

❖ Classical and Nonclassical Carbocations

It is a well-known fact that a large number of chemical reactions proceed via the formation of certain chemical species called carbocations in which one of the carbon carries a positive charge with only six valence electrons. In this section, we will study the generation, structure, stability, and reactivity of two main types of carbocations called classical and non-classical carbocations one by one.

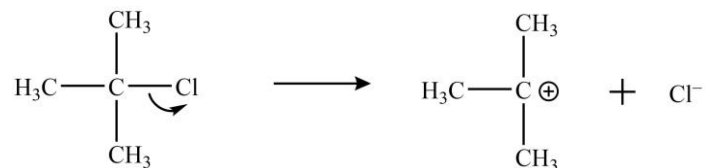
➤ Classical Carbocations

Classical carbocations in the organic chemistry may simply be defined as the carbocations that are stabilized by the delocalization of π -bond, or σ -bond, or lone pair of at conjugated site to the carbon bearing positive charge.

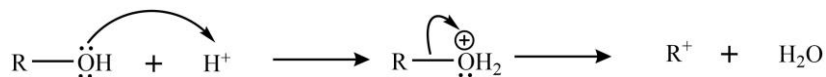
Since the carbon in classical carbocations has only six electrons, it is electron deficient; and therefore, acts as an electrophile in chemical reactions.

1. Generation of classical carbocations: The heterolytic cleavage of the covalent bond is responsible for the generation of most of the classical carbocation species. Some reactions involving the production of carbocations are given.

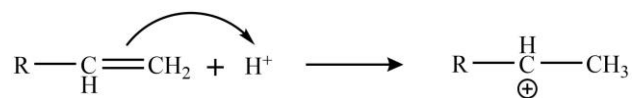
i) Ionization of alkyl halides in polar solvents:



ii) Protonation of alcohols followed by dehydration:



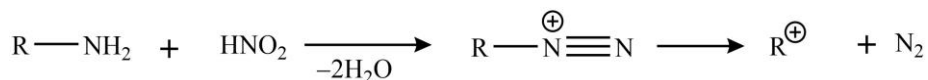
iii) Protonation of unsaturated systems:



iv) Action of superacids on alkyl fluorides:



v) Deamination of primary aliphatic amines by nitrous acid:



2. Orbital structure of classical carbocations: It has been experimentally found that the classical carbocations are trigonal planar around the carbon bearing positive charge. Now valence bond theory, as well as molecular orbital theory, easily accounted for such structure, it is more comfortable to discuss the valence bond approach. The carbon with the positive charge is in sp^2 hybridization with three hybrid orbitals oriented at 120° in a plane with empty p_z -orbital at a perpendicular.

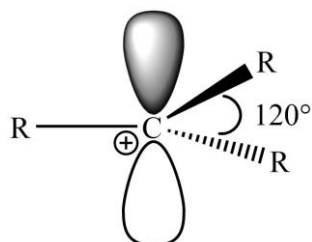
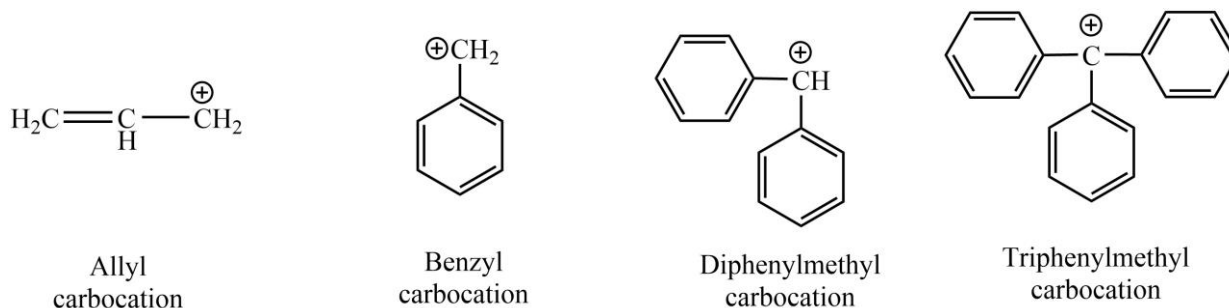


Figure 1. Orbital structure of a classical carbocation.

3. Stability of classical carbocations: Before we discuss the stability of classical carbocations, we need to classify them based on saturation. The first case is alkyl carbocations which are given below.



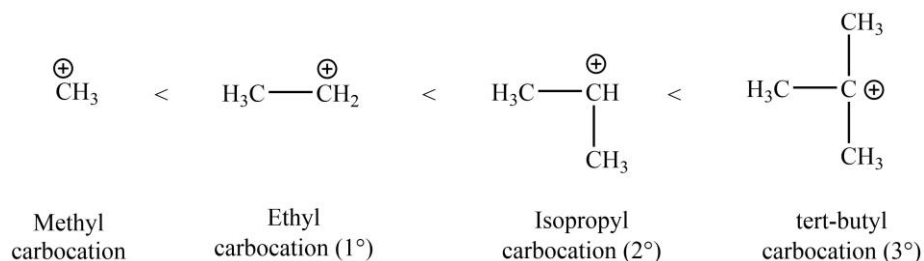
The second case is of unsaturated classical carbocations where the carbon bearing positive charge is directly connected to a carbon participating in multiple bonds i.e.



Since the carbon in carbocations has only six electrons, it is electron deficient; and therefore, any effect that can compensate for the deficiency will stabilize the carbocation.

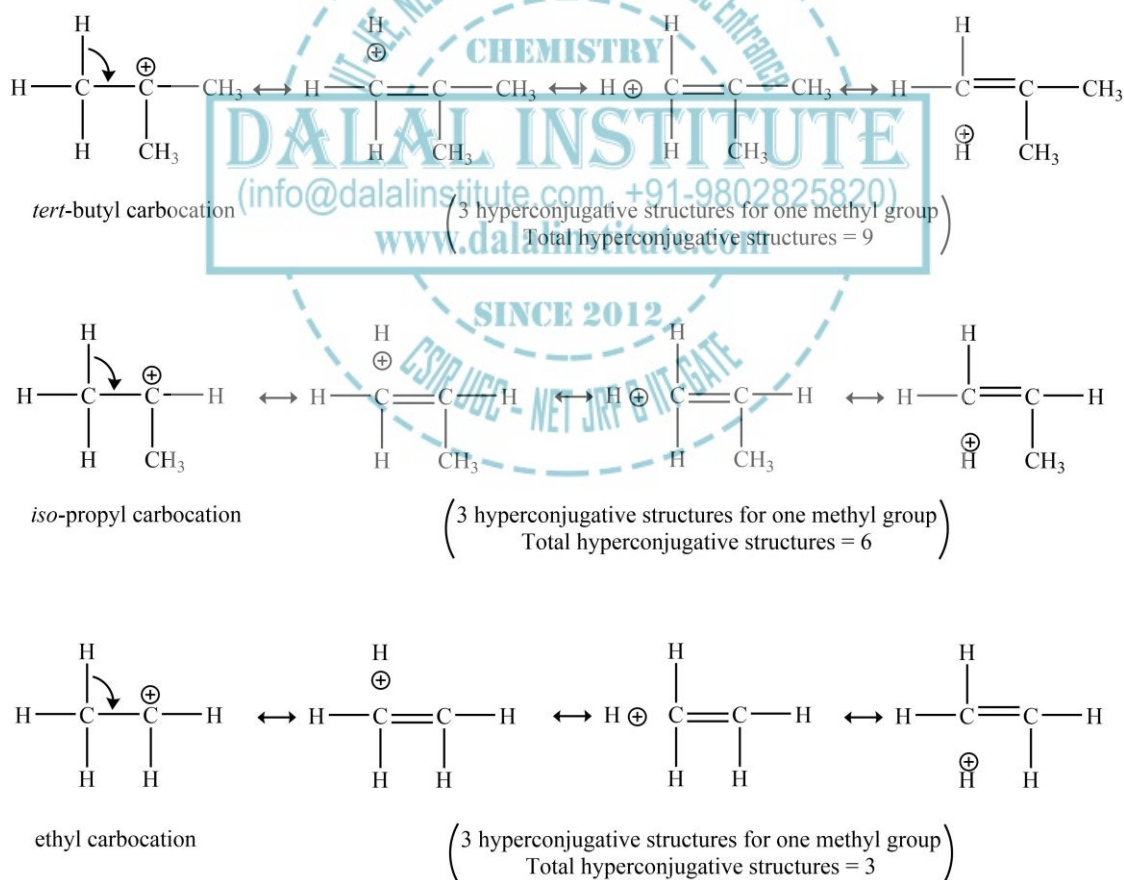
i) Stability of alky carbocations on the basis of inductive effect:

Since the alkyl group has an electron-donating effect (+I), the stability of the classical carbocation will increase as the number of attached donating groups increases. The stability order of alky carbocations based on inductive effect is given below.



ii) Stability of alky carbocations on the basis of hyperconjugation:

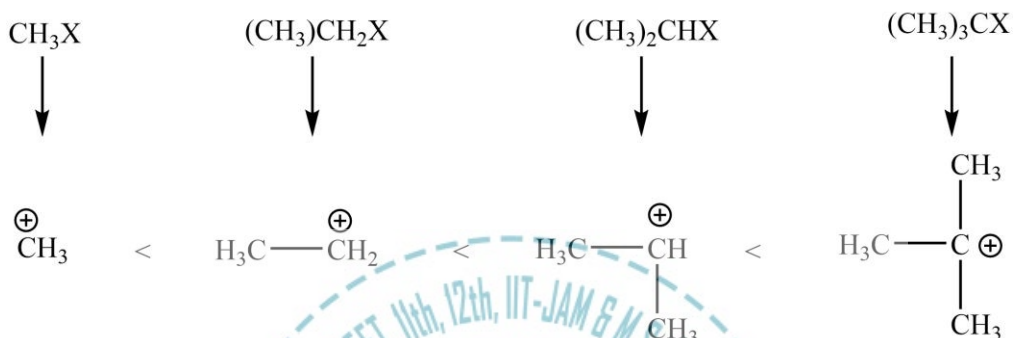
The existence of the hyperconjugation effect can be used to rationalize the relative stability of different carbocations as shown below.



Hence, as far as the number of possible hyper-conjugative structures possible is concerned, tertiary carbocation should be more stable than secondary, which in turn should be more stable than primary.

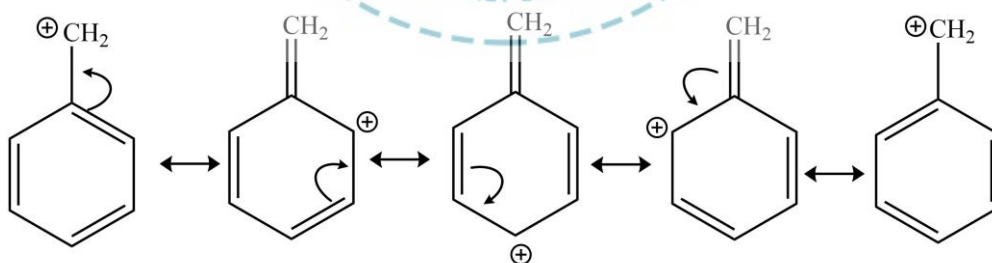
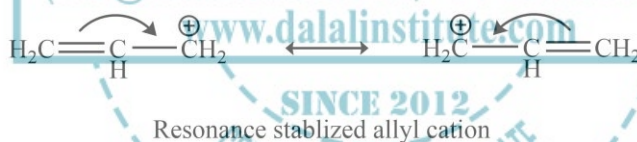
iii) Stability of alkyl carbocations on the basis of steric effect:

Since the alkyl carbocations are primarily obtained from alkyl halides with tetrahedral geometry, a link between the steric relief and carbocation formed can be established. During the formation of carbocations in such cases, the carbon-carbon bond angles change from $109^{\circ}28'$ to 120° . Therefore, the carbon with bulky groups around is expected to get more relief from this carbocationic conversion. The stability order of alkyl carbocations on the basis of steric effect is given below.



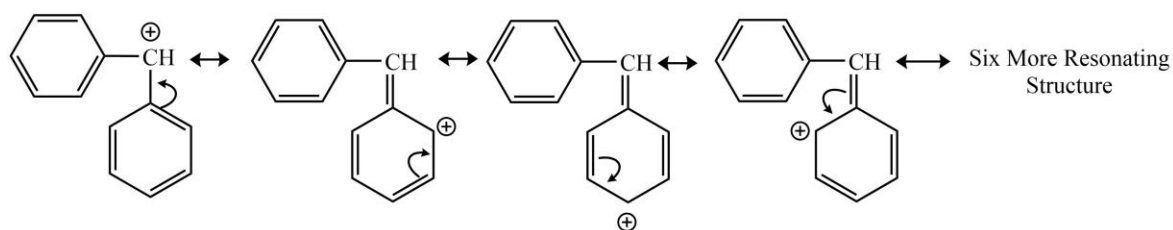
iv) Stability of allyl and benzyl carbocations:

The stability of the carbocations in which the carbon bearing positive charge is adjacent to the double or triple bond can be rationalized in terms of resonance effect. First of all, let us draw the resonance structures allyl and benzyl carbocations.

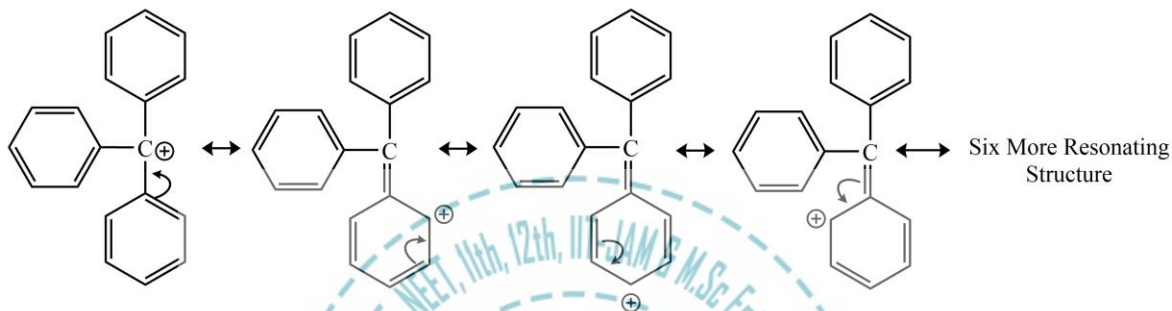


Resonance stabilized benzyl cation

Now, as the number of phenyl groups attached to carbon bearing positive charge increases, the number of resonating structures will also increase, and hence the stability.

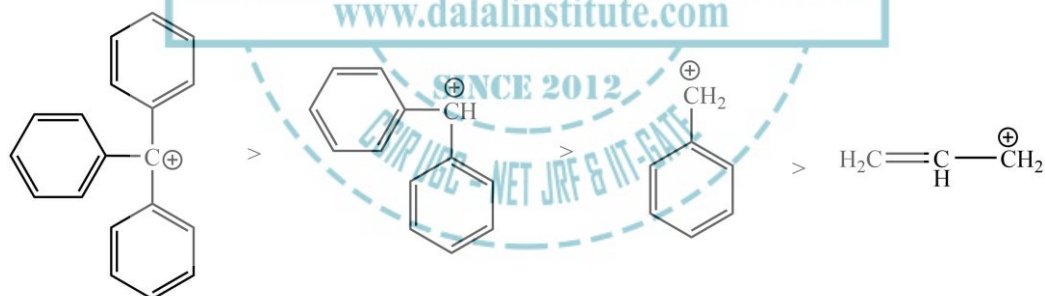


Resonance stabilized diphenylmethyl carbocation



Resonance stabilized triphenylmethyl carbocation

Therefore, the expected order of the stability of unsaturated systems with carbon bearing positive charge should be as given below.



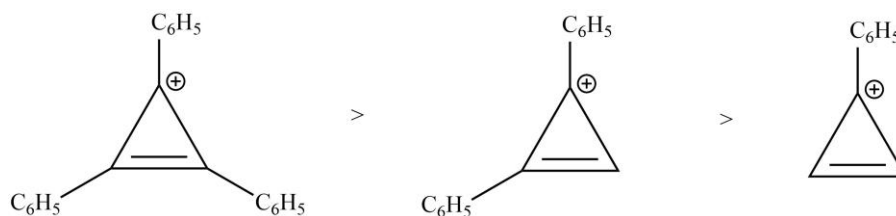
Triphenylmethyl carbocation

Diphenylmethyl carbocation

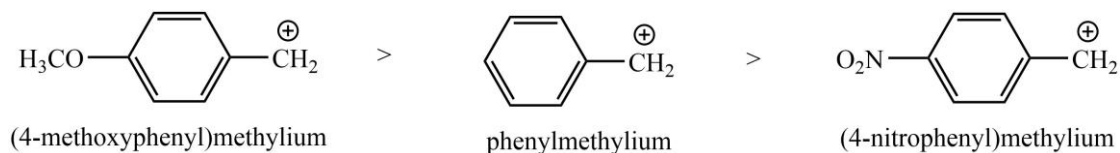
Benzyl carbocation

Allyl carbocation

Similarly, the order of stability in phenylcyclopropenyl, diphenylcyclopropenyl and triphenylcyclopropenyl should follow the following order.



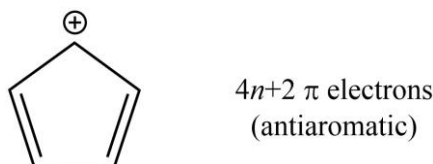
v) *Stability of substituted benzyl carbocations:* Since the carbon with positive charge is electron deficient in nature, any group with +R effect will stabilize the system and vice-versa. The order of stability of some typically substituted carbocations is given below.



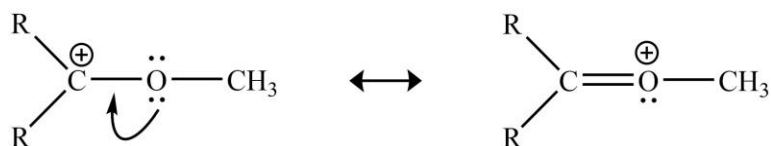
vi) *Stability of tropylium ion:* The cycloheptatrienyl cation or tropylium ion is exceptionally stable due to its aromatic character (planar and $4n+2$ π electrons). According to molecular orbital theory, its delocalization energy is significantly greater than the delocalization energy of its acyclic counterpart. Similarly, the valence bond theory can also explain its exceptional stability on the basis of resonance as given below.



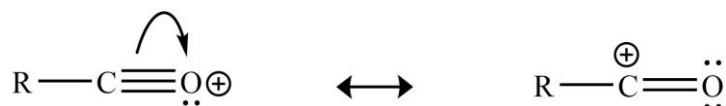
vii) *Instability of cyclopentadienyl cation:* The cyclopentadienyl cation is very unstable due to its antiaromatic character (planar and $4n$ π electrons). According to molecular orbital theory, its delocalization energy is significantly less than the delocalization energy of its acyclic counterpart.



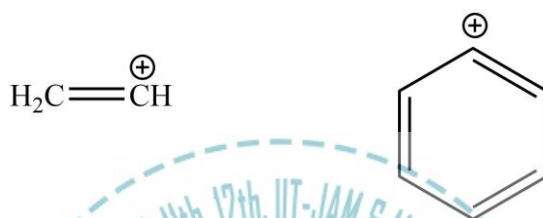
viii) *Stability of alkoxyalkyl cation:* If the positive charge bearing carbon in the carbocationic species is connected to a hetero atom with lone pair of electrons, the resonance will get it stabilized.



ix) *Stability of acyl cation*: Just like alkoxyalkyl cation, the resonance will also stabilize the acyl cation as shown below.

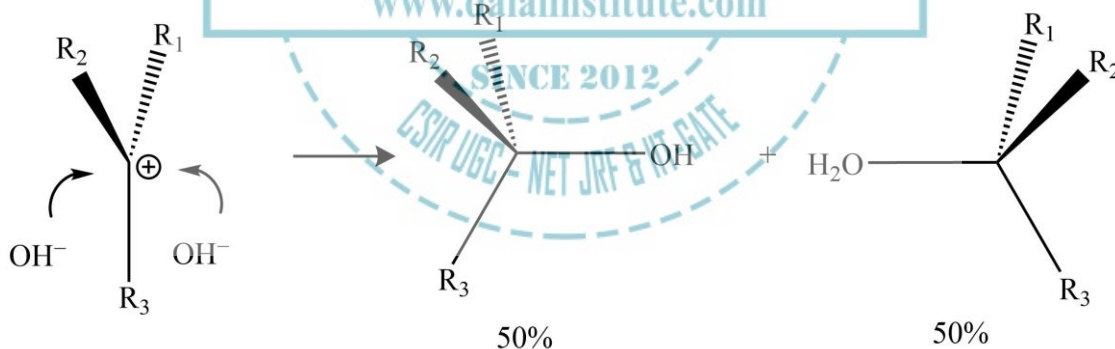


x) *Instability of phenyl and vinyl cation*: If the positive charge is on the double-bonded carbon atom, the system cannot be stabilized because the sp^2 orbital carrying positive charge will be perpendicular to the orbital of the double bond.

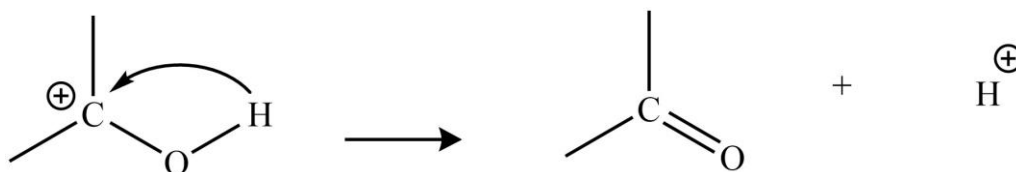


4. Reactivity of classical carbocations: The principal routes by which the carbocations can react to give rise to stable products are given below.

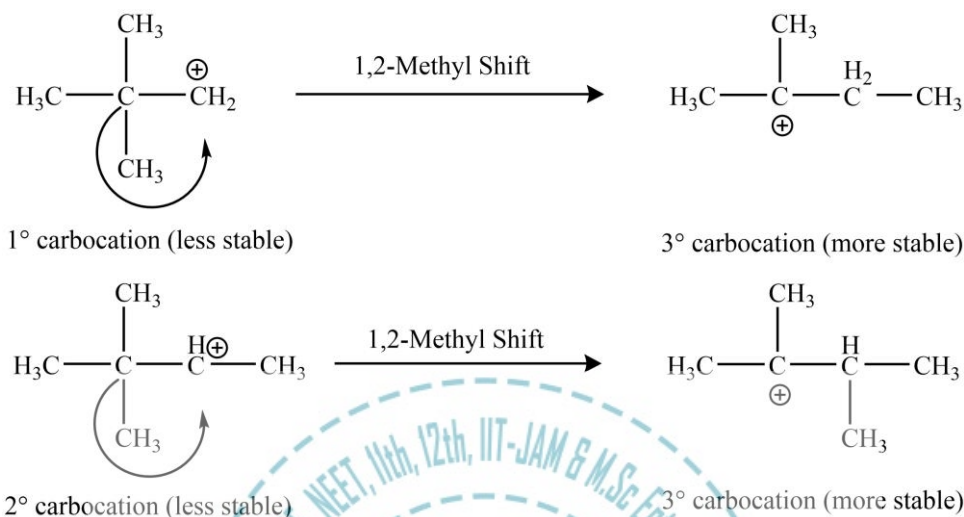
i) *Nucleophilic attack*: In these types of reactions, a carbocation may combine with a species by accepting an electron pair. Furthermore, it should also be noted that if all the three groups on the carbocation are different, a racemic mixture will be obtained.



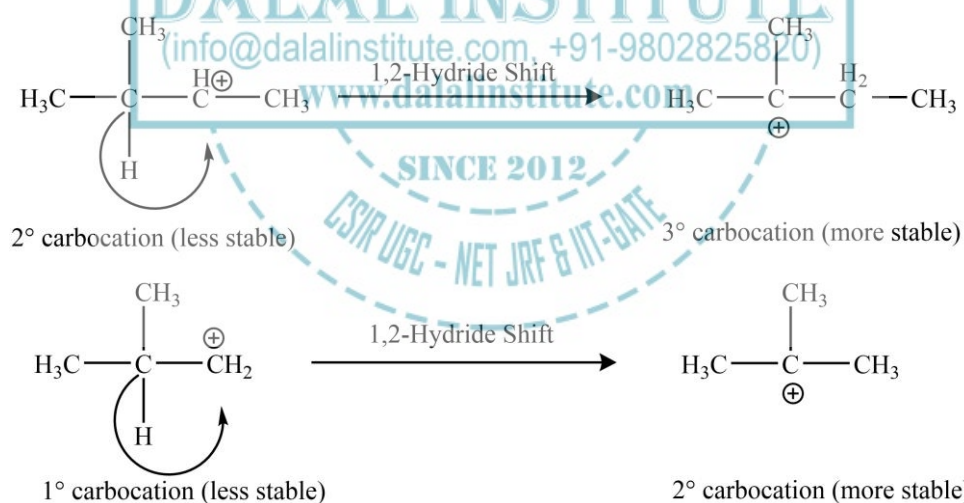
ii) *Proton removal*: In these types of reactions, a carbocation may result in the removal of a proton from the adjacent atom forming a double bond.



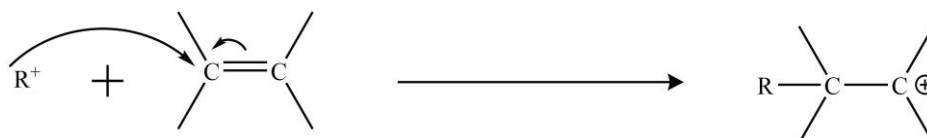
iii) *Rearrangement reaction*: 1-2 methyl shift or 1-2 hydride shifts are very common in carbocation chemistry to attain a more stable counterpart. For instance, a primary and secondary carbocation will prefer to rearrange themselves into a more stable tertiary carbocation via methyl shifts as given below.



Similarly, primary and secondary carbocation can also rearrange themselves into a more stable tertiary carbocation via hydride shift.



iv) *Addition reactions*: A carbocation may attack at the triangular face of a double bond to create a new positively charged center as shown below.



➤ Non-Classical Carbocations

Non-classical carbocations in the organic chemistry may simply be defined as the carbocations in which the π -bond is not conjugation with the carbon bearing positive charge, and gets stabilized by neighboring group participation by π - or σ -bond.

Like classical carbocations, the carbon in a non-classical carbocation has only six electrons, it is also electron deficient; and therefore, acts as an electrophile in chemical reactions. Now, whether the neighboring participant is σ -bond or π -bond (not conjugated), non-classical carbocations can be divided into two categories.

1. Generation of non-classical carbocations: The generation of non-classical carbocations takes place mainly in neighboring group participation via π - or σ -bond. Some reactions involving the production of non-carbocations are given.

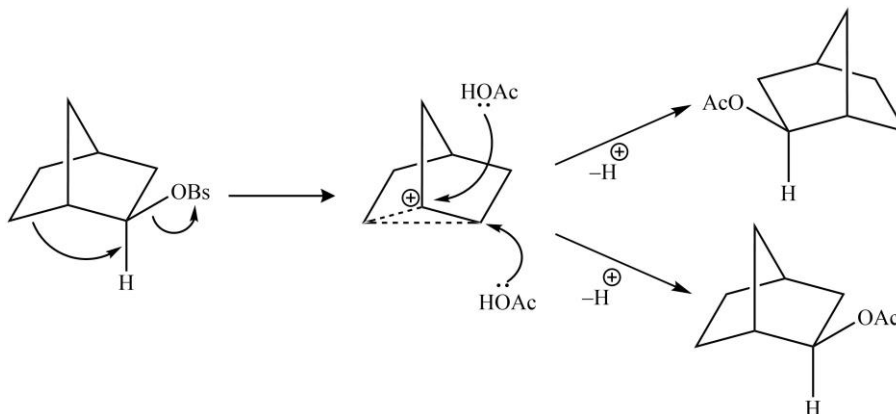
i) Neighbouring group participation via π -bond:

In the case of a benzyl halide, the reactivity is higher because the S_N2 transition state enjoys a similar overlap effect to that in the allyl system. An aromatic ring can assist in the formation of a carbocationic intermediate called a phenonium ion by delocalizing the positive charge.



ii) Neighbouring group participation via σ -bond:

The aliphatic C–H or C–C bonds can also give rise to delocalization of charge if these bonds are close enough and antiperiplanar to the leaving group. The intermediates corresponding to these mechanisms are nonclassical in nature; and the 2-norbornyl system is the most popular of such type. More precisely, the acetolysis of exo-2-norbornyl brosylate yields a racemic mixture of exo-acetates only and no endo product; suggesting neighboring group participation from σ -bond. Furthermore, a very slow rate is observed if we use endo-2-norbornyl brosylate confirming our guess.



2. Orbital structure of non-classical carbocations: One of the first (and popular) examples of non-classical ions was the 2-norbornyl cation. Non-classical carbocations are simply the organic cations where the electron density of a filled bonding molecular orbital is distributed over three or more atomic centers and have some sigma-bond property. Satisfying all the requirements, the 2-norbornyl cation is considered an archetypal case.

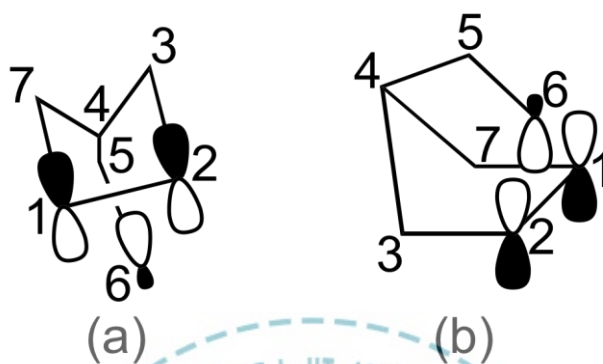
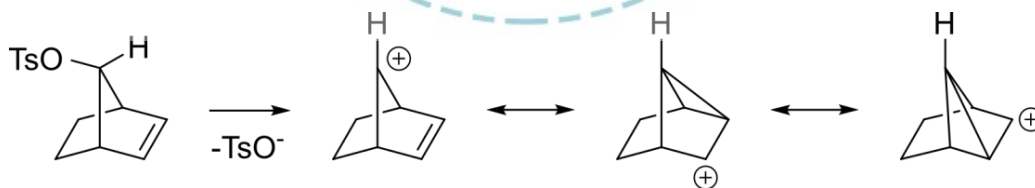


Figure 2. Orbital structure of a non-classical carbocation (2-norbornyl).

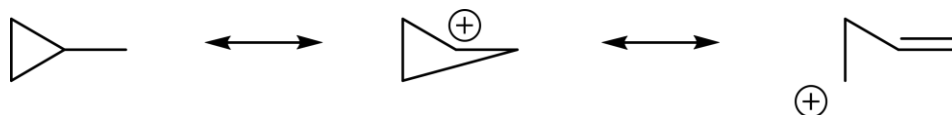
The most widely accepted molecular orbital structure of the 2-norbornyl cation is having two p -type orbitals (on carbons 1 and 2) interacting with an sp^3 -hybridized orbital on carbon 6 to form the hypervalent bond. Extended Hückel Theory calculations for the 2-norbornyl cation suggest that the orbital on carbon 6 could instead be sp^2 -hybridized, though this only affects the geometry of the geminal hydrogens.

3. Stability of non-classical carbocations: The stability profile of nonclassical carbocations can be rationalized by the delocalization of σ - or π -bonds as discussed below.

i) Stability gain via the delocalization of π -bond: The typical example of this type of stabilization is 2-norbornyl cation which is shown below.

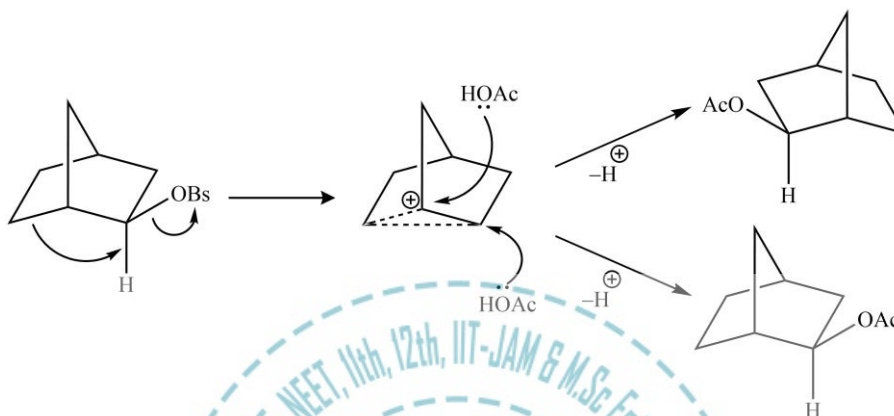


ii) Stability gain via the delocalization of σ -bond: The treatment of cyclopropylmethyl (or cyclobutyl chloride or homoallyl chloride) chloride with dilute ethyl alcohol yields a mixture of 5% homoallyl alcohol, 47% cyclobutanol, and 48% cyclopropylmethyl alcohol. All this suggests that the carbocationic intermediate present in all three reactions must be the same, which in turn, is responsible for the same resulting products.

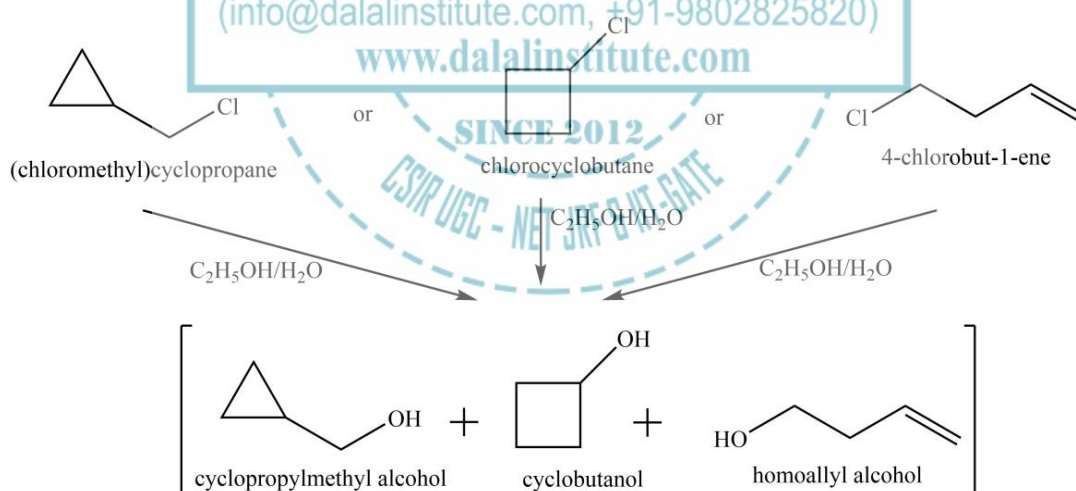


4. Reactivity of non-classical carbocations: The principal routes by which the non-classical carbocations can react to give rise to stable products are given below.

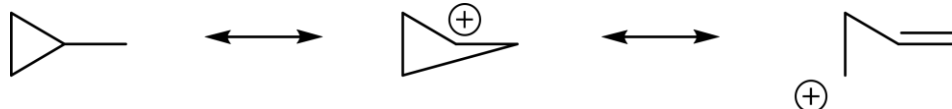
i) *Nucleophilic attack:* In these types of reactions, a non-classical carbocation may combine with a species by accepting an electron pair. Furthermore, it should also be noted that if all the three groups on the carbocation are different, a racemic mixture will be obtained.



ii) *Rearrangement reactions:* The treatment of cyclopropylmethyl (or cyclobutyl chloride or homoallyl chloride) chloride with dilute ethyl alcohol yields a mixture of 5% homoallyl alcohol, 47% cyclobutanol and 48% cyclopropylmethyl alcohol.



All this suggests that the carbocationic intermediate present in all three reactions must be the same, which in turn, is responsible for the same resulting products.



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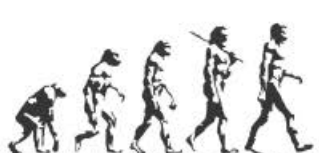
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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ISBN: 978-81-952427-3-3



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