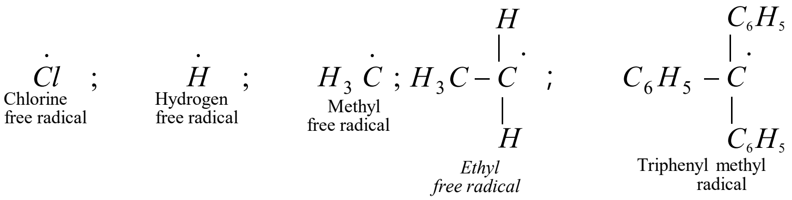
Reaction Intermediates.

Short lived fragments called reaction intermediates result from homolytic and Heterolytic bond fission. The important reaction intermediates are free radicals, carbocations, carbonions, carbenes, benzyne and nitrenes.

Free radicals

A free radical may be defined as an atom or group of atoms having an odd or unpaired electron. These result on account of homolytic fission of a covalent bond and are denoted by putting a dot (.) against the symbol of atom or group of atoms.



$\dot{Cl}$; $\dot{H}$; $H_3\dot{C}$; $H_3C-\dot{C}H_2$; $(C_6H_5)_3\dot{C}$

Chlorine free radical ; Hydrogen free radical ; Methyl free radical ; Ethyl free radical ; Triphenyl methyl radical

The first stable organic free radical was triphenyl methyl radical and it was prepared by **Gomberg**.

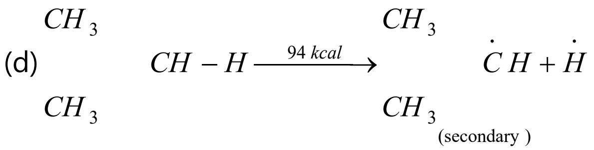
(1) **Characteristics of free radical**.

(i) The formation of free radical is initiated by heat, light or catalysts.

(a) $Cl:Cl \xrightarrow[\text{sunlight}]{\text{Energy}} \dot{Cl} + \dot{Cl}$

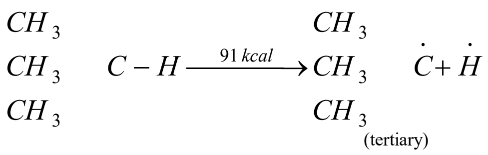
(b) $H_3C:H \xrightarrow{102\ kcal} H_3\dot{C} + \dot{H}$

(c) $H_3C-CH_2-H \xrightarrow{97\ kcal} H_3C-\dot{C}H_2 + \dot{H}$ (primary)



(d) $(CH_3)_2CH-H \xrightarrow{94\ kcal} (CH_3)_2\dot{C}H + \dot{H}$ (secondary)

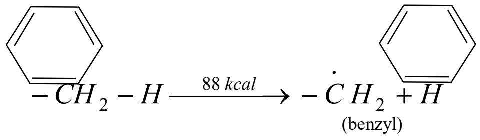
(e)



$$\begin{matrix}CH_3\\ CH_3\\ CH_3\end{matrix}\; C-H \xrightarrow{91\,kcal} \underset{\text{(tertiary)}}{\begin{matrix}CH_3\\ CH_3\\ CH_3\end{matrix}}\; \dot{C}+\dot{H}$$

(f) $CH_2=CH-CH_2-H \xrightarrow{86\,kcal} CH_2=CH-\underset{\text{(allyl)}}{\dot{C}H_2}+\dot{H}$

(g)



(h) $CH_3-NH_2 \xrightarrow{heat\,/\,light} \dot{C}H_3+\dot{N}H_2$

(ii) Free radicals are generally electrically neutral.

(iii) There are seven electrons in the out most orbit of carbon of carbon free radicals.

(iv) Owing to the presence of an odd electron; a carbon radical is paramagnetic in nature. Due to this reason free radicals are highly reactive.

(v) Free radicals are neutral electrophiles.

(vi) Chemical reactions which takes place with the formation of free radical as an intermediate are known as free radical reactions. These reactions takes place in three steps,

(a) Initiation
(b) Propagation and
(c) Termination

Each of these steps, in turn, may involve two or more steps.

(a) Initiation step**:** In this step, homolytic bond fission takes place in the presence of initiator, i.e., peroxide, $h\nu$, heat etc. The process is always endothermic.

$$Cl-Cl \xrightarrow[\Delta]{h\nu\ or} \dot{C}l+\dot{C}l \quad \Delta H=+ve$$

(b) Propagation step**:** Propagation step is always two or more than two step process and **all propagation steps should be exothermic, otherwise free radical reactions would not take place**.

Propagation step I: In this step, formation of free radical as reaction intermediate takes place. For example,

$$CH_3-H+\dot{C}l \longrightarrow \dot{C}H_3+HCl \qquad \Delta H=\text{Negative}$$

Propagation step II: Reaction intermediate reacts with reagent to give the product.

$$\dot{C}H_3+Cl-Cl \longrightarrow CH_3-Cl+\dot{C}l \qquad \Delta H=\text{Negative}$$

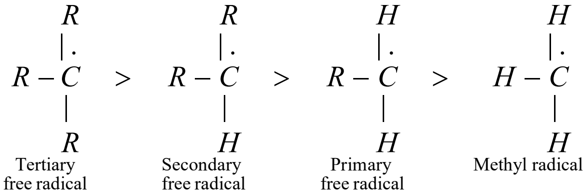
(c) Termination step **:** In this step, free radical formed in the last propagation step (generally propagation step II) is destroyed by the addition of free radical or by the addition of some impurities like $CHCl_3$ or CCl_4.

$$\dot{C}l+\dot{C}l \longrightarrow Cl_2$$

Reaction velocity of free radical reaction is very-very high.

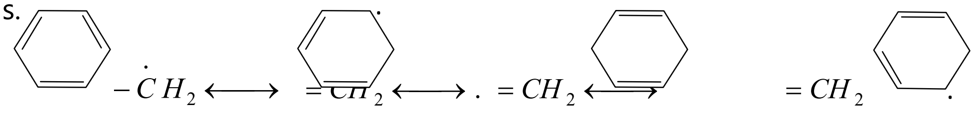
Note: Certain compounds, known as inhibitor, retar velocity of free radical reactions. Common inhibitors are O_2, I_2 p-benzoquinone and diphenylamine.

(2) **Relative stabilities of free radicals:** The tertiary alkyl free radicals are most stable and methyl free radial is least stable, i.e., the free radical formed easily has greater stability.



$$\underset{\text{Tertiary free radical}}{R_3\dot{C}} > \underset{\text{Secondary free radical}}{R_2H\dot{C}} > \underset{\text{Primary free radical}}{RH_2\dot{C}} > \underset{\text{Methyl radical}}{H_3\dot{C}}$$

Benzyl and allyl free radicals are resonance stabilized hence are more stable than alkyl free radicals.



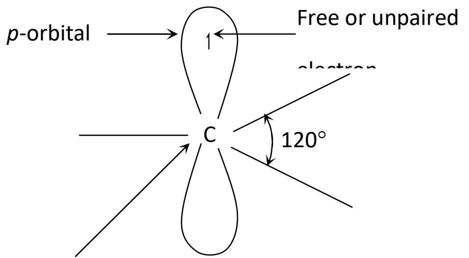
Benzyl free radical

$$CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2 \text{ (Allyl)}$$

Relative stability of free radicals are: Benzyl > allyl > $3^o > 2^o > 1^o$ > methyl, vinyl

The stability of various free radicals can be compared from their bond dissociation energies (the energy required for the homolytic cleavage of the covalent bond in the molecule to form two radicals). In general, the smaller the amount of energy required for bond breaking, the more stable is the radical.

(3) **Structure of alkyl free radicals:** The carbon atom of alkyl free radicals which is bonded to only three atoms or groups of atoms is sp^2 hybridized. Thus, free radicals have a planar structure with odd electron situated in the unused p-orbital at right angles to the plane of hybrid orbitals.



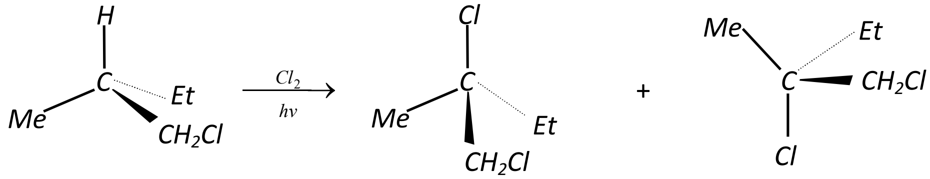
Sp^2 hybridised c-atom

However, in the substituted alkyl radicals the 's' character of these orbitals has been found to increase, thus, tending to the pyramidal shape.

$$\dot{C}H_3 < \dot{C}H_2F < \dot{C}HF_2 < \dot{C}F_3.$$

So, CF_3 is essentially pyramidal in shape.

(4) **Stereochemistry of free radicals:**To learn about the stereochemistry of free radical reaction. We choose the reaction, chlorination of 1-chloro-2-methyl butane. The reaction products are,



If we review the insight of the reaction, it is clear that the reaction involves racemization at the reaction center. The free radical should have the sp^2 hybridization. Obviously a Cl_2 molecule could attack either the upper or lower lobe of the p-orbital with equal chances, leading to racemic mixture.

Intermediate $\xrightarrow{Cl_2} \underset{(50\%)}{d-\text{form}} + \underset{(50\%)}{l-\text{form}}$

(5) **Reactions involving free radicals,**

- (i) Chlorination of alkanes
- (ii) Pyrolysis of alkanes
- (iii) Wurtz reaction

(iv) Anti-markownikoff rule

(v) Kolbe electrolytic synthesis

(vi) Polymerization initiated by free radical.

Carbonium ions (carbocations)

Carbocation is defined as a group of atoms which contain positively charged carbon having only six electrons. It is obtained by Heterolytic fission of a covalent bond involving carbon atom. It is denoted by putting a positive charge (+) against the symbol of group of atoms.

$$CH_3^{\oplus} \qquad C_2H_5^{\oplus} \qquad (CH_3)_2CH^{\oplus} \qquad (CH_3)_3C^{\oplus}$$

$$\underbrace{\text{Methyl carbonium ion} \quad \text{Ethyl carbonium ion}}_{\text{Primary}} \qquad \underbrace{\text{Isopropyl carbonium ion}}_{\text{Secondary}} \qquad \underbrace{\text{Tert. Butyl carbonium ion}}_{\text{Tertiary}}$$

(1) **Characteristics of carbocations**

(i) The formation of carbocations can be done,

(a) By heterolysis of halogen compounds: $(CH_3)_3-C-Cl \longrightarrow (CH_3)_3\overset{\oplus}{C} + \overset{\ominus}{Cl}$

(b) By protonation of alkenes or alcohols: $CH_2=CH_2 \overset{H^{\oplus}}{\rightleftharpoons} \overset{\oplus}{C}H_2-CH_3$

$$R-O-H \overset{H^{\oplus}}{\rightleftharpoons} R-\overset{\oplus}{O}H_2 \overset{-H_2O}{\rightleftharpoons} R^{+} + H_2O$$

(c) By decomposition of Diazo compounds: $C_6H_5-N_2-Cl \xrightarrow{-Cl} C_6H_5\overset{\oplus}{N}_2 \xrightarrow{-N_2} \overset{\oplus}{C}_6H_5 + N_2$

(ii) Carbocations are not electrically neutral.

(iii) There are six electrons in the out most orbit of carbon of carbocation i.e., 2 electrons less than octet.

(iv) A carbocation is diamagnetic in nature due to all paired electrons.

(v) Carbocations are charged electrophiles i.e., they react with nucleophilic reagents. The order of reactivity of carbocations is, Primary (1°) > Secondary (2°) > Tertiary (3°)

(2) **Types of carbocations**: Carbocations can be classified into the following types,

(i) **Alkyl carbocations**

(a) When positive charge is present on the alkyl carbon, carbocation is known as alkyl carbocation.

(b) Alkyl carbocation is of four types

$\overset{\oplus}{C}H_3$ Methyl carbocation

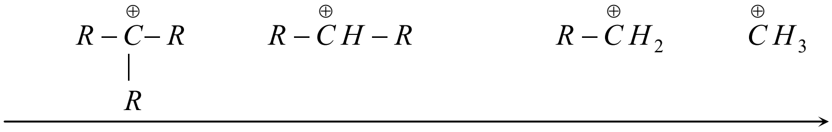
$R-\overset{\oplus}{C}H_2$ Primary alkyl carbocations

$R-\overset{\oplus}{C}H-R$ Secondary alkyl carbocations

$R_3\overset{\oplus}{C}$ Tertiary alkyl carbocations

(c) Stability of alkyl carbocations can be explained by
Inductive effect and hyper conjugation.

(d) According to these two effects the stability order is as follows:

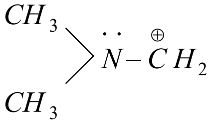


$$\underset{R}{\underset{|}{R-\overset{\oplus}{C}-R}} \qquad R-\overset{\oplus}{C}H-R \qquad R-\overset{\oplus}{C}H_2 \qquad \overset{\oplus}{C}H_3$$

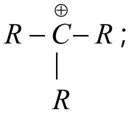
Stability in decreasing order

(e) If α -atom with respect to carbocationic carbon has one or more than one lone pair of electrons then lone pair of electrons strongly stabilizes a carbocation due to the delocalization.

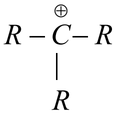
Alkoxy and amino groups are important substituents for such type of carbocations.



$(CH_3)_2\ddot{N}-\overset{\oplus}{C}H_2$ is more stable than



$\underset{R}{\underset{|}{R-\overset{\oplus}{C}-R}}$; $CH_3-\ddot{\underset{\cdot\cdot}{O}}-\overset{\oplus}{C}H_2$ is more stable than



$\underset{R}{\underset{|}{R-\overset{\oplus}{C}-R}}$

(ii) **Vinyl carbocation**: When positive charge is present on vinylic carbon then carbocation is known as vinyl carbocation, $CH_2=\overset{\oplus}{C}H$

This carbocation is the least stable because positive charge is present on the electronegative carbon.

(iii) **Allyl carbocation:** $(CH_2=CH-\overset{\oplus}{C}H_2)$

(a) When positive charge is present on the allylic carbon of the allyl group, the carbocation is known as allyl carbocation.

(b) Allyl carbocations are more stable than the alkyl carbocations due to the resonance. Allyl carbocations are stabilized by delocalization (or resonance).

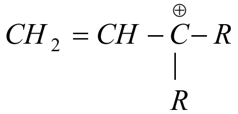
(c) Allyl carbocations are of the following types,

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

Primary

$CH_2=CH-\overset{\oplus}{C}H-R$

Secondary



$CH_2=CH-\underset{R}{\overset{\oplus}{C}}-R$

Tertiary

(d) Stability of primary, secondary and tertiary allyl carbocations can be compared by, Inductive effect and Hyper conjugation. Thus, tertiary is more stable than secondary which is more stable than primary allyl carbocation.

(iv) **Phenyl methyl carbocations**

(a) When positive charge is present on benzyl carbon, carbocation is known as phenyl methyl carbocation.

(b) Phenyl methyl carbocations are of three types,

$C_6H_5-\overset{\oplus}{C}H_2$

Benzyl carbocation

or

Phenyl methyl carbocation

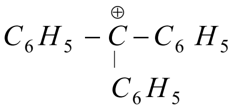
(1°-carbocation)

$C_6H_5-\overset{\oplus}{C}H-C_6H_5$

Diphenyl methyl

carbocation

(2°-carbocation)



$C_6H_5-\underset{C_6H_5}{\overset{\oplus}{C}}-C_6H_5$

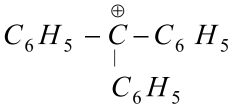
Triphenyl methyl

carbocation

(3°-carbocation)

(c) Stability of phenyl methyl carbocations can be explained by resonance.

Structure :



$C_6H_5-\underset{C_6H_5}{\overset{\oplus}{C}}-C_6H_5$

$C_6H_5-\overset{\oplus}{C}H-C_6H_5$

$C_6H_5-\overset{\oplus}{C}H_2$

No. of resonating structures : 10 7 4

(i) Number of resonating structures in decreasing order

(ii) Stability in decreasing order.

(d) Phenyl methyl carbocations are more stable than allyl carbocations due to the number of resonating structures.

(v) **Aromatic carbocations**

(a) Cations in which positive charge is present on carbon of aromatic system is known as aromatic carbocation.

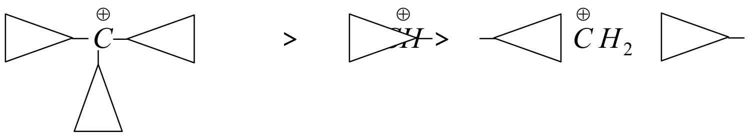
(b) Aromatic carbocations are so stable that even their solid states are known. For example tropolium carbocation as tropolium bromide is a yellow solid. It fact tropolium carbocation is about 10^{11} times more stable than triphenyl methyl carbocation.

(c) Cations obeying Huckel (4n+2) rule are stable because they are aromatic and there is complete delocalization of positive charge.

(vi) **Cyclopropyl methyl carbocations**

(a) These carbocations are very stable carbocations. They are more stable than benzyl carbocations.

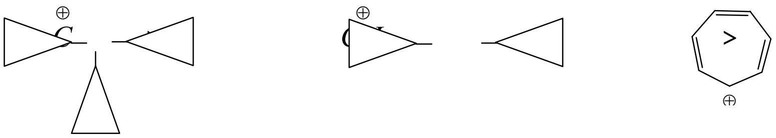
(b) Stability of Cyclopropyl methyl carbocations increases with every Cyclopropyl group. Thus additional Cyclopropyl group has cumulative additive effect on the stability. Thus,



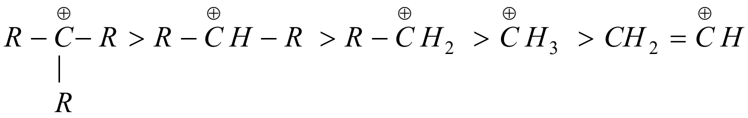
Stability in decreasing order

(c) The special stability is a result of conjugation between the bent orbitals of the Cyclopropyl ring and the vacant- p -orbital of the cationic carbon.

(3) **Relative:**Stability of different types of carbocations in decreasing order



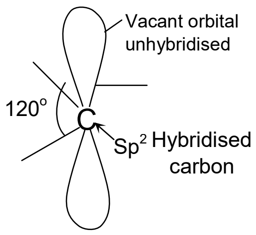
$$(C_6H_5)_3\overset{\oplus}{C} > (C_6H_5)_2\overset{\oplus}{C}H > C_6H_5-\overset{\oplus}{C}H_2 \geq CH_2=CH-\overset{\oplus}{C}H_2 \geq$$



$$R-\overset{\oplus}{\underset{\underset{R}{|}}{C}}-R > R-\overset{\oplus}{C}H-R > R-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H$$

Note: More stable is a carbocation, the more easily it is formed.

(4) **Structure of carbocation:** The carbon atom in carbocation is sp^2 hybridized. The three sp^2 hybrid orbitals form three σ bonds with hydrogen or other carbon atoms of alkyl groups. The unhybridised p-orbital of carbon remains vacant. Since it involves sp^2 hybridization, its structure is planar with a bond angle of 120^o.



Planar structure of carbocation

(5) **Reactions involving carbocations**

(i) Electrophilic addition reactions

(ii) SN^1 Reactions

(iii) Electrophilic substitution reactions

(iv) Molecular rearrangement reactions, e.g., Pinacole-Pinacolone rearrangement.

(6) **Rearrangement in carbocations**

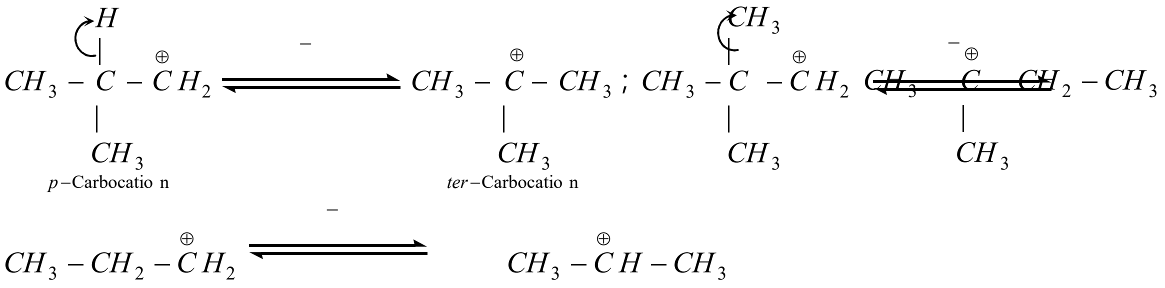
(i) Rearrangement takes place in primary and secondary carbocations.

p-carbocation $\xrightleftharpoons{\text{Rearrangement}}$ ter-carbocation or sec. carbocation

Driving force for rearrangement is the stability factor (Less stable species wants to convert into more stable species).

(ii) For rearrangement, carbocation should have at least three carbons. (α, β and γ).

(iii) If β-carbon has hydrogen as well as alkyl group then rearrangement is due to the migration of hydrogen in the form of hydride ion from β to α-carbon. If β-carbon has only hydrogens then hydrogen migrates. If β-carbon has only alkyl groups then alkyl group migrates from β to α-carbon.

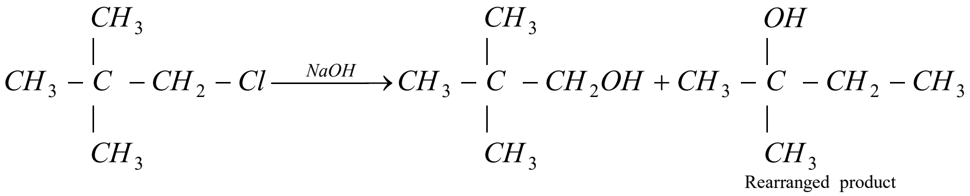


$$CH_3-\underset{CH_3}{\overset{H}{C}}-\overset{\oplus}{C}H_2 \overset{-}{\rightleftharpoons} CH_3-\underset{CH_3}{\overset{\oplus}{C}}-CH_3\ ;\ CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2 \overset{-}{\rightleftharpoons} CH_3-\underset{CH_3}{\overset{\oplus}{C}}-CH_2-CH_3$$

p–Carbocation *ter*–Carbocation

$$CH_3-CH_2-\overset{\oplus}{C}H_2 \overset{-}{\rightleftharpoons} CH_3-\overset{\oplus}{C}H-CH_3$$

Note: If the number of products of the reaction is more than the expected products then product formation takes place by formation of carbocation and there is rearrangement in carbocation.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-Cl \xrightarrow{NaOH} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH+CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-CH_3$$

Rearranged product

Carbanions

A carbanion may be defined as a species containing a carbon atom carrying a negative charge. These are generated by the Heterolytic fission of covalent bond involving carbon atom in which the atom linked to carbon goes without the bonding electrons.

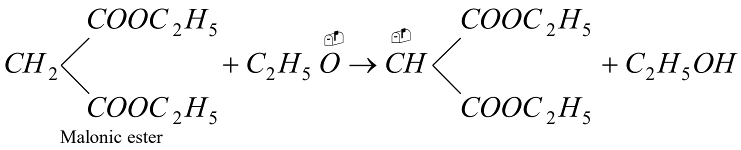
It is denoted by putting a negative charge (–) against the symbol of group of atoms.

$$\underbrace{\underset{\text{Methyl carbanion}}{CH_3^{\ominus}} \qquad \underset{\text{Ethyl carbanion}}{C_2H_5^{\ominus}}}_{\text{Primary}} \qquad \underbrace{\underset{\text{Isopropyl carbanion}}{(CH_3)_2CH^{\ominus}}}_{\text{Secondary}} \qquad \underbrace{\underset{\text{Tert. butyl carbanion}}{(CH_3)_3C^{\ominus}}}_{\text{Tertiary}}$$

(1) **Characteristics of carbanions,**

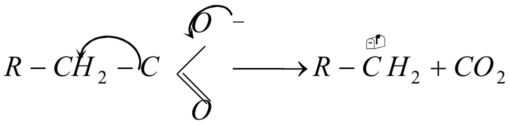
(i) The formation of carbanions can be done,

(a) By attack of base on hydrogen atom : Organic compounds which possess a labile or acidic hydrogen have the tendency to produce carbanions as in the case of reactive methylene compounds which lose proton in presence of sodium ethoxide (C_2H_5ONa).



$$CH_2(COOC_2H_5)_2 + C_2H_5\overset{\ominus}{O} \rightarrow \overset{\ominus}{C}H(COOC_2H_5)_2 + C_2H_5OH$$

(b) By decarboxylation of carboxylate ion:



$$R-CH_2-C(=O)O^- \longrightarrow R-\overset{\ominus}{C}H_2 + CO_2$$

(c) By the formation of organometallic compound;

$$CH_3-Cl \xrightarrow{Mg/ether} CH_3MgCl \longrightarrow \overset{\ominus}{C}H_3 + Mg^{\oplus}Cl^{\ominus}$$

(ii) Carbanions are not electrically neutral.

(iii) There are eight electrons in the outermost orbit of carbanionic carbon hence its octet is complete.

(iv) A carbanion is diamagnetic in nature due to all paired electrons.

(v) Carbanions are charged nucleophiles i.e., they react with electrophilic reagents. The order of reactivity of carbanions is, Tertiary (3°) > Secondary (2°) >Primary (1°) (Decreasing order)

(2) **Stability of carbanions:** The stability of carbanion may be explained by

(i) **Electronegativity of carbanionic carbon**

Stability $\propto$ Electronegativity of carbanionic carbon $\propto$ % s -character of carbanionic carbon

$$CH_3-\underset{\underset{sp^3}{\uparrow}}{\overset{\ominus}{C}}H_2 \qquad CH_2=\underset{\underset{sp^2}{\uparrow}}{\overset{\ominus}{C}}H \qquad CH\equiv\underset{\underset{sp}{\uparrow}}{\overset{\ominus}{C}}$$

$$\xrightarrow{\hspace{8cm}}$$

% s -character in increasing order.

Stability in increasingorder.

(ii) **Inductive effect:** Stability of carbanions depends on the +I or – I group as follows:

(a) Stability $\propto \dfrac{1}{+I \text{ power of the group}}$

$$\overset{\ominus}{C}H_3 \qquad R \rightarrow \overset{\ominus}{C}H_2 \qquad R \rightarrow \overset{\ominus}{C}H_2 \leftarrow R \qquad R \rightarrow \underset{\underset{R}{\uparrow}}{\overset{\ominus}{C}} \rightarrow R$$

$$\xrightarrow[\hspace{10cm}]{}$$

+ I power in increasing order.

Stability in decreasing order.

(b) Stability of carbanions $\propto - I$ power of the group.

For example:

$$I \longrightarrow \overset{\ominus}{C}H_2 \quad Br \longrightarrow \overset{\ominus}{C}H_2 \quad Cl \longrightarrow \overset{\ominus}{C}H_2 \quad F \longrightarrow \overset{\ominus}{C}H_2$$

$$\xrightarrow[\hspace{10cm}]{}$$

– I power of halo group is in increasing order

Stability is in increasing order

(iii) **Delocalization or Resonance:** Allyl and benzyl carbanions are stabilized by delocalization of negative charge.

$$\underset{2}{CH_2 = CH - \overset{\ominus}{C}H_2} \quad \underset{4}{C_6H_5 - \overset{\ominus}{C}H_2} \quad \underset{7}{(C_6H_5)_2\overset{\ominus}{C}H} \quad \underset{10}{(C_6H_5)_3\overset{\ominus}{C}}$$

$$\xrightarrow[\hspace{10cm}]{}$$

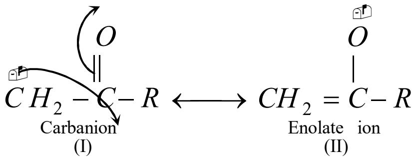
Number of resonating structures is in increasing order

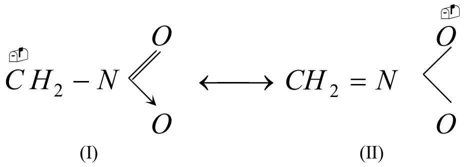
Stability is in increasing order.

(iv) **Stabilization by sulphur and phosphorous:** Attachment of carbanionic carbon of a sulphur and phosphorus atom causes an increase in carbanion stability.

The cause of stability is due to the delocalization of negative charge of carbanion by vacant d -orbital $p\pi - d\pi$ bonding) of phosphorus and sulphur.

(v) **Stabilization by >C=O, –NO$_2$ and CN groups present on carbanionic carbon: These** groups stabilize carbanion by resonance effect.





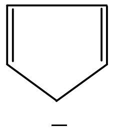
Contribution of structure (II) will be more than (I) because in (II) negative charge is present on electronegative oxygen.

(vi) **Stability of Aromatic carbanions**

(a) Anions in which negative charge is present on carbon of aromatic system is known as aromatic carbanions.

(b) Aromatic carbanions are most stable carbanions.

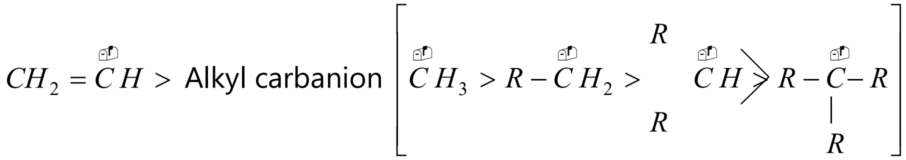
(c) Anions obeying Huckel rule are stable because they are aromatic and there is complete delocalization of negative charge.



Cyclopentadienyl anion

(3) **Relative stability of different types of carbanions in decreasing order**

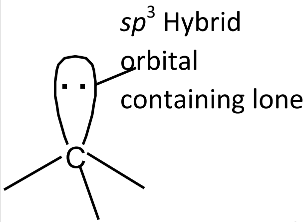
Aromatic carbanion > Benzyl carbanion > Allyl carbanion > $CH \equiv \overset{\ominus}{C}$ >



$CH_2 = \overset{\ominus}{C}H >$ Alkyl carbanion $\left[\overset{\ominus}{C}H_3 > R-\overset{\ominus}{C}H_2 > \begin{matrix} R \\ \\ R \end{matrix}\!\!>\overset{\ominus}{C}H > R-\overset{\ominus}{\underset{R}{\underset{|}{C}}}-R \right]$

(4) **Structure of carbanion:**

The negatively charged carbon atom in carbanion is sp^3 hybridized. Therefore, it has a pyramidal structure. Three of the four sp^3 hybridized orbitals form 3σ bonds with hydrogen or carbon atom of the alkyl group. The fourth sp^3 hybrid orbital contains the lone pair of electrons.

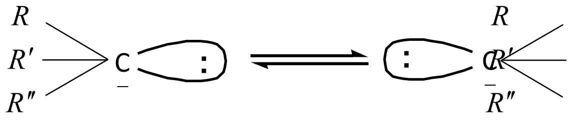


Pyramidal structure of carbanion

Note: Geometry of allyl and benzyl carbanion is almost planar and hybridization is sp^2.

Methyl anion is isostructural (pyramidal) and isoelectronic (eight valency electrons) with ammonia.

The carbanions having three different bulky groups are not optically active. It is due to pyramidal structure of carbanion which is not rigid and shows a rapid equilibrium between following two enantiomeric pyramidal structures.



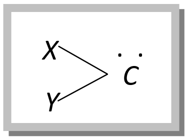
(5) **Reactions involving carbanions**

(i) Condensation reactions of carbonyl compounds, i.e., Aldol condensation, Perkin reaction, Reformatsky reaction etc.

(ii) Condensation reaction of ester; Claisen condensation.

(iii) Witting reaction.

Carbenes



A carbene may be defined as a species in which carbon atom has six electrons in the outer shell (electron deficient), out of which two constitute a lone pair and two are shared. So they are divalent carbon species containing two unpaired electrons and possess no charge.

The simplest carbene is $\ddot{C}H_2$ which known as methylene. Substituted carbenes are simply named as derivative of carbenes. For example, $\underset{\text{Phenyl carbene}}{C_6H_5-\ddot{C}H}$ $\underset{\text{Dialkyl carbene}}{R-\ddot{C}-R}$ $\underset{\text{Dichloro carbene}}{\ddot{C}Cl_2}$

(1) **Characteristics of carbnes**

(i) Carbenes can be formed,

(a) By the photochemical decomposition or pyrolysis of aliphatic diazo compounds or ketenes.

$$\underset{\text{Diazo methane}}{CH_2N_2} \xrightarrow[(UV)]{h\nu \text{ or heat}} \underset{\text{Carbene}}{:CH_2} + N_2; \qquad R-CHN_2 \xrightarrow{h\nu \text{ or heat}} \underset{\text{Alkyl carbene}}{RCH:} + N_2$$

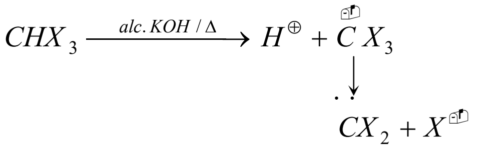
$$RCO-CHN_2 \xrightarrow{h\nu \text{ or heat}} \underset{\text{Acyl carbene}}{RCO-CH:} + N_2; \; \underset{\text{Ketene}}{CH_2=C=O} \longrightarrow \underset{\text{Carbene}}{:CH_2} + CO$$

(b) By the action of a base on suitable polyhalogen compound.

$$\underset{\text{Chloroform}}{CHCl_3} + C_2H_5ONa \longrightarrow \underset{\text{Dichloro carbene}}{:CCl_2} + C_2H_5OH + NaCl$$

$$CHCl_3 + \underset{\text{Tert. butoxide ion}}{(CH_3)_3CO^{\ominus}} \rightleftharpoons (CH_3)_3C-OH + :CCl_3 \longrightarrow :CCl_2 + Cl^-$$

(ii) Carbenes are related to carbanions through the α -elimination reaction.



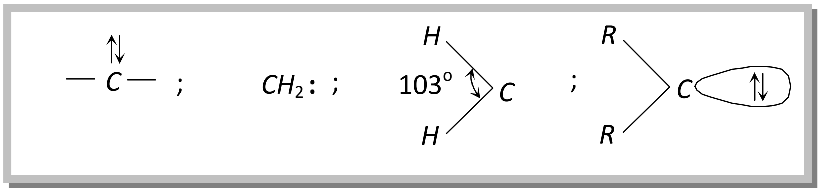
$$CHX_3 \xrightarrow{alc.KOH/\Delta} H^{\oplus} + \overset{\ominus}{C}X_3 \longrightarrow \ddot{C}X_2 + X^{\ominus}$$

(iii) Carbenes are neutral, divalent, highly reactive carbon intermediates. They works as electrophiles.

(2) **Types and stability of carbenes**

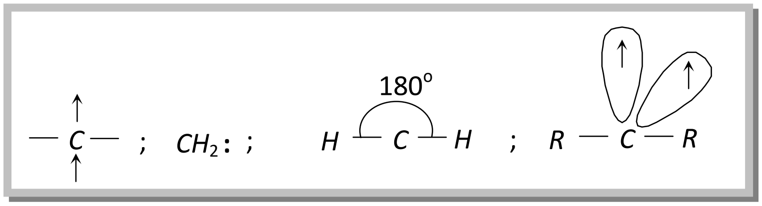
Carbenes are of two types

(i) **Singlet**: When both the electrons go into one orbital and have opposite spin (antiparallel), i.e., the unshared electrons are paired in one orbital and has a bent structure.



The singlet state is actually found to have $H-C-H$ bond angle 103^o (between 90^o to 120^o) and a $C-H$ bond length of 1.12Å. It is generally considered as the less stable.

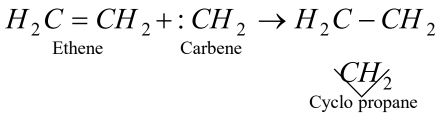
(ii) **Triplet**: When the two electrons go into different orbitals and have same spin (parallel), i.e., the unshared electrons are not paired. Such carbene would have a permanent magnetic moment and would exist in three closely grouped energy state, if it were placed in a magnetic field. Such a state is called triplet state and is believed to be a linear molecule.



With $H-C-H$ bond angle 180^o and a $C-H$ bond length of 1.03Å, it might be considered as a free diradical and is more stable.

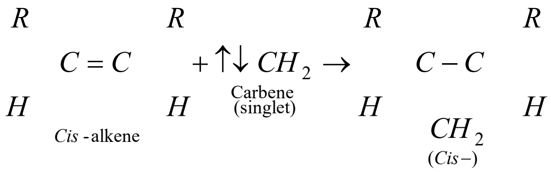
(3) **Reactions involving carbenes**

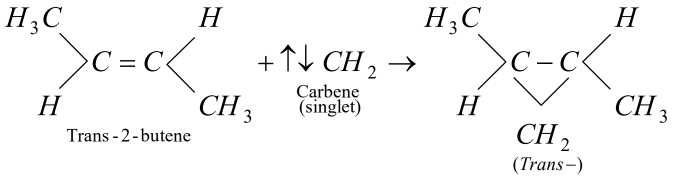
(i) **Addition to alkenes:** Formation of cyclo alkane derivatives, e.g.,

(a) 

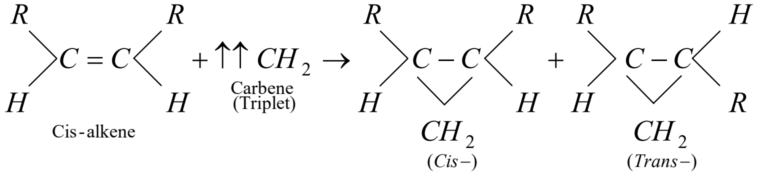
$$\underset{\text{Ethene}}{H_2C=CH_2}+\underset{\text{Carbene}}{:CH_2}\rightarrow \underset{\underset{\text{Cyclo propane}}{CH_2}}{H_2C-CH_2}$$

(b) 

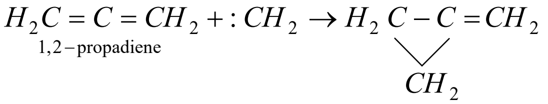


(c) 

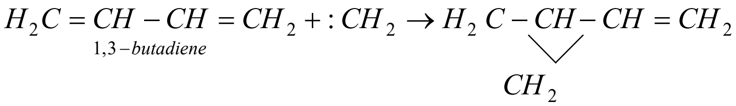
(d) Conversely, the triplet carbenes add on alkenes in a non-stereo specific manner to form both (cis- and trans-) products.



(e) In case of conjugated or cumulative, the addition always occurs exclusively at 1, 2-position.

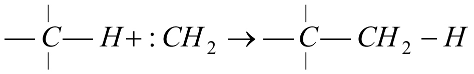


$$\underset{\text{1,2-propadiene}}{H_2C=C=CH_2}+:CH_2\rightarrow H_2\underset{\underset{CH_2}{\diagdown\!\diagup}}{C-C}=CH_2$$

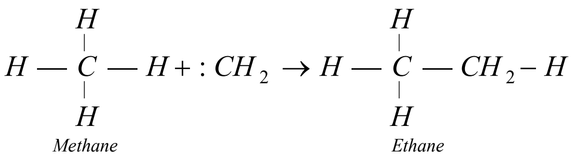


$$\underset{1,3-\textit{butadiene}}{H_2C=CH-CH=CH_2}+:CH_2\rightarrow H_2\underset{\underset{CH_2}{\diagdown\!\diagup}}{C-CH}-CH=CH_2$$

(ii) **Insertion reactions:**Carbenes are also used in its insertion between the $C-H$ bond, e.g.,

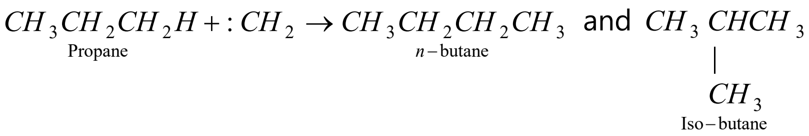


$$-\overset{|}{\underset{|}{C}}-H+:CH_2\rightarrow-\overset{|}{\underset{|}{C}}-CH_2-H$$ (Next homologue)



$$\underset{Methane}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H} + :CH_2 \rightarrow \underset{Ethane}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-H}$$

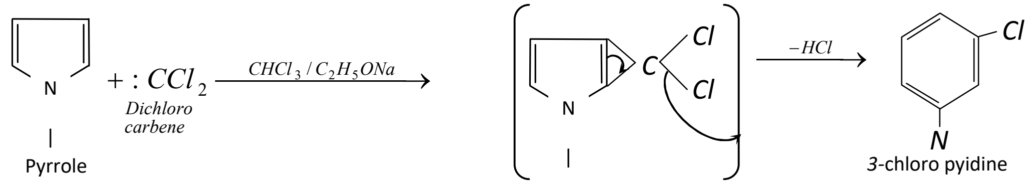
Further it can be inserted in all the possible positions (pri-, sec-, tert-).



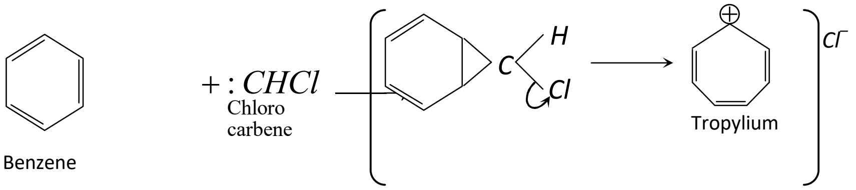
$$\underset{\text{Propane}}{CH_3CH_2CH_2H} + :CH_2 \rightarrow \underset{n-\text{butane}}{CH_3CH_2CH_2CH_3} \text{ and } \underset{\text{Iso}-\text{butane}}{CH_3\underset{\underset{CH_3}{|}}{CH}CH_3}$$

(iii) **Ring expansion reactions:** These involve the addition of a halogeno carbene across a double bond followed by rearrangement.

(a)



(b)



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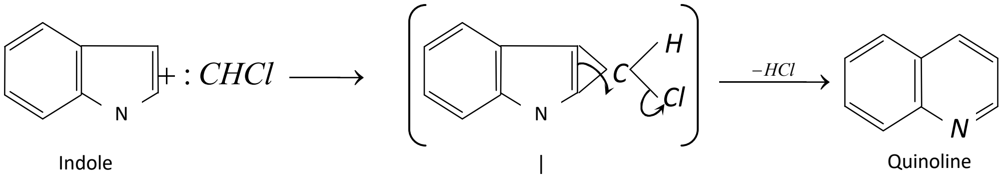
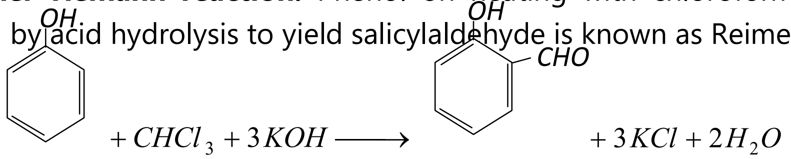


(iv) **Carbylamine reaction:**By heating a mixture of primary amine and chloroform with ethanolic potassium hydroxide to form isocyanide (carbylamine) is known as carbylamine reaction.

$$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$$

Mechanism: $$CHCl_3 \xrightarrow[(-H_2O)]{OH^-} :\overset{\ominus}{C}Cl_3 \longrightarrow \underset{\text{Dichloro carbene}}{:CCl_2} + Cl^-$$

(v) **Reimer-Tiemann reaction:** Phenol on heating with chloroform and aqueous alkali followed by acid hydrolysis to yield salicylaldehyde is known as Reimer-Tiemann reaction.



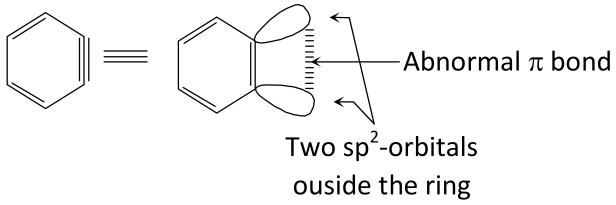
Comparison of Free radical, Carbocation, Carbanion and Carbene

Characteristic	**Free radical**	**Carbocation**	**Carbanion**	**Carbene**
Nature	Neutral having odd electron	Positive charge on C	Negative charge on C	Neutral, divalent with 2 unshared electrons
Hybridization	sp^2	sp^2	sp^3 (non-conjugated) sp^2 (Conjugated)	(i) sp^2 (singlet) (ii) sp (triplet)
Structure	Planar	Planar	Pyramidal/Planar	(i) Planar (singlet) (ii) Linear (triplet)
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	(i) Diamagnetic (ii) Paramagnetic
Stability order	$Ph_3\dot{C} > Ph_2\dot{C}H > Ph\dot{C}$ $CH_2 = CH - \dot{C}H_2 > 3^o >$ $1^o > \dot{C}H_2 > CH_2 = \dot{C}H$	$Ph_3\overset{+}{C} > Ph_2\overset{+}{C}H >$ $Ph\overset{+}{C}H_2 > CH_2 = CH - \overset{+}{C}H$ $3^o > 2^o > 1^o > CH_3$	$Ph_3\overset{\ominus}{C} > Ph_2\overset{\ominus}{C}H >$ $Ph\overset{\ominus}{C}H_2 > \text{Allyl} >$ $\overset{\ominus}{C}H_2 > 1^o > 2^o > 3^o$	Triplet > singlet

Benzyne

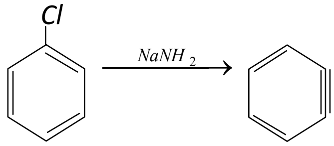
(1) 1, 2-Didehydrobenzene, C_6H_4 and its derivatives are called benzyne or arynes and the simplest member is benzyne.

(2) It is neutral reaction intermediate derived from benzene ring by removing two substituents, of ortho positions, one in the form of electrophile and other in the form of nucleophile leaving behind two electrons to be distributed between two orbitals.



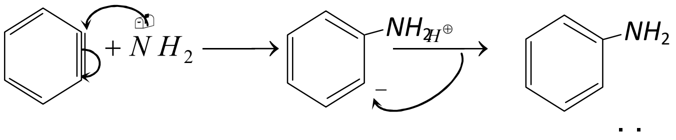
(3) Benzye intermediate is aromatic in character.

(4) When halobenzene is heated with sodamide formation of benzyne takes place.



(5) (i) It behaves as dienophile and gives Diels-Alder reaction with diene.

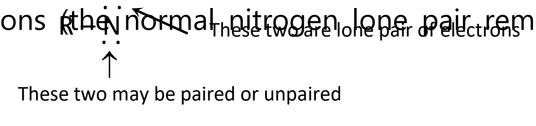
(ii) It reacts with strong nucleophile like $\overset{\ominus}{NH}_2$



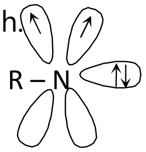
Nitrenes (R – N :)

(1) The nitrogen analogous of carbenes are called nitrenes.

(2) There is possibility of two spin states for nitrenes depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel.



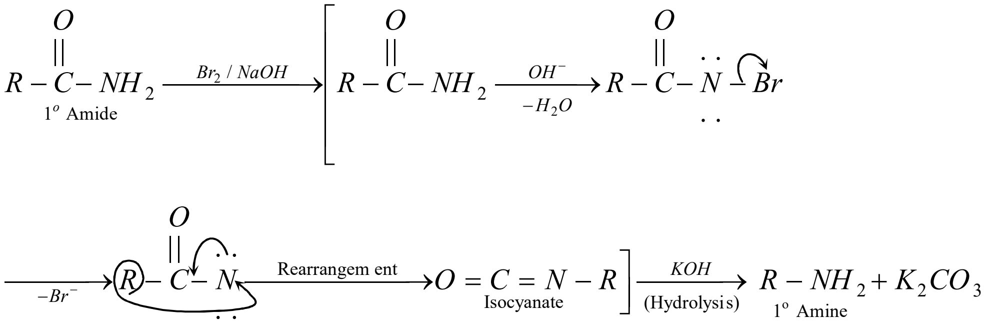
(3) In general nitrenes obey Hunds rule and are ground state triplet with two degenerate sp -orbitals containing a single electron each.



Sp-Triplet nitrene

(4) Nitrenes can be generated, in situ, by the following methods,

(i) **By action of Br_2 in presence of a base on a 1^o amide** (Hofmann-bromamide reaction),



$$\underset{1^o\ \text{Amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow{Br_2\,/\,NaOH} \left[R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[-H_2O]{OH^-} R-\overset{\overset{O}{\|}}{C}-\underset{..}{\overset{..}{N}}-Br \xrightarrow[-Br^-]{} R-\overset{\overset{O}{\|}}{C}-\underset{..}{\overset{..}{N}} \xrightarrow{\text{Rearrangement}} \underset{\text{Isocyanate}}{O=C=N-R} \right] \xrightarrow[\text{(Hydrolysis)}]{KOH} \underset{1^o\ \text{Amine}}{R-NH_2} + K_2CO_3$$

(ii) **By decomposition of azides in presence of heat or light.**

$$\underset{\text{Alkylazide}}{R-\overset{..}{N}=\overset{+}{N}=\overset{..}{N}:^-} \xrightarrow{\Delta\, or\, \text{h}\nu} \underset{\text{Alkylnitrene}}{R-\overset{..}{N}:} + N\equiv N$$

(iii) Unsubstituted nitrene $(H-\overset{..}{N}:)$ can be obtained by photolysis of (or by passing electric discharge through) NH_3, N_2H_4 or N_3H.