

Nucleophiles ①

⊗ Nucleophilicity and Basicity -

⇒ Nucleophilicity increases due to the presence of electron donating groups, whereas electron withdrawing group decreases it.



⇒ As moving down the group, nucleophilicity increases, although basicity decreases.



⇒ Along a period from left to right, nucleophilicity decreases. $R_3C^- > R_2N^- > RO^- > F^-$

⇒ A nucleophile with a negative charge is a more powerful nucleophile than its conjugate acid.

e.g. Both H_2O & OH^- are nucleophiles, but

OH^- is more powerful than H_2O .

NH_2^- " " " " NH_3 .

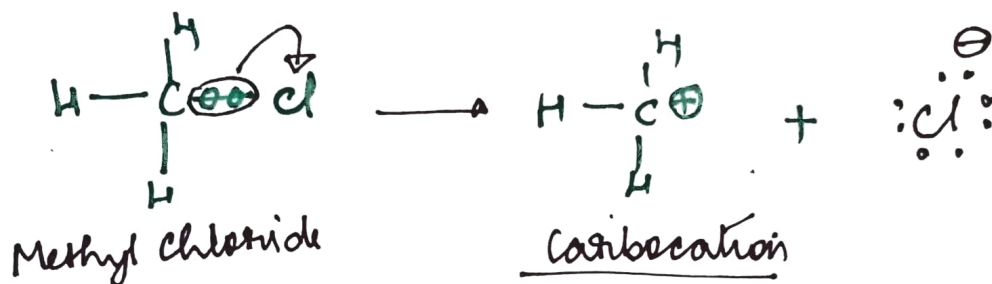
IONIC INTERMEDIATES

(2)

⊗ Homolytic and heterolytic bond fission result in the formation of short lived fragments, called reaction intermediates.

① Carbocations or Carbonium ions :-

A carbonium ion is positively charged ion in which the positive charge is carried by a carbon atom with six electrons in its valence shell.



⊗ Nomenclature :-

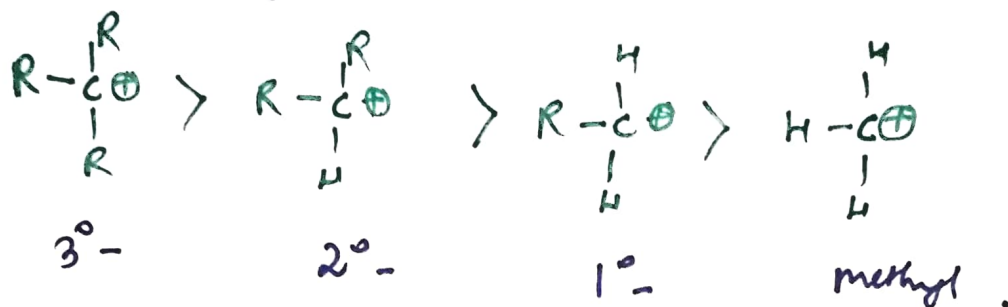
<u>Formula</u>	<u>Carbonium System</u>	<u>Cationic System</u>
CH_3^+	Carbonium ion	methyl cation
CH_3CH_2^+	Methyl Carbonium ion	Ethyl cation
$(\text{CH}_3)_2\text{CH}^+$	Dimethyl Carbonium ion	Isopropyl cation
$(\text{CH}_3)_3\text{C}^+$	Trimethyl Carbonium ion	tert-butyl cation
$\text{C}_6\text{H}_5\text{CH}_2^+$	Phenyl Carbonium ion	benzyl cation
$\text{CH}_2=\text{CH}-\text{CH}_2^+$	Vinyl Carbonium ion	Allyl cation

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* Based on Inductive effect :-

The relative stabilities of carbocation can also be explained on the basis of inductive effect. -

The relative order is -



The 3° -Carbocation ion having three electron donating alkyl group attached to the positively charged carbon is most stable. It is because the total positive charge on carbon gets dispersed on four carbon atoms due to the +I effect of three alkyl groups.

On the other hand, in 2° -carbocation ion, the total positive charge is dispersed over three C-atom which is less stable than 3° -carbocation ion.

* Based on Resonance :-

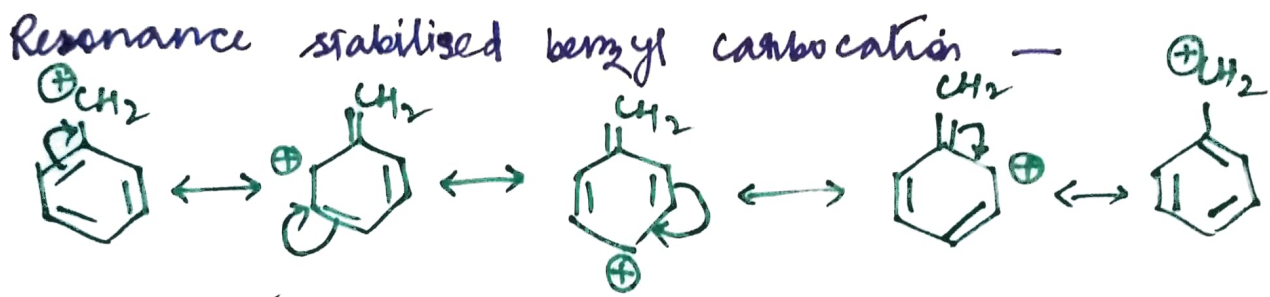
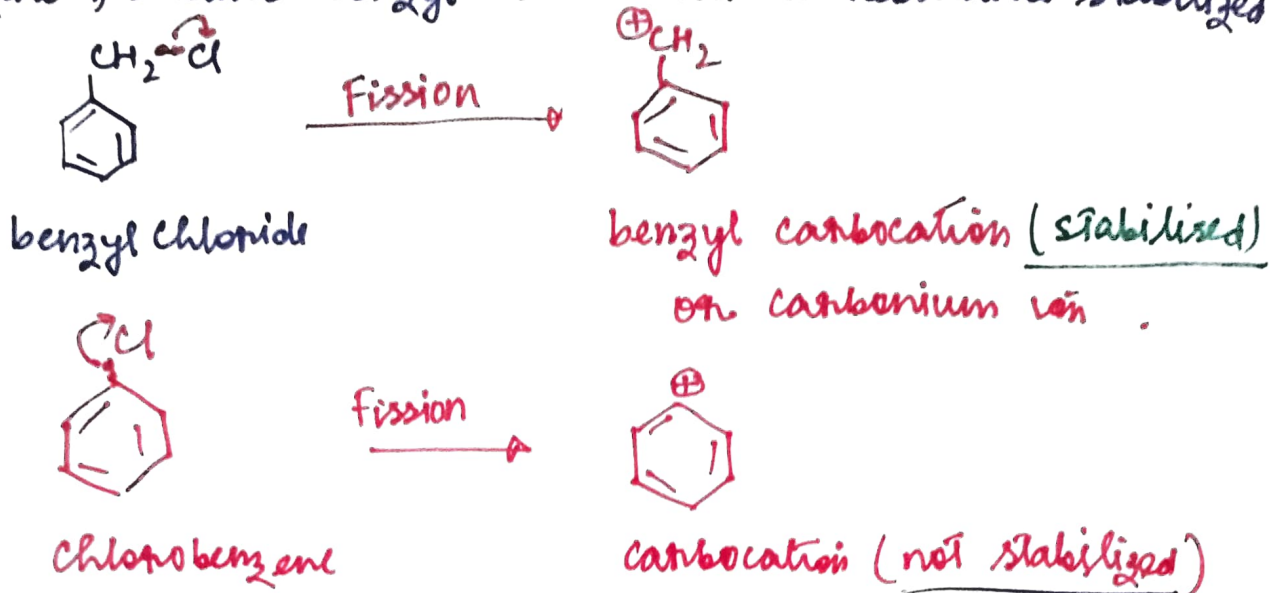
The conjugation due to the resonance of double bond also leads to stability.

e.g. allyl halide ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$) is more reactive than alkyl chloride ($\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Cl}$), because, allyl carbocation formed from allyl halide is resonance stabilised.



⊗ Stability of carbonium ion based on resonance -

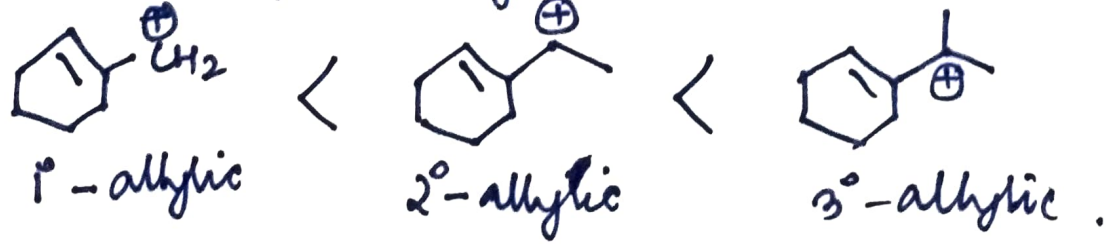
Example:- benzyl chloride is more reactive than chlorobenzene, because benzyl carbocation is resonance stabilized.



⊗ The relative stabilities of carbocations has the following order -

Tropylium cation > triphenyl carbocation > diphenylmethyl carbocation > benzyl carbocation > allyl carbocation > 3°-butyl carbocation > isopropyl carbocation > Ethyl carbocation > methyl carbocation.

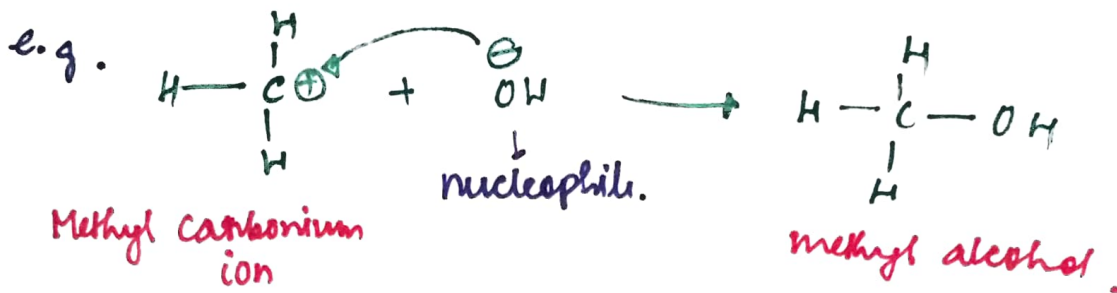
⊗ The stability of allyl carbocation has the order -



⊙ Properties of carbonium ion :-

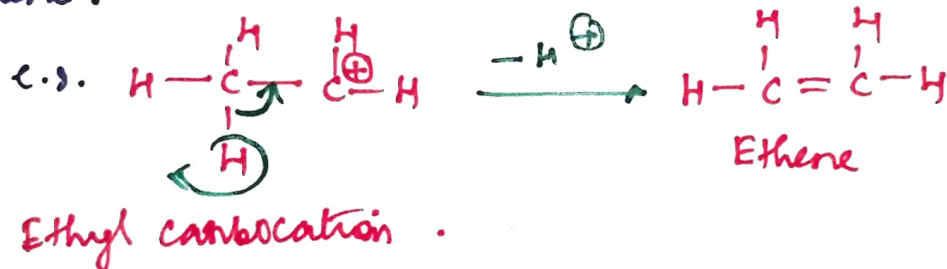
① Combination with nucleophiles :-

A carbonium ion combines with nucleophiles to acquire a pair of e⁻s.

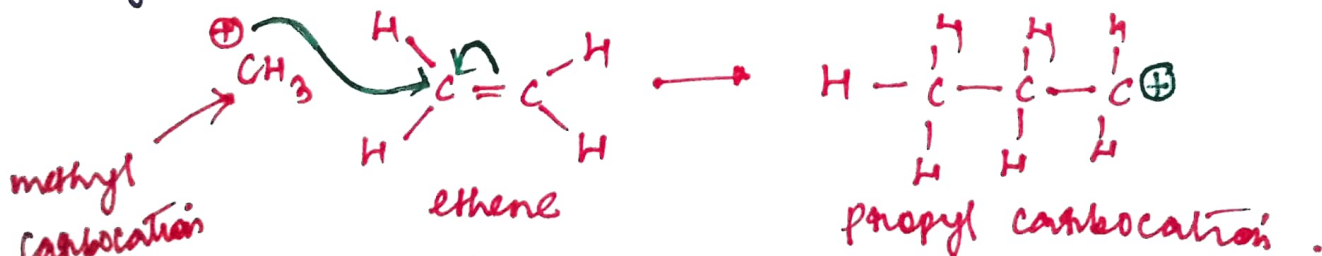


② Proton Loss :-

A carbonium ion loses a proton to form an alkene.



③ Addition to an alkene :- A carbonium ion may add to an alkene to produce another carbonium ion with higher molecular mass.



④ Molecular rearrangement :- A 1° or 2° carbocation undergoes rearrangement to form 3° carbocation (stable).

