# Reactive Intermediates



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#### REACTIVE INTERMEDIATES

The intermediates formed during the reactions: short lived, mostly non isolable, quickly converted into more stable molecule.







Carbocations have six electrons in their valence shell, and are electron deficient. ⇒ Carbocations are Lewis acids.

Most carbocations are **short-lived** and **highly reactive**.

# CARBOCATIONS

For many years they were called as carbonium ions; in **1902** it was suggested inappropriate to use suffix 'onium' ion for lesser covalency which is often used for higher covalency than neutral atom. e.g. ammonium, hydronium ion. *Finally accepted by IUPAC in 1987 after Olah's discovery.* 



In 1962, George A. Olah (Nobel Laureate in chemistry in 1994; now at theUniversity of Southern California) and co-workers published the first of a series of papers describing experiments in which alkyl cations were prepared in an environment in which they were reasonably stable and in which they could be observed by a number of spectroscopic techniques.

### THE RELATIVE STABILITIES OF CARBOCATIONS



The relative stabilities of carbocations is  $3^{\circ} > 2^{\circ} > 1^{\circ} >$  methyl.

### **THE RELATIVE STABILITIES OF CARBOCATIONS**

Allyl cation and benzyl cation are more stable than most other carbocations. Molecules which can form allyl or benzyl carbocations are especially reactive. Stable allylic cations have been obtained by the reaction between alkyl halides, alcohols, or alkenes (by hydride extraction) and SbF<sub>5</sub> in SO<sub>2</sub> or SO<sub>2</sub>CIF.







## THE RELATIVE STABILITIES OF CARBOCATIONS



Vacant p-orbital and cyclopropyl bonds are parallel to each other



Acyl or acetyl cation is as stable as tert-butyl cation.

Q. Which of the following carbocations do not exist? Which one is more stable?



It is impossible to form carbocation at bridgehead atoms in [2.2.1] systems since they can not be planar.

Larger bridgehead carbocations can exist.

Cyclopropyl group provides extra stability already discussed in previous slide.

## CARBOCATION

#### How they exist?

More stable ones can be prepared in solution and in some case they even exist as solid salts.

➢ In solution, carbocations may be free i.e. in case of polar solvents they are solavated.

➢ In non-polar solvents they exist as an ion pair i.e. closely associated with negative ion/counter ion/gegenion.

#### Commercially available carbocation



Aryl methyl carbocations are further stabilized by electron donating groups at ortho and para postion (s).

## **PREPARATION OF CARBOCATIONS**

No matter how they are generated, study of the simple alkyl cations has provided dramatic evidence for the stability. Both propyl fluorides gave the isopropyl cation; all four butyl fluorides gave the *tert*-butyl cation. Butane, in superacid, gave only the *tert*-butyl cation.



## Structure of carbocation:



demonstrating planar geometry



Negatively charged Organic species in which carbon carries three bond pairs and one lone pair, is known as cabanion.

Carbanions donate their electron pair to a proton or some other positive center to neutralize their negative charge.

The conjugate bases of weak acids, strong bases, excellent nucleophiles.

# **Characteristic of Carbanions**

Hybridisation and geometry : Alkyl carbanion has three bond pairs and one lone pair. Thus hybridisation is sp3 and geometry is pryamidal.



- There are eight electrons in the outermost orbit of carbanionic carbon hence its octet is complete.
- It behaves as charged nucleophile.
- It is diamagnetic in character because all eight electrons are paired.
- It is formed by heterolytic bond fission.
- It reacts with electrophiles.

# **Stability of carbonions**

Carbanions are destabilized by alkyl groups



Stability of carbanions depends on the +I or –I group as follows
1. with increase in +I effect stability decreases
2. with increase in –I effect stability increases

# **Stability of carbonions**

#### **Delocalistion or Resonance**

Allyl and benzyl carbanions are stabilised by delocalisation of negative charge.



(i) Number of resonating structures in increasing order (ii) Stability in increasing order

# **Stability of carbanions**

### Stability of Aromatic Carbanions

- (i) Anions in which negative charge is present on carbon of aromatic system is known as aromatic carbanions.
- (ii) Aromatic carbanions are most stable carbaions.
- (iii) Anions obeying Huckel rule are stable because they are aromatic and there is complete delocalisation of negative charge.



Cyclopentadienyl anion

# **Stability of different type of carbanions in decreasing order**

Aromatic carbanion > Benzyl carbanion > Allyl carbanion > CH= > CH2 = > Alkyl carbanion

# FREE RADICALS

 Definition: Any chemical species with one or more unpaired electrons. These are paramagnetic due to the presence of unpaired electron. They are generated by the homolysis of covalent bond by heat or light.  The first organic free radical identified was triphenylmethyl radical, by Moses Gomberg (the founder of radical chemistry) in 1900.





Moses Gomberg 1866-1947

#### II. THE GENERATION AND FATE OF FREE RADICALS

- The formation of radicals may involve breaking of covalent bonds homolytically, a process that requires significant amounts of energy.
- Homolytic bond cleavage most often happens between two atoms of similar electronegativity.

#### III. RADICAL IONS

- A radical ion is a free radical species that carries a charge.
- Many aromatic compounds can undergo one-electron reduction by alkali metals.
- Sodium naphthalenide: the reaction of naphthalene with sodium in an aprotic solvent.



# **Stability of Free Radicals**



#### Due to hyperconjugation or Inductive effect

 Radicals next to functional groups, such as carbonyl, nitrile, and ether are even more stable than tertiary alkyl radicals.



# Structure of Free radicals:



#### Planar structure

Neutral divalent carbon species in which the carbon is bonded to two monovalent atoms and is surrounded by sextet of electrons

arhenes

 $CH_2$   $CCI_2$ 

# Structure of Carbenes:



#### Sp hybridised carbon

#### Singlet Carbene

**Triplet Carbene** 

Triplet carbenes are generally stable in the gaseous state, while singlet carbenes occur more often in aqueous media.

#### II. REACTIVITY

 Singlet and triplet carbenes exhibit divergent reactivity. Singlet carbenes generally participate in cheletropic reactions. Singlet carbenes with unfilled p-orbital should be electrophilic. Triplet carbenes can be considered to be diradicals, and participate in stepwise radical additions.

Addition to C=C:

![](_page_24_Figure_3.jpeg)

stepwise radical addition, may be stereoselective

III. GENERATION OF CARBENES

 Disintegration of diazoalkanes and their analogs, via photolytic, thermal, or transition metal (Rh, Cu)-catalyzed routes.

![](_page_25_Figure_2.jpeg)

• Base-induced α-elimination

![](_page_26_Figure_1.jpeg)

Carbenes are intermediates in the Wolff rearrangement.

![](_page_26_Figure_3.jpeg)

![](_page_27_Picture_0.jpeg)

Nitrenes are uncharged, electron deficient molecular species that contain a monovalent nitrogen atom surrounded by a sextet of electrons. Nitrenes, RN, are the nitrogen analogs of carbenes. Nitrenes are too reactive for isolation under ordinary conditions.

![](_page_27_Figure_2.jpeg)

 Singlet state: carbocation-like in nature, trigonal planar geometry, electrophilic character
 Triplet state: diradical-like in nature, linear geometry

- Formation of nitrenes
- from <u>thermolysis</u> or photolysis of <u>azides</u>.
- from isocyanates, with expulsion of CO.

![](_page_28_Figure_3.jpeg)

# Arynes or benzynes

**Arynes** or **benzynes** are highly reactive species derived from an aromatic ring by removal of two substituents.

![](_page_29_Figure_2.jpeg)

![](_page_30_Figure_0.jpeg)

![](_page_31_Figure_0.jpeg)

compound formed in this step is called benzyne

![](_page_32_Figure_0.jpeg)

Angle strain is relieved. The two *sp*-hybridized ring carbons in benzyne become *sp*<sup>2</sup> hybridized in the resulting anion.

![](_page_33_Figure_0.jpeg)

![](_page_34_Picture_0.jpeg)