

Topic: General Organic Chemistry (GOC)

STUDY MATERIAL

***For
Bachelor's of Science
(1st Semester)
Students***

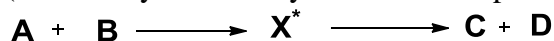
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Reaction intermediates are short lived, high energy reactive species which are formed from hemolytic or heterolytic bond fissions during the course of a chemical reaction. These reactive intermediates generally cannot be isolated but can be detected by spectroscopic techniques such as Infra-red Spectroscopy (IR), Nuclear Magnetic Resonance (NMR), Raman Spectroscopy (RS), Electron Spin Resonance (ESR) etc. or can be trapped chemically. The detection of nitronium ion (NO_2^+) reactive intermediate during the nitration of benzene was predicted by using Raman spectroscopy similarly free radicals and triplet intermediates can be detected by ESR and CIDNP (chemically induced dynamic nuclear polarization) techniques.

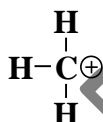


Where A and B are reactants, X^* is reactive intermediate, C and D are products. The various types of reaction intermediates which are encountered during the course of organic reactions are as follows:

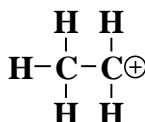
1. Carbocations
2. Carbanions
3. Free-radicals
4. Carbenes
5. Benzyne
6. Nitrenes

Carbocations:

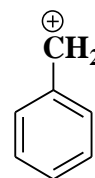
- ❖ Carbocations are those species in which carbon atom bears a positive charge and is bonded to three other atoms.
- ❖ Carbocations are unstable because they don't have eight electrons to satisfy the octet rule.
- ❖ Carbocations behaves as Electrophiles as they have only six electrons in outermost shell.



Methyl carbocation



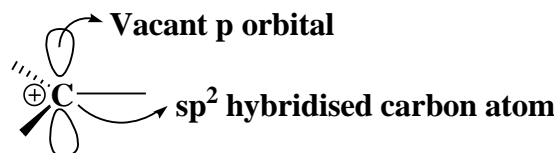
Ethyl carbocation



Benzyl carbocation

Structure of Carbocation:

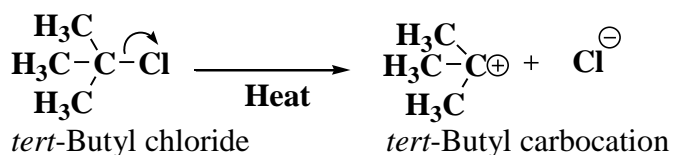
- ❖ In carbocations the carbon atom bearing positive charge is sp^2 hybridized and it uses all its three hybridized orbitals for forming bonds with other atoms. The remaining p_z orbital is empty and is perpendicular to the plane of the other three bonds.
- ❖ Carbocation possess **Trigonal Planar** geometry with bond angle of 120° .



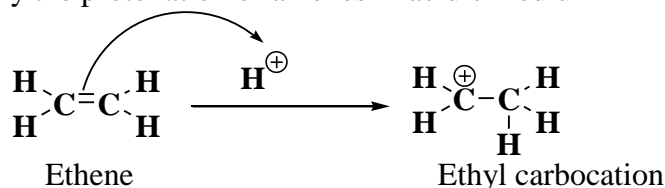
Generation of Carbocations:

Carbocations have been observed as reaction intermediates in a no. of reactions. Following are some of the methods which are generally used to generate carbocations:

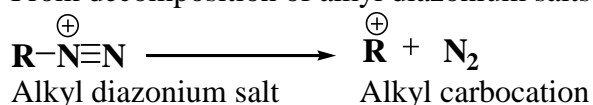
(i) By the heterolysis of C-X bond in alkyl halides.



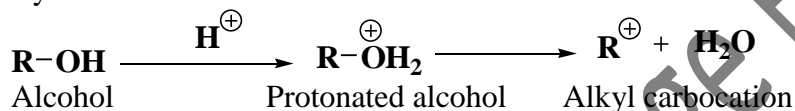
(ii) By the protonation of alkenes in acidic medium



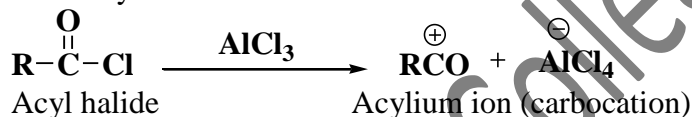
(iii) From decomposition of alkyl diazonium salts



(iv) By treatment of alcohols with concentrated acids

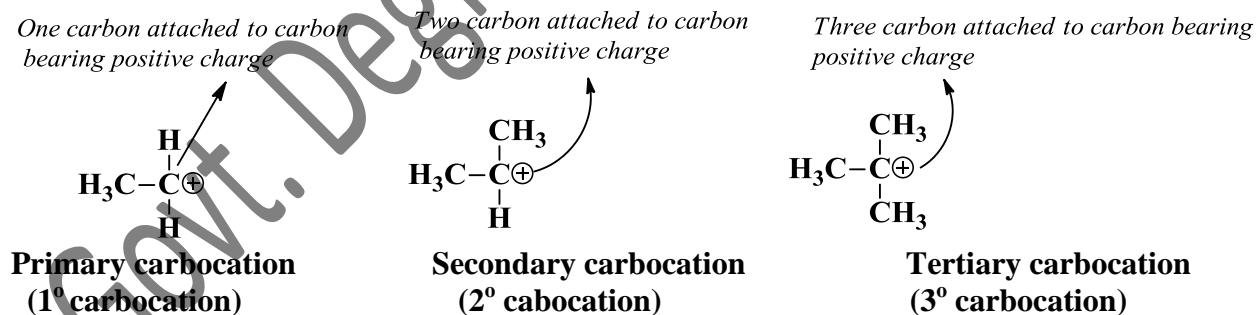


(v) From acyl halides



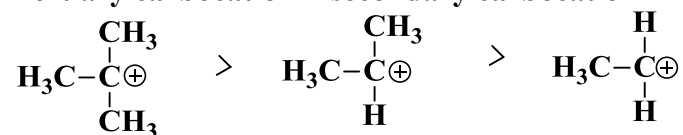
Types and Stability of Carbocations:

There are three types of carbocations: **Primary carbocation**, **Secondary carbocation** and **Tertiary carbocation** classified on the basis of no. of carbon atoms attached to a carbon bearing positive charge



The stability order of three types of carbocations is shown as:

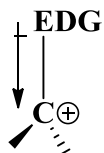
Tertiary carbocation > secondary carbocation > Primary carbocation



The above stability order of carbocations can be explained on the basis of Inductive effect and Hyperconjugation effect.

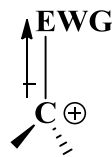
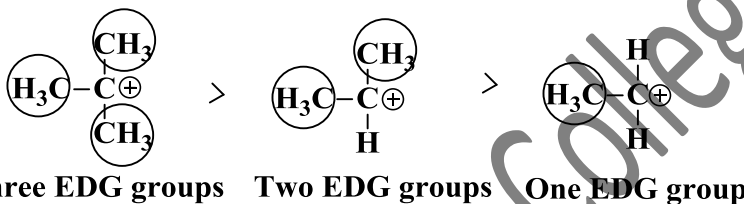
Inductive Effect:

Electron donating groups (EDG) when attached to positively charged carbon tend to decrease the intensity of positive charge on carbon thereby stabilizing the carbocation. However electron withdrawing groups (EWG) when attached to positively charged carbon atom will tend to increase the intensity of positive charge on it and finally will destabilize it. The alkyl groups are electron releasing in nature. Thus more the no. of alkyl groups attached to positively charged carbon more will be the stability of carbocation.



Electron donating group stabilizes the carbocation

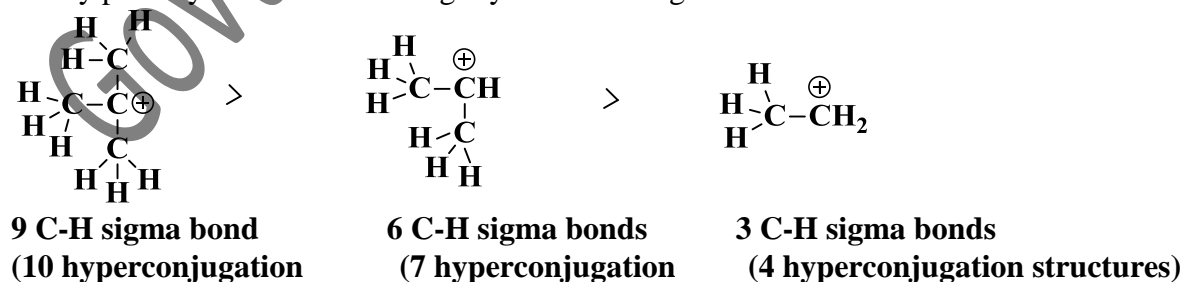
On the basis of inductive effect stability of alkyl carbocations is as follows:



Electron withdrawing group destabilize the carbocation

Hyperconjugation Effect:

Hyperconjugation effect is also helpful in predicting the stability of carbocations. In case of carbocations the C-H sigma bonds of the alkyl groups attached directly to the carbon bearing positive charge can participate in delocalisation, This effect is known as **Hyperconjugation effect** or **No bond resonance** or **Baker-Nathan effect** or **Hetero-valent effect**. Greater the no. of C-H sigma bonds adjacent to carbon bearing positive charge greater is the stability due to higher no. of hyperconjugation structures. On this basis tertiary carbocation is most stable having nine C-H sigma bonds, followed by secondary carbocation having six C-H sigma bonds and finally primary carbocation having only three C-H sigma bonds.

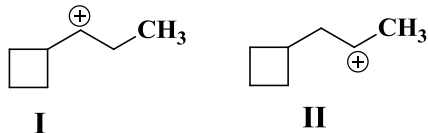


Problems based on carbocations

Q1. Most stable carbocation is:

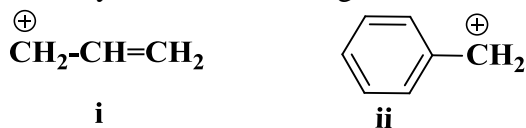
- a) $\text{CH}_3\text{-CH}_2^+$ b) $\text{Br-CH}_2\text{-CH}_2^+$ c) $\text{Cl-CH}_2\text{-CH}_2^+$ d) $\text{F-CH}_2\text{-CH}_2^+$

Q2. Correct stability order is:



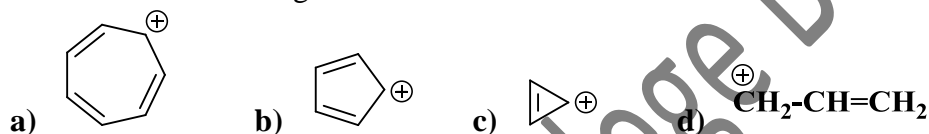
- a) i > ii b) ii > i c) Both are equally stable d) None

Q3. Stability order of following carbocations is:

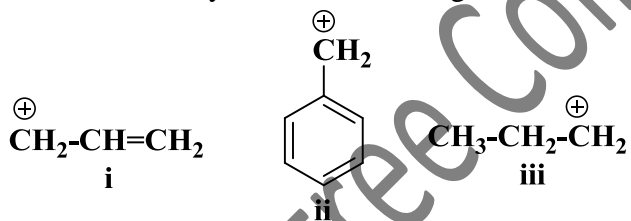


- a) i > ii b) ii > i c) Both are equally stable d) None

Q4. Which of the following is most stable carbocation:

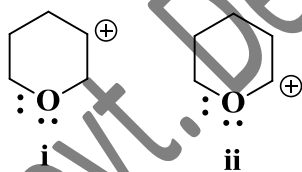


Q5. Correct stability order of following carbocations is:



- a) i > ii > iii b) ii > iii > i c) ii > i > iii d) None

Q6. Predict stability order:



- a) i > ii b) ii > i c) Both are equally stable d) None

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