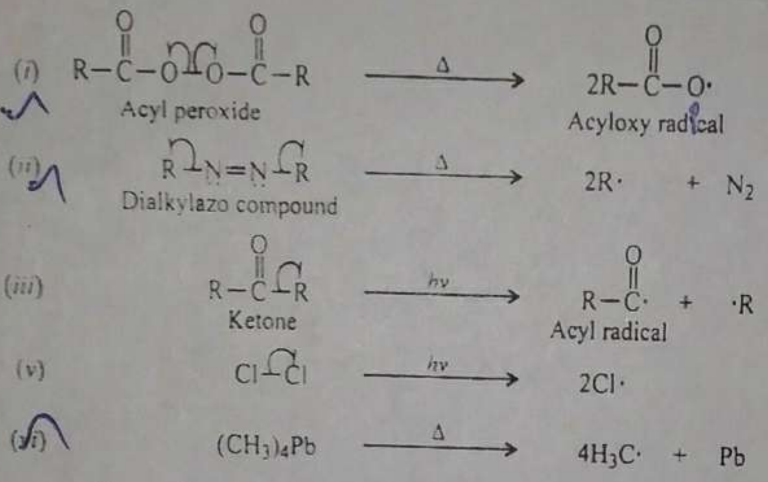
3.10.1. FREE RADICALS*

The paramagnetic species containing an atom or a group of atoms with one or more odd and unpaired electrons is called a **free radical.** Organic reactions which are either initiated by free radicals or involve free radical intermediates are called **free radical reactions.**

(a) Formation

Free radicals are generally produced in reactions carried out at **high temperature** or under the influence of high energy radiations such as **ultraviolet light.** The formation of free radicals is particularly easy if the bonds undergoing symmetrical cleavage are relatively weak. For example,



(i) $\underset{\text{Acyl peroxide}}{R-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-R} \xrightarrow{\Delta} \underset{\text{Acyloxy radical}}{2R-\overset{\overset{O}{\|}}{C}-O\cdot}$

(ii) $\underset{\text{Dialkylazo compound}}{R-N=N-R} \xrightarrow{\Delta} 2R\cdot + N_2$

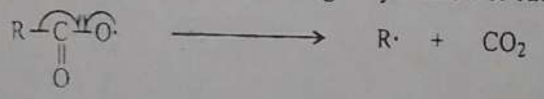
(iii) $\underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-R} \xrightarrow{h\nu} \underset{\text{Acyl radical}}{R-\overset{\overset{O}{\|}}{C}\cdot} + \cdot R$

(v) $Cl-Cl \xrightarrow{h\nu} 2Cl\cdot$

(vi) $(CH_3)_4Pb \xrightarrow{\Delta} 4H_3C\cdot + Pb$

[Homolytic cleavage is generally indicated by fish hook (⌒)]

Occasionally, a free radical cleaves further to give yet another radical. For example,



$R-\underset{\underset{O}{\|}}{C}-O\cdot \longrightarrow R\cdot + CO_2$

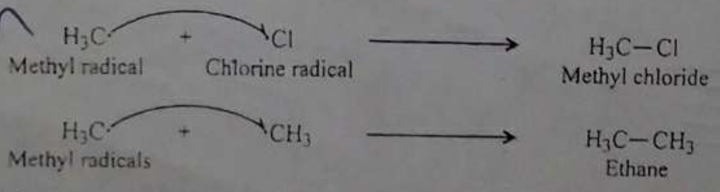
Free radicals are sometimes formed also by the reaction between radical and a molecule. For example,

$\underset{\text{Chlorine radical}}{Cl\cdot} + \underset{\text{Methane}}{H-CH_3} \longrightarrow \underset{\text{Methyl radical}}{\cdot CH_3} + HCl$

(b) Reactions

The important reactions of free radicals can be outlined as follows :

(1) **Coupling of free radicals to form neutral molecules.** Two free radicals readily couple (or combine) to form a stable, neutral molecule. These are the usual **termination reactions** *in free radical chemistry.* For example,



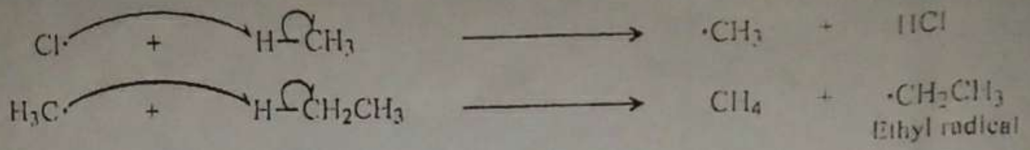
$\underset{\text{Methyl radical}}{H_3C\cdot} + \underset{\text{Chlorine radical}}{\cdot Cl} \longrightarrow \underset{\text{Methyl chloride}}{H_3C-Cl}$

$\underset{\text{Methyl radicals}}{H_3C\cdot + \cdot CH_3} \longrightarrow \underset{\text{Ethane}}{H_3C-CH_3}$

(2) **Reaction with a neutral molecule.** A free radical may abstract an atom from a neutral molecule to form a *new* free radical. The new radical usually reacts further to *propagate* a free radical reaction. For example,

---

*These free radicals can be detected by electron spin resonance spectroscopy (ESR). The detail of this aspect is beyond the scope of this book.



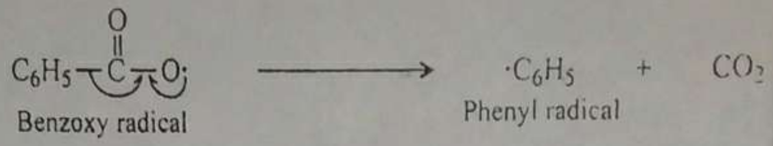
$$Cl\cdot + H-CH_3 \longrightarrow \cdot CH_3 + HCl$$

$$H_3C\cdot + H-CH_2CH_3 \longrightarrow CH_4 + \cdot CH_2CH_3$$

Ethyl radical

Such reactions are usually referred to as propagation reactions in free radical chemistry

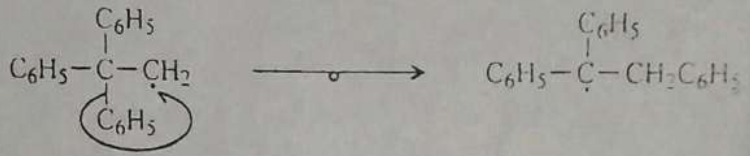
(3) **Decomposition.** A free radical may cleave to give another radical. For example,



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow \cdot C_6H_5 + CO_2$$

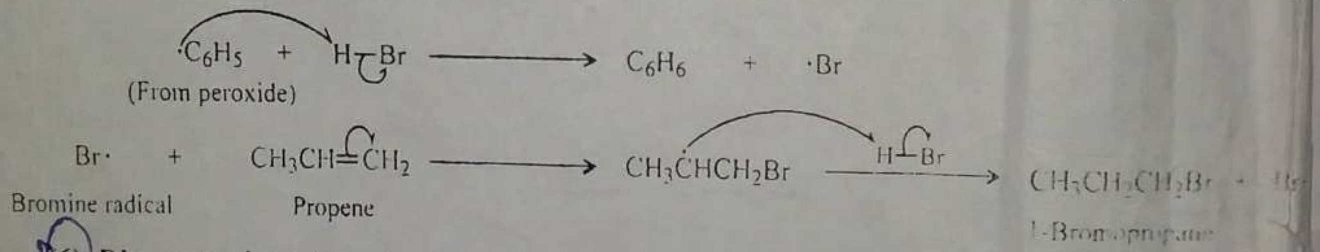
Benzoxy radical　　Phenyl radical

(4) **Rearrangement.** A free radical may rearrange, though less readily than a carbocation, another radical. For example,



$$C_6H_5-\underset{C_6H_5}{\overset{C_6H_5}{C}}-\dot{C}H_2 \longrightarrow C_6H_5-\overset{C_6H_5}{\dot{C}}-CH_2C_6H_5$$

(5) **Addition to a multiple bond.** A free radical can add to a multiple bond like a typical electrophile. The abnormal addition of HBr to propene in the presence of peroxide is one such example.



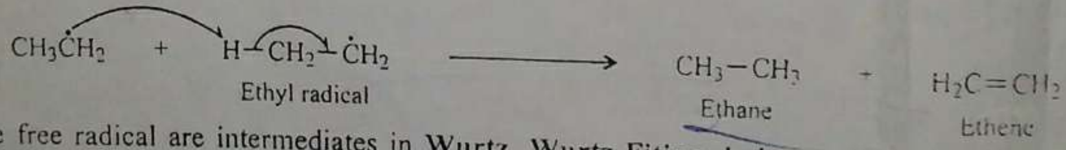
$$\cdot C_6H_5 + H-Br \longrightarrow C_6H_6 + \cdot Br$$

(From peroxide)

$$Br\cdot + CH_3CH=CH_2 \longrightarrow CH_3\dot{C}HCH_2Br \xrightarrow{H-Br} CH_3CH_2CH_2Br + Br\cdot$$

Bromine radical　　Propene　　1-Bromopropane

(6) **Disproportionation.** A free radical may undergo disproportionation to form two or more neutral molecules. For example,



$$CH_3\dot{C}H_2 + H-CH_2-\dot{C}H_2 \longrightarrow CH_3-CH_3 + H_2C=CH_2$$

Ethyl radical　　Ethane　　Ethene

These free radical are intermediates in **Wurtz, Wurtz-Fiting, halogenation of alkanes, Pyrolysis** reactions, etc. These will be discussed in concerned chapters.

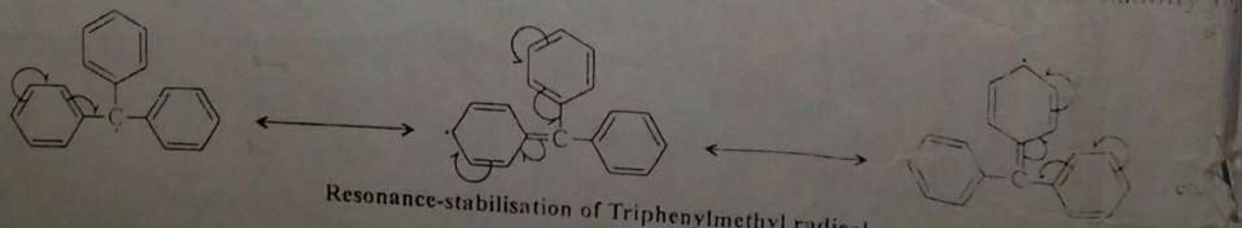
(*c*) Stability.

(1) *The decreasing order of stability of alkyl free radicals is : Tertiary > Secondary > Primary*

The above order of stability has already been explained in terms of **hyperconjugation** (see sec 3.5

(2) Allyl and benzyl radicals are more stable than simple alkyl radicals due to increased stabilisa by resonance as explained under sec. **3.3.1**.

(3) Diphenylmethyl and triphenylmethyl radicals, in which resonance-stabilisation is much m marked (see the resonance forms of triphenylmethyl radical, for example), should show stability of rather high order.



Resonance-stabilisation of Triphenylmethyl radical

Actually, **triphenylmethyl** and similar radicals are stable enough to exist in solution at room temperature.

To sum up, the **decreasing order** of stability of radicals is :

Triphenyl methyl > Diphenyl methyl > Benzyl > Allyl > Tert-alkyl > Sec-alkyl > Prim-alkyl

(d) Structure.

Simple alkyl radicals are believed to have a *planar* structure with the central carbon being *sp*^{2} hybridised. The odd unpaired electron is situated in the unused *p* orbital (**Fig. 3.3**).

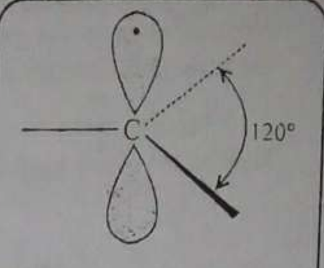
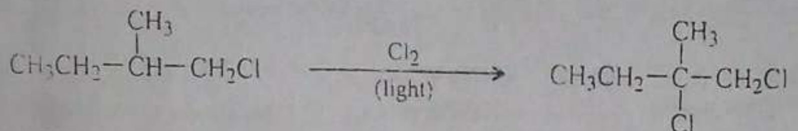


Fig. 3.3. Structure of an alkyl free radical.

Evidence in support of the planar structure. That simple alkyl radicals have planar structure is supported by the following experimental observations :

When (+)-1-chloro-2-methylbutane was chlorinated, (±)-1,2-dichloro-2-methylbutane was the product.



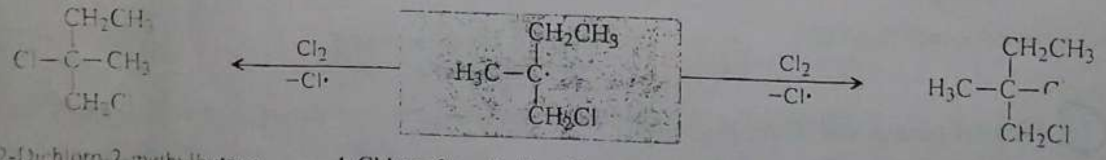
$$CH_3CH_2-\overset{CH_3}{CH}-CH_2Cl \xrightarrow[\text{(light)}]{Cl_2} CH_3CH_2-\overset{CH_3}{\underset{Cl}{C}}-CH_2Cl$$

(+)-1-Chloro-2-methylbutane (±)-1,2-Dichloro-2-methylbutane

The loss of optical activity in the above reaction can be explained by the planar structure of the alkyl radical intermediate. The chlorine molecule can attack the *flat* alkyl radical from both sides with equal ease and the product should therefore, be a racemic compound.

$$CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2Cl + \cdot Cl \longrightarrow CH_3CH_2-\overset{CH_3}{\dot{C}}-CH_2Cl + HCl$$

(+)-1-Chloro-2-methylbutane 1-Chloro-2-methylbutyl radical (3°) (**flat**)

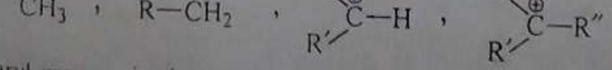


$$Cl-\overset{CH_2CH_3}{\underset{CH_2Cl}{C}}-CH_3 \xleftarrow[-Cl\cdot]{Cl_2} H_3C-\overset{CH_2CH_3}{\underset{CH_2Cl}{C\cdot}} \xrightarrow[-Cl\cdot]{Cl_2} H_3C-\overset{CH_2CH_3}{\underset{CH_2Cl}{C}}-Cl$$

(+)-1,2-Dichloro-2-methylbutane **1-Chloro-2-methylbutyl radical (3°) (flat)** (–)-1,2-Dichloro-2-methylbutane

3.10.2. CARBOCATIONS / CARBONIUM IONS*

The cationic species in which the positive charge is borne by carbon is called a **carbocation** *or* **carbonium ion**. For example,



$$\overset{\oplus}{C}H_3 \;,\; R-\overset{\oplus}{C}H_2 \;,\; \overset{R}{\underset{R'}{}}\!\!>\overset{\oplus}{C}-H \;,\; \overset{R}{\underset{R'}{}}\!\!>\overset{\oplus}{C}-R''$$

(R, R' and R'' are alkyl/aryl groups, simple or substituted. They may contain multiple bonds also).

---

*These carbocations can be detected by **NMR** spectroscopy. For example,

$$(CH_3)_3F + SbF_5 \xrightarrow{\text{liq. } SO_2} (CH_3)_3\overset{\oplus}{C}\,Sb\overset{\ominus}{F_6}$$

δ_{ppm} = 3 (High field) δ_{ppm} = 4.3 (Low field)

Limitation of Definition. In examples given above, carbon is trivalent. The ending ***onium ion*** is generally used for a covalency higher than normal covalency of the charged atom (*e.g.*, ammonium ion for $^{\oplus}NH_4$, oxonium ion for $R\overset{\oplus}{\ddot{O}}H_2$, etc.). Therefore, the name ***carbonium ion*** for the carbocation with trivalent carbon is misleading. Therefore, it has been suggested that the term **carbocations** be used for *carbonium ions* with **trivalent** carbon. Since this suggestion has not been adopted universally so far, the term carbonium ion continues to be used in literature for carbocations with even trivalent carbon.

> **Caution !** Although the more scientific term *carbocation* has been used in this book, users of the book should keep this limitation in view while reading other books or even examination papers.

(*a*) Nomenclature.

Two systems of nomenclature have been proposed. Under the **carbonium ion system**, the simplest carbocation $^{\ominus}CH_3$ is called 'carbonium ion' and the related carbocations are named as derivatives of this 'carbonium ion'. Under the **cationic system**, these species are named as alkyl (or aryl) cations, as illustrated below :

Formula	Name Under	
	Carbonium ion system	**Cationic system**
$\overset{\oplus}{C}H_3$	Carbonium ion	Methyl cation
$CH_3\overset{\oplus}{C}H_2$	Methylcarbonium ion	Ethyl cation
$(CH_3)_2\overset{\oplus}{C}H$	Dimethylcarbonium ion	Isopropyl cation
$(CH_3)_3\overset{\oplus}{C}$	Trimethylcarbonium ion	*tert*-Butyl cation
$H_2C{=}CH{-}\overset{\oplus}{C}H_2$	Vinylcarbonium ion	Allyl cation
$C_6H_5{-}\overset{\oplus}{C}H_2$	Phenylcarbonium ion	Benzyl cation

Caution ! (1) Avoid using names like isopropyl carbonium ion for dimethylcarbonium ion, and *tert*-butylcarbonium ion for trimethylcarbonium ion. Under the carbonium ion system, the correct formulae for isopropyl and *tert*-butyl carbonium ions are really $(CH_3)_2CH{-}\overset{\oplus}{C}H_2$ and $(CH_3)_3C{-}\overset{\oplus}{C}H_2$ respectively. It may be noted that many of these names are still used in current literature rather loosely.

(2) Encourage the use of names recommended under the cationic system.

(*b*) Structure.

The ~~central~~ carbon of a carbocation is sp^2 hybridised. The three sp^2 hybrid orbitals are utilised in forming bonds to three atoms or groups. The remaining unused p orbital remains vacant. The carbocation is thus *a flat species having all the three bonds in one plane with a bond angle of 120° between them* (Fig. 3.4).

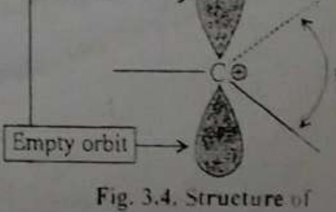


Fig. 3.4. Structure of a carbocation

(*c*) Stability.

The stability of a carbocation is determined to a large extent by its structure.

(1) **Simple alkyl cations.** Among simple alkyl cations, the decreasing order of stability is

Tertiary > Secondary > Primary > Methyl

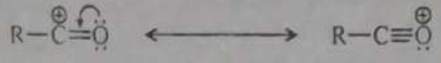
It has already been explained in terms of **hyperconjugation** (sec. 3.5.) and the concept of **inductive effect** (sec. 3.2.1 page 39).

(2) **Allyl cation.** It is highly **resonance-stabilised**, as already explained under sec. 3.3.1 (page 44).

(3) **Benzyl cation.** This is also a **resonance-stabilised** species, as already explained under sec. 3.3.1 (page 44).

(4) **Triphenylmethyl cation.** This is among the most stable carbocations known due to *extensive dispersal of the positive charge*, as already explained under sec. 3.3.1 (page 44).

(5) **Acyl cations (Acylium ions).** These carbocations are also resonance-stabilised, as shown below:

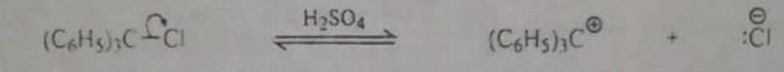


$$R-\overset{\oplus}{C}=\ddot{\underset{\cdot\cdot}{O}} \longleftrightarrow R-C\equiv\overset{\oplus}{\underset{\cdot\cdot}{O}}$$

(*d*) **Formation.**

Carbocations are formed in one of the following ways :

(1) **Unsymmetrical cleavage.** For example,



$$(C_6H_5)_3C-Cl \xrightleftharpoons{H_2SO_4} (C_6H_5)_3C^{\oplus} + :\overset{\ominus}{Cl}$$

Triphenylmethyl chloride (*Colourless*) — Triphenylmethyl cation (*Yellow*)

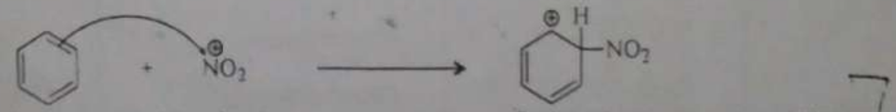
(2) **Polar additions to multiple bonds.** For example,

(*i*)

$$H_3C-CH=CH_2 + \overset{\oplus}{H} \longrightarrow H_3C-\overset{\oplus}{C}H-CH_3$$

Propene — Isopropyl cation

(*ii*)

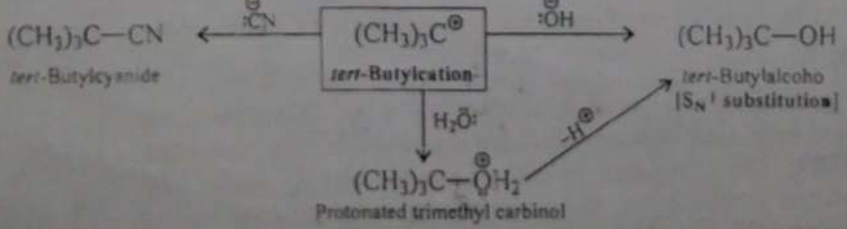


Benzene — Nitronium ion — **Carbocation :** ***resonance stabilised***

(*e*) **Reactions.**

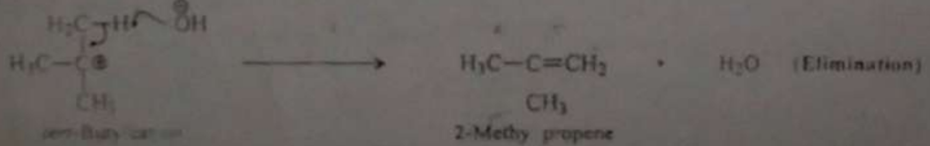
Some representative reactions of carbonium ions/carbocations are :

(1) **Combination with anions or electron-rich species (nucleophiles).** For example,



These **cations** are intermediates in the **nucleophilic substitution** reactions of alkyl halides governed by S_N1 mechanism.

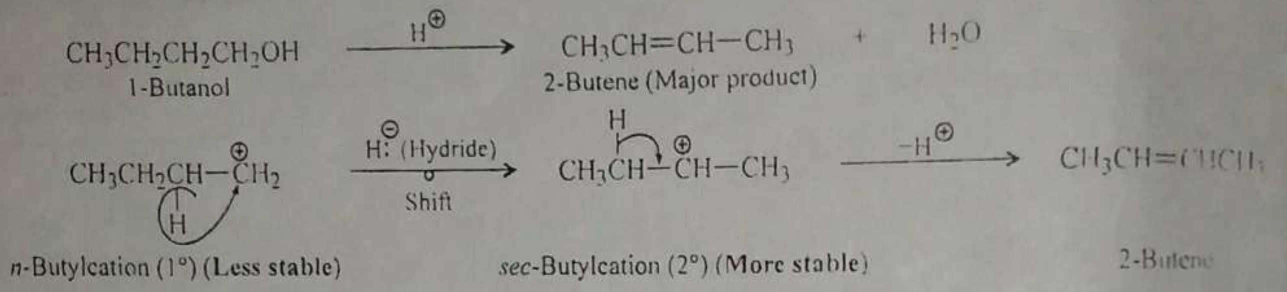
(2) **Loss of a proton ~~or a cation from the adjacent atom.~~** For example,



Such *carbocation intermediates* are generated in elimination reactions of **alkyl halides and alcohols** in the presence of alc. KOH and conc. H_2SO_4 respectively.

(3) **Rearrangement* reaction.** A hydrogen or an alkyl or aryl group may migrate alongwith its electron pair to the positive centre in the carbocation and a new carbocation may be formed, provided the new carbocation is **more stable** than the original carbocation. For example,

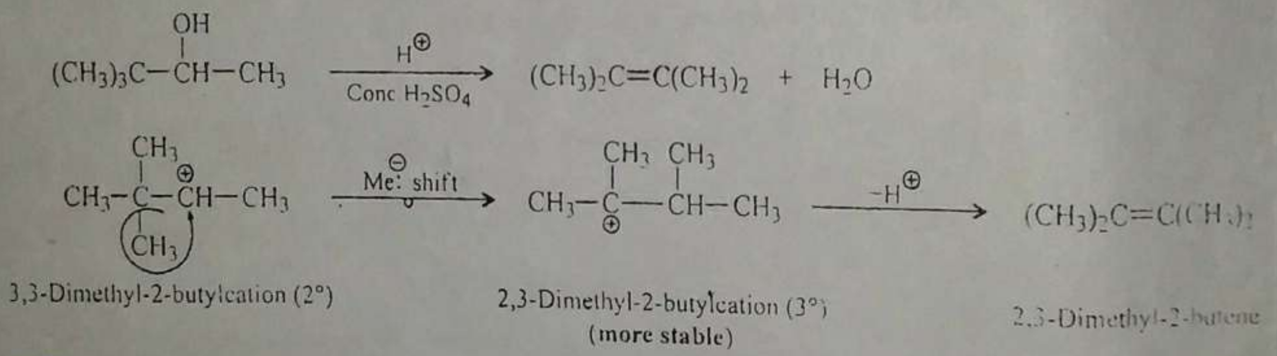
(*a*) the **dehydration** of 1-butanol give 2-butene instead of 1-butene in the presence of conc. H_2SO_4 involves **hydride ion** ($:H^{\ominus}$) transfer to give **more stable** carbocation intermediate.



$$CH_3CH_2CH_2CH_2OH \xrightarrow{H^{\oplus}} CH_3CH{=}CH{-}CH_3 + H_2O$$

$$CH_3CH_2CH{-}\overset{\oplus}{C}H_2 \xrightarrow[\text{Shift}]{\overset{\ominus}{H:}\text{ (Hydride)}} CH_3CH{-}\overset{\oplus}{C}H{-}CH_3 \xrightarrow{-H^{\oplus}} CH_3CH{=}CHCH_3$$

(*b*) the **dehydration** of 3,3-dimethyl-2-butanol in the presence of conc. H_2SO_4 involves $Me:^{\ominus}$ shift to give more stable *tert*. carbocation which give 2, 3-dimethyl-2-butene.

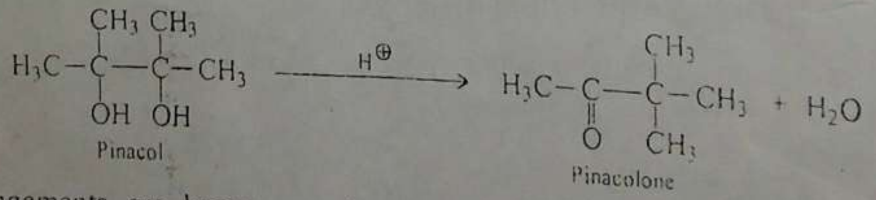


$$(CH_3)_3C{-}\overset{OH}{CH}{-}CH_3 \xrightarrow[\text{Conc }H_2SO_4]{H^{\oplus}} (CH_3)_2C{=}C(CH_3)_2 + H_2O$$

$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\overset{\oplus}{C}H{-}CH_3 \xrightarrow{\overset{\ominus}{Me:}\text{ shift}} CH_3{-}\underset{\oplus}{\overset{CH_3}{C}}{-}\overset{CH_3}{CH}{-}CH_3 \xrightarrow{-H^{\oplus}} (CH_3)_2C{=}C(CH_3)_2$$

(c) Pinacol pinacolone rearrangement

It involves *acid catalysed dehydration of* 1, 2-*glycols* (**pinacols**), followed by a *rearrangement* the carbon skeleton to form ketones (pinacolones).



$$H_3C{-}\underset{OH}{\overset{CH_3}{C}}{-}\underset{OH}{\overset{CH_3}{C}}{-}CH_3 \xrightarrow{H^{\oplus}} H_3C{-}\underset{\|\atop O}{C}{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3 + H_2O$$

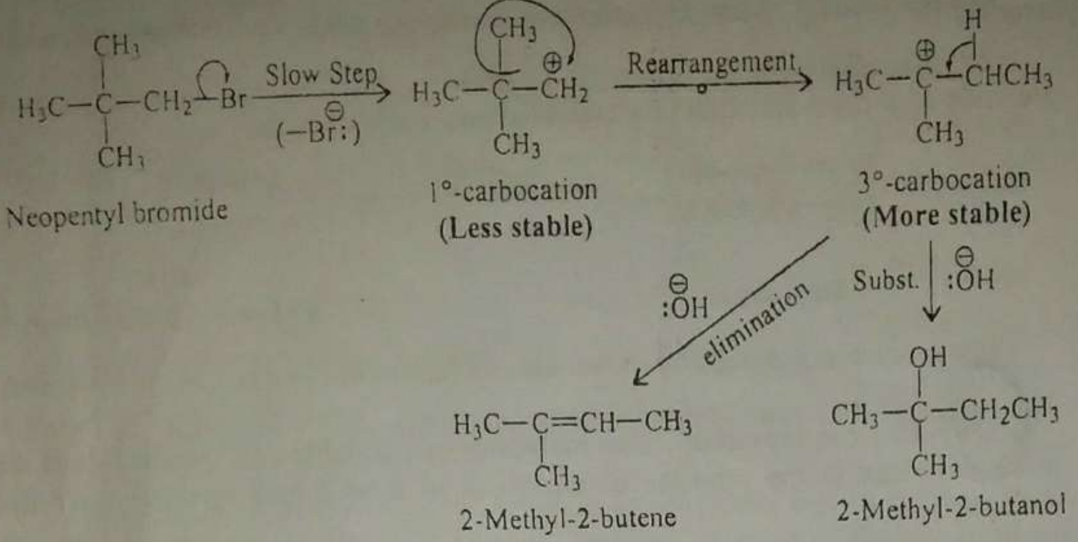
Such rearrangements are known as **pinacol-pinacolone rearrangements** or simply **pinacol rearrangements**. The detailed mechanism of this rearrangement is given under sec **19.4.1**, page 443.

(d) Wagner-Meerwein rearrangement (Neopentyl rearrangement).

It is observed that neopentyl bromide on hydrolysis does not give neopentyl alcohol but gives 2-methyl-2-butanol and 2-methyl-2-butene due to rearrangement of intermediate 1°-**carbocation** into **more stable** 3°-carbocation that can undergo substitution and elimination reactions as shown ahead

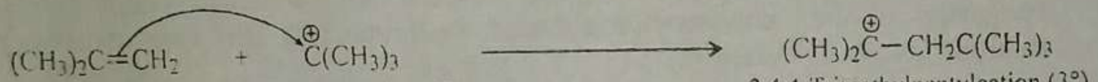
---

* Rearrangement step is generally shown by crooked arrow ($\xrightarrow[\circ]{}$) notation



Such rearrangements are known as **Wagner-Meerwein** rearrangements.*

(4) **Addition to a multiple bond.** A carbocation may add to a multiple bond to form a new carbocation. For example,



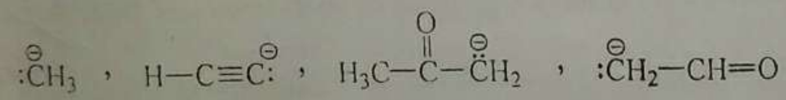
$$(CH_3)_2C{=}CH_2 + \overset{\oplus}{C}(CH_3)_3 \longrightarrow (CH_3)_2\overset{\oplus}{C}{-}CH_2C(CH_3)_3$$

2-Methylpropene *tert*-Butylcation (3°) 2,4,4-Trimethylpentylcation (3°)

The new carbocation may combine with an anionic species to form a stable product or it may add to yet another molecule of the alkene to form a still larger carbocation. (**Vinyl polymerisation**)

3.10.3. CARBANIONS

The anionic species containing a trivalent carbon with a lone pair of electrons is called a **carbanion**. For example,



$$:\overset{\ominus}{C}H_3\ ,\quad H{-}C{\equiv}\overset{\ominus}{C}:\ ,\quad H_3C{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{\ddot{C}}H_2\ ,\quad :\overset{\ominus}{C}H_2{-}CH{=}O$$

A carbanion is necessarily a **base** (Lewis base) and also a **nucleophile**.

(*a*) **Structure**

It is likely that the central carbon in a carbanion is sp^3-hybridised. The unshared pair of electrons occupies one of four sp^3 orbitals, the other three are involved in the formation of three bonds. Thus, carbanions would have *tetrahedral* structures (Fig. 3.5).

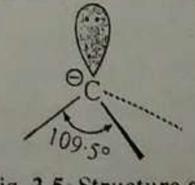


Fig. 3.5. Structure of a carbanion

(*b*) **Stability**

The stability of a carbanion is determined by its structures, as illustrated below :

(1) **Simple alkyl carbanion.** The order of stability of alkyl carbanions is

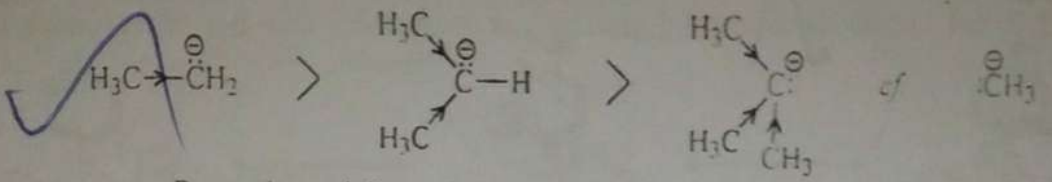
Methyl > Primary > Secondary > Tertiary carbanions

Explanation. The increasing number of electron-releasing alkyl groups in the above series increases the negative charge density at the central carbon atom of the carbanion, and thereby decreases the

---

* Since the starting material is neopentyl bromide. This reaction is also referred to as "**Neopentyl rearrangement**".

carbanion stability, as illustrated below :



Decreasing stabilities of 1°, 2° and 3° carbanions

(2) **Carbanions derived from alkynes, alkenes, and alkanes.** Consider the following series of carbanions and also their relative *s* characters :

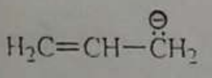
	$HC\equiv\overset{\ominus}{C}:$	$H_2C=\overset{\ominus}{\ddot{C}}H$	$H_3C-\overset{\ominus}{\ddot{C}}H_2$
s character (%)	50	33	25

The higher the *s* character, the closer the electrons are to the nucleus and hence of lower energy. Therefore, the stability order in the above series of carbanions should be, and actually is, as follows :

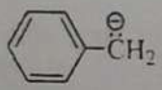
$$HC\equiv\overset{\ominus}{C}: \;>\; H_2C=\overset{\ominus}{\ddot{C}}H \;>\; H_3C-\overset{\ominus}{\ddot{C}}H_2$$

In general, stability of carbanions **increases with increase in the amount of 's' character** at the carbanionic carbon.

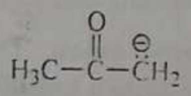
(3) **Carbanions in which the unshared electron pair is conjugated with an unsaturated bond.** Consider the following carbanions (I to IV) in which the unsaturated bond is situated α to the carbanionic carbon :



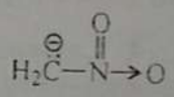
I



II

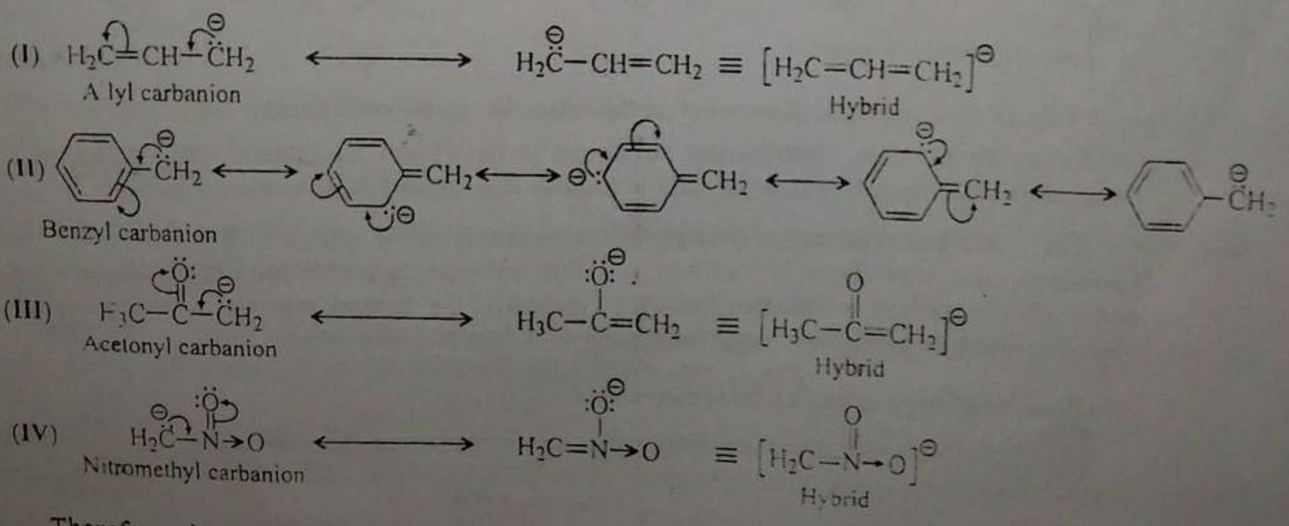


III



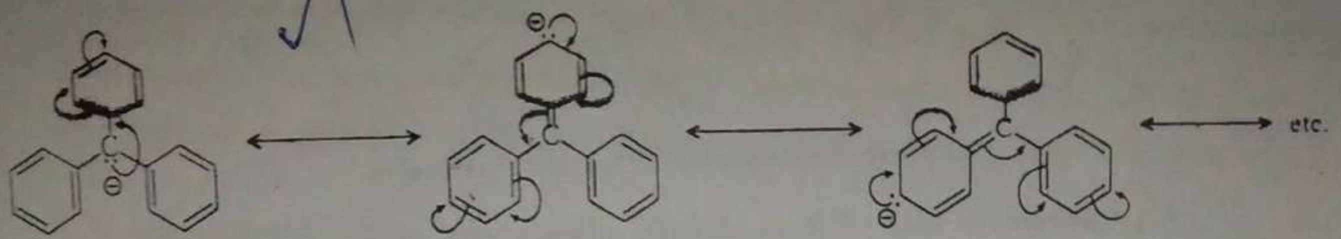
IV

Each of these carbanions is **stabilised by resonance**, as shown below :



Therefore, these carbanions should be ***more stable*** than simple alkyl carbanions.

In diphenylmethyl and triphenylmethyl carbanions, resonance-stabilisation would be even more pronounced than in benzyl carbanion (II), as illustrated ahead in the case of **triphenylmethyl** carbanion.



Resonance stabilisation of triphenylmethyl carbanion

Obviously, the stability order among these carbanions should be as follows :

Triphenylmethyl > Diphenylmethyl > Benzyl carbanions

Actually, diphenyl and triphenylmethyl carbanions can be kept in solution indefinitely if water is excluded rigorously.

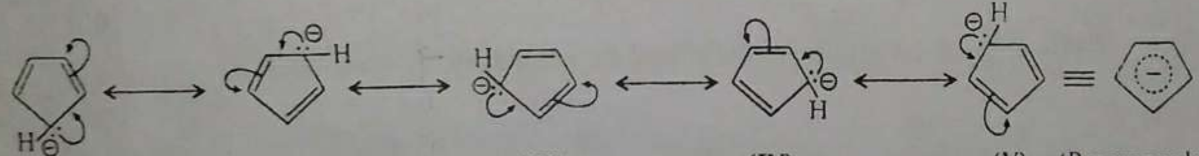
As a natural corollary, the **decreasing acidity** of the corresponding hydrocarbons should be, and actually is, as follows :

Triphenylmethane > Diphenylmethane > Toluene

Compared to allyl and benzyl carbanions (I and II above) III and IV should show greater stability because the electronegative atoms oxygen and nitrogen in these are more capable of bearing a negative charge than carbon. Actually, the carbanions III and IV are more stable than even triphenylmethyl carbanion.

To sum up, **carbanions in which the unshared pair of electrons is conjugated with an unsaturated bond show enhanced stability due to resonance.**

(4) **Cyclopentadienyl anion.** This carbanion, also known as *cyclo-pentadienide ion*, is highly resonance-stabilised, as shown below :


(I) (II) (III) (IV) (V) (Resonance hybrid)

Resonance stabilisation in Cyclopentadienide ion

Since, all the five contributing structures (I to V) are equivalent, this carbanion should show remarkable stability (*cf.* aromatics) and is usually represented as a resonance hybrid.

The calculated resonance energy of cyclopentadienide ion is 175 kJ/mole (*cf.* benzene with resonance energy of about 151 kJ/mole). Thus, cyclopentadienide ion represents an aromatic system and it should exhibit **aromatic** character. Actually, the typical aromatic substitution reactions have been successfully performed on this carbanion.

Reaction involving carbanion intermediates :

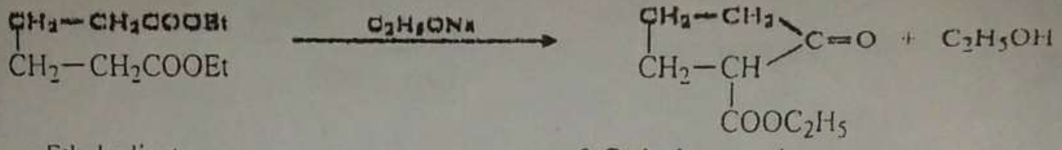
(1) ***Claisen ester condensation.** The condensation of two molecules of ethyl acetate to form ethyl acetoacetate, in presence of sodium ethoxide is known as claisen ester condensation.

$$\underbrace{CH_3COOC_2H_5 + CH_3COOC_2H_5}_{\text{Ethylacetate (2 moles)}} \xrightarrow{C_2H_5ONa} \underbrace{CH_3COCH_2COOC_2H_5}_{\text{Ethyl acetoacetate}} + C_2H_5OH$$

***L. Claisen** (1851-1930). A German chemist. Professor of Chemistry at the University of Bonn. Best known for the above-noted condensation reaction and rearrangement of allyl phenyl ethers.

This reaction is governed by **carbanion** mechanism will be discussed in detail under sec. **26.2.1** page

(2) **Dieckman condensation.** It involves *cyclisation* of a suitable aliphatic carboxylic es presence of sodium ethoxide to a 2-carboalkoxy cycloalkanone.



Ethyl adipate

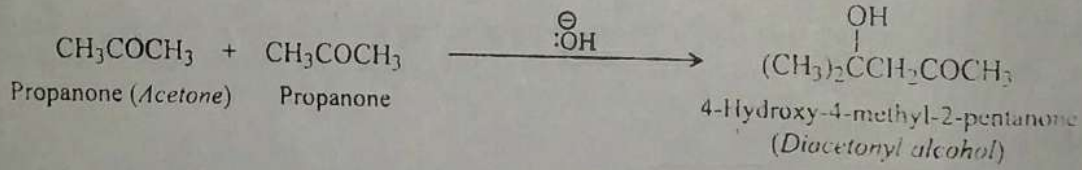
2-Carbethoxy cyclopentanone

This reaction is governed by **carbanion** mechanism will be discussed in detail under sec. **9.1** page

(3) **Aldol condensation.** Two molecules of a suitable aldehyde or ketone containing α-*hydr* *atom* combines in the presence of dil. alkali to form β-*hydroxyaldehyde* or β-*hydroxyketone*. example,

$$\underset{\text{Ethanal}}{CH_3CHO} + \underset{\text{Ethanal}}{HCH_2CHO} \xrightarrow{\overset{\ominus}{:OH}} \underset{\text{3-Hydroxybutanal (Acetaldol)}}{CH_3CH(OH)CH_2CHO}$$

This reaction is called aldol condensation as the product (3-hydroxybutanal) contains a hydroxyl group and an aldehyde group. Similar condensation of two molecules of ketones is designated as aldol condensation although the product in that case contains keto rather tha aldehyde group. For example,



$$\underset{\text{Propanone (Acetone)}}{CH_3COCH_3} + \underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow{\overset{\ominus}{:OH}} (CH_3)_2\overset{\overset{OH}{|}}{C}CH_2COCH_3$$

4-Hydroxy-4-methyl-2-pentanone (*Diacetonyl alcohol*)

These reactions governed by **carbanion** mechanism will be discussed later under sec. **22.9**, page 5

The product **aldol** on heating loses a molecule of water to form α, β-unsaturated aldehyde.

$$CH_3\underset{\underset{OH}{|}}{CH}-CH_2CHO \xrightarrow{\Delta} CH_3\overset{\beta}{C}H=\overset{\alpha}{C}H-CH=O + H_2O$$

Acetaldol

Crotonaldehyde (a α, β-unsaturated aldehyde)

Aldol condensations may also take place between two different aldehydes or ketones, an ald and a ketone containing **α-hydrogens**. Such condensations are called **cross aldol condensat** These reaction may give a mixture of possible products and may also be catalysed by an acid or of an alkali. For detailed mechanism see sec. **22.9**, page 518.

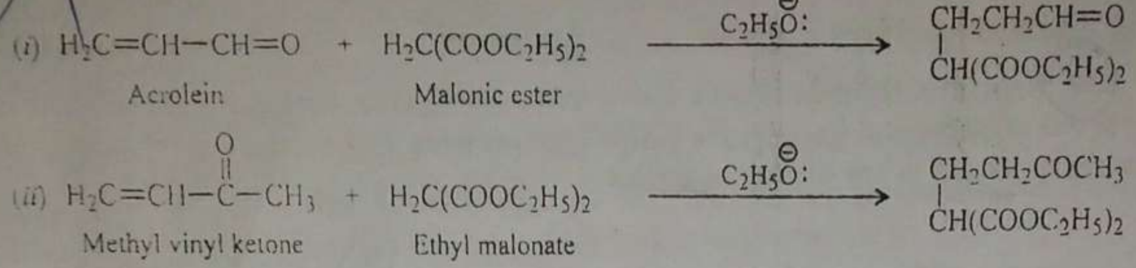
Problem. Give the various products formed between condensation of following paired compounds

(*i*) $CH_3CH{=}O + CH_3COCH_3 \xrightarrow{\overset{\ominus}{:OH}}$ ....

(*ii*) $CH_3COCH_3 + CH_3COCH_3 \xrightarrow{HCl}$ ....

(*iii*) $C_6H_5CH{=}O + CH_3COCH_3 \xrightarrow{\overset{\ominus}{:OH}}$ ....

(4) **Michael Addition.** It involves the **addition of carbanions** to **α, β-unsaturated carbonyl compounds.** The carbanions are generally generated from *difunctional* compounds such as **malonic ester, acetoacetic ester** and **cyanoacetic ester** or *mono-functional* compounds such as nitromethane in the presence of sodium ethoxide. For example,



$$(i)\ \underset{\text{Acrolein}}{H_2C{=}CH{-}CH{=}O} + \underset{\text{Malonic ester}}{H_2C(COOC_2H_5)_2} \xrightarrow{C_2H_5\overset{\ominus}{O}:} \begin{array}{l}CH_2CH_2CH{=}O\\ |\\ CH(COOC_2H_5)_2\end{array}$$

$$(ii)\ \underset{\text{Methyl vinyl ketone}}{H_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + \underset{\text{Ethyl malonate}}{H_2C(COOC_2H_5)_2} \xrightarrow{C_2H_5\overset{\ominus}{O}:} \begin{array}{l}CH_2CH_2COCH_3\\ |\\ CH(COOC_2H_5)_2\end{array}$$

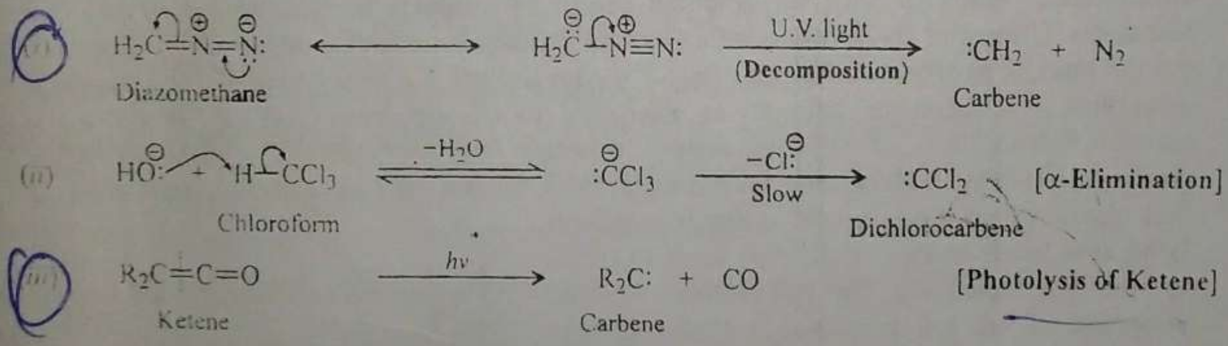
The detailed mechanism of this reaction, governed by carbanion intermediate will be given later under sec. 26.1.2, part III, page 643.

Reactions other than mentioned above involve carbanion intermediates are - **Knoevenagel reaction, Perkin reaction, Claisen reaction, Stobbe condensation,** reactions of **active methylene compounds** and **Grignard reagent.*** These reactions will be discussed under concerned chapters (see sec. 22.9)

3.10.4. CARBENES

These

These are *highly reactive* neutral species *in which the carbon atom has six electrons in the valence shell of which two are unshared.* Carbenes are intermediates in many organic reactions, as illustrated below :



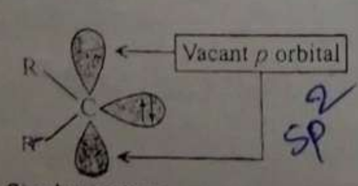
$$(i)\ \underset{\text{Diazomethane}}{H_2C{=}\overset{\oplus}{N}{=}\overset{\ominus}{N}:} \longleftrightarrow H_2\overset{\ominus}{C}{-}\overset{\oplus}{N}{\equiv}N: \xrightarrow[\text{(Decomposition)}]{\text{U.V. light}} \underset{\text{Carbene}}{:CH_2} + N_2$$

$$(ii)\ H\overset{\ominus}{O}: + \underset{\text{Chloroform}}{H{-}CCl_3} \underset{}{\overset{-H_2O}{\rightleftharpoons}} :\overset{\ominus}{C}Cl_3 \xrightarrow[\text{Slow}]{-Cl^{\ominus}} \underset{\text{Dichlorocarbene}}{:CCl_2}\quad [\alpha\text{-Elimination}]$$

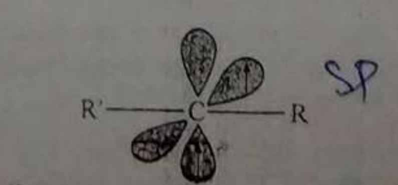
$$(iii)\ \underset{\text{Ketene}}{R_2C{=}C{=}O} \xrightarrow{h\nu} \underset{\text{Carbene}}{R_2C:} + CO \quad [\text{Photolysis of Ketene}]$$

(*a*) **Structure.**

Carbenes have two possible structures namely ***singlet*** and ***triplet*** carbenes. In singlet state carbon atom is believed to be sp^2 hybridised in which one of the sp^2 hybrid orbital contains the unshared pair of electrons with opposite spins and two sp^2 hybrid orbitals form two covalent bonds. The remaining p orbitals are vacant. The carbon atom in *triplet* carbene is believed to be sp hybridised with nearly ***linear*** shape. The two sp hybrid orbitals are utilised in the formation of two covalent bonds and remaining two electrons with parallel spins occupy mutually perpendicular p_y and p_z orbitals. See structures given below :



Singlet carbene



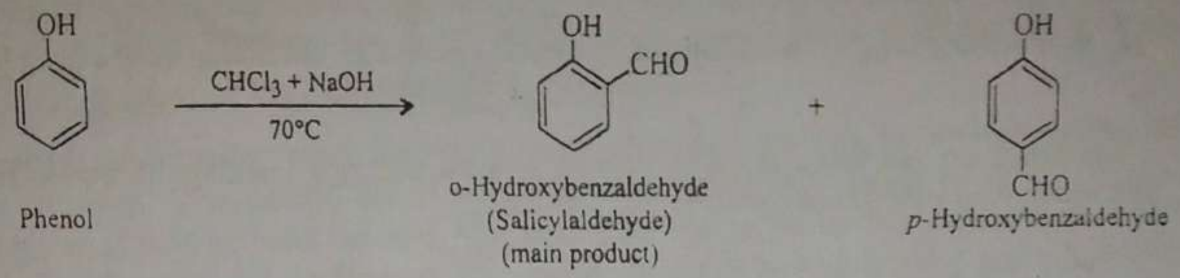
Triplet carbene (*Biradical structure*)

---

* See chapter on Organometallic compounds.

(*b*) **Reactions involving carbenes as intermediates.**

(1) **Reimer-Tiemann reaction.** An aldehyde group is introduced, generally *ortho* to the –OH group, when a phenol is treated with chloroform and sodium hydroxide solution. For example,



Phenol

o-Hydroxybenzaldehyde (Salicylaldehyde) (main product)

p-Hydroxybenzaldehyde

This reaction involving **carbene intermediate** will be discussed under phenols (sec. **20.4.6**, page 467).

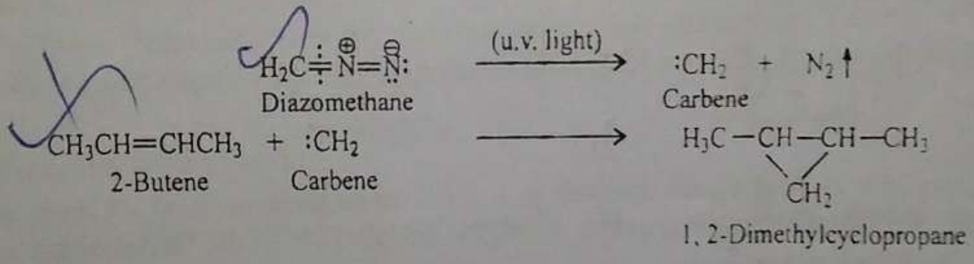
(2) **Carbylamine reaction.** When warmed with chloroform and potassium hydroxide, a primary amine forms an **isocyanide** or a **carbylamine** characterised by a highly unpleasant odour.

$$R\ddot{N}H_2 + CHCl_3 + 3KOH \longrightarrow \underset{\boxed{\text{Isocyanide}}}{RN \equiv C} + 3KCl + 3H_2O$$

(R is an alky /aryl group)

This reaction is *not* given by a *secondary* or a *tertiary* amine and is therefore used *as a diagnostic test for primary amines*. This reaction involves carbene as intermediate will be discussed later under chapter on **amines** (section **28.9.6**, page 711).

(3) **Addition of carbenes to alkenes.** (*a*) When treated with diazo-methane in the presence of ultraviolet light, cyclopropanes are formed by the addition of methylene across the double bond. For example,



$$\underset{\text{Diazomethane}}{H_2\ddot{C}=\overset{\oplus}{N}=\overset{\ominus}{\ddot{N}}:} \xrightarrow{\text{(u.v. light)}} \underset{\text{Carbene}}{:CH_2} + N_2\uparrow$$

$$\underset{\text{2-Butene}}{CH_3CH=CHCH_3} + \underset{\text{Carbene}}{:CH_2} \longrightarrow H_3C-CH-CH-CH_3 \;(\text{ring }CH_2)$$

1, 2-Dimethylcyclopropane

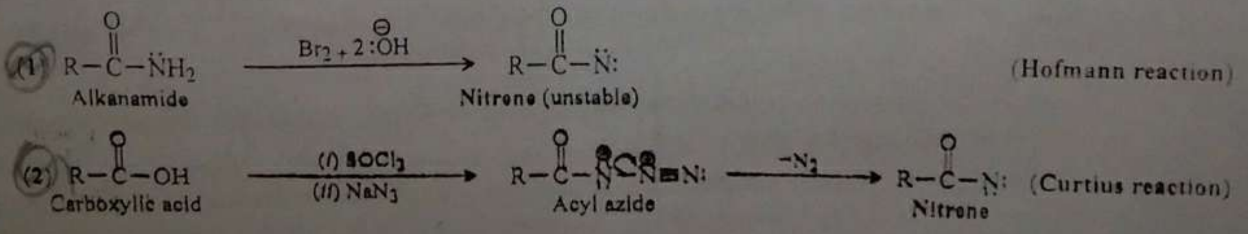
The mechanism of this reaction will be discussed under chapter on **alkenes** (section **10.4.1**, page 212).

3.10.5. BENZYNE

These will be discussed later under chapter on **organic halogen compounds II** (sec. **18.5.1**, page 406).

3.10.6. NITRENES

These are ***neutral, monovalent,*** electron deficient nitrogen containing species. These formed as intermediates in **Hofmann, Curtius, Schmidt** and **Lossen** rearrangements.



$$(1)\ \underset{\text{Alkanamide}}{R-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2} \xrightarrow{Br_2 + 2:\overset{\ominus}{\ddot{O}}H} \underset{\text{Nitrene (unstable)}}{R-\overset{O}{\overset{\|}{C}}-\ddot{N}:}$$

(Hofmann reaction)

$$(2)\ \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow[(ii)\ NaN_3]{(i)\ SOCl_2} \underset{\text{Acyl azide}}{R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{\ddot{N}}-\overset{\oplus}{N}\equiv N:} \xrightarrow{-N_2} \underset{\text{Nitrene}}{R-\overset{O}{\overset{\|}{C}}-\ddot{N}:}$$

(Curtius reaction)