CARBANIONS & THEIR STABILITY

By:
Dr. Muhammad Imran Shaikh
Lecturer,
Dow College of Pharmacy,
Dow University of Health Sciences,
Karachi.
Objectives:

At the end of this topic students will be able to,

- Define carbanion.
- Explain chemical ways for carbanion formation.
- State factors affecting stability of Carbanions.
- Interpret stability of different carbanions on the basis of chemical structure.
- Discuss different reactions that carbanions undergo, like aldol condensation, wittig reactions and favorskii rearrangement.
Carbanions are units that contain a negative charge on a carbon atom.

The negative charge gives good nucleophilic properties to the unit that can be used in the formation of new carbon-carbon bonds.
“In theory any organic compound can function as an acid in classical sense by donating a proton to a suitable base, the resultant acid being a carbanion."

\[ R_3C-H + B: \leftrightarrow R_3C^\Theta + BH^\Theta \]
Carbanion formation:

- The most general method of forming a carbanion is by removal of atom or group, leaving its bond electron pair behind.
- Leaving group can be,
  - A hydrogen (i.e. a proton).
  - CO₂ from the decarboxylation of alkyl acetate.
Stability:

stability of carbanion is affected usually by following factors,

- Increase in ‘s’ character at the carbanion carbon.
- Electron withdrawing inductive effects.
- Conjugation of carbanion lone pair with polarized multiple bond.
- Aromatization.
1. Increase in ‘s’ character at the carbanion carbon:

\[ \text{CH}_3\text{--CH}_3 \text{ < CH}_2\text{=CH}_2 \text{ < HC≡CH; } \]

Above mentioned is the trend of increasing acidity from alkanes towards alkynes due to the presence sp hybrid orbitals of alkyne where s character is maximum due to the fact that in sp hybrid orbitals bonding electrons are at least distance from the nucleus making carbon more electronegative for those electrons and hence more acidic.
2. Electron withdrawing inductive effects:
3. Conjugation of carbanion lone pair with polarized multiple bond:

\[
\begin{align*}
&\text{B} \equiv \text{H} \\
&\text{CH}_2 \equiv \text{C} \equiv \text{N} \iff \left[ \text{CH}_2 \equiv \text{C} \equiv \text{N} \iff \text{CH}_2 = \text{C} = \text{N}^\ominus \right] + \text{BH}^\ominus \\
&\text{B} \equiv \text{H} \quad \text{Me} \\
&\text{CH}_2 \equiv \text{C} = \text{O} \iff \left[ \text{Me} \equiv \text{Me} \right] + \text{BH}^\ominus \\
&\text{B} \equiv \text{H} \\
&\text{CH}_2 \equiv \text{N} = \text{O} \iff \left[ \text{N} = \text{O} \equiv \text{O} = \text{N} \equiv \text{O}^\ominus \right] + \text{BH}^\ominus
\end{align*}
\]
4. Aromatization:

an example of stabilization via aromatization (resonance) is of cyclopentadiene

★ Huckel rule

\[ 4n+2 \]
Carbanion reactions
Aldol condensation:

Aldehydes containing α hydrogen undergo self addition in the presence of a dilute base to form products called **aldols**. The reaction is called aldol condensation.

\[
\begin{align*}
\text{CH}_3\text{C} &= \text{H} + \text{CH}_2\text{C} &= \text{H} \\
\text{Acetaldehyde} & & \text{Acetaldehyde} \\
\text{CH}_3\text{C} &= \text{CH} &= \text{CH}_2\text{C} &= \text{H} \\
\text{3-Hydroxybutanal} & & \text{aldol}
\end{align*}
\]
Mechanism of reaction

Step 1.

\[
\begin{align*}
H-CH_2-C-H + \ddot{\text{O}}H & \rightleftharpoons \dddot{\text{C}}H_2-C-H + H_2O \\
\end{align*}
\]

Acetaldehyde

(Nucleophile)

Step 2. The enolate ion attacks the carbonyl carbon of another un-ionised aldehyde molecule.

\[
\begin{align*}
\delta^- & \rightleftharpoons \dddot{\text{C}}H_2-C-H \\
\end{align*}
\]

Step 3. The negative oxygen in the product accepts a proton from water to give aldol.

\[
\begin{align*}
\text{Acetaldehyde} \\
\end{align*}
\]

\[
\begin{align*}
\text{3-Hydroxybutanal} \\
\end{align*}
\]
The product in all aldol condensations has several common structural characteristics:

- The product is a larger molecule that contains newly formed carbon-carbon bond.
- The newly formed C-C bond occurs between the α-carbon of one aldehyde molecule and what was originally the carbonyl carbon of the second aldehyde molecule.
- The product contains two functional groups: one carbonyl group and one hydroxyl group.
- The hydroxyl group is always attached to the β-carbon.
Acetone + Acetone = ?
Benzaldehyde + acetaldehyde = ?
Benzaldehyde + acetone = ?
Benzaldehyde + acetophenone = ?
Propanaldehyde + Propanaldehyde = ?
Wittig reaction:

- An extremely useful reaction for the synthesis of alkenes from carbonyl compounds.
- The heart of the synthesis is the nucleophilic attack on carbonyl carbon by an ylid / ylide to form a betaine which undergoes elimination to yield the product.
- Ylid / ylide: Molecule with adjacent opposite charges.
- Betaine: neutral chemical compound with positive charge cation functional group which bears no hydrogen negative charge functional group which may not be adjacent to positive charge.
Formation of phosphonium ylid.

Addition of phosphonium ylid to carbonyl compound.
Favorskii rearrangement:

These are base induced rearrangements involving carbanions that proceed via 1-3 elimination to form cyclopropanone intermediates.

[Diagram showing the rearrangement process involving α-haloacetone and cyclopropanone intermediate, leading to carboxylate anion end-product.]