

BASICS OF REACTION MECHANISM

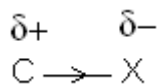
Electronic effect in a covalent bond

(A) Inductive effect (I-effect)

When an electron withdrawing or electron releasing group is attached to the carbon chain, the displacement of σ – electrons along the saturated carbon chain takes place due to the difference in electro negativities. This induces a permanent polarity in the compound. This is called as inductive effect or simply I –effect. This effect weakens with the increasing distance from electronegative atom and becomes negligible after three carbon atoms.

(i)- I effect

When an electron withdrawing group is attached to the carbon chain, it pulls the electron towards itself and renders the carbon chain with partial positive charge. Thus electron withdrawing group is said to exert a -I effect



Some important electron withdrawing groups in order of –I effect in the order of decreasing inductive effect are as follows

$-\text{NR}_3^+$, $-\text{SR}_2^+$, $-\text{NH}_3^+$, $-\text{NO}_2$, $-\text{SO}_2\text{R}$, $-\text{CN}$, $-\text{CO}_2\text{H}$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OAr}$, $-\text{COOR}$, $-\text{OR}$, $-\text{COR}$, $-\text{SH}$, $-\text{C}\equiv\text{CR}$, $-\text{Ar}$, $-\text{CH}=\text{CR}_2$

Amongst sp , sp^2 , sp^3 hybridized carbon, the order of -I effect is $sp > sp^2 > sp^3$

Because of –I effect (electron withdrawing group) electron density decreases hence
-basic nature of compound decreases

Acidic nature of compound increases

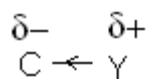
Phenol is more acidic than water because of electron withdrawing nature of benzene ring.

Acidic strength of various haloacetic acid is in the order

$\text{F}-\text{CH}_2\text{COOH} > \text{Cl}-\text{CH}_2\text{COOH} > \text{Br}-\text{CH}_2\text{COOH} > \text{I}-\text{CH}_2\text{COOH}$

ii)+I effect

When an electron releasing group is attached to the chain, it develops negative charge on the chain and said to exert +I effect



Some important electron releasing group in order of their +I effect are as follows

$-\text{O}^- > -\text{COO}^- > -\text{C}(\text{CH}_3)_3 > -\text{CH}(\text{CH}_3)_2 > -\text{CH}_2\text{CH}_3 > -\text{CH}_3 > \text{D} > \text{H}$

Because of +I effect (electron releasing group) electron density on the carbon chain increases, hence

-basic nature of compound is increases

-acidic nature of compound is decreases

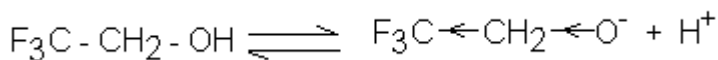
Eg. methanol is more basic than water because of +I effect of C_2H_5 group

Solved problem

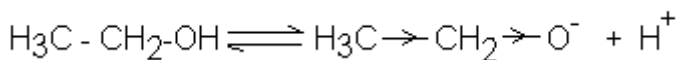
Q) Of the ethanol and trifluoro ethanol which is more acidic?

Solution

Trifluoro ethanol is more acidic because strong $-I$ effect of trifluoromethyl group stabilizes the anion of trifluoroethanol.



While $+I$ effect of ethyl group destabilizes the anion of ethanol



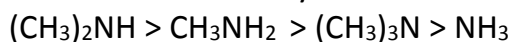
Q) Write the order of basicity of NH_3 , CH_3NH_2 , $(CH_3)_2NH$, $(CH_3)_3N$ in aqueous medium

Solution

$(CH_3)_2NH$ (dimethyl amine) is more basic than CH_3NH_2 (methyl amine), which is more basic than NH_3 because of $+I$ effect of CH_3 group, which increases the availability of lone pairs on the nitrogen atom

However $(CH_3)_3N$ is less basic than dimethyl amine and methyl amine due to steric hindrance of three bulky methyl groups and less solvation effect

Thus order of basicity

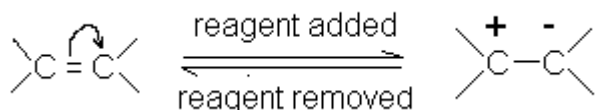


Electromeric effect

It is a temporary effect involving complete transfer of π -electrons of a multiple bond towards one of the bonded atoms in the presence of an attacking reagent

If attacking reagent is removed, charge disappears and compound regains its original form.

Therefore this effect is temporary and reversible

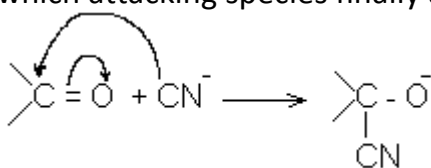


a) $+E$ effect

If π -electrons transfer towards the atom to which attacking species attacks, the effect is known as $+E$ effect



b) If π -electrons transfer towards the atom of the double bond other than the one to which attacking species finally attaches, the effect is known as $-E$ effect.

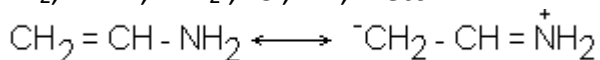


Resonance effect or mesomeric effect (M-effect or R effect)

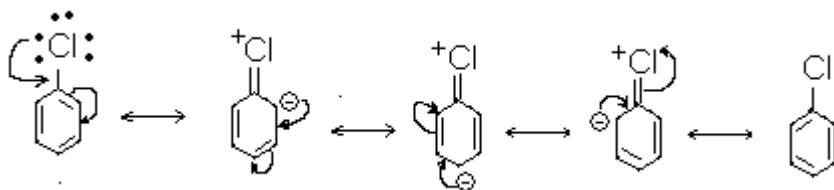
Mesomeric effect takes place in conjugated system i.e. having alternate σ and π –bonds or in system having lone pair in conjugation with π bond. It is defined as permanent polarization effect in which electron pair get displaced from one part of the conjugated system to another part, thus producing polarity in the molecule.

a) +M effect or +R effect

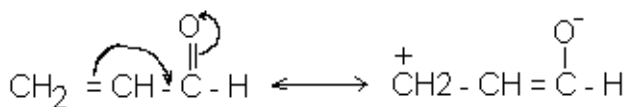
a group is said to have +M effect if flow of electrons is away from it e.g. –OH, –OR, –SH, –NH₂, –NHR, –NR₂, –Cl, –Br, –I etc



This effect extends the degree of delocalization and thus imparts stability to the molecule +M effect of halogen atom explains the low reactivity of vinyl chloride and aryl chloride.

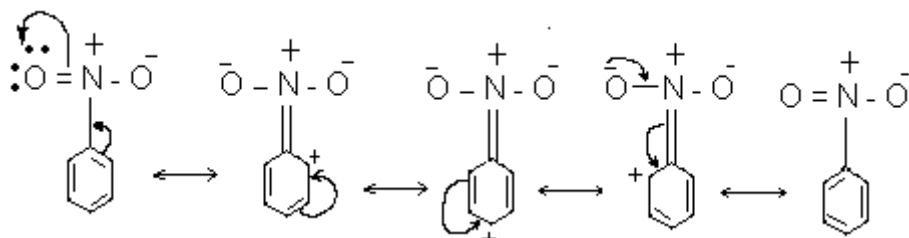


b) –M effect or –R effect



A group is said to have –M effect if electrons are displaced towards that group. Electron withdrawing group exert –M effect

e.g >C=O, –CHO, –COOR, –CN, –NO₂ etc



Conditions for writing resonance structures

The following are essential conditions for writing resonating structures

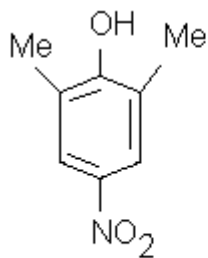
- 1.The contributing structure should have same atomic positions
- 2.The contributing structures should have same number of unpaired electrons
- 3.The contributing structures should have nearly same energy
- 4.The structures should be so written that negative charge is present on an electronegative atom and positive charge is present on an electropositive atom
- 5.In contributing structures, the like charges should not reside on adjacent atoms

Resonance energy = Actual bond energy – energy of the most stable resonating structures

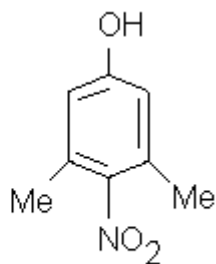
For example, the resonance energy of carbon dioxide is 138 kJ/mol. This means that the actual molecule of CO₂ is about 138kJ/mol more stable than the most stable structure among the contributing structures.

Solved problem

Q) Which phenol is more acidic



(I)



(II)

Solution

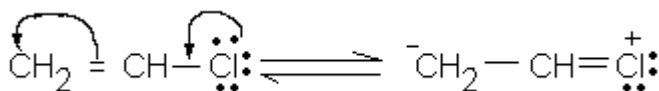
2,6-dimethyl-4-nitrophenol(I) is more stable than 3,5-dimethyl-4-nitrophenol(II)

The phenoxide of (I) is stabilized by -I and -R effect of NO_2 group and destabilized by +I effect of the two Me groups at the ortho positions. The major contribution comes from -R effect of NO_2 group. The phenoxide ion of (II) is stabilized by -I effect of NO_2 and destabilized by two Me groups at meta positions. The NO_2 group in (II) is not coplanar with benzene ring due to the bulky methyl group attached to the adjacent C-atoms. Thus, the -R effect of NO_2 group is ruled out

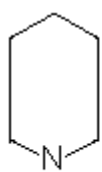
Q) $\text{CH}_2=\text{CH}-\text{Cl}$ does not give $\text{CH}_2=\text{CH}-\text{OH}$ easily on treatment with OH^- explain

Solution

As C-Cl bond acquires double bond character due to resonance, substitution of Cl^- by OH^- is difficult



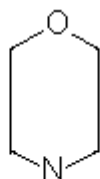
Q) State the order of basicity of the following compounds



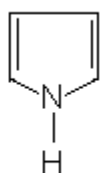
(I)



(II)



(III)



(IV)

In iv, lone pair of electrons are involved in aromaticity so least easily available for donation.

In II, lone pair of electrons is involved in resonance.

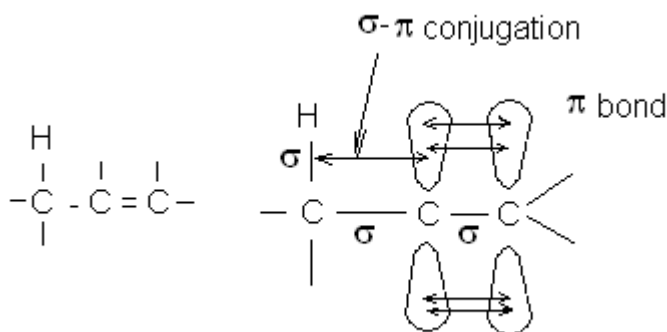
In I and III availability of lone pair is maximum but presence of highly electronegative oxygen in atom (iii) makes it comparatively less readily available for donation. Thus order of basicity is

I > III > II > IV

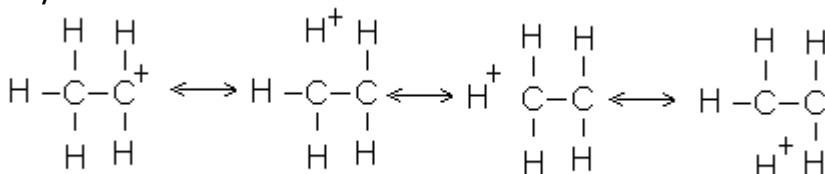
Hyperconjugation effect

This involves the conjugation between σ – electrons of a single carbon-hydrogen bond and the π -electron of the adjacent multiple bond.

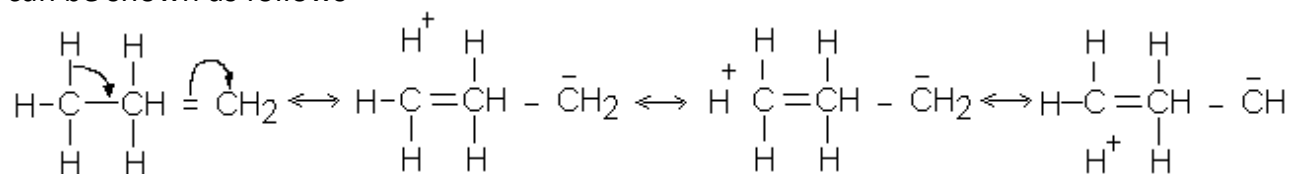
p-orbital of the double bond overlaps with σ orbital of α C-H bond of alkyl group, thus there occurs delocalization of 4 electrons over 4 atom. 1 hydrogen and 3-carbon atoms



It is also called as no bond resonance because in the different canonical form, no bond exists between carbon and H-atom of the alkyl group. For example, resonance structure of ethyl cation can be shown as follows



Hyperconjugation is also possible in alkenes and alkyl arenes. For example, for propene can be shown as follows



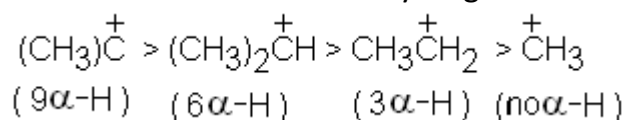
Significance of hyperconjugation

(a) Stability of alkenes

Greater the number of α – H atom in an alkene. Greater will be its stability. i.e more the number of alkyl groups attached to the doubly bonded carbon atom are more stable

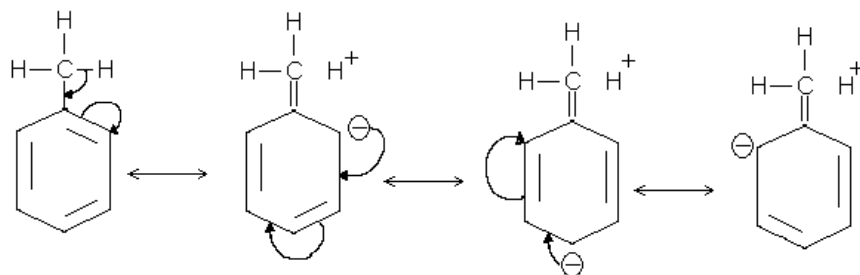
(b) Stability of carbocation and alkyl free radicals

On the basis of number of hydrogen atoms order of stability of carbocations is given by



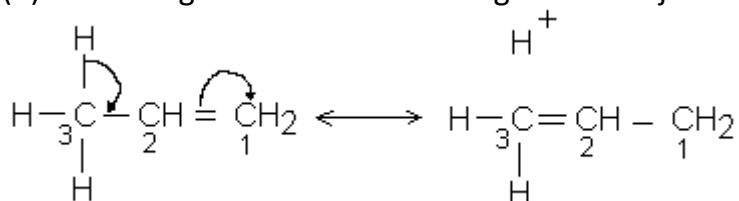
(c) Directive influence of alkyl groups

The o,p- directive influence of an alkyl group can be explained on the basis of hyperconjugation



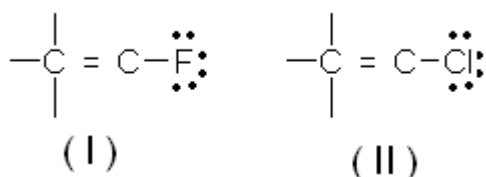
Since electron density at o and p-position with respect to CH₃ group is more and thus electrophilic substitution takes place preferentially at o, p-position with respect to CH₃ or any alkyl group

(d) Shortening of carbon-carbon single bond adjacent to multiple bond



Because of hyperconjugation C₃C₂ single bond acquires some double bond character and C₃-C₂ bond length (1.49Å) becomes slightly shorter than a normal single C-C bond length (1.54Å)

Solved problems



In which case lone pair - π conjugation will be more preferred?

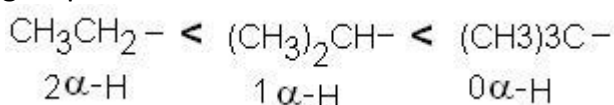
Solution

Lone pair - π conjugation in structure (I) is preferred because the overlapping of 3p orbital of chlorine with 2p orbital of carbon atom does not take place effectively due to the difference in energy states of the orbitals involved

Q) Arrange (CH₃)₃C-, (CH₃)₂CH-, CH₃CH₂- when attached to benzene or an unsaturated group in increasing order of inductive effect is

Solution

When above groups are attached to benzene or an unsaturated group, there occurs hyperconjugation and hyperconjugative effect and thus inductive effect given by alkyl group follows the order

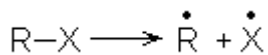


Cleavage of covalent bonds

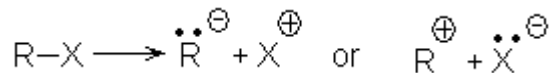
A covalent bond can be cleaved in two different ways

a) Homolytic cleavage

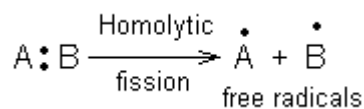
In homolytic cleavage each atom separate with one electron leading to the formation of highly reactive intermediate called free radicals. Such type of cleavage occurs generally in a gas phase or in solution in non-polar solvents and is catalyzed by ultraviolet light or high temperature or by radical initiators like peroxides. Free radicals are paramagnetic in nature and are extremely reactive.

**b) Heterolytic cleavage or fission**

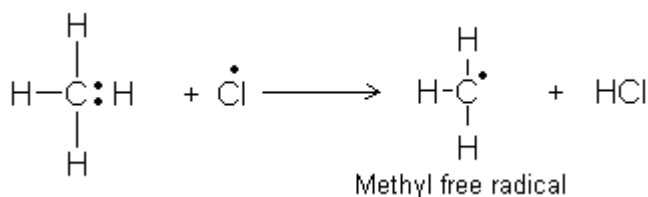
In heterolytic cleavage both the electrons of a covalent bond (shared pair of electrons) are taken away by one of the more electronegative atom. That's why it is also known as unsymmetrical fission. Such cleavage occurs in polar solvents because of the ease of separation of charge and stabilization of the resultant ion-pair through solvation. In such heterolytic fission, the charged species formed are either carbon bearing positive charge called carbocation or carbon bearing negative charge called carbanion

**c) Free radical**

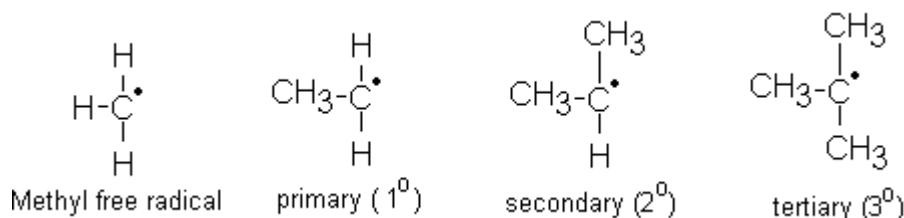
A free radical may be defined as an atom or group of atoms having an unpaired electron. These are produced during the homolytic fission of a covalent bond



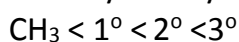
These free radicals are very reactive. This is because of the fact that they have a strong tendency to pair up their unpaired electron with another electron from wherever available. These are short lived and occur only as reaction intermediate during reaction. The alkyl free radical may be obtained when free radical chlorine attack methane.



The free radicals may be classified as primary, secondary or tertiary depending upon whether one, two or three carbon atoms are attached to the carbon atom carrying the odd electron

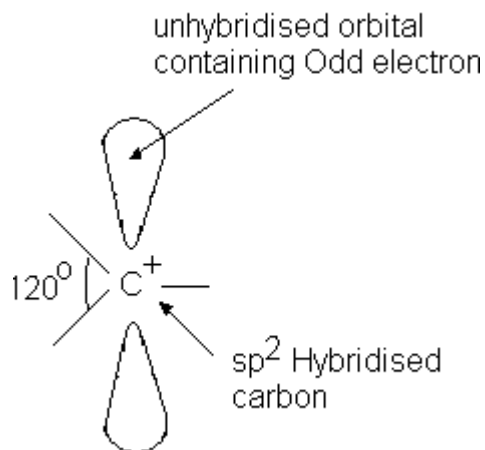


Stability of free radicals: the order of stability of alkyl free radicals is



This order of stability can easily be explained on the basis of hyperconjugation. Larger the number of alkyl groups attached to the carbon atom carrying the odd electron, greater this the delocalization of electrons and hence more stability of free radical.

Structure of alkyl free radical



The carbon atom in alkyl free radicals involves sp^2 hybridisation. Therefore, it has planar structure. The three hybrid orbitals are used in the formation of three σ bonds with three H atoms or alkyl group. The unpaired electron is present in unhybridised p-orbital

Attacking reagents

There are basically two types of reagents used in organic chemistry, the electrophiles and nucleophiles. In organic chemistry, the interaction of electrophile i.e. electron pair acceptors and nucleophiles i.e. electron pair donors are generally observed. Electrophiles in other words are called lewis acids and nucleophiles are called lewis bases

Electrophiles

Electrophiles are electron loving chemical species. (Electro-electron, phile loving). Therefore electrophiles are electron deficient species in search of electrons. These can be either positively charged or neutral. Or have an empty orbital or a heterolytically breakable bond (to a leaving group)

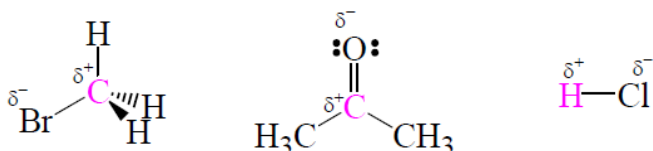
Positive Electrophiles

H^+ , H_3O^+ , NO_2^+ , NO^+ , R^+ , Cl^+ , Br^+ , RCO^+ etc

Neutral Electrophiles

BF_3 , $AlCl_3$, $FeCl_3$, $ZnCl_2$, SO_3 , $SnCl_4$, $R\cdot$ (free radicals), $:CR_2$ (carbenes), $:NR$ (nitrenes), $BeCl_2$

Polar



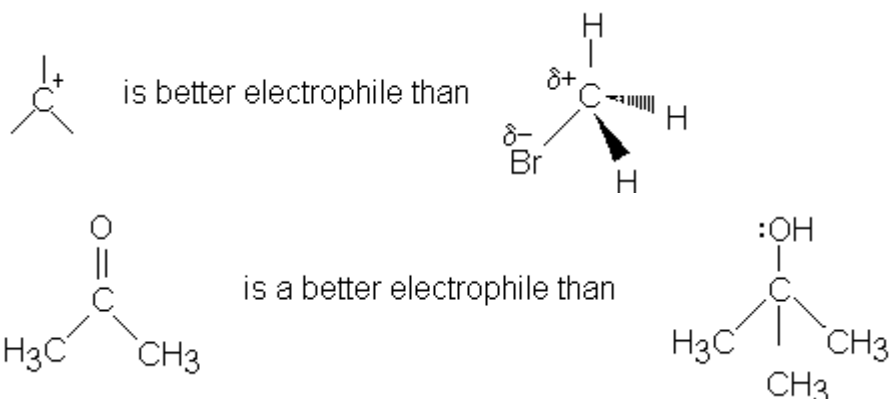
Polarizable

$Br-Br$, $Cl-Cl$, $I-I$

Since electrophiles are electron deficient species they are also termed as Lewis acids

Electrophiles strength

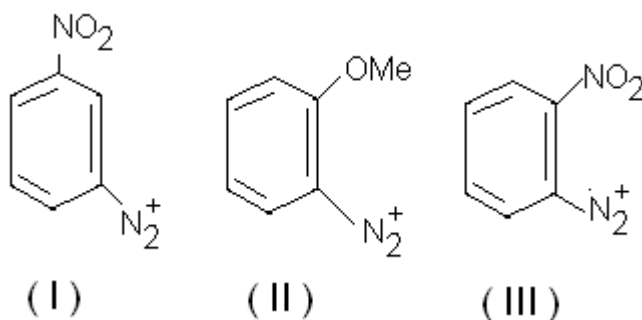
Given the same electrophilic atom, a greater degree of positive charge gives a stronger Electrophile



The strength of electrophiles without empty orbitals (to which a bond must be broken before another can form) is also influenced by the nature of the group to which the bond will be broken (leaving group)

Solved problem

Q) Arrange the following electrophiles in the decreasing order of electrophilicity



Solution

(III) is the strongest electrophile because of $-R$ effect of nitro group is also operative along with its $-I$ effect but (I) has greater $+R$ effect (lesser $-I$ effect) and NO_2 from metaposition will only show $-I$ effect. Thus, the decreasing order of electrophilicity is (III) > (I) > (II)

Nucleophiles

Nucleophiles are electron rich species in the search of nucleus or positive centre or have π bonds Therefore they can be positively charged or neutral

Negative nucleophiles

OH^- , H^- , CN^- , Cl^- , Br^- , I^- , RCOO^- , $\text{RC}\equiv\text{C}^-$, NH_2^- , SR^- , S^{2-}

Neutral nucleophiles

H_2O , ROH , NH_3 , RNH_2 , RSH , ROR , H_2S

Pi bonds

C_2H_4 , C_2H_2 , C_6H_6

Since nucleophiles are electron rich chemical species, these are also regarded as Lewis bases

Relative nucleophilic strength : depends on Charge , Solvent, aprotic solvent

Strength depending on Charge

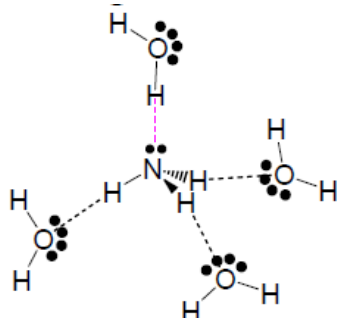
Given two nucleophiles with the same nucleophilic atom, a negative charge makes the atom more reactive In more general terms, the stronger base is the stronger nucleophile (given the same nucleophilic atom)

OH^- is better nucleophile than H_2O

Br^- is better nucleophile than HBr

Strength depending on Solvent

Hydrogen-bonding solvents (protic solvents) reduce nucleophilicity by interacting with the free electrons in the nucleophile



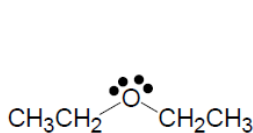
This effect is particularly strong for small atoms with concentrated charges, thus larger atoms are more nucleophilic in protic solvents (~opposite basicity)

$\text{HS}^- > \text{HO}^-$

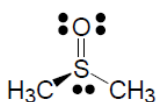
$\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

Strength depending on aprotic solvent

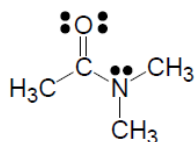
Aprotic solvents



diethyl ether



Dimethylsulfoxide



Dimethylacetamide (DMA)

In solvents that can accept, but not donate hydrogen bonds, nucleophiles are not solvated (but the cations providing countercharges are)

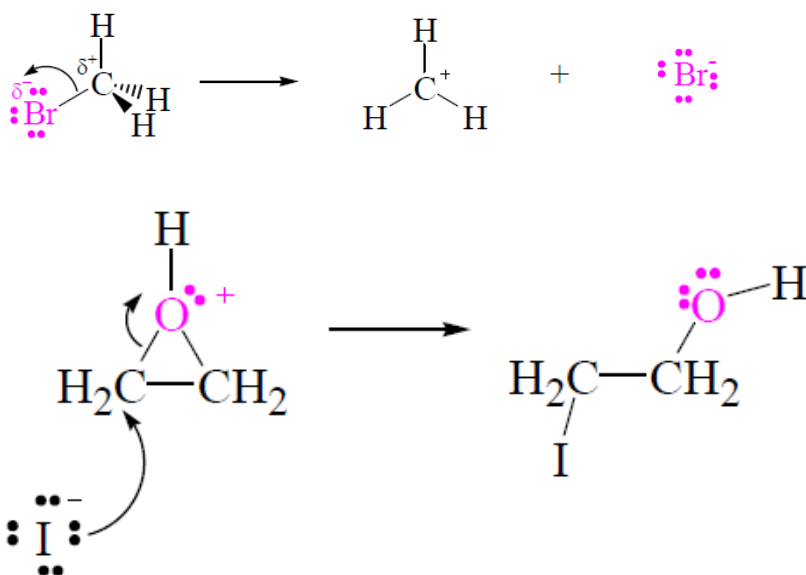
Thus the nucleophilicity and basicity are more closely correlated:

$\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

Basicity is a thermodynamic property and nucleophilicity is a kinetic property thus Strong nucleophiles tend to be strong bases, but these properties are not measured the same way

Leaving Groups

Leaving groups are the fragments that retain the electrons in a heterolytic bond cleavage:



Leaving Group Stability

- Weaker bases are more stable with the extra pair of electrons and therefore make better leaving groups

$\text{H}_2\text{O} > \text{OH}^-$

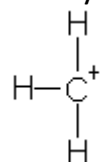
$\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

Various intermediates

Whenever reaction takes place in organic chemistry, the reactants are not directly transformed into the products. The reaction proceeds via some intermediates, which are formed during the course of reaction and not very stable species. Intermediates are formed, by the attack of a reagent or by covalent fission in a reacting molecule. Some important reaction intermediates are discussed below

1. Carbocations (carbonium ions)

A carbocation is molecule in which a carbon atom bears three bonds and a positive charge. Carbocations are generally unstable because they do not have eight electrons to satisfy the octet rule.

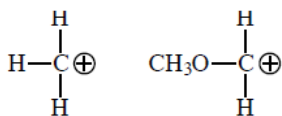


Carbocation Classification

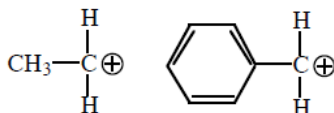
In order to understand carbocations, we need to learn some basic carbocation nomenclature. A primary carbocation is one in which there is one carbon group attached to the carbon bearing the positive charge. A secondary carbocation is one in which there are two carbons attached to the carbon bearing the positive charge. Likewise, a tertiary

carbocation is one in which there are three carbons attached to the carbon bearing the positive charge

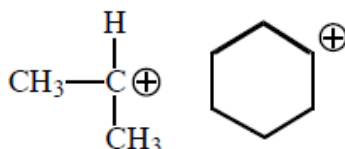
Methyl carbocations
No C-C⁺ bonds



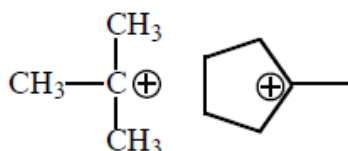
Primary (1°) carbocations
One C-C⁺ bond



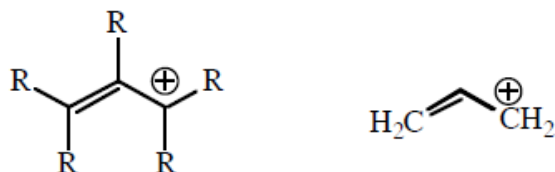
Secondary (2°) carbocations
Two C-C⁺ bonds



Tertiary (3°) carbocations
Three C-C⁺ bonds



If the carbon bearing the positive charge is immediately adjacent to a carbon-carbon double bond, the carbocation is termed an allylic carbocation. The simplest case (all R = H) is called the allyl carbocation.



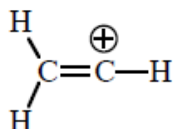
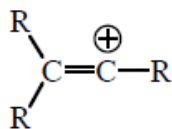
Generic allylic carbocation The allyl carbocation

If the carbon bearing the positive charge is immediately adjacent to a benzene ring, the carbocation is termed a benzylic carbocation. The simplest case is called the benzyl carbocation.



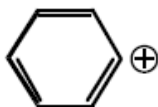
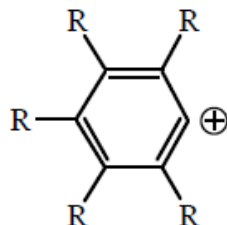
Generic benzylic carbocation The benzyl carbocation

If the carbon bearing the positive charge is part of an alkene, the carbocation is termed a vinylic carbocation. The simplest case is called the vinyl carbocation. Note that the carbon bearing the positive charge has two attachments and thus adopts sp hybridization and linear geometry



Generic vinylic carbocation The vinyl carbocation

If the carbon bearing the positive charge is part of a benzene ring, the carbocation is termed an aryl carbocation. The simplest case is called the phenyl carbocation.



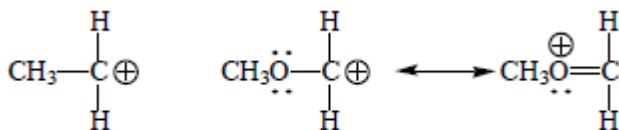
Generic aryl carbocation The phenyl carbocation

Carbocation Stability

The stability of carbocations is dependent on a few factors

Resonance

Resonance is a stabilizing feature to a carbocation because it delocalizes the positive charge and creates additional bonding between adjacent atoms. Decreasing the electron deficiency increases the stability



No resonance

Resonance

The structure on the left does not have any resonance contributors in which electrons are donated to the carbon with the open octet. Compare this with the carbocation that has resonance and a delocalized positive charge. Charge delocalization imparts stability, so the structure with resonance is lower in energy.

In the example shown above, an oxygen atom lone pair is involved in resonance that stabilizes a carbocation.

In general, any adjacent lone pair or π bond can also be involved in resonance delocalization of a carbocation positive charge.

Allylic and benzylic carbocations enjoy resonance stabilization by delocalization of the positive charge to the adjacent π bond(s).

Vinylic and aryl carbocations do not enjoy resonance stabilization because their π electron clouds are perpendicular to the vacant p orbital of the carbocation. (Recall that resonance requires the interacting orbitals to be parallel so they can overlap. Without overlap there can be no resonance.)

Note the influence of inductive effect versus resonance on the energies of these molecules. The oxygen atom that is bonded to the carbocation on the right is more

electronegative than the corresponding hydrogen atom in the left-hand structure. We would think that the inductive effect would pull electron density away from the carbocation, making it higher in energy. In actuality, resonance usually (but not always) outweighs other factors. In this case, carbocation stabilization by resonance electron donation is a more significant factor than carbocation destabilization by inductive electron withdrawal.

Inductive effect

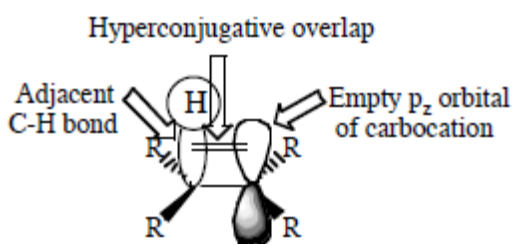
Methyl and primary carbocations without resonance are very unstable, and should never be involved in a reaction mechanism unless no other pathway is possible. More stable carbocations (secondary or tertiary with resonance, or any carbocation with resonance) is sufficiently stable to be formed in a mechanism under reasonable reaction conditions.

The second factor that should be considered when thinking about carbocation stability is the number of carbons attached to the carbon carrying the positive charge.

CH_3^+ (methyl; less stable) < RCH_2^+ (1°) < R_2CH^+ (2°) < R_3C^+ (3° ; more stable)

Hyperconjugation

We look at the number of bonding electrons that are attached to the carbocation because those bonding electrons will help in alleviating the positive charge. Bonding electrons from adjacent σ bonds may overlap with the unoccupied p orbital of the carbocation.



This phenomenon is termed hyperconjugation. Since the overlap supplies electron density to the electron-deficient carbocation carbon, we predict that increasing the number of hyperconjugative interactions increases carbocation stability.

Extending this idea, we predict that increasing the number of bonds adjacent to the carbocation by increasing the number of alkyl groups attached to the carbocation carbon results in an increase in carbocation stability. For example, a tertiary carbocation should be more stable than a secondary carbocation. This prediction is accurate.

Our simple prediction suggests that any adjacent bonding electron pair will participate in carbocation hyperconjugation. However, only C-H and C-C bonds provide a significant level of increased stability.

When considering the importance of hyperconjugation versus resonance as the more important stabilizing feature, resonance usually wins out. For example, a primary carbocation with resonance is more stable than a secondary carbocation without

resonance. A secondary carbocation with resonance is usually more stable than a tertiary carbocation without resonance.

In vinylic carbocations, the positive charge is assigned to a carbon with sp hybridization. How does this influence the carbocation's stability? An sp orbital has more s character than an sp^2 orbital. Electrons in an s orbital are closer to the nucleus and therefore more tightly held than electrons in a p orbital. This can be taken to mean that the electronegativity of carbon increases with increasing s character.

Thus:

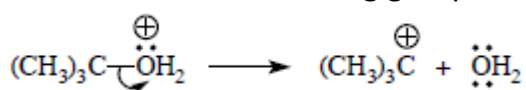
sp carbon (most s character; most electronegative) $>$ sp^2
 $>$ sp^3 (least s character; least electronegative).

Electronegativity is a measure of electron attraction. So the stability of a cation is influenced by the electronegativity of the atom bearing the positive charge. The more electronegative the atom the less stable the cation. A vinylic carbocation carries the positive charge on an sp carbon, which is more electronegative than an sp^2 carbon of an alkyl carbocation. Therefore a primary vinylic carbocation is less stable than a primary alkyl carbocation.

Similar reasoning explains why an aryl carbocation is less stable than a typical secondary alkyl carbocation such as cyclohexyl carbocation. Because of their reduced stability, vinyl and aryl carbocations are not often encountered.

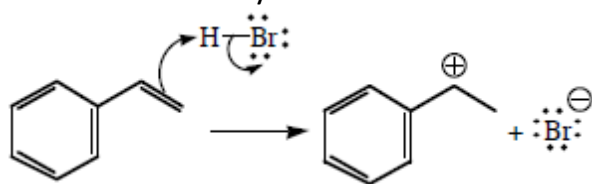
Carbocation Formation

Ionization of a Carbon - Leaving Group Bond. When a bond between a carbon atom and a leaving group ionizes, the leaving group accepts the pair of electrons that used to be shared in the covalent bond. This may leave the carbon atom with an open octet, resulting in a carbocation. The ionization is indicated with a curved arrow starting at the bond and pointing to the leaving group atom that accepts the electron pair. Better leaving groups or formation of a more stable carbocation result in lower activation energy and faster ionization. Carbon - leaving group bonding ionization is illustrated using an oxonium ion



Electrophilic Addition to a π Bond. When an electrophile attacks a π bond, the π electron pair may form a new σ bond to the electron-deficient atom of the electrophile. (Not all additions to π bonds involve electrophiles or carbocations.) The other π bond carbon no longer shares the π electron pair, resulting in a carbocation. This addition is indicated with a curved arrow starting at the π bond and ending at the electron deficient atom of the electrophile. More powerful electrophiles or the formation of more stable carbocations result in lower activation energy and faster addition. Electrophilic addition to a π bond is illustrated by the reaction of HBr (an electrophile) with styrene ($\text{PhCH}=\text{CH}_2$). Note that the more stable carbocation (secondary with resonance) is

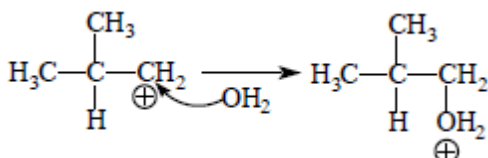
formed. This is a key mechanistic feature of Markovnikov's Rule.



Three Facts of a Carbocation

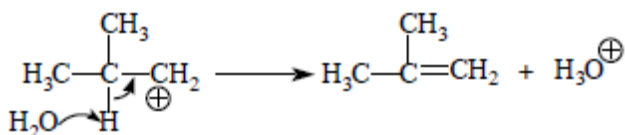
Now we consider how carbocations behave in reaction mechanisms. Generally speaking, carbocations are unstable due to their open octets and positive charges. Thus, their reactions will be strongly influenced by filling the octet of the carbon bearing the positive charge, or at least making this positive charge more stable. There are three common mechanism pathways (or ways) by which carbocations may achieve this stability. These ways are (a) capture a nucleophile, (b) lose a proton to form a π bond, and (c) rearrange. Note in each case that the carbon bearing the open octet gains a pair of electrons thus completing its octet.

Capture a nucleophile. The carbocation is electrophilic because it has a positive charge and (in most cases) a carbon atom with an open octet. The positive charge is neutralized when an electron pair is accepted and a new covalent bond is formed. By definition, a species that donates a pair of electrons to form a new covalent bond is a nucleophile. Because carbocations are very reactive, even weak nucleophiles such as water can be captured with ease.

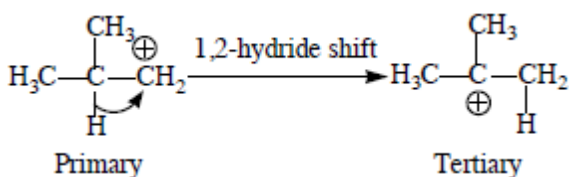


When carbocation deprotonation can lead to more than one product, the more stable product is major.

Rearrangement. The bonding electrons of a carbocation may shift between adjacent atoms to form a more stable carbocation. For example, rearrangement will occur if a secondary carbocation can be formed from a primary carbocation because a secondary carbocation is more stable than the primary carbocation. There can be two types of rearrangements. Shift of an alkyl group is called a 1,2-alkyl shift.



Shift of a hydrogen atom is called a 1,2-hydride shift. Hydride ion = H^-



Of these two examples, hydride shift leads to a tertiary carbocation whereas alkyl shift leads to a secondary carbocation. Because a tertiary carbocation is more stable than a

secondary carbocation, the hydride shift is favored in preference to the alkyl shift.

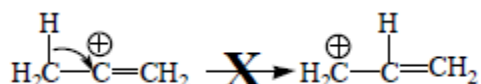
Any C–H or C–C bond adjacent to a carbocation may shift (including C–C bonds that are part of a ring), but only C–C and C–H bonds can migrate during carbocation rearrangement.

The most common carbocation rearrangements involve a carbocation rearranging into a more stable carbocation, such as $2^\circ \rightarrow 3^\circ$

with resonance. (So use these rearrangements with impunity.) Rearrangements that transform a carbocation into another of apparently equal stability are less common, but they do occur. (So before invoking this kind of rearrangement ask yourself if a better rearrangement, or some other mechanism step, is possible.) Rearrangement to a less stable carbocation is very unusual, but also does occur.

(This is the pathway of last very last resort. All other reasonable options must be ruled out first.)

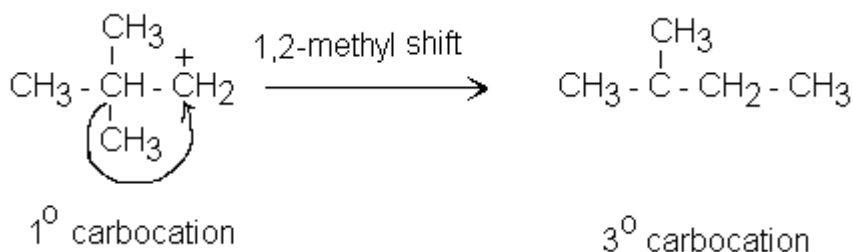
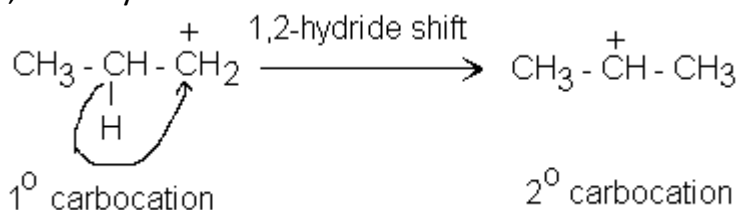
Vinyllic carbocations generally do not rearrange, even if they can become more stable. For example, the rearrangement shown below does not occur, even though a secondary carbocation would rearrange to become a more stable allylic carbocation (primary with resonance).



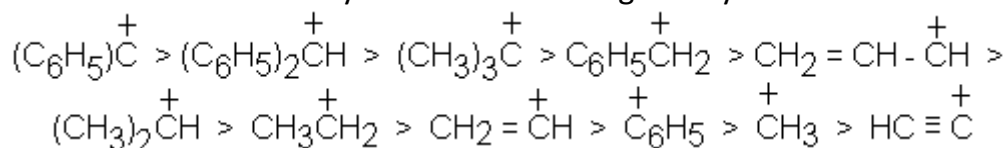
This resistance to rearrangement is probably due to orbital alignment restrictions during the rearrangement transition state.

Rearrangement of carbocations

Carbocations have the property of rearrangement i.e. less stable primary carbocation gets converted to more stable secondary or tertiary carbocation either 1,2 – hydride shift or 1,2-methyl shift

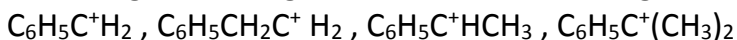


Over all order of stability of carbocations is given by



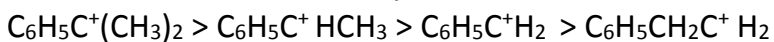
Solved problem

Q) Arrange following carbocations in increasing order of stability



Solution

-C₆H₅ group provide carbocation stabilization through resonance where as alkyl group -CH₃ stabilizes the carbocation by +I effect. Thus order of stability is

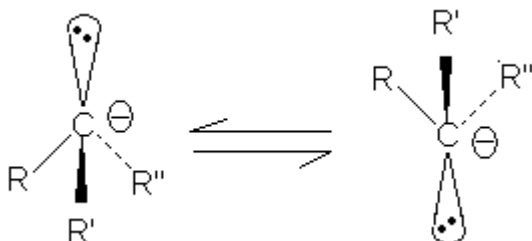


2. Carbanion

These are the chemical species having a trivalent carbon-atom carrying a negative charge and eight electrons in its valance shell

Structure

Carbanion assumes pyramidal configuration, as carbon atom here is sp³ hybridised. The unshared electron pair would be accommodated in an sp³ hybridized orbital. The carbanions readily undergo pyramidal inversion also called umbrella effect



Classification of carbanion

Carbanion are classified as primary (1°), secondary (2°), tertiary (3°) depending upon the nature of carbon atom bearing negative charge

Stability

Inductive effect

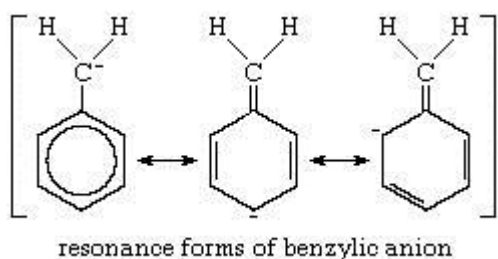
The relative stability of various alkyl carbanion can be explained on the basis of inductive effect. Greater the number of alkyl groups, greater the intensity of negative charge and hence lesser the stability, that why tertiary carbanion are least stable

Hybridization

Since the electronegativity of the carbon increases with increasing s-character of the bonding (that is, in the order sp³, sp², and sp) the carbanion stability follows the same trend.

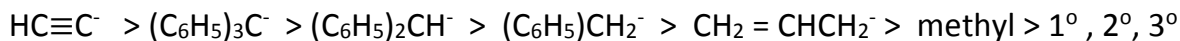
Resonance

Stability of carbanions is also influenced by resonance in those carbanions in which negative charge is in conjugation with the double bond, e.g. stability of benzyl and triphenyl methyl carbanion is explained with the help of resonance



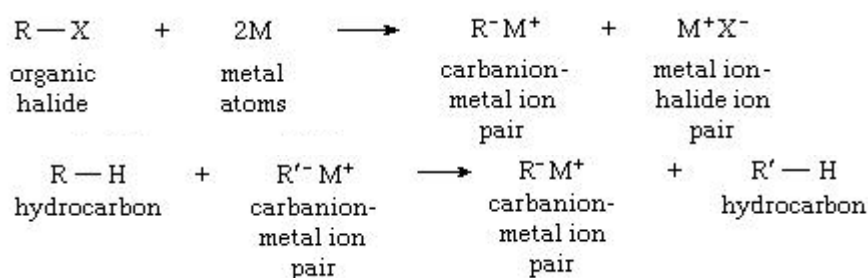
As the number of phenyl groups attached to the carbon atom bearing the negative charge increases, the stability increases due to increase in resonating structure

An electron withdrawing group on the benzene ring increases the stability of aryl carbanion due to inductive effect whereas an electron donating group on the benzene ring decreases the stability. Overall stability order of carbanion is given as



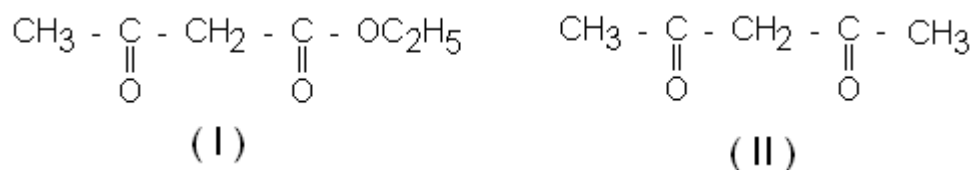
Preparation.

Any preparation of organic-alkali-metal compounds is a source of carbanions. The reaction of organic compounds containing atoms of chlorine, bromine, or iodine with alkali metals is one of the most often used methods. This reaction can be expressed:



Solved Problem

Q) When (I) and (II) are treated with base, separately carbanion results. Which carbanion will be more stable



Solution

Carbanion from (II) will be formed because of more stability due to greater resonance as –COR group is more electron withdrawing than CO₂R

Carbene

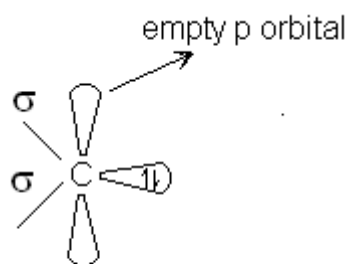
A Carbenes can be defined as neutral, divalent carbon intermediates in which a carbon is covalently bonded to two atoms and have two non-bonded orbitals containing two electrons between them.

Carbenes are short-lived highly reactive chemical species. Since carbenes have only six electrons in the valence shell of central carbon –a atom. These are electron deficient and acts as Lewis acids or electrophiles

Types of carbenes

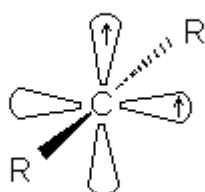
(i) Single carbenes

In the singlet state, a carbon atom is presumed to approximate sp² hybridization. Two of the three sp² hybrid orbitals are utilized in forming two covalent bonds whereas the third hybrid orbital contains the unshared pair of electrons. The remaining p-orbital remains vacant. Thus singlet carbene resembles a carbonium ion very closely.

sp² hybridised carbon

(iii) Triplet carbenes

The central carbon atom is sp hybridised and is in a linear or near-linear species. These two hybrid orbitals are involved in the bond formation with two groups and the remaining two electrons are placed, one each, in the equivalent, mutually perpendicular p_y and p_z orbitals. These electrons have parallel spins and a carbene with this structure is said to be in triplet state.

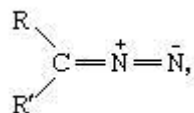


sp hybridised carbon

Triplet carbene is more stable than singlet carbene and expected to be the ground state, because of inter electronic repulsions in singlet carbene. Energy is required to overcome these repulsions which makes the singlet carbene comparatively less stable

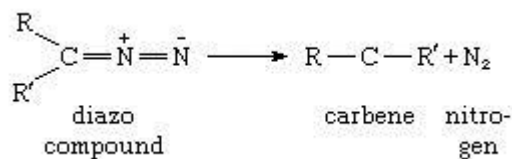
Formation

Because carbenes are molecules with high energy content, they must be made from high-energy precursors, or extra energy must be provided from external sources. Chemical transformations induced by light, so-called photochemical reactions, often are used to prepare carbenes, because the energy of the absorbed light is taken into the high-energy structures. Organic compounds containing a diazo group (two nitrogen atoms joined to one another and to a carbon atom by a double bond) are the most frequently used precursors of carbenes. The molecular structure of diazo compounds is represented by the generalized formula

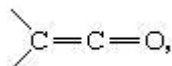


in which R and R' represent two organic groups, which may be the same or different. On either photolysis or pyrolysis (treatment with light or heat, respectively), diazo compounds cleave to yield the corresponding carbene and a free molecule of nitrogen gas. Diazirins, which are ring, or cyclic, compounds, with a structure similar to that of the diazo

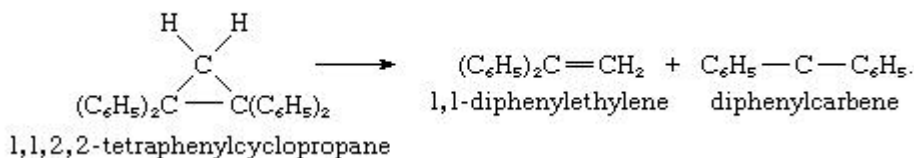
compounds, undergo the same cleavage reaction and are frequently used as precursors of carbenes. The production of a carbene from a diazo compound occurs as shown below:



The photolytic decomposition of certain ketenes, substances the molecules of which contain two carbon atoms and an oxygen atom joined by double bonds,

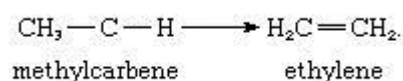


Under certain circumstances, cyclopropanes, the molecules of which contain three-membered carbon rings, can serve as carbene precursors in photochemical reactions. For example, 1,1,2,2-tetraphenylcyclopropane is converted to diphenylcarbene by the reaction



Reactions.

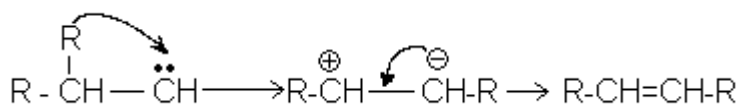
The various chemical reactions that carbenes undergo can be classified as either intramolecular or intermolecular reactions. Intramolecular reactions, or rearrangements, involve only the carbene itself and include no other outside substances; if structurally possible, they lead to stable molecules in which the carbon atom is in its normal, or tetravalent, state. An example of an intramolecular reaction is the rearrangement of methylcarbene to ethylene, in which a hydrogen atom undergoes a shift from one carbon atom to the next:



Intermolecular reactions are those involving two or more separate molecules. Three important classes of intermolecular reaction of carbenes are known: dimerization, addition, and insertion reactions. Dimerization of carbenes—combination of two molecules of the carbene—gives olefins, the molecular formulas of which are exactly twice that of the carbene. An example is the formation of tetramethoxyethylene from dimethoxycarbene

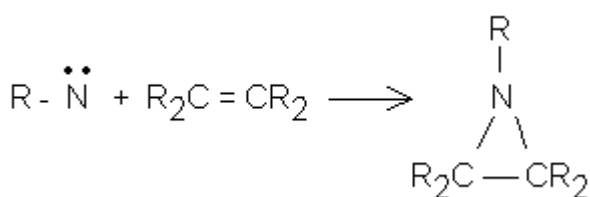
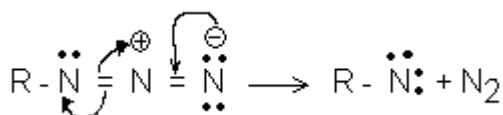


Alkylated and phenylated carbenes can also undergo ready rearrangement, to directly give final product (Alkene)



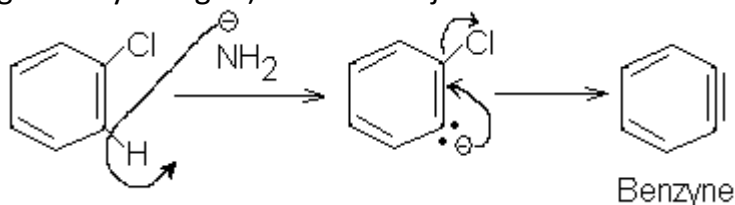
Nitrenes

These are the monovalent nitrogen species in which nitrogen is bonded to only one monovalent atom or group and has two unshared pair of electrons. These nitren contains a nitrogen atom having a six electrons and so it is electron-deficient. These are generally produced by thermolysis of azids



Benzyne

These intermediates are generated by the elimination of α - proton and leaving group (generally halogen) from the adjacent carbons from a benzene ring system. For example



Benzynes are very reactive. Neither benzyne nor any other aryne (substituted benzyne) has yet been isolated under ordinary conditions. The triple bond in benzynes is not identical with the formal triple bond of alkynes because here the two π -bonds are formed by the overlapping of p_z - p_z and sp^2 - sp^2 orbitals whereas in alkynes, they are formed by the overlap of p_z - p_z and p_y - p_y orbitals.