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CHEMISTRY
PAPER No. 5: Organic Chemistry-2 (Reaction Mechanism-1)
MODULE No. 6: Generation, Structure, Stability and Reactivity of Carbocations

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1. Learning Outcomes

After studying this module, you shall be able to:

- Understand what is a carbocation.
- Learn how a carbocation is generated.
- Identify the various types of carbocations and learn about their stability.
- Know about the reactivity of carbocations.

2. Introduction

The heterolytic cleavage in an organic molecule where carbon donates the shared pair of electrons to the leaving group results in the development of positive charge on the carbon atom. Such species where covalency of carbon is three are called carbenium ions or carbocations (e.g. CH_3^+). The carbon atom of carbocation is sp^2 hybridised and it uses the three hybridised orbitals for single bonding to three substituents; the remaining p-orbital is empty. However, the pentacoordinated positively charged species such as CH_5^+ is called carbonium ion. This nomenclature was proposed by G. A. Olah. Carbocations are intermediates in several kinds of reactions. Some stable carbocations have been synthesized in solution (free or ion pair) and some as solid salts.



carbonium
(hypervalent)

5 bonds to C -rare



carbenium
(hypovalent)

3 bonds to C -common

VS

The carbocation has a flat structure having all the three covalent bonds are in plane with a bond angle of 120° between them.

2.1 Classification of carbocations

- Primary carbocation:** In a primary carbocation the carbon bearing the positive charge is attached to one carbon of an alkyl or aryl group.
- Secondary carbocation:** Here carbon with positive charge is attached to two other carbons.
- Tertiary carbocation:** As the name suggests, in this case the positively charged carbon is attached to three carbon atoms.

While a carbocation with the carbon bearing a positive charge and attached to only three hydrogen atoms and no carbon is known as methyl carbocation.

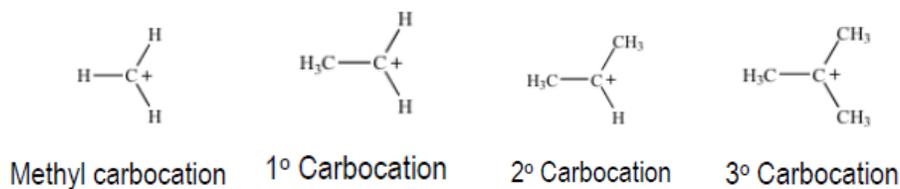


Figure 1: Types of carbocation

2.2 Non-classical Carbocations

A cyclic bridged cation involving three-centre two-electron bonding which three atoms share two electrons is unusual and such species are considered as non-classical carbocations or bridged carbocations. In non-classical carbocation, positive charge is delocalised either by sigma electrons of carbon-carbon or carbon-hydrogen bond or by π electrons of carbon-carbon double bond which is not in allylic position. The examples are 7-norbornenyl cation, norbornyl cation, phenonium ion and cyclopropylmethyl cation.



Figure 2: Non classical carbocation

3. Generation of Carbocation

A number of methods are available to generate stable or unstable carbocation these are ionization, ionization after an initial reaction, attack of π -system on electrophiles.

3.1 Ionization

During direct ionization a leaving group attached to a carbon atom leaves with its pair of electrons resulting in the generation of a carbocation.

For example during solvolysis an alkyl halides ionizes to the intermediate carbocation and the corresponding anion.

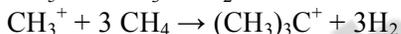
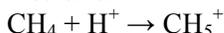


Though, in the case of simple strong acid solution such as H_2SO_4 the carbocation so formed is not very stable, but they can be stored in solutions of fluorosulfuric acid (FSO_3H) and antimony pentafluoride to attain stability. Mixtures, of SbF_5 usually dissolved in SO_2 or SO_2ClF , are strongest acidic solutions known as super acids.

For example the addition of alkyl fluorides to SbF_5 results into the formation of a stable carbocation.



Super acid (FSO_3H-SbF_5) reacts with alkanes as well. For example, at $140^\circ C$ ($284^\circ F$) it converts methane into the tertiary-butyl carbocation, a reaction that begins with the protonation of methane:



3.2 Ionization after an initial reaction

Sometimes the functional groups present in an organic compound first undergo an initial reaction which converts the functional group into a good leaving group, which can then ionize into a carbocation after removal of the leaving group.

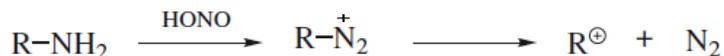
Thus, stable cations can be generated from alcohols in super acid- SO_2 at $-60^\circ C$.

Example:

(a) Protonation of an alcohol gives an oxonium ion which ionizes to a carbocation with loss of water molecule.



(b) A primary amine gets converted into a diazonium salt in the presence of nitrous acid which then ionizes to a carbocation with loss of nitrogen.



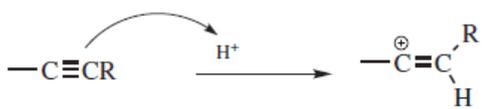
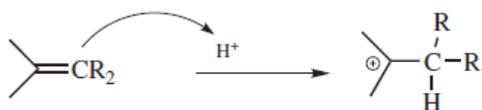
3.3 Attack of π -system on electrophiles

When an electrophile adds to one of the atoms of a π -system the adjacent atom acquires a positive charge. In case the positive atom is a carbon a carbocation is formed.

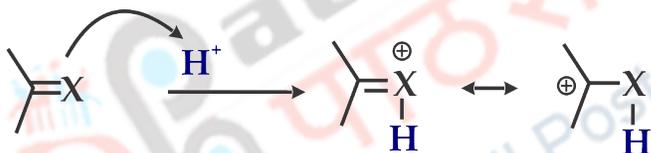
Stable cations can be generated from alkenes by the addition of a proton from super acid or HF-SbF_5 in SO_2 or SO_2ClF at low temperatures.

Example:

(a) Attack of π -system such as alkene or alkyne on an electrophile like proton, bromonium ion etc results in development of positive charge on the adjacent carbon and leads to the formation of carbocation intermediate.

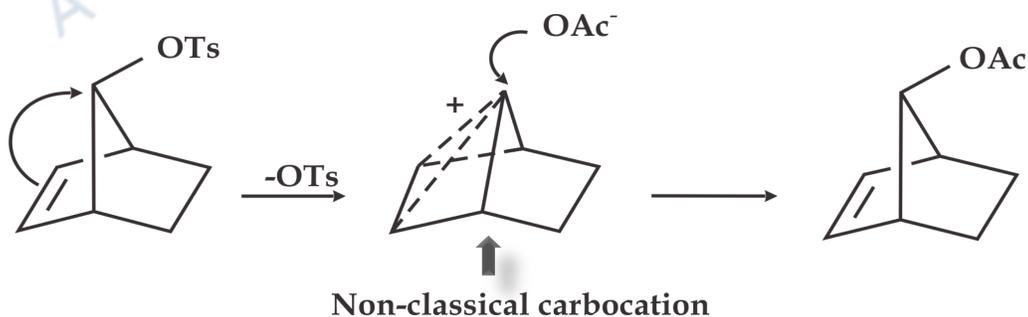


(b) Addition of proton or other positive species to one atom of a C-X bond (X= O, S, N) develops positive charge on adjacent carbon atom.

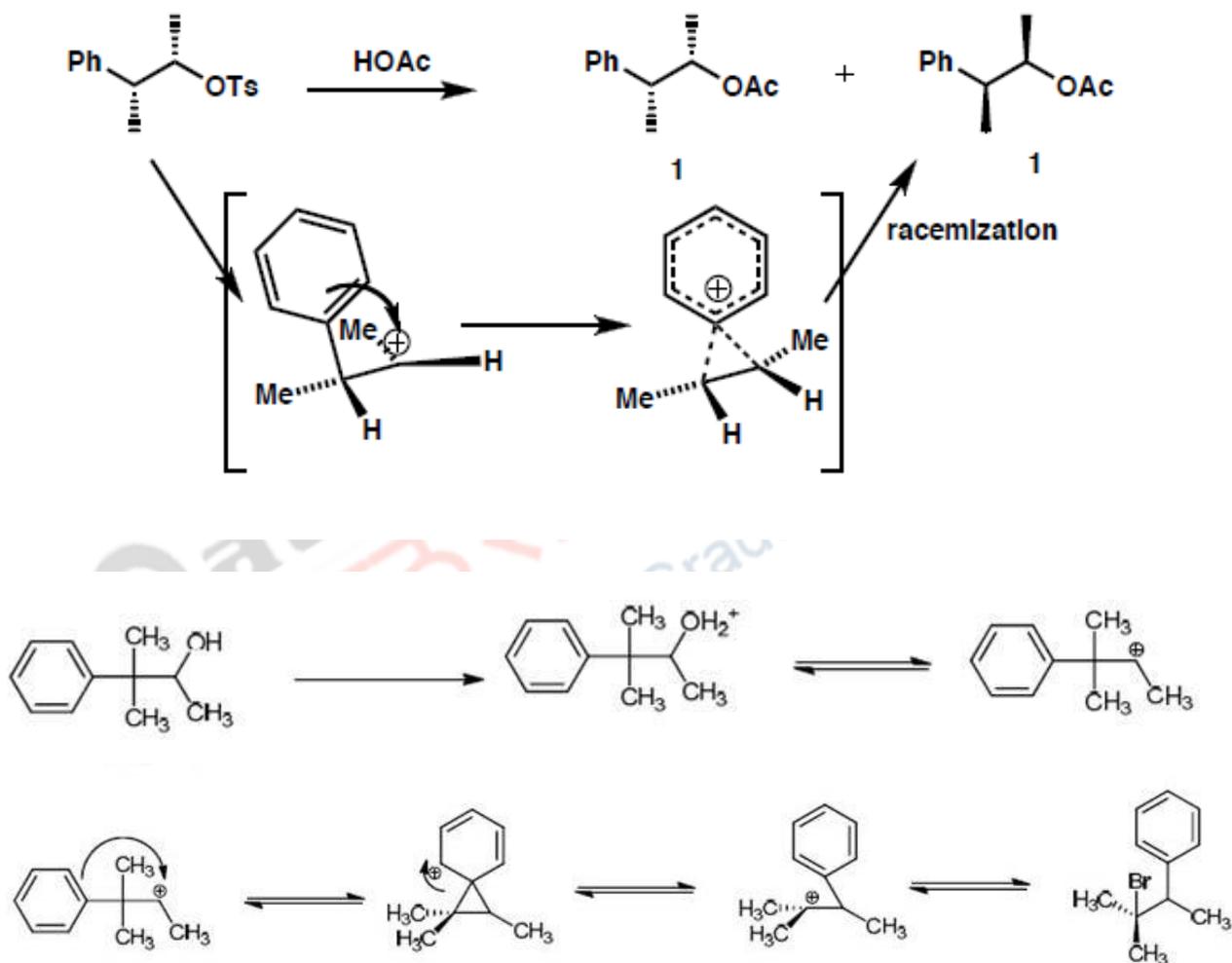


3.4 Generation of Non-classical Carbocations

During acetolysis of anti-tosylate, the tosyl group is removed with strong anchimeric assistance by the double bond, which results into formation of a non-classical carbocation (bridged ion) i.e. 7-norbornenyl cation as shown below. The configuration is retained in such a case.



The phenyl group present adjacent to a leaving group (tosyl group, hydroxyl) participate as a neighboring group during acetolysis and form an intermediate nonclassical carbocation called phenonium ion as shown below.



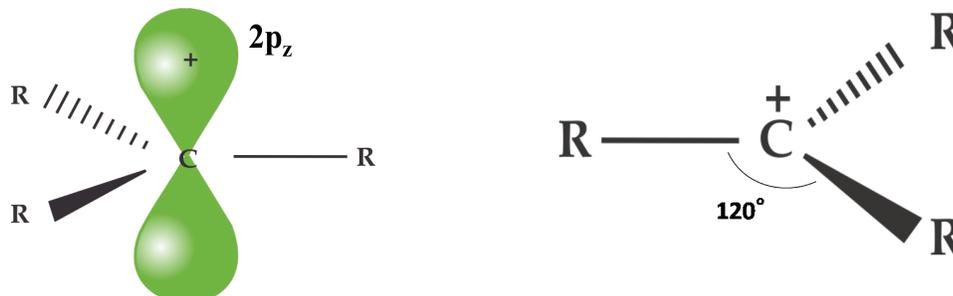
4. Structure of Carbocation

There are six valance electrons in a carbocation. Therefore they have deficiency of electron and they act as Lewis acids.

Features of a carbocation:

- The carbon bearing positive charge of a carbocation is sp^2 hybridized and has vacant unhybridized p orbital.

- It has planar structure having all the three covalent bonds are in plane with the bond angle of 120° between them.



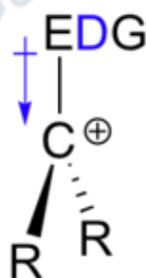
- The positively charged carbon is **trivalent**
- The positive carbon has **sextet of electron** thus it is electron deficient.
- The order of stability of carbocations is $3^\circ > 2^\circ > 1^\circ > \text{methyl}$ carbocation.

5. Stability of Carbocation

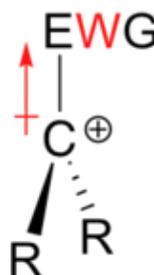
The stability of a carbocation is governed by several factors such as inductive effect, hyperconjugation or resonance effect. Their effect is discussed below:

5.1 Inductive effect

If the groups attached to positively charged carbon are electron releasing they will decrease the intensity of the positive charge on carbon. The electron releasing groups delocalise the positive charge on carbon thereby decreasing its electron deficiency. The alkyl groups are electron releasing in nature (+I effect). More the number of alkyl groups attached more will be the stability of carbocation.



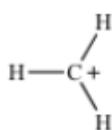
Electron **Donating** Group:
stabilizes a carbocation



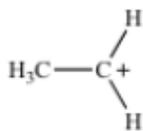
Electron **Withdrawing** Group:
destabilizes a carbocation

Figure 3: Inductive effect in carbocation

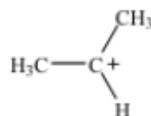
Thus the order of stability of alkyl carbocations is $3^\circ > 2^\circ > 1^\circ >$ methyl carbocation.



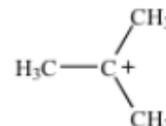
Methyl carbocation



1° Carbocation



2° Carbocation



3° Carbocation

Thus, +I group increases stability of carbocation and is directly proportional to the +I power of the group.

5.2 Hyperconjugation

Hyperconjugation can explain the stability of the carbocation. In case of carbocations the sigma bond in conjugation with vacant p orbital on carbon carrying positive charge participates in delocalisation, thus spreading the charge all over the alkyl groups. This effect is also known as hyperconjugation or no bond resonance.

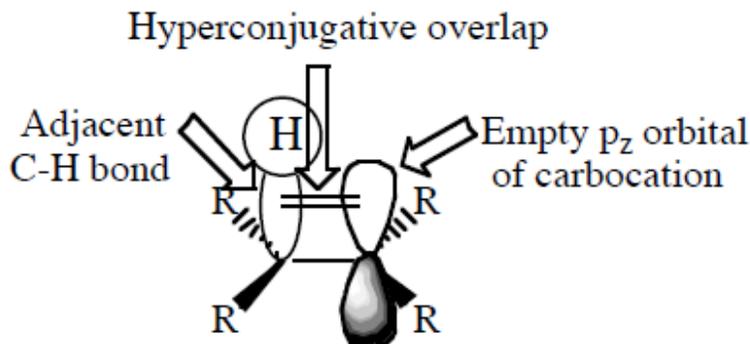
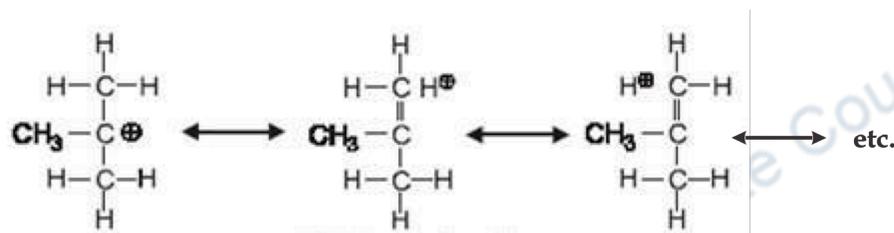
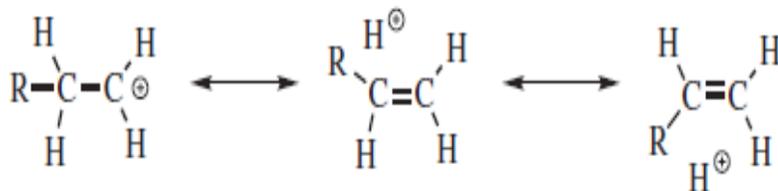


Figure 4: Hyperconjugative overlap of orbital

In tert-butyl cation, $(\text{CH}_3)_3\text{C}^+$ there are nine C-H sigma bonds which participate in delocalisation. In iso-propyl cation, $(\text{CH}_3)_2\text{CH}^+$ six C-H sigma bonds and in ethyl cation, CH_3CH_2^+ three C-H bonds are available. Thus $(\text{CH}_3)_3\text{C}^+$ is more stable than $(\text{CH}_3)_2\text{CH}^+$ which in turn is more stable than CH_3CH_2^+ due to greater number of contributing hyperconjugative structures in former than the latter.

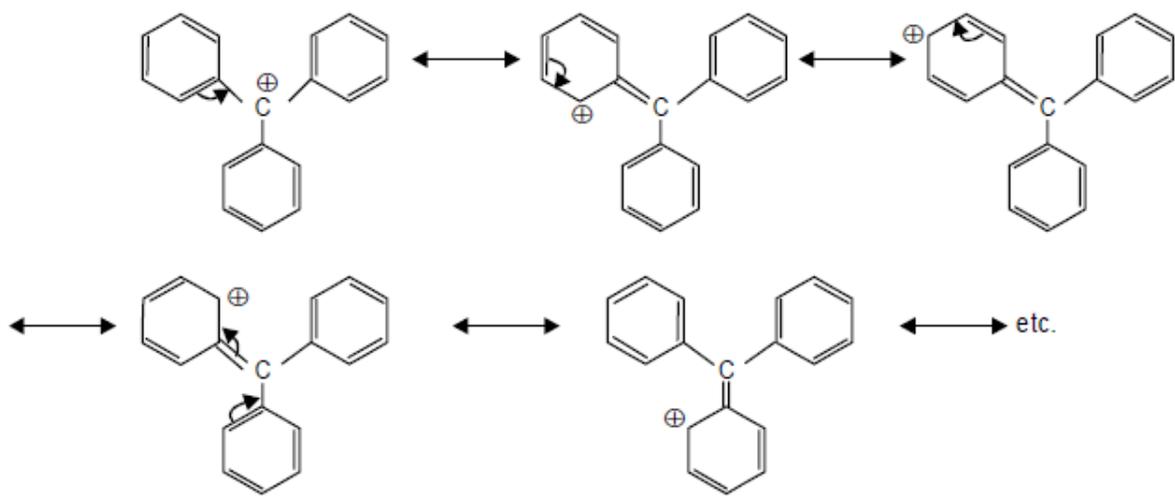


Tertiary Carbocation

Figure 5: Hyperconjugation in carbocation

5.3 Resonance Effects

Conjugation with multiple bond or lone pair of electron increases the stability of a carbocation. For example, triphenylmethyl cation is more stable than diphenylmethyl cation which in turn is more stable than phenylmethyl cation. This due to greater delocalization of positive charge in case of triphenylmethyl cation as it has more number of resonating structures. The salt of triphenylmethyl cation with boron fluoride is stable and exists as solid.



Which is more stable amongst allyl and benzyl carbocations?

Benzyl cation is more stable than allyl cation. In both the cases the vacant p orbital of carbon bearing positive charge is in conjugation with pi bonds and delocalisation of positive charge occurs through p-pi overlap. In benzyl cation, the number of contributing structures are more as compared to allyl cation.

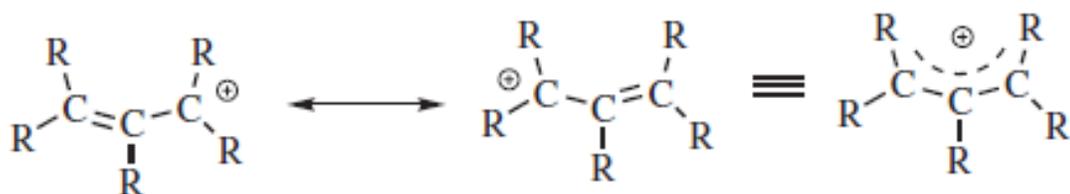
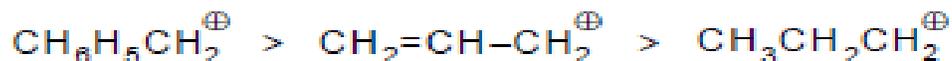


Figure 6: Resonance in allyl carbocation

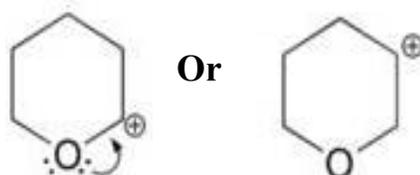


Figure 7: Resonance in benzyl carbocation

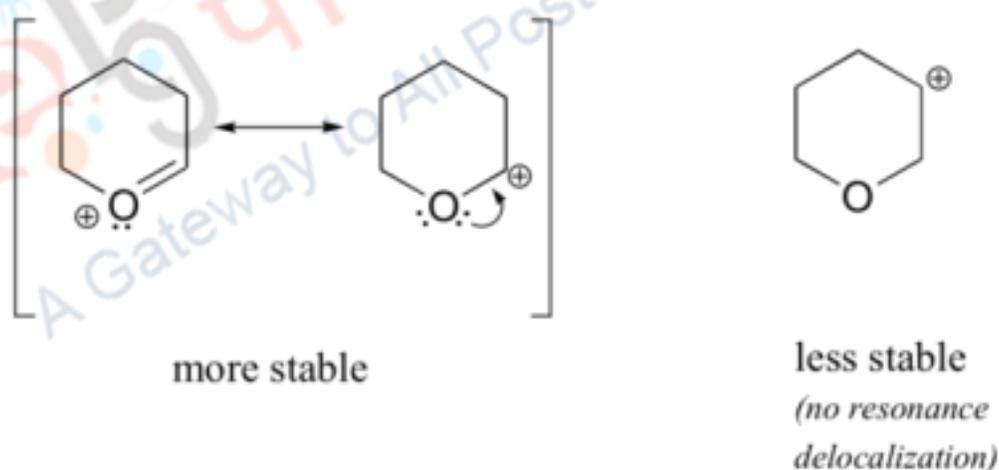
Thus the order of stability is as follows:



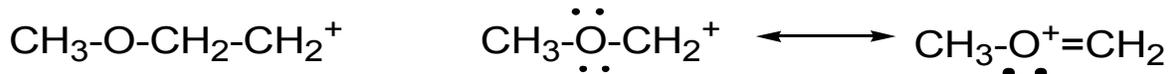
Which is more stable amongst the two tetrahydropyran carbocations ?



If a heteroatom with an unshared pair of electrons is adjacent to the cationic centre then it stabilises the positive charge. Thus the carbocation with positive centre adjacent to the oxygen atom with lone pair of electron is more stable. The lone pair is involved in resonance decrease the electron deficiency of the positive carbon providing it stability. While in the other structure no such stabilisation is present.



Similarly, methoxy methyl cation gains stability due to presence of oxygen atom with lone pair of electron.



If the vacant p orbital of the carbocation is part of a conjugated cyclic ring, it provides greater stability to the carbocation. Hence, tropylium cation and cyclopropenylum cation being aromatic in nature are more stable than cyclopentadienyl cation.

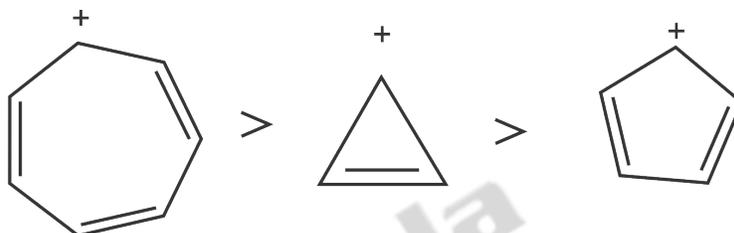
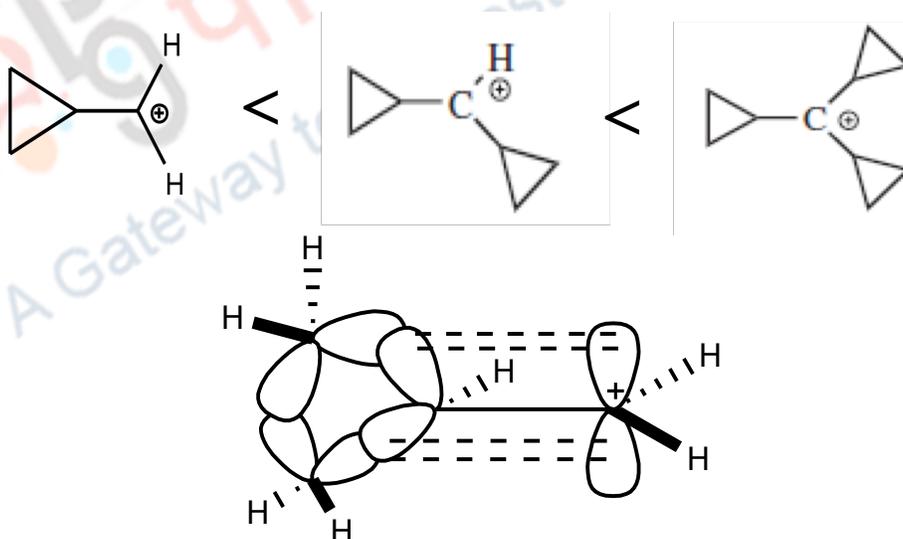


Figure 8: Order of stability of cyclic conjugated carbocation

Cyclopropylmethyl cation is more stable than benzyl cations. The additional cyclopropyl ring further stabilise the carbocation, thus the di- and tri- cyclopropylmethylcations are even more stable. This stability is furnished by the bent orbitals of the cyclopropyl ring, which can overlap effectively with the vacant p orbital of the carbocation, thus reducing its electron deficiency and provides more stability.



Cyclopropyl methyl cation

Figure 9: Order of Stability of mono-, di- and tri- cyclopropyl methyl cations

6. Reactivity of Carbocations

Carbocations are most often short-lived transient species and react further without being isolated. The fate of carbocation depends on its reactivity.

Once a carbocation is formed it may:

- 1) React with a nucleophile to give S_N1 product.
- 2) Lose a proton (H^+) to give an E1 product.
- 3) Rearrange to another carbocation.
- 4) Undergo addition to unsaturated compounds.
- 5) Undergo reaction with leaving group and results in the formation of starting reactant.

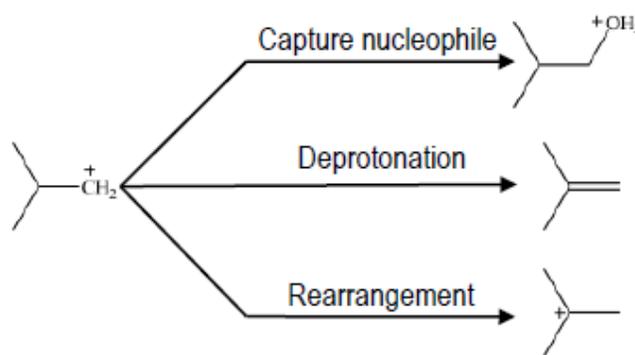
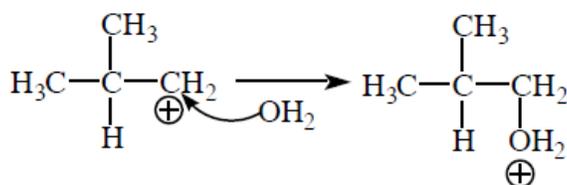


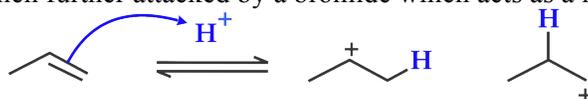
Figure 10: Different fates of a carbocation

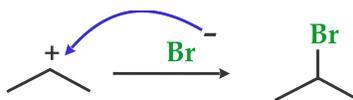
(1) The carbocation may combine with anegative ion orspecies possessing an electron pair (nucleophiles such as OH^- , Cl^- , Br^- , H_2O). These reactions are very fast.



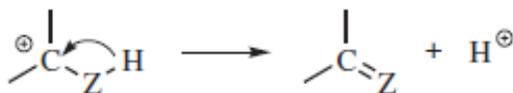
Example:

Addition of HBr to propene according to Markovnikov rule proceeds with formation of a more stable 2° carbocation which further attacked by a bromide which acts as a nucleophile.

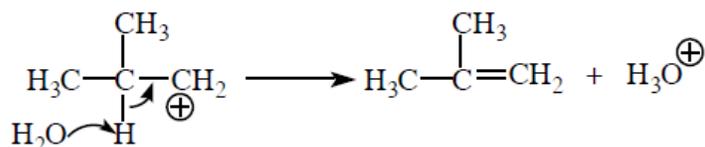




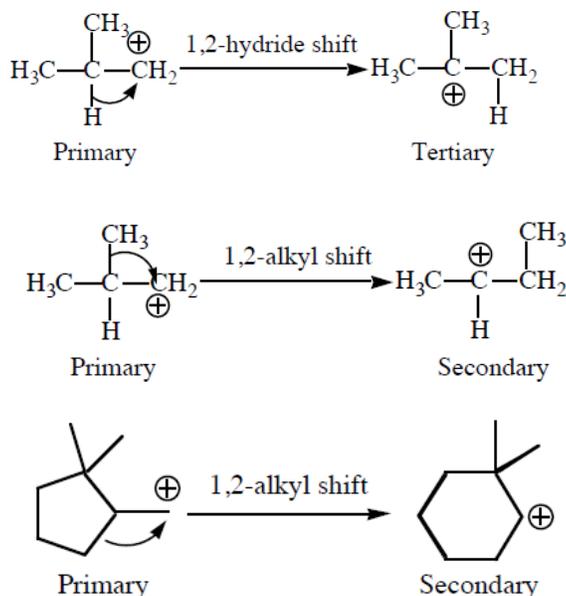
(2) The carbocation formed may undergo loss of proton from the β -carbon to give an alkene, an E1 product.



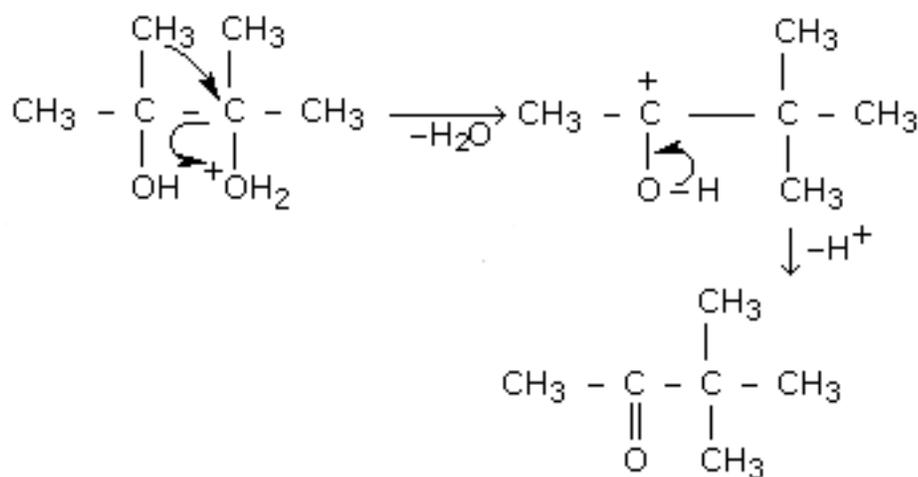
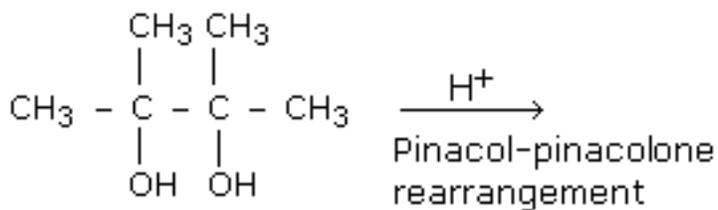
Example: Formation of 2-methylpropene



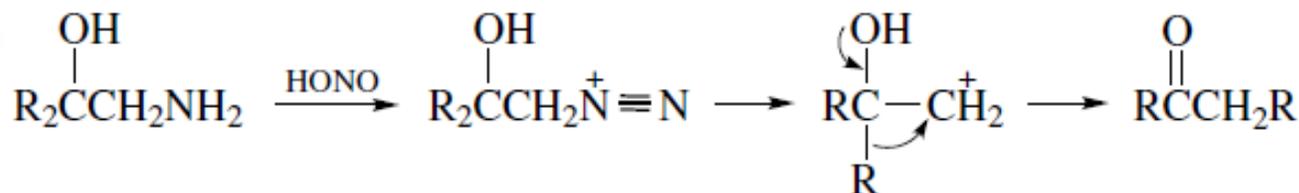
(3) During rearrangement an alkyl or aryl group or hydrogen migrates towards the positively charged carbon with its electron pair, leaving another positive charged more stable carbocation behind. The rearrangement involving migration of hydrogen with its pair of electron is called the **hydride shift** and alkyl group migration by bonding is called the **alkyl shift**. 1,2- shifts are the most common type of rearrangements.



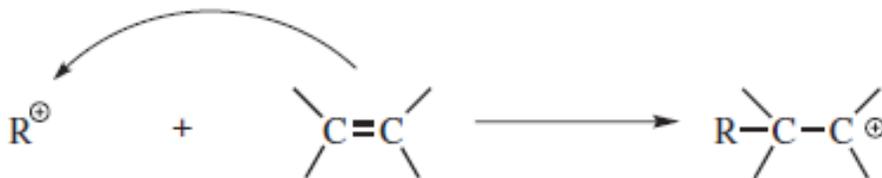
The Pinacol-pinacolone rearrangement: This is common rearrangement in which 1,2-dihydroxy compounds rearrange to give carbonyl compounds. For example conversion of 2,3-dimethylbutane-2,3-diol (pinacol) to t-butyl methyl ketone (pinacolone)



Tiffeneau-Demjanov reaction: This reaction involves conversion of aminomethyl carbinol to ketones on treatment with nitrous acid. It can also be used for synthesis of ring expanded cyclic ketones.



(4) A carbocation may add to a double bond, generating a positive charge at a new position:



6. Summary

In this module you have learnt that:

- Carbocations are reactive intermediates.
- Carbocations are electron deficient species with sextet of electron.
- Stable carbocations can be generated in super acids.
- The order of stability of carbocations is $3^\circ > 2^\circ > 1^\circ > \text{methyl}$.
- Factors such as inductive effect (+I), hyperconjugation and resonance which can decrease the positive charge on carbon stabilize a carbocation.
- Carbocation can undergo various types of reactions such as capturing nucleophile, elimination, rearrangement.

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