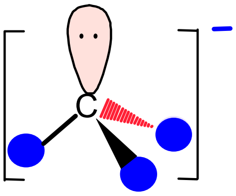


UNIT 12

CARBANIONS

Structure

12.1 INTRODUCTION

The previous two units were dealt with the structural aspects, generation, types and the reactions of carbocation intermediates. In the last unit of this block, we would study about the similar aspects of another intermediate, viz. the carbanions. Carbanions are very significant in organic synthesis because the formation of a new carbon-carbon bond in a reaction requires a nucleophilic carbon for which a carbanion qualifies in a perfect manner. The first section will start with the ways of generation of these intermediates followed by the structure and the factors responsible for their stability. Besides studying the general reactions depicted by these intermediates, you would recall and study some of the rearrangement reactions of carbanions as was done with carbocations in the previous unit. These intermediates have a specific feature of existing as ambident ions. In the last section you would study the general reactions of the ambident ions.

The next and the last block of this course is concerned with four more types of intermediates.

Expected Learning Outcomes

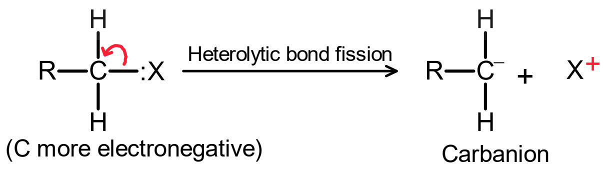
After studying this unit, you should be able to:

- describe and recapitulate some of the general methods of generating carbanions;
- draw and explain the structure of carbanions;
- explain the factors responsible for the stability and reactivity of carbanions;
- compare the relative stabilities of carbanions;
- explain the rearrangement reactions involving carbanions; and
- define ambident ions and describe their structure;
- explain the reactions exhibited by ambident ions.

12.2 GENERATION, STRUCTURE AND STABILITY OF CARBANIONS

It is very well known to you that carbanions are the reactive intermediates in which carbon carries a negative charge (*cf.* carbocations). These are very different from carbocations in many respects except that these are also formed as a result of a heterolytic bond cleavage. We have discussed in Unit 10 that in case of heterolytic bond cleavage, the pair of electrons is retained by more electronegative atom sharing the bond. You have read in case of heterolytic bond cleavage of alkyl halide, a carbocation is formed as carbon is less electronegative than the halogen atom.

In the following general reaction, you can see the electron pair shared between C and X goes to the carbon atom making it electron rich and with a negative charge. The simplest carbanion is obtained from methane and called the methanide ion as given in the following reaction.



$$\underset{\text{Methane}}{CH_4} \rightleftharpoons \underset{\text{Methide ion}}{CH_3^-} + \underset{\text{Proton}}{H^+}$$

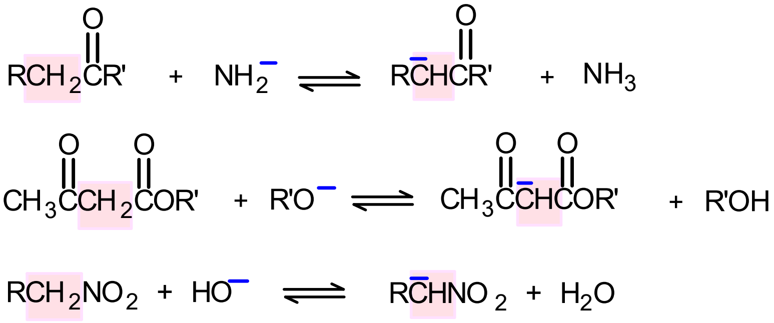
The formation of a carbanion is common in organometallic compounds in which the carbon is covalently bonded to an active metal and the electron pair shared between the two is placed more towards the carbon atom. In the following subsection let us first recall and understand some of the ways of generating carbanions.

12.2.1 Generation of Carbanions

The general reaction of carbanion generation is given in the paragraph above. Following are some of the ways of generating a carbanion.

- **Abstraction of Hydrogen by a Base**

An organic compound containing a C—H bond on treatment with a base like, $NaNH_2$ in liq. NH_3, generates a carbanion. The carbonyl compounds have an acidic hydrogen available that is easy to be abstracted by bases like, OH^-, NH_2^-, RO^- and lead to the formation of a carbanion. Some of the reactions are given below.



$$RCH_2\overset{O}{\overset{\|}{C}}R' + NH_2^- \rightleftharpoons R\bar{C}H\overset{O}{\overset{\|}{C}}R' + NH_3$$

$$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OR' + R'O^- \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}\bar{C}H\overset{O}{\overset{\|}{C}}OR' + R'OH$$

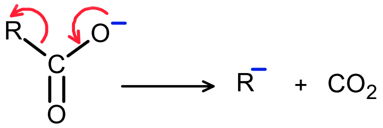
$$RCH_2NO_2 + HO^- \rightleftharpoons R\bar{C}HNO_2 + H_2O$$

Theoretically and following Bronsted concept of acids and bases, any organic compound that contains a C–H bond, can function as an acid in the classical sense by donating a proton to a suitable base, the resultant conjugate base being a carbanion.

It is not possible to abstract a proton from alkanes as they are not acidic in nature. However, it is very easy to abstract a proton from a highly substituted alkane like, triphenyl methane due to the presence of three phenyl groups that help in stabilising the negative ion formed by resonance. Therefore, it is much stronger acid than methane and its pK_a value is 33. The carbanion from triphenylmethane can be obtained from it by the action of sodamide in liquid ammonia. The role of basicity of carbanions will be discussed in detail when we deal with the stability of carbanions in subsection 12.2.3.

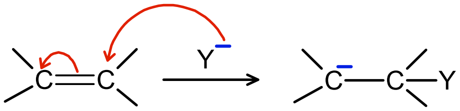
- **Decarboxylation**

Decarboxylation of the carboxylate ion leads to the formation of a carbanion.



- **Addition of nucleophile to an Unsaturated Compound**

A nucleophile adds to one of the carbons of an alkene to generate a carbanion as shown in the following reaction.



- **Reaction of a Metal with an Alkyl halide**

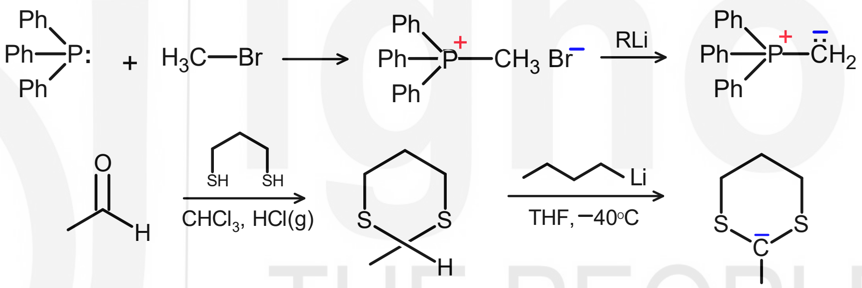
Metals which are less electronegative than carbon react with alkyl halides under appropriate conditions to form a carbon-metal bond. You know that metals are more electropositive as compared to carbon. Due to this the carbon gets a negative charge and metal a positive charge. You must notice here that the carbon and the metal get partial charges in the bond formed. The reversing of the charge on carbon due to the bond formation with a metal is called **umpolung**.

The metals that generally react with alkyl halides are magnesium, lithium, potassium, sodium, zinc, mercury, lead, thallium, etc. You are familiar with the popular Grignard reagent formed as a result of reaction of magnesium metal with alkyl halides in presence of ether as shown in the reaction given below.

$$R—X \xrightarrow[\text{ether}]{\text{Mg}} R.MgX \equiv \overset{\delta-}{R}—\overset{\delta+}{MgX}$$

- **Reactions of Ylides and Dithianes**

Ylides and dithianes react with alkyl metals to form carbanions with partial negative charge as given in the reactions below.

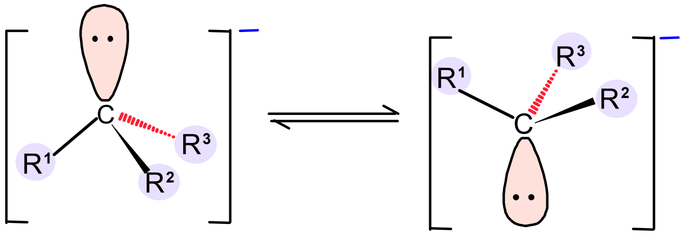


In the following subsection you will recall and learn more about the structure of carbanions.

12.2.2 Structure of Carbanions

The carbanion has an octet of electrons in the outer shell and the negatively charged carbon is trivalent. The experiments have indicated that a simple carbanion of the type R_3C^- may have a **pyramidal** (sp^3) or a planar (sp^2) geometry. The pyramidal geometry is preferred on energy grounds, as the unshared electron pair is accommodated in a sp^3 hybrid orbital rather than in the higher energy, unhybridised *p* orbital in case of a planar geometry. The electron pair remains at the apex of the tetrahedron. There is rapid inversion of configuration between the two pyramidal forms, Fig.12.1.

The tertiary amines (R_3N) also have pyramidal geometry as they are isoelectronic with simple carbanions and show inversion of configuration also.



sp^3 at Transition state of inversion

Fig.12.1: Interconversion of pyramidal forms of carbanions.

The sp^3 nature of the central carbon and its tetrahedral structure comes from the evidence in the ease of reactions which involve the formation of carbanions at bridgeheads. It has been observed that such reactions do not follow the formation of carbocations. 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 it is about 120 kcal/mol.

Carbanions having substituents which allow delocalisation of the electron pair or stabilise the negative charge have planar (sp^2) geometry. For example, in case of Ph_3C^- and $^-CH_2–C{\equiv}N$, the electron pair in *p* orbital allows maximum orbital overlap with those of the substituent. Before studying about the stability of carbanions in the next subsection, you might like to answer the following SAQs.

SAQ 1

Which of the following statements is not true for a carbanion?

a) Carbanions resemble carbocations in that these are also generated by heterolytic fission of a bond.

b) The simplest carbanion formed from methane is called the methanide ion.

c) In a carbon metal bond, the metal gets a negative charge.

d) Generation of carbanion is possible by the abstraction of a proton from a molecule which is acidic enough.

SAQ 2

Fill in the blank spaces in the following with appropriate words.

Carbanion behaves like a charged …………..The carbanionic carbon has ……..electrons in its outermost orbit. There are …….bond pairs and ……lone pair in an alkyl carbanion. A carbanion is …….hybridised and has a ………..geometry.

12.2.3 Stability of Carbanions

You have read in the previous subsection that the carbanion can accept a proton to give its conjugate acid. The ease with which the conjugate acid is formed will decide the stability of the carbanion. We can say that stability of a carbanion depends upon the strength of the conjugate acid. The weaker the acid, the more is its basic strength and less will be the stability of the carbanion.

On the basis of the above given fact, stability of carbanion depends on the following factors.

- ***s*-Character of the Carbanion Carbon**

  You know that carbanion possesses an unshared pair of electrons and is therefore acts as a base. As a result, it can accept a proton to give its conjugate acid. In fact, the stability of a carbanion depends on the strength of this conjugate acid. The weaker is the acid higher will be its pK_a value and higher will be the strength of its conjugate base. It means that the stability of the carbanion as an acid will also be low. The pK_a values of some carbon acids along with their conjugate bases are given in Table 12.1.

Table 12.1: pK_a values for some carbon acids

Carbon acid	**Base**	**pK_a**	**Carbon acid**	**Base**	**pK_a**
CH_4	$\overline{C}H_3$	44	$CH_2(CO_2Et)_2$	$^-CH(CO_2Et)_2$	13.3
$CH_2{=}CH_2$	$CH_2 = \overline{C}H$	37	$(CF_3)_3CH$	$^-C(CF_3)_3$	11
CF_3H	$\overline{C}F_3$	28	$C_6H_5COCH_3$	$C_6H_5CO\overline{C}H_2$	19
$(C_6H_5)_3CH$	$(C_6H_5)_3C^-$	33	CH_3COCH_3	$CH_3CO\overline{C}H_2$	20
$HC{\equiv}CH$	$HC \equiv \overline{C}$	25	$(MeCO)_3CH$	$(CH_3CO)_2\overline{C}H$	6
CH_3CN	$\overline{C}H_2CN$	25	$CH_2(NO_2)_2$	$\overline{C}H(NO_2)_2$	4

The stability of carbanions as carbon acids or the conjugate bases can be explained alternately by the hybridisation of the carbon atom forming the anion. It has been observed that stability follows an order; $sp^3 < sp^2 < sp$. You know that the *s* character in this order is 25%, 33% and 50% respectively. Why is it so and what do you infer by this?

You would recall that the *s* orbitals are closer to the nucleus than the corresponding *p* orbitals, and they are at a lower energy level This difference is carried through into the hybrid orbitals too. The electron pair in a *sp* orbital is thus held closer to the carbon atom than an electron pair in a *sp*^{2} or *sp*^{3} orbital.

Carbanions prefer less alkyl substitution.

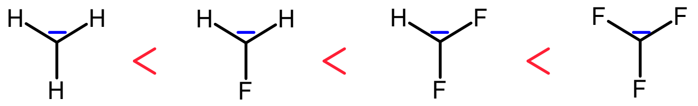
Remember that the stability order for carbocations is the exact reverse of the stability order for carbanions.

The stability of anion depends upon the *s* character of carbanion i.e., more the *s* character, higher will be the stability of anion. The acidity of the hydrogen atom attached to alkane, alkene and alkyne follows the order as the *s* character increases from alkane to alkyne. Thus, the stability order in acetylide, ethenide and ethide carbanion can be given as:

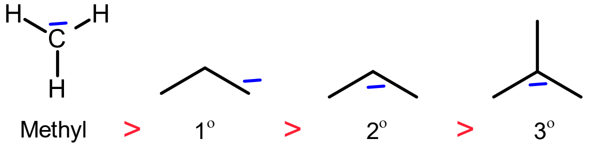
$$\underset{sp^3}{CH_3\overline{C}H_2} < \underset{sp^2}{CH_2{=}\overline{C}H} < \underset{sp}{CH{\equiv}\overline{C}}$$

- **Inductive Effect**

The carbanions being electron rich are very reactive intermediates and readily attacked by electrophiles or the electron-deficient reagents. The stability of the carbanion is increased by the presence of electronegative atoms (F, Cl, Br) or the electron-withdrawing groups like, the C≡N, >C=O, etc. adjacent to the negatively charged carbon which show a -I or a -M effect.



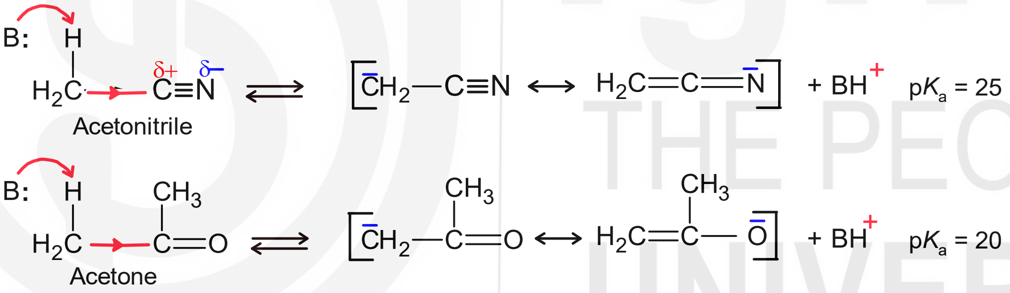
The stability is decreased by electron-donating groups i.e., the ones that show +I or +M effect like alkyl groups. More the number of alkyl groups attached to the carbon bearing the negative charge, lesser will be the stability. Therefore, the order of stability order of alkyl carbanion is: methyl > 1° > 2° > 3° as shown below.



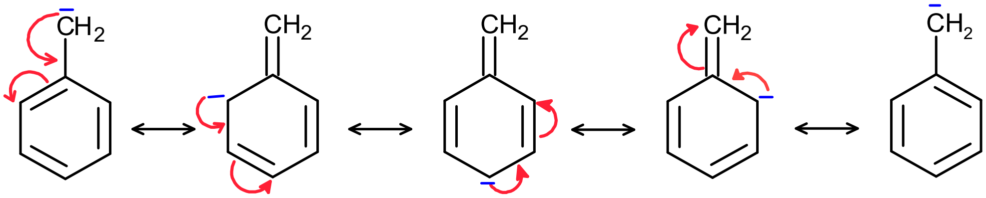
Let us compare the stability of carbanions generated from trifluoromethane, HCF_3 ($pK_a = 28$) and trifluoromethylmethane, $HC(CF_3)_3$ ($pK_a = 11$) viz., $^{-}CF_3$ and $^{-}C(CF_3)$, carbanions. The reason of difference in acidic character is due to the powerful electron-withdrawing inductive effect of the fluorine atoms which make the H atoms more acidic. The fluorine atoms are responsible for the stability of the carbanions.

- **Resonance**

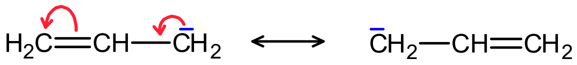
The stability of the carbanion depends on the conjugation of the negative charge of carbanions with a polarised multiple bond like, C≡N, >C=O, etc. The resonance structures are given below.



If we compare the stability of benzyl and allyl carbanions we will observe that the negative charge on the carbon atom is delocalized through resonance in both benzyl and allyl anions. However, the benzyl anion has more number of contributing structures. Therefore, benzyl anion is more stable than the allyl anion.



Canonical forms of benzyl carbanion



Canonical forms of allyl carbanion

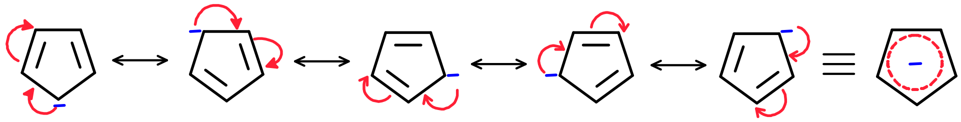
The effect of various groups on the stability of carbanions shows the following order:

NO_2 > RCO > COOR > SO_2 > CN ≈ $CONH_2$ > Halogens > H > R

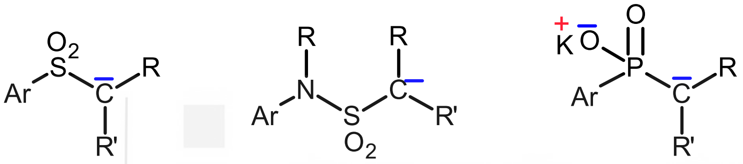
You would recall that cyclopentadiene anion has a 6π electron system which is a 4n+2π Hückel system where n=1 electrons in the anion which are accommodated in three stabilised π molecular orbitals.

- **Aromatisation**

Aromatisation may also lead to the stability of the carbanion. For example, cyclopentadiene has a pK_a of 16 while a simple alkene has pK_a of about 37. On treatment with a base, it gives cyclopentadiene anion. You are well aware that this anion is aromatic in nature. The cyclopentadiene anion is stabilised by aromatisation and shows quasi-aromatic stabilization.



However, some carbanions are stabilised by adjacent sulfur or phosphorus, for example, the structures given below. These moieties are inherently chiral.



In the following section we will discuss some of the reactions that are shown by carbanions. You should proceed further after answering the following SAQ.

SAQ 3

You have read above that the difference of energy barrier between methyl carbanion and trifluoromethyl is 2 to 120 kJmol^{-1}. What is the reason of this large difference?

12.3 REACTIONS OF CARBANIONS

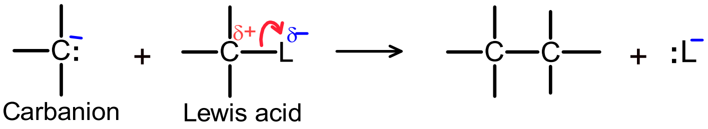
Carbanions exhibit strong basic characteristic behaviour which is depicted in a number of reactions like, displacement, elimination, condensation, addition, rearrangement, polymerisation, etc. We will recall some of the simple reactions in the following subsection and discuss the rearrangement reactions in detail.

12.3.1 General Reactions of Carbanions

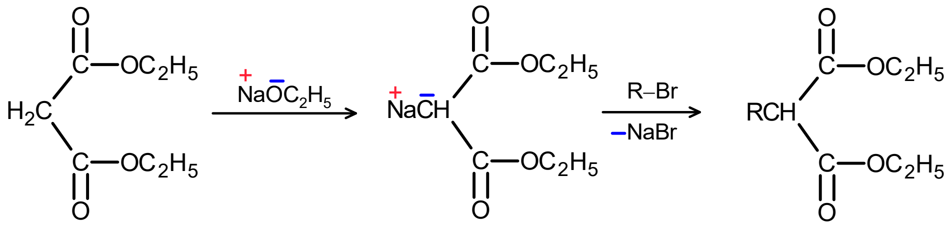
The general reactions are recalled and given in brief here to understand the behavior of these intermediates.

Displacement Reactions

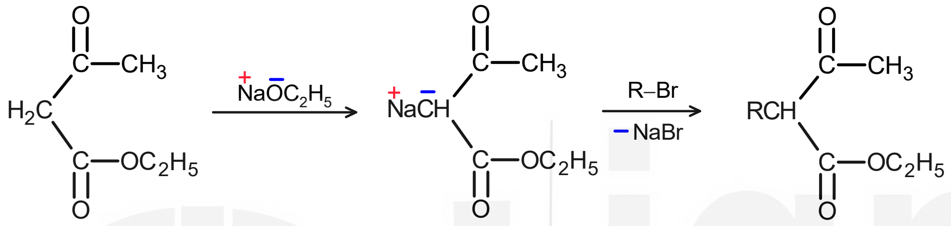
As mentioned above being basic in nature, carbanions act as nucleophiles in a reaction and can combine with positive species in a displacement reaction. The general reaction is shown below.



An example of the displacement reaction is the formation of monoalkyl derivative of diethyl malonate or ethylacetoacetate by the intermediate formation of a carbanion. These reactions have significant synthetic applications. The reactions that take place in the formation of carbanion and further application are given below for diethyl malonate and ethylacetoacetate.



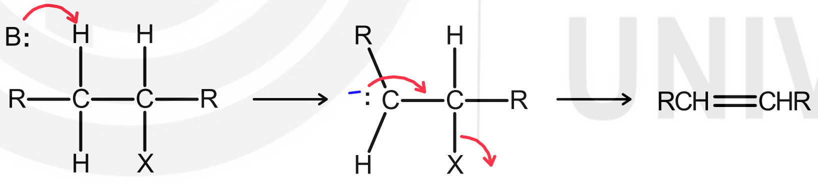
Diethylmalonate



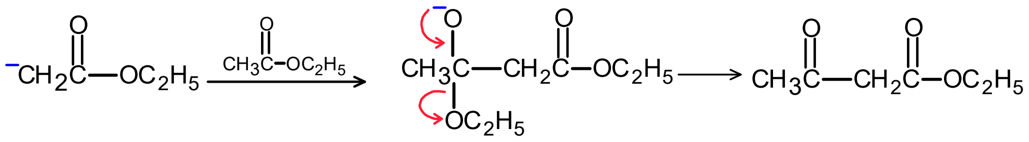
Ethylacetoacetate

Elimination Reactions

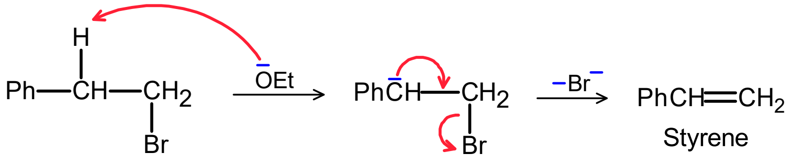
You would recall that a conjugate base elimination reaction, represented as E1cb, is a type of mechanism involved in an elimination reaction. It takes place by the formation of a conjugate base. The carbanion intermediate is also the conjugate base formed by breaking of a C-H bond in an elimination reaction. The negative charge on the carbon assists in the loss of leaving group, leading to the formation of alkene.



A general elimination reaction and the elimination reaction of β-phenylethyl bromide involving the formation of carbanion intermediate are given below. As can be observed in the reaction, β-phenyl ethyl bromide on treatment with a base gives styrene via the intermediate formation of carbanion followed by elimination of Br^-.



Claisen condensation

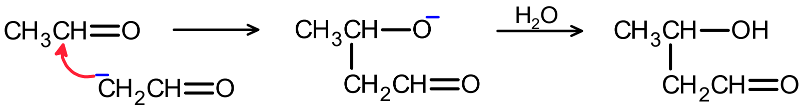


β-Phenylethylbromide Carbanion Styrene

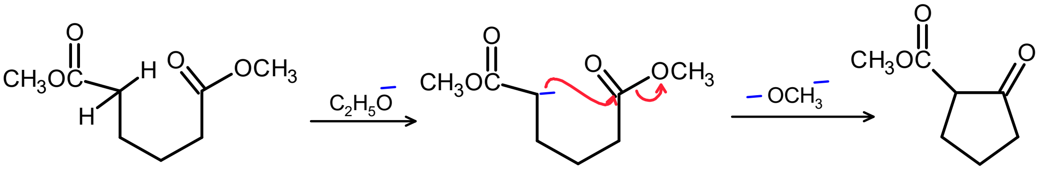
Condensation Reactions

You would recall the aldol, Claisen and Dieckmann condensation reactions that follow the path involving carbanion intermediates. The sample reactions of each type are given below. You should refer back to your B.Sc. notes for this.

Aldol condensation



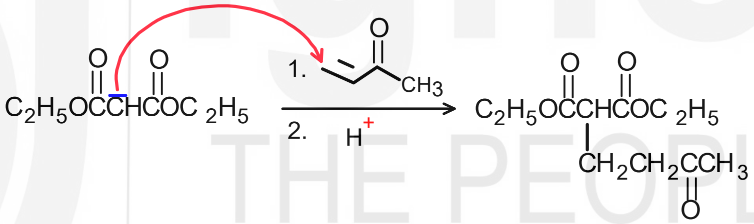
Aldol Condensation



Dieckmann Condensation

Addition Reactions

The carbanions are electron rich therefore, these can add to the double bond of *α, β*-unsaturated carbonyl compounds and form an addition product. This is called the **Michael reaction** or **Michael addition**.



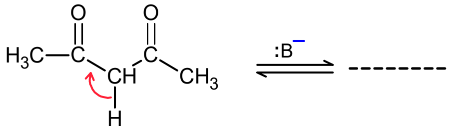
Let us understand some of the rearrangement reactions of carbanions in the following subsection. Before proceeding, you may answer the following SAQ.

SAQ 4

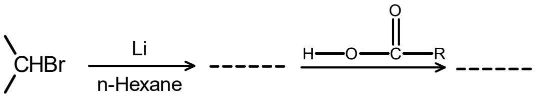
Complete the following reactions indicating the charges.

a) $R{-}X \xrightarrow[\text{ether}]{Mg}$ --------

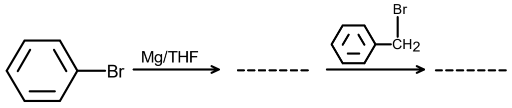
b)



c)



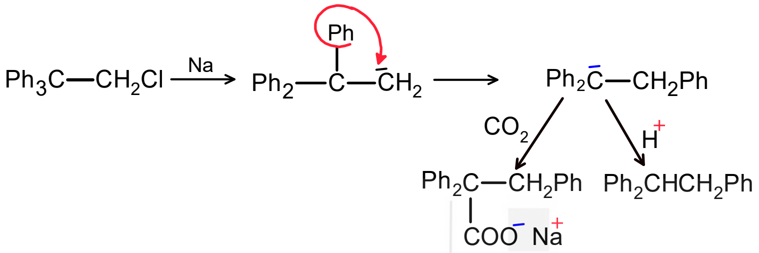
d)



12.3.2 Rearrangement Reactions of Carbanions

You have studied the rearrangement reactions of carbocations which are very common and have a good synthetic importance. You know that the rearrangement involves migration of a group or an atom that leads to the formation of a stable carbocation. You will recall that the carbanions do not undergo rearrangements to that extent. The group in case of a carbocation migrates with a pair of electrons while in case of carbanion rearrangement the group migrates without a pair of electrons.

As an example, the reaction of triphenylethyl chloride in presence of sodium is shown below.

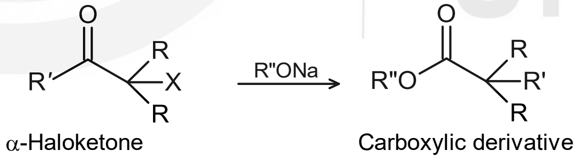


Thus the 1,2 alkyl shifts from one carbon to the other are not known in carbanions. However, there are some rearrangements in which the 1,2 alkyl shifts from N or S to carbanion carbon, are known to exist. The rearrangement reactions of these types of the carbanions are given below.

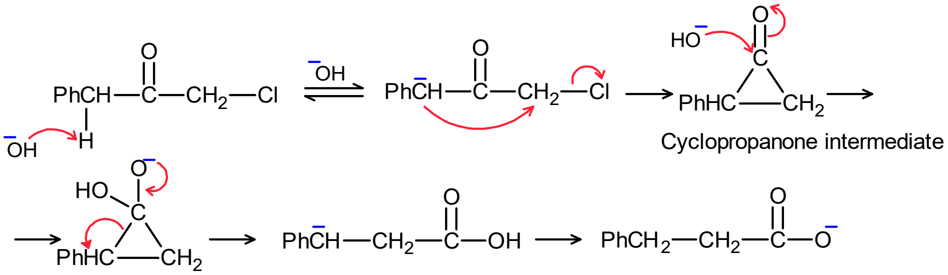
Favorskii Rearrangement

Favorskii rearrangement is a pinacol type rearrangement in *α*-halo ketones which involves the migration of a substituent as an anion to give a new C-C bond *α* to the carbonyl group. The starting *α*-halo ketone is transformed, via carbanion intermediates, into a carboxylic acid or its derivative.

A simplified representation of the reaction is outlined below where R and R' can be H, alkyl or aryl groups and X is generally Cl or Br.

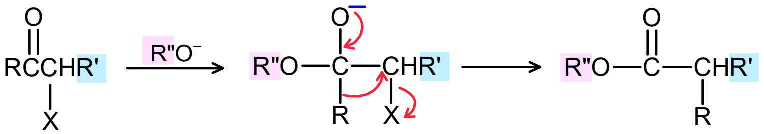


The Favorskii rearrangement is most useful for the preparation of branched-chain aliphatic carboxylic acids and their derivatives. If in the reaction R'' is H then the products are carboxylic acids and if R'' is an alkyl group then the products are esters. The reaction is believed to proceed through the steps given below.

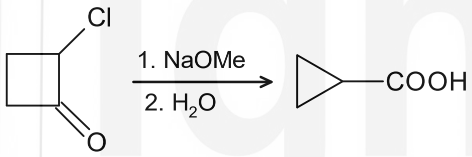


There is evidence that the rearrangement involves cyclopropanones as reaction intermediates as can be seen in the above reaction. These intermediates undergo subsequent addition of OH^-, followed by ring opening to yield the more stable of the two possible carbanions.

There is also a mechanism that can operate in the absence of an acidic hydrogen. This process, called the ***semibenzilic rearrangement***, is closely related to the pinacol rearrangement. A tetrahedral intermediate is formed by nucleophilic addition to the carbonyl group and the halide serves as the leaving group. The reaction is as follows.

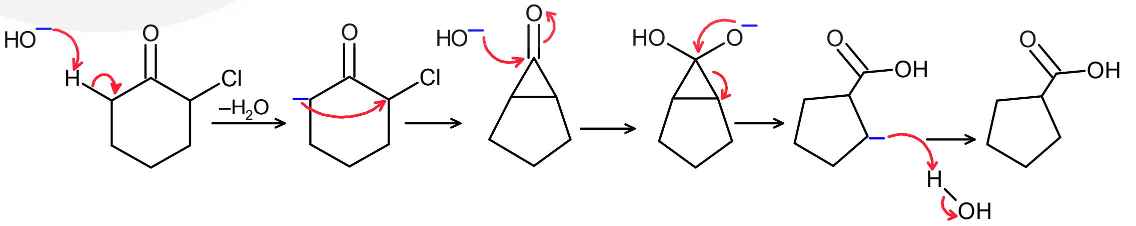


If this reaction is carried on cyclic ketones, it results in ring contraction due to rearrangement. For example, 2-chlorocylobutanone on treatment with sodium methoxide followed by hydroylsis is converted into cyclopropane carboxylic acid as per the following reaction.



Cyclobutanone Cyclopropane carboxyllic acid

The mechanism can be explained by taking cyclic α-chlorohexanone as an example. The reaction involves abstraction of alpha proton by base to give a carbanion intermediate, which is resonance stabilised with its enolate form. This carbanion or enolate cyclizes to a cyclopropanone intermediate which is then attacked by the hydroxide nucleophile which by a sequence of further electronic movements and in presence of water subsequently forms the carboxylate derivative. The reaction along with its mechanism can be given as follows.



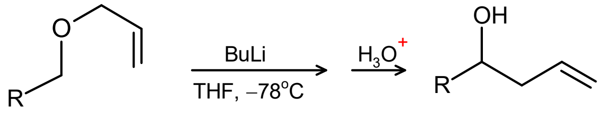
α-Cyclohexanone Carbanion Intermediate Cyclopropanone Intermediate Carboxyllate derivative

Although the 1,2 alkyl shifts from one carbon to the other are not very common in carbanions, however, there are some rearrangements in which the 1,2-alkyl shift occurs from O, N or S to carbanion carbon. Some of the rearrangement reactions of these types of carbanions are discussed below.

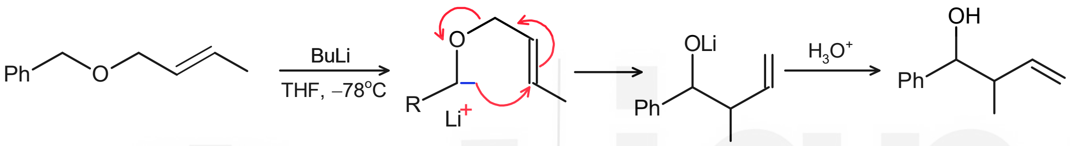
[2,3]-Wittig Rearrangement

The [2,3]-Wittig Rearrangement allows the synthesis of homoallylic alcohols by the base-induced rearrangement of allyl ethers at low temperatures.

Homoallylic alcohol is an aliphatic alcohol where the hydroxy carbon is β to a double bond. The most common base used in this reaction is butyl lithium and a general reaction can be represented as follows.

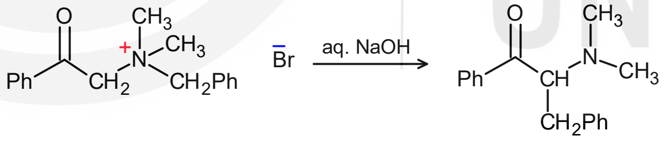


The [2,3]-Wittig rearrangement is a [2,3]-sigmatropic reaction, a thermal isomerization that proceeds through a six-electron, five-membered cyclic transition state. The first step in the reaction is abstraction of hydrogen atom forming an anion. The transformation of this deprotonated allyl ether into homoallylic alcohol involves a [2,3]-sigmatropic rearrangement and is therefore termed [2,3]-Wittig rearrangement which is shown in the following reaction sequence.



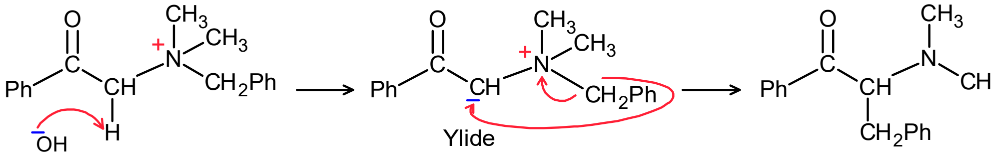
Stevens Rearrangement

This rearrangement takes place in a quaternary ammonium salt. This salt does not have an alkyl group having a β-hydrogen atom but has alkyl group with an electron-withdrawing group placed β to the nitrogen atom. It undergoes base-catalyzed rearrangement to yield a tertiary amine. The rearrangement involves migration of a group, without a pair of electrons, from nitrogen to carbon having negative charge. For example, phenacylbenzyldimethylammonium bromide (a) gives α - dimethylamino-β - phenylpropiophenone (b) on treatment with aqueous sodium hydroxide.



(a) **(b)**

The rearrangement follows an intramolecular mechanism via the formation of ylide as can be shown below.



The role of the electron-withdrawing carbonyl group is to stabilize the ylide formed in the first step by abstraction of H from the ammonium salt. You are familiar with the priorities of the migrating groups. Thus, here the benzyl group migrates in preference to alkyl group. The ylide rearranges to give tertiary amine. You would also observe that the rearrangement occurs with retention of absolute stereochemistry at the migrating centre.

It has been observed that the quaternary ammonium salts having a β-hydrogen atom undergo elimination with base to give alkene and tertiary amine. The reaction is known as the **Hofmann elimination.**

A variant of the Stevens rearrangement is the rearrangement of sulfur ylides.

In the Units 10, 11 and 12 you have studies about two important intermediates that have an important synthetic significance. You learnt the way the positively or negatively charged carbon ion can be attacked by a reagent that could be a neutral species or a charged one. In all these cases the charge is located on one atom being attacked. In the following section you would study about the types of ions which can be attacked from more than one side of the same molecule. You can proceed after answering the following SAQ.

SAQ 5

Complete the following sentences with appropriate words.

a) Favorskii rearrangement involves the migration of a substituent as an anion to give a new C-C bond ------------.

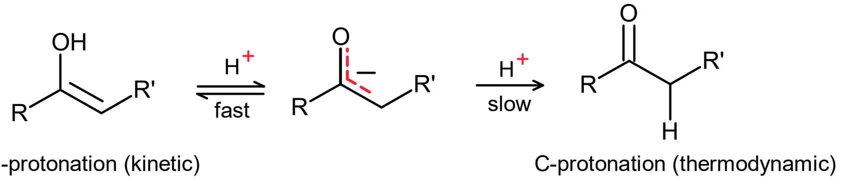
b) The ------------ involves the synthesis of homoallylic alcohols by the base-induced rearrangement of allyl ethers at low temperatures.

c) The base-catalyzed rearrangement to yield a tertiary amine starting from a quarternary ammonium salt is called the -----------------.

d) The ------- shifts from one carbon to the other are not known in carbanions.

12.4 AMBIDENT IONS AND THEIR REACTIONS

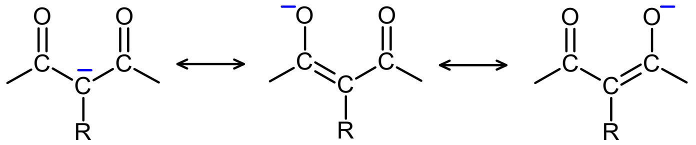
In the previous section you have read that being electron rich, carbanions act as nucleophiles in their reactions. The reaction takes place at the site of the negative charge. You might have read that sometimes the lone pair in a carbanion or the nucleophile can be shared between more than two atoms in the same molecule. As a result we can say that the reaction can take place at more than one site in the molecule. Such nucleophiles are called the ambident nucleophiles. The name comes from '*ambi* ' in Latin meaning "both" and '*dent* ' in Latin means "teeth". The reaction with such reagents depends upon the reaction conditions, and a possibility of getting mixtures is always there. A common example of ambident nucleophile is enolate ion with oxygen and carbon as two nucleophilic centres as is shown below.

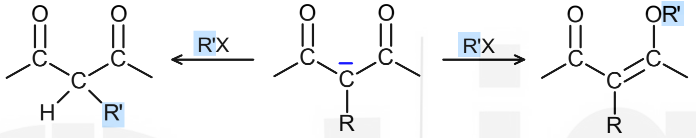


In the reactions of ambident nucleophiles, the reaction stops after one of the sites has reacted and formed a product. Some of the nucleophiles like cyanates (NCO^-) generally form only one type of products viz., isocyanates

(RNCO) and do not form the isomeric cyanates (ROCN). These types of reactions that give rise to one type of product when there is a possibility of formation of two products are called **regioselective**. Some of the ambident ion types are briefly explained in the following paragraphs.

Ions with two keto groups on either side: These ions are obtained by the removal of a proton from molecules having two carbonyl groups e.g., malonic esters, β-keto esters, β-diketones, etc. The ions generated in case of a diketo ester is shown below with the possible resonating structures. As you can see the ion can be attacked at C centre or the O centre. In an alkylation reaction given below, the product may be a C-alkylated or an O-alkylated product.





In the case of unsymmetrical carbonyl groups, three products are obtained due to the attack of carbon and either of the oxygens.

Dicarbanions: These are the ions formed by compounds that can lose two protons with two equivalents of a base as shown by the following reaction.

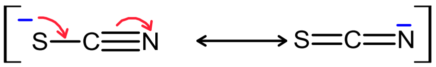
$$H_3C—CO—CH_2—CO— \xrightarrow{\text{2 Equivalents of base}} H_2\bar{C}—CO—\bar{C}H—CO—$$

As can be seen the attack is possible at two carbon ions and it is the more basic carbon which gets attacked faster. You can understand and explain well that the carbon with two adjacent carbonyl groups will be attacked with ease as compared to the other one.

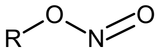
CN$^-$ Ion: It can be nitrile (cyanide, RCN) or an isocyanide and is represented by the following resonance hybrids.

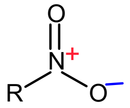
$$\left[—\bar{C}\equiv N \longleftrightarrow :C=\bar{N}\right]$$

Similarly, thiocynanides can also exist in two resonating forms.

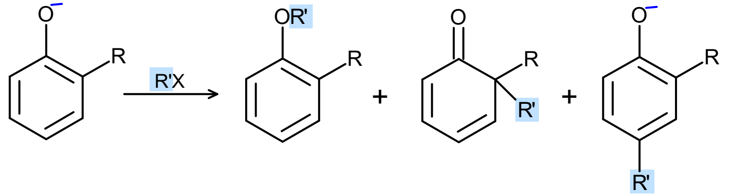


Nitrite Ion: It can also form products in its ester form i.e., nitrite ester, R-O-N=O or non-ester form i.e., nitro compounds RNO_2.


Alkylnitrile


Nitroalkane

Phenoxide Ions: These are analogous to enolate anions. These can undergo C-alkylation or O-alkylation as indicated below.



Let us now understand the factors that govern the reactions of the ambident nucleophiles.

12.4.1 Reactivity of Ambident Nucleophiles

The reactivity of the ambident nucleophiles depends mainly on two factors, viz., polarisability of the nucleophile and the nature of the solvent. You have read in Unit 9 about the hard and soft acid base (HSAB) concept and you know that it is related to the polarisability of the compound. Let us understand the two factors in the following paragraphs.

Polarisability of the Nucleophile: We know that according to the HSAB principle hard acids prefer hard bases and soft acids prefer soft bases during a reaction. The same principle is followed in an ambident nucleophile where the more electronegative atom is a harder base than the less electronegative atom. For example, as can be relooked into the previous subsection, in an enolate anion the more electronegative oxygen atom with negative charge is harder base than the carbon atom bearing negative charge.

Let us consider a nucleophilic reaction in which the nucleophile attacks the carbocation. When the reaction takes place by S_N1 mechanism the positive charge bearing carbon is the hard acid while in the case of S_N2 mechanism, the carbon being attacked is the soft acid. You should be able to answer the following question.

In the case of enolate anions which anionic atom will attack the carbocation and which one will attack the carbon in S_N2 reactions?

The answer is simple as you might have guessed also. The carbocation being a hard base would prefer attack by a hard base i.e., attack by oxygen of enolate. In case of S_N2 reaction the reacting carbon is a softer acid and would preferably be attacked by carbon atom of enolate ion.

Nature of the solvent: It is known that the ions get solvated in presence of a solvent in the reaction mixture. If the ambident nucleophile is not well surrounded by the solvent molecules, it attacks from its more electronegative ion. However, when it is well solvated or surrounded by the counter positive ions then the attack from the less electronegative ion takes place. In protic solvents, the more electronegative atom is better solvated due to hydrogen bonding. In polar aprotic solvents, neither atom of the nucleophile is solvated to a good extent, but these solvents are very effective in solvating cations. Therefore, in case of the polar aprotic solvents the more electronegative ion becomes available for attack.

The effect of solvent can be explained by an example. When benzyl bromide is reacted with β- naphthoxide, the products obtained are different in different solvents. Thus, in dimethyl sulfoxide, 95% O-alkylated product is obtained whereas in 2,2,2-trifluoroethanol, 85% C-alkylated product is obtained.

Another example that shows the effect of various solvents in the reactivity of ambident nucleophiles is the reaction of anion of pyrrole with butenyl bromide in a number of solvents. As you would observe the nature of solvent affects the type of product formed. The reaction and the percent formation of N- and C-alkylated products with the change in solvent is given in Table 12.1.

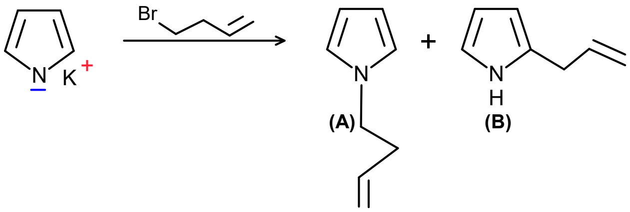
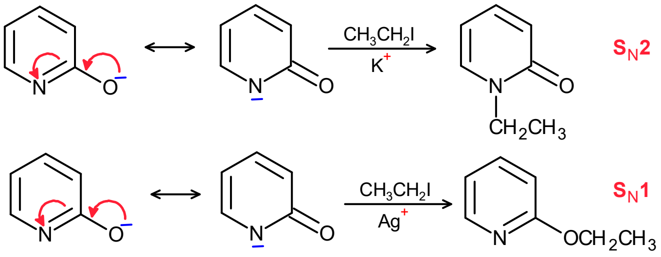


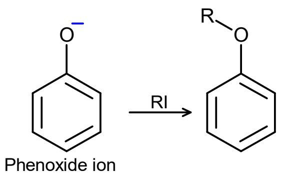
Table 12.1: Percent formation of N- and C-alkylated products with the change in solvent

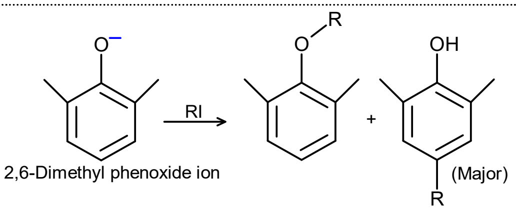
Sr. No.	Solvent	% A	% B
1	Tetrahydrofuran	81	19
2	Dioxane	71	29
3	Di-isopropyl ether	21	79
4	Benzene	15	85
5	Toluene	14	86
6	*n*-Heptane	14	86

It was mentioned above that the nature of counter ions also influences the attack of the nucleophile. For example, the alkylation of the enolate ion of 2-hydroxypyridine with ethyl iodide follows a S_N2 mechanism when the reaction was carried out with K^+ as the counter ion. The reaction takes place at the soft N atom centre with the formation of 73%product. When the same reaction is carried out in the presence of Ag^+ ions, 83% of the O-alkylated product is obtained. The reason is the ability of Ag^+ ions to coordinate with the leaving group iodide ion, as a result of which the reaction is found to follow the S_N1 mechanism. The reactions of the enolate ion of pyridine with K^+ and Ag^+ counter ions are given below.



Steric Effects: Sometimes the steric hindrance at the nucleophilic centre may become a predominating factor in the reactivity of the nucleophile. For example, the alkylation of phenol with RI gives O-alkylated product. However, when the reaction centre is crowded C-alkylation is favoured over O-alkylation. For example, 2,6-dimethyl phenol has a O^- in between two methyl groups, it results into C-alkylation as depicted in the following reaction.

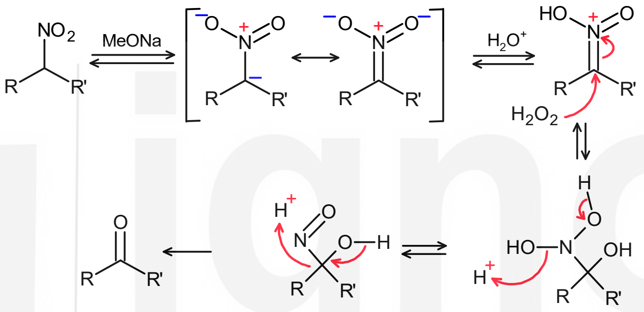




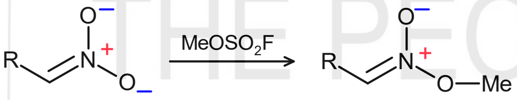
12.4.2 Reactions of Ambident Nucleophiles

Some of the reactions of ambident nucleophiles are given below.

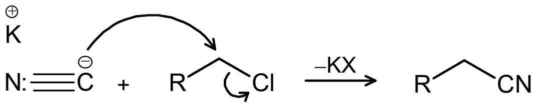
Nef Reaction: The reaction involves conversion of a nitro compound to carbonyl compound in the presence of a base. The nitronate anion is formed as an ambident nucleophile during the reaction. When the reaction is carried out in presence of sodium methoxide, the reaction takes place at the carbon centre anion which happens to be the soft base. The reaction is given below.



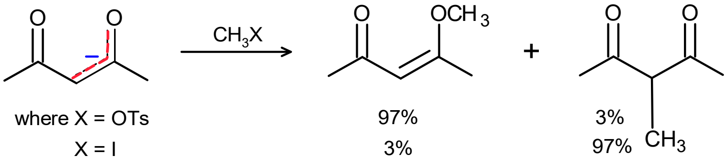
When a strong alkylating agent like $MeOSO_2F$ is used, there is a probability of O-alkylated product as shown below.



Kolbe nitrile Synthesis: The reaction is between primary aliphatic halides with alkali metal cyanides to give nitriles as per the reaction given below. As can be seen in the reaction, the ambident nucleophile is cyanide that forms an isocyanide in the presence of Ag^+ and Cu^+ ions.



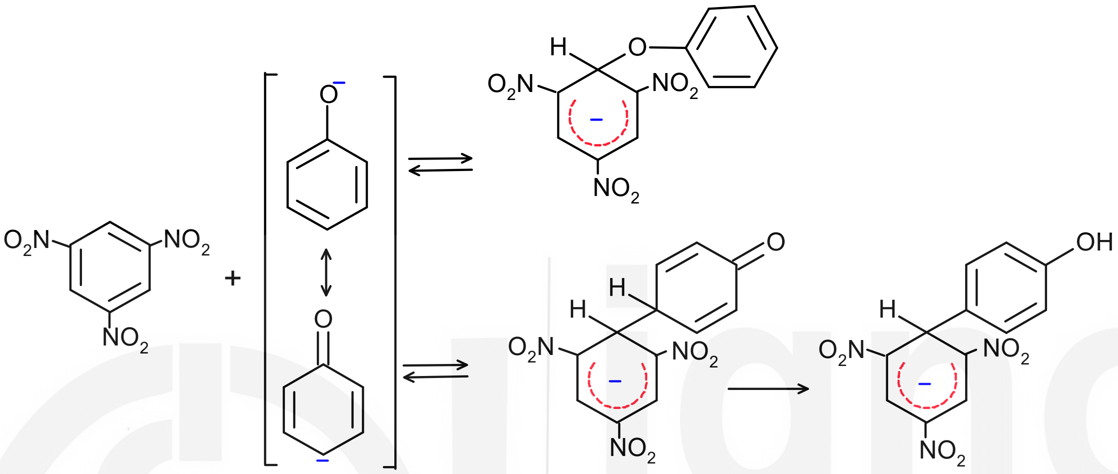
Alkylation with Active Methylene Groups: The reaction takes place in the compounds like acetylacetone which forms enolate ion. The C- or O- alkylation depends upon many factors, like the polar effect of the substituent, steric nature of the alkyl group and the nature of the leaving group.



In this reaction the O-/C-alkylation ratio decreases in the following order if the soft leaving groups like, bromide, chloride or fluoride are used.

$CH_3CH_2CH_2CH_2 > (CH_3)_2CH > CH_3CH_2 > CH_3$

Reaction with Phenoxide Ion: When the ambident nucleophile, viz., the phenoxide ion is reacted with 2,4,6-trinitrobenzene both O- and C-alkylation products are obtained. The attack through oxygen end is found to be reversible and kinetically preferred as the formation of the adduct does not disturb the aromaticity. While in the case of C-bonded adduct it initially loses the aromaticity. However, the aromaticity is regained rapidly by proton loss in the next step. Therefore, this route was found to be effectively irreversible and considered to be a product of thermodynamic control. Both the routes are depicted in the reactions given below.



Let us summarise all about carbanions discussed in this unit.

12.5 SUMMARY

Carbanions are one of the important intermediates formed by the heterolytic cleavage of a bond. These are different from the carbocations in many respects.

The carbanions can be generated by a number of methods that include abstraction of proton from an alkyl halide by a base, reaction of an alky halide with a metal, a decarboxylation reaction, addition of a nucleophile to an unsaturated compound and reactions of ylides and dithianes.

Some of the general reactions of carbanions are displacement, elimination, condensation, addition, polymerization and rearrangement. The rearrangement reactions shown by carbanions are very few as compared to those of carbocations. The 1,2 alkyl shifts from one carbon to the other as observed in carbocation rearrangements are not known in carbanions. However, there are some rearrangements in which the 1,2 alkyl shifts from N or S to carbanion carbon are known to exist. These reactions of carbanions are Stevens, Hofmann and Favorskii rearrangements.

The lone pair in a carbanion or the nucleophile can be shared between more than two atoms in the same molecule resulting in the reaction at more than one site in the molecule. Such nucleophiles are called the ambident nucleophiles. The ambident ions can be the ions with two keto groups on either side, dicarbanions, cyanide ion, nitrite ion and phenoxide ions.

The reactivity of the ambident nucleophiles depends mainly on two factors, viz., polarisability of the nucleophile and the nature of the solvent. The polarisability is based on the HSAB principle. According to this concept the hard acids prefer hard bases and soft acids prefer soft bases during a reaction. As far as the effect of solvent is concerned if the ambident nucleophile is not well surrounded by the solvent molecules, it attacks from its more electronegative negative ion. However, when it is well solvated or surrounded by the counter positive ions then the attack from the less electronegative ion takes place.

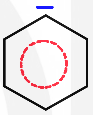
The reactions shown by the ambident nucleophiles given in this unit are, Nef reaction, Kolbe nitrile synthesis, alkylation with active methylene groups and the reaction with phenoxide ion.

12.6 TERMINAL QUESTIONS

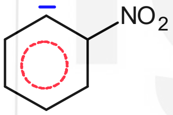
1. Compare the stability of carbanions formed from HCF_3 and HCl_3.

2. Which one is more aromatic out of cyclopentadienyl anion and cyclo-octatrienyl anion? Draw the structures and explain your answer.

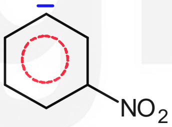
3. Arrange the following carbanions in the decreasing order of stability.



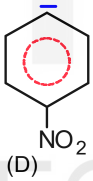
(A)



(B)



(C)



(D)

4. Write the alkylation reaction of enolate anion of cyclohexanone in the gas phase. Explain the formation of the product in the reaction.

5. Complete the following reaction and explain the formation of the preferred product.

$$C_2H_5COCH_2COOEt \xrightarrow{\text{2 Equivalents of base}} ? \xrightarrow{R'X} ?$$

6. Differentiate between a carbocation and a carbanion.

12.7 ANSWERS

Self Assessment Questions

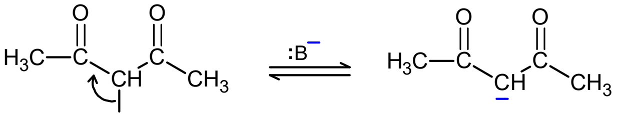
1. c)

2. nucleophile, eight, three, one, *sp*^{3}, tetrahedral

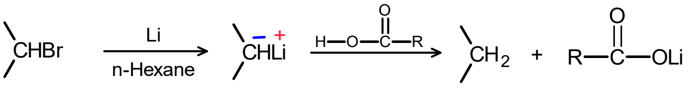
3. The higher energy barrier of trifluoromethyl carbanion is due to the more electronegativity of fluorine atom which is more stabilizing than a hydrogen atom.

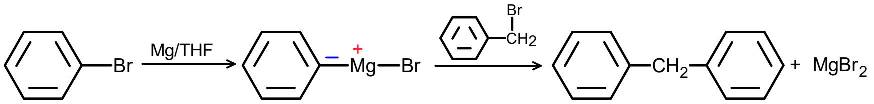
4. a)

$$R{-}X \xrightarrow[\text{ether}]{\text{Mg}} \overset{\delta-}{R}{-}\overset{\delta+}{Mg}\,X$$

b) 

resonance stabilised cabanion

c) 

d) 

5. a) *α* to the carbonyl group

   b) [2, 3]- Wittig rearrangement

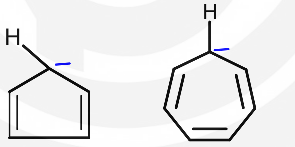
   c) Stevens rearrangement

   d) 1,2 alkyl

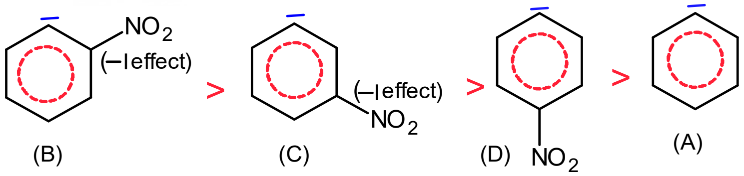
Terminal Questions

1. In the formation of $^-CCl_3$ from $HCCl_3$, an electron-withdrawing inductive effect is seen. However, the electron-withdrawing inductive effect of Cl is less than that of F, and $^-CF_3$ is more stabilised than $^-CCl_3$.

2. Cyclopentadienyl anion is more stable as it attains aromaticity while the other one is antiaromatic.



Aromatic Anti-aromatic

3. 

(B) (C) (D) (A)

Stability Order: B > C > D > A

4. Alkylation of the enolate anion of cyclohexanone in the gas phase shows only O-alkylation being more electronegative and no C-alkylation. The reason of sole O-alkylation is that the reaction is in gas phase therefore, the nucleophile is completely free and the ion is not solvated.

5 The anion at the CH_2 between two carbonyl groups is preferably formed due to it being more stable, therefore the preferred product.

$$C_2H_5COCH_2COOEt \xrightarrow{\text{2 Equivalents of base}} C_2H_5CO\bar{C}H\,COOEt \xrightarrow{R'X} C_2H_5COCHR'COOEt$$

Carbanion	Carbocation
Are reactive intermediates that have carbon atoms containing eight electrons	Are reactive intermediates that have carbon atoms containing six electrons
Cabanions have a negative charge.	Carbocations have a positive charge.
It is sp^3 hybridised.	It is sp^2 hybridised.
Geometry of carbon atom is pyramidal	Geometry of carbon atom is trigonal planar
Acts as a nucleophile	Acts as an electrophile
Stability order: Methyl carbanion > primary carbanion > secondary carbanion > tertiary carbanion	Stability order: Methyl carbocation < primary carbocation < secondary carbocation < tertiary carbocation