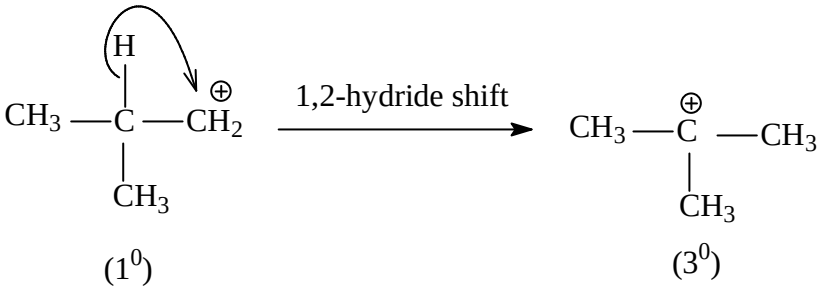
. The bent orbitals in cyclopropyl ring release electrons to be vacant 'p'-orbital of carbocation (σ - conjugation)

Rearrangement of carbocation

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

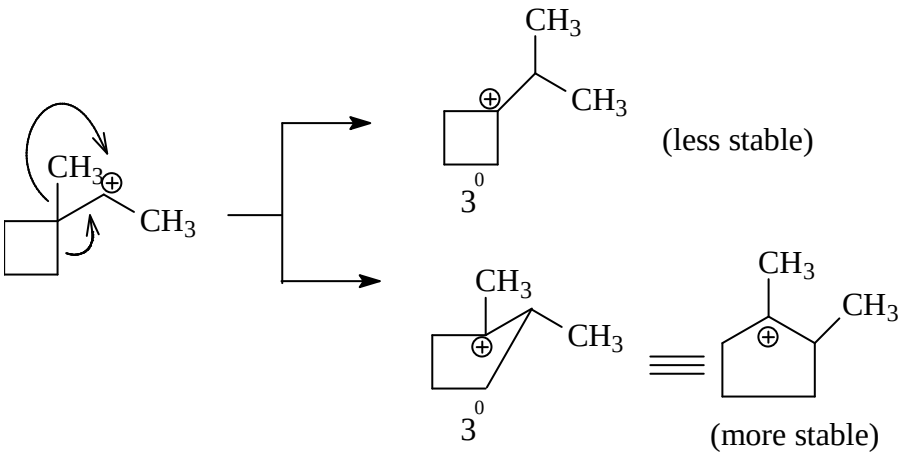


($\grave{1}^0$) ($\grave{3}^0$)



(1^0) (3^0)

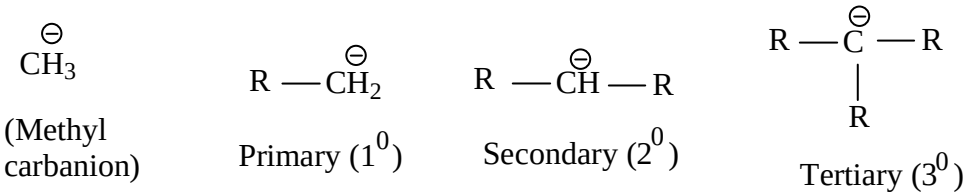
RING EXPANSIONS DURING REARRANGEMENT OF CARBOCATIONS



2. Carbanion

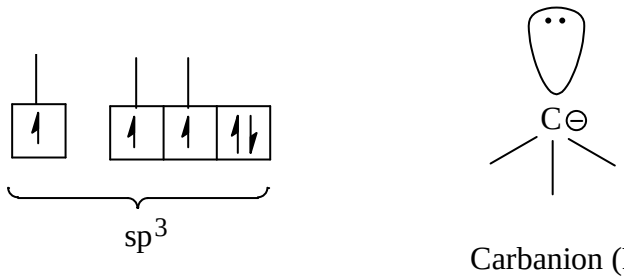
They are intermediate species carrying a negative charge on carbon.

Classification



Structure

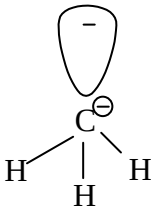
In carbanions, carbon is in sp^3 hybridised state. The three half filled sp^3 hybridised orbitals form 3σ bonds. 4^{th} sp^3 hybridised orbital contains a pair of electrons. But in resonance stabilised carbanions like, allyl, benzyl etc the negatively charged carbon is sp^2 hybridised.



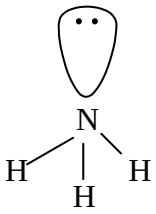
$\therefore$ The carbon in carbanion are associated with 8 electrons in its valence shell.

NOTE:

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



(10 electrons)



(10 electrons)

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. ∴ The stability of carbanion is in the order.

$CH_3^- > 1^0 > 2^0 > 3^0$

$$\overset{\ominus}{C}H_3 > R-\overset{\ominus}{C}H_2 > R_2-\overset{\ominus}{C}H > R_3-\overset{\ominus}{C}$$

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

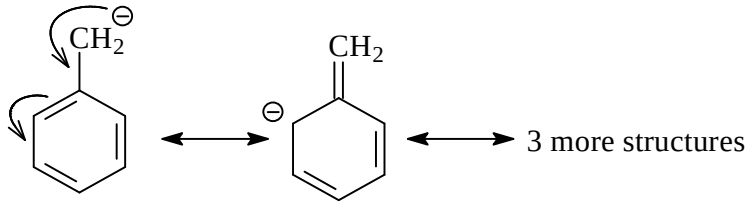
$$CH_3 \rightarrow \overset{\ominus}{C}H_2 \quad < \quad CF_3 \leftarrow \overset{\ominus}{C}H_2$$

Stability in terms of resonance

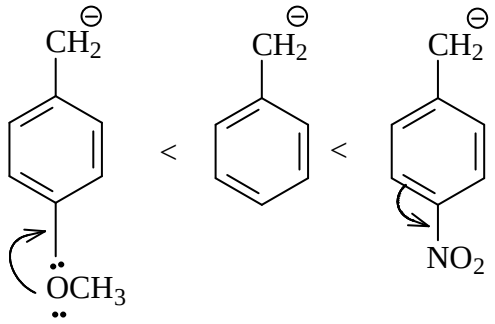
a) Resonance stabilisation of allylic carbanion

$$CH_2=CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH_2$$

b) Resonance stabilisation of benzylic carbanion

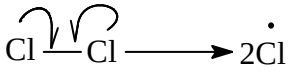


The magnitude of -ve charge is located at ortho-para positions. Therefore electron withdrawing groups at ortho-para positions increase the stability of benzylic carbanion and electron releasing group at ortho- para positions decreases their stability.

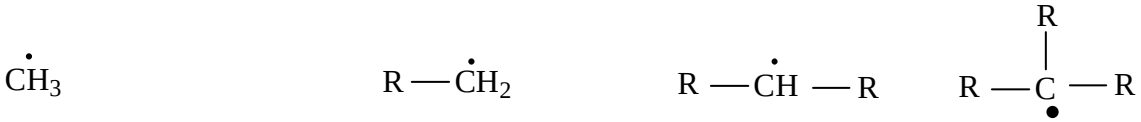


3. Free radicals

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



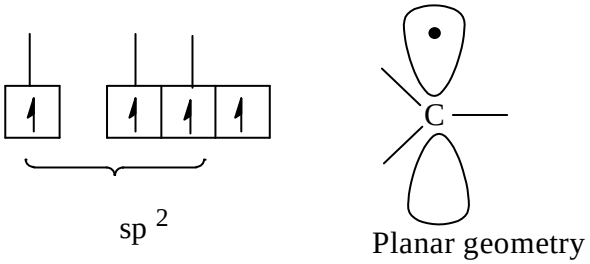
Classification



Methyl freeradical 1^0 2^0 3^0

Structure

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



sp^2 Planar geometry

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

Stability

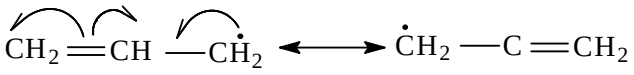
Stability in terms of hyperconjugation

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 $3^0 > 2^0 > 1^0 >$ $\dot{C}H_3$

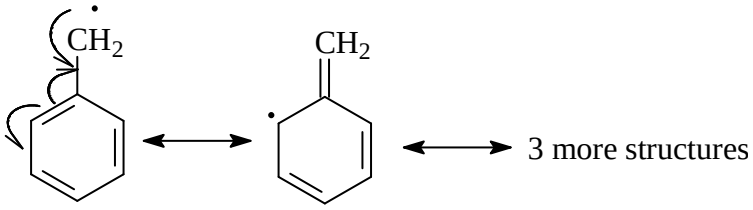
$$\underset{\text{No } \alpha-\text{hydrogen}}{\dot{C}H_3} < \underset{3\alpha-\text{hydrogen}}{CH_3-\dot{C}H_2} < \underset{6\alpha-\text{hydrogen}}{CH_3-\dot{C}H-CH_3} < \underset{9\alpha\text{-hydrogen}}{CH_3-\overset{\bullet}{\underset{|}{C}}(CH_3)_2}$$

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.

$$C_6H_5-\dot{C}H_2 < (C_6H_5)_2-\dot{C}H < (C_6H_5)_3\dot{C}$$

4. Carbenes

They are neutral, electron deficient chemical species carrying two unshared electrons on carbon.

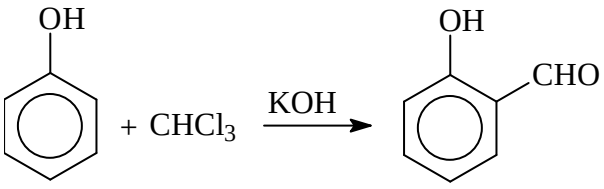
Eg: $:CH_2$ - Methylene, $:CCl_2$ - Dichlorocarbene

Carbenes are the reaction intermediates in the following reactions

A. Carbyl amine reaction

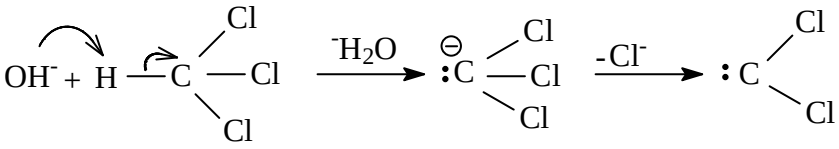
$$R-\ddot{N}H_2 + CHCl_3 + 3KOH \longrightarrow R-NC + 3KCl + 3H_2O$$

B. Riemer-Tiemann reaction



Salicylaldehyde

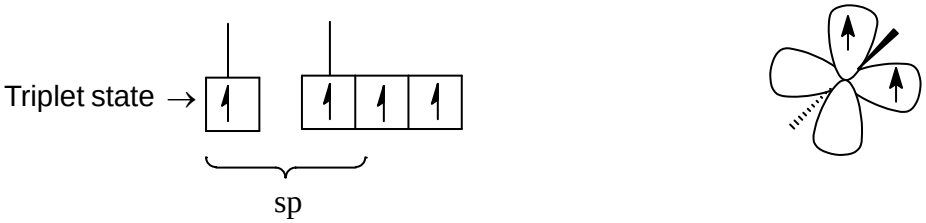
Both Riemer-Tiemann reaction and carbylamine reaction involves a dichloro carbene intermediate.



Structure

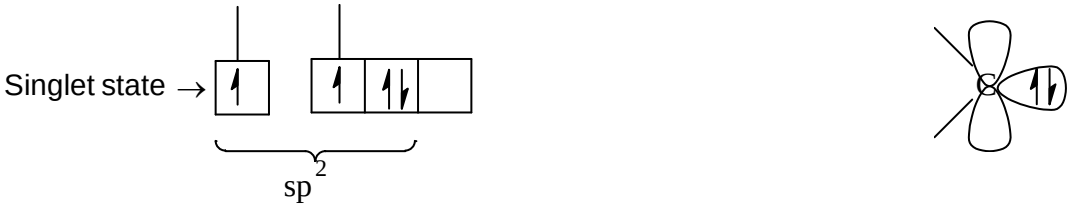
A carbene is known to exist in two states. If the two unshared electrons goes to two different orbitals (parallel spin) the carbene is in triplet state.

- In triplet state of carbene the carbon is in 'sp' hybridised state
- The two half filled 'sp' hybridized orbitals form 2σ bonds
- The two unshared electrons are present in two different unhybridised 'p' orbitals.
- There is a net magnetic moment in this state



If the two unshared electrons goes to a single orbital (antiparallel state) the carbene is in singlet state.

- In this form of carbon is in sp^2 hybridised state
- The two half filled sp^2 hybridised orbitals form of 2σ bonds
- The two unshared electrons are present in the third sp^2 hybridised orbital
- The unhybridised 'p' orbital is unoccupied

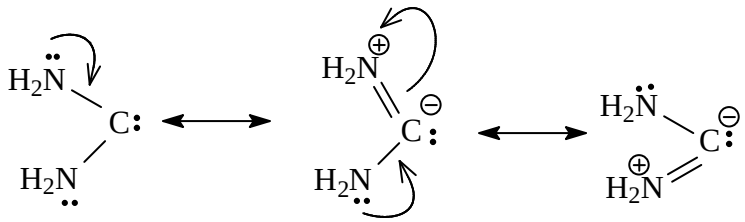


Stability

The ground state of carbene is considered to be the triplet state, because for the formation of singlet state electron must be paired. It requires some extra energy to overcome the electron-electron repulsion

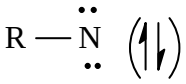
NOTE:

If the carbon in carbene is bonded to two groups, each containing a lone pair, the carbene is stabilised by resonance.

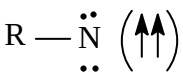


5. Nitrenes

They are the nitrogen analogous of carbenes

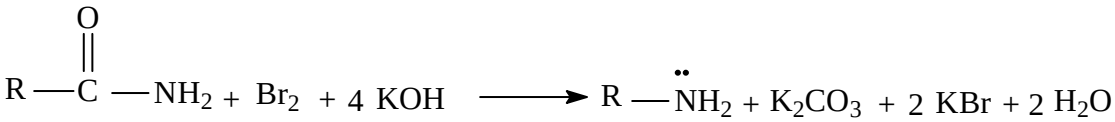


Singlet

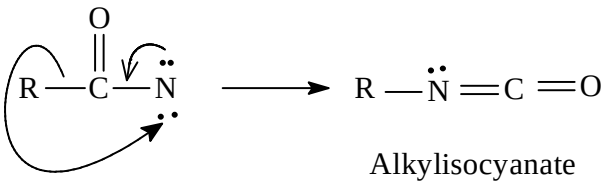


Triplet

Nitrenes are the reaction intermediates in Hoffmann's bromamide reaction



The reaction involves an acylnitrene intermediate and is rearranges to an alkyl isocyanate



Alkylisocyanate

Acylnitrene

(Unstable)

ELECTROPHILES AND NUCLEOPHILES

Electrophiles are electron loving chemical species (electron deficient)

Eg: $R^{\oplus}$, $H^{\oplus}$, $NO_2^{\oplus}$, NO^{+}, $X^{\oplus}$, ... (+ve ions)

$\dot{R}$, $:CH_2$, $R-\ddot{N}:$, BF_3, $AlCl_3$, $FeBr_3$, SO_3.... (Neutral)

Nucleophiles are nucleus loving chemical species (electron rich)

Eg: OH^-, NH_2^-, CN^-, R^-, X^-, ... (-ve ion)

$H_2\ddot{O}:$, $R-\ddot{O}H$, $\ddot{N}H_3$, $R-\ddot{N}H_2$,..... (Neutral)

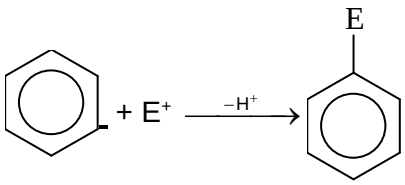
Different types of organic reactions

1. Substitution reaction

a. Electrophilic substitution reaction (S.E. reaction)

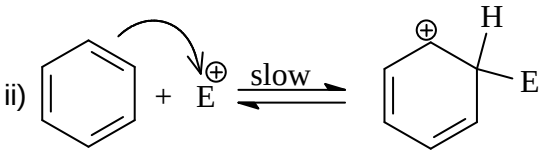
The substitution reaction is carried out by an electrophile

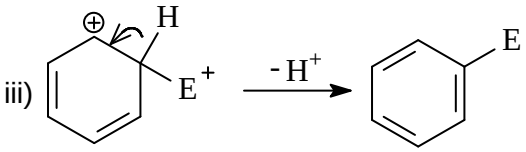
Eg: - Electrophilic substitution reaction in benzene



Mechanism

i) Reagent $\longrightarrow E^{\oplus}$



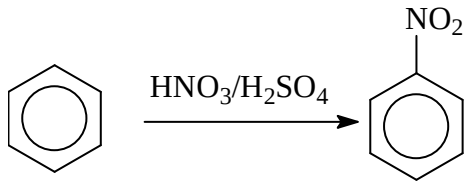


The second step is the slowest step and it is therefore the rate determining step

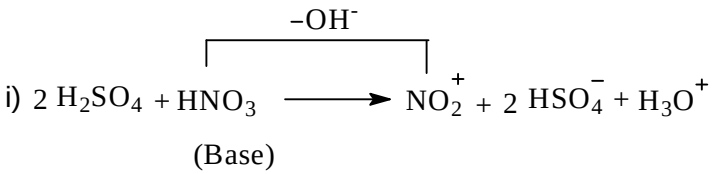
Application

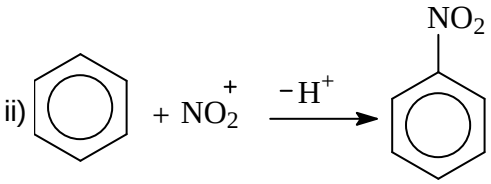
• Benzene and hexadeuteriobenzene gives a particular electrophilic substitution reaction exactly at the same rate, because cleavage of proton is not involved in rate determine step

1. Nitration

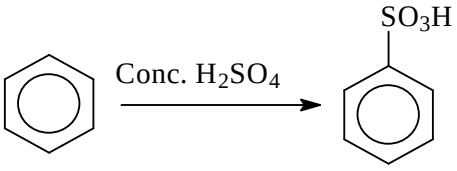


Mechanism

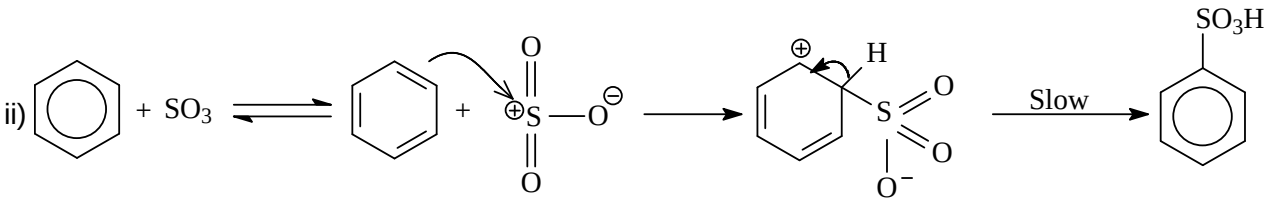




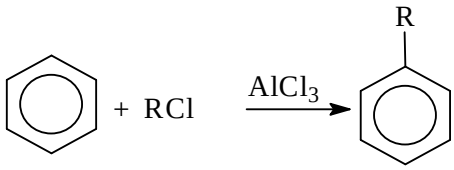
2. Sulphonation



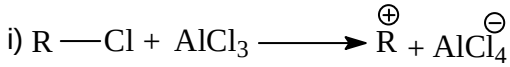
Mechanism:

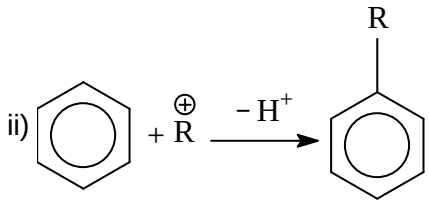


Friedel craft's reaction



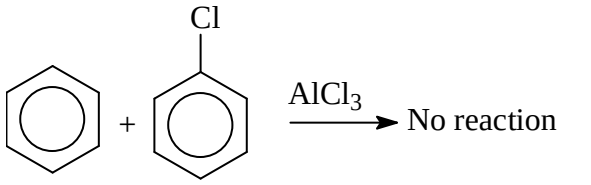
Mechanism:

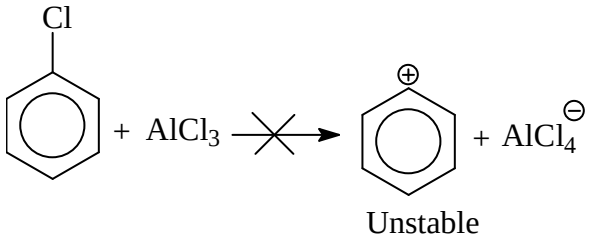




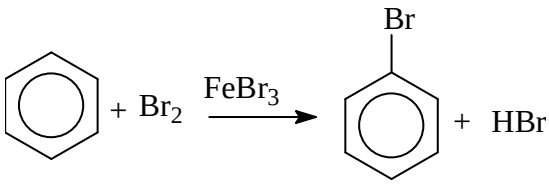
Application:-

Benzene with chlorobenzene doesn't give friedel craft's reaction because the phenyl carbocation is highly unstable.



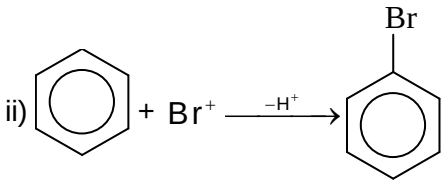


Halogenation



Mechanism:

i) $Br_2 + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$



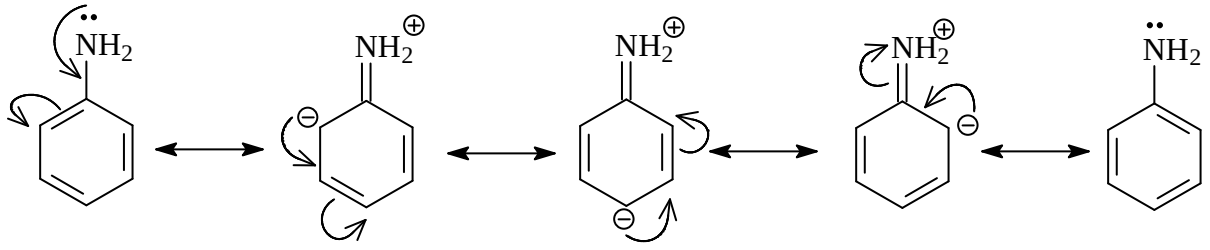
Ring activating groups for electrophilic substitution

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

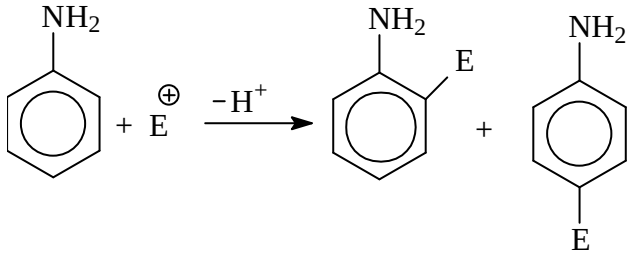
Eg: $-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{O}H$, $-\ddot{O}R$ ..... (+R effect)

Alkyl groups (+I and hyperconjugation)

Ring activating effect of $-\ddot{N}H_2$ group



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



(major)

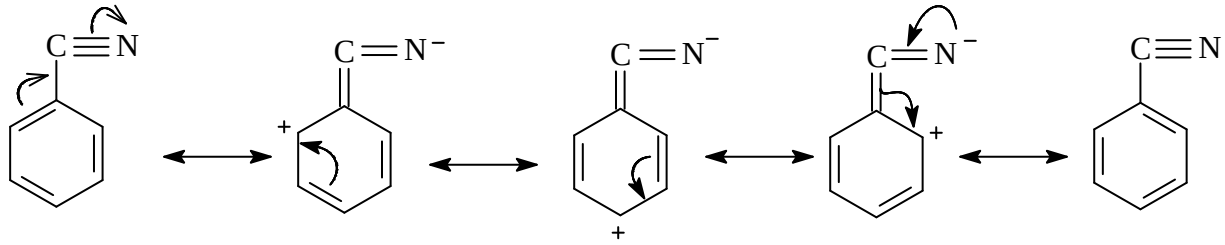
Ring deactivating groups for electrophilic substitution

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

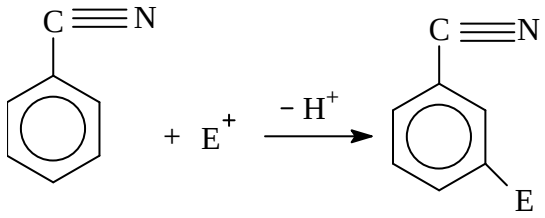
Eg:- NO_2, -CN, $-SO_3H$, -CHO, -COOH .... (-I and -R effect)

Halogens (-I effect)

Ring deactivating effect of cyanide group

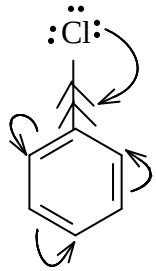


The magnitude of +ve chargee is located at ortho-para positions . ∴ Ring deactivating groups are meta directing groups for electrophiles



Anomalous behavior of halogens

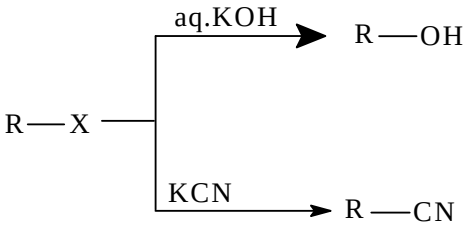
Halogens are ring deactivating groups through their strong -I effect. But orthopara directing groups for electrophiles through their weak +R effect. ∴ Halogens are ortho-para directing deactivators. i.e., th reactivity of the ring is controlled by strong -I effect of halogen and orientation of the electrophile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



b. Nucleophilic substitution reaction

The substitution reaction carried out by nucleophile.

Eg:-



Some steriochemical aspects

1. **Optical activity**

The ability of a compound to rotate the plane of vibration of plane polarised light is called optical activity.

Towards right $\rightarrow$ Dextro rotatory $\left(d/_{(+)}\right)$

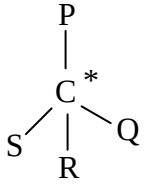
Towards left $\rightarrow$ Laevo rotatory $\left(d/_{(-)}\right)$

2. **Chirality**

The objects that gives non-superimpossable mirror images are called chairal object and phenomenon is known as chairality.Chirality of the molecule is the necessary condition for optical activity

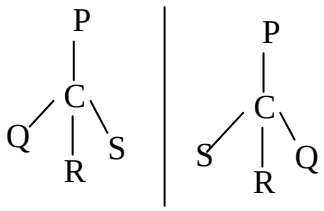
3. **Asymmetric carbon**

In 1874 Vant-Hoff and Le-Bell pointed out that the 4- valancies of a carbon are directed towards the corners of a regular tetrahedron.If the valancies are satisfied by 4-different groups or atoms, the molecule become chiral and is therefore optically active. Such type of a carbon is called an asymmetric carbon.



4. **Enantiomers**

They are the optical isomers of the same compound and rotate the plane vibration of plane polarised light equally but through opposite directions. They are nonsuper impossible mirror images of each other



5. **Racemic mixture**

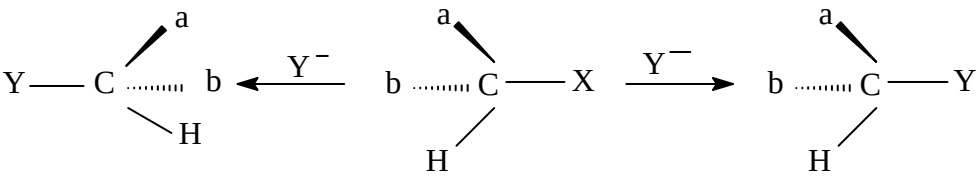
An equimolar mixture of enantiomers are called racemic mixture. Optical activity of racemic mixture are zero due to external compensation

6. **Racemisation**

The process of conversion of an optically active isomer into its racemic modification is called racemisation

7. **Configuration**

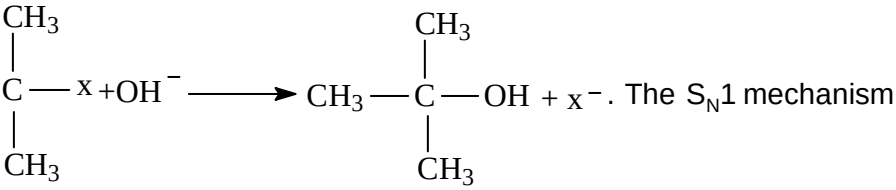
The spacial arrangement of different, groups or atoms around a central carbon is called configuration. In a chemical reaction, if the configuration of different bonds around the central carbon is preserved, it is called retention of configuration. In a chemical reaction if the configuration of different bonds around the central carbon is not preserved, it is called inversion configuration.



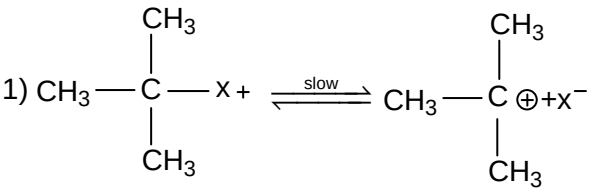
(Inversion) (Retention)

Mechanism of nucleophilic substitution reaction

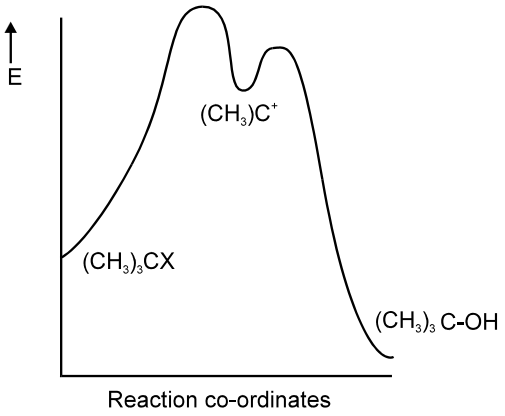
S_N1 mechanism (substitution nucleophilic unimolecular mechanism)

Consider the reaction 

. The S_N1 mechanism for this reaction can be explained as



2) $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\oplus + OH^- \xrightarrow{fast} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$



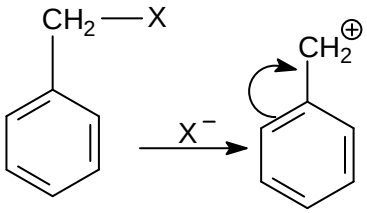
The first step is the slowest step and it is therefore the rate determining step. This step involves only a single reactant molecule. Therefore the mechanism is called as unimolecular.

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 $3^o > 2^o > 1^o > CH_3^+$. $\therefore$ The reactivity of various alkylhalide towards S_N1 reaction follows the order $3^o > 2^o > 1^o > CH_3x$

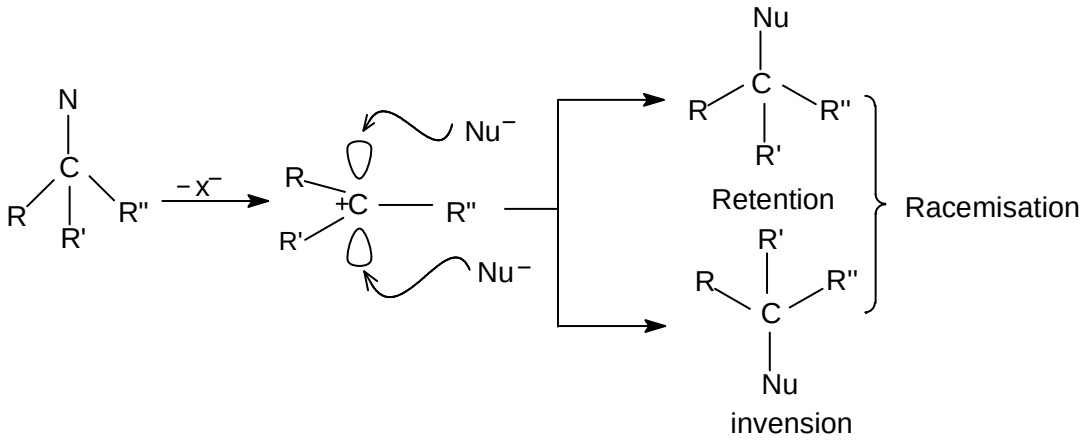
Note:

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

$CH_2=CH-CH_2-X \xrightarrow{-X^-} CH_2=CH-\overset{\oplus}{C}H_2$



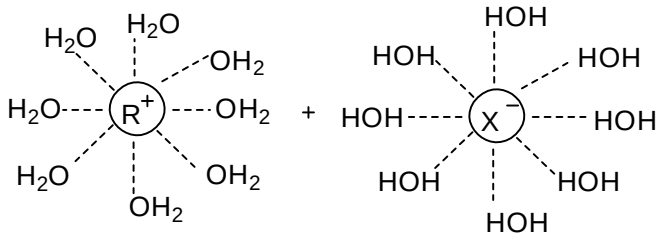
Steriochemistry in S_N1 reaction



$\therefore$ S_N1 reaction at an optically active centre gives a partial racemisation with slight excess of inversion product (The attack of nucleophile through the side of leaving group is partially hindered by leaving X^- ions from this position)

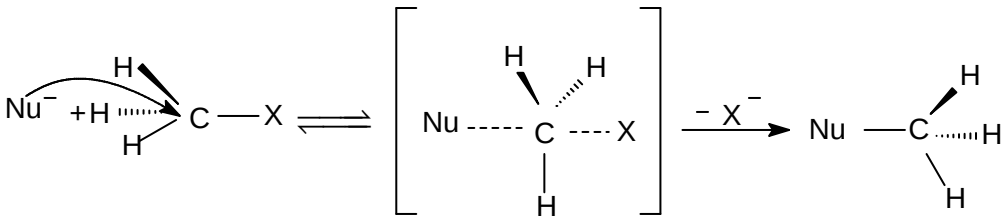
Effect of solvents on S_N1 reaction

The rate determining step of S_N1 reaction involves the formation of two ions (R^+ and x^-) polar solvents easily solvate these two ions. So rates S_N1 reactions are greater in polar solvents. Polarprotic solvents such as alcohol, water etc. are even more effective solvents for S_N1 reaction because the x^- ions forms hydrogen bonds with the hydrogen of the OH group and R^+ ions co-ordinate with the oxygen of the OH group using its non bonding electron.

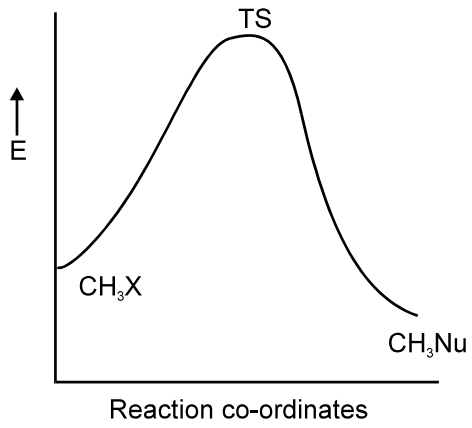


S_N2 Mechanism (Substitution nucleophilic bimolecular mechanism)

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



(Transition state)



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

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

$$CH_3 - X > 1^O > 2^O > 3^O$$

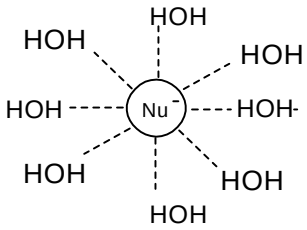
Note:

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

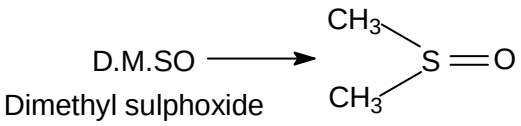
S_N2 reaction at an optically active centre gives a single sterio isomer and its direction of optical activity is unpredictable (may be dextro or laevo)

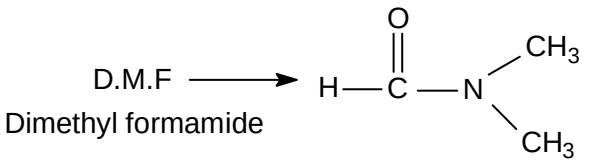
Effect of solvents on S_N2 reaction

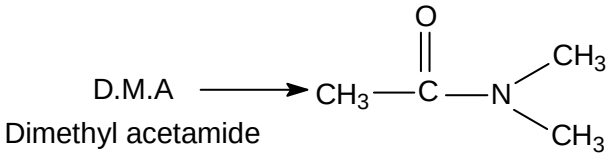
The rate determining step of S_N2 reaction involves the nucleophite also. In polar prototic solvents the nucleophile forms, H-bonds with the solvent molecules.

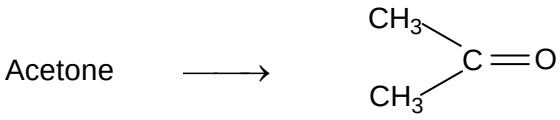


$\therefore$ The nucleophile in a cage of H-bonds and therefore it have less nucleophilicity. $\therefore$ S_N2 reactions are slow in polar protic solvents. The commonly used solvents for S_N2 reactions are polar aprotic solvents such as









S_N1 Vs S_N2

S_N1	S_N2
➢ Nucleophilic strength unimportant	➢ Nucleophiles with high nucleophilicity
➢ $3^o>2^o>1^o>CH_3$-x	➢ $CH_3x>1^o>2^o>3^o$
➢ Polar protic solvents	➢ Weakly polar (aprotic)solvents
➢ Rate=K[R–X]	➢ Rate =K[R–X] [Nu^-]
➢ Rearrangements are possible	➢ Rearrangement is not possible

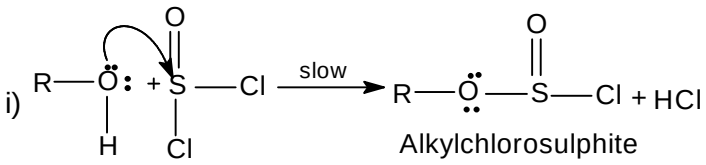
S_Ni Mechanism (Internal nucleophilic substitution)

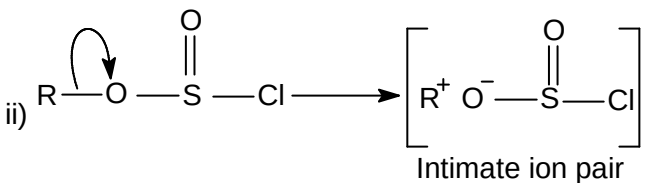
In S_N1 mechanism both retention and invension of configurations are present, in S_N2 mechanism inversion configuration takes place only. There is a 3rd possibility in which complete retention of configuration occurs (S_Ni mechanism)

The action of alcohols with thionyl chloride is a typical example for this reaction.

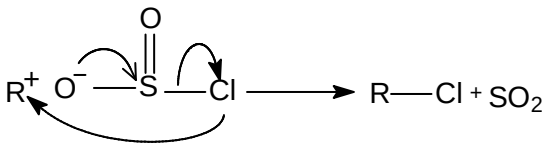
$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$$

Mechanism





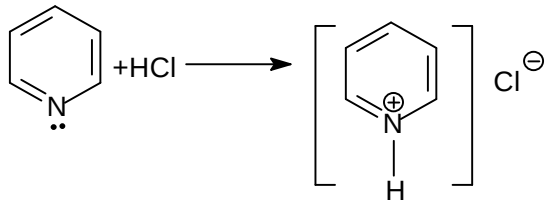
iii) Intimate ion pair gives internal nucleophilic substitution



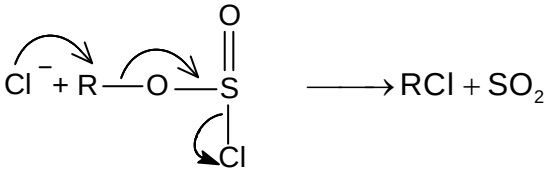
The geometry of the intimate ion pair force the Cl^- ions to attack from the same side in which the R-O bond is originally located. There fore we get a 100% retention product

Note:

If the reaction takes place in pyridene medium, (Darzenes process), protonation of pyridene takes place



$\therefore$ The medium contains good concentration of Cl^- ions. These Cl^- ions gives S_N2 reaction on alkylchlorosulphite and produce the corresponding inversion product.



Free radical Substitution Reaction

Substitution reaction is carried out by a free radical

Eg: $CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

Mechanism

i) $Cl-Cl \xrightarrow{hv} 2\dot{Cl}$ Initiation

ii) $\dot{C}l + CH_4 + \longrightarrow \dot{C}H_3 + HCl$

iii) $\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \dot{C}l$

} Propagation

iv) $\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$

v) $\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$

} Termination

➢ $CH_3—CH_2—CH_3 + Cl_2 \xrightarrow{h\upsilon} CH_3—\underset{Cl}{\underset{|}{CH}}—CH_3 + CH_3—CH_2—Cl$

(Major)

Mechanism:

➢ $CH_3—CH_2—CH_3 + \dot{Cl}$ → $CH_3—\dot{C}H—CH_3$ (2^o (More Stable)) $\xrightarrow{\dot{Cl}}$ $CH_3—\underset{Cl}{\underset{|}{CH}}—CH_3$ (Major)

→ $CH_3—CH_2—\dot{C}H_2$

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 $3^o > 2^o > 1^o$. ∴ The reactivity of various hydrogen atoms towards free radical substitution reaction follows the order $3^o > 2^o > 1^o$:

➢ $CH_3—\underset{CH_3}{\underset{|}{CH}}—CH_3 + Cl_2 \longrightarrow CH_3—\underset{CH_3}{\underset{|}{CH}}—CH_2—Cl$

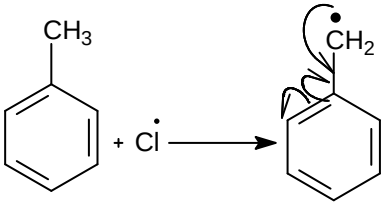
(Major)

Different type of H-atoms	Primary	Secondary	Tertiary
Reactivity of corresponding H-atoms	1	3.8	5
Total no.of corresponding H-atoms	9	0	1
Total possibility of corresponding products	9	0	5
% yield of correspondig products	$\frac{9}{14}\times 100$	0	$\frac{5}{14}\times 100$

Note

Allylic and benzylic free radicals are resonance stabilised. There fore reactivity of allylic and benzylic hydrogen towards free radical substitution reaction are greater than that of 3^o H.

$CH_2=CH_2—CH_3^+\dot{Cl} \xrightarrow{-HCl} CH_2=CH—\dot{C}H_2$



Addition Reaction

1. Electrophilic addition reaction

The addition reaction is initiated by an electrophile

Eg: $CH_2=CH_2 + HX \longrightarrow CH_3-CH_2-X$

Mechanism:

i) $HX \longrightarrow H^+ + X^-$

ii) $CH_2=CH_2 + H^+ \longrightarrow \overset{+}{C}H_2-CH_3$

iii) $CH_3-\overset{+}{C}H_2 + X^- \longrightarrow CH_3-CH_2-X$

Application:

$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-CH_2-CH_2-Br + CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

(Major) (Markovnikov's rule)

Mechanism:

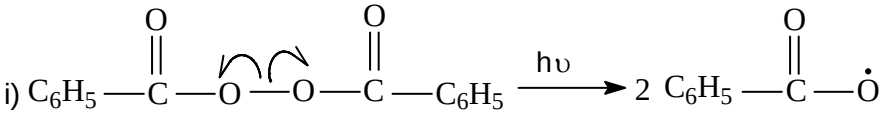
$$CH_3-CH=CH_2 + H^+ \longrightarrow \begin{cases} CH_3-\overset{+}{C}H-CH_3 \xrightarrow{Br^-} CH_3-CHBr-CH_3 \\ \quad 2^0 \text{ (stable more)} \qquad \text{Major} \\ CH_3-CH_2-\overset{+}{C}H_2 \\ \quad 1^0 \end{cases}$$

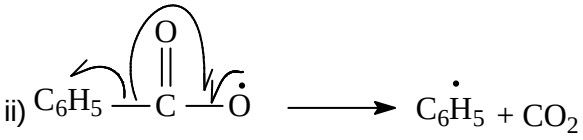
Note:

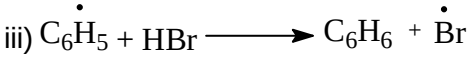
The addition of HBr (not other HX) to an unsymmetrical alkene in presence of a peroxide takes place against Markonikov's rule and is called the anti-Markovnikov's addition or peroxide effect or Kharasch effect.

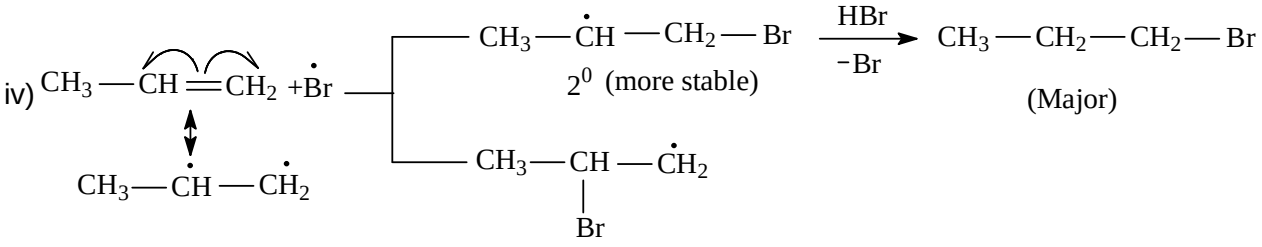
$$CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2-Br$$

Mechanism:

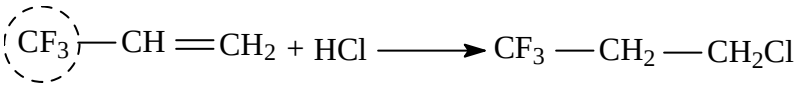




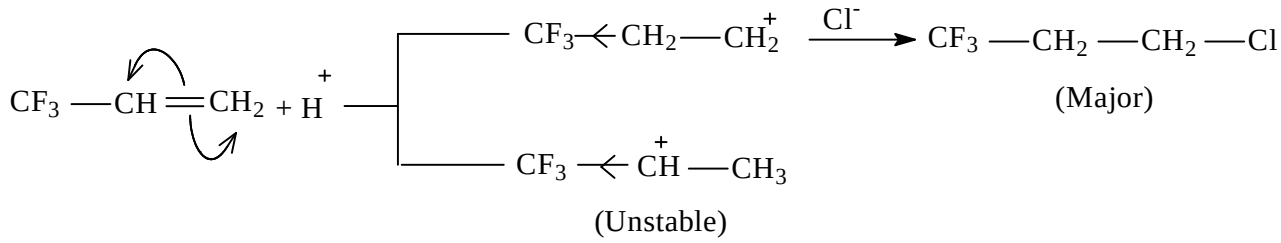




Note: Presence of electron withdrawing groups on unsaturated carbon gives anti- markonikov's addition

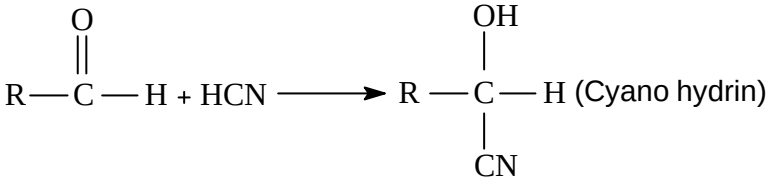


Mechanism:



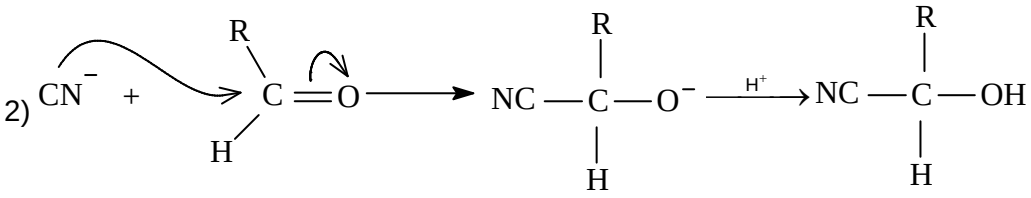
Nucleophilic addition reaction

The addition reaction is initiated by a nucleophile



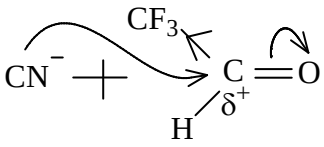
Mechanism:

1) $HCN \longrightarrow H^+ + CN^-$



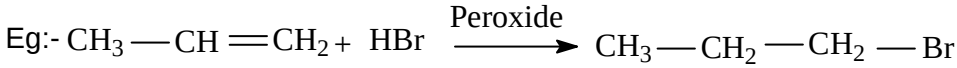
Note:

Presence of electron withdrawing groups on carbonyl carbon increases the rates of nucleophilic addition reaction.



Free radical addition reaction

The addition reaction is initiated by a free radical

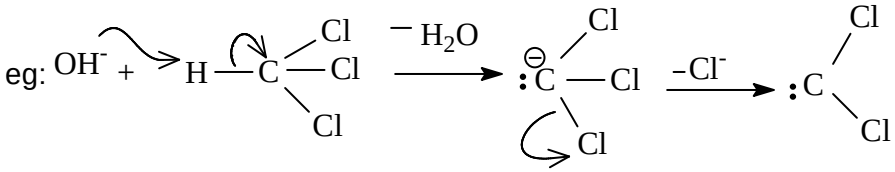


ELIMINATION REACTION

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;

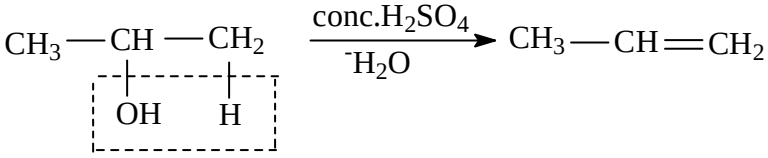
The loss of two atoms or groups occurs from the same atom



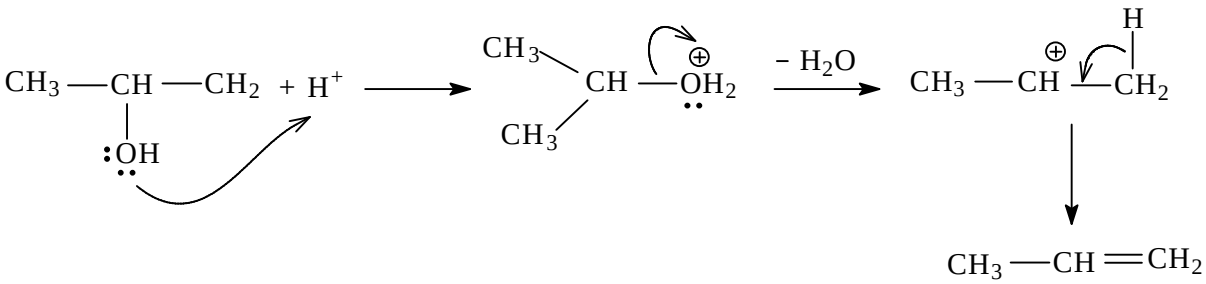
β – Elimination reaction:

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

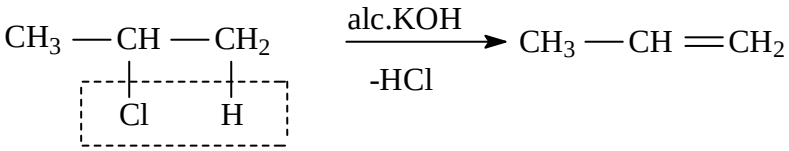
1. Dehydration of alcohols



Mechanism



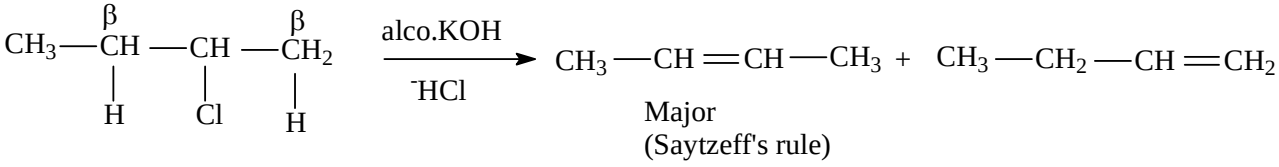
2. Dehydrohalogenation reaction



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.

Saytzseff's Rule

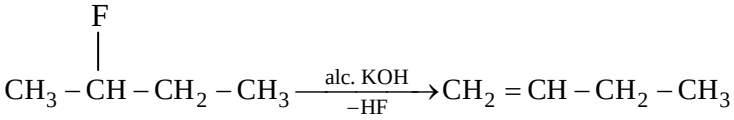
In a dehydrohalogenation reaction, the more substituted alkene will be the major product



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

Exceptions for Saytzseff's elimination

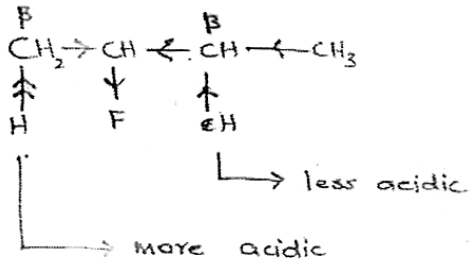
1. Dehydrofluorination reaction (Hoffmann's elimination)



Reason

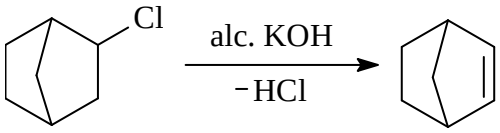
The C – F bond strength is greater than C – H bond strength

$\therefore$ The more acidic $\beta - H$ (less sterically crowded $\beta - H$) will be eliminated in first step.



2. Bredt's rule

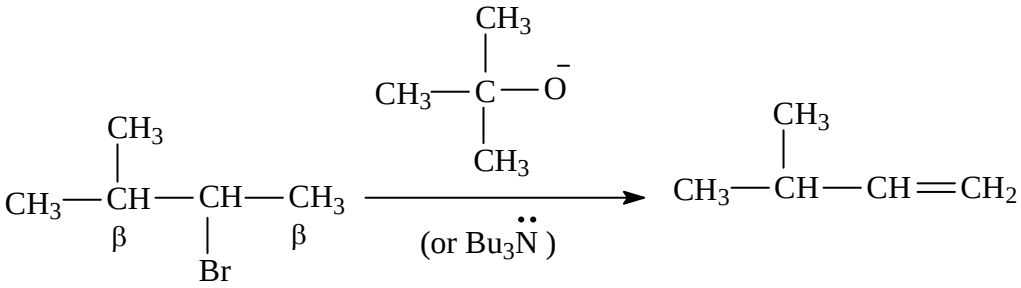
Bridgehead carbon has pyramidal geometry. In order to maintain pyramidal geometry, its hybridisation should be sp^3. Double bonds on bridgehead carbon makes the hybridisation sp^2 (planar). Therefore double bonds are not formed through bridgehead carbon.



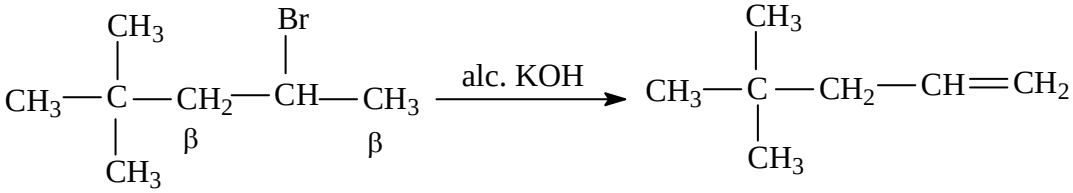
NOTE

Nucleophilic substitutions (both S_N1 and S_N2) are also difficult on bridgehead carbon.

3. Bulkier bases prefer to attack less sterically crowded $\beta - H$ and produce corresponding Hoff-man elimination.

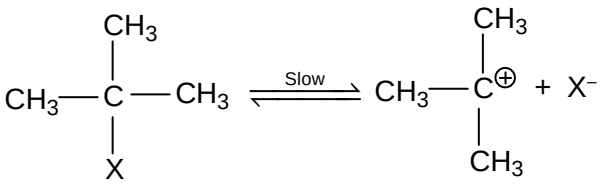


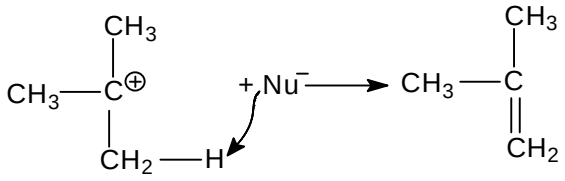
4. Bulkness around a particular $\beta - H$ directs the incoming base to another $\beta - H$ which is less sterically crowded and produce corresponding Hoffmann's elimination product.

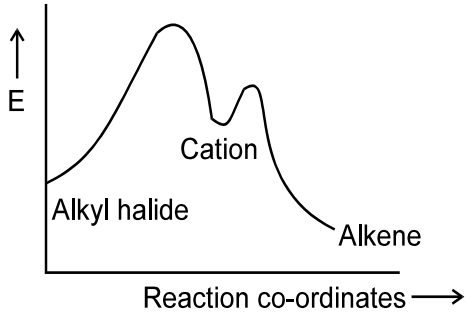


Mechanism of β-elimination reactions

1. E_1 Mechanism (elimination unimolecular mechanism)

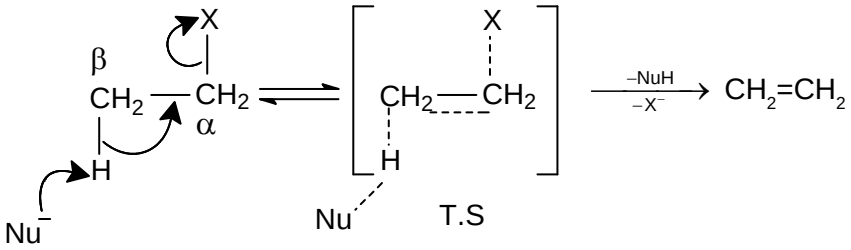
i. 

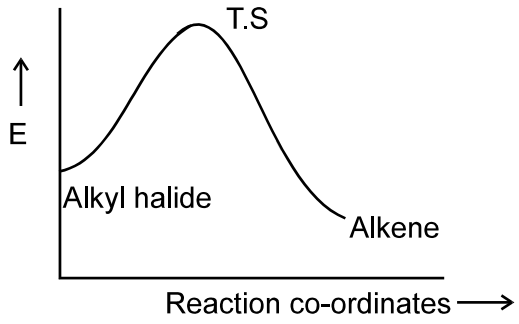
ii. 



Since the rate determining step of E_1 reaction involves the formation of a carbocation intermediate, the E_1 reactivity order of various alkyl halides follows the sequence $3^0 > 2^0 > 1^0$

2. E_2 mechanism (elimination biomolecular mechanism)





Bulkness at α-carbon sterically retards the backside attack of nucleophile on that carbon and directs the incoming nucleophile to β-hydrogen. $\therefore$ The E_2 reactivity of various alkyl halides follows the order $3^0 > 2^0 > 1^0$

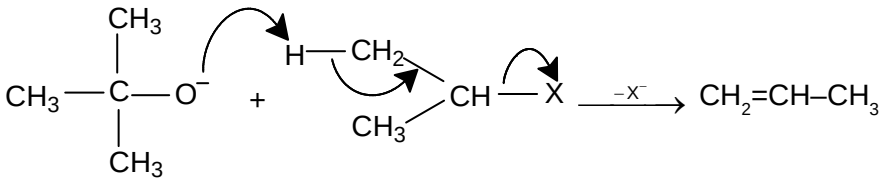
E_1 Vs E_2

E_1	E_2
Weak Base	Strong Base
$3^0 > 2^0 > 1^0$	$3^0 > 2^0 > 1^0$
Polar protic solvents	Nonpolar or weakly polar (aprotic) solvents
Better leaving group required	Better leaving group required
Saytzseff's rule	Saytseff's rule

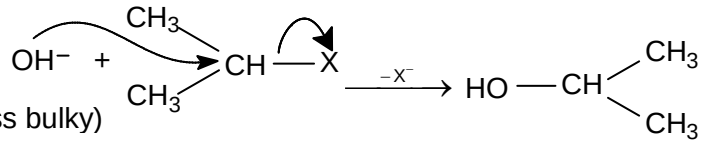
Elimination Vs Substitution Reaction

1. Bulkness of the nucleophile

More bulky nucleophiles gives elimination reaction whereas less bulky nucleophiles gives substitution reaction



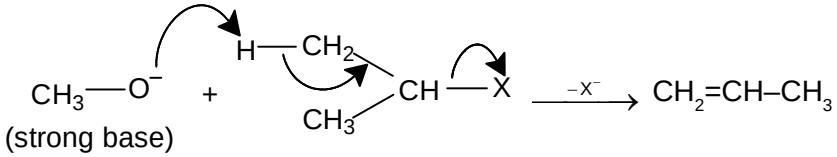
(more bulky)



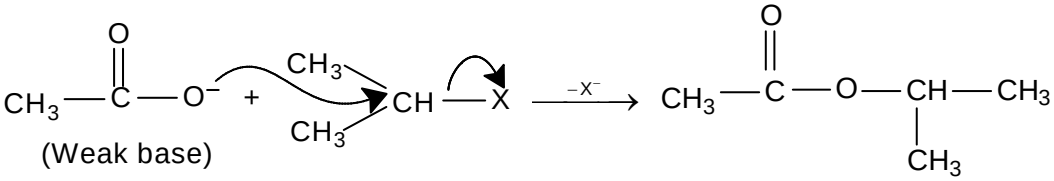
(less bulky)

2. Basicity of the nucleophile

Strong bases gives elimination reaction whereas weak bases gives substitution reaction



(strong base)



(Weak base)

3.Temperature

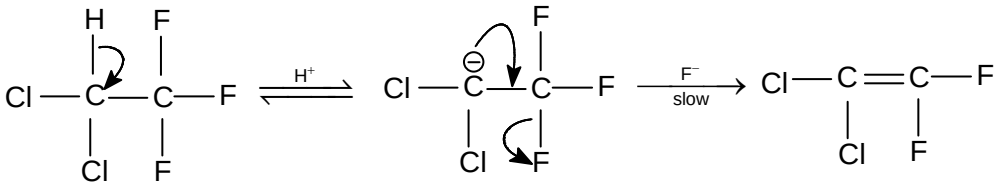
Elimination reaction involves cleavage of large number of bonds. It requires high activation energy. Therefore high temperature favour elimination reaction.

E^1_{cb} Mechanism (Elimination Conjugate Base Mechanism)

In E_1 reaction, the leaving group leaves first and then the β -hydrogen. In E_2 reaction both are eliminated simultaneously. There is another possibility the H^+ ions leaves first and then the leaving group. That is the reaction proceeds through a carbanion intermediate (conjugate base)

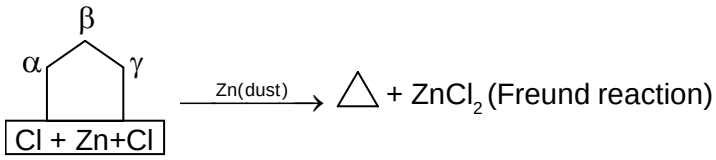
Conditions for E^1_{cb} mechanism

1. Presence of poor leaving group
2. Presence of strongly acidic hydrogen



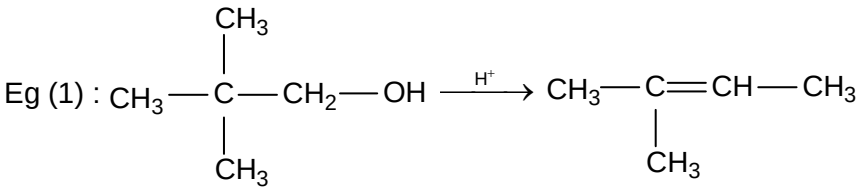
γ - Elimination Reaction

The loss of two atoms or groups occurs from $\alpha - \gamma$ positions

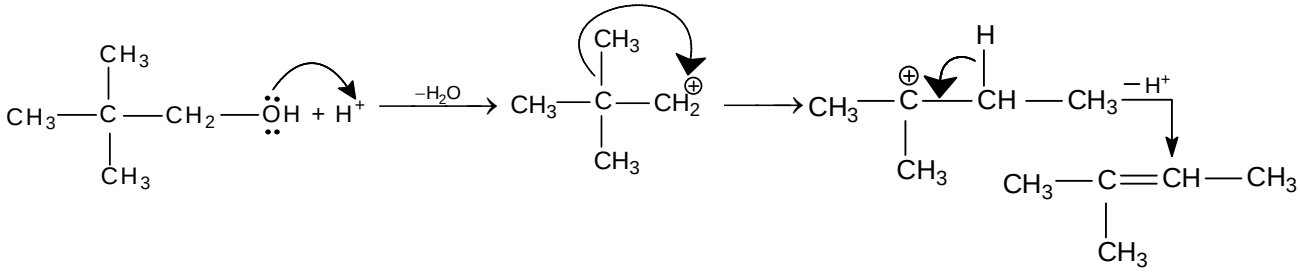


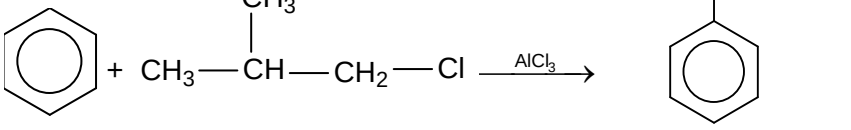
Rearrangement reaction

This type of reactions involve the migration of an atom or a group from one atom to other.

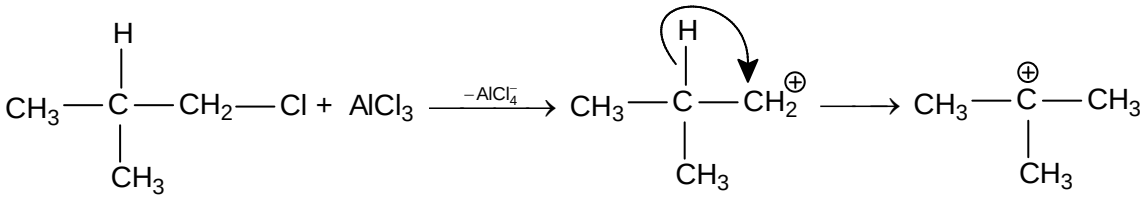


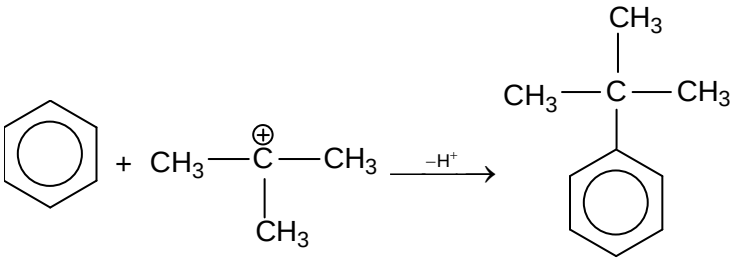
Mechanism

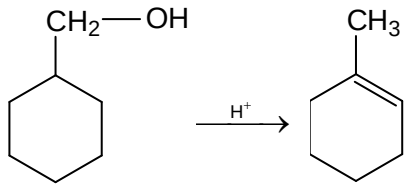


Eg (2) : 

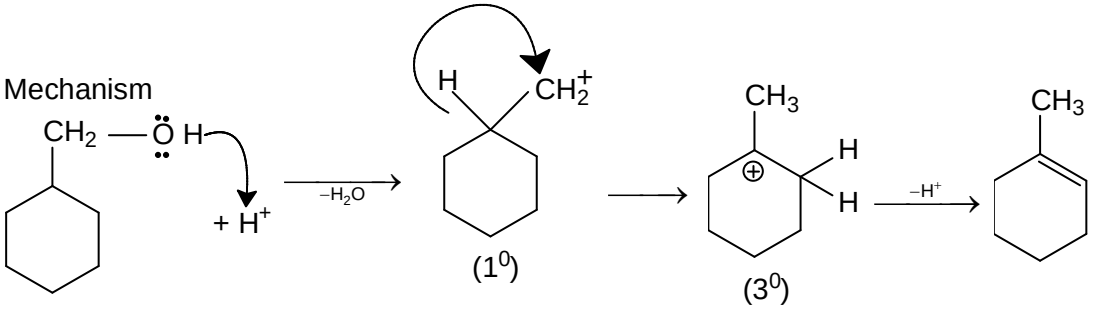
Mechanism

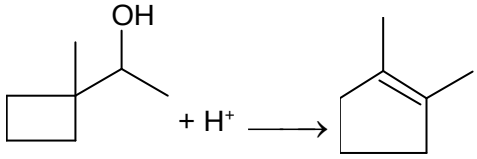
i. 

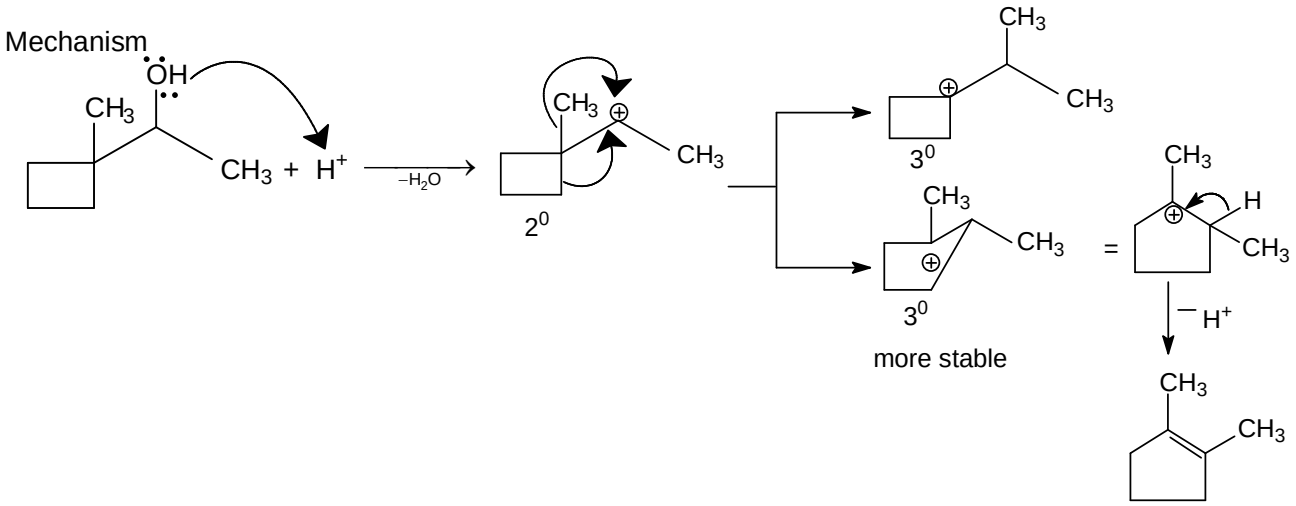
ii. 

Eg(3) : 

Mechanism



Eg (4) : 


Mechanism
OH
CH3
CH3 + H+
−H2O
CH3
CH3
2^0
CH3
CH3
3^0
CH3
CH3
3^0
more stable
=
CH3
H
CH3
− H+
CH3
CH3