Topic: General Organic Chemistry (GOC)

STUDY MATERIAL

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Bachelor's of Science
(Ist Semester)
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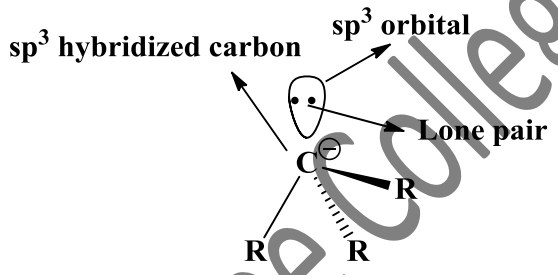
Carbanions

Lecture No. 02

- Carbanion is a species in which carbon bears a negative charge and possesses eight electrons in its valence shell.
- Carbanions behave as Nucleophiles or Lewis bases.
- Carbanion attack at electron deficient site of a substrate molecule.
- Bulky carbanions usually behave as Bases while as carbanions smaller in size behaves as Nucleophiles.
- If all the substituents on the negatively charged carbon are different then carbanion will be chiral.

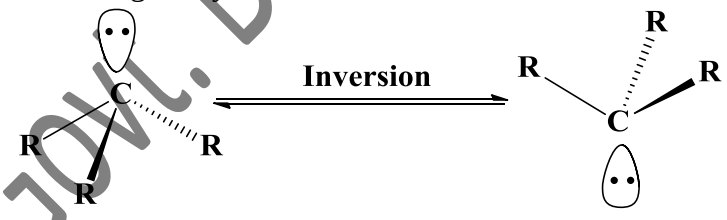
Structure of Carbanion

- In carbanion the carbon atom bearing negative charge is ***sp*^{3}** hybridized and thus possess **Trigonal Pyramidal geometry** with bond angle of **97^o – 100^o**
- Three of the four *sp*^{3} hybridized orbitals form three sigma (**σ**) bonds with monovalent atoms or groups while the fourth *sp*^{3} orbital contain lone pair of electron.
- The carbanions which are stabilized by resonance have **planar** geometry. In these carbanions the carbon atom carrying negative charge is *sp*^{2} hybridized.



Orbital structure of carbanion

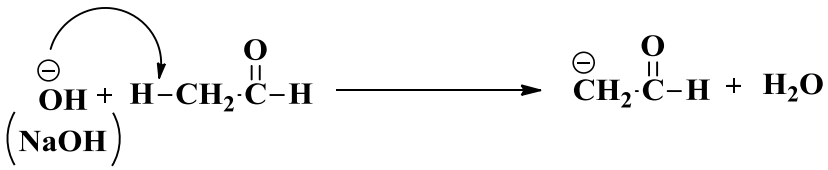
- Carbanion undergoes rapid interconversion between two pyramidal forms. The energy barrier is different for different types of carbanions. For example for a methyl carbanion the energy barrier is **2 kcal/mol**, while for trifluoromethyl carbanion value is around **120 kcal/mol.** The higher energy barrier of trifluoromethyl carbanion is due to the more electronegativity of fluorine atom which is more stabilizing than a hydrogen atom.



Generation of carbanions

Carbanions are important reagents in organic synthesis which are utilized for the synthesis of a large number of organic compounds of medicinal and industrial importance. Carbanions have been generated in a large no. of organic reactions. Following methods are generally used for their generation:

(i) From organic substrates having a C-H bond on treatment with a base.



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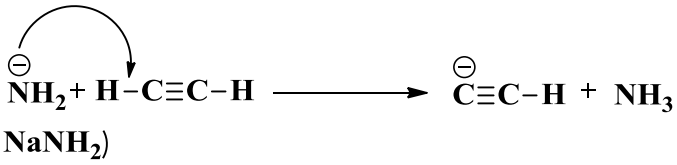

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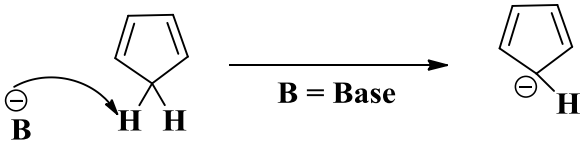
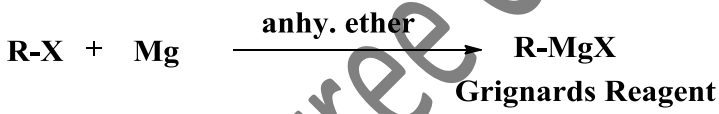


(iv) Addition of a nucleophile to an unsaturated C-C bond generates carbanion.

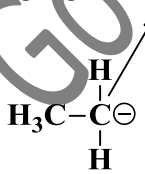
(v) Reaction of an alkyl halide with magnesium in presence of anhydrous ether as a solvent generates Grignards Reagent. The Grignards reagent behaves like a carbanion.



Types and stability of Carbanions

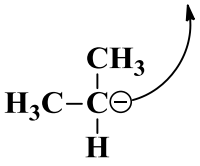
There are three types of carbanions: **Primary carbanion, Secondary carbanion and Tertiary carbanion** classified on the basis of no. of carbon atoms attached to a carbon bearing negative charge.

One carbon attached to carbon bearing negative charge



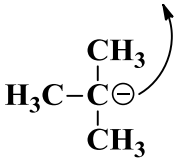
Primary carbanion
(1^o carbanion)

Two carbon attached to carbon bearing negative charge



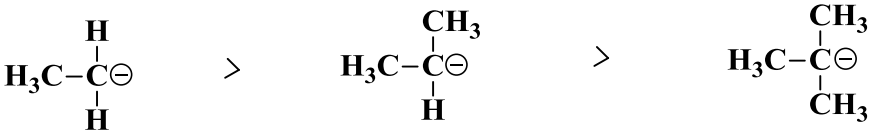
Secondary carbanion
(2^o carbanion)

Three carbon attached to carbon bearing negative charge



Tertiary caranion
(3^o carbanion)

The stability order of three types of carbanions is shown as:
Primary carbanion > secondary carbanion > Tertiary carbanion



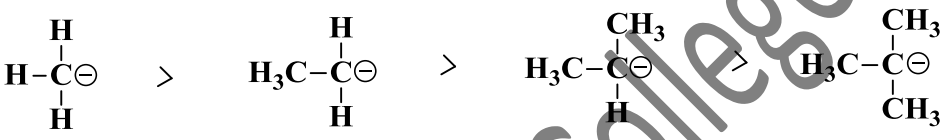
Primary carbanion **Secondary carbanion** **Tertiary carbanion**

The above stability order of carbanions can be explained on the basis of following factors:

- **Inductive effect**
- **Extent of conjugation in anion**
- **Hybridization of the carbanion**
- **Aromaticity**

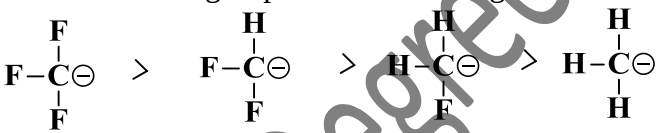
Inductive Effect

Electron donating group (EDG) attached to a carbanion will increase the negative charge on carbon and thus destabilize it. However, electronegative atoms or Electron withdrawing groups (EWG) adjacent to the negatively charged carbon will stabilize the carbanion. The alkyl groups are electron releasing in nature due to inductive effect (+I). More the number of alkyl groups attached to a carbanion, lesser will be the stability. Carbanions prefer a lesser degree of alkyl substitution. Therefore the order of stability order of alkyl carbanion is **methyl carbanion > 1^o > 2^o > 3^o.**



Methyl carbanion **1^o carbanion** **2^o carbanion** **3^o carbanion**

Presence of electronegative atoms (**F, Cl, Br**) or Electron withdrawing groups (NO_2, CN, COOH, CO) close to the negatively charged carbon will stabilize the charge. Thus more the number of such groups in a carbanion greater will be the stability.

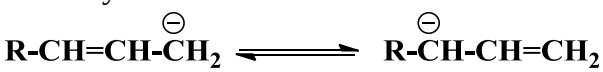


Extent of conjugation in anion

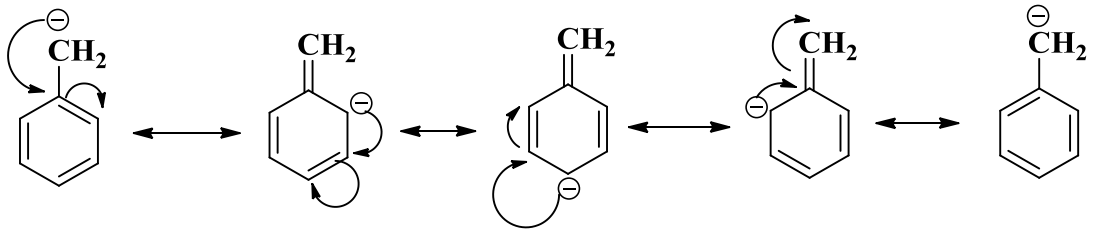
When a negatively charged carbon is in conjugation with a double bond the resonance effect will stabilize the anion by spreading out the charge by rearranging the electron pairs.

☞ **Which is more stable amongst benzyl and allyl carbanions?**

The negative charge is delocalized through resonance in both benzyl carbanion and allyl carbanion. But benzyl carbanion has more number of contributing structures. Thus, benzyl carbanion is more stable than allyl carbanion.



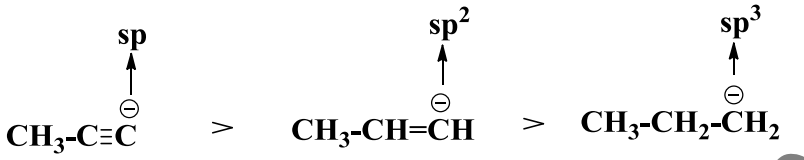
Allyl carbanion



Resonanace structures of Benzyl carbanion

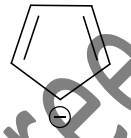
Hybridization of the carbanion

Stability of carbanion will depend upon the *s*-character of carbanion i.e. more the *s*-character, higher will be the stability of carbanion. The percentage of *s*-character in the hybrid orbitals is as follows: **sp (50%) > sp^2 (33%) > sp^3 (25%).**



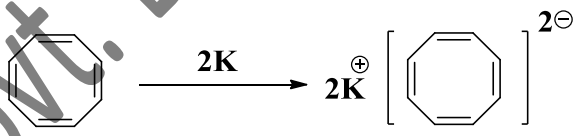
Aromaticity

In some carbanions, the lone pair of electrons of the negative charge is involved in delocalization to add on to the aromatic character of the molecule which gives them extra stability. For example, in Cyclopentadienyl anion there are 6 π electrons and thus it obeys Huckel rule, (4n+2) π electron. This anion is stabilized by aromatization.



Cyclopentadienyl anion

Cyclooctatetraene which is non-aromatic readily reacts with potassium and gets converted to cyclooctatetraenyldianion potassium salt which is 10 π electron system and stable due to aromaticity.



Cyclooctatetraene (COT) (Non-aromatic)

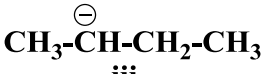
Cyclooctatetraenyldianion potassium salt (Aromatic)

Problems based on Carbanions

☞ Arrange the following carbanions in decreasing order of stability:

i

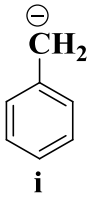
ii



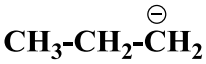
iii

(a) ii > i > iii **b)** i > ii > iii **c)** iii > ii > i **d)** i > iii > ii

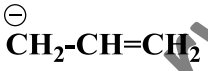
☞ Predict the most stable carbanion:



i



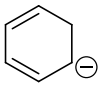
ii



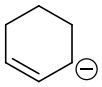
iii

a) i **b)** ii **c)** iii **d)** All are equally stable

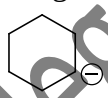
☞ Decreasing order of stability of following carbanions is:



i



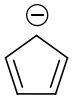
ii



iii

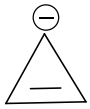
(a) ii > i > iii **b)** i > ii > iii **c)** iii > ii > i **d)** i > iii > ii

☞ Increasing stability order of following molecules is:



i

ii



iii

(a) ii < i < iii **b)** i < ii < iii **c)** iii < ii < i **d)** i < iii < ii

☞ The shape of carbanion is:

a) Tetrahedral **b)** Trigonal pyramidal **c)** Trigonal planar **d)** T-shape