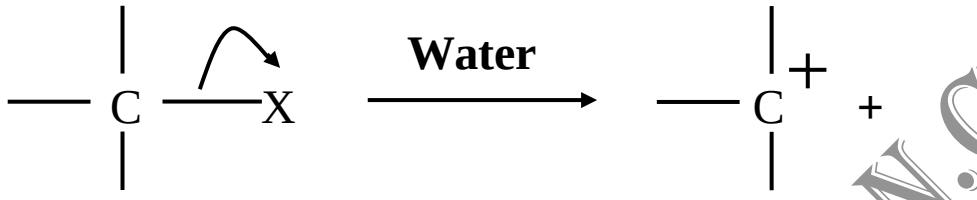
By- SHAILENDRA SHUKLA SIR

Carbonium Ions

"The cations formed by heterolytic bond fission of a covalent bond, where carbon bears positive charge are called carbocations or carbonium ions."

Formation of carbonium ions usually occurs in solution phase and is facilitated by polar solvents like water, alcohol etc. For example,



Haloalkane **Carbonium ion**

(X is more electronegative than C)

Carbonium ions are highly energetic, short lived and highly reactive reaction intermediates, which react further to give final products. Being short lived and highly reactive in general, they could not be isolated and stored.

Since, carbonium ions do not contain unpaired electron, they are not attracted in magnetic field and are diamagnetic in nature. Here, magnetic moment,

$$\mu = \sqrt{n\,(n+2)}\ \text{B.M.}$$

(Where, n = No. Of unpaired electrons)

$$= \sqrt{0\,(0+2)}\ \text{B.M.}$$

$$= 0.00\ \text{B.M.}$$

Characteristics of Carbonium ions

(1) Carbonium ions are positively charged species formed by heterolytic bond fission of a covalent bond, where carbon bears positive charge.

(2) They do not contain any unpaired electron and therefore, they are not attracted in magnetic field and are diamagnetic in nature. The magnetic moment of carbonium ions is zero.

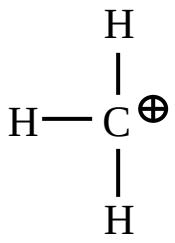
(3)In carbonium ions, carbon bearing positive charge has incomplete octet and contains only six electrons (sextet) in its valence shell. Thus, they are electron deficient and always seek for electrons to complete their octet. It is the reason why they are highly reactive reaction intermediates. Being electron deficient, they act like electrophiles and attack on electron rich centre of substrate molecules.

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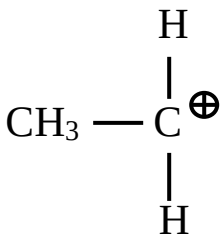
(4) Formation of carbonium ions usually occurs in solution phase and is facilitated by polar solvents like water, alcohol etc.
(5) In alkyl carbonium ions, carbon bearing positive charge is sp^2 hybridized. Hence, alkyl carbonium ions have trigonal planar geometry. They contain an unhybridized and vacant p-orbital which lies perpendicularly above and below the plane formed by sp^2 hybridized orbitals.

Types of Carbonium ions

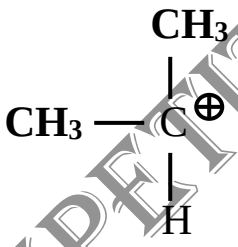
Depending upon the nature of carbon atom bearing positive charge, alkyl carbonium ions may be primary (1^0), secondary (2^0) or tertiary (3^0) in nature. For example,



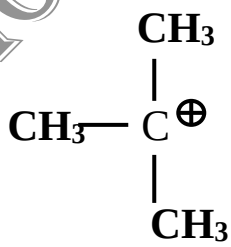
Methyl carbonium ion(1^0)



Ethyl carbonium ion(1^0)



Iso propyl carbonium ion(2^0)



Tert. butyl carbonium ion(3^0)

Geometry of Alkyl Carbonium Ion- In alkyl carbonium ions, carbon bearing positive charge is sp^2 hybridized. Hence, alkyl carbonium ions have trigonal planar geometry where, an unhybridized vacant p-orbital lies perpendicularly above and below the the plane formed by sp^2 hybridized orbitals. Here, bond angle is 120^0 which is normal bond angle of sp^2 hybridization.

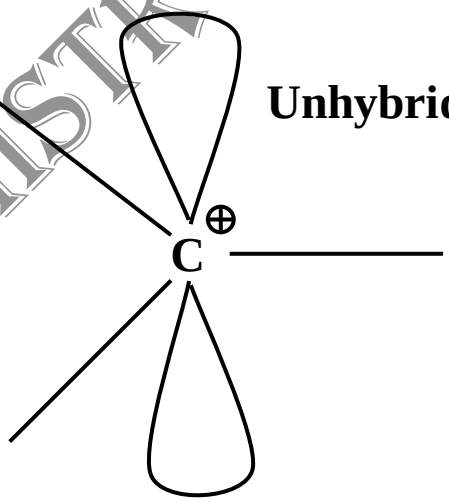


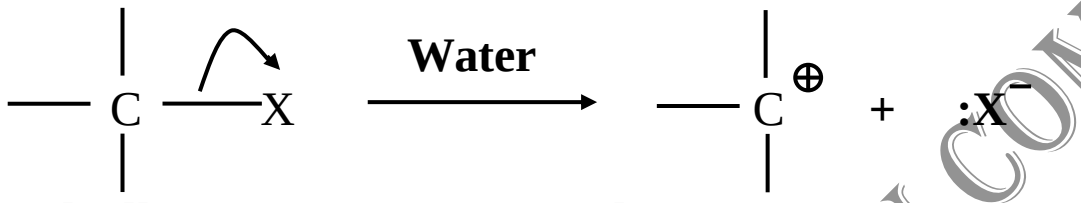
Fig.- Geometry of alkyl carbonium ion (Trigonal Planar)

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Reactions involving Formation of Carbonium ions-

Following reactions involve the formation of carbonium ions as reaction intermediates-

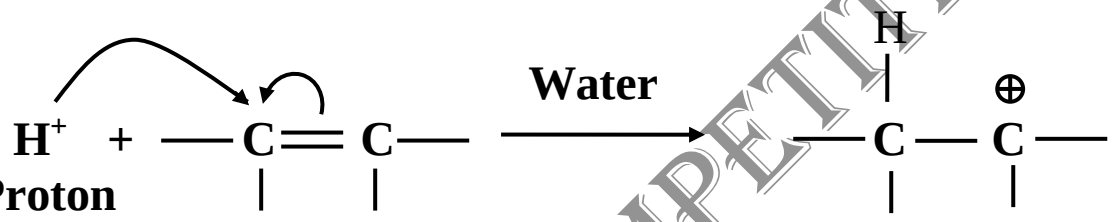
(1) Heterolysis of Haloalkanes-



Haloalkane **Carbonium ion**

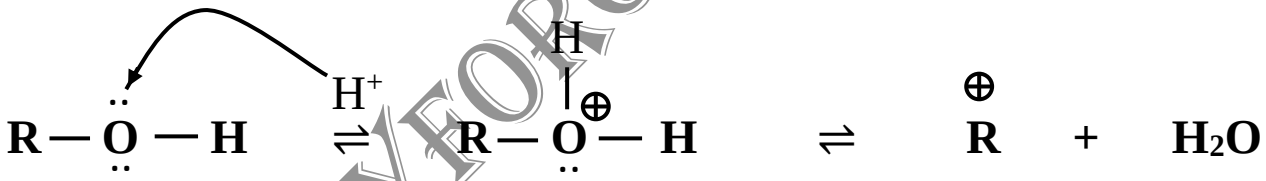
(X is more electronegative than C)

(2) Protonation of Alkenes-



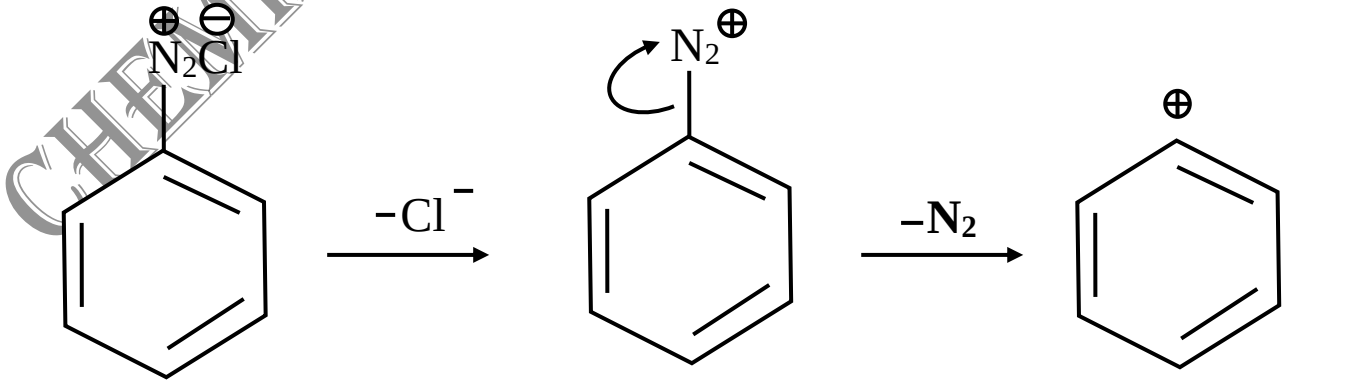
Proton (Electrophile) **Alkene** **Carbonium ion**

(3) Protonation of Alcohols-



Alcohol **Protonated alcohol** **Carbonium ion**

(4) Decomposition of Diazo Compounds-



Benzene diazonium chloride **Benzene diazonium ion** **Phenyl Carbonium ion**

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Stability of Carbonium Ions

Stability of carbonium ions depends upon the dispersal of their positive charge. The greater the dispersal of positive charge of a carbonium, ion more is its stability.

Stability of carbonium ions is explained on following basis-

(i) Inductive effect
(ii) Hyperconjugation
(iii) Resonance

Here, the order of extent of stabilization is as under-

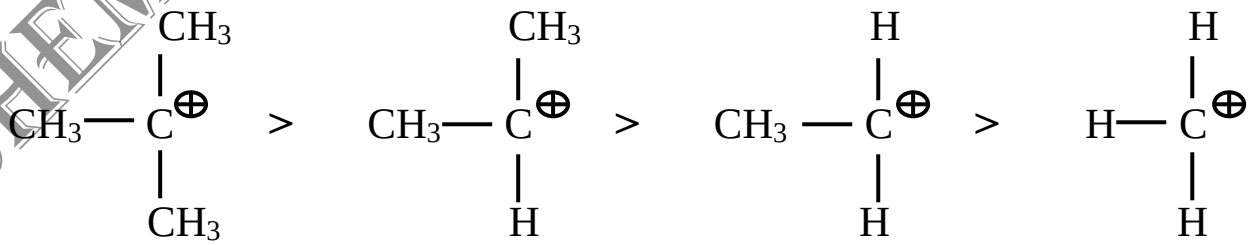
Inductive < Hyperconjugation < Resonance

In fact, +I effect of alkyl groups attached to the positively charged carbon in alkyl carbonium ions, causes dispersal of their positive charge and therefore, increases their stability. Thus, the greater the number of alkyl groups attached to the positively charged carbon, more is stability of alkyl carbonium ion. Thus, the order of stability of different alkyl carbonium ions will be as under.



Tertiary (3^0) carbonium ion > Secondary (2^0) carbonium ion > Primary (1^0) carbonium ion > Methyl (1^0) carbonium ion

This order of stability of alkyl carbonium ions can also be explained on the basis of hyperconjugation. The greater the number of Hyperconjugated forms possible for a carbonium ion, more is dislocalization of its positive charge and therefore, more is its stability. For example, the order of stability of methyl, ethyl, isopropyl and tertiary butyl carbonium ions is as under-



Tert butyl carbonium ion > Isopropyl carbonium ion > Ethyl carbonium ion > Methyl carbonium ion

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Here, methyl carbonium ion does not contain any α-hydrogen atom and therefore, it has no hyperconjugated form while, ethyl carbonium ion contains three α- hydrogen atoms and therefore, it has three Hyperconjugated forms. Thus, ethyl carbonium ion will be more stable than methyl carbonium ion.

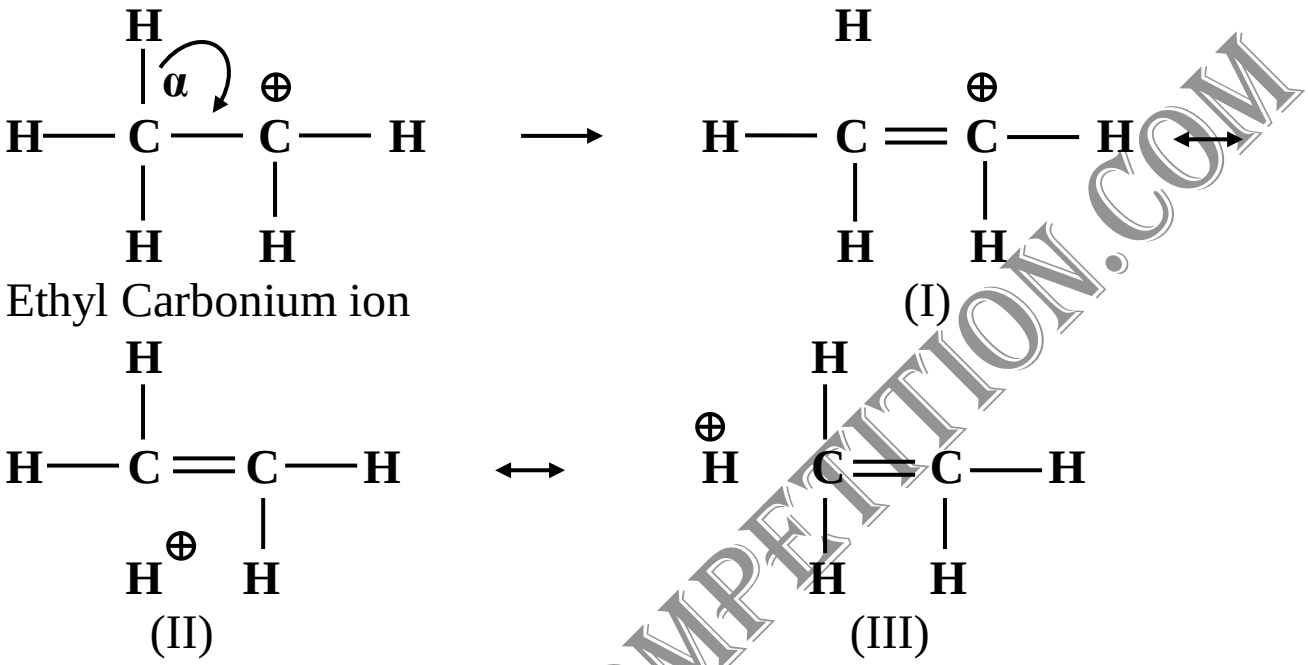


Fig.- Hyper-conjugation in Ethyl Carbonium ion

Similarly, isopropyl carbonium ion (2^0) having six α-hydrogen atoms has six hyper-conjugated forms and is more stable than ethyl carbonium ion (1^0) and tertiary butyl carbonium ion (3^0) having nine hyper-conjugated forms is intern more stable than isopropyl carbonium ion (2^0).

There are certain carbonium ions which gain stability by resonance and are more stable than primary and secondary alkyl carbonium ions. For example, allyl carbonium ion is more stable than isopropyl carbonium ion.

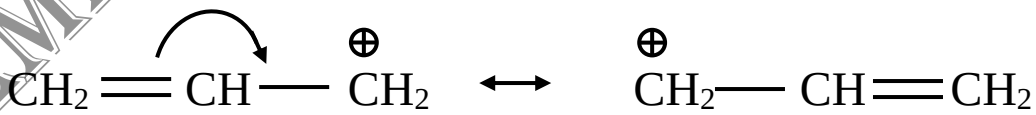
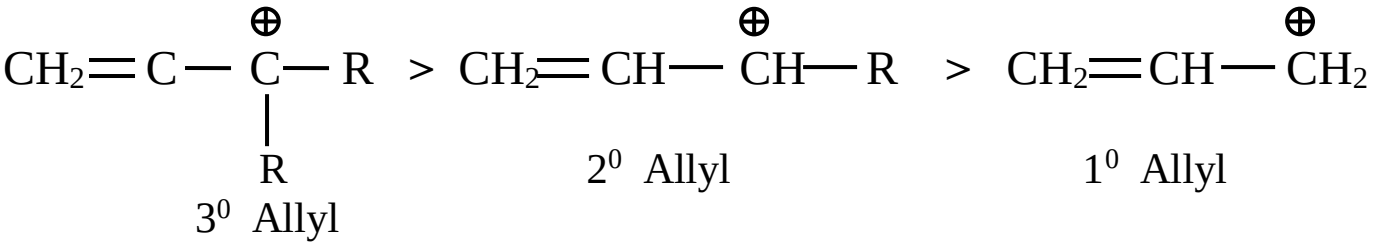


Fig.-Resonance in allyl carbonium ion

Here, secondary allyl carbonium ion is more stable than primary allyl carbonium ion and tertiary allyl carbonium ion is intern more stable than secondary allyl carbonium ion. Thus, the order of stability of allyl carbonium ions will be as follows-

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Benzyl carbonium ion also gains stability by resonance and is more stable than allyl carbonium ion due more extension of resonance.

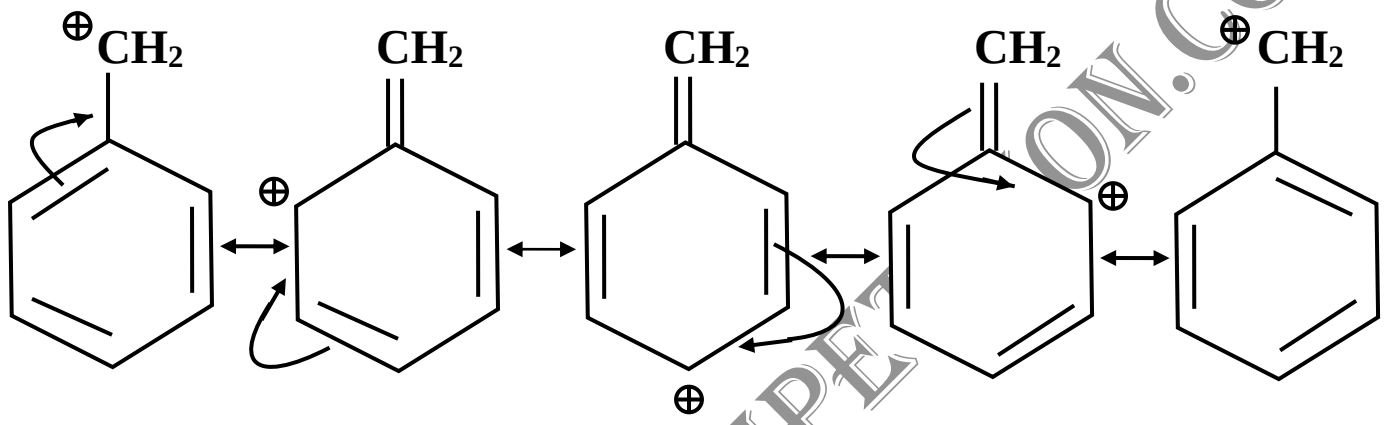
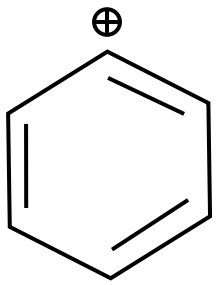


Fig.- Resonance in Benzyl Carbonium ion

In the same way, diphenyl methyl carbonium ion having 10 resonance forms is more stable than benzyl carbonium ion and triphenyl methyl carbonium ion is in tern more stable than diphenyl methyl carbonium ion.

Here also, secondary benzyl carbonium ion is more stable than primary benzyl carbonium ion and tertiary benzyl carbonium ion is intern more stable than secondary benzyl carbonium ion.

If carbon bearing positive charge is a part of benzene ring then carbonium ion is called aryl carbonium ion. For example,



Phenyl Carbonium ion

In aryl and vinyl carbonium ions, π electron cloud of double bond is perpendicular to the vacant p-orbital of positively charged carbon atom. Hence,

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they are not stabilized by resonance. It is the reason why these carbonium ions are highly unstable in nature and therefore, they do not encounter in reaction mechanism. In fact, for resonance the interacting orbitals must be parallel so that they can overlap effectively together. If there is no effective overlap of orbitals, there would be no resonance.

The stability of carbocations also depends upon the electronegativity of carbon bearing positive charge. The greater the electronegativity of carbon bearing positive charge, lesser is dispersal of positive charge and therefore, lesser is stability of respective carbocation. For example, the stability of primary vinylic carbocation is lesser than primary alkyl carbocation.

$$\underset{\text{Ethyl carbocation}}{CH_3-\overset{\oplus}{C}H_2} \quad > \quad \underset{\text{Vinyl carbocation}}{CH_2=\overset{\oplus}{C}H}$$

sp^2 (33.33% s-character) sp (50 % s-character)

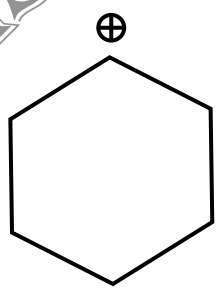
Here, the greater the extent of s-character in hybridized orbital of a carbon atom, more is its electronegativity and therefore, lesser is stability of respective carbocation.

Similarly, Alkynyl carbonium ions are found to be less stable than vinyl carbonium ion.

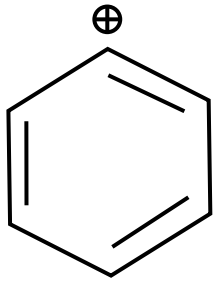
Thus, the order of stability of alkyl, vinyl and ethyne carbonium ions will be as under-

$$\underset{\text{Ethyl carbocation}}{CH_3-\overset{\oplus}{C}H_2} \quad > \quad \underset{\text{Vinyl carbocation}}{CH_2=\overset{\oplus}{C}H} \quad > \quad \underset{\text{Ethynyl carbocation}}{H-C\equiv\overset{\oplus}{C}}$$

For the same reason, aryl carbocation is less stable than cyclohexyl carbocation, which is a secondary alkyl carbocation.



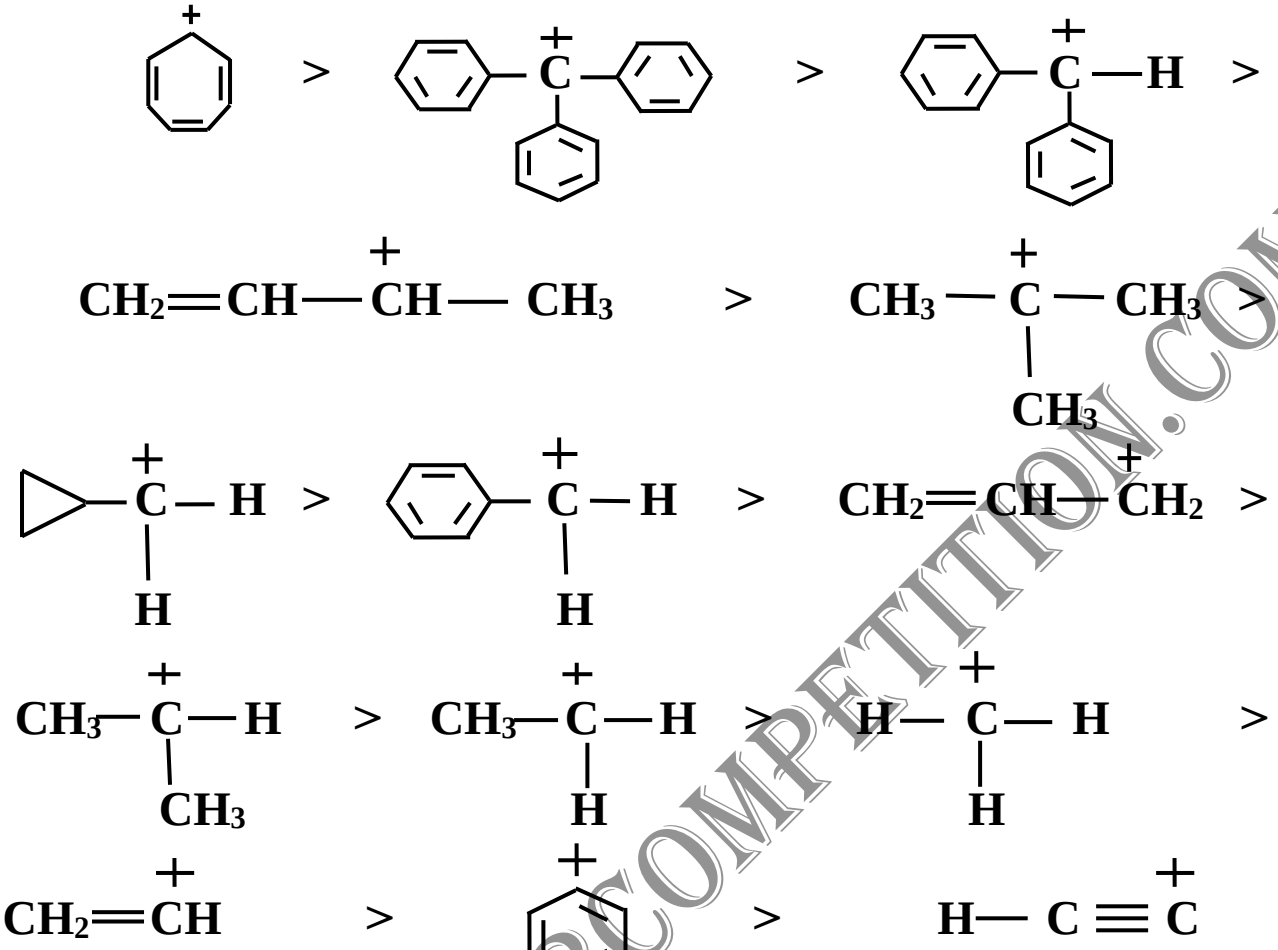
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Cyclohexyl carbocation Aryl carbocation

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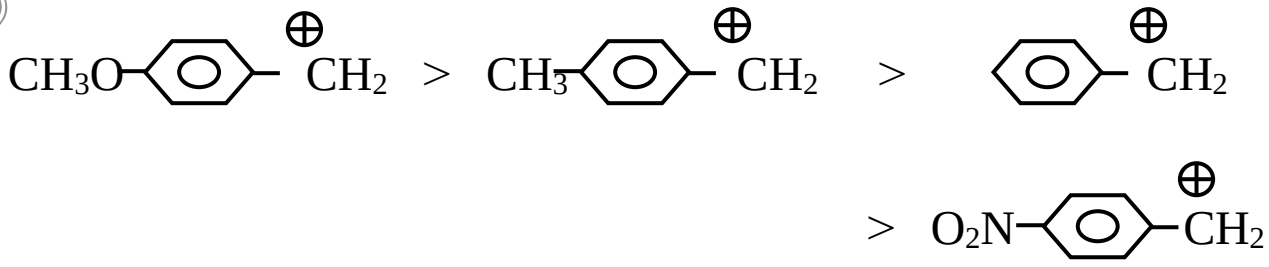
The relative stability of some most common carbonium ions is as under-



Here, stability of primary benzylic and primary allylic carbocations is almost same to that of secondary alkyl carbocations.

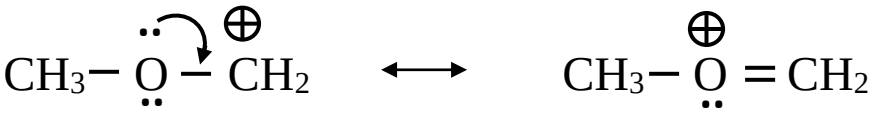
In vinylic carbocations, doubly bonded carbon is sp^2 hybridized. Hence, it has more electronegativity and act like atom having –I effect. It increases positive charge on positively charged carbon and therefore, it decreases the stability of vinylic carbocations. Thus, vinylic carbocations are highly unstable in nature.

On the other hand, the atoms or groups having –I effect, such as –Cl, -Br, $-NO_2$ etc. intensify positive charge on positively charged carbon and therefore, decrease the stability of carbocations. For example, the order of stability of para–substituted benzyl carbonium ion is as under-

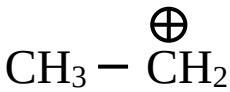


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If all the three factors i.e. inductive effect, hyperconjugation and resonance are operating in different carbocations, then resonance is preferred for deciding their relative stability. For example, methoxy methyl carbocation involves resonance and is more stable than ethyl carbocation where resonance is not possible though it involves +I effect and hyperconjugation.



Resonance in methoxy methyl carbocation



Ethyl carbocation having no resonance

Methyl and primary carbocations involving no resonance are relatively unstable and therefore, they should not be invoked in a reaction mechanism, unless no other path is possible.

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