Reaction Intermediate

Three important reaction intermediates are –

① Free radical
② Carbanions
③ Carbenium ion

Carbonium ion or Carbenium ion

methanonium = $CH_5^{\oplus}$

Homolytic fission:- $A - B \rightarrow A^{\cdot} + B^{\cdot}$

when A and B are usually of similar electronegativity.

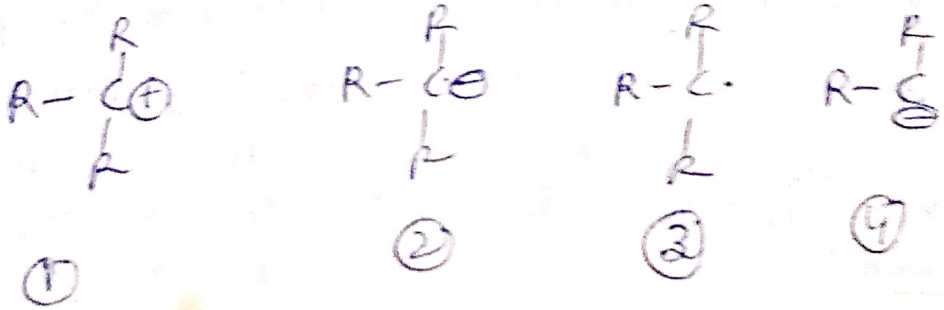
Heterolytic fission:- $A - B \rightarrow A^{\oplus} + B^{\ominus}$

$A : | B \rightarrow A : + B^{\ominus}$ pair

* There are four types of organic species in which a carbon atom has a valency of only 2 or 3.
* They are very short lived and most exist only as intermediates that are quickly converted to more stable molecules However some are more stable than others.

The four type of species are –

(1) Carbocations (2) Carbanions (3) Free radical
(4) Carbenes out of the four only Carbanions have a complete octet around the Carbon.



① ② ③ ④

Other Nitrene $R - \bar{N}$ ⑤

(2)

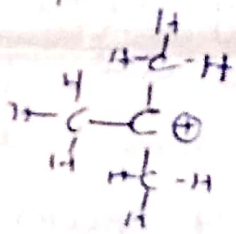
Carbocations:- Any organic species which has a carbon atom bearing only six electrons is called Carbocation.

* In most of the cases Carbonium ion cannot be isolated but it is a reactive intermediate in many chemical reactions.
* The carbon atom of the carbonium ion is sp^2 hybridized
* The remaining p orbital is empty.

eg:- In simple alkyl Carbocations the order of stability is
tert -> sec -> primary

* The stability order can be explained by hyperconjugation and by field effect

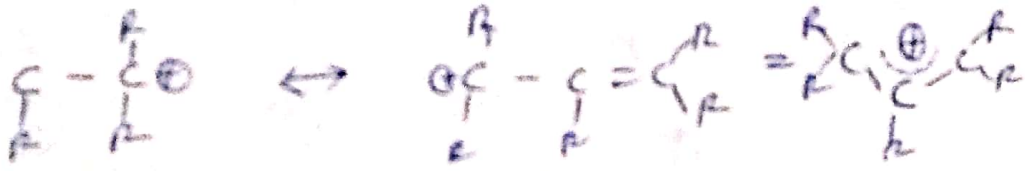
R = CH_3



The field effect:- +I effect of alkyl gp.

eg ②:- The positive carbon is in conjugation with a double bond the stability is greater because of increased delocalization due to resonance and because the positive charge is spread over two atoms instead of one.

acyclic allylic cation



cyclic allylic cation

Benzylic Cation - Canonical forms

(9) Both triphenylmethyl and diphenylmethyl cations have been isolated as solid salts $Ph_3C^{\oplus}$ $Ph_2CH^{\oplus}$

Generation :- * Carbocations, stable or unstable, are usually generated in one of two general ways:

1 A direct ionization, in which a group attached to a carbon atom leaves with its pair of electrons.

$$R-\overset{\frown}{X} \longrightarrow R^{\oplus} + X^{\ominus}$$

2 A proton or other positive species adds to one atom of an unsaturated atom, leaving the adjacent carbon atom with a positive charge.

$$-C=\overset{\frown}{C} + H^{\oplus} \longrightarrow -\overset{\oplus}{C}-C-H$$

The two Chief Pathway by which carbocations react to give stable products

① The carbocation may combine with a species possessing an electron pair. $R^+ + Y^{\ominus} \rightarrow R-Y$.

② The carbocation may lose a proton -

$$-\overset{\oplus}{C}-\overset{\frown}{C}-H \rightarrow -C=C + H^{\oplus}$$

③ Rearrangement :- $CH_2-\overset{H}{\overset{\frown}{CH}}-\overset{\oplus}{C}H_2 \rightarrow CH_2-\overset{\oplus}{C}H-CH_2$

④ addition :- A carbocation may add to a double bond, generating a positive charge at a new position.

$$R^+ + -C=C- \Rightarrow R-\overset{|}{C}-\overset{|}{C}^{\oplus}$$