GENERAL ORGANIC CHEMISTRY - III

Section (A) : Solvents, Reagents and Leaving groups

1. Solvents

(a) Non polar solvents (examples: Benzene, hexane, toluene, CCl_4 etc.)

(b) Polar solvents: (i) polar protic (ii) polar aprotic

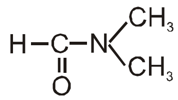
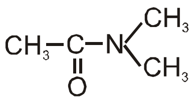
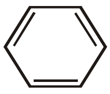
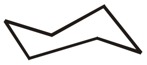
(i) Polar protic : A polar solvent which has acidic hydrogen and donate H^+ ion.
(examples: H_2O, ROH, RCOOH etc.)

(ii) Polar aprotic : A polar solvent which does not have acidic hydrogen.
(examples: Ether, acetone, DMF, DMA, DMSO etc.)

Note : Non polar solvents are always aprotic in nature.

Worksheet-1

Tick mark (✓) in right columns

S.No.	Solvents	Polar	Protic	Aprotic	Remarks
1.	H_2O				Polar protic solvent
2.	CH_3OH				Polar protic solvent
3.	CH_3CH_2OH				Polar protic solvent
4.	H–COOH				Polar protic solvent
5.	CH_3–COOH				Polar protic solvent
6.	NH_3				Polar protic solvent
7.	CH_3COCH_3 (Acetone)				Polar aprotic solvent
8.	$(CH_3)_2S=O$ (DMSO)				Polar aprotic solvent
9.	 Dimethyl formamide (DMF)				Polar aprotic solvent
10.	 Dimethyl acetamide (DMA)				Polar aprotic solvent
11.					Non-polar solvent
12.					Non-polar solvent
13.	CH_3–CH_2–CH_2–CH_2–CH_3				Non-polar solvent

2. Reagents

Reagent generates three type of attacking species.

(a) Electrophiles: Electrophiles are electron deficient species, which can accept a pair of electron.

(b) Nucleophiles: Nucleophiles are electron rich species having atleast one unshared pair of electron.

(c) Radicals: It is an electron deficient species with odd electron around an atom.

$\dot{C}H_3$, $C_2H_5^{\bullet}$, $C_2H_5O^{\bullet}$, $CH_3COO^{\bullet}$, $X^{\bullet}$ etc.

2.1 Nucleophiles

Nucleophiles are electron rich species having atleast one unshared pair of electron. It can be neutral or negatively charged. It also acts as Lewis base.

CN^-, OH^-, Br^-, I^-, $\ddot{N}H_3$, $H_2\ddot{\underset{\cdot\cdot}{O}}$ etc.

** Ambident nucleophiles

The species which have more than one nucleophilic sites for reaction are called ambident nucleophiles.

$:\overset{\ominus}{C}\equiv N:$, $:\overset{\ominus}{\underset{\cdot\cdot}{\ddot{O}}}-\ddot{N}=\underset{\cdot\cdot}{\ddot{O}}$, $:\overset{\ominus}{\underset{\cdot\cdot}{\ddot{O}}}-CH=\underset{\cdot\cdot}{\ddot{S}}$, $HSO_3^{\ominus}$

** **Nucleophilicity:** The tendency to give e^- pair to an **electron deficient carbon** atom is defined as nucleophilicity.

Criteria for Nucleophilicity

1. The factors which increases e^- density (+I, +M groups) at donor atom increases nucleophilicity.
2. The more polarisable donor atom is the better nucleophile. Therefore size of donor atom increases, nucleophilicity also increases.

(a) Periodicity

Nucleophilicity decreases from left to right in a period because electron negativity of atoms increases.

$CH_3^- > NH_2^- > OH^- > F^-$

Top to bottom in a group nucleophilicity increases because size of donor atom and polarizability increases.

** **Basicity decreases from top to bottom in a group.**

Acidic strength: HI > HBr > HCl > HF

Basic strength: $F^- > Cl^- > Br^- > I^-$

Nucleophilicity: $F^- < Cl^- < Br^- < I^-$

(Due to smaller size of F^- it is more solvated (hydration) by polar protic solvent).

Hydration or solvation decreases gradualy down the group.

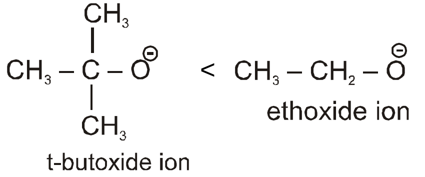
** **Negative charge density increases, nucleophilicity increases.**

(b) Nucleophilicity of halogens in polar aprotic solvents

Polar aprotic solvents do not hydrate or solvate the anions therefore nucleophilicity of smaller anion is higher than that of larger anion. Hence order of nucleophilicity of halide ions is **$F^- > Cl^- > Br^- > I^-$**

(c) Steric effects on nucleophilicity

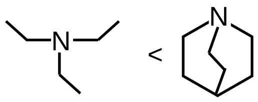
If the steric crowding becomes very high, the nucleophilicity becomes so poor that the base may be regarded as non-nucleophilic.

(i) 

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\ominus} < CH_3-CH_2-O^{\ominus}$

t-butoxide ion

ethoxide ion

(ii) 

Note-

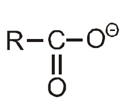
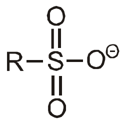
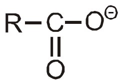
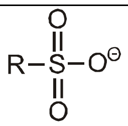
(1) Strong bases but weak nucleophiles are t-BuO⁻, LDA [N(iPr)₂Li], NEt₃.

(2) Strong nucleophiles but very weak bases are $\overset{\ominus}{I}$, $\overset{\ominus}{Br}$.

(3) Strong nucleophiles but moderate bases are $H\overset{\ominus}{S}$, N_2H_4 .

Worksheet – 2

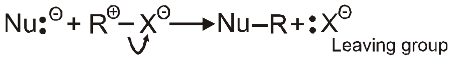
Certain species are mentioned in each column in the table below. The student should mark “>”, “<” or “=” signs in between given species to generate the correct order of the property mentioned at the top.

	Nucleophilicity	**Basicity**	**Remarks / Reasons**
Def.	The tendency to give e^- pair to an electron deficient carbon atom is defined as nucleophilicity. It is kinetic controlled property (KCP)	A base is a substance that can accept a proton by donating a pair of electrons. It is thermodynamic controlled property (TCP)	Basicity can be determine by value of pK_b and pK_{aH}. (We use pK_{aH} to mean the pK_a of the conjugate acid)
1	CH_3^- NH_2^- OH^- F^-	CH_3^- NH_2^- OH^- F^-	If donor atoms belong to same period, then nucleophilicity and basicity order is same
2	SiH_3^- PH_2^- SH^- Cl^-	SiH_3^- PH_2^- SH^- Cl^-	" " "
3	F^- Cl^- Br^- I^-	F^- Cl^- Br^- I^-	Down the group nucleophilicity increases while basicity decreases.
4	OH^- SH^-	OH^- SH^-	" " "" " "
5	RO^- RS^-	RO^- RS^-	" " "
6	RO^- HO^-	RO^- HO^-	If donor atom is same, then generally nucleophilicity and basicity order is also same.
7	$RCOO^-$ PhO^- HO^- RO^-	$RCOO^-$ PhO^- HO^- RO^-	" " "
8	 $R-\underset{\underset{O}{\|}}{C}-O^{\ominus}$  $R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{\ominus}$	 $R-\underset{\underset{O}{\|}}{C}-O^{\ominus}$  $R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{\ominus}$	" " "
9	HO^- H_2O	HO^- H_2O	Anion is better nucleophile and better base.
10	NH_2^- NH_3	NH_2^- NH_3	

2.2 Leaving groups and leaving ability (Nucleofugality)

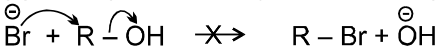
Weaker bases are always good leaving groups (nucleofuse).

A good leaving group always stabilize the transition state and lowers its energy of activation hence increases the rate of the reaction.

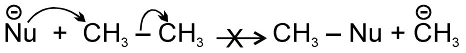


$$Nu{:}^{\ominus} + R^{\oplus}\!-\!X^{\ominus} \longrightarrow Nu\!-\!R + {:}\underset{\text{Leaving group}}{X^{\ominus}}$$

Note: (1) Strong bases rarely act as leaving group.



$\overset{\ominus}{Br} + R-OH \not\longrightarrow R-Br + \overset{\ominus}{OH}$ (Strong base, poor leaving group)



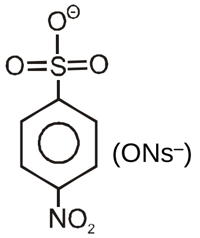
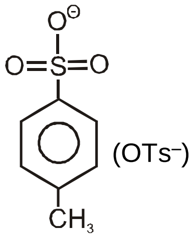
$\overset{\ominus}{Nu} + CH_3-CH_3 \not\longrightarrow CH_3-Nu + \overset{\ominus}{CH_3}$ (Strong base but does not act as a leaving group)

(2) The leaving group should have lower bond energy with carbon.

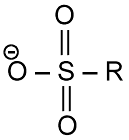
(3) Negative charge is stabilized either by dispersal or delocalization in leaving group.

Worksheet – 3

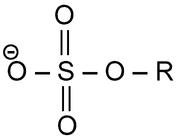
The student should mark ">", "<" or "=" signs in between given species to generate the correct leaving group ability order.

1.	$\overset{\ominus}{I}$ $\overset{\ominus}{Br}$ $\overset{\ominus}{Cl}$ $\overset{\ominus}{F}$	6.	NR_3^+ SR_2^+
2.	CH_3^- NH_2^- OH^- F^-	7.	$CF_3SO_3^-$ $PhCOO^-$ PhO^- EtO^-
3.	$R\text{–}COO^-$ PhO^- HO^- RO^-	8.	H_2O OH^-
4.	SH^- OH^-	9.	N_2 NH_2^-
5.	 (ONs⁻)  (OTs⁻)	$ONs^- \rightarrow$ Nosylate $OTs^- \rightarrow$ Tosylate $OBs^- \rightarrow$ Brosylate		

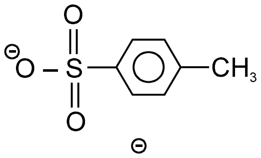
Other good leaving groups are -



Alkanesulphonate ion



Alkyl sulphate ion



Tosylate ion ($\overset{\ominus}{OTs}$)

$CF_3\overset{\ominus}{SO_3}$

Triflate ion
(a super leaving group)

2.3 Electrophiles

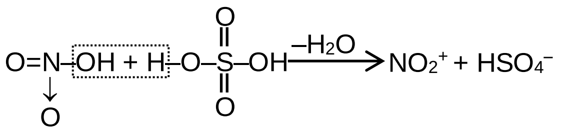
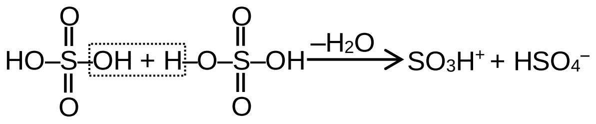
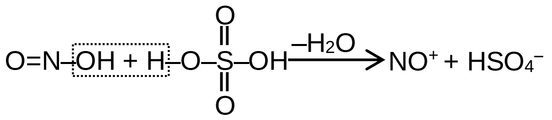
Electrophiles are electron deficient species, which can accept a pair of electron.

(a) Positively charged species are $\overset{\oplus}{H}, \overset{\oplus}{Cl}, \overset{\oplus}{Br}, \overset{\oplus}{NO_2}, \overset{\oplus}{CH_3}, \overset{\oplus}{H_3O}$

(b) Species with vacant orbital at central atom are PCl_5, $AlCl_3$, SO_2, SO_3, BH_3 and carbenes.

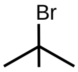
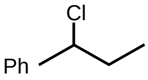
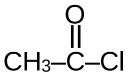
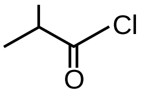
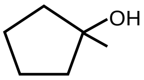
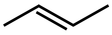
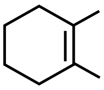
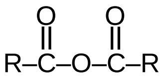
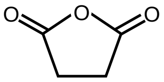
(c) Disociable σ and π bonds are CO_2 and RCOCl.

Generation of electrophiles

Compounds	**Reagents**	**Electrophile**	**Chemical reaction to generate electrophile**
1. Alkane			NA
2. Alkene	H^+ (H_2SO_4…..)	Carbocation	$R–CH{=}CH_2 \xrightarrow{H^+} R-\overset{+}{C}H-CH_3$
3. Alkyne	H^+ (H_2SO_4…..)	Carbocation	$R–C{\equiv}CH \xrightarrow{H^+} R-\overset{+}{C}=CH_2$ (rarely formed)
4. Alcohol	H^+ (H_2SO_4…..)	Carbocation	$R–CH_2–OH \xrightarrow{H^+} R-\overset{+}{C}H_2$
5. Alkylhalide	Lewis acid ($AlCl_3$, $ZnCl_2$, BF_3,$FeBr_3$ …)	Carbocation	$RCH_2X \xrightarrow{AlCl_3} R-\overset{+}{C}H_2 + AlCl_3X^-$
6. Acid halide	Lewis acid ($AlCl_3$, $ZnCl_2$, BF_3……)	Acyl Carbocation	$R–COX \xrightarrow{AlCl_3} R-\overset{+}{C}=O+AlCl_3X^-$
7. Acid	Lewis acid ($AlCl_3$, $ZnCl_2$, BF_3……)	Acyl Carbocation	$R–COOH \xrightarrow{AlCl_3} R-\overset{+}{C}=O+AlCl_3OH^-$
8. Halogen (Cl_2,Br_2,I_2, ICl,IBr,BrCl)	Lewis acid ($AlCl_3$, $ZnCl_2$, BF_3……)	Halonium ion (X^+)	$X_2 \xrightarrow{AlCl_3} X^+ + AlCl_3X^-$
9. Carbonyl Compound	H^+	Carbocation	$R_2C{=}O \xrightarrow{H^+} R_2\overset{+}{C}–OH$
10. For nitration reaction	conc.HNO_3 + conc.H_2SO_4	Nitronium ion NO_2^+	 $O{=}\underset{\downarrow\atop O}{N}–\boxed{OH + H}–O–\overset{O\atop \|}{\underset{\|\atop O}{S}}–OH \xrightarrow{-H_2O} NO_2^+ + HSO_4^-$
11. For sulphonation reaction	Conc. H_2SO_4	$SO_3(SO_3H^+)$	 $HO–\overset{O\atop \|}{\underset{\|\atop O}{S}}–\boxed{OH + H}–O–\overset{O\atop \|}{\underset{\|\atop O}{S}}–OH \xrightarrow{-H_2O} SO_3H^+ + HSO_4^-$
12. For nitrosation reaction	$HNO_2 + H^+$	NO^+	 $O{=}N–\boxed{OH + H}–O–\overset{O\atop \|}{\underset{\|\atop O}{S}}–OH \xrightarrow{-H_2O} NO^+ + HSO_4^-$
13. For Gattermann Koch reaction	CO + HCl + $AlCl_3$	$H-\overset{+}{C}=O$	$CO + HCl + AlCl_3 \longrightarrow H-\overset{+}{C}=O + AlCl_4^-$
14. For Gattermann reaction	HCN + HCl + $AlCl_3$	$H-\overset{+}{C}=NH$	$HCN + HCl + AlCl_3 \longrightarrow H-\overset{+}{C}=NH + AlCl_4^-$

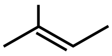
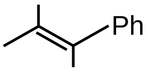
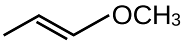
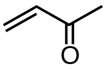
Worksheet-4 (A)

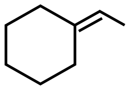
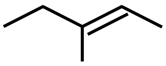
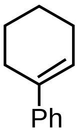
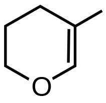
Generation of electrophiles :

S.N.	Reactant	Reagent	Electrophile
1		$\xrightarrow{AlCl_3}$	
2		$\xrightarrow{AlCl_3}$	
3	 $CH_3-\overset{\overset{O}{\|}}{C}-Cl$	$\xrightarrow{\text{Anhyd. } AlCl_3}$	
4		$\xrightarrow{AlCl_3}$	
5		$\xrightarrow{H_2SO_4}$	
6		$\xrightarrow{H_2SO_4}$	
7		$\xrightarrow{H_2SO_4}$	
8	 $R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$	$\xrightarrow{AlCl_3}$	
9		$\xrightarrow{AlCl_3}$	

Worksheet-4 (B)

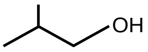
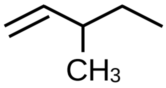
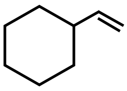
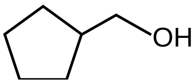
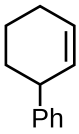
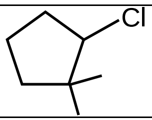
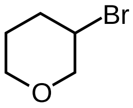
Generation of electrophiles:

S.N.	Reactant	Reagent	Electrophile
1	$CH_3-CH_2-CH=CH_2$	$\xrightarrow{H_2SO_4}$	
2		$\xrightarrow{H_2SO_4}$	
3		$\xrightarrow{H_2SO_4}$	
4		$\xrightarrow{H^+}$	
5		$\xrightarrow{H^+}$	

6		$\xrightarrow{H^+}$	
7		$\xrightarrow{H^+}$	
8		$\xrightarrow{H^+}$	
9		$\xrightarrow{D^+}$	

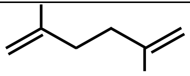
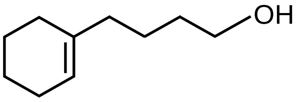
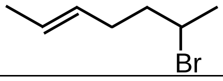
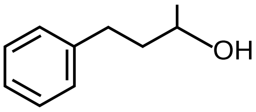
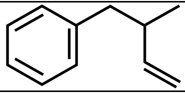
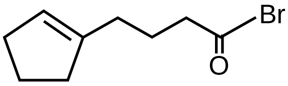
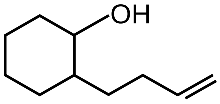
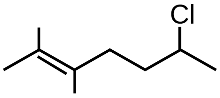
Worksheet-4 (C)

Generation of electrophiles :

S.N.	Reactant	Reagent	Electrophile
1	$CH_3–CH_2–CH_2–Cl$	$\xrightarrow{\text{Anhy. }AlCl_3}$	
2	$CH_3–CH_2–CH_2OH$	$\xrightarrow{\text{Conc.}H_2SO_4}$	
3		$\xrightarrow{\overset{\oplus}{H}, H_2SO_4}$	
4		$\xrightarrow{H^+}$	
5		$\xrightarrow{H^+}$	
6		$\xrightarrow[-H_2O]{H^+}$	
7		$\xrightarrow{H^+}$	
8		$\xrightarrow{AlCl_3}$	
9		$\xrightarrow{FeBr_3}$	

Worksheet-4 (D)

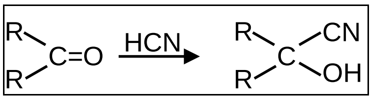
Generation of electrophiles :

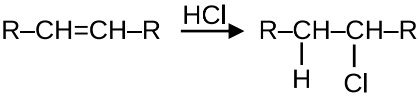
S.N.	Reactant	Reagent	Electrophile
1		$\xrightarrow{H^+}$	
2		$\xrightarrow{HF,\ BF_3}$	
3		$\xrightarrow{FeBr_3}$	
4		$\xrightarrow{H_2SO_4}$	
5		$\xrightarrow{H^+}$	
6		$\xrightarrow{AlCl_3}$	
7		$\xrightarrow{H^+}$	
8		$\xrightarrow{FeCl_3}$	

Section (B) : Types of organic reactions

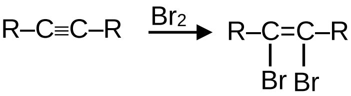
3.1 On the basis of nature of reactants

(a) **Addition reaction:** Where two or more molecules combine to form a larger one (the adduct). Addition reaction include such reactions as **halogenation, hydrohalogenation, hydration etc**.



(i) 

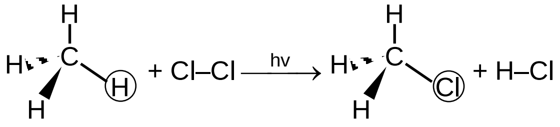
$$R\text{–}CH{=}CH\text{–}R \xrightarrow{HCl} R\text{–}\underset{H}{CH}\text{–}\underset{Cl}{CH}\text{–}R$$

(ii) 

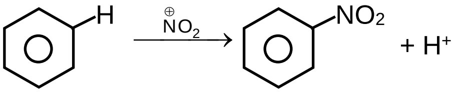
$$R\text{–}C{\equiv}C\text{–}R \xrightarrow{Br_2} R\text{–}\underset{Br}{C}{=}\underset{Br}{C}\text{–}R$$

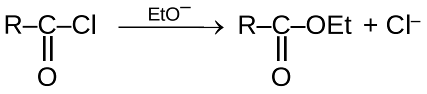
(b) **Substitution reaction:** In which one group in a chemical compound is replaced by another group. Such reaction follows free radical substitution, aromatic electrophilic substitution (S_E), nucleophilic substitution (**S_N1, S_N2, S_Ni, S_N2Th**) etc.

$R–L \xrightarrow{Y} R–Y + L$

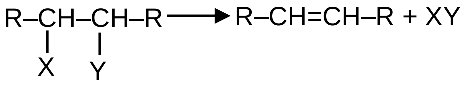
(1)


(2) $R–CH_2–Br \xrightarrow{NaOH} R–CH_2–OH + NaBr$

(3)


(4)

$R–\underset{\underset{O}{\|}}{C}–Cl \xrightarrow{EtO^-} R–\underset{\underset{O}{\|}}{C}–OEt + Cl^-$

(c) **Elimination reaction:** In which two substituent groups or atoms are removed from a molecule either in a one or two-step mechanism. Such reactions include dehydration, dehalogenation etc.


$R–\underset{X}{\underset{|}{C}H}–\underset{Y}{\underset{|}{C}H}–R \rightarrow R–CH=CH–R + XY$

3.2 On the basis of electronic nature of reagents

(a) **Nucleophilic reaction:** When attacking reagent is nucleophile in first step of mechanism then the reaction is generally called nucleophilic reaction.

(b) **Electrophilic reaction:** When attacking reagent is electrophile in first step of mechanism then the reaction is generally called electrophilic reaction.

(c) **Free radical reaction:** When attacking reagent is free radical then reaction is called free radical reaction.

Types of reagents :

(a) Nucleophile ($\ddot{N}u^{\ominus}$): Electron rich species having lone pair of electrons & complete octet at donor atom.

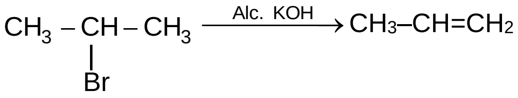
(b) Electrophile ($E^{\oplus}$): Electron deficient species having vacant p or d-orbitals.

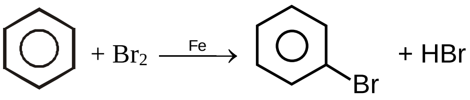
(c) Free radical ($R^{\bullet}$): Electron deficient species having odd electron in valence shell.

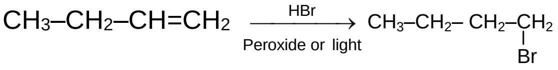
Worksheet-5

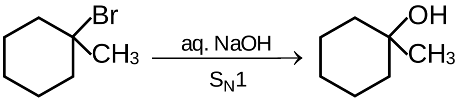
Write the type of reactions for the followings.

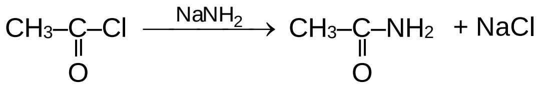
1. $CH_3–CH_2–Br \xrightarrow{NaOH} CH_3–CH_2–OH$ [...]

2.

$CH_3–\underset{Br}{\underset{|}{C}H}–CH_3 \xrightarrow{Alc.\ KOH} CH_3–CH=CH_2$ [...]

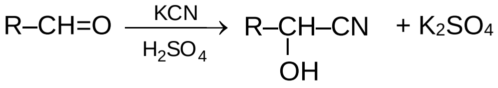
3.

[...]

4.

$CH_3–CH_2–CH=CH_2 \xrightarrow[\text{Peroxide or light}]{HBr} CH_3–CH_2–CH_2–\underset{Br}{\underset{|}{C}H_2}$ [...]

5.

[...]

6. 

$CH_3-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{NaNH_2} CH_3-\underset{\underset{O}{\|}}{C}-NH_2 + NaCl$ [………………………………………………………]

7. 

$R-CH=O \xrightarrow[H_2SO_4]{KCN} R-\underset{\underset{OH}{|}}{CH}-CN + K_2SO_4$ [………………………………………………………]

8. Isopentane $\xrightarrow[h\nu]{Br_2}$ 2-Bromo-2-methylbutane [………………………………………………………]

Section (C) : Applications of chemical kinetics in organic chemistry

Chemical kinetics is the branch of physical chemistry that deals with the study of rate of reactions and the factors governing rate of reaction.

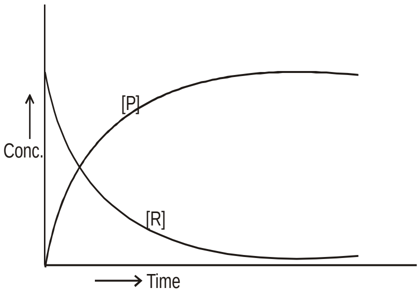
4.1 Rate of chemical reaction

The rate of reaction is the change in concentration of reactants or products per unit time.

$$\text{Rate} = \frac{\text{Change in concentration}}{\text{Time taken}} = \frac{\Delta c}{\Delta t} = \frac{\text{mol / lit.}}{\text{time}} = \text{mol lit}^{-1}\ \text{time}^{-1}$$

Rate is always defined in such a manner so that it is always positive value.

For a reaction $R \longrightarrow P$



$$\text{Rate} = \frac{\Delta c}{\Delta t} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

Relation between the rates of reactions of different species taking part in a chemical reaction

Rate of reaction of all the species taking part in a chemical reaction are not equal as evident from their stochiometric coefficients. Rate of reaction is always defined for a balanced chemical equation.

$aA + bB \longrightarrow cC + dD$

$$\textbf{Rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Ex. $N_2 + 3H_2 \longrightarrow 2NH_3$

***** From above we can have the following relation between the rate of reactions of different species

$$\text{Rate of reaction} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

4.2 Molecularity

Molecularity is defined only for the elementary reactions which is equal to number of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy.

No elementary reactions involving more than three molecules are known, because of very low probability of near-simultaneous collision of more than three molecules.

The rate law for the elementary reaction

$aA + bB \longrightarrow$ products

rate = $k[A]^a[B]^b$, where a + b = 1, 2 or 3.

The mechanism of any complex reaction is always written in terms of elementary steps, so molecularity of each of these steps will be defined but net molecularity of complex reaction has no meaning.

4.3 Order of reaction

Let there be a reaction

$$n_1 A + n_2 B \longrightarrow \text{products.}$$

✧ Rate of reaction:

$$R \propto [A]^p [B]^q \quad \text{............ (i)}$$

$$R = k [A]^p [B]^q \quad \text{.......... (ii)}$$

(Rate law equation) where k = rate constant

✧ Where p & q may or may not be equal to n_1 & n_2.

✧ p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p + q) is overall order of the reaction.

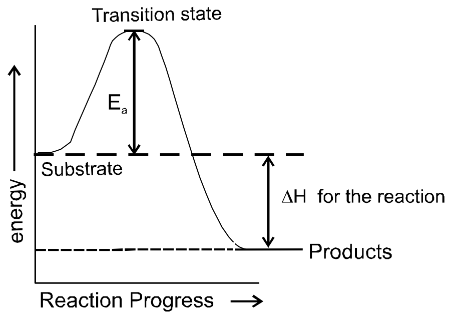
✧ **Order of reaction is experimentally determined & may be positive, negative, zero or fractional**.

Comparison between molecularity and order of reaction

Molecularity of reaction	**Order of reaction**
1. It is defined as the **no. of molecules** of reactant taking part in a particular step.	1. It is defined as the sum of the **power of concentration terms** that appear in the rate law equation.
2. It is always a **whole number**. It can neither be **zero** nor **fractional**.	2. It may be **zero, fractional** or any integer.
3. It is derived for **slowest step** in the mechanism of reaction generally.	3. It is derived from **rate expression**.
4. It is **theoretical** value.	4. It is **experimental** value.

4.4 Transition state & Activated complex

The transition state is the transitory of molecular structure in which the molecule is no longer a substrate but not yet a product.
All chemical reactions must go through the transition state to form a product from a substrate molecule.
The transition state is the state corresponding to the highest energy along the reaction co-ordinate.

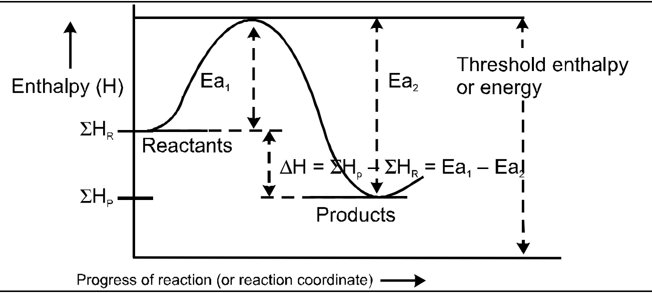


Transition state is unstable and cannot be isolated.
In equation : $S \rightarrow X \rightarrow P$,
X is the transition state, which is located at the peak of the curve on the Gibbs free energy graph.

4.5 Activation energy

"**It can be defined as, the minimum amount of energy that is required to activate atoms or molecules to a condition in which they can undergo chemical transformation".**

In terms of transition state theory, the activation energy is the difference in energy content between atoms or molecules in an activated or transition state configuration and the corresponding atoms and molecules in their initial configuration.

	ΣH_R = Summation of enthalpies of reactants ΣH_P = Summation of enthalpies of products ΔH = Enthalpy change during the reaction Ea_1 = Energy of activation of the forward reaction Ea_2 = Energy of activation of the backward reaction

Threshold energy: The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur is known as threshold energy.

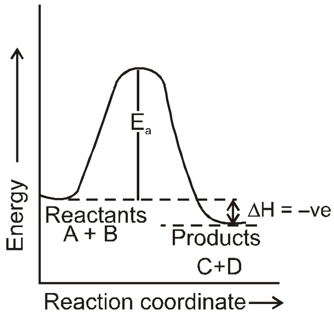
E_a = Threshold energy – Actual average energy of reactants

E_a is expressed in kcal mole^{-1} or kJ mole^{-1}.

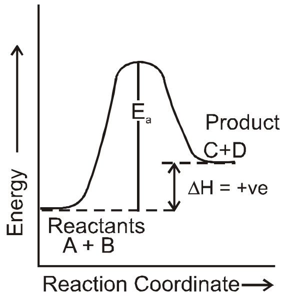
Greater the height of energy barrier, greater will be the energy of activation and slower will be the reaction at a given temperature.

4.6 Reaction profile

The energy change as a function of the progress of the reaction is known as reaction profile or energy diagram.

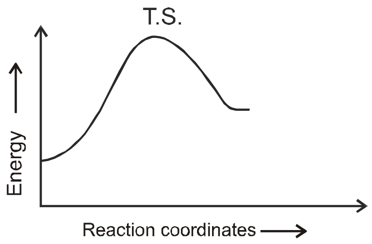


(Exothermic)



(Endothermic)

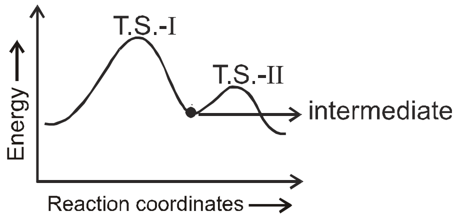
Elementary reactions: These reactions take place in single step without formation of any intermediate.

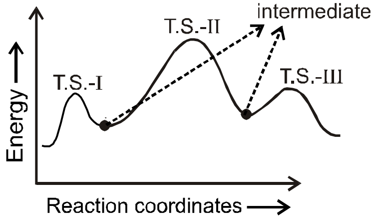


T.S. = Transition state

In case of elementary reactions the sum of stoichiometric coefficients is equal to order of the reactions.

Complex reactions: Reaction which proceed in more than one steps are known as complex reaction. These reactions take place in a sequence of a number of elementary reactions.





For complex reactions order is to be experimentally calculated.

4.7 Factors affecting rate of chemical reaction

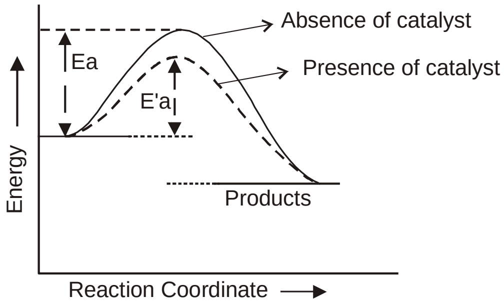
(i) Effect of concentration: It is seen by rate law equation which is experimental data.

$r = k[A]^m\,[B]^n$

(ii) Chemical nature of reactants: This is the point of detailed study in organic chemistry.
(In general rate: Gaseous > Liquid > Solid medium)

(iii) Effect of catalyst: Presence of positive catalyst lower down the activation energy hence increases the rate of reaction.

(iv) Effect of temperature: rate of reaction generally increases with temperature.



4.8 Rate determining step

The **slowest step** of the mechanism is called rate determining step of the reaction. Rate law of reaction is calculated with the help of rate determining step (R.D.S).

Section (D) : Organometallic compounds and Grignard reagent

Organometallic compounds are the organic compounds in which a metal atom is directly attached to carbon atom through covalent bond or ionic bond.

For example C–M or $\overset{-}{C}\overset{+}{M}$ (R-MgX, R_2CuLi, R_2Zn, RNa, RLi)

Note: (1) RONa (Sodium alkoxide). CH_3COONa (Sodium acetate), CH_3COOAg (Silver acetate), RSK (Potassium mercaptide) RNHK (N-Alkylpotassamide), $(CH_3COO)_4Pb$ (Lead tetraacetate), etc are **not** organometallic compounds.

(2) It should be noted that $(CH_3)_4Si$ (Tetramethylsilane, TMS) is also not an organometallic compound because silicon is a nonmetal.

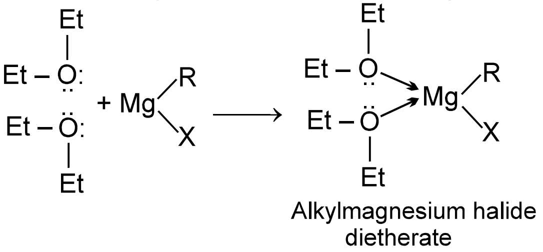
(3) Most important examples of organometallic compounds are **Grignard reagents.** In Grignard reagent, the carbon and magnesium atom are bonded with each other through polar covalent bond (35% ionic character) and magnesium atom is also attached to halogen by ionic bond.

5.1 Grignard reagent

(a) Preparation of Grignard reagent (G.R.)

$$RX + Mg \xrightarrow[\text{Ether}]{\text{Dry and pure}} RMgX$$

Dry ether is used as a solvent because it is a Lewis base that donates its lone pair of electrons to electron-deficient magnesium atom, therefore providing stability to the Grignard's reagent.



Process: To an etherial solution of alkyl halide Mg metal is added at very low temp. (0-5°C). A vigorous reaction takes place, and a solution of G.R. is obtained. It cannot be evaporated to get it in solid state because reaction will be explosive. It is stable only in solution state.

Reactivity order with respect to X (For preparation of RMgX)

$$R - I > \underbrace{R - Br}_{\substack{\text{Most} \\ \text{commonly} \\ \text{used}}} > R - Cl > \underset{\substack{\downarrow \\ \text{(No G.R. formation)}}}{R - F}$$

(b) Examples of Grignard's reagent

1. Saturated Aliphatic Grignard's reagent

$R–MgX$ (Alkylmagnesium halide)

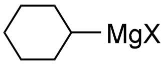
$CH_3–MgI$ (Methylmagnesium iodide)

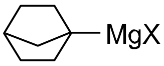
2. Unsaturated Aliphatic Grignard's reagent

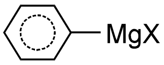
(i) Alkenyl Grignard's reagent: $CH_2=CH–MgX$

(ii) Alkynyl Grignard's reagent: $CH_3–C\equiv C–MgX$

(iii) Allylmagnesium halide: $CH_2=CH–CH_2–MgX$

3. Alicyclic Grignard's reagent: 

, 

4. Aromatic Grignard's reagent: 

(Phenylmagnesium halide)

(c) Reactivity of Grignard reagent

* On having same hydrocarbon radical, the order of reactivity of Grignard's reagent will be as follows-
RMgI > RMgBr > RMgCl

* Reactivity order with different alkyl part is-

RMgX : ($R = 3^o > 2^o > 1^o > CH_3 > C=C > C\equiv C$)

* Reactivity order of Grignard reagent with respect to different reactants (Substrates) is-
Acidic hydrogen > RCOCl > RCHO > RCOR > RCOOR'

Note: (1) Except halogens all other functional groups which can react with Grignard reagent [including $–NO_2$, –CN, CHO] must be **absent** in the alkyl group otherwise G.R. will be destroyed by internal reactions.

(2) If the alkyl part has more stable negative charge, then RMgX is more stable and it will be less reactive.

(d) Synthesis of other organometallic compounds from Grignard reagent

$R–Mg–X + ZnCl_2 \longrightarrow R_2Zn + MgX(Cl)$

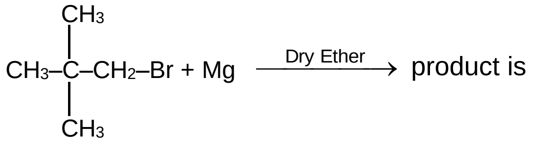
$R–Mg–X + HgCl_2 \longrightarrow R_2Hg + MgX(Cl)$

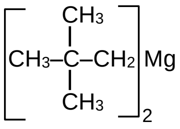
$R–Mg–X + SnCl_4 \longrightarrow R_4Sn + MgX(Cl)$

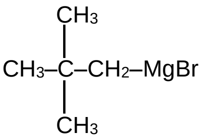
$R–Mg–X + PbCl_4 \longrightarrow R_4Pb + MgX(Cl)$

$R–Mg–X + CdCl_2 \longrightarrow R_2Cd + MgX(Cl)$

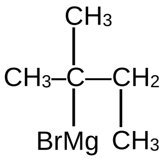
Illustrations

1. 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Br + Mg \xrightarrow{\text{Dry Ether}}$ product is

(A) 
$\left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2\right]_2 Mg$

(B) 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-MgBr$

(C) $(CH_3)_3C-MgBr$

(D) 
$CH_3-\overset{CH_3}{\underset{BrMg}{C}}-\underset{CH_3}{CH_2}$

2. CH_3MgBr reacts most easily with -
(A) Phenol (B) Acetone (C) Ethyl ethanoate (D) CH_3-CH_2-Br

3. Which of the following Grignard reagent is most reactive?
(A) RMgCl (B) RMgBr (C) RMgI (D) All have same reactivity

4. Which of the following is not organometallic compound?
(A) $(CH_3)_2Cd$ (B) $(CH_3CH_2)_2Zn$ (C) Ph-MgBr (D) C_6H_5-ONa

5. Reactivity and stability of following Grignard reagents is -
(1) CH_3-CH_2-MgX (2) $CH_2=CH-MgX$ (3) $CH_3C\equiv C-MgX$

Ans. 1. (B) 2. (A) 3. (C) 4. (D)
5. Reactivity order : 1 > 2 > 3 ; Stability order : 1 < 2 < 3

Section (E) : Acid base reaction

6.1 Test of acidic hydrogen (Liberation of H_2 on reaction with Na metal)

All active-H (attached with O, S, X, C_{sp} and active methylene) gives H_2 gas with Na or K metals.
$CH_3COOH + Na \longrightarrow CH_3COONa + \frac{1}{2}H_2\uparrow$

Illustrations

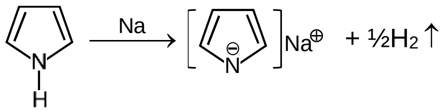
1. $H-O-H \xrightarrow{Na} NaOH + \frac{1}{2} H_2\uparrow$

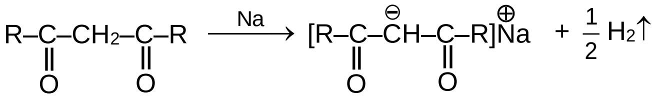
2. $R-O-H \xrightarrow{Na} R-ONa + \frac{1}{2} H_2\uparrow$

3. $RSH \xrightarrow{Na} RSNa + \frac{1}{2}H_2\uparrow$

4. $NH_3 \xrightarrow{Na} NaNH_2 + \frac{1}{2}H_2\uparrow$

5. $CH_3CONH_2 \xrightarrow{Na} CH_3CONHNa + \frac{1}{2}H_2\uparrow$

6. 

7. 
$R-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-R \xrightarrow{Na} [R-\underset{O}{\underset{\|}{C}}-\overset{\ominus}{C}H-\underset{O}{\underset{\|}{C}}-R]\overset{\oplus}{Na} + \frac{1}{2}H_2\uparrow$

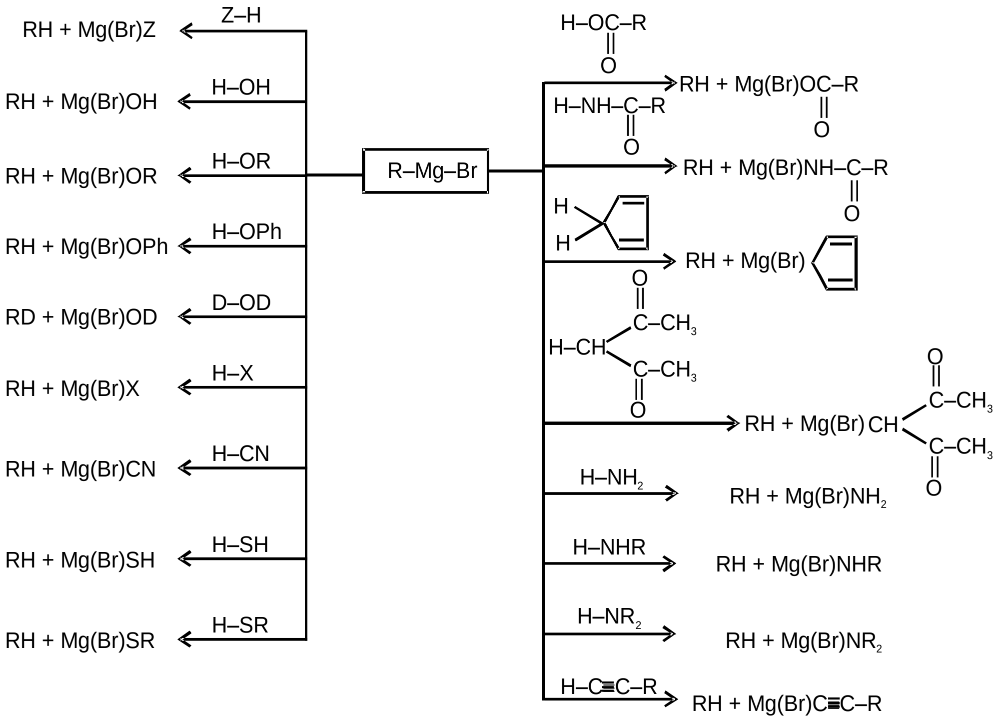
6.2 Acid base reaction with Grignard reagent

Compounds having reactive or acidic hydrogen give acid base reaction with grignard reagent.

$Z-H + R-MgX \longrightarrow R-H + Z-MgX$

Note : If R = CH_3 in R–Mg–Br then methane gas is released.

The reaction is used for estimation of active hydrogen atoms present in a molecule. This method is called **Zerewitinoff method** for estimation of active hydrogen atoms.



6.3 Feasibility of reactions

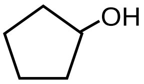
Reaction is feasibile if product is more stable than reactant.

1. Write the products, if reaction is feasible.

(i) $CH_3SO_3H \xrightarrow{NaHCO_3} CH_3SO_3Na + H_2O + CO_2$

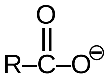
(ii) $PhCOOH \xrightarrow{NaH\overset{14}{C}O_3} PhCOONa + H_2O + \overset{14}{C}O_2$

(iii) $PhCH_2OH \xrightarrow{NaH\overset{14}{C}O_3}$ No reaction

(iv)

$\xrightarrow{NaHCO_3}$ No reaction

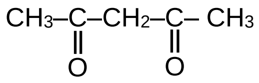
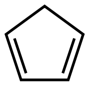
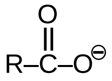
Worksheet-6(A)

Mark E or Y or N, where *(E = Equilibrium, Y = Yes, N = No)

Bases \ Acids	Ph–SH	Ph–OH	R–OH	R–C≡C–H	NH_3	R–NH_2
1.  $R–\overset{O}{\overset{\|\|}{C}}–O^{\ominus}$ (Weak base in water)						
2. Ph–$O^{\ominus}$ (Weak base in water)						

3. $OH^{\ominus}$ (Strong base in water)						
4. $R\text{–}O^{\ominus}$ (Strong base)						
5. $R\text{–}C\equiv C:^{\ominus}$ (Strong base)						
6. $H^{\ominus}$ (Very Strong base)						
7. $NH_2^{\ominus}$ (Very Strong base)						
8. $R^{\ominus}$ (Strongest base)						

Worksheet-6(B)

Bases / Acids	$Ph\text{–}SO_3H$	$R\text{–}COOH$	H_2CO_3	 $CH_3\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_2\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_3$	H_2O	
9.  $R\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}O^{\ominus}$ (Weak base in water)						
10. $Ph\text{–}O^{\ominus}$ (Weak base in water)						
11. $OH^{\ominus}$ (Strong base in water)						
12. $R\text{–}O^{\ominus}$ (Strong base)						
13. $R\text{–}C\equiv C:^{\ominus}$ (Strong base)						
14. $H^{\ominus}$ (Very Strong base)						
15. $NH_2^{\ominus}$ (Very Strong base)						
16. $R^{\ominus}$ (Strongest base)						

Answers

Worksheet-1

	Polar	Protic	Aprotic		Polar	Protic	Aprotic		Polar	Protic	Aprotic
1.	✓	✓	–	6.	✓	✓	–	10.	✓	×	✓
2.	✓	✓	–	7.	✓	×	✓	11.	×	×	✓
3.	✓	✓	–	8.	✓	×	✓	12.	×	×	✓
4.	✓	✓	–	9.	✓	×	✓	13.	×	×	✓
5.	✓	✓	–								

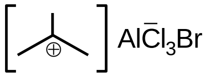
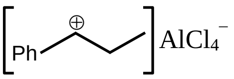
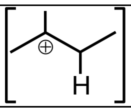
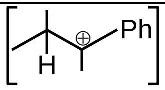
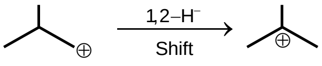
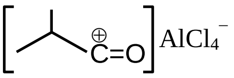
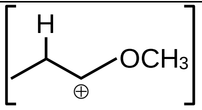
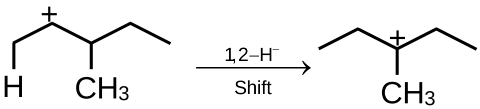
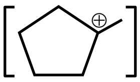
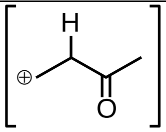
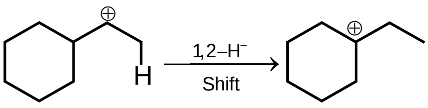
Worksheet – 2

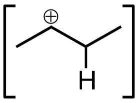
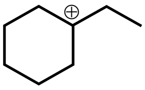
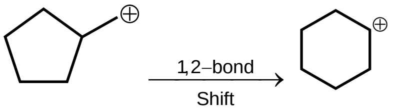
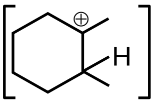
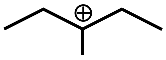
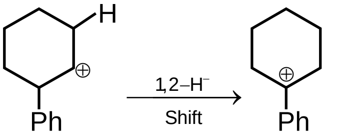
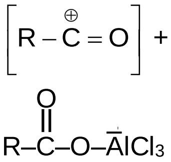
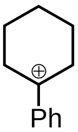
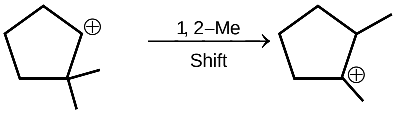
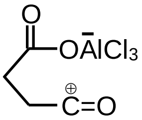
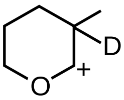
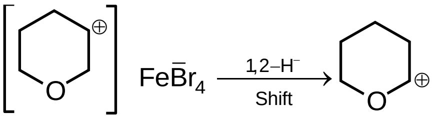
	Nucleophilicity	Basicity		Nucleophilicity	Basicity
1	$CH_3^- > NH_2^- > OH^- > F^-$	$CH_3^- > NH_2^- > OH^- > F^-$	6	$RO^- > HO^-$	$RO^- > HO^-$
2	$SiH_3^- > PH_2^- > SH^- > Cl^-$	$SiH_3^- > PH_2^- > SH^- > Cl^-$	7	$RCOO^- < PhO^- < HO^- < RO^-$	$RCOO^- < PhO^- < HO^- < RO^-$
3	$F^- < Cl^- < Br^- < I^-$	$F^- > Cl^- > Br^- > I^-$	8	$RCOO^- > RSO_3^-$	$RCOO^- > RSO_3^-$
4	$OH^- < SH^-$	$OH^- > SH^-$	9	$HO^- > H_2O$	$HO^- > H_2O$
5	$RO^- < RS^-$	$RO^- > RS^-$	10	$NH_2^- > NH_3$	$NH_2^- > NH_3$

Worksheet – 3

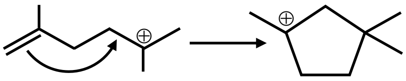
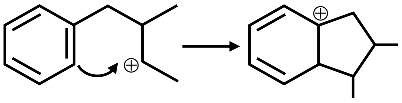
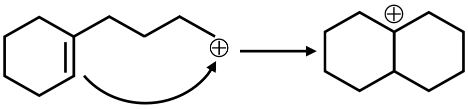
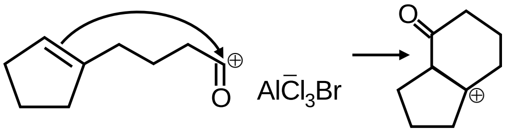
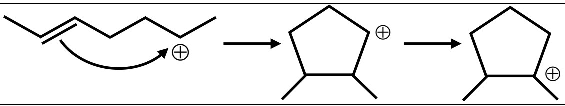
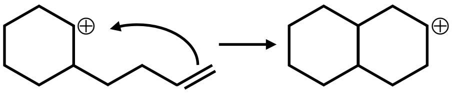
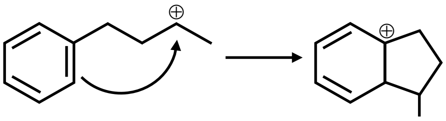
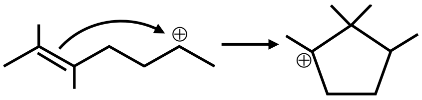
1.	$\overset{\ominus}{I} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} > \overset{\ominus}{F}$	6.	$NR_3^+ < SR_2^+$
2.	$CH_3^- < NH_2^- < OH^- < F^-$	7.	$CF_3SO_3^- > PhCOO^- > PhO^- > EtO^-$
3.	$R{-}COO^- > PhO^- > HO^- > RO^-$	8.	$H_2O > OH^-$
4.	$SH^- > OH^-$	9.	$N_2 > NH_2^-$
5.	(ONs^-) > (OTs^-)		

Worksheet-4 A,B,C

S.N.	Electrophile(4-A)	Electrophile(4-B)	Electrophile(4-C)
1		$CH_3CH_2\overset{\oplus}{C}HCH_3$	$\left[CH_3-CH_2-\overset{\oplus}{C}H_2\right]Al\bar{C}l_4 \xrightarrow[\text{Shift}]{1,2-H^-} CH_3-\overset{\oplus}{C}H-CH_3$
2			$\left[CH_3-CH_2-\overset{\oplus}{C}H_2\right] \xrightarrow[\text{Shift}]{1,2-H^-} CH_3-\overset{\oplus}{C}H-CH_3$
3	$CH_3-\overset{\oplus}{C}=O+Al\bar{C}l_4$		
4			
5			

6			
7			
8			
9			

Worksheet-4D

1		**5**	
2		**6**	
3		**7**	
4		**8**	

Worksheet-5.

1. Substitution reaction. **2.** Elimination reaction. **3.** Substitution reaction. **4.** Addition reaction.
5. Substitution reaction. **6.** Substitution reaction. **7.** Addition reaction. **8.** Substitution reaction.

Worksheet-6A

1.	**N**	**N**	**N**	**N**	**N**	**N**
2.	Y	**N**	**N**	**N**	**N**	**N**
3.	Y	Y	E	**N**	**N**	**N**
4.	Y	Y	E	**N**	**N**	**N**
5.	Y	Y	Y	**N**	**N**	**N**
6.	Y	Y	Y	Y	**N**	**N**
7.	Y	Y	Y	Y	**N**	**N**
8.	Y	Y	Y	Y	Y	Y

Worksheet-6B

9.	Y	E	**N**	**N**	**N**	**N**
10.	Y	Y	Y	E	**N**	**N**
11.	Y	Y	Y	Y	E	E
12.	Y	Y	Y	Y	E	E
13.	Y	Y	Y	Y	Y	Y
14.	Y	Y	Y	Y	Y	Y
15.	Y	Y	Y	Y	Y	Y
16.	Y	Y	Y	Y	Y	Y

Types of Reactions

[I] Substitution reaction

[A group is replaced by another group]

(a) Nucleophilic substitution

[Nucleophile substitutes leaving group]

(i) S_N1 Reaction

- Intermediate is carbocation
- Rearrangement is possible
- Racemisation

* Alkyl halide, Alcohol & Ether

(ii) S_N2 Reaction

- No intermediate , no rearrangement
- Inversion of configuration

* Alkyl halide, Alcohol & Ether

(iii) S_Ni Reaction

- Retaintion of configuration

* Alcohol

(iv) S_N2Th Reaction

- Tetrahedral intermediate is formed

* Acid & Acid derivatives

(v) S_N2Ar Reaction

- Intermediate is carbanion

* Aryl halide

(b) Electrophilic substitution

[Electrophile substitutes leaving group]

* Aromatic compounds

(c) Free radical substitution

[Free radical substitutes leaving group]

* Alkane

[II] Addition reaction

[Groups are added to substrate]

(a) Electrophilic addition

* Alkene & Alkyne

(b) Nucleophilic addition

- Racemisation

* Carbonyl compounds

(c) Free radical addition

- Anti Markovnikov product

* Alkene & Alkyne with HBr in presence of peroxides.

[III] Elimination reaction

[Groups are eliminated from substrate]

(a) E1 Reaction

- Intermediate is carbocation
- Rearrangement is possible

* Alkyl halide, Alcohol & Ether

(b) E2 Reaction

- No intermediate
- No rearrangement
- Anti elimination

* Alkyl halide

(c) E1cB Reaction

- Intermediate is carbanion
- D-Exchange is observed

(d) Ei Reaction

- No intermediate
- No rearrangement
- Syn elimination

* Ester

Types of reagents :

(a) Nucleophile : Electron rich species having pair of electrons.

(b) Electrophile : Electron deficient species having vacant p or d-orbital.

(c) Free radical : Electron deficient species having seven electrons in valence shell.