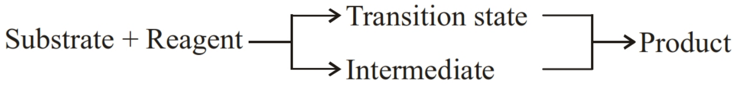
REACTION MECHANISM



Substrate : Part of reactant which is underattack.

Reagent : Part of reactant which attacks over substrate.

Reagents

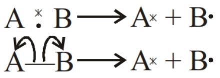
Electrophile	Nucleophile	Free radicals
Electron pair seeking groups. e.g. $^{+}CH_3$, ^{+}H, $^{+}\ddot{\underset{\cdot\cdot}{Cl}}\!:$ $AlCl_3$, BF_3, And all lewis acids	Electron pairdonors. e.g. $^{\ominus}\!:\!CH_3$, $^{\ominus}\!:\!H$, $^{\ominus}\!:\!\ddot{\underset{\cdot\cdot}{Cl}}\!:$ $:\!NH_3$, $H_2\ddot{O}\!:$ And all lewis bases	Species having at least one unpaired e^-. E.g. $\cdot H$, $\cdot CH_3$, $\cdot\ddot{\underset{\cdot\cdot}{Cl}}\!:$

When reagent attacks over substrate they cause bond cleavage

Bond cleavage (fission)

Homolytic

Shared electrons are taken away by both the bonding atoms equally, leading to formation of two radicals.



$A \overset{\times}{\cdot} B \longrightarrow A^{\times} + B^{\cdot}$

$A - B \longrightarrow A^{\times} + B^{\cdot}$

Nonpolar nature of bond and solvent favours homolysis.

Necessary & sufficient condition:

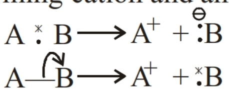
(i) very high temperature, or

(ii) light, or

(iii) source of radical

Heterolytic

Shared electrons are taken away by only one bonding atom forming cation and anion.



$A \overset{\times}{\cdot} B \longrightarrow A^{+} + \overset{\ominus}{:}B$

$A - B \longrightarrow A^{+} + \overset{\times}{\cdot}B$

polar nature of bond and solvent favours heterolysis.

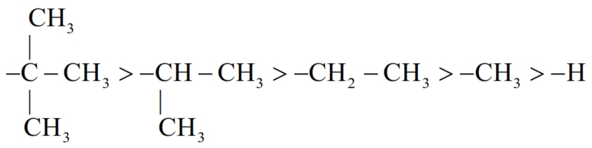
ELECTRON DISPLACEMENT :

Inductive effect : - Permanent effect in which polarisation of one bond induces polarisation in all the neighbouring bonds but with the decreasing efficiency as we move farther from the group is called as inductive effect.

–I group : Electron withdrawing groups.

$$-NO_2 > -COOH > -F > -Cl > -Br > -I > -OR > -NHR > -OH > -NH_2$$

+I group : Electron repelling groups :

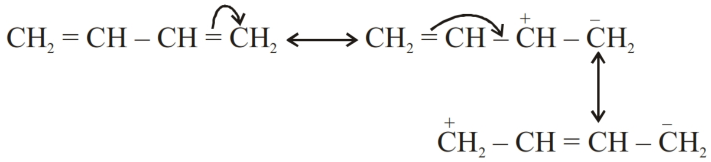


$$-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 > -\underset{CH_3}{\underset{|}{CH}}-CH_3 > -CH_2-CH_3 > -CH_3 > -H$$

Mesomesic Effect :

Shifting of π-electrons in conjugate system giving permanent polarity on the chain.

e.g.,



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

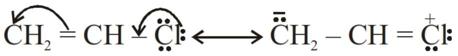
Delocalisation of π-electrons as a result of mesomeric effect giving a number of resonance structure. Due to this effect terminal carbon is almost as positive as the first carbon. This is quite different from Inductive effect due to which charge decreases as one moves away from the source.

Types :

(a) Positive Mesomeric Effect (+M) :

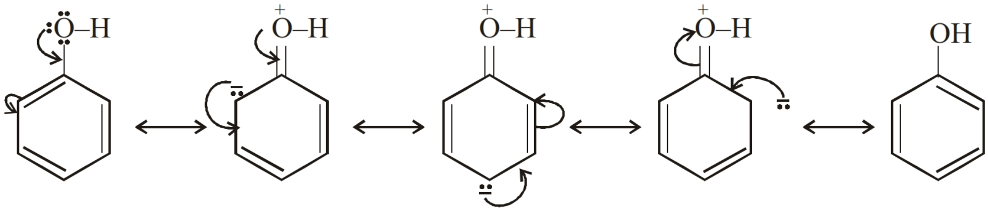
- The direction of electron displacement is away from the group or atom having lone pair of electrons.
- They release the electron pair for conjugation with an attached conjugated system.

e.g. $-\ddot{O}H$, $-\ddot{O}R$, $\ddot{N}H_2$, $-\ddot{S}R$, $-\ddot{X}:$ etc. show +M effect.



$$CH_2=CH-\ddot{Cl}: \longleftrightarrow \overset{-}{C}H_2-CH=\overset{+}{Cl}:$$

- In case of aromatic compound they are ortho and para directors. (Ring activators)

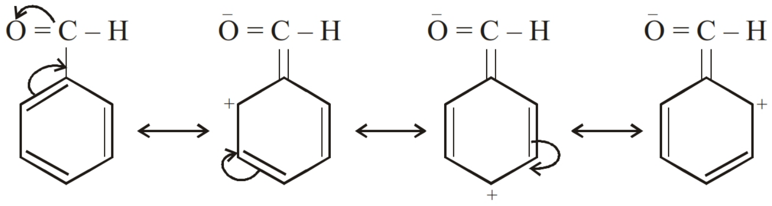


Note : Electron density increases at o & p-positions, electrophile attacks at o and p positions.

(b) Negative Mesomeric effect (–M effect)

- Displacement of π-electron takes palce away from conjugate system.
- –M effect deactivates the conjugate system for S_E (Electrophilic substitution reaction)
- –M effect decreases electrons density in the conjugate system thus in case of aromatic compound these are meta director.

- Eg. –CN, –CHO, –COOH, $-\overset{+}{N}H_3$, etc show -M effect.

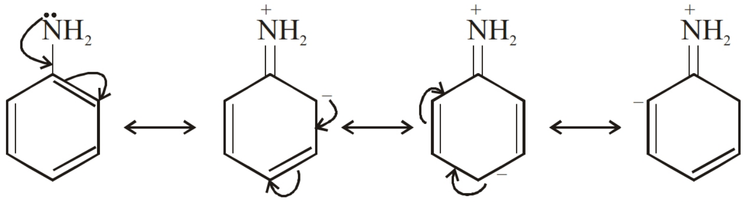


Note : Conjugate compounds can be represented by two or more than two possible structures due to the delocalisation of conjugated electrons. These possible structures are known as Resonating structures. The real structure of conjugated compounds is a hybrid of all resonating structures. This phenomenon is known as resonance. Thus resonance is hybridisation of resonating structures.

$$\underset{(I)}{CH_2=CH-\bar{C}H_2} \quad \text{and} \quad \underset{(II)}{\bar{C}H_2-CH=CH_2}$$

I and II are Resonating structures of allyl carbanion.

- Resonating structures are not the real structures of conjugated compounds.



I II III IV

I to IV are the resonating structures of aniline. The real structure of aniline will be a resonance hybrid of all these four structures.

Effect of resonance on the conjugate functional group of the compound.

(a) Resonance decreases bond length of functional group thus increases bond energy.

(b) Bond length of functional group $\propto \dfrac{1}{\text{No.of resonating structures}}$

(c) Bond strength $\propto$ No. of resonating structures.

(d) Reactivity of functional group due to bond breaking $\propto \dfrac{1}{\text{No.of resonating structures}}$

(e) Stability of conjugated compounds $\propto$ No. of resonating structures.

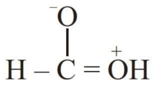
Contribution of Resonating Structures :

It depends upon the stability of structure and the stability depends upon

(i) Neutral species is more stable than the charged (or dipolar species).

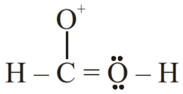
(ii) Species having complete octet is more stable than the species having incomplete octet.

(iii) If all structures 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.



$$H-\overset{\overset{-}{O}}{\overset{|}{C}}=\overset{+}{O}H$$

(I)

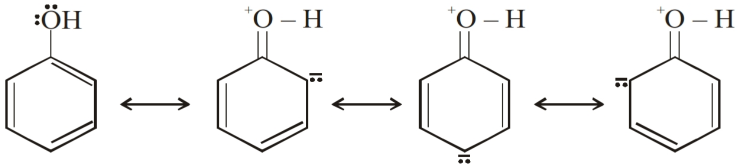


$$H-\overset{O^{+}}{\overset{|}{C}}=\underset{\cdot\cdot}{\ddot{O}}-H$$

(II)

(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.

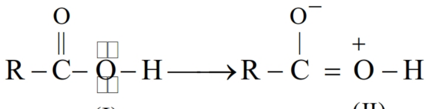


I II III IV

I > II $\equiv$ IV > III (stability order)

Conditions of Resonating Structures :

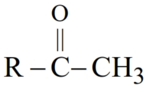
1. All resonating structures must have the same arrangement of atomic nuclei



$$R-\overset{O}{\overset{\|}{C}}-O-H \longrightarrow R-\overset{O^{-}}{\overset{|}{C}}=\overset{+}{O}-H$$

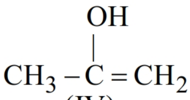
(I) (II)

- N. B.: Position of atomic nuclei in (I) and (II) are same,



$$R-\overset{O}{\overset{\|}{C}}-CH_3$$

(III)

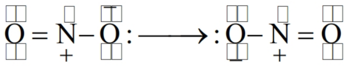


$$CH_3-\overset{OH}{\overset{|}{C}}=CH_2$$

(IV)

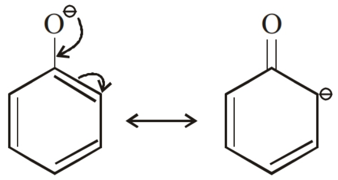
- Position of H-nuclei in (III) and (IV) are different, hence (III) and (IV) are not the resonating structures.

2. The resonating structures must have the same numbers of paired and unpaired electrons. However, they differ in the way of distribution of electrons.



$$O=\overset{+}{N}-O: \longrightarrow :O-\overset{+}{N}=O$$

3. The energies of the different resonating structures must be the same or nearly the same.
4. All atoms that are part of the delocalisation system must be planar.
5. All atoms of the resonating structures should follow the octet rule.

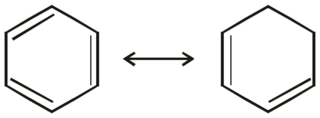


I II

6. Bond order in compounds which exhibit resonance

$$= \frac{\text{Total no. of bonds on central atom among all resonating structures}}{\text{No. of resonating structures}}$$

e.g.,

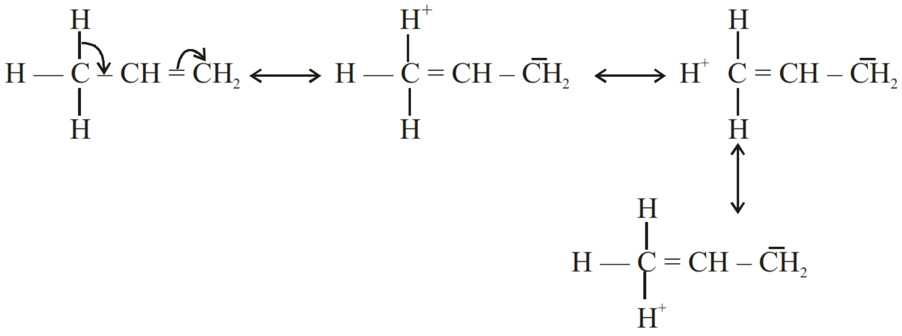


I II

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

Hyperconjugation/No Bond Resonance/Baker - Nathan Effect/$\sigma-\pi$ Conjugation

- When sp^3 carbon containing at least one H is in conjugation with sp^2 carbon.
- Compound should have at least one sp^2-hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.
- Resonating structures due to hyperconjugation may be written involving "no bond" between the alpha carbon and H-atoms.
- No bond resonance can be represented as



Electromeric Effect (Temporary effect) :

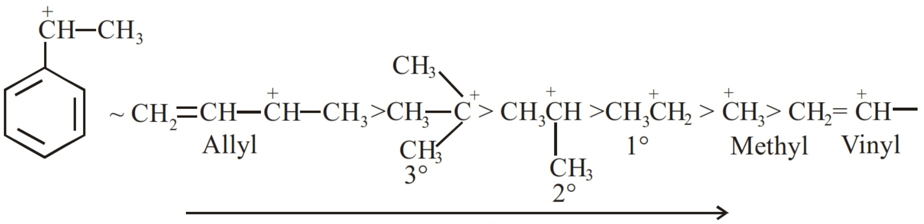
When a compound having π bond is approached by a charged reagent (electrophile or nucleophile), the electrons of the bond are completely polarised or displaced towards one of the constitutent atoms due to electrostatic attraction or repulsion.

Type of reactions :

Organic Reaction Intermediates

1. Carbon Free Radicals :

- Formed due to homolytic fission
- Carbon atom having one odd electron.
- Incomplete octet so highly reactive towards other free radicals.
- Carbon free radical is sp^2 hybridised.
- H–C–H bond angle in $\dot{C}H_3$ is 120° and three C–H coplanar.
- Stability order of different types of carbon free radicals are



$$C_6H_5\overset{+}{C}H-CH_3 \sim \underset{\text{Allyl}}{CH_2=CH-\overset{+}{C}H-CH_3} > \underset{3^\circ}{CH_3-\overset{+}{C}(CH_3)-CH_3} > \underset{2^\circ}{CH_3\overset{+}{C}H(CH_3)} > \underset{1^\circ}{CH_3\overset{+}{C}H_2} > \underset{\text{Methyl}}{\overset{+}{C}H_3} > \underset{\text{Vinyl}}{CH_2=\overset{+}{C}H-}$$

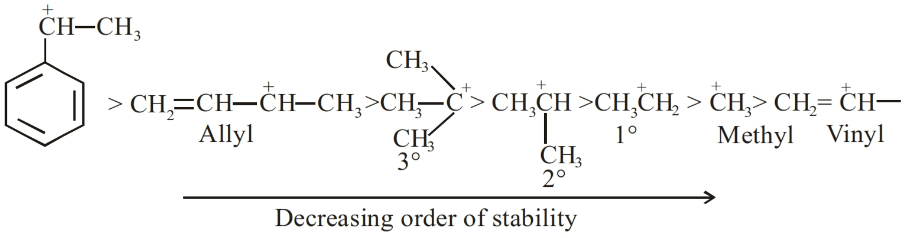
Decreasing order of stability

Note : (i) Greater the stability easier will be formation of that species.

(ii) Stability of allyl and benzyl carbon free radical is explained by resonance and stabilityof 3°, 2°, and 1° carbon free radicals is explained by hyperconjugation i.e. number of hyperconjugation effect $\propto$ stability.

2. Carbocation / Carbonium Ion :

- * Results due to hetrolytic fission.
- * Carbon atom having positive charge
- * Incomplete octet thus reactive towards electron rich species (Nucleophiles).
- * Stability order of different types of carbocations.



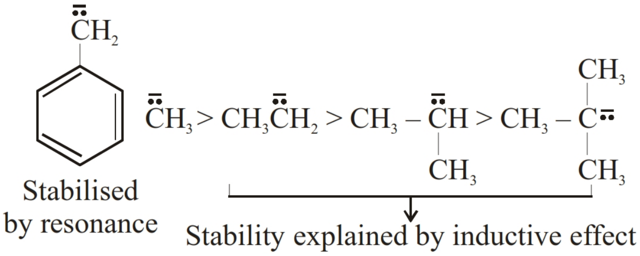
Note : Stability of allyl and benzyl carbocation is explained by hyperoconjugation and inductive effect.

Number of hyperconjugation effect $\propto$ stability

3. Carbanion :

* An organic ion with a pair of available electrons and a negative charge ont he central carbon atom is called a carbanion.

- Carbanion is sp^3 hybridised. Its geometry is pyramidal like NH_3. It is an electron rich species, thus reactive towards electron deficient species (electrophiles).
- Stability order of different types of carbanions:



- Presence of electron-attracting group (–CN, NO_2) increases stability and presence of electron-releasing group ($-CH_3$) etc decreases stability of carbanion.

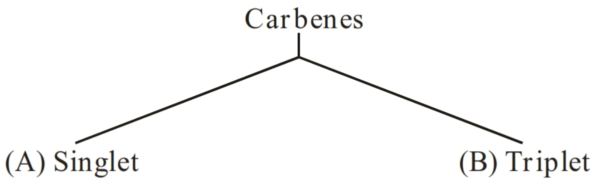
4. Carbenes :

- Obtained by photolysis of either diazomethan (CH_2N_2) or keten ($CH_2=C=O$)
- Incomeplete octet thus highly reactive.

$$CH_2=\overset{+}{N}-\overset{-}{N} \xrightarrow[-N_2]{\text{light}} :CH_2 + N_2$$

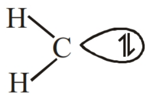
$$CH_2=C=O \xrightarrow[-CO]{\text{light}} :CH_2 + CO$$

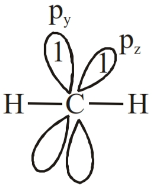
- Exists in two forms.

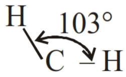


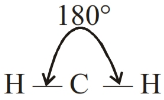
1. In this case unshared electrons are paired (sp^2 hybridised)

2. Unshared electrons are not paired (sp hybridised) These are present in two unhybridised p-orbital.





2. 

2. 

3. Bond length between C–H is 1. 12 Å.
4. Less stable
5. an electrophile

3. Bond length between C–H is 1. 12 Å.
4. More stable
5. A free diradical

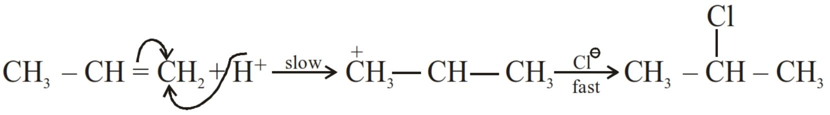
DIFFERENT REACTION

1. Addition reactions:

Formation of two new σ-bonds due to breaking of a π-bond.

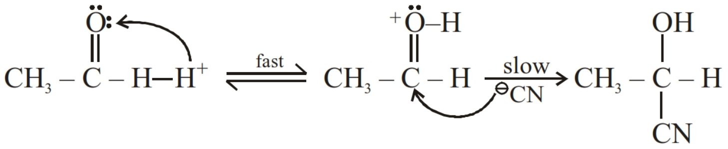
It is of three types :

(i) Electrophilic addition : If electrophile attacks in the show step while addition, it is electrophillic addition.



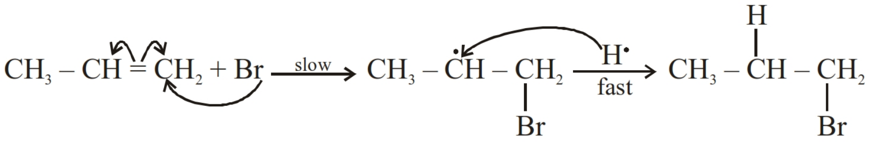
$$CH_3-CH=CH_2+H^+\xrightarrow{slow}\overset{+}{C}H_3-CH-CH_3\xrightarrow[fast]{Cl^\ominus}CH_3-\overset{\overset{Cl}{|}}{C}H-CH_3$$

(ii) Nucleophillic addition : If nucleophile attacks in the slow step while addition.



$$CH_3-\overset{\overset{\ddot{O}:}{||}}{C}-H \;\; H^+\underset{}{\overset{fast}{\rightleftharpoons}} CH_3-\overset{\overset{+\ddot{O}-H}{||}}{C}-H\xrightarrow[{}^\ominus CN]{slow}CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CN}{|}}{C}}-H$$

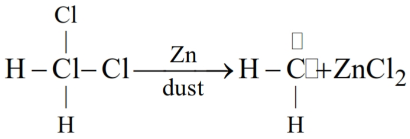
(iii) Radical addition : If radical attacks in the slow step while addition.



$$CH_3-CH=CH_2+Br\xrightarrow{slow}CH_3-\dot{C}H-\underset{\underset{Br}{|}}{CH_2}\xrightarrow[fast]{H^\bullet}CH_3-\overset{\overset{H}{|}}{C}H-\underset{\underset{Br}{|}}{CH_2}$$

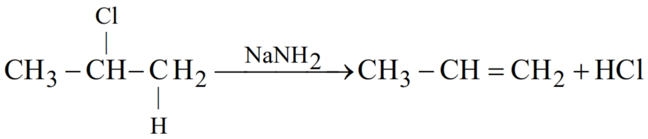
2. Elimination reaction : If two σ-bonds are broken from any molecule, reaction is called as elimination reaction. It is of three types :

(i) α-elimination : Two σ-bonds are broken from the same atom forming a carbene.



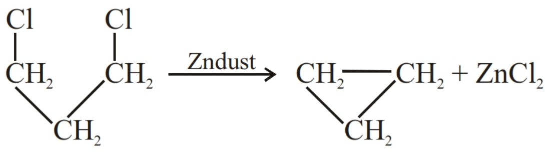
$$H-\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C}}-Cl\xrightarrow[dust]{Zn}H-\underset{\underset{H}{|}}{C}+ZnCl_2$$

(ii) β-elimination : Two σ-bonds are broken from consecutive atoms, forming a π-bond.



$$CH_3-\overset{\overset{Cl}{|}}{C}H-\underset{\underset{H}{|}}{C}H_2\xrightarrow{NaNH_2}CH_3-CH=CH_2+HCl$$

(iii) γ-elimination : Two σ-bonds are broken from alternate atoms, forming a three membered ring.

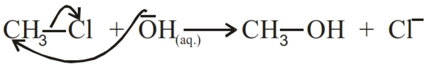


3. Substitution reaction :

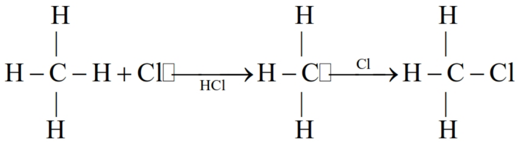
When any group comes in place ofanother group, reaction is called as substitution group.

It is of three types :

(i) Nucleophillic Substitution (S_N) : When any nucleophile replaces another nucleophile.

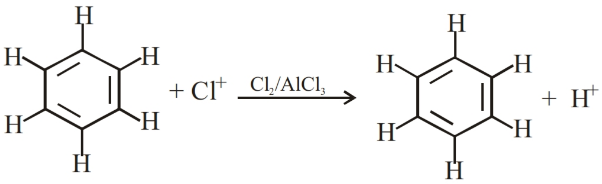


(ii) Radical Substitution (S_R) : When any radical replaces another radical.



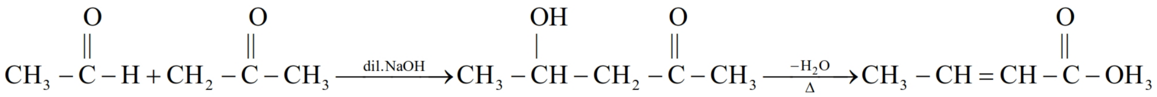
$$H-\underset{H}{\overset{H}{C}}-H+Cl\square \xrightarrow[HCl]{} H-\underset{H}{\overset{H}{C}}\square \xrightarrow{Cl} H-\underset{H}{\overset{H}{C}}-Cl$$

(iii) Electrophillic Substitution (S_E) : When any electrophile replaces another electrophile.



4. Condensation Reaction :

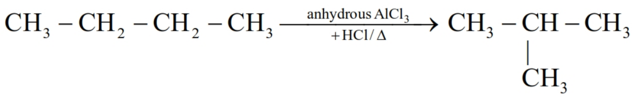
Two or more reactants are combined to form a product with or without the elimination of simple molecules like H_2O, HCl, NH_3, R–OH etc.



$$CH_3-\overset{O}{\overset{\|}{C}}-H+CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{dil.NaOH} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{-H_2O} CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-OH_3$$

5. Rearrangement reaction :

Structure is rearranged.



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[+HCl/\Delta]{anhydrous\ AlCl_3} CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_3$$

6. Polymerisation reaction :

Smaller molecules are combined to form bigger molecule.

$$nCH_2=CH_2 \xrightarrow[\Delta]{} (-CH_2-CH_2)_n$$