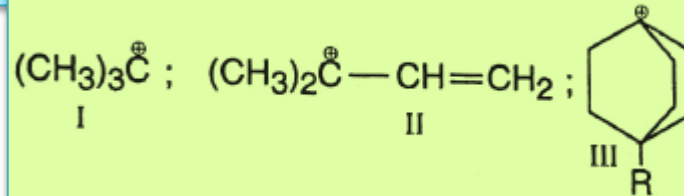
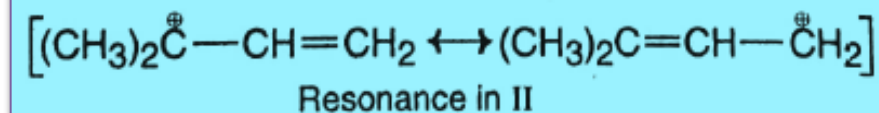


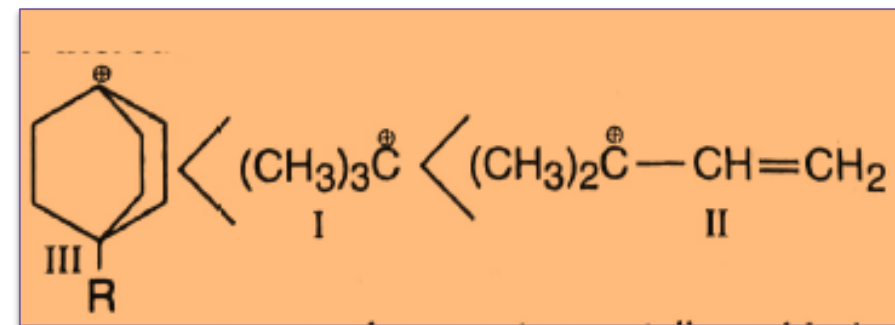
Question: Arrange the following carbocations in order of their increasing stability and provide reason.



- ❖ The carbocation I is stabilized by the +I effects of three $-\text{CH}_3$ groups and hyperconjugative effect involving nine C-H bonds.
- ❖ The carbocation III is similarly stabilized by +I effect of three ring bonds.
- ❖ However, it is not stabilized by hyperconjugation because formation of a double bond at the bridgehead position is not possible (Bredt's rule).
- ❖ Again, the carbocation suffers from angle strain because the angle between bonds is somewhat less than the sp^2 bond angle, i.e., 120° .
- ❖ The carbocation II is the most stable one because it is highly stabilized by resonance and also by both inductive and hyperconjugative effects of two methyl groups.

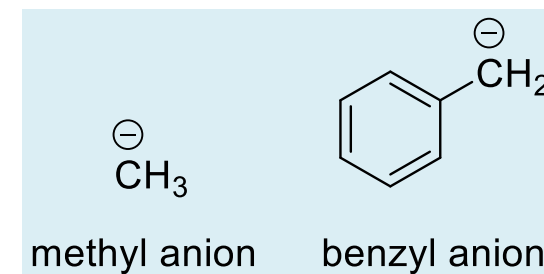


Hence, the order of their increasing stability is:



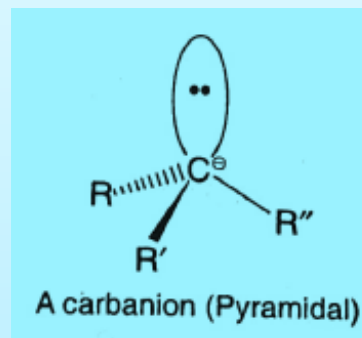
Carbanions

The species containing negatively charged carbon atom is known as carbanion. For example:



Structure:

- ❖ The central carbon atom of a carbanion is sp^3 hybridized.
- ❖ It is surrounded by three bonding pairs and one unshared pair of electrons which occupies an sp^3 orbital. Thus, a carbanion is expected to have the tetrahedral shape.



- ❖ However, the shape is not exactly that of a tetrahedron. It is found to have the pyramidal shape.
- ❖ Since the repulsion between the unshared pair and any bonding pair is greater than the repulsion between any two bonding pairs, the angle between two bonding pairs (i.e., two sp^3 - σ bonds) is slightly less than the normal tetrahedral value of 109.5° and because of this, a carbanion appears to be shaped like a pyramid with the negative carbon at the apex and the three groups at the corners of a triangular base.
- ❖ However, the resonance-stabilized carbanions, such as allylic and benzylic carbanions are sp^2 hybridized and they assume trigonal planar structure.

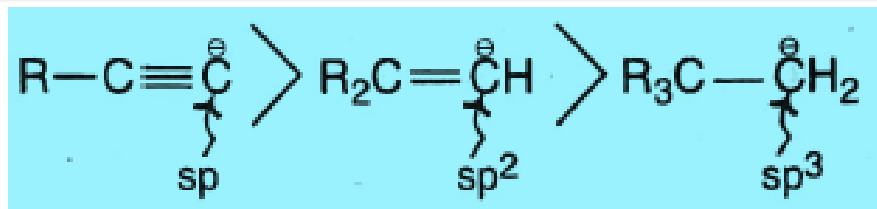
The factors responsible for carbanion stability are -

The structural features responsible mainly for the increased stability of carbanions are :

- (i) the amount of 's' character of the carbanion carbon atom,**
- (ii) inductive electron withdrawal,**
- (iii) conjugation of the non-bonding electron pair with an unsaturated system, and**
- (iv) constituting an aromatic system.**

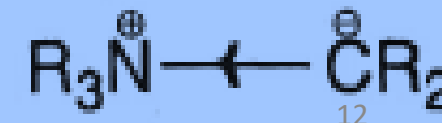
(i) The amount of 's' character of the carbanion carbon atom

- ❖ An s orbital is closer to the nucleus than the p orbital in a given main quantum level and it possesses lower energy.
- ❖ An electron pair in an orbital having large s character is, therefore, more tightly held by the nucleus and hence of lower energy than an electron pair in an orbital having small s character.
- ❖ Hence, a carbanion at an sp hybridized (50% s character) carbon atom is more stable than a carbanion at a sp² hybridized (33.33% s character) carbon atom, which in turn is more stable than a carbanion at an sp³ hybridized (25% s character) carbon atom. Thus, the order of carbanion stability is:



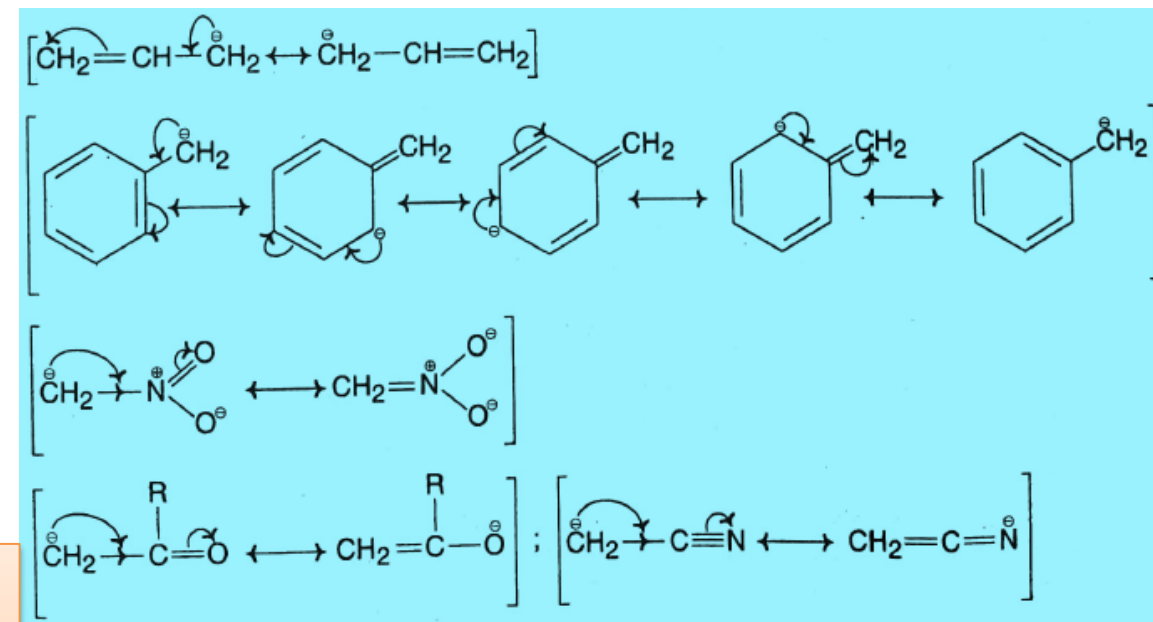
(ii) Inductive electron withdrawal

- ❖ Groups having electron-withdrawing inductive effects (H) stabilize a carbanion by dispersing the negative charge.
- ❖ In a nitrogen ylide, for example, the carbanion is stabilized by the -I effect of the adjacent positive nitrogen.



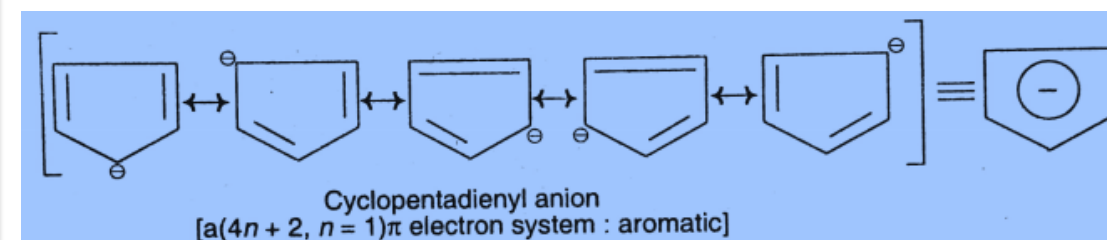
(iii) Conjugation of a non-bonding electron pair with an unsaturated system

- ❖ Where there is a double or triple bond α to the carbanion carbon atom, the anion is stabilized by delocalization of its negative charge with the π orbitals of the multiple bond.
- ❖ Thus, allylic and benzylic carbanions and the carbanions attached to the functional groups such as $-\text{NO}_2$, $-\text{C}\equiv\text{N}$, $>\text{C}=\text{O}$, etc. are stabilized by resonance.

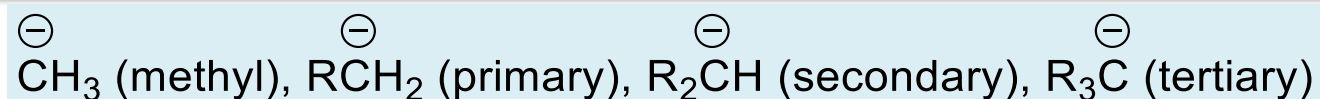


(iv) Constituting an aromatic system

- ❖ The unshared pair of a carbanion may be involved in constituting a planar $(4n + 2)\pi$ electron system where $n = 0, 1, 2, \dots$ etc., i.e., a carbanion may be stabilized by constituting an aromatic system
- ❖ Cyclopentadienyl anion, for example, is unusually stable because it is a 6π electron system and aromatic.



Question: Give the order of stability of the following simple carbanions :



Because of the destabilizing influence of the electron-donating inductive effect of alkyl groups, the order of stability of these simple carbanions is as follows:

