

GENERAL ORGANIC CHEMISTRY & ISOMERISM

A chemical equation is a symbolic representation of a chemical change. It indicates the initial reactants and final products involved in a chemical change. Reactants generally consist of two species:

- (i) One which is being attacked; it is called a **substrate**.
- (ii) Other which attacks the substrate; it is referred to as a **reagent**. These two interact to form products.

Substrate + Reagent \rightarrow Products

It is important for us to know not only what happens in a chemical change but also known how it happens. Most of the reactions are complexes and take place via intermediates which may or may not be isolated. The intermediates are generally very reactive. They react readily with other species present in the environment to form the final products. **The detailed step by step description of a chemical reaction is called its mechanism.**

Substrate $\rightarrow \rightarrow \rightarrow$ intermediates $\rightarrow \rightarrow \rightarrow$ Products

Mechanism is only a hypothesis which explains various facts regarding a chemical change.

The reactions of organic compounds essentially involve changes in the existing covalent bonds present in their molecules. These changes may involve electronic displacements in the bonds, breaking of the bonds, energy changes accompanying the cleavage and formation of new bonds. To understand clearly the mechanism of various organic reactions, it is thus essential to have knowledge about the following well established concepts:

- (i) Electronic displacements in bonds,
- (ii) Cleavage (fission or breaking) of covalent bonds,
- (iii) Nature of attacking reagents.

1. ELECTRON DISPLACEMENT IN ORGANIC MOLECULES:

In organic molecules different reactions depend on the electron density in their molecules. Since majority of attacking reagents are polar, i.e. nucleophilic (or) electrophilic, hence in organic compounds permanent (or) temporary polarity is developed by temporary (or) permanent electron displacements.

The different electronic effects which operate in covalent bonds are

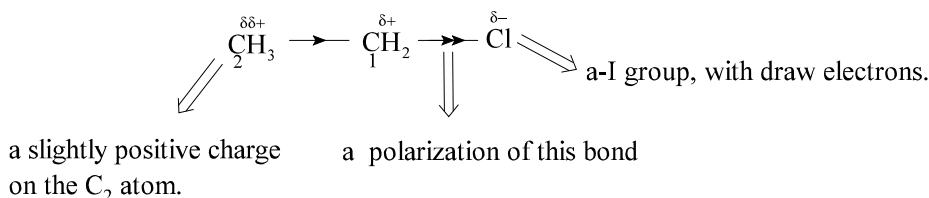
- | | |
|-----------------------------|------------------------------------|
| (a) Inductive effect | (b) Mesomeric and resonance effect |
| (c) Electromeric effect and | (d) Hyper conjugation |

(a) Inductive Effect

In a covalent single bond between unlike atoms, electron pair forming the σ bond is never shared absolutely equally between the two atoms; it tends to be attracted a little more towards the more electronegative atom of the two. Thus in an alkyl chloride, electron density tends to be greater nearer chlorine than carbon, as the former is the more electronegative; this is generally represented as in



If the carbon atom bonded to chlorine is itself attached to further carbon atoms, the effect can be transmitted further. For example $\text{C}_2\text{H}_5 - \text{Cl}$.



Electron displacement along the chain

In ethyl chloride the effect of the chlorine atom, partial appropriation of the electrons of the carbon chlorine bond is to leave C₁ slightly electron deficient this it seeks to rectify by in turn, appropriating slightly more than its share of the electrons of the σ bond joining it to C₂, and so on down the chain. The effect of C₁ on C₂ is less than the effect of Cl on C₁. However it decreases as the distance from source (more electronegative atom) increases. From practical point of view, it may be neglected after third carbon atom.

Inductive effect is denoted by the symbol 'I' and represented by a straight arrow (\longrightarrow), the arrow head pointing towards the source.

The inductive effect causes certain degree of polarity in the bond which in term renders the bond much more liable to be attached by other charged atoms (or) group.

The characteristic of inductive effect are

- (i) A permanent effect
- (ii) The electron never leave their original atomic orbital
- (iii) Operates through σ bond
- (iv) Polarisation of electrons is always in single direction.
- (v) Its magnitude (i.e. electron with drawing or donating power) decreases with increase in distance

Atoms (or) groups which attract electrons more strongly than hydrogen are called attracting (or) withdrawing groups and produce -I effect. The following is the order of decreasing -I effect.

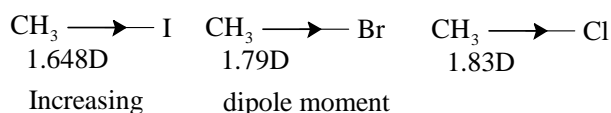
NR₃⁺, SR₂⁺, NH₃⁺, NO₂, CN, SO₃H, CHO, CO, COOH, COCl, COOR, CONH₂, OH, OR, F⁻, Cl, Br, I, NH₂, C₆H₅, CH₂=CH₂, H.

Atoms (or) groups which attract electrons less strongly than H are called as electron releasing or repelling groups and produce +I effect. Following is the decreasing order of +I effect.

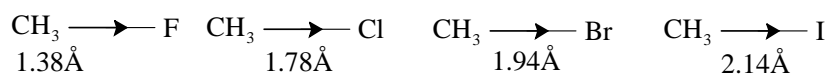
C₆H₅O⁻, COO⁻, R₃C, CHR₂, CH₃, H

Applications of Inductive Effect

- (i) **Dipole moment:** Since, inductive effect leads to a dipolar character in the molecule, it develops some dipole moment in the molecule, which increases with the increase in the inductive effect.



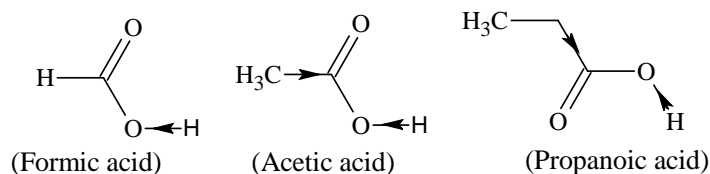
- (ii) **In Bond Length:** With increase in inductive effect, the bond length usually decreases because of increased ionic character,



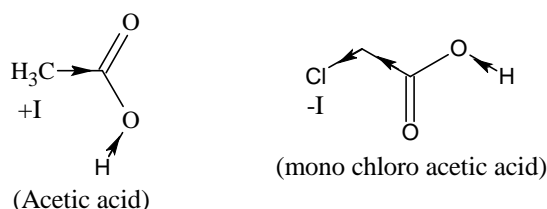
- (iii) **Strength of Fatty Acids:** As the number of alkyl groups attached to -COOH group increases, the acid

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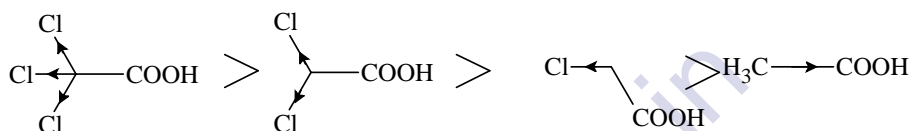
strength decreases. Thus formic acid is stronger acid than acetic acid which is stronger than propionic acid and so on, due to increasing +I effect of alkyl groups.



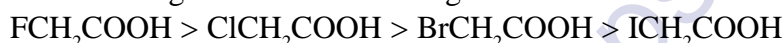
- (iv) **Strength of Substituted Acids:** Chlorinated acetic acids are stronger than acetic acid due to the –I effect of chlorine atom.



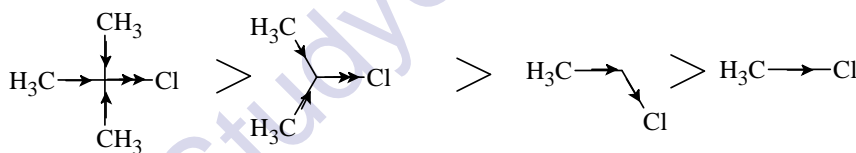
Larger the number of chlorine atoms, the greater will be –I and the stronger will be the acid.



The relative strength of the different halogen substituted acids is



- (v) **Reactivity of Alkyl Halides:** The carbon-halogen bond in tertiary alkyl halides is most reactive while it is least reactive in primary alkyl halides. This can be explained on the basis of greater +I effect in t-alkyl halides which pushes the –I effect; hence the bond becomes highly polar and most weak.



(b) Mesomeric Effect or Resonance:

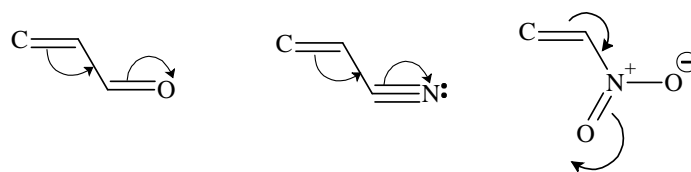
Special properties are associated with systems in which a π -bond is conjugated either with a second π -bond (or) with an atom which possesses a pair of electrons in a p-orbital. These are: stabilization energy, single bond lengths which are shorter than those in non-conjugated compounds, and (in some cases) the modification of dipolar properties.

- (i) **f-bond-f bond conjugation:** The simplest example is butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$. This is symmetrical molecule and conjugation does not lead to the appearance of a dipole. In valence bond language, contributions from ionic structures $\text{CH}_2^+-\text{CH}=\text{CH}-\text{CH}_2^-$ and $\text{CH}_2^--\text{CH}=\text{CH}-\text{CH}_2^+$ are necessarily equal and their dipoles therefore, nullify each other. This is not true, however, when π -bonds of different types are in conjugation. For example in an α, β unsaturated carbonyl compound such as butenal the contribution of structure (A) is greater than that of (B) because oxygen is significantly more electronegative than carbon the carbonyl group thus polarizes the $\text{C}=\text{C}$ bond.

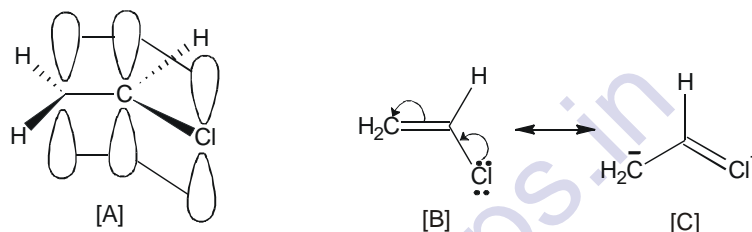


A group such as carbonyl which withdraws electrons from an adjacent group via the π -bonding framework is described as having a –M effect, the –ve sign indicating electron withdrawal and M

standing for mesomeric. Other groups of –M type include ester, nitrile and nitro etc., and the curved arrows in the representations denote the direction of the mesomeric effect.



- (ii) **f-bond-p-orbital conjugation:** In vinyl chloride (chloroethene) the p-orbital on the carbon which is attached to chlorine can overlap with both the p-orbital on the second carbon atom and one of the filled p-orbitals on chlorine three delocalized MO's are established of which the two of lowest energy are occupied. Since the p-orbital on chlorine is initially filled, its participation in the delocalized π system leads to the partial removal of electrons from chlorine and the appearance of a dipole moment directed from chlorine towards carbon. This is opposed to the dipole established in C – Cl σ bond as a result of the –I effect of chlorine, with the overall result that the dipole moment of vinyl chloride (1.44D) is considerably smaller than that of ethyl chloride (2.0D) in which the –I effect is operative. The capacity of chlorine for donating electrons into a molecular π -system is described as a +M effect.



In VB terminology, vinyl chloride is described as a hybrid of the structures (B) and (C), the latter symbolizing the +M effect of chlorine. Both descriptions also indicate that C—Cl bond should be shorter than in a saturated alkyl chloride, as is found.

Other elements with unshared p-electrons which take part in forming delocalized π -systems include other halogens, oxygen and nitrogen, e.g.,



In each case the substituent has a + M effect.

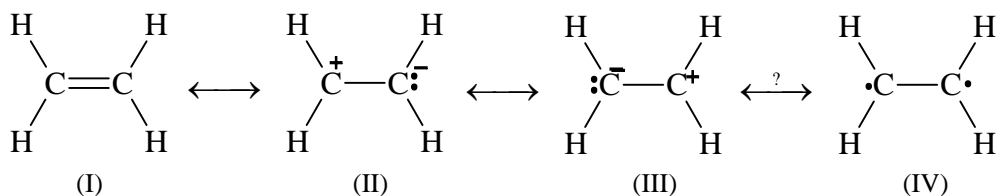
Rules for Drawing valence Bond Resonance Structures

We have already said that resonance effects are encountered mainly in molecules with multiple (i.e. π) bonds. Except in a few special molecules, the σ -bond framework is not involved in significant resonance interactions.

This fact can be rationalized by noting that electrons in π bonds are higher in energy than those in σ bonds, making the π -bonding electrons more reactive and also more polarizable than σ -bonding electrons.

When a species contains multiple bond(s) it may have several resonance contributors for example, even a molecule as simple as ethylene has several resonance.

But not all resonance structures contribute equally to the hybrid's properties. For example, here are four structures we might write for ethylene:



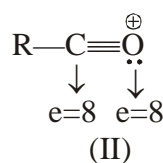
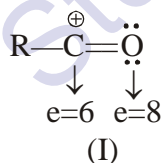
The first structure (I) is by far the main contributor. Structure II and III are minor contributors for three reasons: the π bond has been broken, there are charge separations not present in the major contributor, and the valence of the +vely charged carbon is unsatisfied. Structure IV does not contribute at all not only are both carbons' valences unsatisfied, but previously paired electrons have become unpaired. From considerations such as these we can derive a list of rules that will help us determine if a given resonance contributor has a valid structure, and how important its relative contribution is.

1. In going from one resonance structure to another no nuclei can change position; only electrons (bonds) can move.
2. No atom in any resonance structure can ever have more electrons around it than will fill its valence shell; that is, there should be no more than eight electrons around any second period element.
3. Most organic structures have no unpaired electrons. But if there are unpaired electrons, the no. of unpaired electrons cannot change from one structure to the next.
4. The most important resonance contributor's are those with the maximum no. of covalent bonds and the minimum number of charge separations.
5. When Zwitterionic charges are present negative charges prefer to be on the electronegative atoms, with positive charges on the more electro positive atoms. Rules 1, 2 and 3 determine whether a structure is "legal", while rules 4 and 5 determine the relative contribution by a resonance structure.

Contribution of Resonating structures:

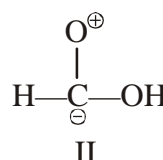
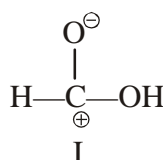
The contribution of an individual factors:

- (i) Neutral species is more stable than the charged (or dipolar species).
- (ii) Species having complete octet is more stable than the species having incomplete octet

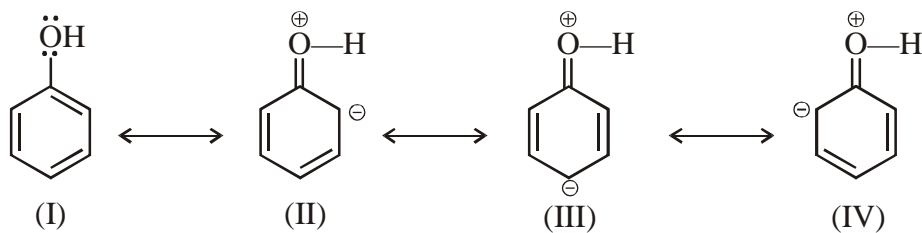


(I) and (II) are resonating structure of acyl cation. (II) will be more stable than (I).

- (iii) If all structure have formal charge, the most stable one is that in which the positive and negative charges reside on the most electropositive and most electronegative atoms of the species respectively.



- (iv) Resonating structure with a greater number of covalent bonds is more stable.
- (v) increase in charge separation decreases the stability of a resonating structure.



Hence stability of II and IV will be the same and both will be more stable than III. The order of stability of resonating structures in decreasing order will be as follows :



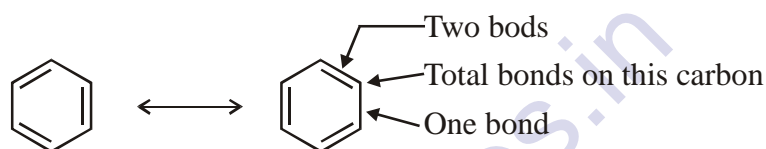
Ø **Note :** All the resonating structure do not contribute equally to the real molecule . Their contribution is a direct function of their stability.

Resonance and Bond order :

Bond order in conjugated compound or bond order in compounds which exhibit resonance =

$$\frac{\text{Total number of bonds on central atom}}{\text{Number of resonating structures}}$$

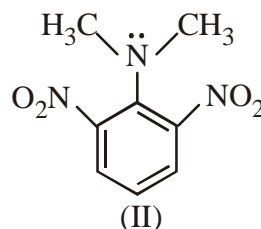
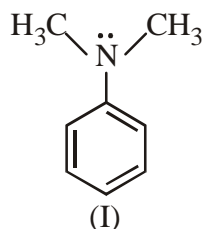
For example :



$$\text{Bond order of carbon in benzene} = \frac{2+1}{2} = 1.5$$

Steric Inhibition of Resonance:

The most important condition for resonance to occur is that the involved atoms in resonating structure must be coplanar or nearly coplanar for maximum resonance. If this condition does not fulfill, the involved orbitals cannot be parallel to each other and as a consequence delocalisation of electrons or positive charge cannot occur. The planarity of orbitals are inhibited by the bulky groups present on adjacent atoms. This phenomenon is known as **steric inhibition of resonance**. For example, in dimethyl aniline (I) the orbital having lone pair of electrons present on nitrogen atom is in the plane of the benzene ring hence lone pair of electrons present on nitrogen atom is in the plane of the benzene ring hence lone pair takes part in the delocalisation.

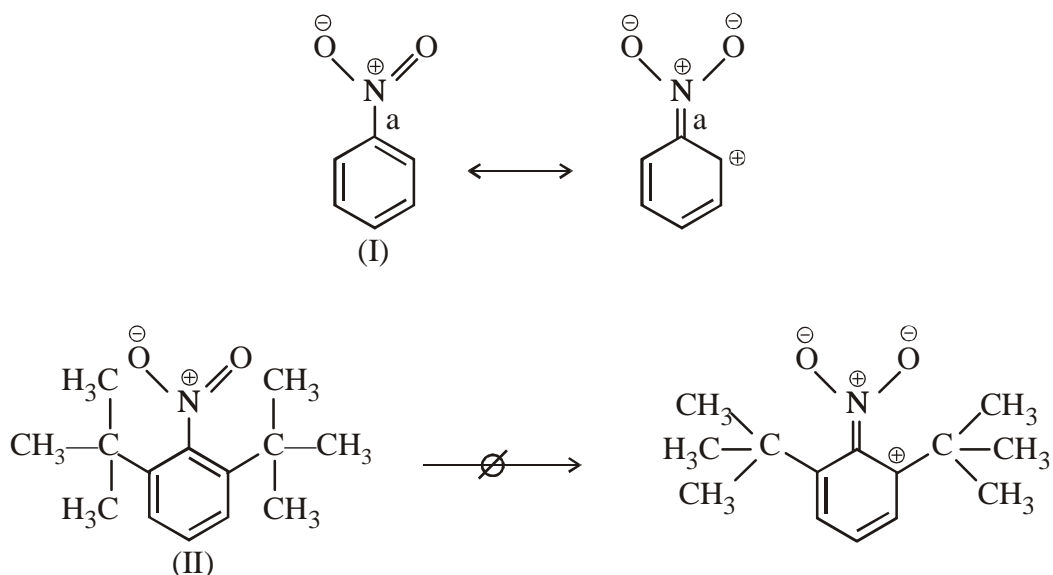


In N, N-dimethyl-2, 6-dinitroaniline (II) the $\ddot{\text{N}}(\text{CH}_3)_2$ groups is out of the plane of the benzene ring owing to the presence of the two bulky nitro groups and consequently the lone pair of electrons on the nitrogen atoms of $\ddot{\text{N}}(\text{CH}_3)_2$ group cannot get delocalised through lone pair, π conjugation.

Thus bulky groups present at ortho position inhibit delocalisation of lone pair of electrons or positive charge present on key atom of the molecule. Steric inhibition of resonance has profound effect on:

- | | | |
|---------------------------------------|---------------------------|-----|
| (i) Physical properties | (ii) Acidity and Basicity | and |
| (iii) Reactivity of organic compounds | | |

In nitro-benzene (I) bond length between carbon-nitrogen (bond -a) is in between single and double due to the resonance but in compound (II) bond length between carbon-nitrogen is only of single bond due to the inhibition of resonance.



Two further points should be noted. First, bond strength is dependent on the extent of the overlap of the combining atomic orbitals, so that in these conjugated systems the more nearly equal in size the p-orbitals are, the more effective is the π -orbital overlap. Hence fluorine is more effective than chlorine in conjugating with carbon, and oxygen is more effective than sulphur. Hence the order of +M effects is :



+M effect possessing groups are:



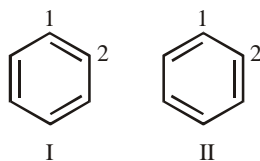
-M effect possessing groups are:



APPLICATION OF MESOMERIC OR RESONANCE

(i) Effect of resonance on the structure :

Resonance decreases bond length of single bond and increases bond length of double bond in real structure. Consider structure of benzene:

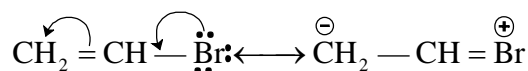


I and II are resonating structure of C_6H_6 .

- According to resonating structure I, C—C bond length between C_1 and C_2 will be 1.33 \AA
- According to resonating structure II, C—C bond length between C_1 and C_2 will be 1.54 \AA
- According to resonance, bond length between C_1 and C_2 will neither be 1.33 nor 1.54 \AA but will be in between 1.33 & 1.54 \AA , i.e., bond length between C_1 & C_2 is > 1.33 & $< 1.54 \text{ \AA}$.
- experimental value is 1.40 \AA , this result coincides with the result obtained by resonance

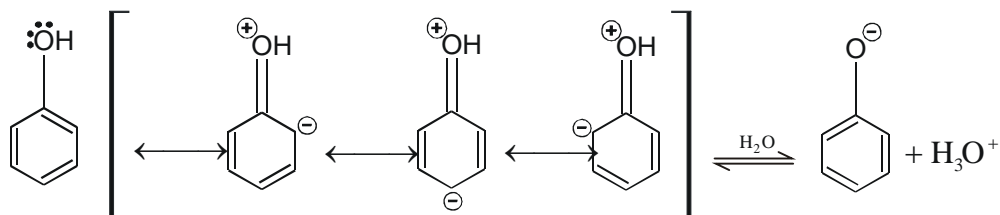
(ii) The low reactivity of halogens :

The low reactivity of halogens bonded to unsaturated carbon is due to the +M effect of the halogen. The C—Br bond in vinyl bromide has a partial double-bond character due to the +M effect of bromine with consequent low reactivity of bromine.

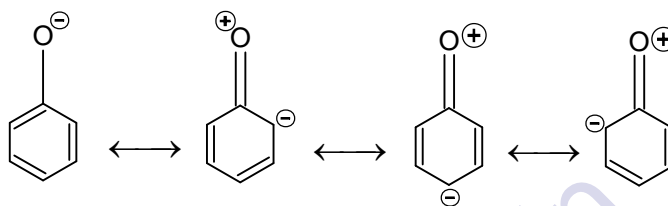


(iii) Acidity of phenol :

The acidity of phenol is due to the +M effect of OH group. The mesomeric transfer of the lone pair on the oxygen atom of phenol to the π electrons of the benzene ring results in several resonance structures with positive charge on the oxygen atom. This aids the hydrogen atom of OH group will leave as proton.



The ionization is specially aided due to the formation of the relatively more stable phenoxide ion. The charge delocalization in phenoxide ion affords greater stability over phenol in which charge separation occurs in the canonical forms.


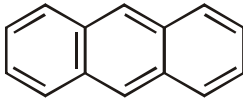
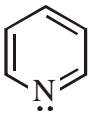



Hence, phenol prefers to ionize, i.e. it is acidic.

(iv) Aromatic character of compounds

According to the **Hückel rule**, a compound will be aromatic if it fulfils the following four conditions:

- (i) Compound should be cyclic
- (ii) Compound should be planar
- (iii) Compound should be conjugated
 - (a) Double bond, Single bond, Double bond
 - (b) Double bond, Single bond, electron pair
 - (c) Double bond, single bond, positive charge
- (iv) Compound should have $(4n + 2) \pi$ conjugated or delocalised electrons where n is a whole number $n = 0, 1, 2, 3, \dots, 4n$

Structure	No. of conjugated electrons
	6π
	14π
	6π
	2π


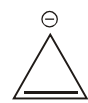



6π

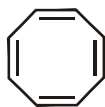
Anti-Aromatic compounds

According to Huckel rule, compound will be anti aromatic if it will fulfil the following four conditions:

- (i) Compound should be cyclic
- (ii) Compound should be planar
- (iii) compound should be conjugated and
- (iv) Compound should have $(4n)\pi$ conjugated or delocalised electrons where n is whole number
 $n = 1, 2, 3, 4, 5, 6$

n	$(4n)\pi$
Structure	$(4n)\pi$
	4π
	4π
	4π

Exception : Although cyclooctatetraene has $(4n)\pi$ electrons even then it is not an anti aromatic. Geometry of this compound is non planar

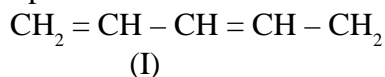


Cyclooctatetraene

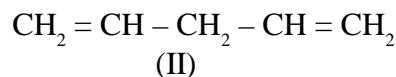
Note: Aromatic compounds are diamagnetic in character whereas anti-aromatic compounds are paramagnetic in character:

(v) Stability of conjugated species :

- (1) Stability of a conjugated compound is more than the corresponding non-conjugated compound.
 For example



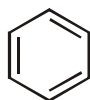
Conjugated compound



Non-conjugated compound

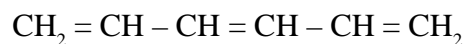
Hence (I) will be more stable than (II)

- (2) Stability of an aromatic compound is more than the corresponding non-aromatic conjugated compound. For example (III) is more stable than (IV)



(III)

Aromatic compound



(IV)

Conjugated non-aromatic compound

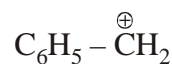
Thus stability series of different compounds in decreasing order is as follows :

Aromatic compound > conjugated non-aromatic compound

> non-conjugated compound > anti aromatic



Number of resonating structure = 2



Number of resonating structure = 4

Hence the benzyl carbocation is more stable than the allyl carbocation.

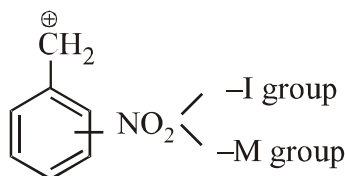
(vi) Stability of substituted benzyl carbocations:

Stability of substituted benzyl carbocation depends on the nature of group present in the benzene ring.

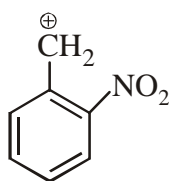
The group may be $+I$, $-I$, $+R$ or $-R$.

Case I : When ring has a group which is $-I$ and $-M$ group.

$-I$ group withdraws electrons, increases magnitude of positive charge, decreases stability.



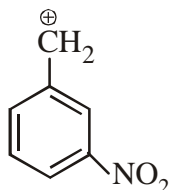
$-M$ group (When present at *o*- or *p*-position) withdraws electrons, increases magnitude of positive charge, decreases stability.



(I)

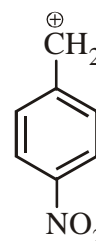
- (i) Increase in the magnitude of positive charge by $-I$ and $-M$ effect

- (ii) $-I$ and $-M$ power is maximum



(II)

- (i) Increase in positive charge only by $-I$ effects



(III)

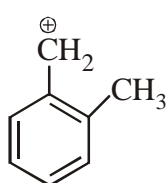
- (i) Increase in positive charge by $-I$ and $-M$ effect

- (ii) $-I$ and $-M$ power is minimum

Hence (II) is more stable than (III) which is more stable than (I).

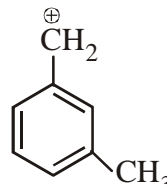
Thus *meta* derivative is more stable than *p*-derivative which is more stable than *o*-derivative.

Case II : When ring has a group which is $+I$ and $+R$ group.



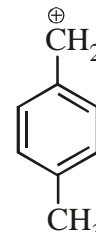
(I)

Positive charge is decreased by $+I$ and $+M$ group or stability by $+I$ and



(II)

Stabilised by $+I$ group only



(III)

Stabilised by $+I$ and $+M$ effect

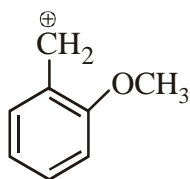
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+M group.

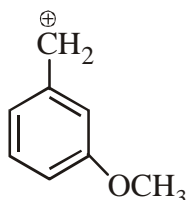
Hence (I) is more stable than (III) which is more stable than (II).

Thus *o*-derivative is more stable than *p*-derivative which is more stable than *m*-derivative.

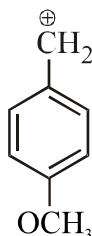
Case-III : When group has +M effect and –I effect.



Stabilised by +M effect
destabilised by – I effect
–I power is maximum (due to distance)



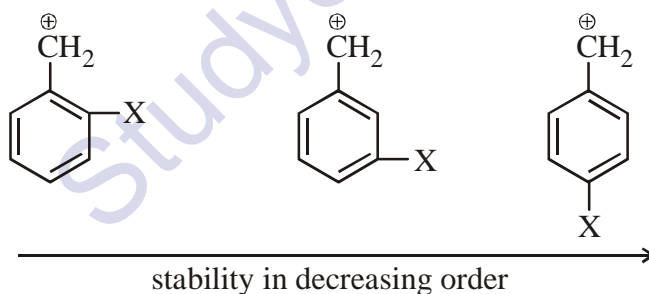
Destabilised by –I effect



Stabilised by +M effect
destabilised by – I effect
–I power is minimum (due to distance)

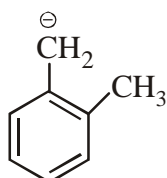
Hence *p*-derivative is more stable than *o*-derivative which is more stable than *m*-derivative

Note : In case of halo derivatives, result depends only on –I power of the group.

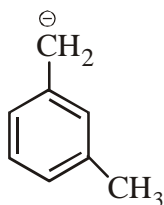


(vii) Stability of substituted Benzyl carbanions

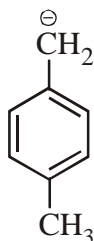
Case I : When group has + M and + I effect.



+M effect decreases stability
+I effect also decreases stability
+I power is maximum



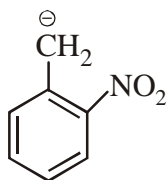
Destabilised only by +I effect



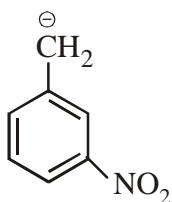
destabilised by +M effect and +I effect, +I power is minimum

Hence *m*-derivative is more stable than *p*-derivative which is more stable than *o*-derivative

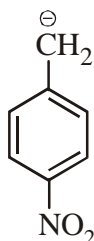
Case-II : When group has –R and –I effect.



Stabilised by –M and –I effect
(– I power is maximum)

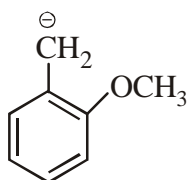


Stabilised by –I effect

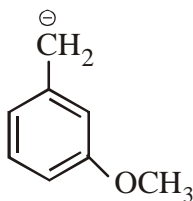


Stabilised by –M and –I effect
and – I power is minimum

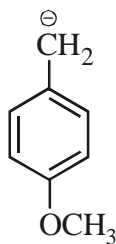
Thus *o*-derivative is more stable than *p*-derivative which is more stable than *m*-derivative.



Destabilised by + M effect and
stabilised by –I effect
–I power is maximum



Stabilised by –I effect

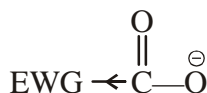


Destabilised by +M effect
stabilised by -I effect and
-I power is minimum

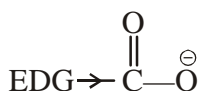
(viii) Acidity of Aromatic Acids

As we know acidity of carboxylic acids depends on the stability of acid anion thus.

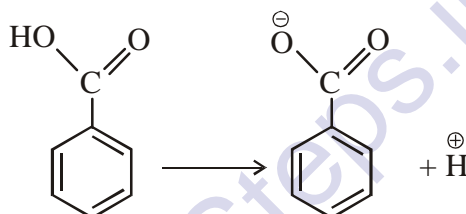
Electron withdrawing group stabilises anion, hence increases acidity



Similarly, electron donating group destabilises anion, hence decreases acidity.



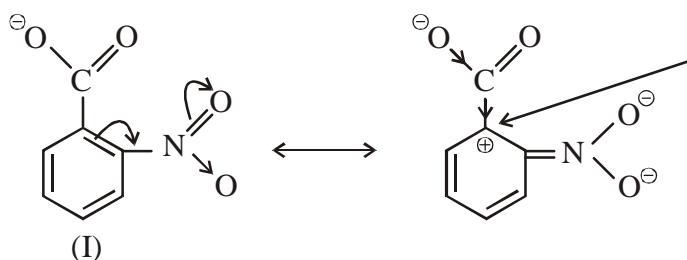
The First member of aromatic acid is a benzoic acid which dissociates as follows



Thus acidity of benzoic acid will depends on the stability of benzoate anion which is only stabilised by inductive effect and not by resonance because **carboxylic group and carboxylate ion are not in the plane of the ring**. These two groups will not take part in the delocalisation with the benzene ring. In substituted benzoic acid there is no direct interaction between COO^- and substituent.

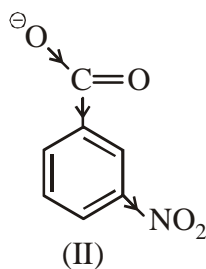
Acidity of substituted Acids: Ortho substituted benzoic acid is always a strong acid than *m*- and *p*-derivative due to the ortho effect.

Case I : When group is -M and -I group.

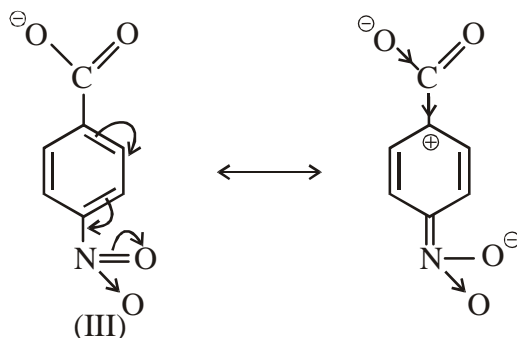


Carbon becomes electron deficient due to resonance effect of NO_2 group. This electron deficient carbon withdraws electrons from the carboxylate group by inductive effect.

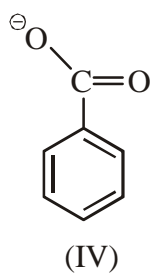
Thus, anion is stabilised by -M and -I effect and -I power is maximum



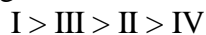
Anion is stabilised only by -I effect of NO₂ group



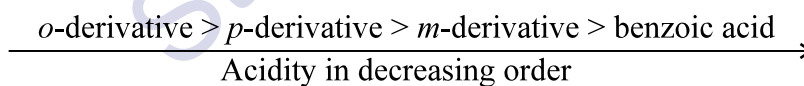
Anion is stabilised by -M and -I effect of NO₂ group



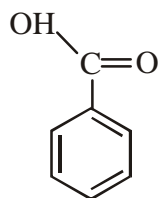
Thus decreasing order of the stability of these anions is follows:



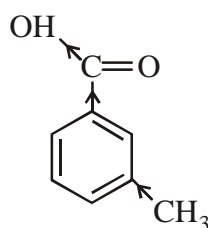
We know that *ortho* derivative is the most acidic therefore decreasing order of acidity of these acids is as follows :



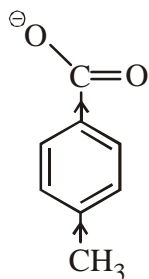
Case II : When group has +M and +I effect.



Ortho derivative will be most acidic due to ortho effect.



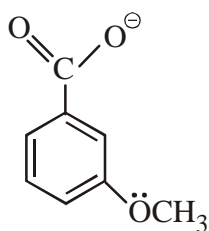
Anion is destabilised due to +I effect



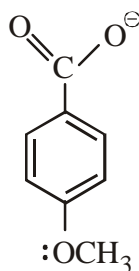
Anion is destabilised by +M and +I effect and +I power is minimum

Thus $\xrightarrow{\text{benzoic acid} > o\text{-derivative} > m\text{-derivative} > p\text{-derivative}}$
Acidity in decreasing order

Case III : When group has +M and -I effect



Stabilised by -I effect



Destabilised by +M effect stabilised by -I effect

Thus $\xrightarrow{o\text{-derivative} > p\text{-derivative} > m\text{-derivative} > \text{benzoic acid}}$
Acidity in decreasing order

(ix) Basicity of Aromatic amines :

- (a) Basicity of nitrogen containing compounds \propto electrons on nitrogen
In aromatic amines, lone pair of electrons present on nitrogen is delocalised. hence, electron density decreases due to resonance.

Thus Basicity $\propto \frac{1}{\text{Number of resonating structures}}$

Structure	Number of resonating structure
$\text{C}_6\text{H}_5\ddot{\text{N}}\text{H}_2$	4
$\text{C}_6\text{H}_5\ddot{\text{N}}\text{H}-\text{C}_6\text{H}_5$	7
$\text{C}_6\text{H}_5\ddot{\text{N}}(\text{C}_6\text{H}_5)_2$	11

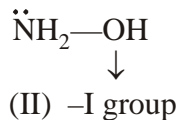
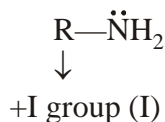
- (b) Basicity of other Nitrogen containing compounds: Basicity depends on the following factors:
(1) Electronegativity of nitrogen

$$\text{Basicity} \propto \frac{1}{\text{Electronegativity of nitrogen}}$$

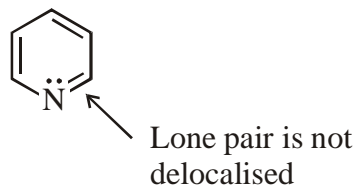
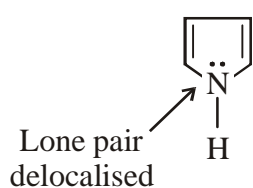
(2) Inductive effect:

$$\text{Basicity} \propto +I \text{ power of the group on nitrogen}$$

$$\text{Basicity} \propto \frac{1}{-I \text{ power of the group on nitrogen}}$$



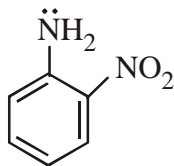
(3) Resonance : Delocalisation of lone pair of electrons present on nitrogen decreases basicity.



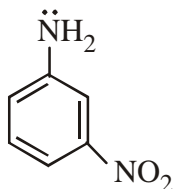
Hence (II) is more basic than (I)

(c) Basicity of Substituted Anilines: Para substituted aniline is more basic than ortho substituted aniline and the effect is known as **para effect**.

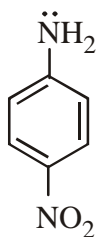
Case I : When group has $-R$ and $-I$ effect.



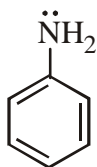
Decrease in electron density nitrogen by
 $-R$ and $-I$ effect and
 $-I$ effect is maximum
 (minimum electron density on nitrogen)



Decrease in electron density on nitrogen by
 $-I$ effect only

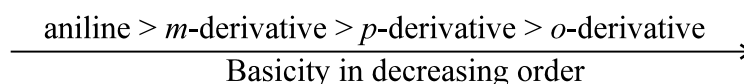


Decrease in electron density on nitrogen by
 $-R$ and $-I$ effect and
 $-I$ power is minimum



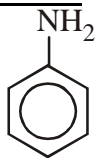
no group

Thus order of basicity is as follows :

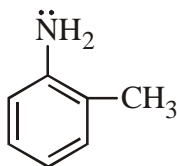


Case II : When group is $+R$ and $+I$ group .

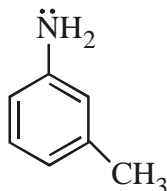
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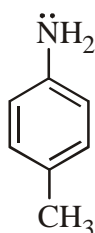
No group, hence electron density does not change due to group.



Increase in electron density on nitrogen by + R and +I group and +I power is maximum

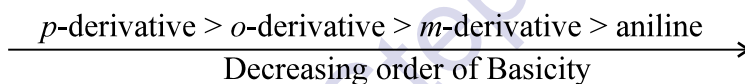


Increase in electron density on nitrogen by +I group



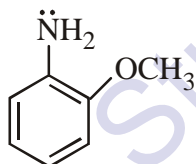
Increase in electron density on nitrogen by +I group and +I group and +I power is minimum.

Thus aniline will be least basic and p-derivative will be most basic hence order of basicity is as follows

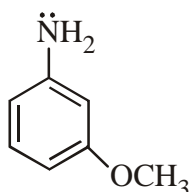


Note : p-derivative is more basic than ortho derivative due to a para effect.

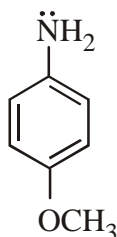
Case III : When group + R and – I group.



Increase in electron density on nitrogen by +R effect
Decrease in electron density on nitrogen by – I effect
– I power is maximum.

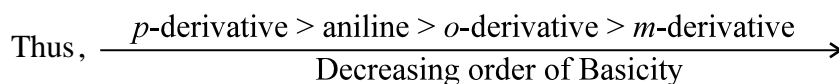


Decrease in electron density on nitrogen by – I effect

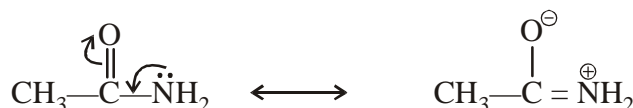


Increase in electron density on nitrogen by + R effect
decrease in electron density on nitrogen by – I effect
– I power is minimum

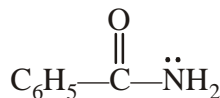
p-derivative is more basic than ortho derivative due to para effect.



(4) Effect of cross conjugation on basicity:



Due to delocalisation and –I effect of CO group, amides are less basic than amines.



In this amide there is cross conjugation which increase basicity; thus $\text{C}_6\text{H}_5\text{CONH}_2$ is more basic than CH_3CONH_2 . π bond of $\text{C}=\text{O}$ group is in conjugation to benzene ring as well as lp of NH_2 groups.

(x) Acidity of α -Hydrogens :

α -Hydrogen of carbonyl compounds, nitrites, acids, nitro compounds are acidic in character. In other words we can say that

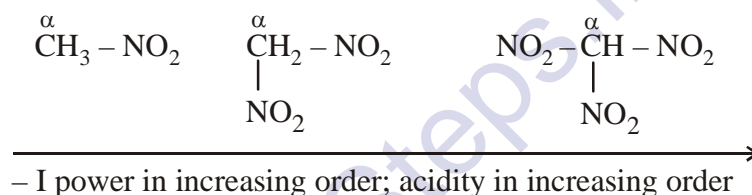
- (i) α -Hydrogens are acidic in character when –I group is present on the α -carbon.
- (ii) Acidity of α -hydrogens depends on the stability of carbanion which is obtained by the ionisation of the compound

Thus acidity depends on the stability of CH_2G^- .

Stability of anion depends on two factors.:

- (a) Stability of carbanion \propto –I power of the group present on α -carbon

For example;



- (b) Stability of carbanion \propto number of resonating structures.

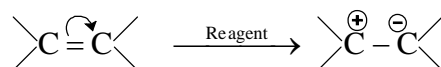


Thus α -hydrogen of nitro methane is acidic due to inductive effect as well as delocalisation of negative charge.

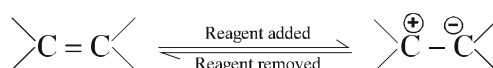
(c) Electromeric Effect :

On the close approach of a reagent, the electronic system of an unsaturated molecule is deformed. when the reagent is removed without allowing the reaction to takes place, the electronic system reverts to the original ground state of the molecule. This kind of polarizability of multiple bonds is known as electromeric effect.

Electromeric effect causes complete transfer of the π electrons from one carbon to the other consequently, one end is positively charged and the other negatively charged which aid the reagent to attack. The shift of the electrons is shown by a curved arrow (?) indicating the direction of the electron shift.



The effect is temporary since the electrons revert to the original state on removing the reagent.



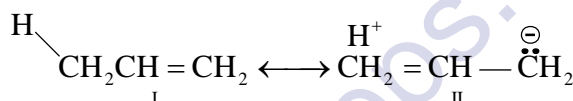
When the multiple bond is between two dissimilar elements the shift of electrons takes place towards the more E.N of the two. Inductive effect may also determine the direction of the shift of electrons e.g.,



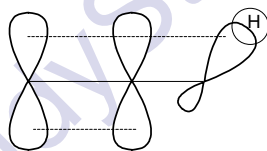
(d) Hyperconjugation

Unlike the usual delocalization which involves electrons, a different type called hyper conjugation involves σ electrons. This another type of resonance (hyper conjugation) is often invoked to account for the stabilizing and electron donating effect of an alkyl group. Hyper conjugation involves delocalization of C—H sigma electrons into an adjacent pi system. Thus propene may be described as a hybrid of structures I and II. In canonical forms which involve hyper conjugation there is no bond between the carbon and hydrogen and therefore this effect has also been called no bond resonance [sacrificial hyper conjugation, since in II, there is one less real bond]. Alternatively, the molecular description is that this effect arises from the overlap of σ orbitals in the alkyl group with the π system.

The evidence for hyper conjugation is that in propene e.g., the C—C single bond is slightly shorter than in ethane. Thus it is reasoned that C—C single bond in propene acquires some double bond character. Moreover the heat of hydrogenation of propene (30.1 Kcal/mol i.e., 126 kJ/mol) is less than that of ethene (32.8 kcal/mol i.e., 137 kJ/mol). Hyper conjugation is however, no longer believed to make any significant contribution to the stability of substituted alkenes. In fact at present the evidence is against hyper conjugation in the ground states of neutral molecules. Evidence is there to show that hyper conjugation is indeed important and significantly accounts for the stability of carbocations and free radicals.



Sacrificial hyper conjugation

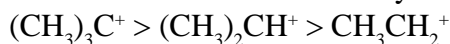


Hyperconjugation in an alkene: overlap between σ and π orbitals.

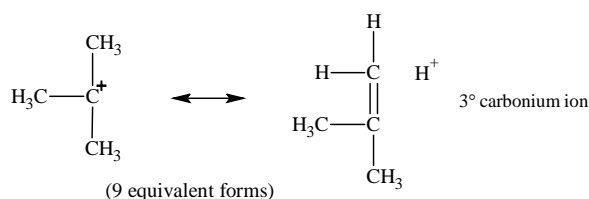
Thus in hyperconjugation in the ground state of neutral molecules, the canonical forms invoke not only no-bond resonance but a charge separation as well which however not possessed by the main form.

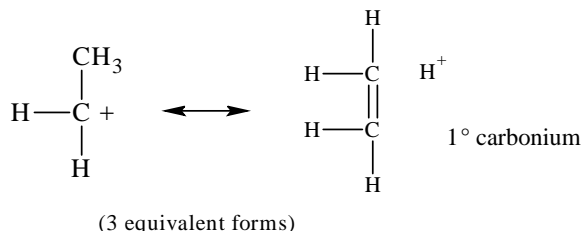
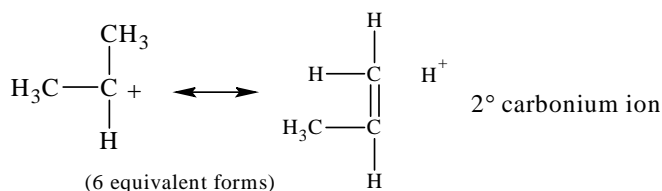
Effects of Hyperconjugation :

1. Stability of Carbonium ions: The order of stability of carbonium ions is as follows



above order of stability can be explained by hyper conjugation. In general greater the number of hydrogen atoms attached to α -carbon atoms, the more hyper conjugative forms can be written and thus greater will be the stability of carbonium ions.



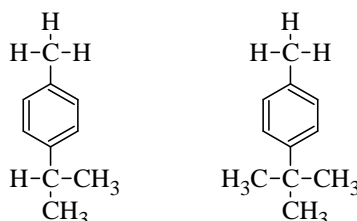


- Stability of free radicals: Stability of free radicals can also be explained as that of carbonium ions.
 $(\text{CH}_3)_3\dot{\text{C}} > (\text{CH}_3)_2\dot{\text{C}}\text{H} > \text{CH}_3\dot{\text{C}}\text{H}_2 > \dot{\text{C}}\text{H}_3$
- Bond lengths : The bond length in a molecule changes if there is hyper conjugation, e.g., in propene $\text{}^3\text{CH}_3 - \text{}^2\text{CH} = \text{}^1\text{CH}_2$, the $\text{C}_1 - \text{C}_2$ bond length is found to be more than 1.34\AA while the $\text{C}_2 - \text{C}_3$ bond distance is less than 1.54\AA ($\text{C}-\text{C}$ single bond length).
- Dipole moment: since hyper conjugation causes the development of charges, it also affects the dipole moment of the molecule.
- Orientation influence of methyl group : The o, p directing influence of the methyl group in methyl benzenes is attributed partly to inductive and partly of hyper conjugation effect.



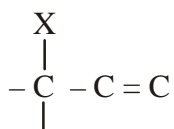
[Orientation influence of the methyl group due to +I effect]

The role of hyper conjugation in O, P directing influence of methyl group is evidence by the fact that nitration of P-isopropyl toluene and p-tert-butyl toluene from the product in which $-\text{NO}_2$ group is introduced in the ortho position with respect to methyl group and not to isopropyl or t-butyl group although the latter groups are more electron donating than methyl groups i.e. the substitution takes place contrary to inductive effect. Actually this constitutes an example where hyper conjugation overpowers inductive effect.



Reverse Hyperconjugation :

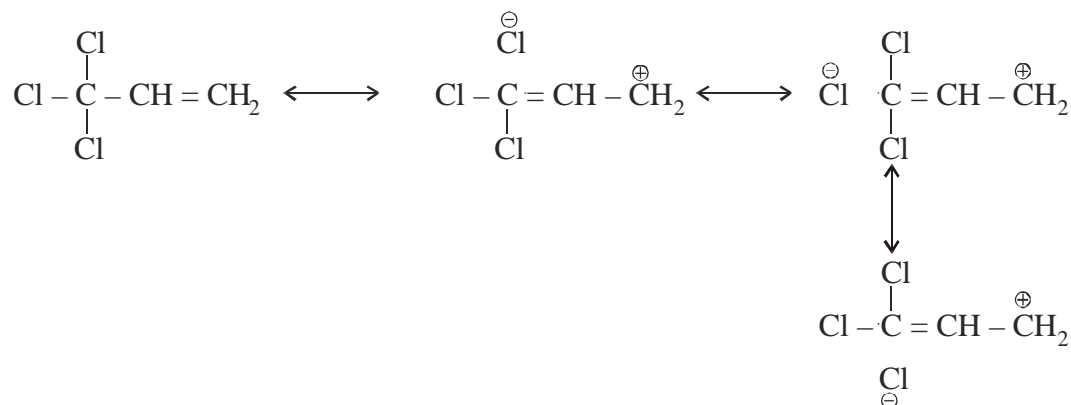
The phenomenon a of hyperconjugation is also observed in the system given below:



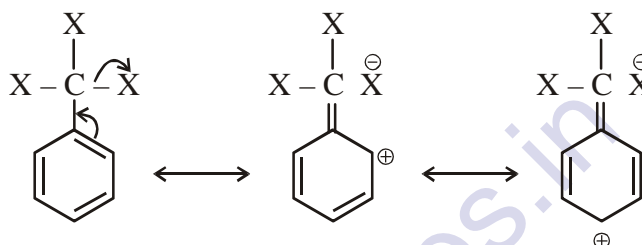
where X = halogen

In such system the effect operates in the reverse direction . Hence the hyperconjugation in such

system is known as reverse hyperconjugation .

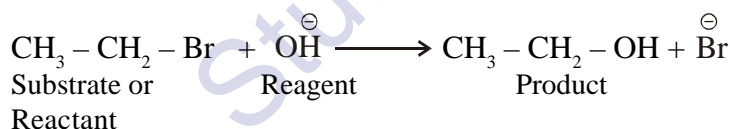


The *meta* directing influence and deactivating effect of CX_3 group for electrophilic aromatic substitution reaction can be explained by this effect.



2. CLEAVAGE OF COVALENT BOND

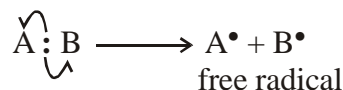
Organic reaction is a process in which breaking and formation of covalent bond/bonds take place. In organic reaction, the main organic compound which is converted into a new compound by breaking and formation of covalent bonds is known as the **reactant** or **substrate** and the new compound formed is known as the **product**. The chemical species which causes the change is called the **reagent**.



Breaking of covalent bond of the compound is known as **bond fission**. A bond can be broken by two ways:

(a) Homolytic fission or Homolysis

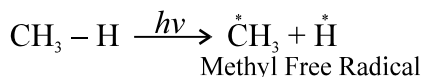
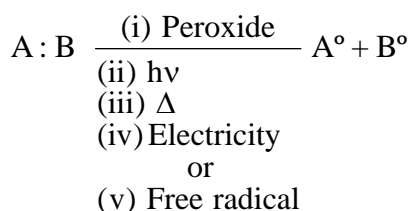
In this fission, the covalent bond is broke in such a way that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.



The factor which favours homolysis is zero or a small difference in electronegativity between A and B. Homolytic bond fission takes place in gaseous phase or in the presence of non polar solvents (CCl_4 , CS_2)

Condition for homolytic bond Fission : Homolysis takes place in the presence of peroxide. UV

light, heat ($\geq 500^\circ\text{C}$), electricity and free radical. The process is known as initiation of free radical reaction.



- (i) Homolytic bond fission gives free radical as the reaction intermediate.
- (ii) Reaction mechanism of the reaction is known as free radical or homolytic mechanism.

(b) Heterolytic Bond Fission or Heterolysis

In heterolysis, the covalent bond is broken in such a way that one species (i.e., less electronegative) is deprived of its own electron, while the other species gains both the electrons.



Thus formation of opposite charged species takes place. In case of organic compounds, if positive charge is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**. Carbocation and carbanion are the reaction intermediates. The factor which favours heterolysis is a greater difference of electronegativity between A and B.

Thus

- (1) Heterolytic bond fission gives carbocation or carbanion as reaction intermediate.
- (2) Mechanism of the reaction in which heterolytic bond fission takes place is known as heterolytic mechanism or ionic mechanism.
- (3) The energy required for heterolytic bond fission is always greater than that for homolytic bond fission due to electrostatic force of attraction between ions,

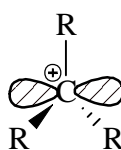
(c) Reactive Intermediates

A great majority of organic reactions are multistep processes involving intermediates whose life time are usually very short. An understanding of the structures and properties of these intermediates which are normal covalent compounds, ions or radical's is of paramount importance to an understanding of organic reaction mechanisms. As we shall see in the energy profile diagrams, intermediates possess sufficiently low energy to be formed under the reaction conditions, but in most of the cases are not stable enough to permit isolation. This is especially true of those intermediates in which carbon has fewer than four covalent bonds. A brief description of some common kinds of intermediates is given below.

Carbocations

Carbocations are the key intermediates in several reactions and particularly in nucleophilic substitution reactions.

Structure : Generally, in the carbocations the positively charged carbon atom is bonded to three atoms and has no lone pairs on carbon. Carbon has six valence electrons. It is sp^2 hybridized with a planar structure and bond angles of about 120° .

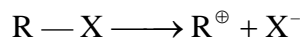


Orbital picture of carbocation

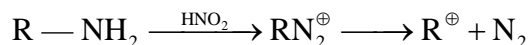
There is a vacant unhybridized p orbital which e.g., in the case of CH_3^+ lies perpendicular to the sp^2 hybridised plane..

Formation : Carbocations can be generated in a variety of way's some of the reactions in which carbocations are formed are summarized below.

1. Solvolysis of C—X bond (X = halogens, OBs, etc]



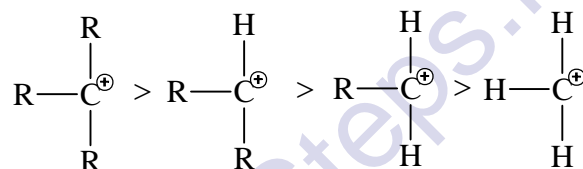
2. Deamination of amines by nitrous acid.



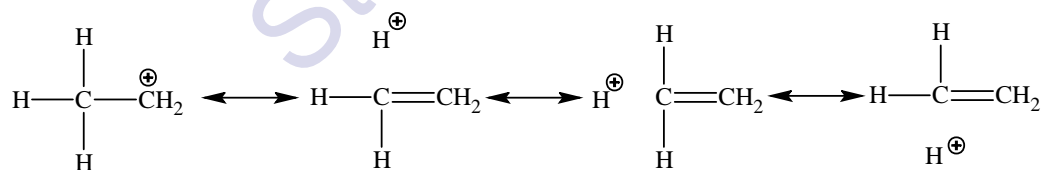
3. Protonation of alcohols followed by dehydration



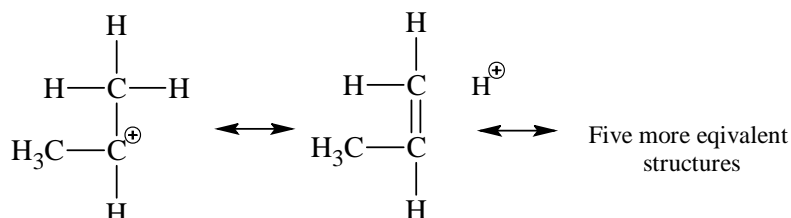
Stability: There is strong evidence, both physical and chemical, that alkyl groups are more electron-donating than hydrogen. It, therefore, follows that when these groups are attached to the electron-deficient carbon of the carbocation, they tend to release electrons and partially compensate for the electron-deficiency of the positive carbon. The positive charge thus gets dispersed over all the alkyl groups and this dispersal of charge increases the stability of the whole system. Accordingly, tertiary carbocations are more stable than secondary ones which in turn are stabler than primary carbocations.

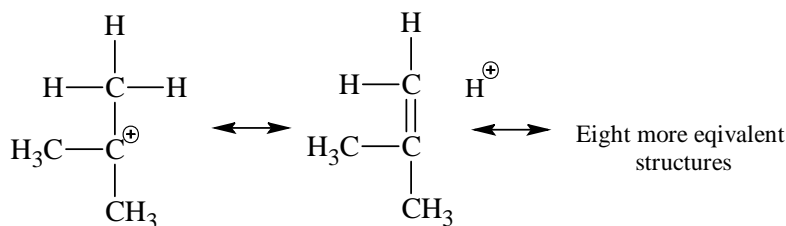


The greater stability of alkyl substituted carbocations is sometimes partly ascribed to the phenomenon of hyperconjugation. According to this, the σ electrons of an α C—H bond can be delocalized into the unfilled p orbital of the positive carbon atom, thus spreading the charge over all such bonds. For an alkyl-substituted carbocation, several hyperconjugative resonance forms can be written each having the same number of covalent bonds as the first structure.

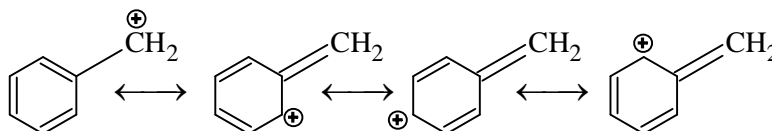
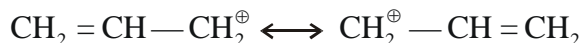


In case of a secondary carbocation, more equivalent structures can be written than for a primary carbocation whereas still greater number of such structures can be written for a tertiary carbocation.

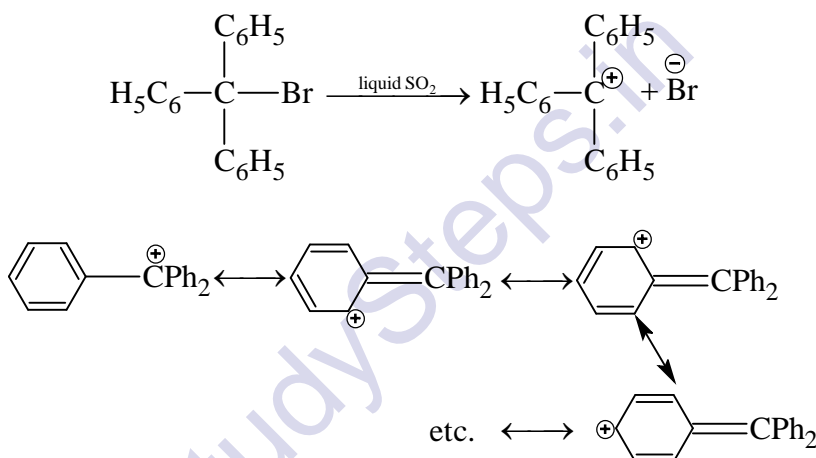




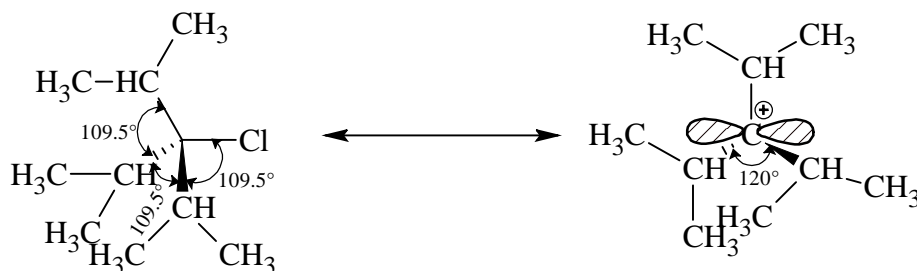
Resonance is an important factor that enhances the stability of a carbocation by delocalization of its charge in systems like allyl and benzyl carbocations.



Triphenyl carbocation is so stable that when triphenylmethyl bromide is placed in liquid sulphur dioxide (a solvent with which carbocation does not react) it is possible to determine it quantitatively by measuring the electrical conductivity of the solution.



Steric effects also play key role in the ease of formation and stability of carbocations derived from highly substituted substrates. The stability of such carbocations is attributed to the steric relief. In substrates such as tri-isopropyl chloride, the three bulky isopropyl groups are pushed together due to sp^3 angle of 109.5° . This pushing together results in a strain called B strain (or back strain). When this ionizes, the angle expands from 109.5° (sp^3) to 120° (sp^2) resulting in the relief of this strain due to increase in space between the alkyl groups.



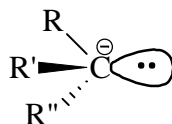
Such a carbocation would resist addition of a nucleophile as it would result in the crowding of bulky groups together.

Carbanions

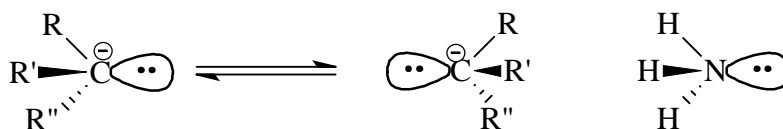
Carbanions are anions of carbon, generated by the removal of one of the groups attached to a carbon without removing the bonding electrons. Thus, every carbanion possesses one unshared pair of electrons

GOC - ISOMERISM

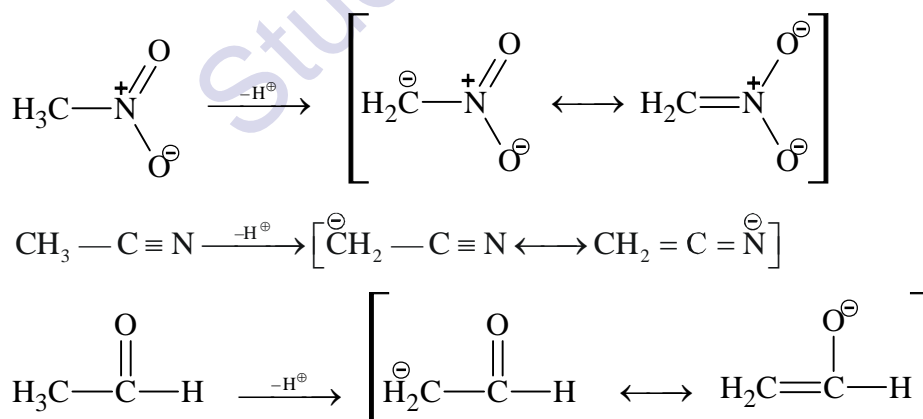
and three pairs of bonding electrons around the central carbon atom which is sp^3 hybridized.



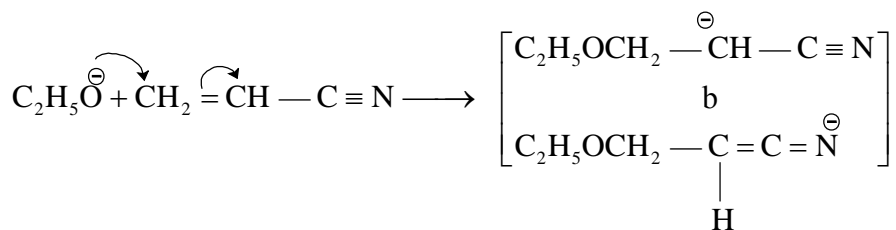
We know that the non-bonding electron pair repels the bonding pair more than the bonding pairs repel each other and because of this, there is reduction of the angle between bonding pairs to a value slightly lesser than the tetrahedral value of 109.5° . The configuration of simple carbanions such as the methyl anion thus appears to be pyramidal just like that of ammonia with which the methyl anion is isoelectronic. With this picture of carbanion, one can infer that if the three substituents are different, the carboanion should be asymmetric and consequently there should be retention of configuration in the reactions involving a carbanion intermediate. However, it could not be demonstrated experimentally as the unshared pair and the central carbon rapidly oscillate from one side of the plane to the other. This rapid equilibrium between enantiomeric pyramidal structure thus explains the loss of optical activity associated with the asymmetric carbanions.



Formation : As there is little difference between the electro negativities of carbon and hydrogen (2.5 and 2.1, respectively) the polarity of the C—H bond is very small. The heterolytic fission of this covalent bond to form an anion and a proton should then be a very difficult process. In other words, a hydrogen atom bound to an sp^3 carbon atom shows negligible acidity. However, the presence of electron attracting substituents such as nitro, cyano or carbonyl groups on the same carbon renders the hydrogen relatively acidic. The increase in acidity is not only due to the electron-withdrawing ability of these substituents, but also due to their ability to delocalize the negative charge of the anion. Thus hydrogens on the carbon atom alpha to nitro, cyano or carbonyl groups have acidic character and can be removed as protons leaving resonance stabilized anions.

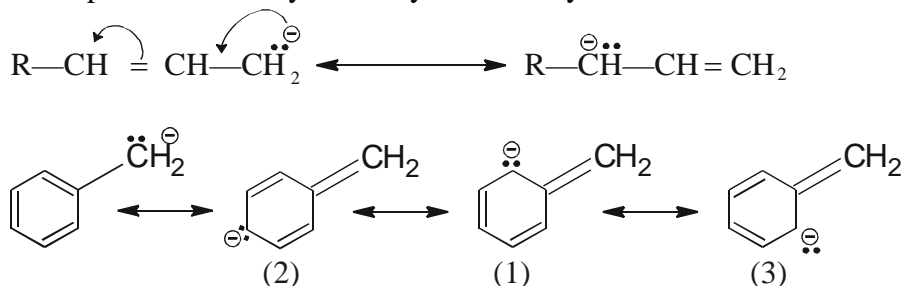


Carboanions are also formed when a nucleophile adds to a carbon-carbon double bond.

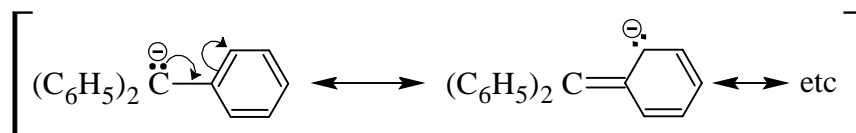
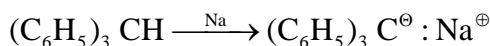


Stability : As we have already seen, carboanions are stabilized by electron-withdrawing substituents. Generally speaking, a carbanion is stabilized by resonance if a double bond is located α to the anionic

carbon. This explains the stability of the allylic and benzylic carbanions.



Ready conversion of triphenylmethane to the triphenylmethyl carbanion can be similarly explained.

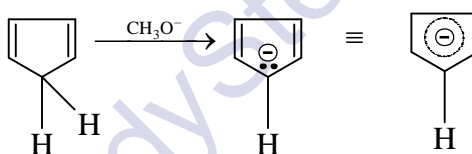


The order of stability of the simple carbanions is : methyl > primary > secondary > tertiary

Another factor that contributes to the stability of carbanions is the extent of s-character of the bonding orbitals of the carboanionic carbon. Carbanion stability, thus, has been found to be in the order:

$\text{RC}\equiv\text{C}^\ominus > \text{R}_2\text{C}=\text{CH}^\ominus > \text{R}_3\text{C}-\text{CH}_2^\ominus$. We have already seen that the carbon atom in acetylene is sp hybridized (50% s character) and hence hydrogen atom attached to it should be more acidic than that of ethylene where the carbon is sp^2 hybridized (33% s character).

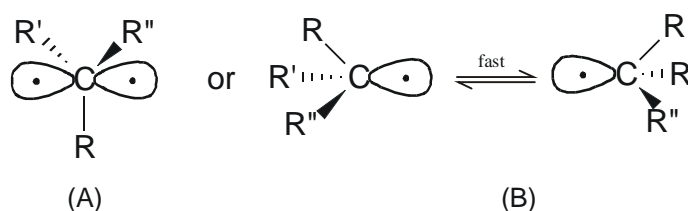
An interesting example is cyclopentadiene which readily loses a proton to form the cyclopentadienyl anion.



The unusual stability of cyclopentadienyl anion is explained by the fact that although it has only four π electrons, two more electrons become available to it by the heterolysis of the C—H bond thus forming a system of six electrons. These electrons are spread over all the five carbon atoms like the delocalized aromatic system of benzene ring, thus conferring on it stability so characteristic of the aromatic compounds.

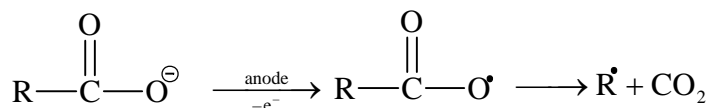
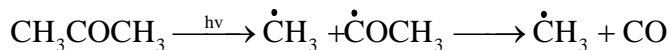
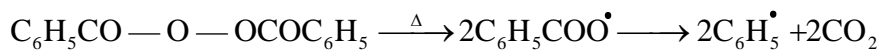
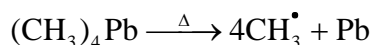
Free Radicals

There are two possible structures for simple alkyl radicals. Either a free radical may be a planar species (A) in which the carbon atom bearing the odd electron is sp^2 hybridized (as in carbocations) and the odd electron remains in the p-orbital, or it could have a shape resembling a shallow pyramid (B) which is neither planar nor tetrahedral and the orbital containing unpaired electron is some sort of a hybrid between a p and an sp^3 orbital.

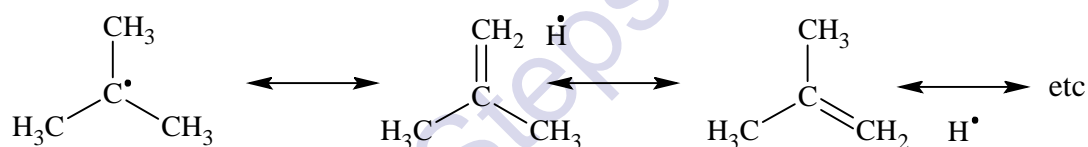


The question as to whether free radicals exist in a planar configuration or in a rapid equilibrium between the two pyramidal forms (B) is difficult to answer with certainty. However, available evidence indicates that the unpaired electron is in a p orbital. Resonance stabilized free radicals certainly exist in planar configuration.

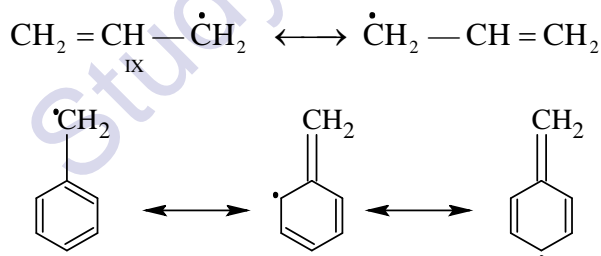
Formation : Free radicals are often produced when a molecule is supplied with sufficient energy—thermal or photochemical—to cause homolysis of a covalent bond. In addition oxidation-reduction reactions involving the gain or loss of a single electron can also generate radicals. Some typical reactions producing free radicals are given below:



Stability: In general, it has been found that the stability of alkyl radicals is in the order $(\text{CH}_3)_3\text{C}^\bullet > (\text{CH}_3)_2\text{CH}^\bullet > \text{CH}_3 - \text{CH}_2^\bullet$. The reason for the stabilizing influence of alkyl groups is not far to seek if we consider that in going from methyl to t-butyl, there is increasing tendency for electron release due to hyperconjugation. As we have seen that the carbon atom carrying an unpaired electron has a half-filled orbital that gives the radical its characteristic unstability; the hyperconjugative mechanism tends to fill this orbital and thus stabilizes the radical to some extent. Various hyperconjugative contributing forms of tert-butyl radical are given below :



Allyl and benzyl radicals are particularly stable because of resonance involving π electrons of the double bond or aromatic ring.



Another factor that is responsible for the increased stability of tertiary radicals may be steric. Formation of a tert-butyl radical by the removal of a hydrogen atom from isobutane, $(\text{CH}_3)_3\text{CH}$, is favoured as the steric repulsion between the methyl groups is relieved to a certain extent by an increase in bond angles from 109.5° to about 120° . Clearly this steric relief should be the greatest in the formation of a tertiary radical.

Carbenes

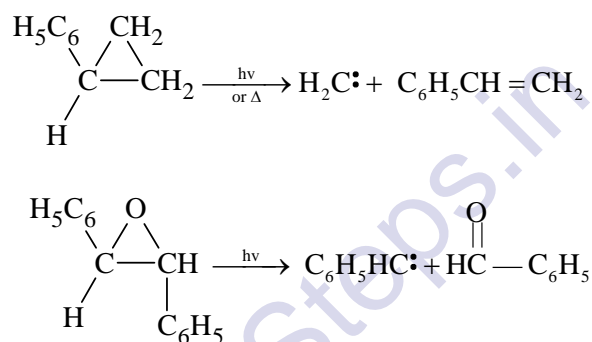
Carbenes can be defined as neutral, divalent carbon intermediates in which a carbon is covalently bonded to two atoms and has two non-bonding orbitals containing two electrons between them. Theoretical considerations suggest that there are two possible kinds of carbenes, singlet and triplet carbenes. In the singlet state, a carbon atom is presumed to approximate sp^2 hybridization. Two of the three sp^2 hybrid orbitals are utilized in forming two covalent bonds whereas the third hybrid orbital contains the unshared pair of electrons. The unhybridized p orbital remains vacant. Thus singlet carbene (A) resembles a carbocation very closely. On the other hand, carbon atom of a triplet carbene (B) is sp

hybridized and it is a linear or near-linear species. These two hybrid orbitals are involved in the bond formation with two groups and the two electrons are placed one each, in the equivalent, mutually perpendicular p_y and p_z orbitals. Since these electrons have parallel spins, a carbene with this structure is said to be in a triplet state.

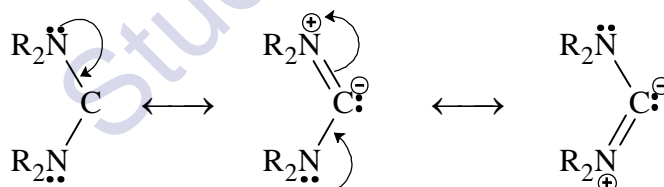


At first sight, it appears that a singlet carbene has lower energy as the unshared electron pair is in a sp^2 hybrid orbital; but the considerations of the electron repulsion energy that must be overcome to pair two electrons in a single orbital places it at the higher energy level than a triplet structure. It is, therefore, reasonable to believe that the triplet state of a carbene is more stable than the singlet state and should be expected to be the ground state.

Formation : Photochemical or thermal cleavage of cyclopropanes and oxiranes is a common method for the generation of carbenes.

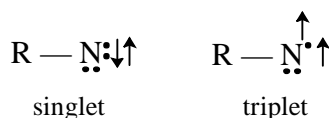


Stability: Carbenes in which the carbene carbon is attached to two atoms, each bearing an unshared pair of electrons, are somewhat more stable due to resonance.



Nitrenes

Nitrenes are electron-deficient monovalent nitrogen species in which the nitrogen atom has a sextet of electrons in its outer shell. There are two possible forms in which a nitrene can exist, the singlet and triplet states.

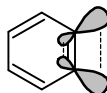


Arynes

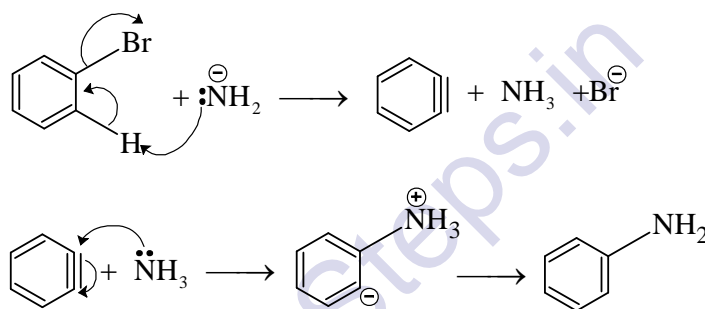
Arynes may be defined as aromatic compounds containing a formal carbon-carbon triple bond. The best known aryne is benzyne which may be regarded as the aromatic counterpart of acetylene or in other words, it is benzene minus two ortho hydrogens and can also be called as dehydrobenzene.



The benzyne bond is not like the triple bond of acetylene where the two carbons form a σ bond using sp orbitals and the remaining p orbitals are used to form π bonds. Such a structure is not possible in benzyne because of the hexagonal geometry associated with the benzene ring. Most probably the new bond of benzyne is formed by the overlap of sp^2 orbitals belonging to two neighbouring carbon atoms. These sp^2 orbitals are orthogonal to the π molecular orbital of the benzene ring.



Formation: Benzyne has been shown to be intermediate in several important organic reactions. For example, in the presence of a strong base, aryl halides eliminate HX from 1, 2-positions to produce benzyne which then rapidly reacts with the available nucleophile to regenerate the aromatic system.



Stability: The new bond of benzyne, formed by the overlap of sp^2 orbitals belonging to two neighbouring carbon atoms is unstable, and therefore benzyne is an extremely reactive chemical species.

3. NATURE OF ATTACKING REAGENTS

Organic reagents can be classified into two categories:

Electrophile: Electron deficient species or electron acceptor to form a covalent bond is electrophile.

Nucleophile: Electron rich species or electron donor to form a covalent bond is nucleophile.

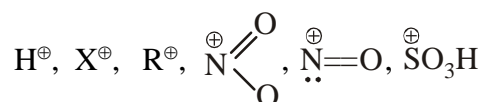
(a) Electrophiles

It can be classified into two categories:

(A) Charged electrophiles

(B) Neutral electrophiles

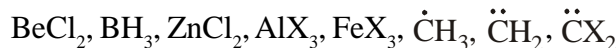
(A) **Charged electrophiles:** Positively charged species in which central atoms have an incomplete octet is a charged electrophile.



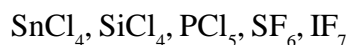
⇒ **Note:** All cations are charged electrophiles except cations of I A, II A group elements, Al^{+++} and NH_4^+

(B) Neutral electrophiles : It can be classified into three categories:

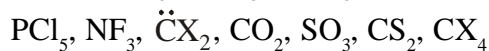
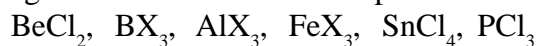
(I B) Neutral covalent compound in which central atom has incomplete octet is neutral electrophile.



(II B) Neutral covalent compound in which central atom has complete or expended octet and central atom has unfilled-d-sub-shell is neutral electrophile



(III B) Neutral covalent compound in which central atom is bonded only with two or more than two electronegative atoms is neutral electrophile.



⇒ **Note :** (i) Cl_2 , Br_2 and I_2 also behave as neutral electrophiles.

(ii) Electrophiles are Lewis acids.

(b) Nucleophiles

Nucleophiles can be classified into three categories:

(A) Charged nucleophiles: Negatively charged species are charged nucleophiles.

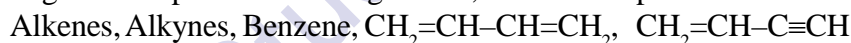


(B) Neutral nucleophiles: It can be classified into two categories:

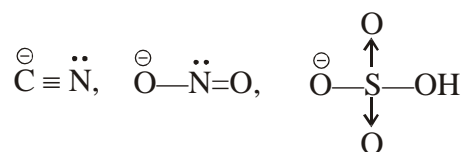
(IB) Neutral covalent compound, in which central atom has complete octet, has at least one lone pair of electrons and all atoms present on central atom should not be electronegative, is neutral nucleophile.



(IIB) Organic compound containing carbon, carbon multiple bond/bonds behaves as nucleophile.



(C) **Ambident nucleophiles:** Species having two nucleophilic centres, one is neutral (complete octet and has at least one lone pair of electrons) and other is charged (negative charge) behaves as ambident nucleophile



Note : (1) Organometallic compounds are nucleophiles.

(2) Nucleophiles are Lewis bases.

Organic compounds which behave as electrophile as well as nucleophile: Organic compound in which carbon is bonded with electronegative atom (O, N, S) by multiple bond/bonds behaves as electrophile as well as nucleophile.





Note : During the course of chemical reaction electrophile reacts **with nucleophile**.

TYPE OF ORGANIC REACTIONS

The reactions of organic compounds can be classified into four main types:

- | | |
|---|---|
| (i) Substitution or displacement reactions
(iii) Elimination reactions | (ii) Addition reactions
(iv) Rearrangement reactions |
|---|---|

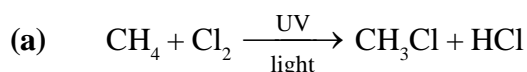
(i) Substitution or displacement reactions:

Substitution or displacement reactions are those reactions in which an atom or group of atoms attached to a carbon atom in a substrate molecule is replaced by another atom or group of atoms. During the reaction no change occurs in the carbon skeleton, i.e., no change in the saturation or unsaturation of the initial organic compound.

Depending on the mechanism, the substitution reactions are further classified into three types:

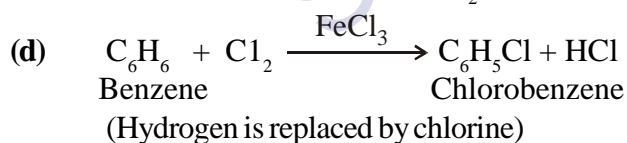
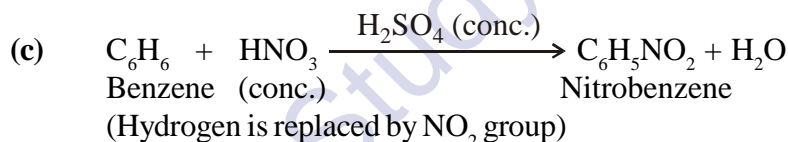
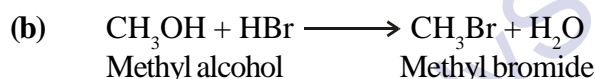
- | | |
|--|---|
| (a) Free radical substituting reactions
(c) Nucleophilic substituting reactions | (b) Electrophilic substituting reactions |
|--|---|

Some of the examples of substitution reactions are :



methane

(Hydrogen atom is replaced by chlorine)



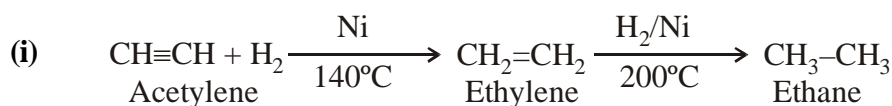
(ii) Addition reactions :

Addition reactions are those in which the attacking reagent adds up to the substrate molecule without elimination. Such reactions are given by those compounds which possess double or triple bonds. In the process a triple bond may be converted into double bond or single bonds and a double bond is converted into single bond. For each π -bond of the molecule two sigma bonds are formed and the hybridisation state of carbon atoms changes from sp and sp^2 and sp^2 to sp^3 .

Like substitution reactions, addition reactions are also of three types:

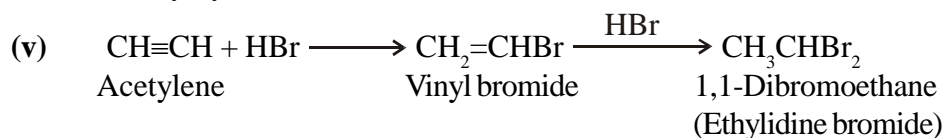
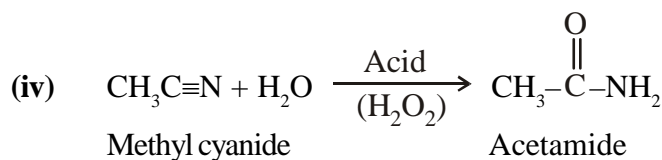
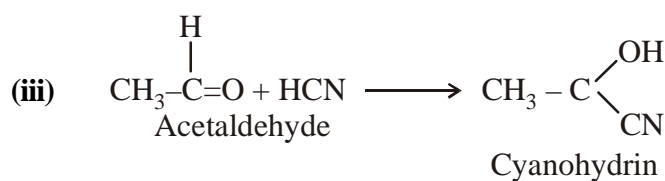
- | | |
|---|--|
| (a) Free radical addition reactions.
(c) Electrophilic addition reactions. | (b) Nucleophilic addition reactions |
|---|--|

Some of the examples of addition reactions are:



Ethylene

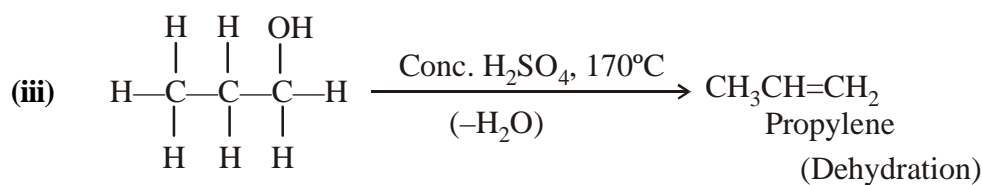
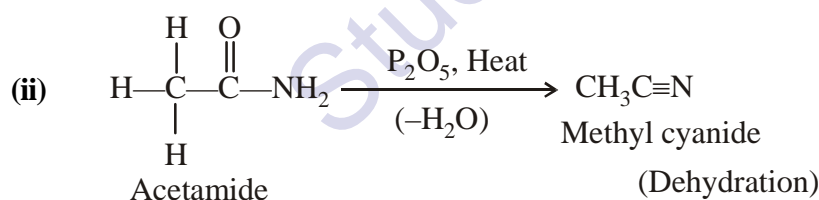
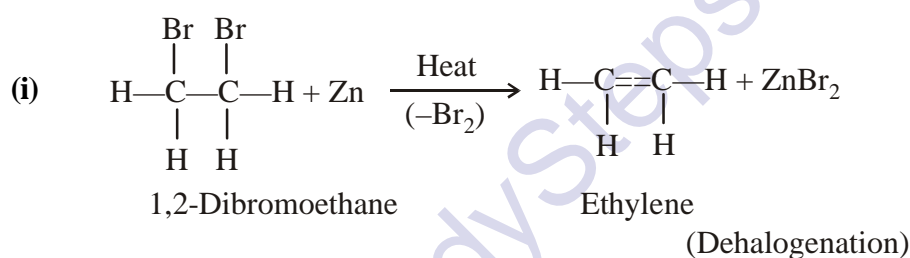
1,2-Dibromoethane
(Ethylene bromide)



(iii) Elimination reactions

The reverse of addition reactions are termed as elimination reactions. In these reactions generally atoms or groups from two adjacent carbon atoms in the substrate molecule are removed and multiple bond is formed. In the process two sigma bonds are lost and a new π -bond is formed, i.e., state of hybridization of carbon atom changes from sp^3 and sp^2 to sp .

Some example are :

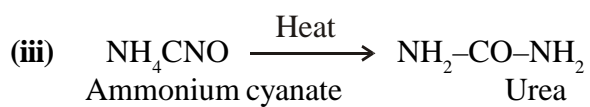
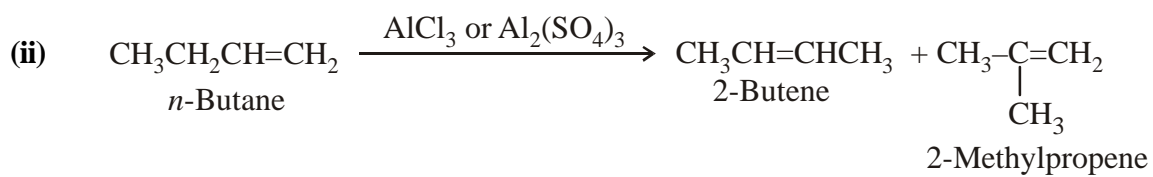
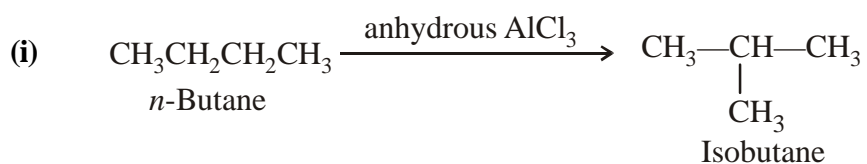


(iv) Rearrangement reactions:

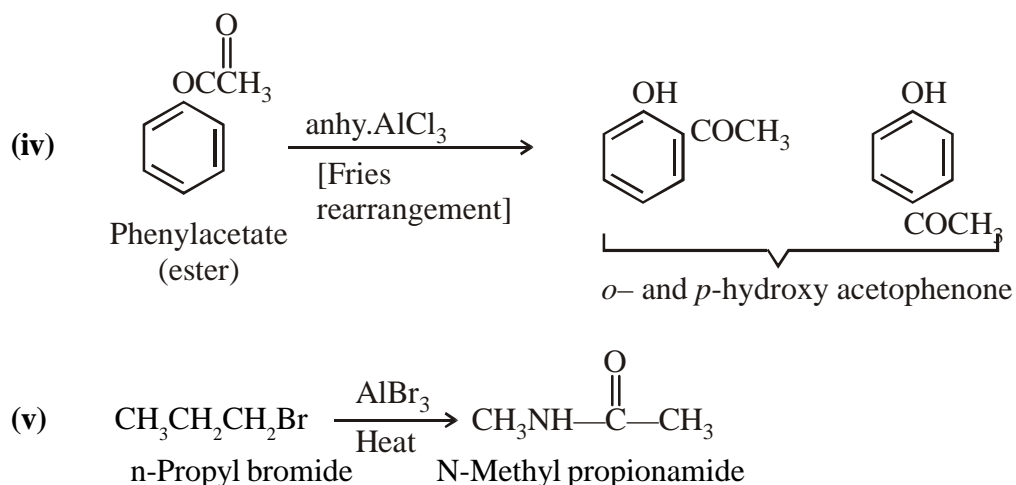
The reaction which involve the migration of an atom or group from one site to another within the molecule (nothing is added from outside and nothing is eliminated) resulting in a new molecular structure are known as rearrangement reactions. The new compound is actually the structural isomer of the original one.

Some of the examples are :

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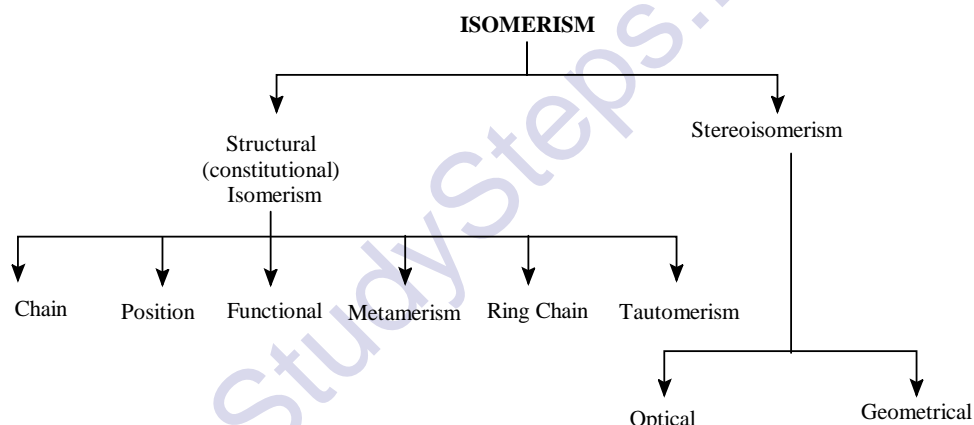


StudySteps.in



ISOMERISM

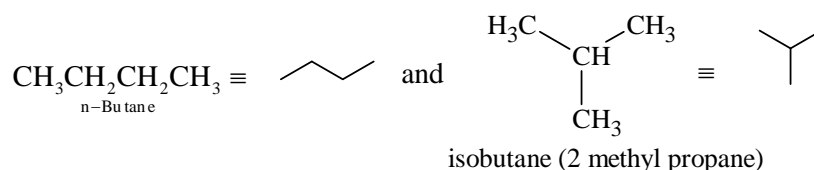
Different organic compounds with the same molecular formula but different physical and chemical properties are called isomers and the general phenomenon is known as isomerism. It is classified as follows.

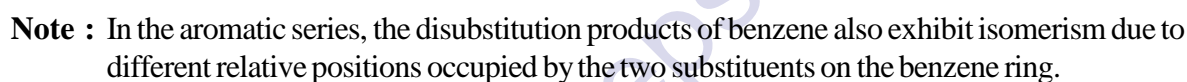


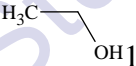
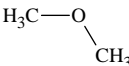
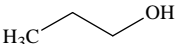
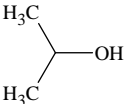
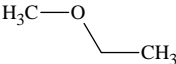
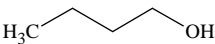
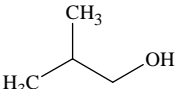
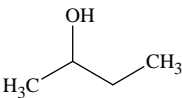
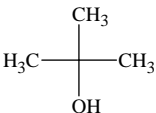
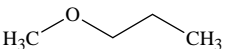
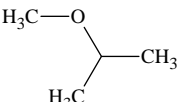
Structural Isomerism

Compounds which possess the same molecular formula but differ in bonding arrangement of atoms (or) groups within the molecule i.e. differ in structure [A structural formula for a compound conveys which atom is directly linked to which other atom. It, however, tells nothing about the shape of the molecule but indicates the groups of elements present which provide clues to the properties of the substance], are structural isomers and this phenomenon is known as structural isomerism.

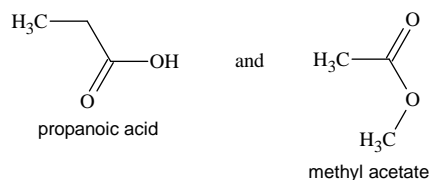
- (i) **Chain or Nuclear Isomerism:** In this type the isomers differ in the variation of the carbon chain (or) skeleton of the molecule. The same molecular formula may represent a straight chain of carbons as well as a branched chain. The molecular formula C_4H_{10} stands for two isomers namely n-butane and isobutane.



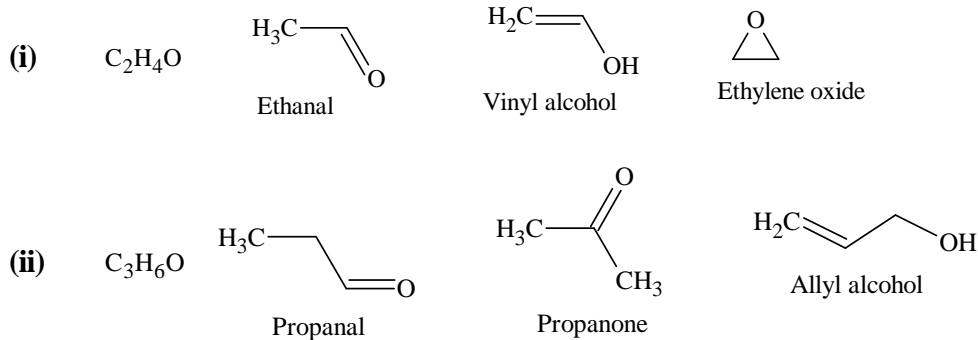


a)	Molecular formula	p-alcohol	s-alcohol	t-alcohol	Ethers
	C_2H_6O	 ethanol	—	—	 dimethyl ether
	C_3H_8O			—	
	$C_4H_{10}O$	 			 

b) Monocarboxylic acids and esters are functional isomers

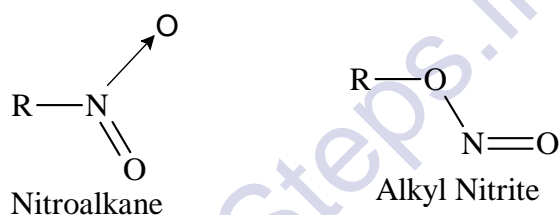


c) Aldehydes, ketones, unsaturated alcohols and alkene oxides are functional isomers.

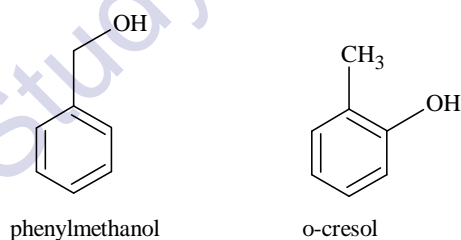


(iii) Cyanides are isomeric with isocyanides
 RCN (Alkyl cyanide) RNC (alkyl isocyanide)

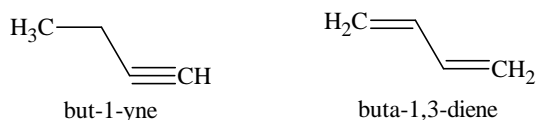
(iv) Nitroalkanes are isomeric with alkyl nitrites



(v) Aromatic alcohols may be isomeric with phenols



(vi) Sometimes a double bond containing compound may be isomeric with a triple bond containing compound. This is also called as functional isomerism. Thus butyne is isomeric with butadiene (Molecular formula C_4H_6)



(vii) Primary, secondary and tertiary amines of some molecular formula are also the functional isomers.

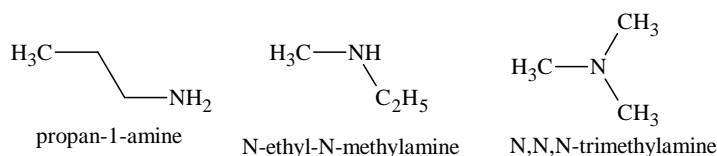
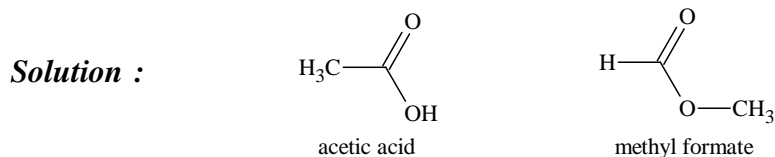
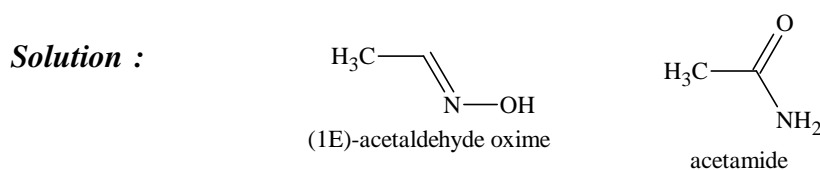


Illustration 4 : Give the functional isomer for acetic acid



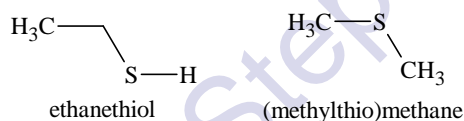
Monocarboxylic acids and Ester's are functional isomers.

Illustration 5 : Give the functional isomer for acetaldoxime.



Oximes and amides are functional isomers.

Illustration 6 : Give the functional isomer for ethyl thioalcohol.



Thioalcohols and thio ethers are functional isomers.

(iv) **Metamerism :** It arises when different alkyl radicals are joined with the same divalent functional group present in the molecule, e.g. ethers, thioethers, secondary amines, ketones, esters etc.

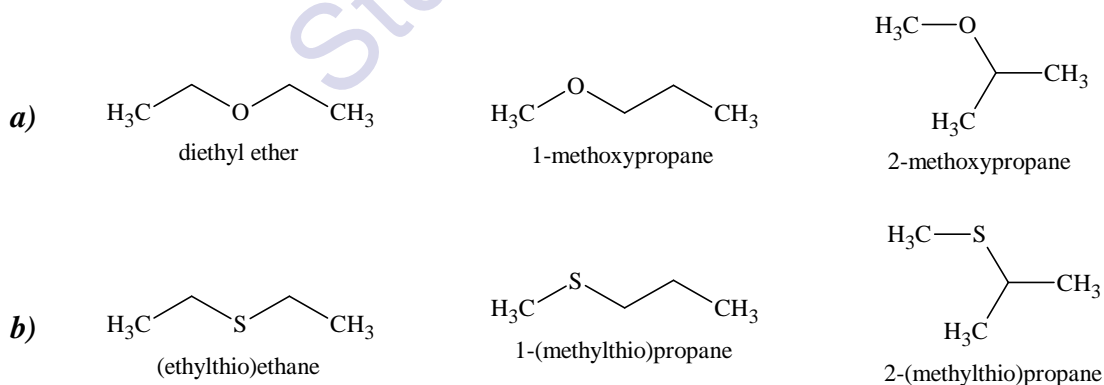
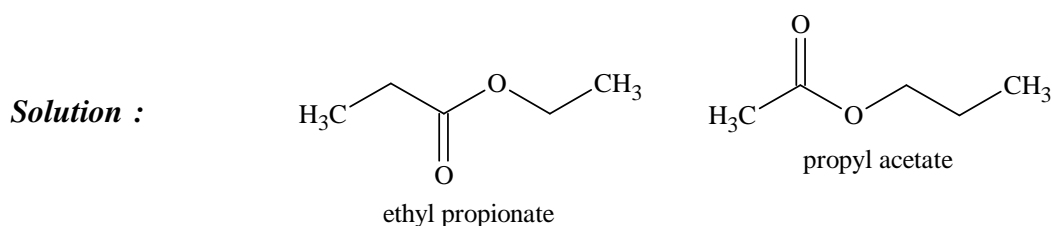


Illustration 7 : Give the metamer for ethyl propionate.

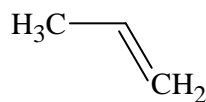


(v) **Ring Chain Isomerism :** This type of isomerism is due to difference in way of linking of carbon atoms and the isomers may have either open chain (or) closed chain structure e.g. alkenes and

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cycloalkanes.

a) C_3H_6

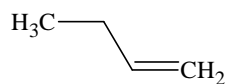


prop-1-ene

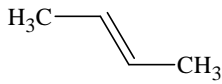


cyclopropane

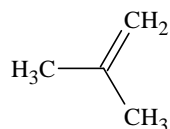
b) C_4H_8



but-1-ene



but-2-ene



2-methylprop-1-ene

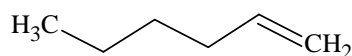


cyclobutane

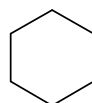


methylcyclopropane

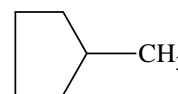
c) C_6H_{12}



hex-1-ene



cyclohexane



methylcyclopentane

Note: Ring chain isomers are always functional isomers.

Tautomerism

It is a special type of functional isomerism in which the isomers are readily interchangeable and maintain a dynamic equilibrium with each other. Hence, the name dynamic isomerism. Both the isomers represent one and a single substance. Reversibility of change is due to mobility of a group or atom which can move from one position to another in the molecule, often with rearrangement of a double bond. These two forms are called **tautomers** and **tautomerides** of each other.

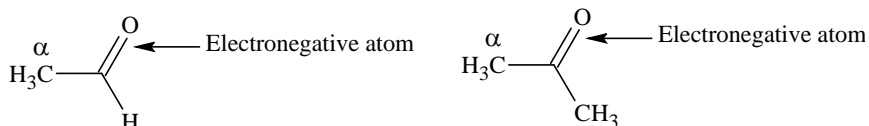
Various terms used for tautomerisms

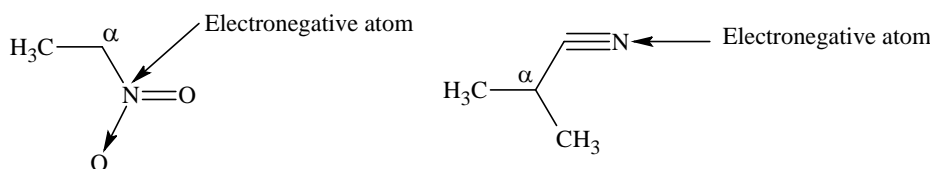
- | | |
|------------------|--|
| (a) Desmotropism | [desmos = bond ; tropos = turn , (From Greek)] |
| (b) Pseudomerism | (c) Kryptomerism |
| (d) Metamerism | (e) Allelotropism |

Structural requirement for tautomerism

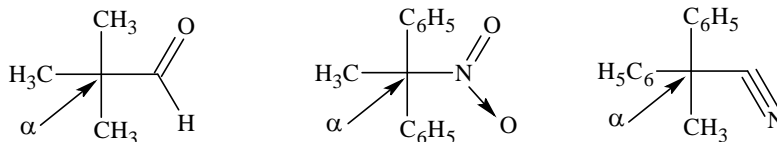
- (i) Compound should have electronegative atom bonded with multiple bond (i.e. N and O).
- (ii) Compound should have at least one acidic hydrogen present on α -carbon of the molecule.

If the compound favours these two conditions it will show tautomerism. For example.



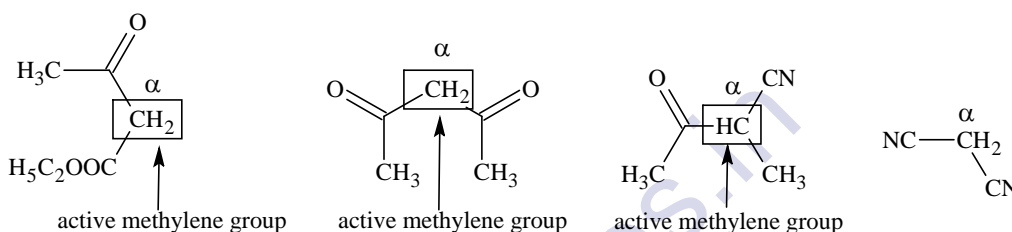


These compounds fulfill both the conditions, hence these will show tautomerism.



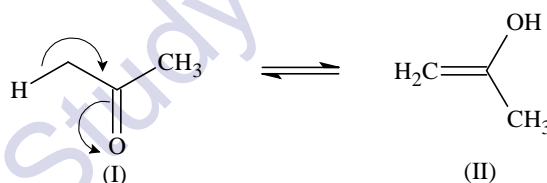
In these compounds electronegative atom is bonded with multiple bond but compound has no hydrogen on α -carbon hence these compounds will not show tautomerism.

If compound has active methylene group (or) active methyne group then α -carbon for tautomerism is always carbon of active methylene (or) methyne group. For example



These compounds will also show tautomerism because these compounds fulfill both structural requirements.

Cause of tautomerism : Migration of acidic hydrogen from α -carbon to electronegative atom which is bonded with multiple bond is the cause of tautomerism and this phenomenon is known as tautomerism.



- (i) Both (I) and (II) are isomers known as tautomers.
- (ii) Tautomers are always in equilibrium state.
- (iii) Number of sigma, pi and lone pair of electrons in both tautomers are always same.
- (iv) Tautomerism is a chemical phenomenon which takes place only in liquid state.
- (v) Tautomerism is catalysed by acid as well as base.
- (vi) Tautomers are always reversible functional groups, functional isomers.

Distance between tautomerism and resonance

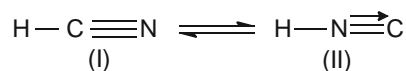
- Tautomers of a compound actually exist and can be separated. On the other hand, resonating structures are imaginary and question of separation of such structure even does not arise.
- Tautomers are different in the position of at least one atom relative to other atoms in the molecule. **Chief difference is the position of electrons and f -electrons or unshared e^- not the atom.**
- Position of ions in tautomers differ in bond length, i.e., migratory part has different bond lengths in two cases of its attachment in appreciable difference. In resonating structure, difference is not more than 0.3\AA , i.e., two extreme case in benzene are 1.54\AA and 1.33\AA .
- Tautomers are in dynamic equilibrium \rightleftharpoons interconvertible and no such equilibrium in resonance.
- Tautomerism has no contribution on stabilization of a molecule resonance has its effect on stabilization.
- Tautomerism may occur in planar or non-planar while resonance only in planar.

Tautomerism is of several types the two important types are dyad and triad systems :

Dyad System: It involves the oscillation of hydrogen between two polyvalent atoms, e.g., hydrogen

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cyanide (I) and hydrogen isocyanide (II).

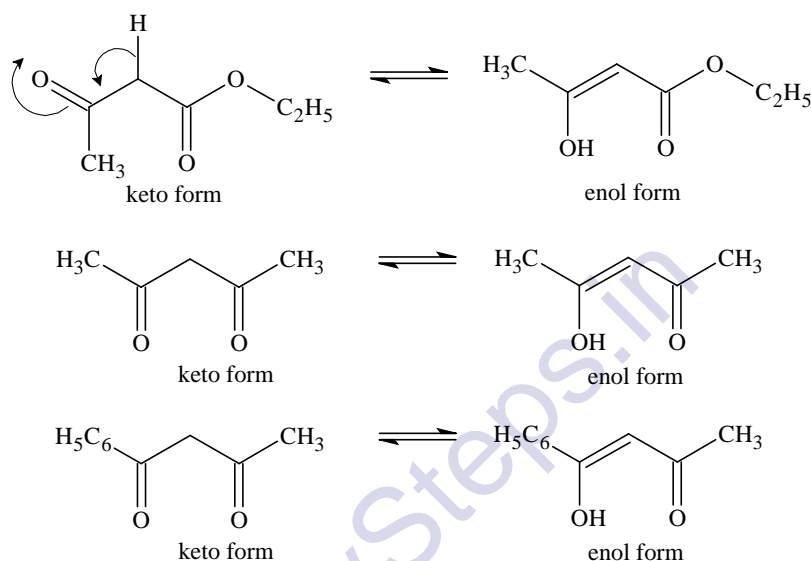


In the above example the H atom vibrates between carbon and nitrogen atoms. The alkyl derivatives of (I) are called cyanides while those of (II) isocyanides.

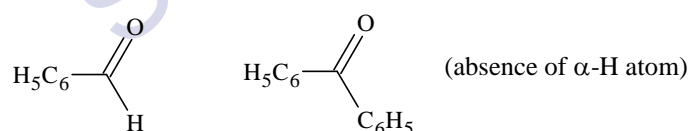
(b) **Triad System:** In it one H atom oscillates between three polyvalent atoms.

(i) **Keto-enol tautomerism:** In this case the polyvalent atoms are one oxygen and two carbon atoms, e.g. aceto acetic ester, acetyl acetone, benzoyl acetone, acetaldehyde, acetone, phenol etc.

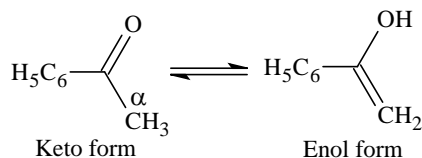
The form containing keto (oxo) group is called keto while that having alkene and -ol functions is called an enol form.



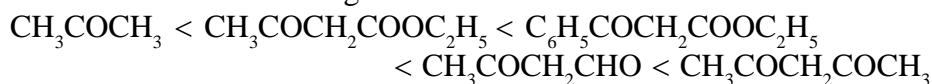
The conversion of a keto form into enol form is known as enolization. It is catalysed by the presence of acid (or) alkali. This dynamic isomerism is shown only by those aldehydes, ketones or esters which have at least one labile α -hydrogen atom. For example, benzaldehyde and benzophenone do not have labile α -hydrogen, hence these do not show tautomerism.



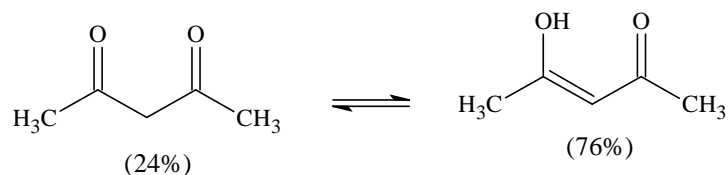
On other hand, acetophenone contains α -H atoms, hence exhibits tautomerism.



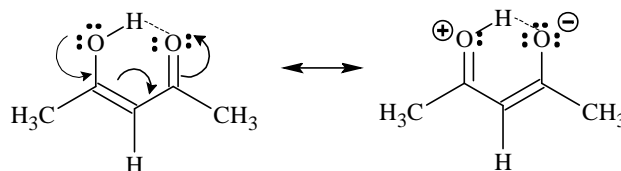
Enolization is in the following order:



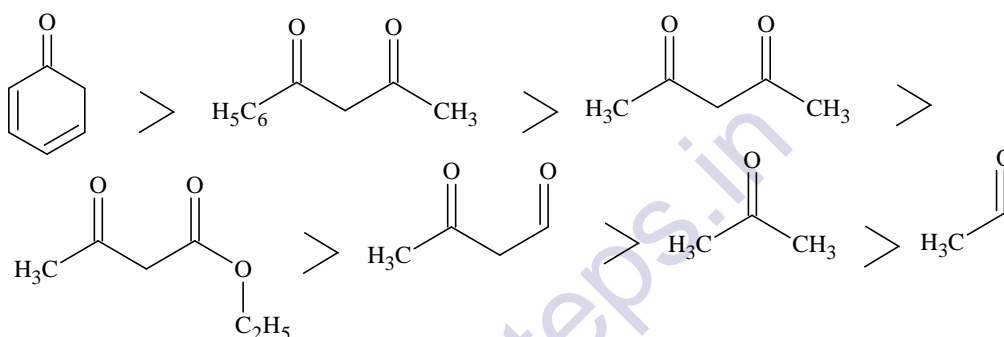
In compounds whose molecules have two carbonyl groups separated by one $-\text{CH}_2-$ group (called β -dicarbonyl compounds), the amount of enol present at equilibrium is far higher e.g.



The greater stability of the enol form of β -dicarbonyl compounds can be attributed to stability gained through resonance stabilization of the conjugated double bonds and (in a cyclic form) through hydrogen bonding.

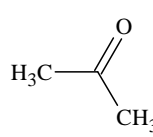
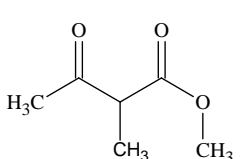
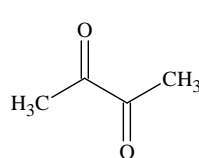
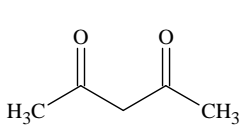
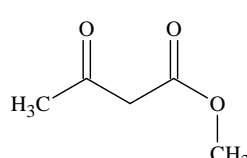
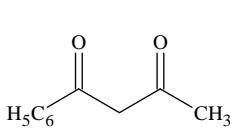


Percentage of enolic contents of some common compounds in decreasing order is given below:

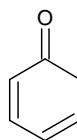
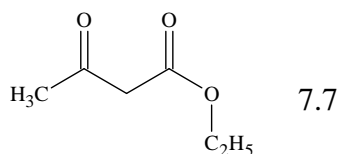


Percentage Composition of Tautomeric Mixture : Percentage of enol contents of some compounds is given below in the table.

Enol content of some compounds

Compound	Enol Percentage	Compound	Enol Percentage
	0.00025		31.00
	0.0056		80.4
	4.8		89.0

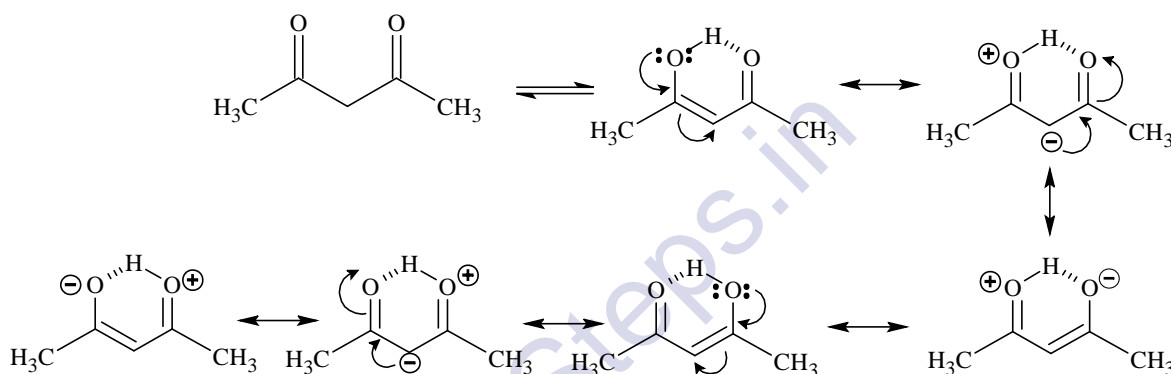
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99.99

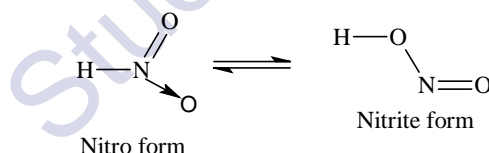
The conversion of a keto form into an enol form is known as enolisation and the enolisation of a compound has been found to depend upon various factors such as structural factor, temperature and nature of solvent. However, the most important is the structural factor (resonance and hydrogen bonding).

- (a) Ketonic form predominates in simple monocarbonyl compounds like acetaldehyde, acetone and cyclohexanone. This is due to the greater bond strength of $C=O$ ($>C=O$, 365 kJ/mole) present in keto form than the carbon-carbon double bond ($C=C$, 250 kJ/mole) present in enolic form.
- (b) Enolic form predominates in β -di ketones due to intramolecular hydrogen bonding and resonance. Intramolecular hydrogen bonding stabilizes enol form by 7 kcal/mole and resonance stabilizes enol form by 15 kcal/mole. Thus enol form is more stable than keto form by 22 kcal/mole in 1,3-diketones.



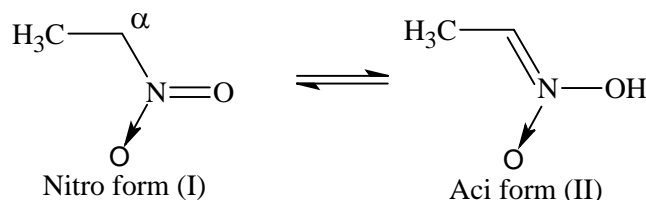
(ii) Triad System containing Nitrogen

- (a) Nitrous acid exists in two tautomeric forms:

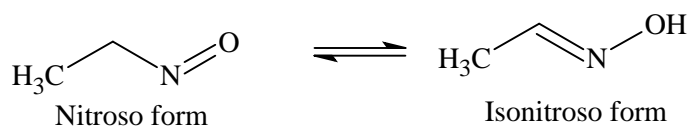


The alkyl derivatives of nitro form and nitrite form are called as nitro alkanes and alkyl nitrites, respectively.

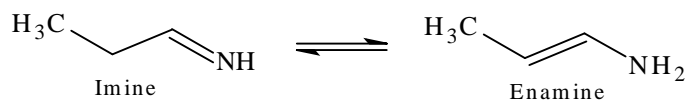
- (b) Primary and secondary nitroalkanes have liable α -H atom, hence exhibit nitro-ac nitro type of tautomerism.



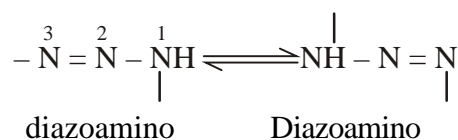
- (c) **Nitroso-oximino System:** In this system one tautomer exists as nitroso while the other tautomer exists as an isonitroso (oxime) form.



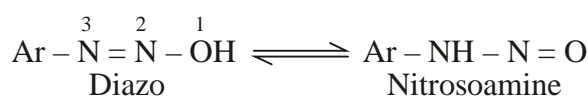
(d) Imine-Enamine System



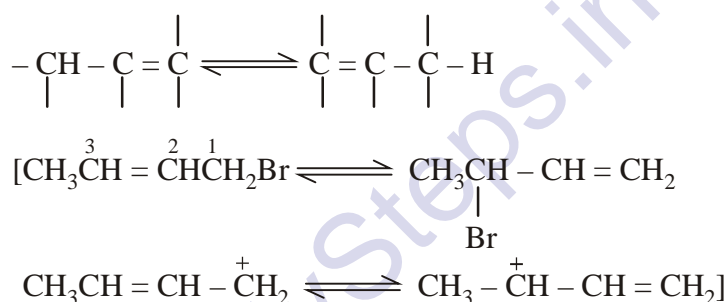
(e) Diazo-amino: Triazen system or Mesohydric tautomerism:



(f) Diazo-nitrosamine system :

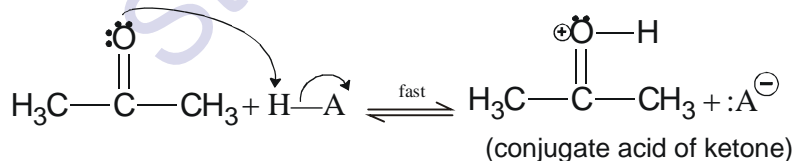


(g) Three carbon system:

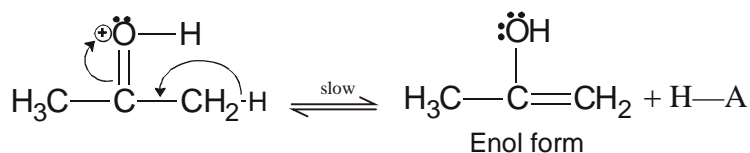


Mechanism of tautomerism : Acid catalysed tautomerism is a two step process.

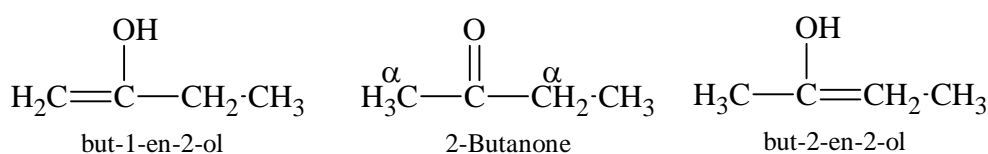
- (i)** Proton transfer from the acid catalyst, H—A, to the carbonyl oxygen forms the conjugate acid of the aldehyde (or) ketone.



- (ii)** Proton transfer from the α -carbon to the base, A^- gives the enol and generates a new molecule of the acid catalyst, H—A.



with unsymmetrical ketones, enolization may occur in either of two directions.



the ketone is by far the most abundant species present at equilibrium. Both enols are also present, but in very small concentrations. The enol with the more highly substituted double bond is the more stable of

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the two enols and is present in higher concentration than the other.

- * Percent enol content \propto conjugation
 - \propto / Temperature
 - \propto / Hydrogen bonding
 - \propto / Base strength

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