

❖ Generation, Structure, Stability and Reactivity of Carbocations, Carbanions, Free Radicals, Carbenes and Nitrenes

A number of chemical reactions proceed via the formation of certain chemical species which are formed somewhere during the overall pathway. These species are called as reaction intermediates and are actual molecules that are short-lived and unstable. Sometimes they are called temporary reactants or products because they are neither present in actual reactants nor the actual products. Here, we will study the generation, structure, stability, reactivity of carbocations, carbanions, free radicals, carbenes, and nitrenes.

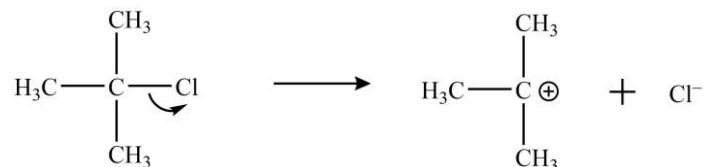
➤ Carbocations

The term carbocations in organic chemistry may simply be defined as the chemical species that carries a positive charge on the carbon with only six valence electrons.

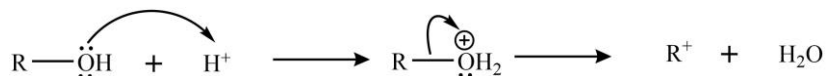
Since the carbon in carbocations has only six electrons, it is electron deficient; and therefore, acts as an electrophile in chemical reactions.

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

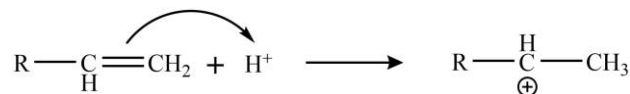
i) Ionization of alkyl halides in polar solvents:



ii) Protonation of alcohols followed by dehydration:



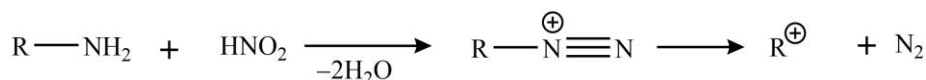
iii) Protonation of unsaturated systems:



iv) Action of super acids on alkyl fluorides:



v) Deamination of primary aliphatic amines by nitrous acid:



2. Structure of carbocations: It has been experimentally found that the 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 a positive charge is in sp^2 hybridization with three hybrid orbitals oriented at 120° in a plane with an empty p_z orbital at the perpendicular.

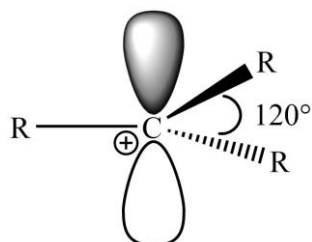
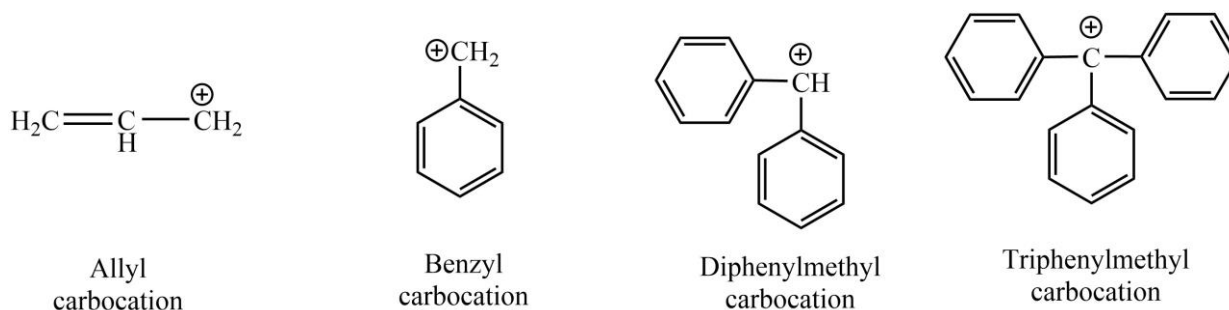


Figure 9. Orbital structure of carbocation.

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



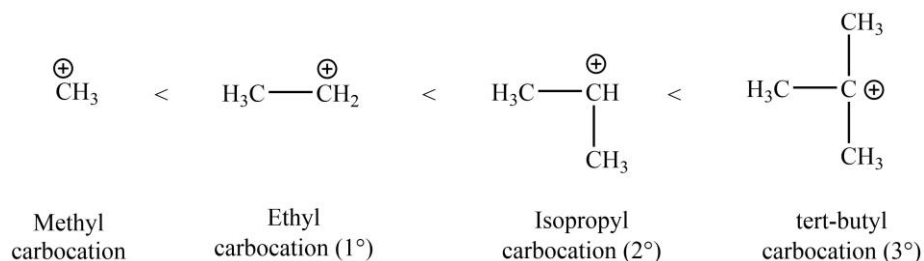
The second case is of unsaturated carbocations where the carbon bearing positive charge is directly connected to a carbon participating in multiple bond i.e.



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.

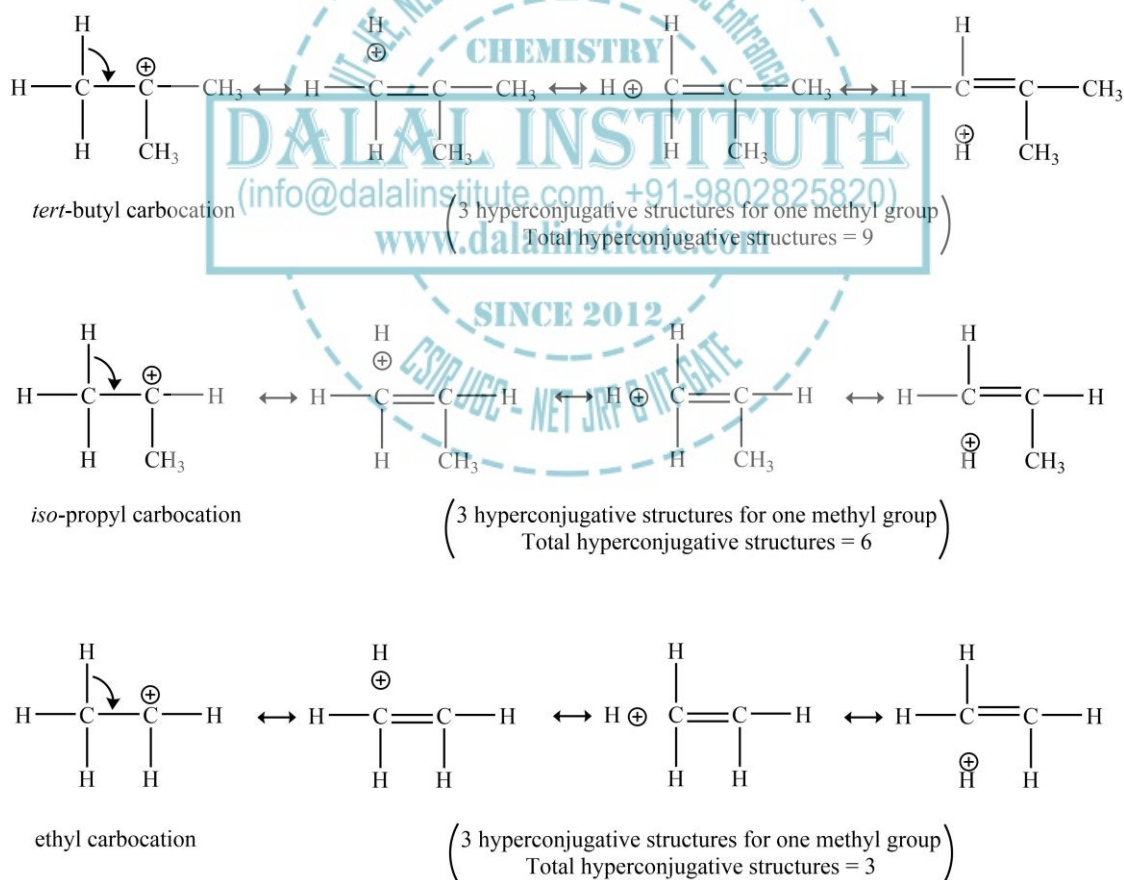
i) Stability of alky carbocations on the basis of inductive effect:

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



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

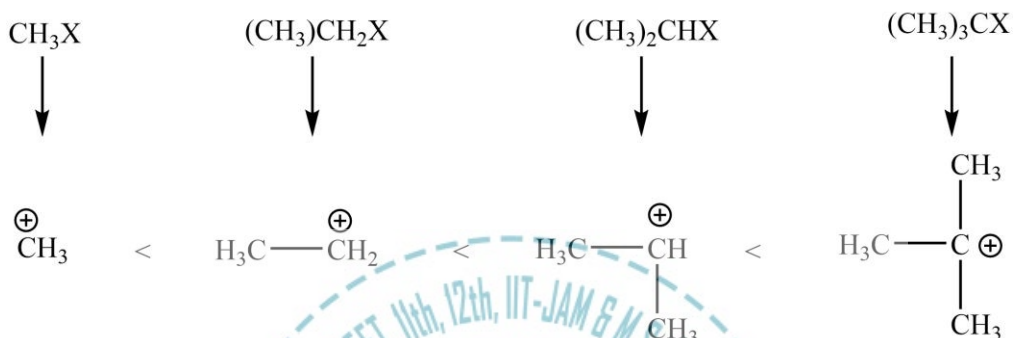
The existence of the hyperconjugation effect can be used to rationalize the relative stability of different carbocations as shown below.



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.

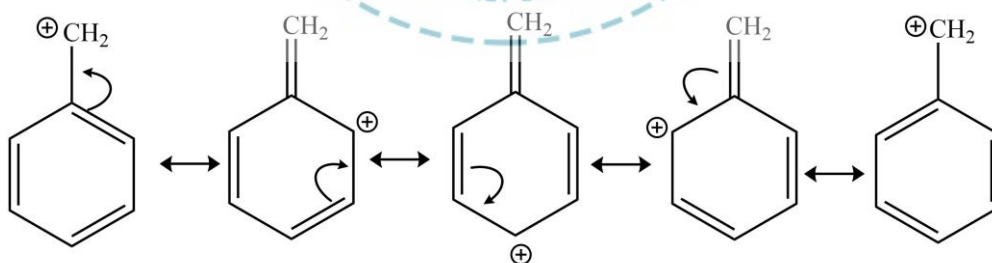
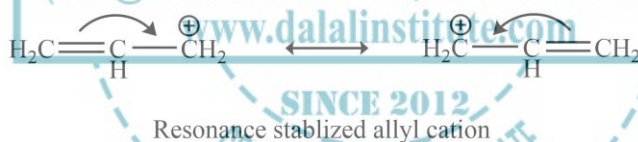
iii) Stability of alkyl carbocations on the basis of steric effect:

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.



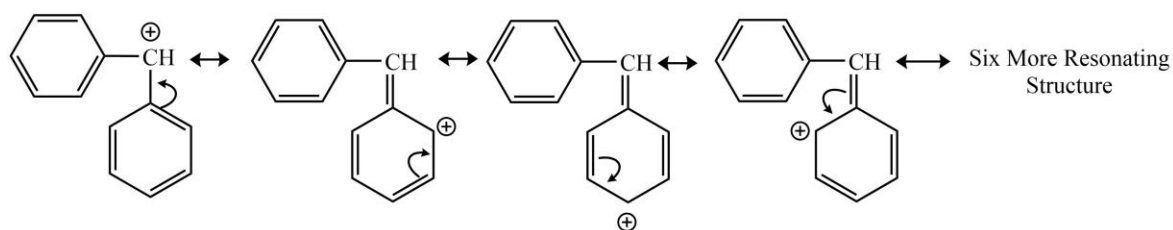
iv) Stability of allyl and benzyl carbocations:

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.

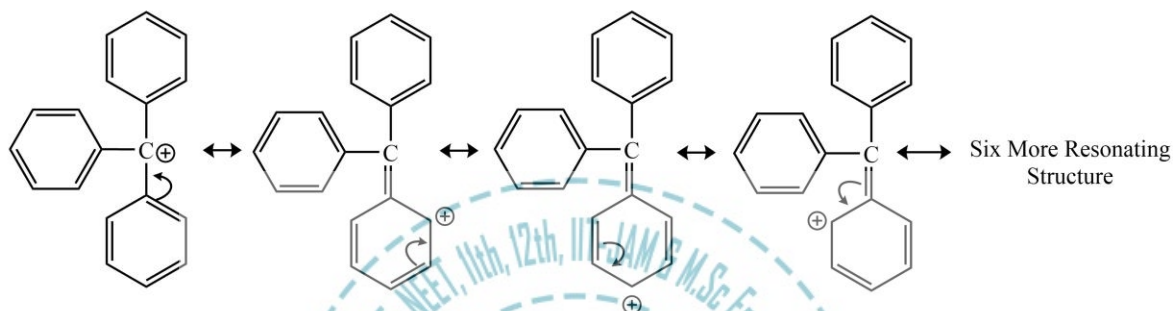


Resonance stabilized benzyl cation

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.



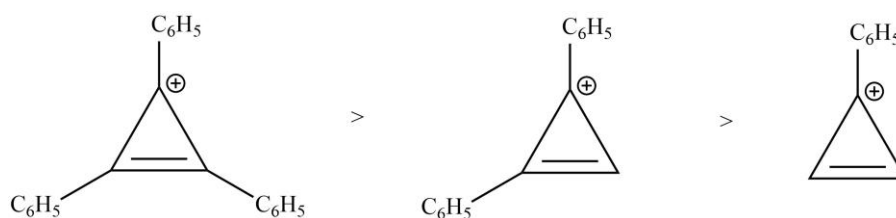
Triphenylmethyl carbocation

Diphenylmethyl carbocation

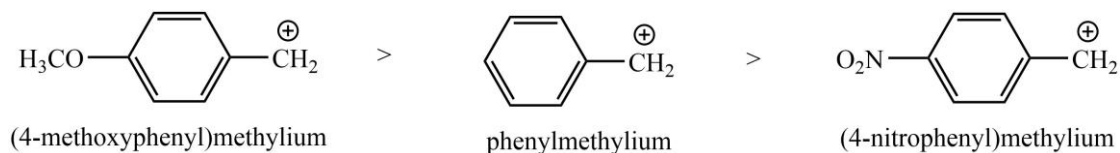
Benzyl carbocation

Allyl carbocation

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



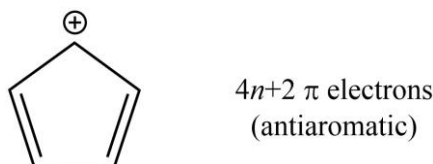
v) *Stability of substituted benzyl carbocations:* Since the carbon with positive charge is electron deficient in nature, any group with +R effect will stabilize the system and vice-versa. The order of stability of some typically substituted carbocations is given below.



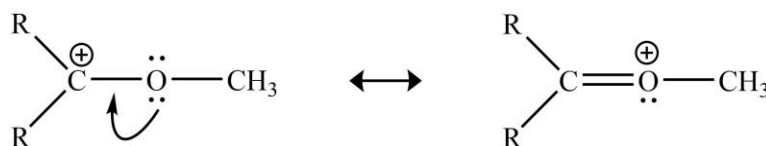
vi) *Stability of tropylium ion:* The cycloheptatrienyl cation or tropylium ion is exceptionally stable due to its aromatic character (planar and $4n+2$ π electrons). According to molecular orbital theory, its delocalization energy is significantly greater than the delocalization energy of its acyclic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



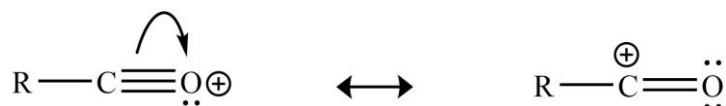
vii) *Instability of cyclopentadienyl cation:* The cyclopentadienyl cation is very unstable due to its antiaromatic character (planar and $4n$ π electrons). According to molecular orbital theory, its delocalization energy is significantly less than the delocalization energy of its acyclic counterpart.



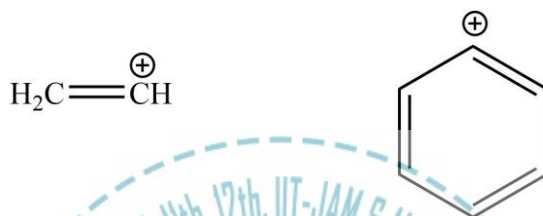
viii) *Stability of alkoxyalkyl cation:* if the positive charge bearing carbon in the carbocationic species is connected to a hetero atom with lone pair of electrons, the resonance will get it stabilized.



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

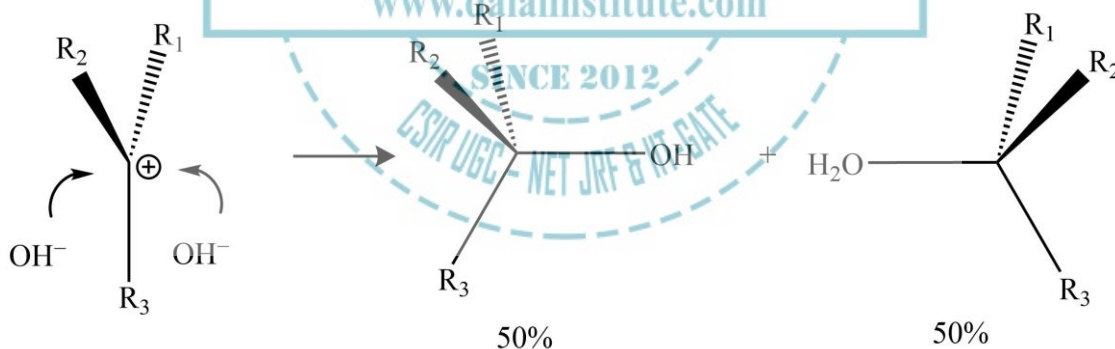


x) *Instability of phenyl and vinyl cation*: If the positive charge is on the double-bonded carbon atom, the system cannot be stabilized because the sp^2 orbital carrying positive charge will be perpendicular to the orbital of the double bond.

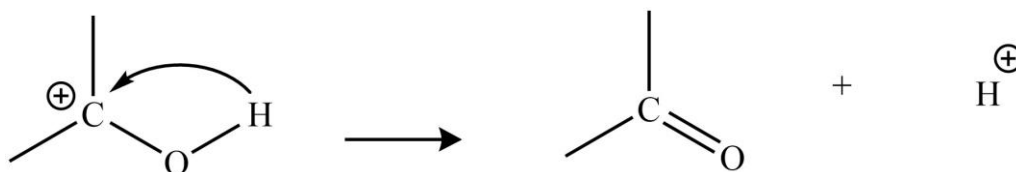


4. Reactivity of carbocations: The principal routes by which the carbocations can react to give rise to stable products are given below.

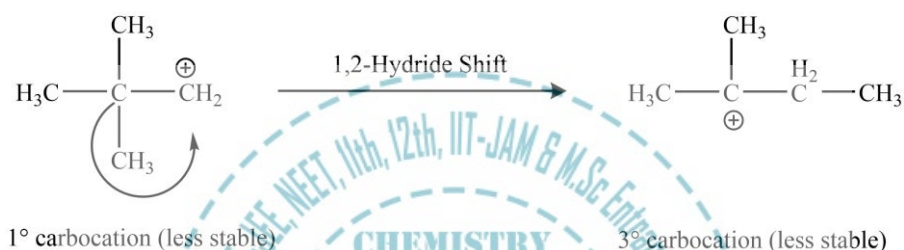
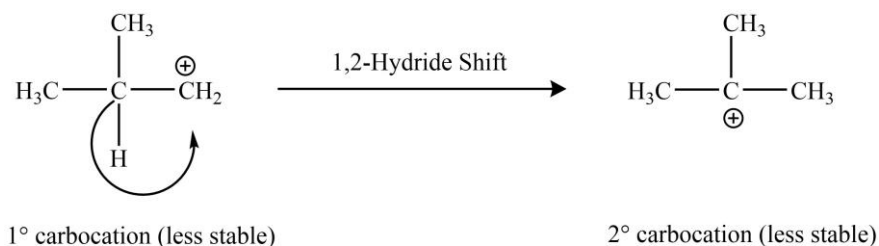
i) *Nucleophilic attack*: In these types of reactions, a carbocation may combine with a species by accepting an electron pair. Furthermore, it should also be noted that if all the three groups on the carbocation are different, a racemic mixture will be obtained.



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 carbocation will prefer to rearrange itself into a more stable tertiary carbocation.



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.



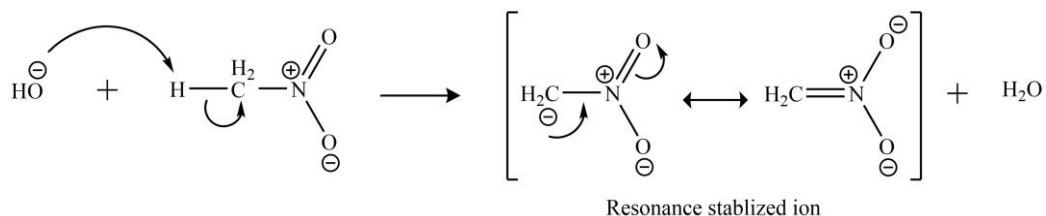
➤ Carbanions

The term carbanions in organic chemistry may simply be defined as the chemical species that carries a negative charge on the carbon with only eight valence electrons.

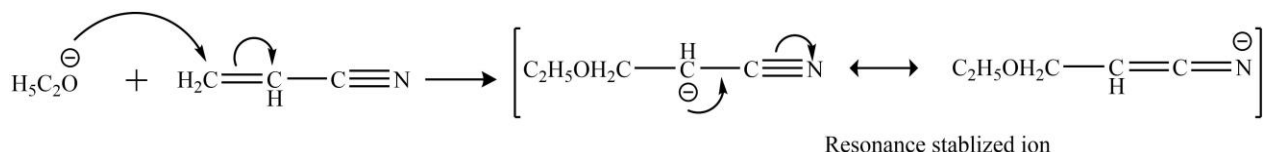
Since the carbon in carbanions has its octet complete, it is electron-rich; and therefore, acts as a nucleophile in chemical reactions.

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

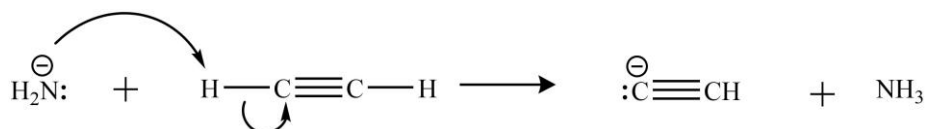
i) *Hydrogen abstraction by a strong base from the carbon alpha to cyano, nitro, or carbonyl groups:*



ii) Nucleophilic addition to α, β -unsaturated species:



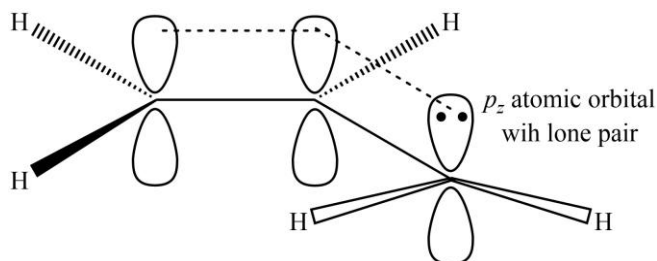
iii) Abstraction of terminal hydrogen from acetylene:



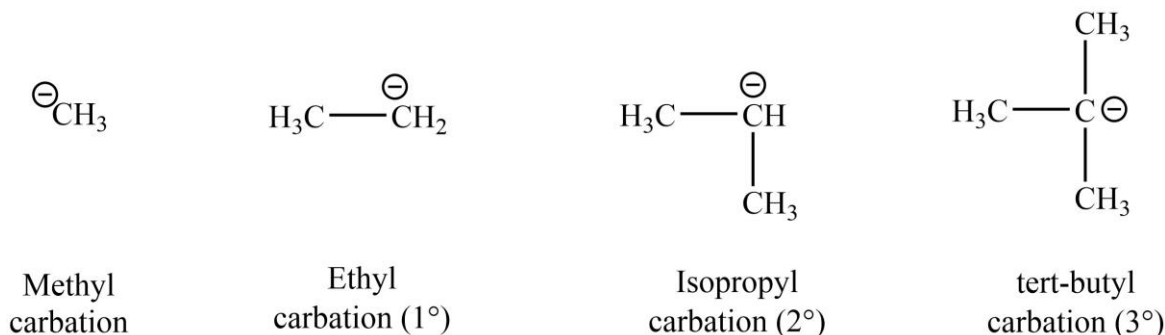
2. Structure of carbanions: It has been experimentally found that the carbanions are trigonal pyramidal around the carbon bearing negative charge. Now valence bond theory, as well as molecular orbital theory, easily accounted for such structure, it is more comfortable to discuss the valence bond approach. The carbon with a negative charge is in sp^3 hybridization with three hybrid orbitals forming bonds and the fourth hybrid orbital containing lone pair of electrons.



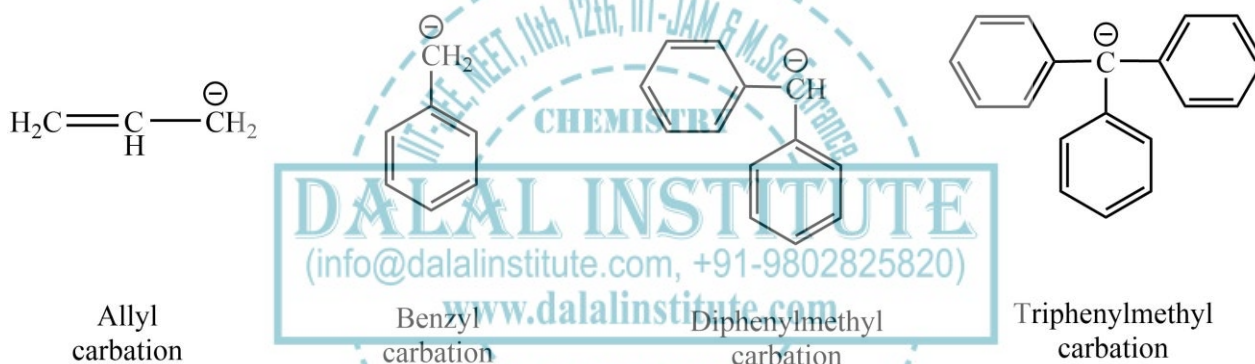
Furthermore, it should also be kept in mind that if the carbon bearing negative charge is adjacent to multiple bonds, the carbanions will adopt a planar structure to get stable by dispersing the negative charge.



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



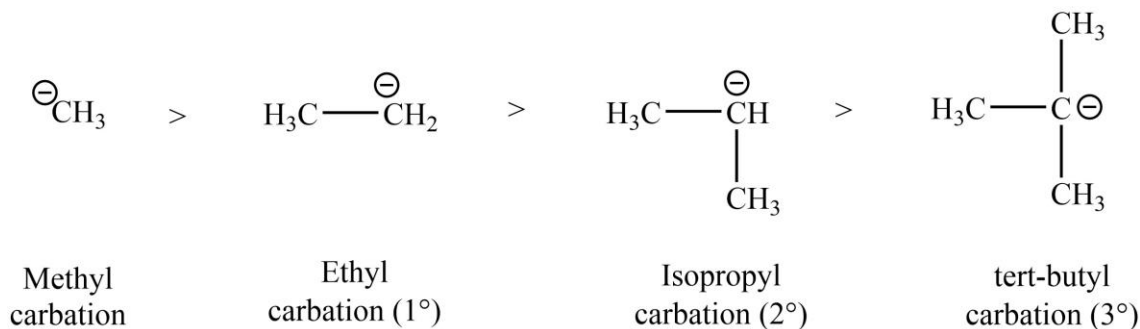
The second case is of unsaturated carbanions where the carbon bearing negative charge is directly connected to a carbon participating in multiple bonds i.e.



Since the carbon in carbanions has eight valence electrons, it is electron-rich; and therefore, any effect that can compensate the electron density accumulation will stabilize the carbanions.

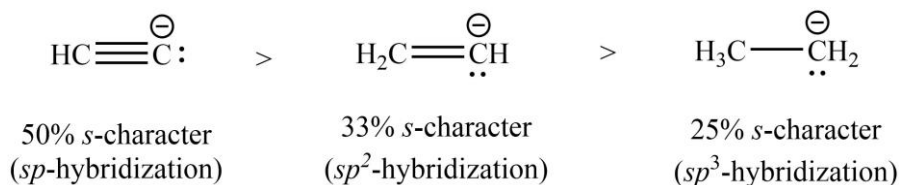
i) Stability of alky carbanions on the basis of inductive effect:

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



ii) Stability of carbanions on the basis of hybridization:

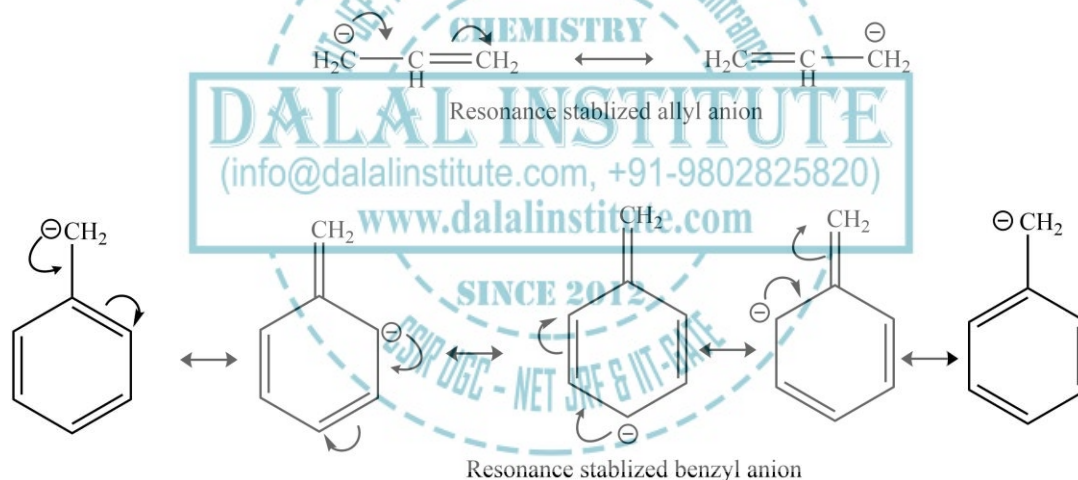
The nature and type of hybridization effect can be used to rationalize the relative stability of different carbanions as shown below.



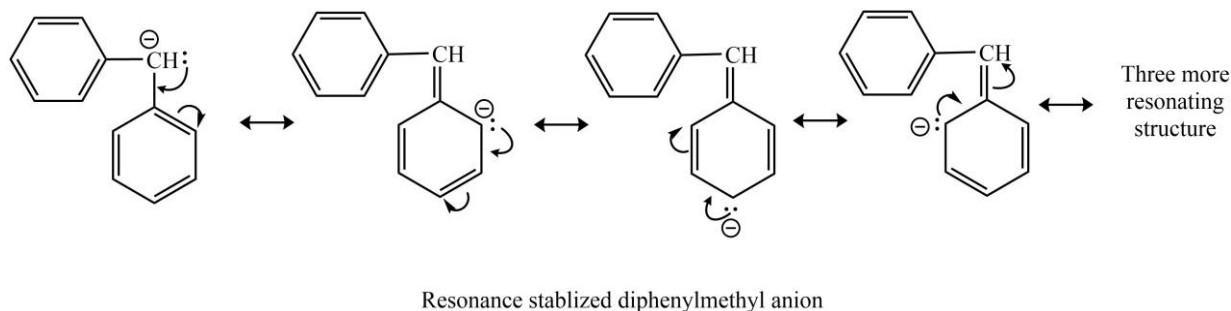
Hence, we can say that as the s-character of carbon bearing negative charge increases, the lone pair gets better stabilization; and therefore, overall carbanionic stability also increases.

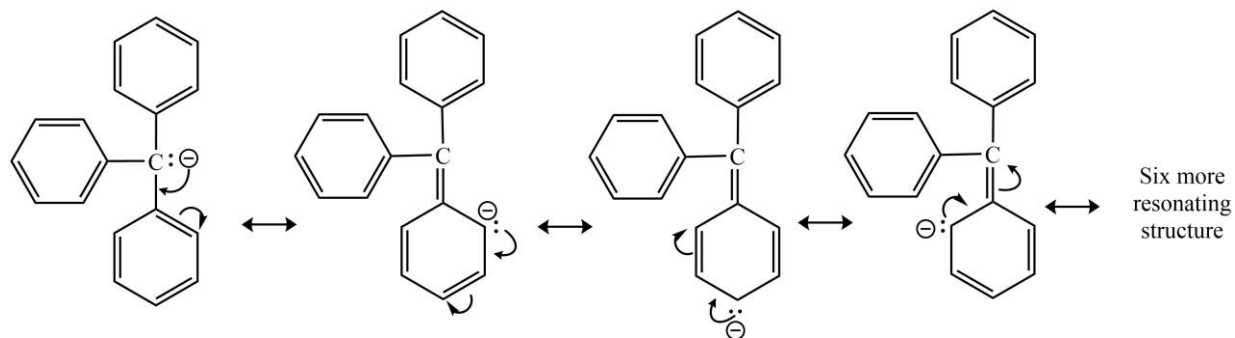
iii) Stability of allyl and benzyl carbanions:

The stability of the carbanions in which the carbon bearing negative 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 of allyl and benzyl carbanions.



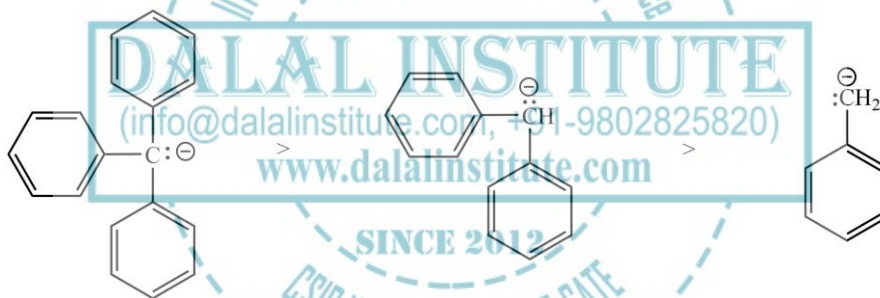
Now, as the number of phenyl groups attached to carbon bearing negative charge increases, the number of resonating structures will also increase, and hence the stability.



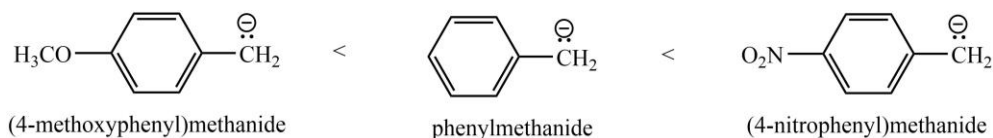


Resonance stabilized triphenylmethyl anion

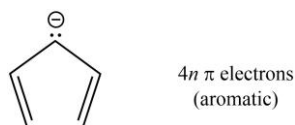
Therefore, the expected order of the stability of unsaturated systems with carbon bearing negative charge should be as given below.



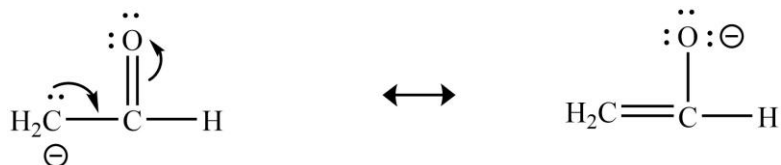
iv) *Stability of substituted benzyl carbanions*: Since the carbon bearing negative charge is electron-rich in nature, any group with $-R$ effect will stabilize the system and vice-versa. The order of stability of some typically substituted carbanions is given below.



v) *Instability of cyclopentadienyl anion*: The cyclopentadienyl anion is very unstable 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.



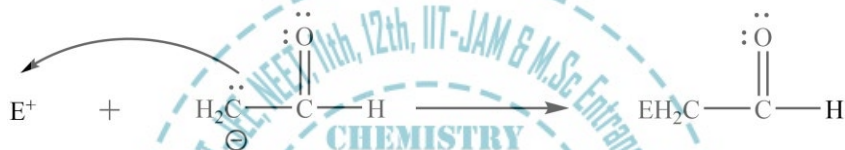
vi) *Stability of carbanions with electron-withdrawing groups:* The presence of electron-withdrawing group will distribute the charge over a wider range; and therefore, will result in a greater stabilization.



Resonance stabilization in acetaldehyde anion

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

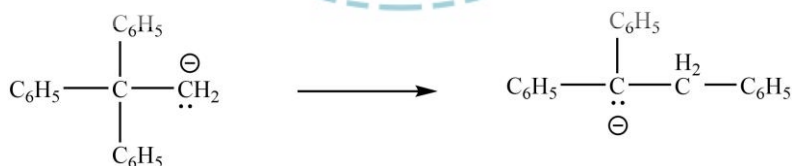
i) *Lone pair donation:* One of the most common pathways of carbanions reaction is the donation of electrons to a positive species like proton, or some species with an empty orbital.



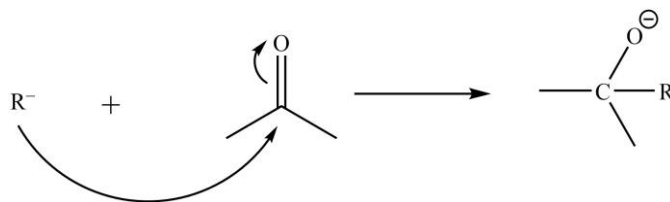
ii) *Associative reaction:* The carbanions can bond with a tetra-coordinated carbon followed by displacement of one of the previously attached groups.



iii) *Rearrangement reaction:* Like carbocations, the carbanions can also undergo rearrangement reaction although it is not very common.



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



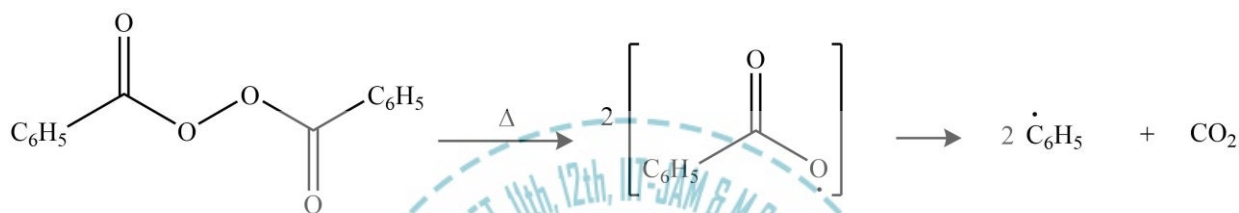
➤ **Free Radicals**

The term free radicals in organic chemistry may simply be defined as the chemical species that carries odd or unpaired electrons on the carbon with only seven valence electrons.

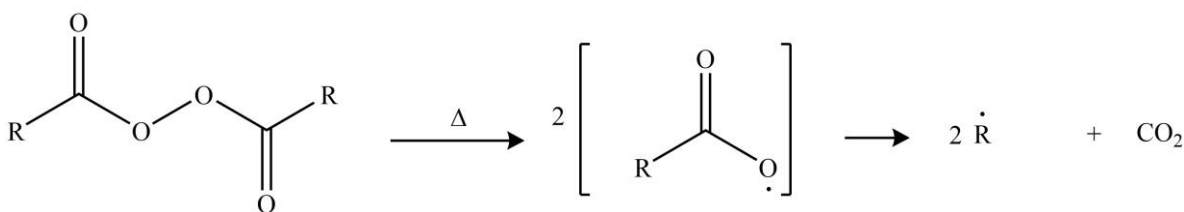
Since the carbon in free radicals has only seven electrons, it is electron deficient; and therefore, acts as an electrophile in chemical reactions.

1. Generation of free radicals: The homolytic cleavage of the covalent bond is responsible for the generation of most of the free radicals species. Some reactions involving the production of free radicals are given below.

i) *Thermal cleavage:*



ii) *Photochemical Cleavage:*



2. Structure of free radicals: It has been experimentally found that the free radicals are trigonal planar around the carbon bearing odd electron. 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 odd electron is in sp^2 hybridization with three hybrid orbitals oriented at 120° in a plane perpendicular to p_z orbital occupied by the odd electron.

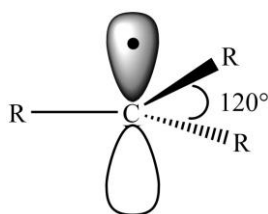
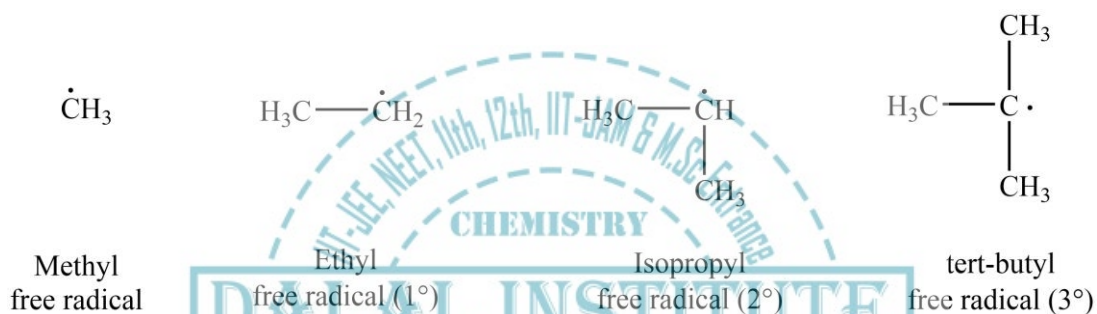
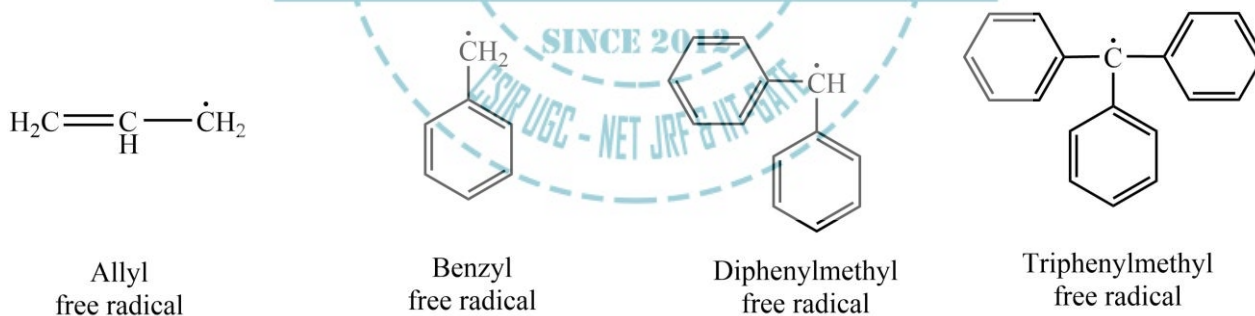


Figure 12. Orbital structure of free radical.

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



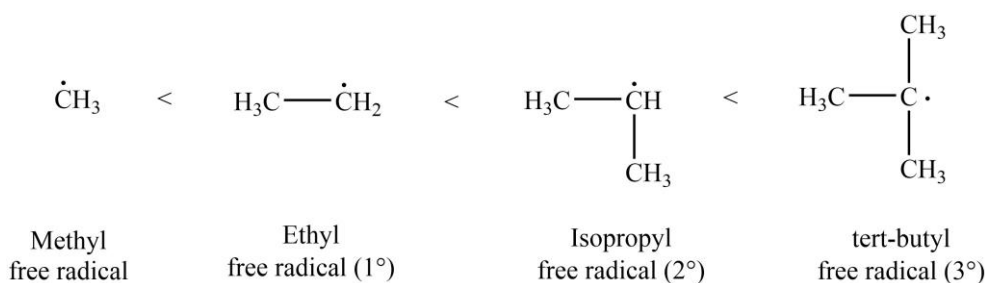
The second case is of unsaturated free radicals where the carbon bearing odd electron is directly connected to a carbon participating in multiple bonds i.e.



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

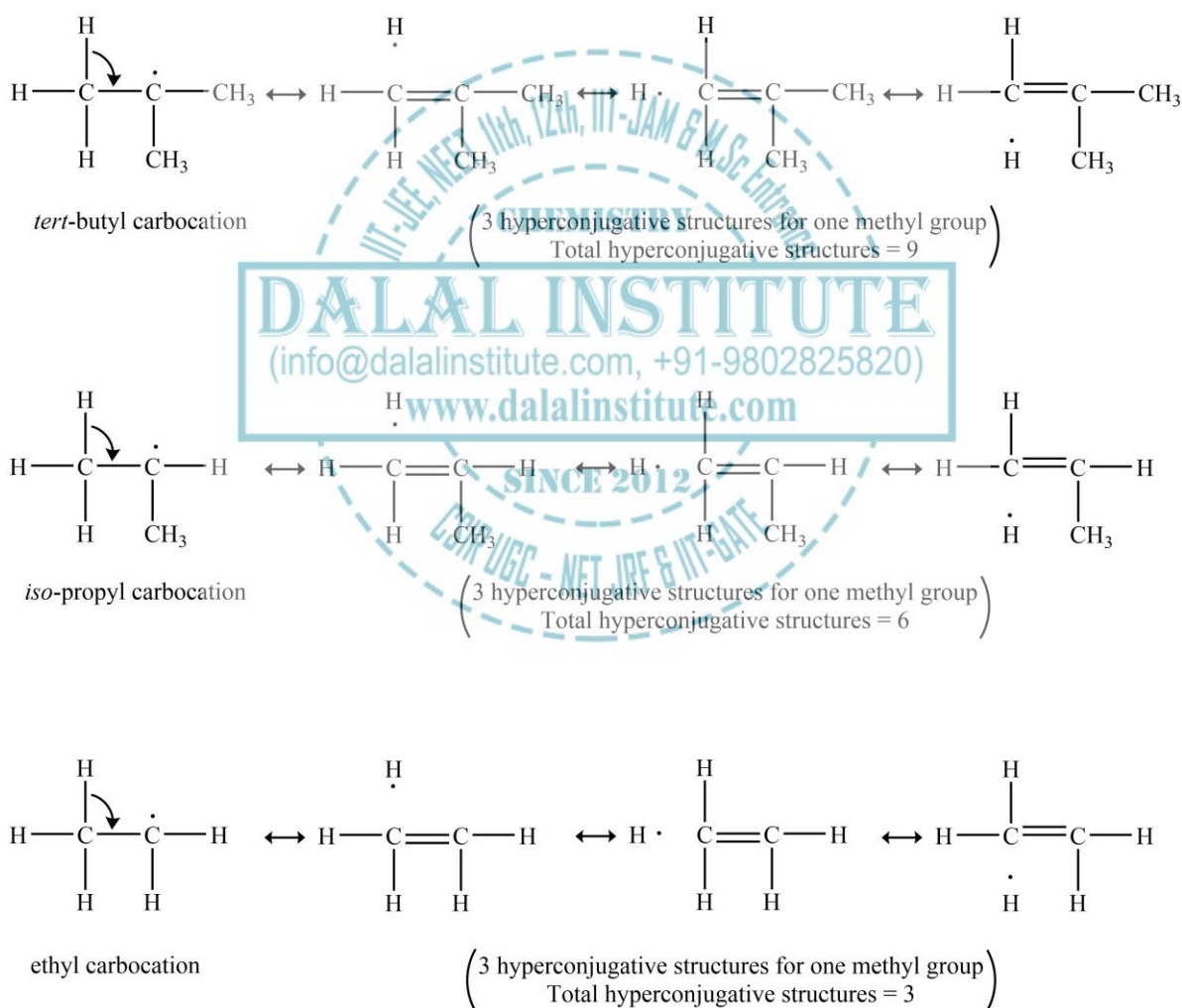
i) Stability of alkyl free radicals on the basis of inductive effect:

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



ii) Stability of alky free radicals on the basis of hyperconjugation:

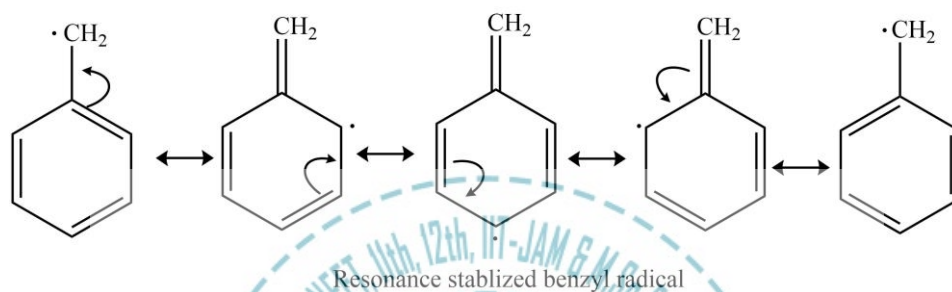
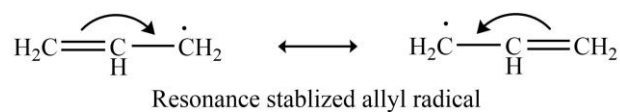
The existence of the hyperconjugation effect can be used to rationalize the relative stability of different free radicals as shown below.



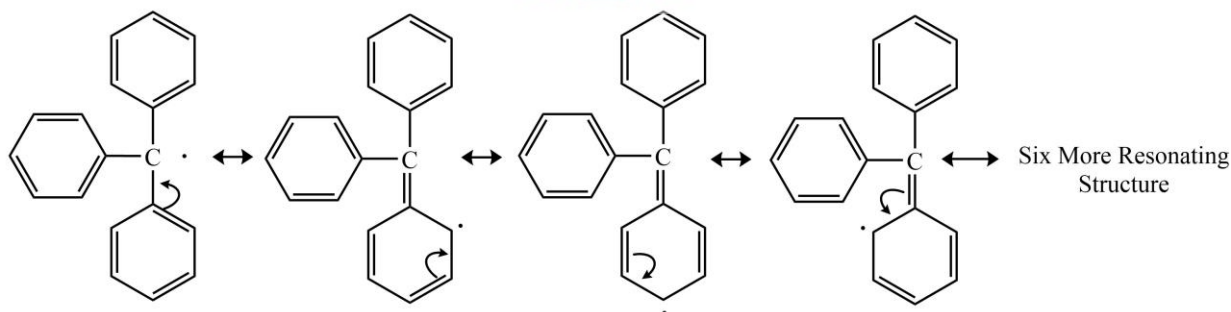
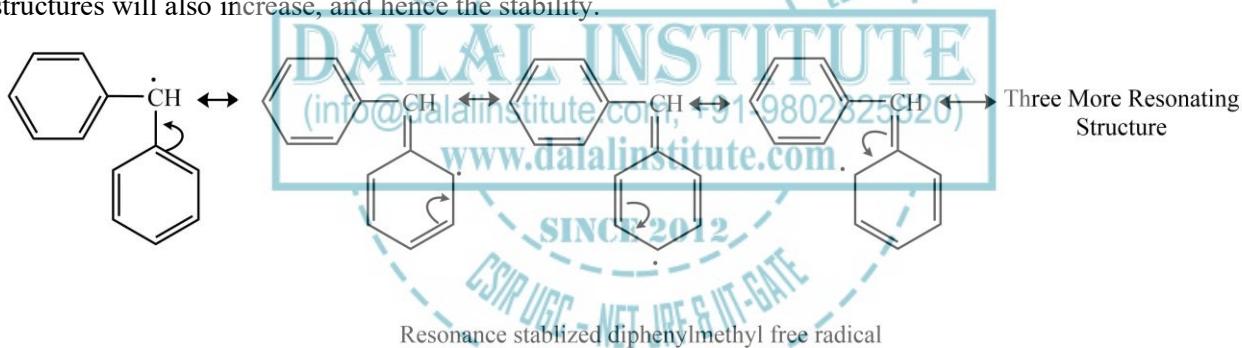
Hence, as far as the number of possible hyper-conjugative structures possible is concerned, tertiary free radicals should be more stable than secondary, which in turn should be more stable than primary.

iii) Stability of allyl and benzyl free radicals:

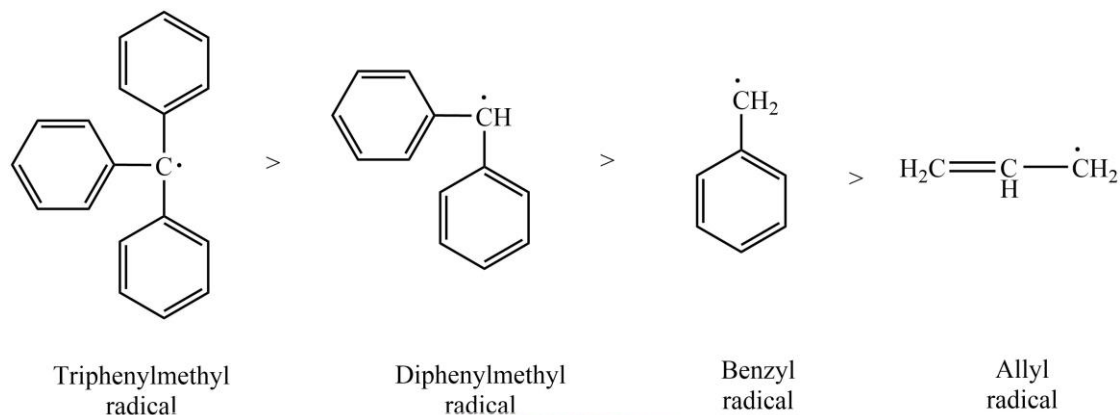
The stability of the free radicals in which the carbon bearing odd electron is adjacent to the double or triple bond can be rationalized in terms of resonance effect. First of all, let us draw the resonance structures of allyl and benzyl free radicals.



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



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



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

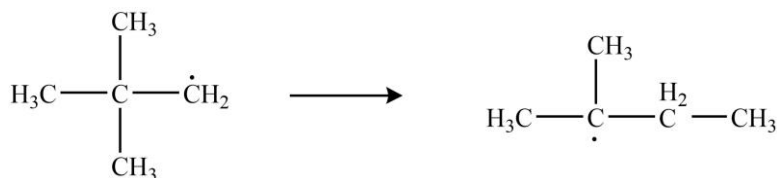
i) *Decomposition reactions:* One of the most common examples of this type of process is the decomposition of the benzyloxy radical.



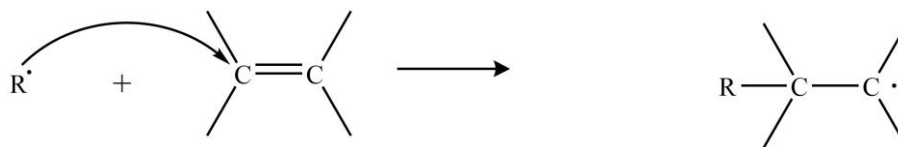
ii) *Hydrogen abstraction:* In these types of reactions, a free radical may result in the removal of a proton from the same (intermolecular process) or another molecule (intramolecular process).



iii) *Rearrangement reaction:* Free radicals may undergo rearrangement reactions to yield different but stable free radical counterparts.



iv) *Addition reactions:* The free radical obtained from an alkene may attack the triangular face of the double bond of another alkene molecule, and the process continues to yield polymers.



➤ Carbenes

The term carbenes in organic chemistry may simply be defined as the chemical species that carries two non-bonding electrons (paired or unpaired) on the carbon with a total of six valence electrons.

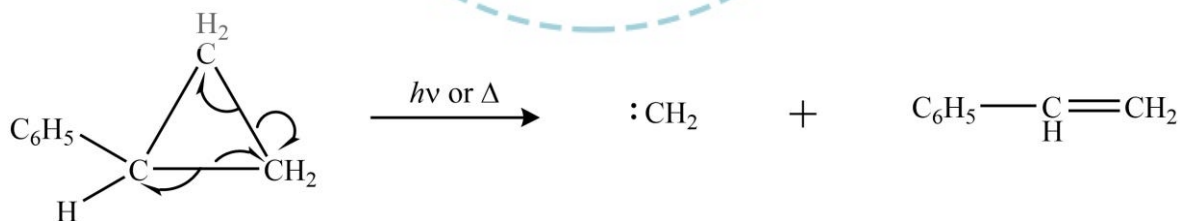
Since the carbon in carbenes has only six electrons, it is electron deficient; and therefore, acts as an electrophile in chemical reactions.

1. Generation of carbenes: Some of the most common pathways involving the production of carbenes are given below.

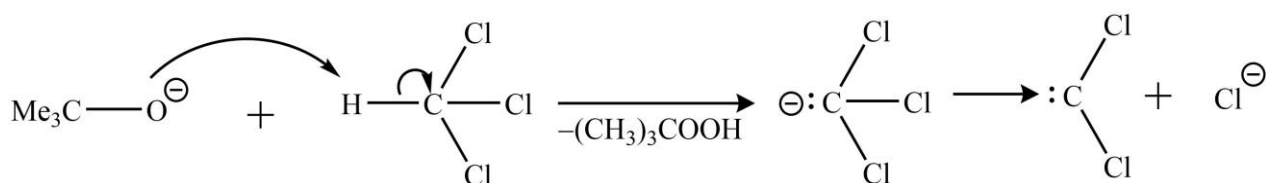
i) *Decomposition of ketones or diazoalkanes:*



ii) *Thermal or photolytic cleavage of cyclopropanes and oxiranes:*



iii) *Attack of strong base on chloroform:*



2. Structure of carbenes: Before we discuss the structure of carbenes, it is better to understand how carbenes can be classified on the basis of the distribution of non-bonding electrons. There are primarily two types carbenes; singlet carbenes and triplet carbenes.

It has been experimentally found that the singlet carbenes are V-shaped and are derivatives of trigonal planar geometry. 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 central carbon is in sp^2 hybridization with three hybrid orbitals oriented at 120° in a plane; two half-filled orbitals participating in bonding whilst the third hybrid orbital contains the lone pair. The p_z orbital remains empty and is perpendicular to the molecular plane.

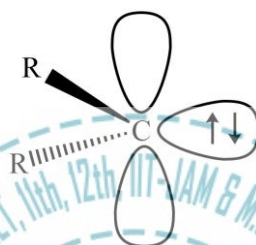


Figure 13. Orbital structure of singlet carbenes.

The triplet carbenes are either linear or V-shaped (depending upon the reaction requirement). 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 central carbon in linear triplet carbene is in sp hybridization with two hybrid orbitals oriented at 180° along the z -axis participating in bonding; whilst the atomic p_x and p_y atomic orbitals containing the unpaired electrons.

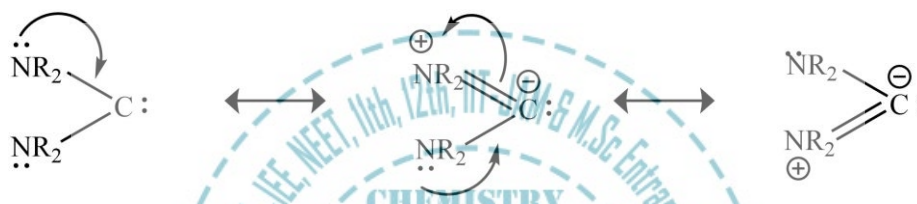


Figure 14. Orbital structure of triplet carbenes.

The central carbon in bent triplet carbene is in sp^2 hybridization with three hybrid orbitals oriented at 120° in a plane; two half-filled orbitals participating in bonding whilst the third hybrid orbital contains an unpaired electron. The other unpaired electron is in the atomic p_z orbital perpendicular molecular plane.

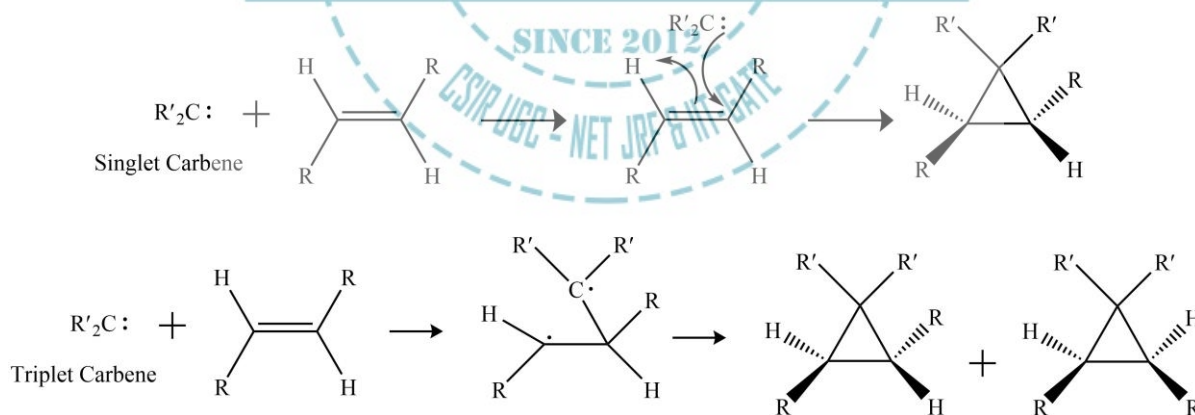
3. Stability of carbenes:

In the case of simple hydrocarbons, triplet carbenes typically have energies 8 kcal/mol less than singlet carbenes due to Hund's rule of maximum multiplicity; and therefore, as a whole, we can conclude that the triplet is the ground state and singlet one is the excited state entities. Also, groups that can donate electron pairs can stabilize the singlet carbene by delocalizing the pair into an empty p_z orbital. Furthermore, the singlet state can become the ground state if its energy is significantly reduced. However, triplet carbenes cannot be stabilized by this strategy. A carbene 9-fluorenylidene is found to exist in a rapid equilibrating mixture of triplet and singlet states with an energy difference of roughly 1.1 kcal/mol. Nevertheless, it is disputed if diaryl carbenes like fluorene carbene are true carbenes since the electrons can be delocalized to such a level that they become biradicals in nature. The experimental studies have suggested that triplet carbenes can be stabilized thermodynamically with heteroatoms of electropositive nature (like in silyl and silyloxy carbenes).

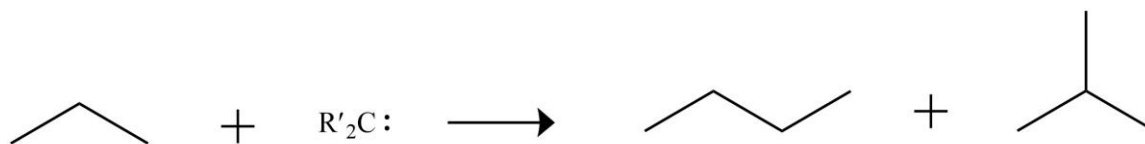


4. Reactivity of carbenes: The principal routes by which the carbenes can react to give rise to stable products are given below.

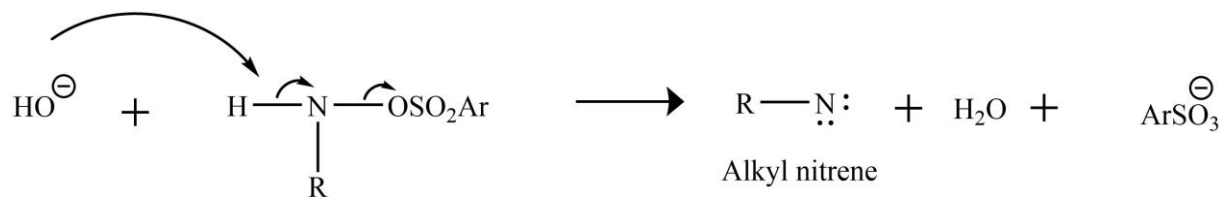
i) *Addition reactions:* besides the carbon-carbon double bonds (including aromatic systems), carbenes may also add to carbon-heteroatom multiple bonds.



ii) *Insertion reaction:* In these reactions, carbenes get inserted into CH bonds to give stable products.



ii) Elimination of sulphonate ion from certain compounds:



2. Structure of nitrenes: Before we discuss the structure of nitrenes, it is better to understand how nitrenes can be classified on the basis of the distribution of non-bonding electrons. There are primarily two types of nitrenes; singlet nitrenes and triplet nitrenes.

It has been experimentally found that the singlet nitrenes are linear and are derivatives of trigonal planar geometry. 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 nitrogen is in sp^2 hybridization with three hybrid orbitals oriented triangularly in a plane; one half-filled hybrid orbital participating in bonding with carbon whilst the second and third hybrid orbitals contain the lone pairs. The p_z orbital remains empty and is perpendicular to the above-mentioned triangular plane.

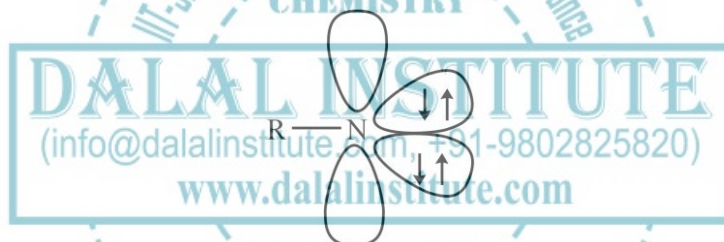


Figure 15. Orbital structure of singlet nitrenes.

The triplet nitrenes are also linear. The nitrogen in triplet nitrenes is in sp hybridization with two hybrid orbitals oriented at 180° along the z -axis; one hybrid orbital (half-filled) participating in bonding whilst the other hybrid orbital contains a lone pair. The atomic p_x and p_y atomic orbitals containing the unpaired electrons.

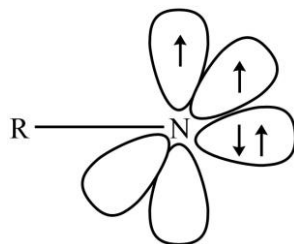
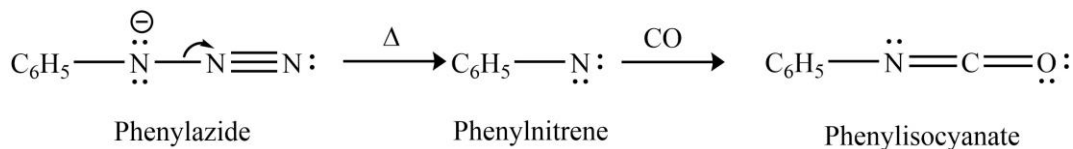


Figure 16. Orbital structure of triplet nitrenes.

3. Stability of nitrenes:

Although nitrenes are too reactive to isolate under normal conditions, in 2019, an authentic triplet nitrene was isolated by Betley and Lancaster, stabilized by coordination to a copper center in a bulky ligand. Furthermore, triplet nitrenes are thermodynamically more stable but react stepwise allowing free rotation and thus producing a mixture of stereochemistry. They are usually detected by adding carbon monoxide as it can form isocyanates with nitrenes which can be isolated easily.



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

i) *Addition reactions:* Nitrenes may add to carbon-carbon multiple bonds to give rise to some stable product.



ii) *Insertion reaction:* In these types of reactions, nitrenes get inserted into CH bonds to give stable products.



iii) *Dimerization reaction:* Nitrenes may undergo dimerization to form diamide.



iv) *Rearrangement reactions:* The nitrenes can also undergo rearrangement reactions to yield very stable products as given below.



v) *Hydrogen abstraction:* Nitrenes are also able to abstract hydrogen or any other groups or atoms to yield free radicals' as given below.



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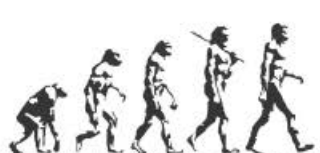
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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