## 3.11 MECHANISMS OF ORGANIC REACTIONS

A detailed description of the changes in structure and bonding that take place in the course of a reaction, and the sequence of such events is called the *reaction mechanism*. A reaction mechanism should include a representation of plausible electron reorganization, as well as the identification of any intermediate species that may be formed as the reaction progresses. These features are elaborated in the following sections.

### 3.11.1 Arrow Notations in Mechanisms

Since chemical reactions involve the breaking and making of bonds, a knowledge of the movement of bonding (and non-bonding) valence shell electrons is essential to this understanding. It is now common practice to show the movement of electrons with curved arrows, and a sequence of equations depicting the consequences of such electron shifts is termed a **mechanism**. In general, two types of curved arrows are used in drawing mechanisms:

(a) A full head on the arrow indicates the movement or shift of an electron pair.

(b) A partial head (fishhook) on the arrow indicates the shift of a single electron.

These are shown below.

A : B is shown as

$\overset{+}{A} + :\overset{-}{B}$ [Both the bond electrons transferred to B]

A : B is shown as

$\dot{A} + \dot{B}$ [One electron goes to A, the other electron to B]

The use of these symbols in bond-breaking and bond-making reactions is illustrated in Fig. 3.50. If a covalent single bond is broken so that one electron of the shared pair remains with each fragment, as in the example, this bond-breaking is called *homolysis*. If the bond breaks with both electrons of the shared pair remaining with one fragment, as in the second and third examples, it is called *heterolysis*.

#### ***Other Arrow Symbols***

Chemists also use arrow symbols for other purposes, and it is essential to use them correctly. The following examples (see Fig. 3.51) illustrate the proper use of these symbols:

**Reaction arrow** ⟶

$$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O + \text{Energy}$$

**Equilibrium arrow** ⇌

**Resonance arrow** ⟷

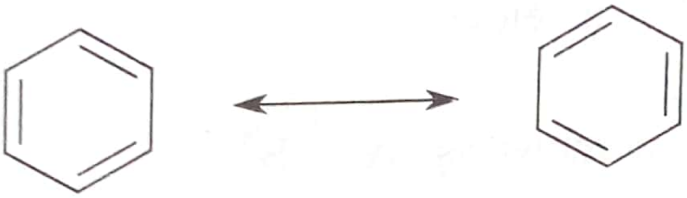


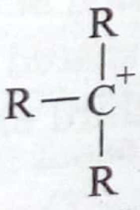
Fig. 3.51

## 3.11.2 Reactive Intermediates in Organic Reactions

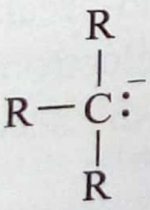
The products of bond breaking, shown above, are not stable in the usual sense, and cannot be isolated for prolonged study. Such species are referred to as *reactive intermediates*, and are believed to be transient intermediates in many reactions. The general structures and names of four such common intermediates are given below.

**Charged intermediates**

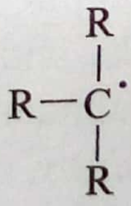
**Uncharged intermediates**



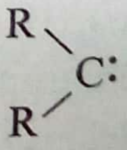
Carbocation



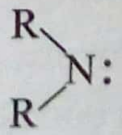
Carbanion



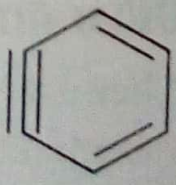
Radical



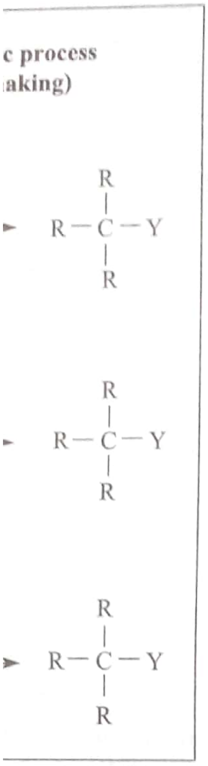
Carbene



Nitrene



**Benzyne**



### 3.11.3 Classification of Reagents

On the basis of the nature of charge carried by ionic reagents, they are classified into two major groups.

(i) Electrophilic reagents or electrophiles, meaning 'electron seeking.

(ii) Nucleophilic reagents or nucleophiles, meaning nucleus (i.e., positive charge) seeking.

#### *Electrophiles*

Reagents which are electron-deficient and have the capability to react with a electron-rich substrate (anion or neutral molecule) to form a new covalent bond by accepting a pair of electrons are known as electrophiles. Electrophiles may be positively charged ions (cations) or electron-deficient neutral molecules. For example, $H^+$, $Cl^+$, $Br^+$, $CH_3^+$, $CH_3CO^+$, $NO_2^+$, $NO^+$, etc., are very known electrophiles, often encountered in organic reactions involving ionic mechanisms. Electrophiles may be considered as acids since they can take up electrons.

Among the neutral but electron-deficient electrophiles, $BF_3$, $BH_3$, $AlCl_3$, $FeCl_3$, etc., are important. They are commonly known as *Lewis acids* and can accept a pair of electrons because of the presence of vacant orbital in B, Al, Fe, etc., as the case may be.

#### *Nucleophiles*

Reagents that are electron rich and can react with electron-deficient substrates (molecules or cations) to produce a new covalent bond through the donation of a pair of electrons are known as nucleophiles. Nucleophiles may be negatively charged anions or electron-rich neutral molecules. For example, common anionic nucleophiles are $OH^-$, $RO^-$, $RS^-$, $CN^-$, $HSO_3^-$, $CH\equiv C^-$, $CH_3O^-$, $I^-$, $Br^-$, $Cl^-$, $F^-$, etc. Nucleophiles are also considered as bases because they can accept $H^+$ from the reaction medium. Among the neutral electron-rich molecules, $H_2O$, ROH, $NH_3$, $RNH_2$, $R_2NH$, $R_3N$ are good nucleophiles. All of them contain a pair of non-bonded electrons, either on O or on N.

### 3.11.4 Nucleophilicity and Basicity of Anions and Electron-rich Neutral Molecules

Since an anion or electron-rich neutral molecule can behave both as a nucleophile and as a base, comparison is often made between the nucleophilic behaviour and basic behaviour of an anion or electron-rich neutral molecule under different reaction conditions.

Nucleophilic character or nucleophilicity is measured by its ability to form a new covalent bond with another reactant through $S_N2$ type substitution (discussed in later part of this chapter). Reactivity order of nucleophilicity of certain anions are as follows:

$$C_6H_5S^- > {}^-C\equiv N > I^- > RO^- > HO^- > Br^- > Cl^- > CH_3COO^- > NO^-$$

Halide ions are often used as good nucleophiles in organic reactions. Among the halide ions, nucleophilicity order is $I^- > Br^- > Cl^- > F^-$.

Causes behind the increased or decreased nucleophilicity of ions demand a detailed discussion on polarizability, nature of substrate, and nature of solvents. In general when in an anion, the atom bearing the negative charge or lone pair of electrons is bigger in size and lower in eletronegativity, the anion serves as a good nucleophile. Thus, when the electron pair of anion is more polarizable, the nucleophilicity is enhanced and vice versa. The nature of solvents also plays an important role in increasing or decreasing the nucleophilicity of anions.

Basicity of anion in organic reactions is measured on the ability of the anion to accept a proton and is measured on the basis of the equilibrium constant, $K_b$ of the reversible reaction as shown below.

$$\bar{B} + \overset{+}{H} \rightleftharpoons BH$$

where, $K_b = \dfrac{[BH]}{[B^-][H^+]}$, $K_b$ = basicity constant of the base $B^-$. $B^-$ would be a strong base if $K_b$ has a very large value, that is, equilibrium shifts to the right. The order of basicity of a few common bases in organic chemistry is given below.

$$(CH_3)_3CO^- > C_2H_5O^- > HO^- > C_6H_5O^- > CH_3COO^-$$

Among the halide ions, basicity order is

$$F^- > Cl^- > Br^- > I^-.$$

It should be remembered that nucleophilicity is a kinetic property, that is, a property which is dependent on the rate of the process, but the basicity is a thermodynamic property—a property which depends on the relative stability of species present in an equilibrium system.

A good nucleophile is not necessarily a good base and vice versa. That is, nucleophilicity and basicity of an anion do not run parallel always.

## 3.11.5 Electrophilic and Nucleophilic Character of Reactive Intermediates

On the basis of the definitions of electrophiles and nucleophiles, it is clear that carbocations are electrophiles or acids and carbanions are nucleophiles or bases. Carbenes have only a valence shell sextet of electrons and are, therefore, electron deficient. In this sense they are electrophiles, but the non-bonding electron pair also gives carbenes nucleophilic character. As a rule, the electrophilic character dominates carbene reactivity.

Carbon radicals have only seven valence electrons, and may be considered electron deficient; however, they do not in general bond to nucleophilic electron pairs, so their chemistry exhibits unique differences from that of conventional electrophiles. Radical intermediates are often called *free radicals*.

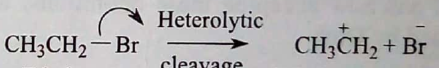
The importance of electrophile/nucleophile terminology comes from the fact that many organic reactions involve at some stage the bonding of a nucleophile to an electrophile, a process that generally leads to a stable intermediate or product. Reactions of this kind are sometimes called *ionic reactions*, since ionic reactants or products are often involved. The shapes ideally assumed by these intermediates become important when considering the stereochemistry of reactions in which they play a role. A simple tetravalent compound like methane, $CH_4$, has a tetrahedral configuration. Carbocations have only three bonds to the charge bearing carbon, so it adopts a planar trigonal configuration. Carbanions are pyramidal in shape (tetrahedral if the electron pair is viewed as a substituent ), but these species invert rapidly at room temperature, passing through a higher energy planar form in which the electron pair occupies a *p* orbital. Radicals are intermediate in configuration, the energy difference between pyramidal and planar forms being very small. Since three points determine a plane, the shape of carbenes must be planar; however, the valence electron distribution varies. Nomenclature, stability, structure and other properties of these reactive intermediates are briefly discussed in the following sections.

## 3.11.6 Structure and Properties of Reactive Intermediates

Heterolytic cleavage of organic compounds generates ion pairs, that is, one anion and one cation. Based on the nature of the charge carried by a carbon on ions, they are classified as carbocations and carbanions.

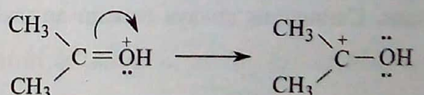
### Carbocations

Cations with an even number of electrons carrying positive charge on the carbon atom are known as carbocations. These may be formed by heterolytic cleavage of a covalent bond between a carbon and any other atom or by electromerization of carbon bearing multiple bonds.



Ethyl bromide

Ethyl cation

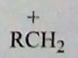


Protonated form of acetone

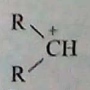
Carbocation

In naming carbocations, the word *cation* is used after the name of alkyl or aryl group. For example, $CH_3^+$ (methyl cation), $CH_3CH_2^+$ (ethyl cation), $(CH_3)_2CH^+$ (isopropyl cation), $(CH_3)_3C^+$ (tertiary butyl cation), $C_6H_5CH_2^+$ (benzyl cation), $:CH^+$ (methylidyne cation).

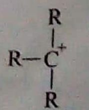
Carbocations are also classified as primary, secondary, and the tertiary according to the number of hydrogen atoms attached to the carbon atom bearing the positive charge.


$\overset{+}{R}CH_2$

Primary carbocation

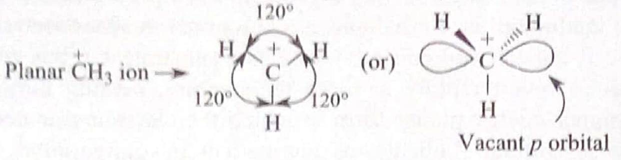


Secondary carbocation

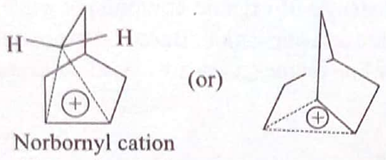


Tertiary carbocation

Stability order of these carbocations is *t*>*s*>*p*. This is due to +I effects of alkyl groups and hyperconjugative resonance. Positively charged carbon atom of any carbocation is $sp^2$ hybridized, therefore the geometric shape of carbocations is always trigonal planar. The structure of $CH_3^+$ may be shown as below.



It should be noted that *carbocations* are again categorized as *carbonium* ions and *carbenium* ions with slight modification in definitions. A carbonium ion is considered to be a hypervalent carbocation, that is, a positively charged carbon having a valency greater than 3, usually pentacoordinated positively charged carbon, that is, $\overset{+}{C}H_5$. It may also be termed as non-classical carbocation or bridged carbocation. But in many literatures of organic chemistry, the term carbonium ion is used as a generic term equivalent to carbocation.



Norbornyl cation
(Carbonium ion)

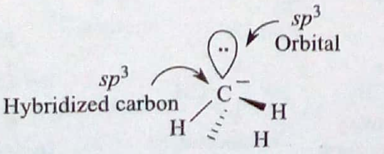
A carbenium ion is an *enium* ion (positively charged) in which the charged atom is carbon. For example, $CH_3^+$ is called simply carbenium ion, but $CH_3CH_2^+$ is called methylcarbenium ion and $C_6H_5CH_2^+$ is phenylcarbenium ion, and so on. IUPAC has now accepted these definitions, which were first proposed by Olah.

### Carbanion

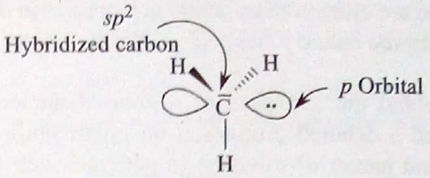
Groups containing negative charge on the carbon atom is known as carbanions. Carbanions always contain an unshared pair of electrons.

$$\underset{\text{Acetaldehyde}}{CH_3-CHO} \xrightarrow{OH^-} \underset{\text{Carbanion}}{:\bar{C}H_2-CHO} + H_2O$$

Carbanions are normally named by adding the word *anion* after the name of alkyl or aryl groups. For example, $:CH_3^-$ (methyl anion), $:C_6H_5^-$ (phenyl anion), $C_6H_5CH_2:^-$ (benzyl anion), $CH_2=CH-CH_2:^-$ (allyl anion). Carbon atom bearing the negative charge in a carbanion may be either $sp^2$ or $sp^3$ hybridized. Therefore, the geometric shape of carbanions may be planar ($sp^2$) or tetrahedral ($sp^3$) or pyramidal.



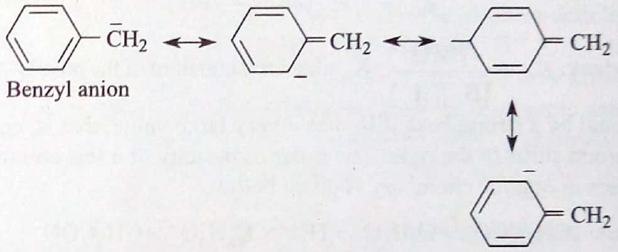
$\bar{C}H_3$ (Tetrahedral or pyramidal form)



$\bar{C}H_3$ (Trigonal planar form)

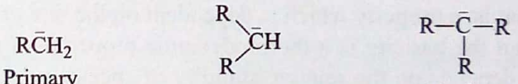
When the negatively charged carbon atom is in conjugation with a multiple bond then the ion becomes very much stabilized by resonance. In such cases, the carbanion always assumes trigonal planar structure.

$$\underset{\text{Allylic carbanion}}{R-CH=CH-\bar{C}H_2} \longleftrightarrow R-\bar{C}H-CH=CH_2$$



Benzyl anion

Like carbocations, carbanions are also classified as primary, secondary, and tertiary.



Primary carbanion — Secondary carbanion — Tertiary carbanion

Stability order of carbanions is just opposite to that of carbocations, that is primary > secondary > tertiary. The stability order of a few known carbanions is as follows.

Vinyl > phenyl > cyclopropyl > ethyl > *n*-propyl > isobutyl > neopentyl > cyclobutyl

## 3.11.7 Free Radicals

Free radicals are reactive intermediates formed by homolytic cleavage of a covalent bond. These are neutral and odd-electron species.

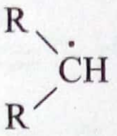
$$CH_3 : Cl \xrightarrow{\text{Homolytic cleavage}} \dot{C}H_3 + \dot{C}l$$

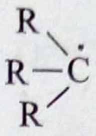
Free radicals are very shortlived and reactive species. Carbon atom of a free radical bearing the unpaired electron may be $sp^3$ or $sp^2$ hybridized, therefore geometric shapes of free radicals may be planar or pyramidal. Free radicals are named as alkyl or aryl group of the corresponding parent compounds.

For example, $CH_3CH_2^{\cdot}$ is ethyl radical, $C_6H_5^{\cdot}$ is phenyl radical.

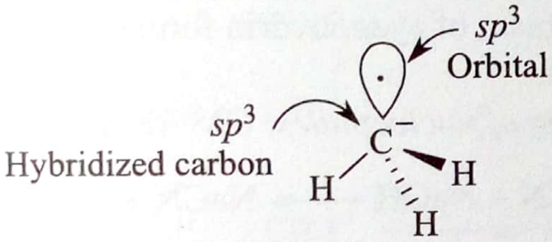
They are classified into primary, secondary, and tertiary free radicals according to the number of hydrogen atoms attached directly to the carbon atom bearing the odd electron.


Primary radical

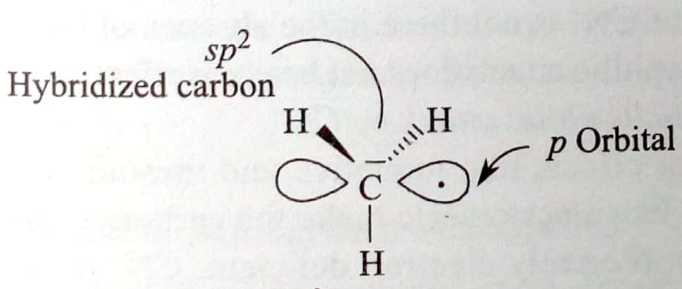

Secondary radical


Tertiary radical

'R' may be H, or an alkyl or aryl group. Like carbanions, free radicals can also have planar as well as tetrahedral structure.



$\dot{C}H_3$ (Tetrahedral form)



$\dot{C}H_3$ (Trigonal planar form)

The stability order of free radicals is $t > s > p$. This is due to hyperconjugative resonance.

Fee radicals, carbocations, and carbanions are important reactive intermediates, which are formed during many organic reactions.

Other important reactive intermediates are carbenes, nitrenes, and benzynes. They are discussed in appropriate chapters of this book.

# Carbenes

Carbenes are highly reactive species, practically all having life-times considerably under 1 sec.

Carbenes are neutral species containing a carbon atom with only six valence electrons.

Carbenes have six electrons: two in each bond and two non-bonding electrons which are often represented as $:CR_2$.

The two non-bonded electrons of a carbene can either be paired or unpaired. If they are paired, the species is a singlet.

↑↓$:CR_2$ singlet carbene

If they are unpaired, the species appears as triplet

↑↑ $:CR_2$ triplet carbene

1) Singlet carbene have R–C–R bond angles of 100–110° and does not have unpaired electrons (ESR spectra inactive).

2) Triplet carbene have R–C–R bond angles of 130–150° and have paired electrons (ESR active)

Type 1: triplet carbene

bond angle (130-150°)

$:CH_2$

$:CHPh$

$:CHR$

$:CPh_2$

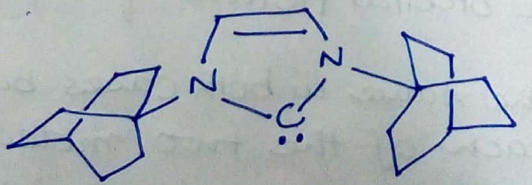
Type 2: singlet carbene

bond angle (100-110°)

$:CCl_2$

$:CHCl$

$:C(OCH_3)_2$

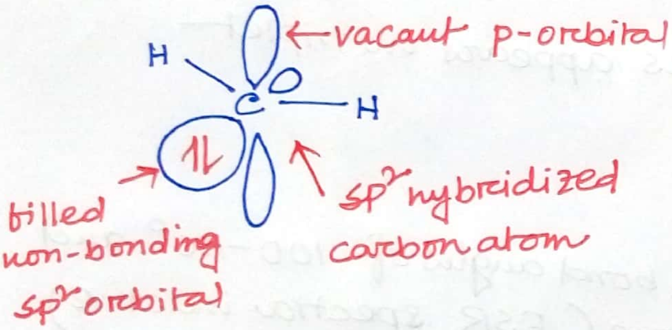


Bond angles of carbenes between 100° and 150°, suggests a trigonal ($sp^2$) hybridization state.

A $sp^2$ hybridized carbene would have three lower energy $sp^2$ orbitals and one high energy p-orbital in which to distribute its six electrons.

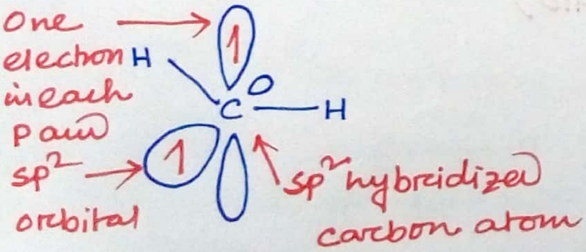
There are two ways of doing this

(i) All of the electrons can be paired, with each pair occupying one of the $sp^2$ orbitals leaving unhybridized p-orbital vacant.



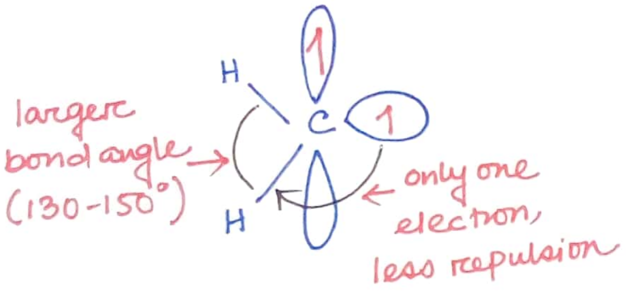
This is the structure of singlet carbene.

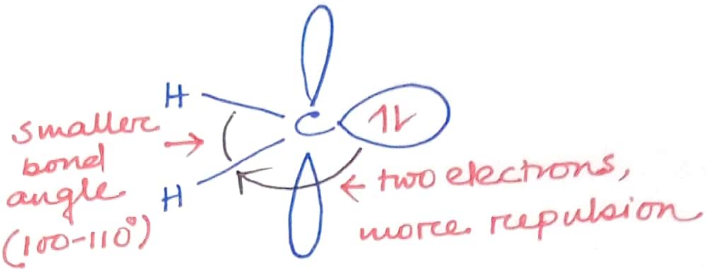
(ii) Two of the electrons remain unpaired, with one electron in each of the p orbitals and one of the $sp^2$ orbitals.



This is the orbital Picture of triplet carbene.

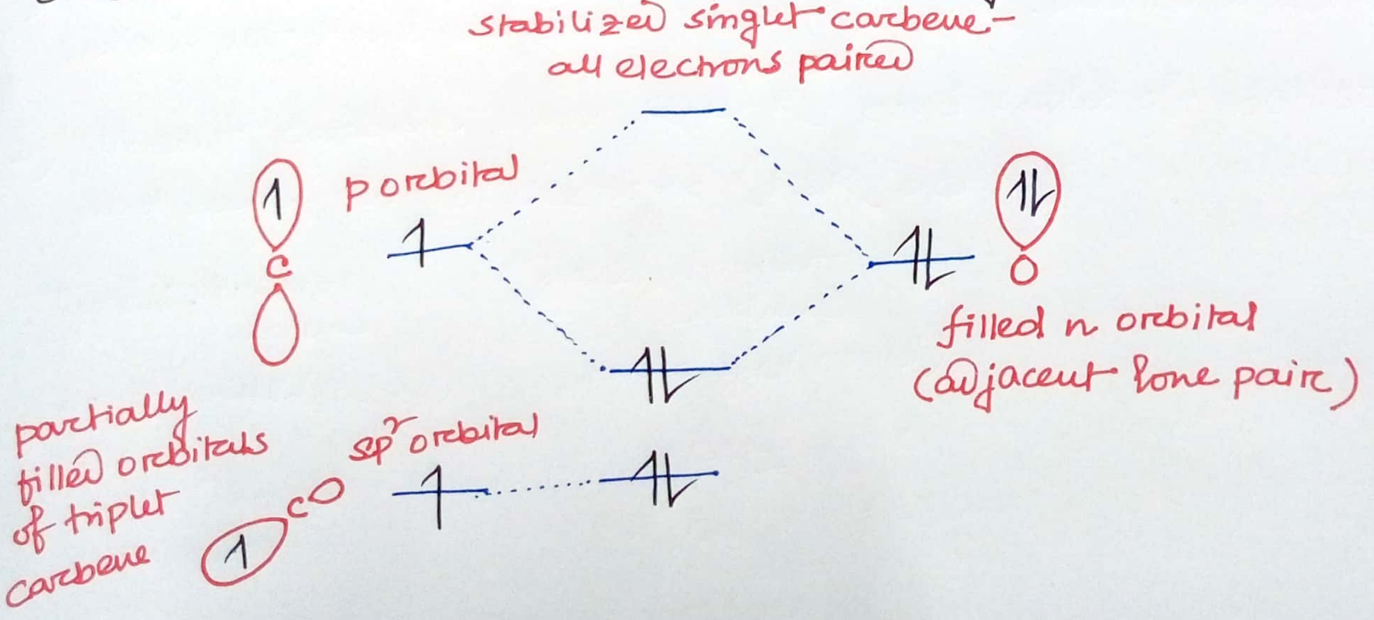
The orbitals are the same in both cases but in triplet carbenes, one electron in each of the two molecular orbitals and in singlet carbenes both electrons go into $sp^2$ orbital





Most types of carbenes are more stable as triplet because the energy to be gained by bringing the electron in the p-orbital down into the sp² orbital is insufficient to overcome the repulsion that exists between two electrons in a single orbitals.

Carbenes that have singlet ground states, all have electron-rich substituents carrying lone pairs adjacent to the carbene centre. These lone pairs can interact with p-orbital of the carbene to produce a new lower-energy orbital which the two electrons occupy.



This molecular orbital formation moves electrons localized on oxygen into orbitals shared between carbon and oxygen.