

Structural Theory in Organic Chemistry

SAIKRISHNA UGGU

Lecturer in Chemistry

P. R. Govt. College (A)
KAKINADA

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- TYPES OF ORGANIC REACTIONS
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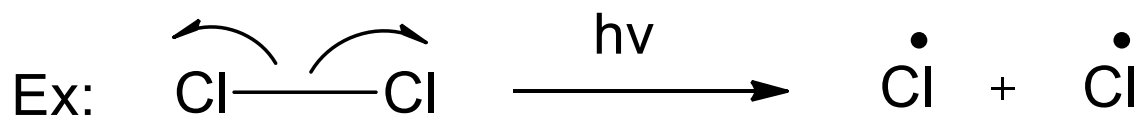
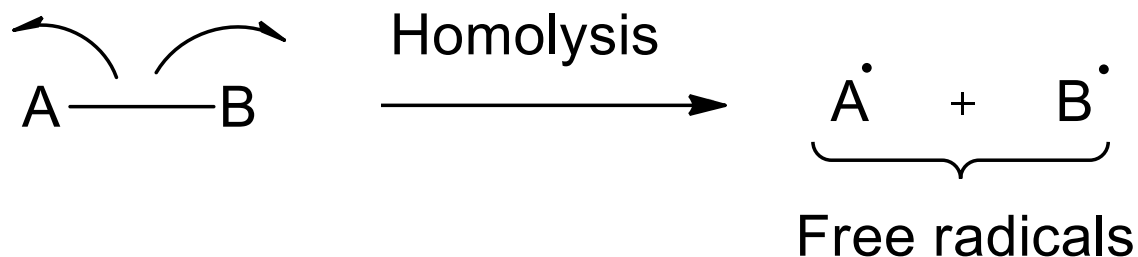
Bond fission

- A covalent bond is formed when two electrons are shared between two atoms.
- Now a chemical reaction takes place when old bonds are broken and new ones are formed.
- Bond making and breaking is takes place by two ways,
- Homolysis and Heterolysis



Homolytic Fission or Homolysis

In this type of fission shared electron pair is distributed equally between two bonded atoms.



Homolytic Fission Characteristics

- It is shown by half headed arrow 
- The two fragments formed in this cleavage are neutral species and each one has one unpaired electron. These species are called as free radicals.
- High temperature, Light ($h\nu$) and peroxides are used in Homolytic fission for the production of free radicals.
- The reactions involved in free radicals as intermediates are called free radical reactions and are proceed through free radical mechanism.

Heterolytic Fission or Heterolysis

- In this case we can see that one of the atoms carry a negative charge after bond cleavage indicating that it has both the electrons of the bond and the other has no electrons at all.
- Hence it is electron deficient thus positively charged. As the electrons are not divided equally after bond cleavage this is called Heterolytic Fission.

Heterolytic Fission

- In a case the C atom carries a positive charge it is called a carbocation and in the case it carries both the electrons of the broken bond and is negatively charged, it is called a Carbanion.
- Carbocation and Carbanions are the most important carbon intermediates in organic chemistry.

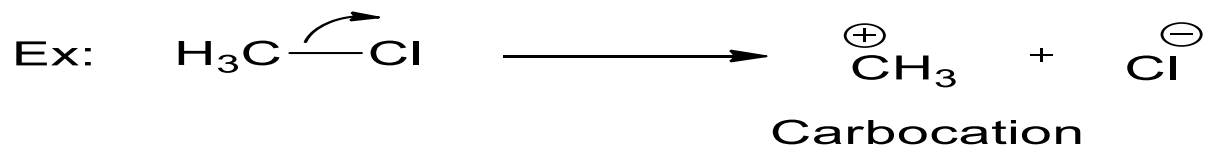
Types of Heterolytic Fission

This Heterolytic fission takes place in two ways based on the electro negativity difference of the two atoms in the compound



Types of Heterolytic Fission

1) If B is More electronegative than A



2) If A is More electronegative than B



Organic Reagents

There are three types of organic reagents

Electrophiles: These are electron deficient species and attacks at centre of maximum electron density or at negatively charged centre of the molecules. These act as Lewis Acids. Electrophiles are of two types ,

a) Positive Electrophiles: these are carrying positive charge

Ex: All carbocations, H^+ , H_3O^+ , Cl^+ , NO^+ etc.

b) Neutral Electrophiles:

These are neutral species

Ex: AlCl_3 , BF_3 , SO_3 etc.



Nucleophiles: These are electron rich in species and attack at the centre of minimum electron density or at positively charged centre of the molecules. These act as Lewis Bases. Nucleophiles are two types,

a) Negative Nucleophiles: these are carrying Negative charge
Ex: All Carbanions, H^- , OH^- , Cl^- , RCOO^- etc.

b) Neutral Nucleophiles: these are Neutral species Ex: H_2O , NH_3 .



Free Radicals: These are Neutral species and contains an unpaired or odd number of electrons

a) These are produced by homolysis of covalent bond

b) Free radicals are paramagnetic in nature due to presence of odd electron

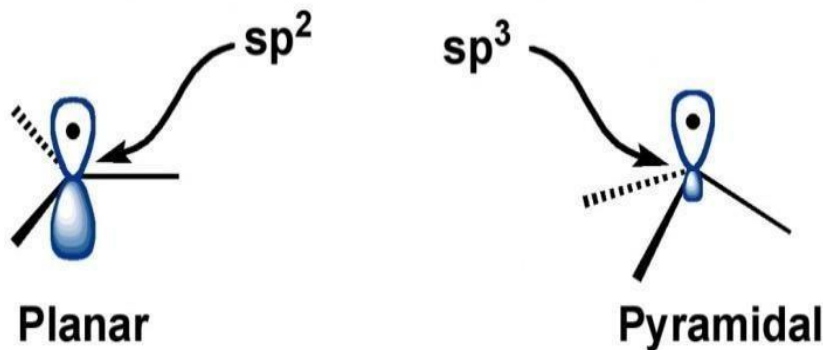
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Ex: $\text{Cl}\cdot$, $\text{CH}\cdot$ etc.

Free radicals

These are neutral intermediates, formed due to homolytic cleavage of a single bond.

Some common bonds which cleave to give free radicals in organic chemistry are shown: C-O, C-CL, C-BR, C-I, C-C, C-H.



Carbocations

Carbocations are formed from the heterolytic cleavage of a carbon- heteroatom bond where the other atom is more electronegative

than carbon like a C-O, C-N, C-X (X can be Cl, Br, I, etc) bond.

After the cleavage if a carbocation is to be formed the two electrons of the bond must go to the other atom. And this is favoured if that other atom is electronegative. Formation of carbocations can be assisted by using cations

Carbanions

These are intermediates formed as a result of heterolysis, but here the electron pair from the bond is kept by the carbon atom.

From what we saw earlier the more electronegative atom keeps the electrons, so in this case carbon must be the more electronegative of the two atoms making up the bond.



ORGANIC REACTIONS

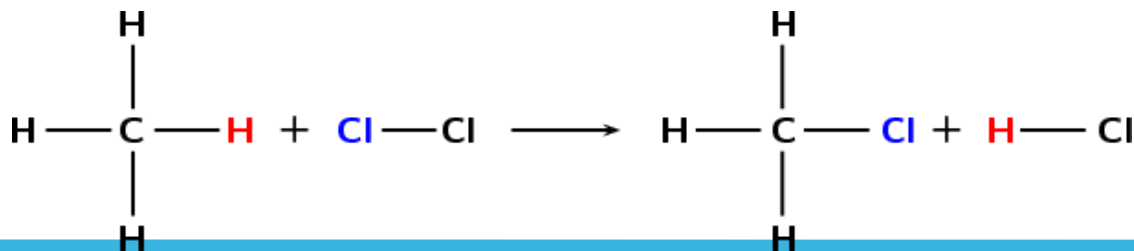
There are four types of organic reactions

1. Substitution reaction
 2. Elimination reaction
 3. Addition reaction
 4. Rearrangement reaction
- 

Substitution reaction

In a substitution reaction one atom or a group of atoms is substituted by another atom or a group of atoms to form a new substance. Example C-Cl bond, in which the carbon atom has partial positive charge due to the presence of highly electronegative chlorine atom.

In a nucleophilic substitution reaction the nucleophile must have a pair of electrons and also should have high affinity for the electropositive species as compared to the substituent which was originally present.



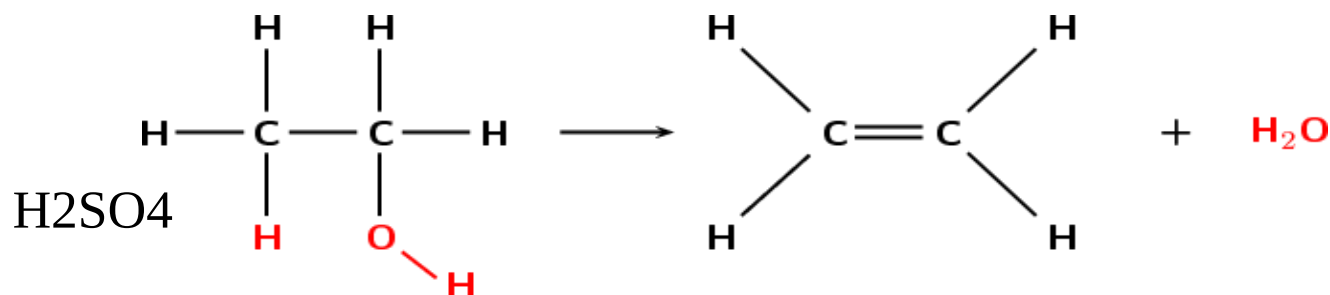
Elimination reaction

There are some reactions which involve the elimination or removal of the adjacent atoms. After these multiple bonds are formed and there is a release of small molecules as products.

One of the examples of elimination reaction is the conversion of ethyl alcohol to ethylene.

Dehydration of an alcohol

During the dehydration of an alcohol the **hydroxyl** ($-\text{OH}$) group and a **hydrogen atom** are **eliminated** from the reactant. A molecule of water is formed as a product in the reaction, along with an alkene.

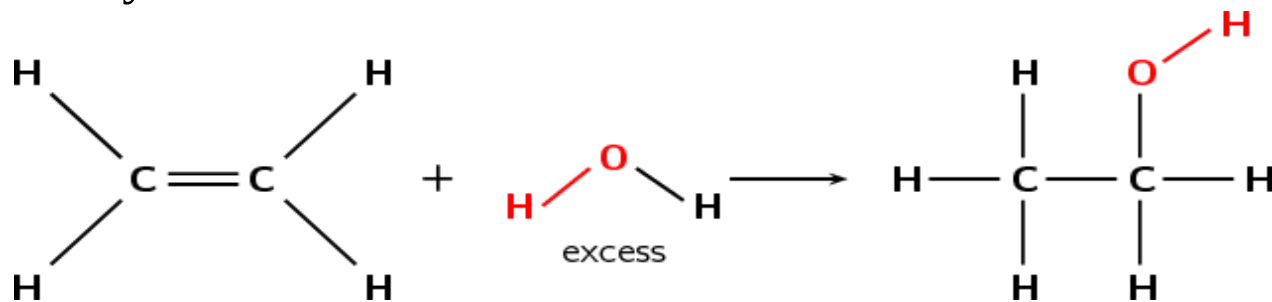


Addition reaction

Addition reaction is nothing but just the opposite of elimination reaction.

An **addition reaction** occurs when two or more reactants combine to form a single product. During addition reaction unsaturated molecules will become saturated.

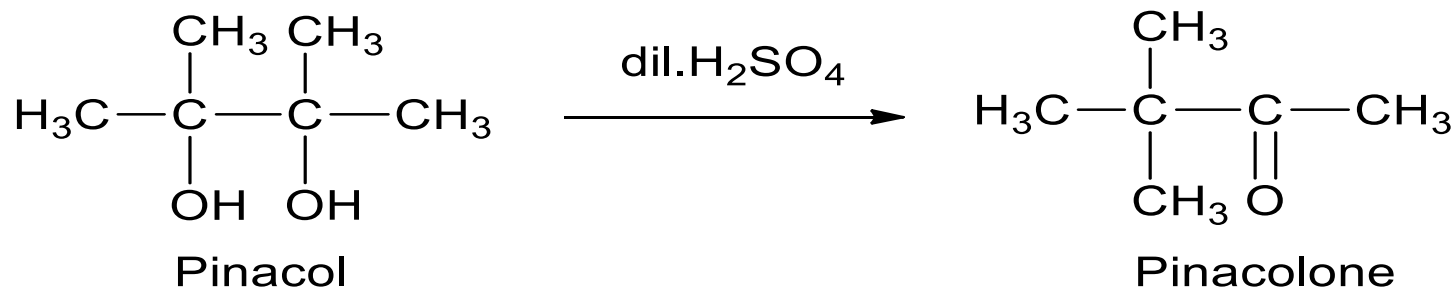
In the reaction given below when HOH is added to ethylene it will give us ethyl alcohol.



Rearrangement Reactions

In these reactions migration of group or atom takes place at intermediate stage as a result rearranged carbon skeleton products are formed.

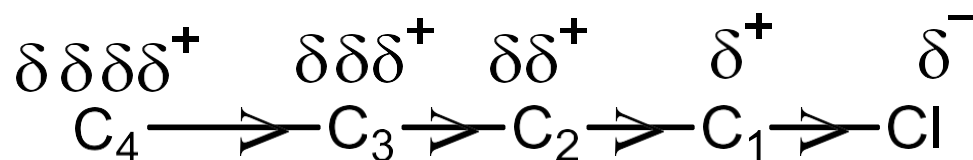
Ex: Pinacol – Pinacolone rearrangement



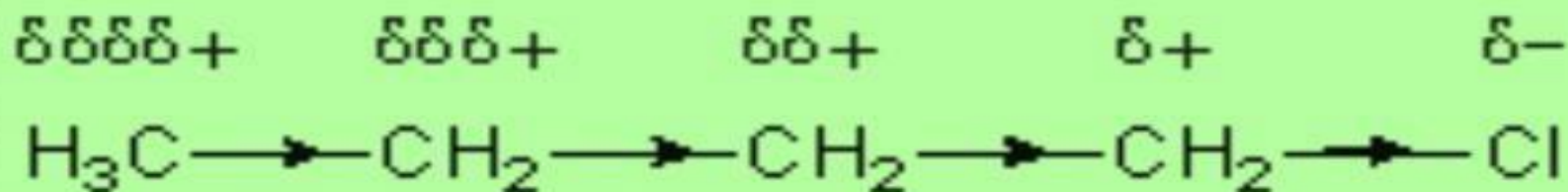
Inductive effect

it is defined as permanent displacement of an electron pair in a sigma bond towards more electronegative atom or group in a carbon chain is called as Inductive effect.

- a) It arises due to electro negativity difference between two atoms forming sigma bond
- b) It is transmitted through sigma bonds and its effect decreases as the carbon chain length increases, significant up to 3 or 4 carbon atoms after that it is negligible.
- c) It is denoted by $\rightarrow$



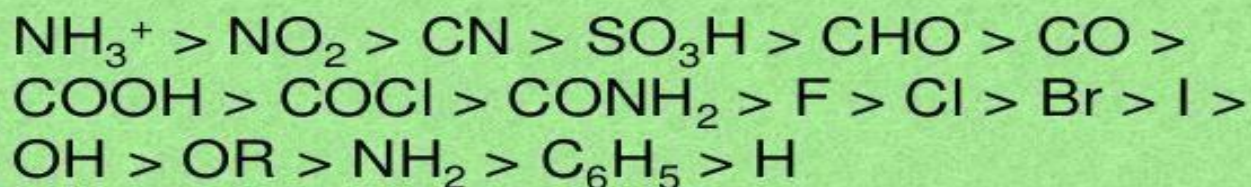
- Inductive effect weakens away along the chain and is not significant beyond 3rd carbon atom



TYPES OF INDUCTIVE EFFECT

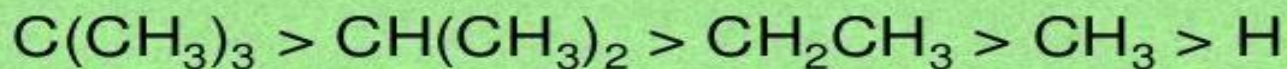
1) Negative inductive effect (-I):

The electron withdrawing nature of groups or atoms is called as negative inductive effect. It is indicated by -I. Following are the examples of groups in the decreasing order of their -I effect:



2) Positive inductive effect (+I):

It refers to the electron releasing nature of the groups or atoms and is denoted by +I. Following are the examples of groups in the decreasing order of their +I effect.

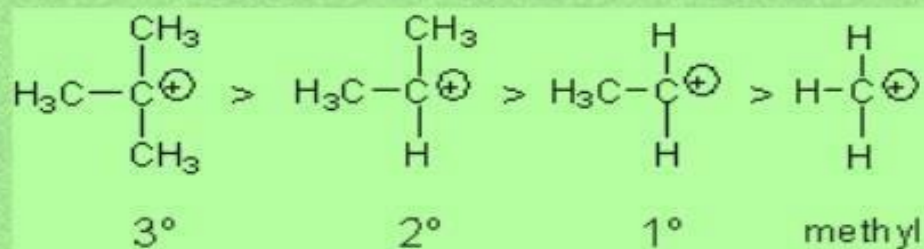


• APPLICATIONS OF INDUCTIVE EFFECT

1. Stability of carbocations:

The stability of carbocations increases with increase in number of alkyl groups due to their +I effect. The alkyl groups release electrons to carbon, bearing positive charge and thus stabilizes the ion.

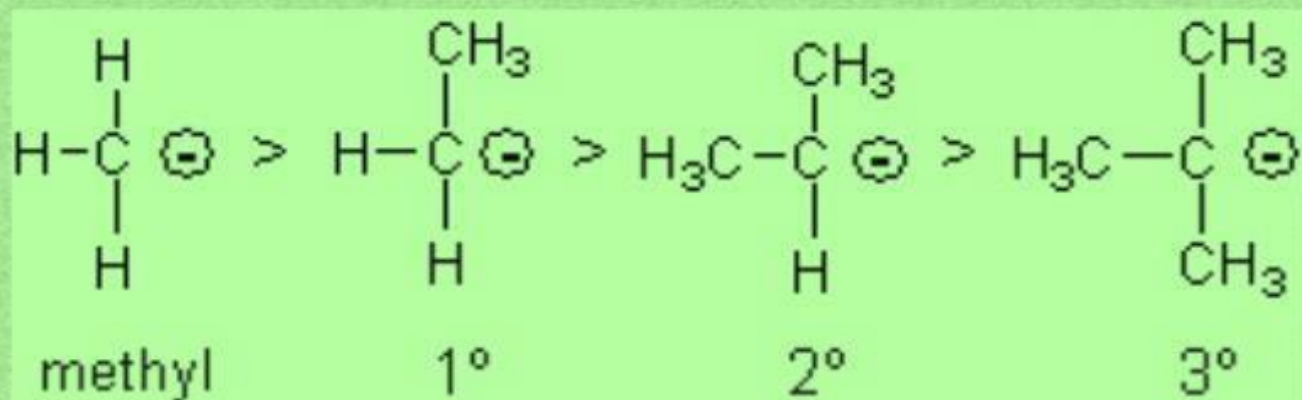
The order of stability of carbocations is :



2. Stability of carbanions:

However the stability of carbanions decreases with increase in the number of alkyl groups since the electron donating alkyl groups destabilize the carbanions by increasing the electron density.

Thus the order of stability of carbanions is:



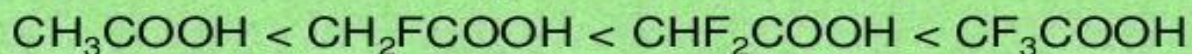
3. Acidic strength of carboxylic acids and phenols:

The electron withdrawing groups (-I) decrease the negative charge on the carboxylate ion and thus by stabilizing it. Hence the acidic strength increases when -I groups are present.

However the +I groups decrease the acidic strength.

E.g.

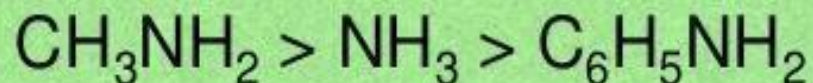
i) The acidic strength increases with increase in the number of electron withdrawing Fluorine atoms as shown below.



ii) Formic acid is stronger acid than acetic acid since the $-\text{CH}_3$ group destabilizes the carboxylate ion.

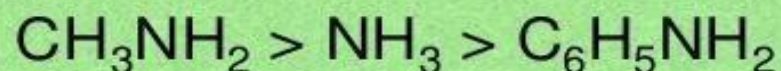
4. Basic strength of amines: The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron withdrawing groups like aryl groups decrease the basic nature. Therefore alkyl amines are stronger Lewis bases than ammonia, whereas aryl amines are weaker than ammonia.

Thus the order of basic strength of alkyl and aryl amines with respect to ammonia is :



4. Basic strength of amines: The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron withdrawing groups like aryl groups decrease the basic nature. Therefore alkyl amines are stronger Lewis bases than ammonia, whereas aryl amines are weaker than ammonia.

Thus the order of basic strength of alkyl and aryl amines with respect to ammonia is :



MESOMERIC OR RESONANCE EFFECT

The flow of electrons from one part of a conjugated system to the other caused by phenomenon of resonance is called resonance effect or mesomeric effect.

-M or -R effect :

When the electron displacement is towards the group.

e.g :-NO₂ , -CHO,

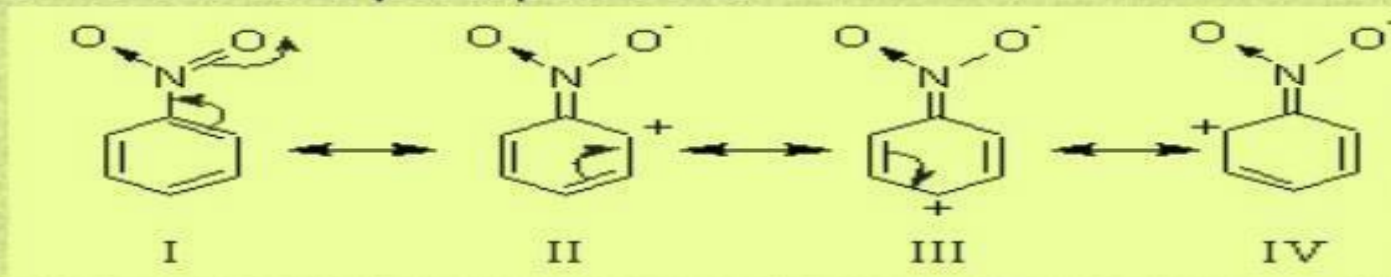
+M or +R effect :

When the electron displacement is away from the group.

e.g :-OH , -OR, -Cl

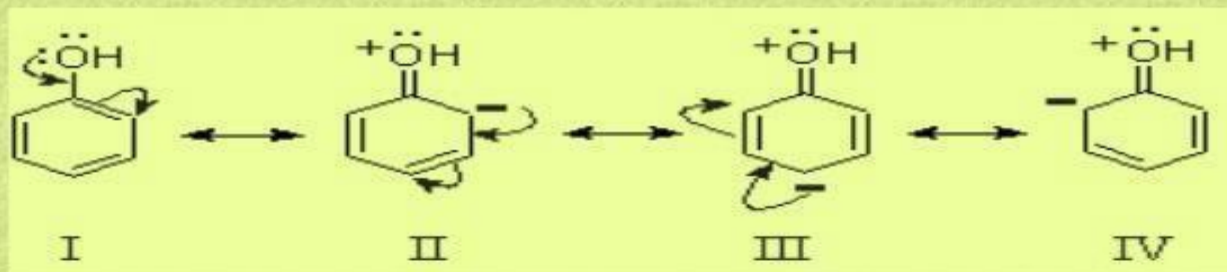


1. The nitro group, $-\text{NO}_2$, in nitrobenzene shows -M effect due to delocalization of conjugated π electrons as shown below. Note that the electron density on benzene ring is decreased particularly on ortho and para positions.



- This is the reason for why nitro group deactivates the benzene ring towards electrophilic substitution reaction.

2) In phenol, the -OH group shows +M effect due to delocalization of lone pair on oxygen atom towards the ring. Thus the electron density on benzene ring is increased particularly on ortho and para positions.



Hence phenol is more reactive towards electrophilic substitution reactions. The substitution is favored more at ortho and para positions.

Essay Questions:

1. Define Inductive Effect. Write Two Applications Of Inductive Effect.
2. Explain Mesomeric Effect With Two Applications.
3. Explain Hyper conjugation With Two Applications.
4. Explain types of organic relations with examples

Short Answer Questions:

1. Write about types of bond fission with examples.
 2. Explain the following a) Electrophilic b) Nucleophilic c) free radical.
Reagents with examples.
 3. Explain the stability of carbenes based on hyper conjugation.
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THANK YOU.....

