

GENERAL ORGANIC CHEMISTRY- III

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JEE(Advanced) Syllabus

Reagents: Electrophiles, Nucleophiles, Radicals.

Common type of Organic reactions: Substitution, Addition, Elimination and Rearrangement reactions.

Grignard reagent: Preparation and the reactions.

JEE(Main) Syllabus

Reagents: Electrophiles, Nucleophiles, Radicals.

Common type of Organic reactions: Substitution, Addition, Elimination and Rearrangement reactions.

Grignard reagent: Preparation and the reactions.



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

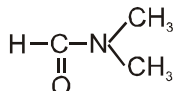
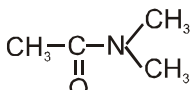
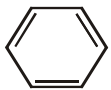
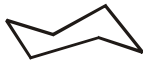
(i) **Polar protic** : A polar solvent which has acidic hydrogen and donate H^+ ion.
(examples: H_2O , ROH , RCOOH etc.)

(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.	$\text{CH}_3\text{CH}_2\text{OH}$				Polar protic solvent
4.	$\text{H}-\text{COOH}$				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.	$(\text{CH}_3)_2\text{S}=\text{O}$ (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.	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$				Non-polar solvent



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.

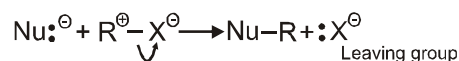
	Nucleophilicity	Basicity	Remarks / Reasons
Def.	The tendency to give e^- pair to an electron deficient carbon atom is defined as nucleophilicity. It is kinetic controlled property (KCP)	A base is a substance that can accept a proton by donating a pair of electrons. It is thermodynamic controlled property (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	$R-\overset{\overset{O}{\parallel}}{C}-O^-$ $R-\overset{\overset{O}{\parallel}}{S}(O)-O^-$	$R-\overset{\overset{O}{\parallel}}{C}-O^-$ $R-\overset{\overset{O}{\parallel}}{S}(O)-O^-$	" " "
9	HO^- H_2O	HO^- H_2O	Anion is better nucleophile and better base.
10	NH_2^- NH_3	NH_2^- NH_3	



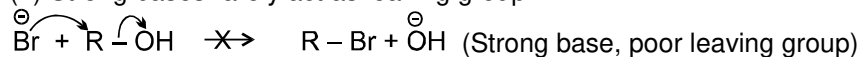
2.2 Leaving groups and leaving ability (Nucleofugality)

Weaker bases are always good leaving groups (nucleofuge).

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



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



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

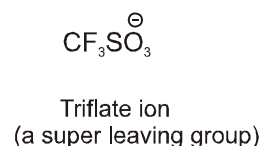
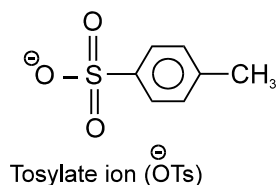
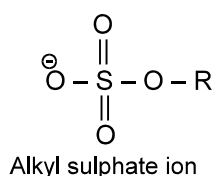
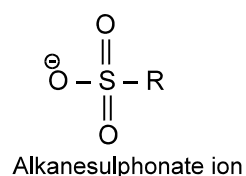
(3) Negative charge is stabilized either by dispersal or delocalization in leaving group.

Worksheet – 3

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

1.	$\text{I}^\ominus \quad \text{Br}^\ominus \quad \text{Cl}^\ominus \quad \text{F}^\ominus$	6.	$\text{NR}_3^+ \quad \text{SR}_2^+$
2.	$\text{CH}_3^\ominus \quad \text{NH}_2^\ominus \quad \text{OH}^\ominus \quad \text{F}^\ominus$	7.	$\text{CF}_3\text{SO}_3^\ominus \quad \text{PhCOO}^\ominus \quad \text{PhO}^\ominus \quad \text{EtO}^\ominus$
3.	$\text{R-COO}^\ominus \quad \text{PhO}^\ominus \quad \text{HO}^\ominus \quad \text{RO}^\ominus$	8.	$\text{H}_2\text{O} \quad \text{OH}^\ominus$
4.	$\text{SH}^\ominus \quad \text{OH}^\ominus$	9.	$\text{N}_2 \quad \text{NH}_2^\ominus$
5.	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> O^\ominus $\text{O}=\text{S}=\text{O}$ NO_2 </div> <div style="text-align: center;"> O^\ominus $\text{O}=\text{S}=\text{O}$ CH_3 </div> </div>	<p>$\text{ONs}^\ominus \rightarrow \text{Nosylate}$</p> <p>$\text{OTs}^\ominus \rightarrow \text{Tosylate}$</p> <p>$\text{OBs}^\ominus \rightarrow \text{Brosylate}$</p>	

Other good leaving groups are -



2.3 Electrophiles

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

(a) Positively charged species are $\text{H}^\oplus, \text{Cl}^\oplus, \text{Br}^\oplus, \text{NO}_2^\oplus, \text{CH}_3^\oplus, \text{H}_3\text{O}^\oplus$

(b) Species with vacant orbital at central atom are $\text{PCl}_5, \text{AlCl}_3, \text{SO}_2, \text{SO}_3, \text{BH}_3$ and carbenes.

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

Compounds	Reagents	Electrophile	Chemical reaction to generate electrophile
1. Alkane			NA
2. Alkene	H ⁺ (H ₂ SO ₄)	Carbocation	$\text{R}-\text{CH}=\text{CH}_2 \xrightarrow{\text{H}^+} \text{R}-\overset{+}{\text{CH}}-\text{CH}_3$
3. Alkyne	H ⁺ (H ₂ SO ₄)	Carbocation	$\text{R}-\text{C}\equiv\text{CH} \xrightarrow{\text{H}^+} \text{R}-\overset{+}{\text{C}}=\text{CH}_2$ (rarely formed)
4. Alcohol	H ⁺ (H ₂ SO ₄)	Carbocation	$\text{R}-\text{CH}_2-\text{OH} \xrightarrow{\text{H}^+} \text{R}-\overset{+}{\text{CH}}_2$
5. Alkylhalide	Lewis acid (AlCl ₃ , ZnCl ₂ , BF ₃ , FeBr ₃ ...)	Carbocation	$\text{RCH}_2\text{X} \xrightarrow{\text{AlCl}_3} \text{R}-\overset{+}{\text{CH}}_2 + \text{AlCl}_3\text{X}^-$
6. Acid halide	Lewis acid (AlCl ₃ , ZnCl ₂ , BF ₃)	Acyl Carbocation	$\text{R}-\text{COX} \xrightarrow{\text{AlCl}_3} \text{R}-\overset{+}{\text{C}}=\text{O} + \text{AlCl}_3\text{X}^-$
7. Acid	Lewis acid (AlCl ₃ , ZnCl ₂ , BF ₃)	Acyl Carbocation	$\text{R}-\text{COOH} \xrightarrow{\text{AlCl}_3} \text{R}-\overset{+}{\text{C}}=\text{O} + \text{AlCl}_3\text{OH}^-$
8. Halogen (Cl ₂ , Br ₂ , I ₂ , ICl, IBr, BrCl)	Lewis acid (AlCl ₃ , ZnCl ₂ , BF ₃)	Halonium ion (X ⁺)	$\text{X}_2 \xrightarrow{\text{AlCl}_3} \text{X}^+ + \text{AlCl}_3\text{X}^-$
9. Carbonyl Compound	H ⁺	Carbocation	$\text{R}_2\text{C}=\text{O} \xrightarrow{\text{H}^+} \text{R}_2-\overset{+}{\text{C}}-\text{OH}$
10. For nitration reaction	conc.HNO ₃ + conc.H ₂ SO ₄	Nitronium ion NO ₂ ⁺	$\begin{array}{c} \text{O} \\ \parallel \\ \text{O}=\text{N}-\boxed{\text{OH} + \text{H}}-\text{O}-\text{S}-\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{NO}_2^+ + \text{HSO}_4^- \\ \downarrow \quad \parallel \\ \text{O} \quad \text{O} \end{array}$
11. For sulphonation reaction	Conc. H ₂ SO ₄	SO ₃ (SO ₃ H ⁺)	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO}-\text{S}-\boxed{\text{OH} + \text{H}}-\text{O}-\text{S}-\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{SO}_3\text{H}^+ + \text{HSO}_4^- \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$
12. For nitrosation reaction	HNO ₂ + H ⁺	NO ⁺	$\begin{array}{c} \text{O} \\ \parallel \\ \text{O}=\text{N}-\boxed{\text{OH} + \text{H}}-\text{O}-\text{S}-\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{NO}^+ + \text{HSO}_4^- \\ \parallel \\ \text{O} \end{array}$
13. For Gattermann Koch reaction	CO + HCl + AlCl ₃	H- $\overset{+}{\text{C}}$ =O	$\text{CO} + \text{HCl} + \text{AlCl}_3 \longrightarrow \text{H}-\overset{+}{\text{C}}=\text{O} + \text{AlCl}_4^-$
14. For Gattermann reaction	HCN + HCl + AlCl ₃	H- $\overset{+}{\text{C}}$ =NH	$\text{HCN} + \text{HCl} + \text{AlCl}_3 \longrightarrow \text{H}-\overset{+}{\text{C}}=\text{NH} + \text{AlCl}_4^-$

**Worksheet-4 (A)**

Generation of electrophiles :

S.N.	Reactant	Reagent	Electrophile
1		$\xrightarrow{\text{AlCl}_3}$	
2		$\xrightarrow{\text{AlCl}_3}$	
3		$\xrightarrow{\text{Anhyd. AlCl}_3}$	
4		$\xrightarrow{\text{AlCl}_3}$	
5		$\xrightarrow{\text{H}_2\text{SO}_4}$	
6		$\xrightarrow{\text{H}_2\text{SO}_4}$	
7		$\xrightarrow{\text{H}_2\text{SO}_4}$	
8		$\xrightarrow{\text{AlCl}_3}$	
9		$\xrightarrow{\text{AlCl}_3}$	

Worksheet-4 (B)

Generation of electrophiles:

S.N.	Reactant	Reagent	Electrophile
1	$\text{CH}_3\text{--CH}_2\text{--CH=CH}_2$	$\xrightarrow{\text{H}_2\text{SO}_4}$	
2		$\xrightarrow{\text{H}_2\text{SO}_4}$	
3		$\xrightarrow{\text{H}_2\text{SO}_4}$	
4		$\xrightarrow{\text{H}^+}$	
5		$\xrightarrow{\text{H}^+}$	



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

Worksheet-4 (C)

Generation of electrophiles :

S.N.	Reactant	Reagent	Electrophile
1	$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--Cl}$	$\xrightarrow{\text{Anhy. AlCl}_3}$	
2	$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{OH}$	$\xrightarrow{\text{Conc. H}_2\text{SO}_4}$	
3		$\xrightarrow{\text{H}^+, \text{H}_2\text{SO}_4}$	
4		$\xrightarrow{\text{H}^+}$	
5		$\xrightarrow{\text{H}^+}$	
6		$\xrightarrow[\text{--H}_2\text{O}]{\text{H}^+}$	
7		$\xrightarrow{\text{H}^+}$	
8		$\xrightarrow{\text{AlCl}_3}$	
9		$\xrightarrow{\text{FeBr}_3}$	





Worksheet-4 (D)

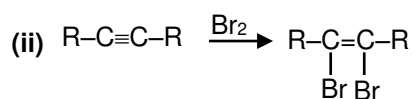
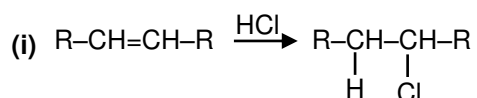
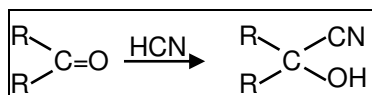
Generation of electrophiles :

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

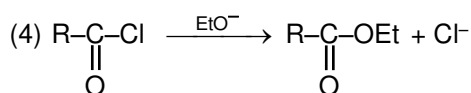
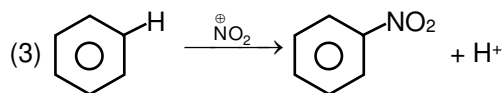
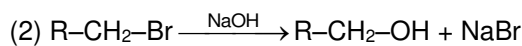
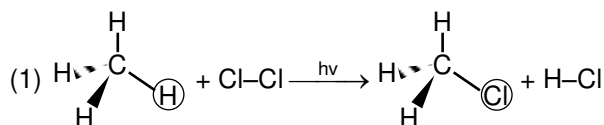
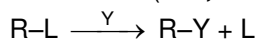
3.1 On the basis of nature of reactants

- (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.**

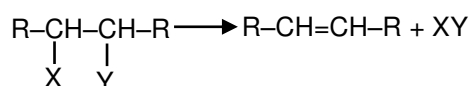




- (b) **Substitution reaction:** In which one group in a chemical compound is replaced by another group. Such reaction follows free radical substitution, aromatic electrophilic substitution (S_E), nucleophilic substitution (S_N1 , S_N2 , S_{Ni} , S_{N2Th}) etc.



- (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.



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 :

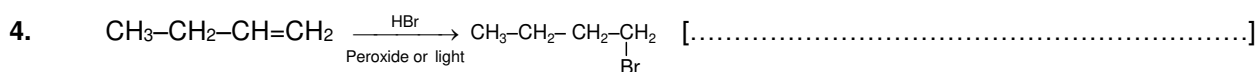
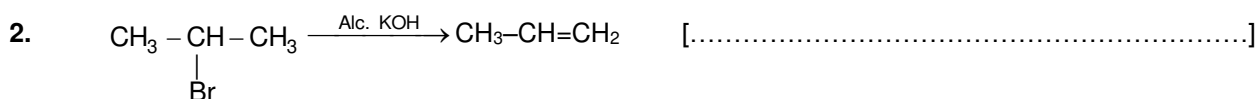
(a) **Nucleophile ($\ddot{\text{Nu}}^\ominus$):** Electron rich species having lone pair of electrons & complete octet at donor atom.

(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.





6. $\text{CH}_3\text{-}\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{C-Cl} \xrightarrow{\text{NaNH}_2} \text{CH}_3\text{-}\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{C-NH}_2 + \text{NaCl}$ [.....]
7. $\text{R-CH=O} \xrightarrow[\text{H}_2\text{SO}_4]{\text{KCN}} \text{R}-\underset{\text{OH}}{\text{CH}}-\text{CN} + \text{K}_2\text{SO}_4$ [.....]
8. Isopentane $\xrightarrow[\text{h}\nu]{\text{Br}_2}$ 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.

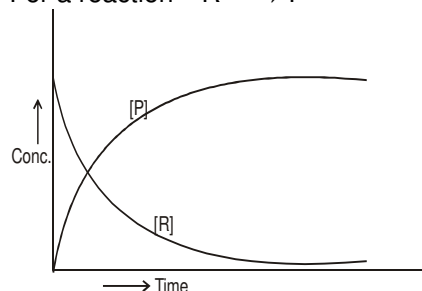
4.1 Rate of chemical reaction

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.

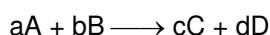
For a reaction $\text{R} \longrightarrow \text{P}$



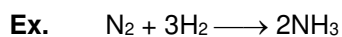
$$\text{Rate} = \frac{\Delta c}{\Delta t} = -\frac{\Delta[\text{R}]}{\Delta t} = \frac{\Delta[\text{P}]}{\Delta t}$$

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 stoichiometric coefficients. Rate of reaction is always defined for a balanced chemical equation.



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



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

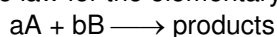
$$\text{Rate of reaction} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

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



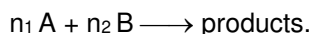
$$\text{rate} = k[\text{A}]^a[\text{B}]^b, \text{ where } a + b = 1, 2 \text{ or } 3.$$

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



✧ Rate of reaction:

$$R \propto [A]^p [B]^q \quad \dots\dots\dots (i)$$

$$R = k [A]^p [B]^q \quad \dots\dots\dots (ii)$$

(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

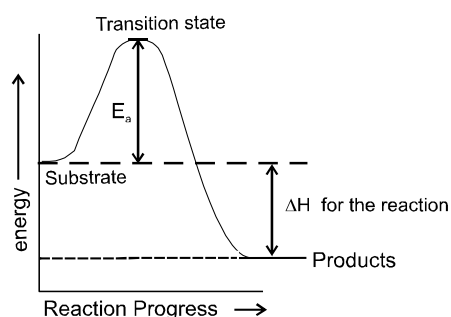
Molecularity of reaction	Order of reaction
1. It is defined as the no. of molecules of reactant taking part in a particular step.	1. It is defined as the sum of the power of concentration terms that appear in the rate law equation.
2. It is always a whole number . It can neither be zero nor fractional .	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.

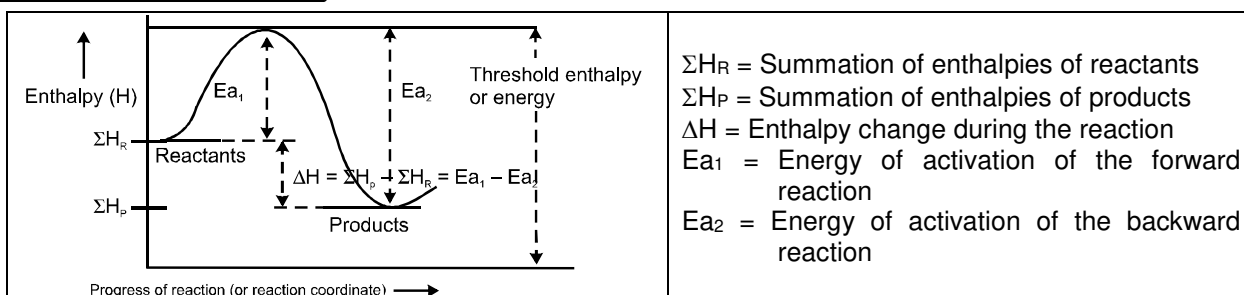
In equation : $S \rightarrow X \rightarrow P$,

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.



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.

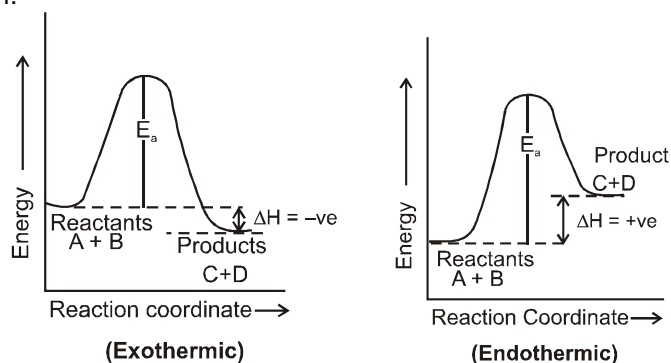
E_a = Threshold energy – Actual average energy of reactants

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

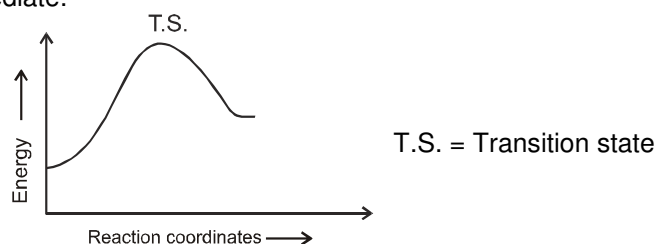
Greater the height of energy barrier, greater will be the energy of activation and slower will be the reaction at a given temperature.

4.6 Reaction profile

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

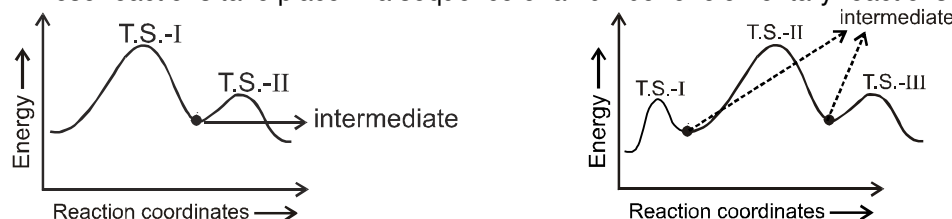


Elementary reactions: These reactions take place in single step without formation of any intermediate.



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.

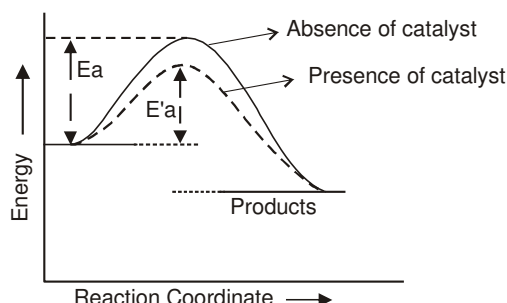
$$r = k[A]^m [B]^n$$

(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

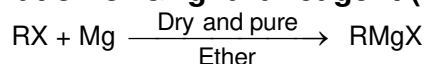
Organometallic compounds are the organic compounds in which a metal atom is directly attached to carbon atom through covalent bond or ionic bond.

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

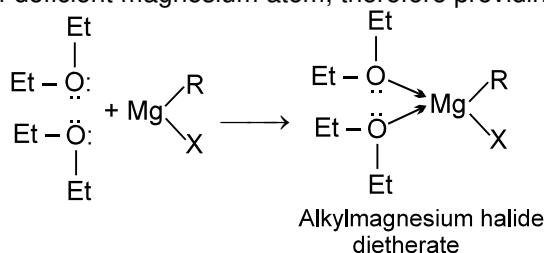
- Note:**
- (1) RONa (Sodium alkoxide), CH_3COONa (Sodium acetate), CH_3COOAg (Silver acetate), RSK (Potassium mercaptide) RNH_2 (N-Alkylpotassiumamide), $(\text{CH}_3\text{COO})_4\text{Pb}$ (Lead tetraacetate), etc are **not** organometallic compounds.
 - (2) It should be noted that $(\text{CH}_3)_4\text{Si}$ (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.)



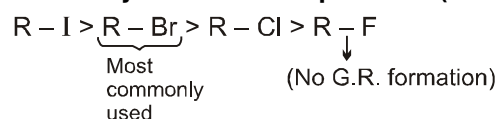
Dry ether is used as a solvent because it is a Lewis base that donates its lone pair of electrons to electron-deficient magnesium atom, therefore providing stability to the Grignard's reagent.





Process: To an ethereal 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)

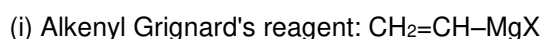


(b) Examples of Grignard's reagent

1. Saturated Aliphatic Grignard's reagent



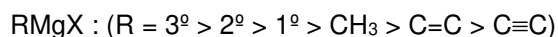
2. Unsaturated Aliphatic Grignard's reagent



(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-

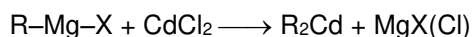
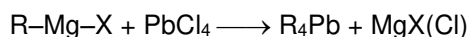
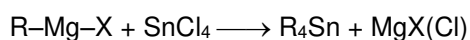
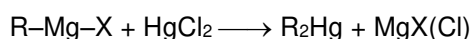
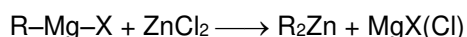


* Reactivity order of Grignard reagent with respect to different reactants (Substrates) is-
 Acidic hydrogen > $RCOCl > RCHO > RCOR > RCOOR'$

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.

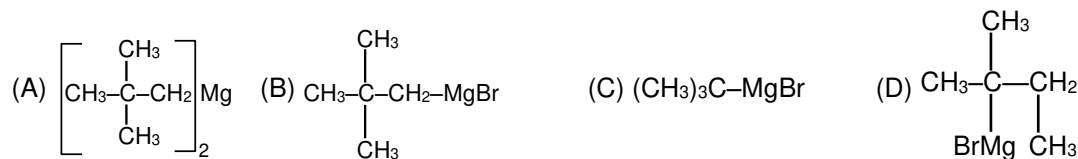
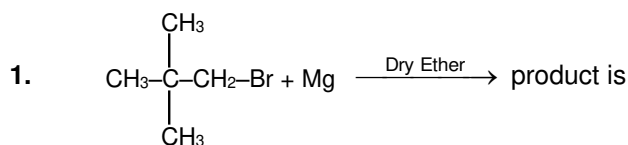
(2) If the alkyl part has more stable negative charge, then $RMgX$ is more stable and it will be less reactive.

(d) Synthesis of other organometallic compounds from Grignard reagent





Illustrations



2. CH_3MgBr reacts most easily with -
 (A) Phenol (B) Acetone (C) Ethyl ethanoate (D) $\text{CH}_3-\text{CH}_2-\text{Br}$
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) $(\text{CH}_3)_2\text{Cd}$ (B) $(\text{CH}_3\text{CH}_2)_2\text{Zn}$ (C) Ph-MgBr (D) $\text{C}_6\text{H}_5-\text{ONa}$
5. Reactivity and stability of following Grignard reagents is -
 (1) $\text{CH}_3-\text{CH}_2-\text{MgX}$ (2) $\text{CH}_2=\text{CH}-\text{MgX}$ (3) $\text{CH}_3\text{C}\equiv\text{C}-\text{MgX}$

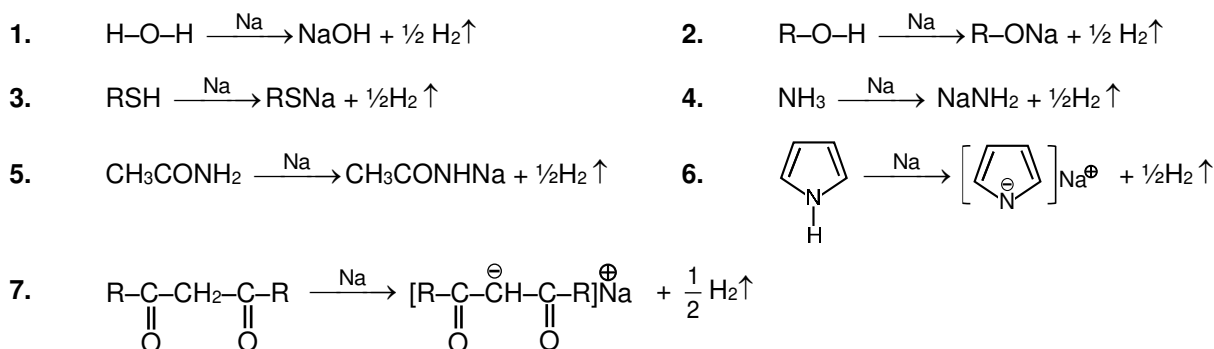
Ans. 1. (B) 2. (A) 3. (C) 4. (D)
 5. Reactivity order : $1 > 2 > 3$; Stability order : $1 < 2 < 3$

Section (E) : Acid base reaction

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

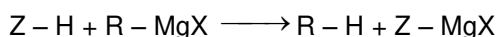
All active-H (attached with O, S, X, C_{sp} and active methylene) gives H_2 gas with Na or K metals.
 $\text{CH}_3\text{COOH} + \text{Na} \longrightarrow \text{CH}_3\text{COONa} + \frac{1}{2}\text{H}_2 \uparrow$

Illustrations



6.2 Acid base reaction with Grignard reagent

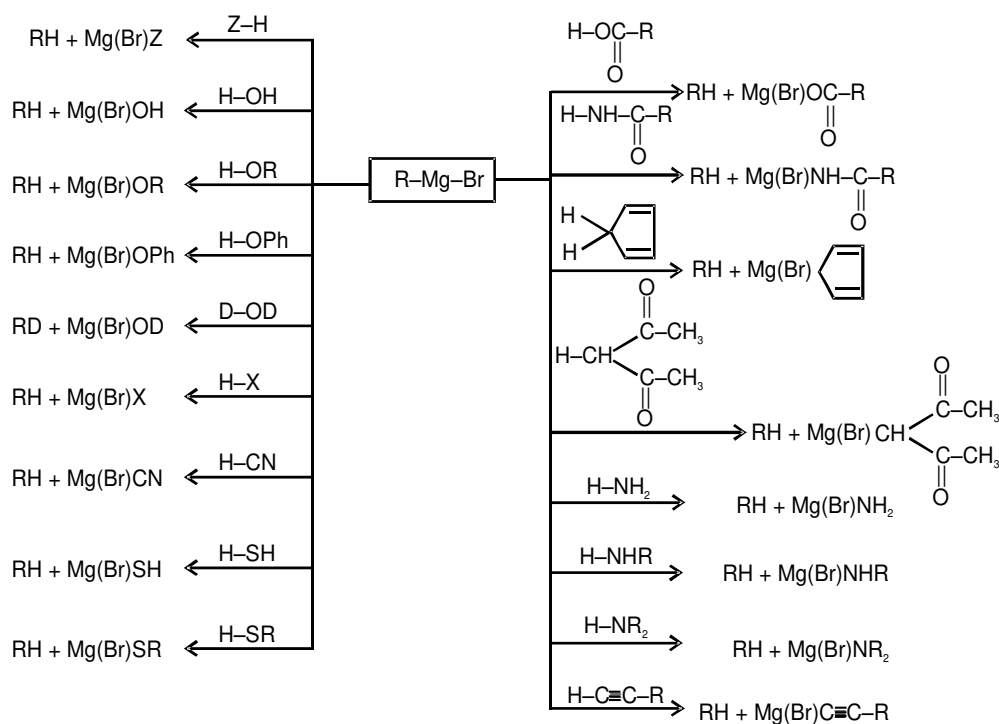
Compounds having reactive or acidic hydrogen give acid base reaction with grignard reagent.



Note : If $\text{R} = \text{CH}_3$ in $\text{R}-\text{Mg}-\text{Br}$ then methane gas is released.



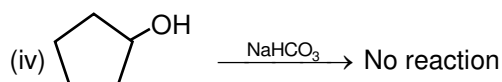
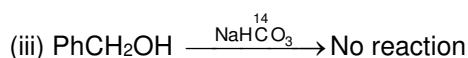
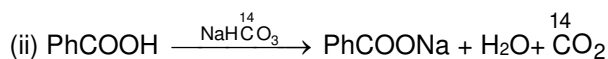
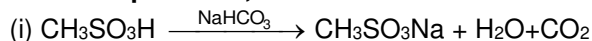
The reaction is used for estimation of active hydrogen atoms present in a molecule. This method is called **Zerewitinoff method** for estimation of active hydrogen atoms.



6.3 Feasibility of reactions

Reaction is feasible if product is more stable than reactant.

1. Write the products, if reaction is feasible.



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. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^\ominus$ (Weak base in water)						
2. $\text{Ph}-\text{O}^\ominus$ (Weak base in water)						





3. OH^\ominus (Strong base in water)						
4. R-O^\ominus (Strong base)						
5. $\text{R-C}\equiv\text{C:}^\ominus$ (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-SO ₃ H	R-COOH	H ₂ CO ₃	CH ₃ -C(=O)-CH ₂ -C(=O)-CH ₃	H ₂ O	
9. R-C(=O)-O^\ominus (Weak base in water)						
10. Ph-O^\ominus (Weak base in water)						
11. OH^\ominus (Strong base in water)						
12. R-O^\ominus (Strong base)						
13. $\text{R-C}\equiv\text{C:}^\ominus$ (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.	✓	✓	—								

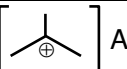
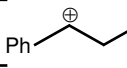
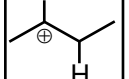
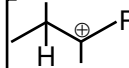
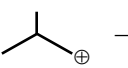
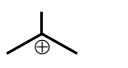
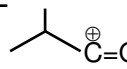
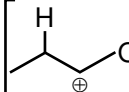
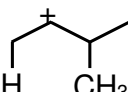
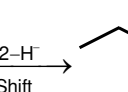
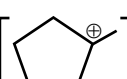
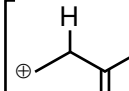
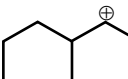
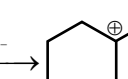
Worksheet – 2

	Nucleophilicity	Basicity		Nucleophilicity	Basicity
1	$\text{CH}_3^- > \text{NH}_2^- > \text{OH}^- > \text{F}^-$	$\text{CH}_3^- > \text{NH}_2^- > \text{OH}^- > \text{F}^-$	6	$\text{RO}^- > \text{HO}^-$	$\text{RO}^- > \text{HO}^-$
2	$\text{SiH}_3^- > \text{PH}_2^- > \text{SH}^- > \text{Cl}^-$	$\text{SiH}_3^- > \text{PH}_2^- > \text{SH}^- > \text{Cl}^-$	7	$\text{RCOO}^- < \text{PhO}^- < \text{HO}^- < \text{RO}^-$	$\text{RCOO}^- < \text{PhO}^- < \text{HO}^- < \text{RO}^-$
3	$\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$	$\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$	8	$\text{RCOO}^- > \text{RSO}_3^-$	$\text{RCOO}^- > \text{RSO}_3^-$
4	$\text{OH}^- < \text{SH}^-$	$\text{OH}^- > \text{SH}^-$	9	$\text{HO}^- > \text{H}_2\text{O}$	$\text{HO}^- > \text{H}_2\text{O}$
5	$\text{RO}^- < \text{RS}^-$	$\text{RO}^- > \text{RS}^-$	10	$\text{NH}_2^- > \text{NH}_3$	$\text{NH}_2^- > \text{NH}_3$

Worksheet – 3

1.	$\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$	6.	$\text{NR}_3^+ < \text{SR}_2^+$
2.	$\text{CH}_3^- < \text{NH}_2^- < \text{OH}^- < \text{F}^-$	7.	$\text{CF}_3\text{SO}_3^- > \text{PhCOO}^- > \text{PhO}^- > \text{EtO}^-$
3.	$\text{R-COO}^- > \text{PhO}^- > \text{HO}^- > \text{RO}^-$	8.	$\text{H}_2\text{O} > \text{OH}^-$
4.	$\text{SH}^- > \text{OH}^-$	9.	$\text{N}_2 > \text{NH}_2^-$
5.	$(\text{ONs}^-) > (\text{OTs}^-)$		

Worksheet-4 A,B,C

S.N.	Electrophile(4-A)	Electrophile(4-B)	Electrophile(4-C)
1	 AlCl_3Br	$\text{CH}_3\text{CH}_2\text{CH}^+\text{CH}_3$	$[\text{CH}_3 - \text{CH}_2 - \text{CH}_2^+] \text{AlCl}_4 \xrightarrow[\text{Shift}]{1,2-\text{H}^-} \text{CH}_3 - \text{CH}^+ - \text{CH}_3$
2	 AlCl_4^-		$[\text{CH}_3 - \text{CH}_2 - \text{CH}_2^+] \xrightarrow[\text{Shift}]{1,2-\text{H}^-} \text{CH}_3 - \text{CH}^+ - \text{CH}_3$
3	$\text{CH}_3 - \text{C}^+ = \text{O} + \text{AlCl}_4^-$		 $\xrightarrow[\text{Shift}]{1,2-\text{H}^-}$ 
4	 AlCl_4^-		 $\xrightarrow[\text{Shift}]{1,2-\text{H}^-}$ 
5			 $\xrightarrow[\text{Shift}]{1,2-\text{H}^-}$ 



6			
7			
8	$\left[\text{R}-\overset{\oplus}{\text{C}}=\text{O} \right] + \text{R}-\text{C}(=\text{O})-\text{O}-\text{AlCl}_3$		
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

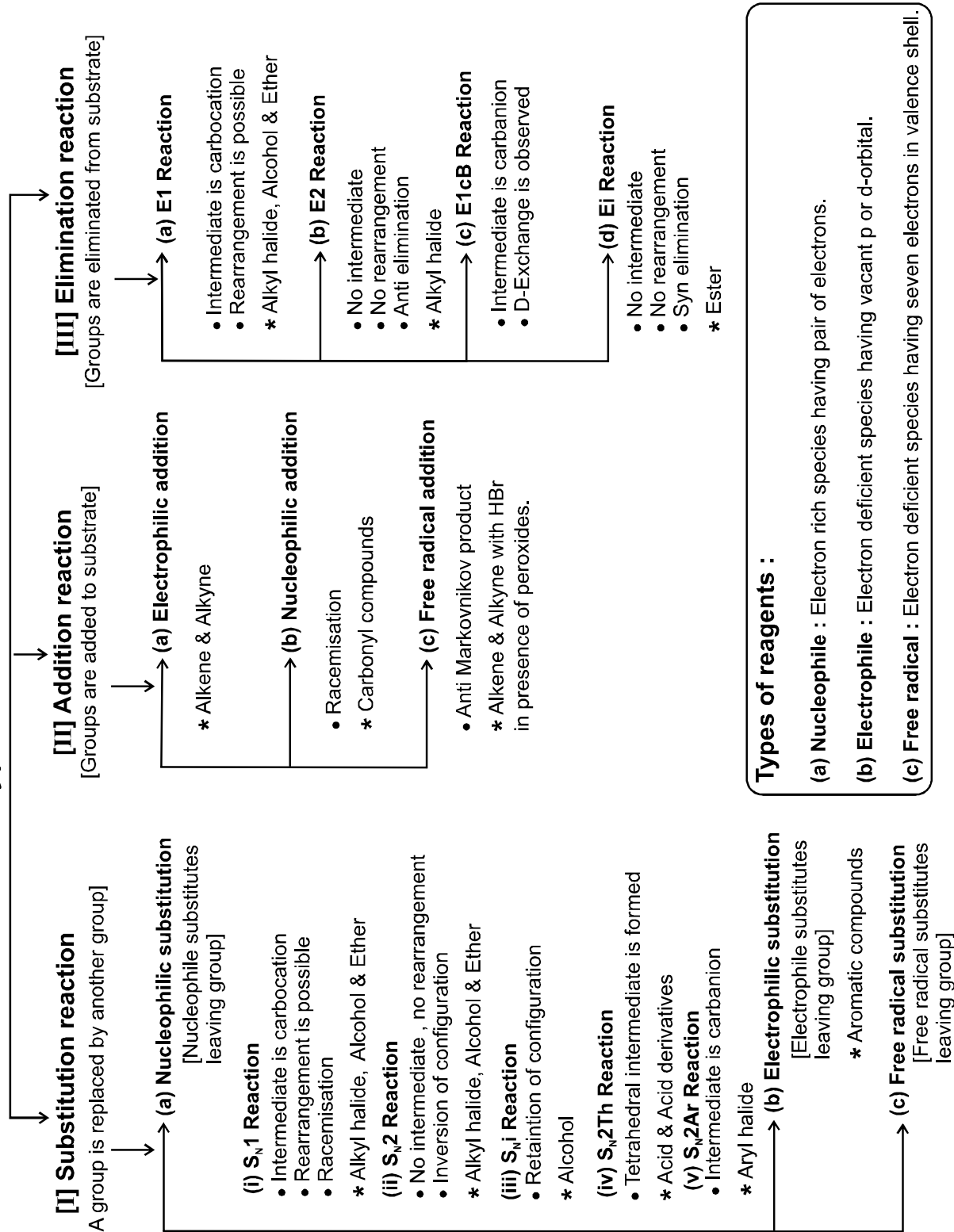
Worksheet-6B

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



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.



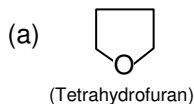
Exercise-1

Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

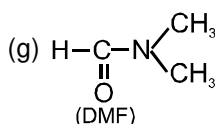
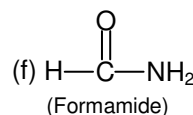
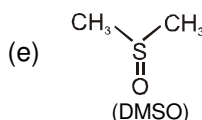
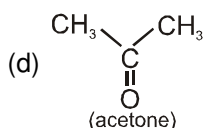
Section (A) : Electrophile, Nucleophile, Nucleophilicity, Leaving group ability & Solvent.

A-1. Label each of the following solvent as **protic or aprotic**.



(b) Acetonitrile

(c) Acetic acid



(h) Cyclohexane

(i) Amonia

A-2. Which of the followings act as nucleophile ?

(a) HS⁻

(b) BF₃

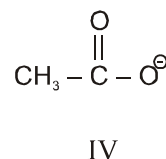
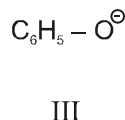
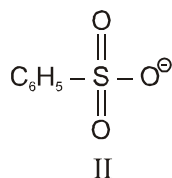
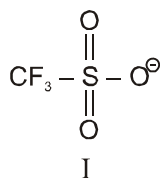
(c) C₂H₅-OH

(d) (CH₃)₃N⁻

(e) :CH₂

A-3. Define ambident nucleophile with an example.

A-4. In nucleophilic substitution reactions the leaving ability order for the following species is (when attached to the sp³ hybridised carbon)-



A-5. Which of the followings act as electrophile ?

(a) CN⁻

(b) H⁺

(c) Br⁺

(d) AlCl₃

(e) BH₃

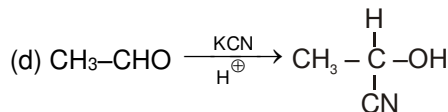
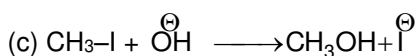
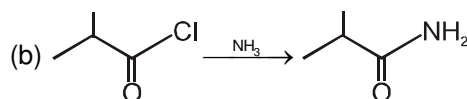
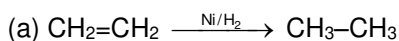
(f) CH₃-C⁺=O

(g) NH₃

(h) NO₂⁺

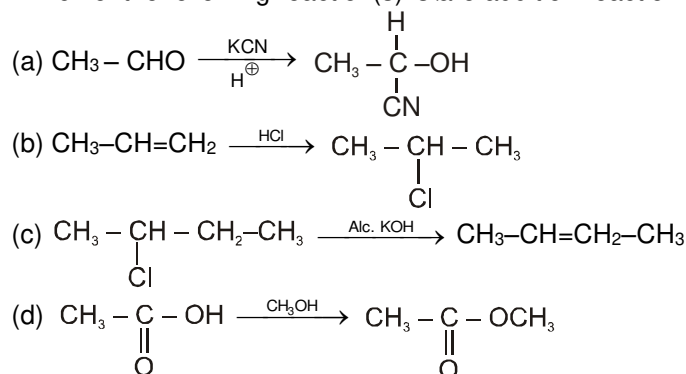
Section (B) : Types of organic reactions

B-1. Which of the following reaction(s) is/are substitution reaction ?

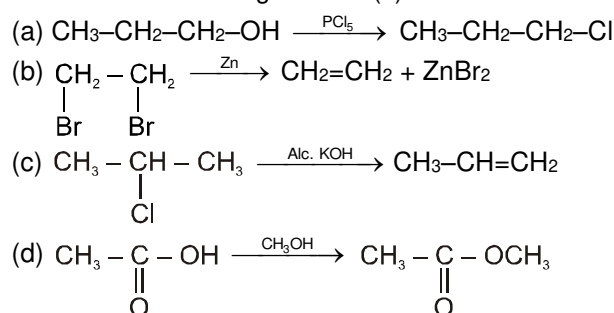




B-2. Which of the following reaction(s) is/are addition reaction ?



B-3. Which of the following reaction(s) is/are elimination reaction ?



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

C-1. Consider the chemical reaction, $2\text{A} + \text{B} \rightarrow \text{C}$.

The rate of this reaction can be expressed in terms of time derivatives of conc. of A, B or C. Give the correct relationship amongst rate expressions.

C-2. Give rate law for the single step reaction $\text{A} + \text{B} + 2\text{C} \rightarrow \text{D}$

C-3. For the reaction $\text{A} + \text{B} \rightarrow \text{Products}$, it is found that the order of A is 2 and of B is 1 in the rate expression. When concentration of both is doubled the rate will increase by a factor of :

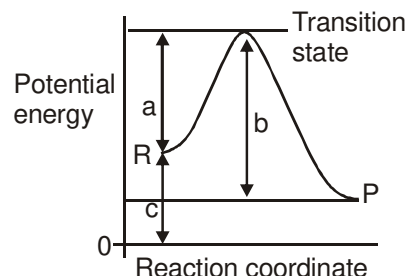
C-4. The rate of certain hypothetical reaction $\text{A} + \text{B} + \text{C} \rightarrow \text{products}$ is given by $r = -\frac{d[\text{A}]}{dt} = k [\text{A}]^{1/2} [\text{B}]^{1/3} [\text{C}]^{1/4}$.
Give the order of the reaction :

C-5. The activation energy for the forward reaction $\text{X} \rightarrow \text{Y}$ is 60 KJ mol^{-1} and ΔH is -20 KJ mol^{-1} . Calculate the activation energy for the backward reaction $\text{Y} \rightarrow \text{X}$.

C-6. The potential energy diagram for a reaction $\text{R} \rightarrow \text{P}$ is given below

Give answer of the following questions:

- Activation energy of forward reaction
- Activation energy of backward reaction
- Enthalpy of reaction
- Threshold energy
- Reaction is exothermic or endothermic.



Section (D) : Grignard reagent and reactions of acidic hydrogen

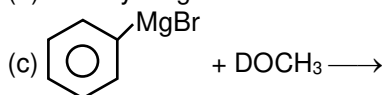
D-1. An organic compound which have molecular formula $\text{C}_4\text{H}_4\text{O}_3$, gives 3 moles of gas on treatment with methyl magnesium bromide. Give structure of the compound.



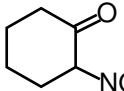
D-2. Predict the product of the following reactions.

(a) Methylmagnesium iodide + $D_2O \longrightarrow ?$

(b) Isobutylmagnesium iodide + Phenylacetylene $\longrightarrow ?$



D-3. Write the products

1.	$RC\equiv CH \xrightarrow{Na}$	6.	$(CH_3)_3N \xrightarrow{Na}$
2.	$RNH_2 \xrightarrow{Na}$	7.	$C_2H_5-O-C_2H_5 \xrightarrow{Na}$
3.	$R_2NH \xrightarrow{Na}$	8.	p-Nitrophenol $\xrightarrow{NaHCO_3}$
4.	$PhOH \xrightarrow{NaNH_2}$	9.	$Ph-C\equiv CH \xrightarrow{NaNH_2}$
5.	 \xrightarrow{Na}	10.	$H-C\equiv CH \xrightarrow{NaOH}$

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Electrophile, Nucleophile, Nucleophilicity, Leaving group ability & Solvent.

A-1. Which of the following is protic solvent ?

- (A) Acetone (B) Ethanol (C) DMF (D) Ether

A-2. Which of the following is polar aprotic solvent ?

- (A) DMF (B) NH_3 (C) H_2O (D) CH_3COOH

A-3. Non polar solvent is :

- (A) DMSO (B) Et_2O (C) DMA (D) CS_2

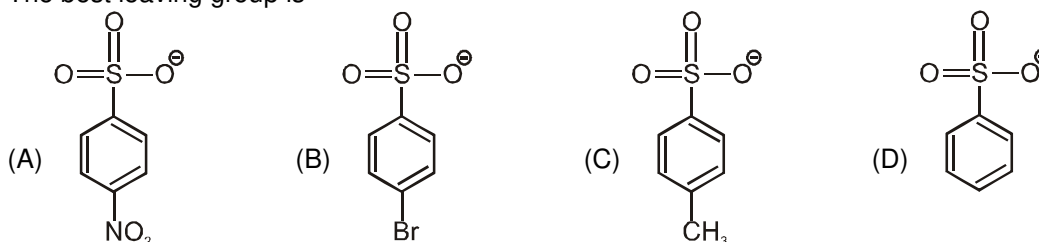
A-4. Which of the following is not a nucleophile ?

- (A) $AlCl_3$ (B) $(CH_3)_2NH$ (C) C_2H_5OH (D) H_2O

A-5. Which one of the following has maximum nucleophilicity ?

- (A) CH_3S^\ominus (B) $C_6H_5O^\ominus$ (C) Et_3N (D) F^\ominus

A-6. The best leaving group is-



A-7. Which of the following is best leaving group?

- (A) PhO^- (B) $PhCH_2O^-$ (C) HO^- (D) EtO^-

A-8. Which of the following is an electrophilic reagent?

- (A) H_2O (B) OH^- (C) NO_2^+ (D) None

A-9. Which of the following is not an electrophile ?

- (A) BH_3 (B) $CH_3-\overset{\oplus}{C}=O$ (C) NH_3 (D) $AlCl_3$

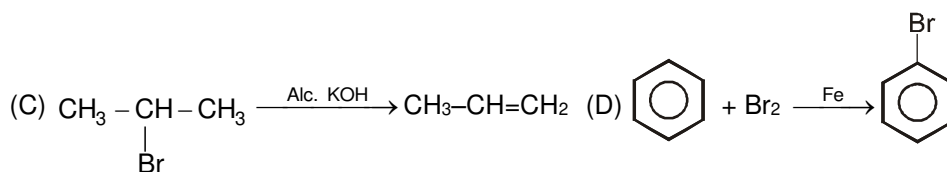
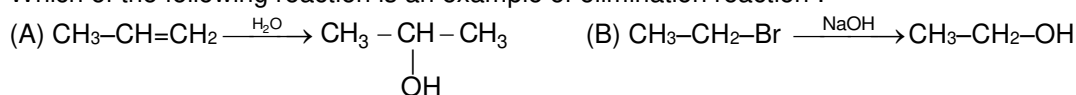
A-10. Which of the following is an electrophilic reagent?

- (A) H_2O (B) PH_3 (C) SO_3 (D) $Et-O-Et$

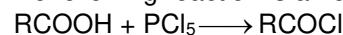


Section (B) : Types of organic reactions

B-1. Which of the following reaction is an example of elimination reaction :



B-2. The following reaction is an example of :



- (A) Acid-base reaction
(C) Addition reaction

- (B) Substitution reaction
(D) Elimination reaction

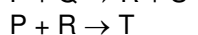
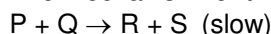
B-3. The following reaction is an example of $\text{CH}_3\text{-}\underset{\text{CH}_3}{\text{C}}\text{=CH}_2 \xrightarrow[\text{H}^+]{\text{H}_2\text{O}} \text{CH}_3\text{-}\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}\text{-CH}_3$

- (A) Acid-base reaction
(C) Addition reaction

- (B) Substitution reaction
(D) Elimination reaction

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

C-1. The mechanism for the reaction ($2\text{P} + \text{Q} \rightarrow \text{S} + \text{T}$) is given below-



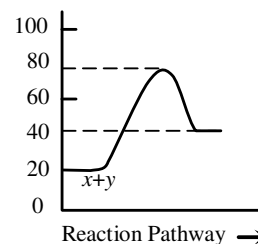
The rate law expression for the reaction is :

- (A) $r = k[\text{P}]^2[\text{Q}]$ (B) $r = k[\text{P}][\text{Q}]$ (C) $r = k[\text{P}][\text{R}]$ (D) $r = k[\text{P}]^2$

C-2. Consider the following energy profile for the reaction $\text{X} + \text{Y} = \text{R} + \text{S}$.

Which of the following statements about the reaction is not correct ?

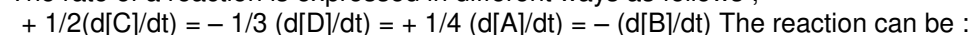
- (A) The energy of activation for the backward reaction is 80 kJ
(B) The forward reaction is endothermic
(C) The energy change of reaction is 20 kJ
(D) The energy of activation for the forward reaction is 60 kJ



C-3. The minimum energy required to permit a reaction is called-

- (A) Internal energy (B) Threshold energy (C) Activation energy (D) Free energy

C-4. The rate of a reaction is expressed in different ways as follows ;



- The reaction can be :
(A) $4\text{A} + \text{B} \longrightarrow 2\text{C} + 3\text{D}$ (B) $\text{B} + 3\text{D} \longrightarrow 4\text{A} + 2\text{C}$
(C) $4\text{A} + 2\text{B} \longrightarrow 2\text{C} + 3\text{D}$ (D) $\text{B} + (1/2)\text{D} \longrightarrow 4\text{A} + 3\text{C}$

C-5. $3\text{A} \rightarrow 2\text{B}$, rate of reaction $\frac{+d[\text{B}]}{dt}$ is equal to :

- (A) $-\frac{3}{2} \frac{d[\text{A}]}{dt}$ (B) $-\frac{2}{3} \frac{d[\text{A}]}{dt}$ (C) $-\frac{1}{3} \frac{d[\text{A}]}{dt}$ (D) $+2 \frac{d[\text{A}]}{dt}$

C-6. For the reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ overall order is found to be 3/2. The rate of reaction can be expressed as:

- (A) $[\text{H}_2][\text{Br}_2]^{1/2}$ (B) $[\text{H}_2]^{1/2} [\text{Br}_2]$ (C) $[\text{H}_2]^{3/2} [\text{Br}_2]^0$ (D) All of these

C-7. The rate law for the single step reaction $2\text{A} + \text{B} \rightarrow 2\text{C}$, is given by

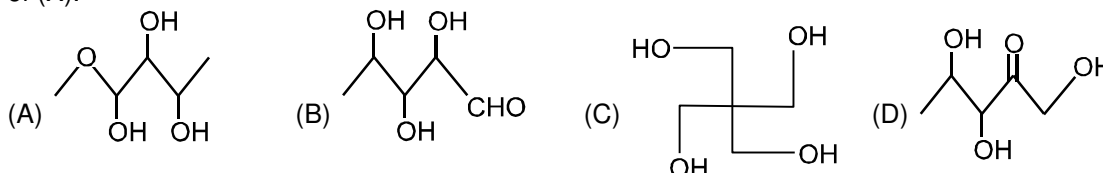
- (A) Rate = $K[\text{A}][\text{B}]$ (B) Rate = $K[\text{A}]^2[\text{B}]$ (C) Rate = $K[2\text{A}][\text{B}]$ (D) Rate = $K[\text{A}]^2[\text{B}]^0$



- C-8.** For a reaction $A + B \longrightarrow \text{products}$, the rate of the reaction was doubled when the concentration of A was doubled, the rate was again doubled when the conc. of A & B were doubled the order of the reaction with respect to A & B are :
- (A) 1, 1 (B) 2, 0 (C) 1, 0 (D) 0, 1

Section (D) : Grignard reagent and reactions of acidic hydrogen

- D-1.** $C_6H_5COOH + CH_3MgI \longrightarrow ?$
 (A) $C_6H_5COOMgI$ (B) CH_4 (C) Both A & B (D) none
- D-2.** $(CH_3)_3CMgCl$ on reaction with D_2O produces :
 (A) $(CH_3)_3CD$ (B) $(CH_3)_3COD$ (C) $(CD_3)_3CD$ (D) $(CD_3)_3COD$
- D-3.** A compound X ($C_5H_{12}O_4$) upon treatment with CH_3MgX gives 4 mole of methane. Identify the structure of (X).



- D-4.** Which of the following does not liberate hydrogen gas with NaH ?
 (A) CH_3-COOH (B) $CH_3-C(=O)-NH_2$ (C) $CH_3-C\equiv CH$ (D) $CH_3-CH_2NH_2$
- D-5.** The product X formed in the following reaction is $C_6H_5MgBr + CH_3OH \rightarrow X$
 (A) benzene (B) methoxybenzene (C) phenol (D) toluene
- D-6.** Which of the following reacts with $NaOH$ easily?
 (A) H_2CO_3 (B) NH_3 (C) $CH_3-C\equiv C-H$ (D) C_2H_5OH
- D-7.** Which of the following is not an organometallic compound?
 (A) CH_3MgX (B) $(CH_3CH_2)_2CuLi$ (C) CH_3-CH_2ZnBr (D) $(CH_3CH_2)_2NLi$
- D-8.** Which of the following R-X does not form Grignard reagent after reaction with Mg in presence of dry ether ?
 (A) CH_3-CH_2-I (B) CH_3-CH_2-Br (C) CH_3-CH_2-Cl (D) CH_3-CH_2-F
- D-9.** Which of the following Grignard reagent is most reactive?
 (A) CH_3-CH_2-MgBr (B) $CH_2=CH-MgBr$ (C) $CH_3-C\equiv CMgBr$ (D) $Ph-MgBr$
- D-10.** $CH_3-\underset{\substack{| \\ CH_3}}{CH}-CH_2-Br + Mg \xrightarrow{\text{Dry ether}} \text{Grignard Reagent}$
 Grignard reagent is-
- (A) $CH_3-\underset{\substack{| \\ CH_3}}{CH}-CH_2-MgBr$ (B) $CH_3-\overset{\substack{CH_3 \\ |}}{C}-MgBr$
 (C) $CH_3-CH_2-CH_2MgBr$ (D) $CH_3-CH_2-\underset{\substack{| \\ CH_3}}{CH}-MgBr$

PART - III : MATCH THE COLUMN

1. Match the List-I with List-II :

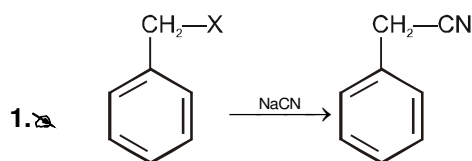
	List-I		List-II
(A)	I^\ominus	(p)	Strong nucleophile
(B)	$CF_3SO_3^\ominus$	(q)	Strong base
(C)	H_2O	(r)	Good leaving group
(D)	$CH_3CH_2O^\ominus$	(s)	Weak base



Exercise-2

Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE



In the above reaction rate is fastest, when (X) is :

- (A) $-\text{OH}$ (B) $-\text{NH}_2$ (C) $-\text{SO}_2\text{CH}_3$ (D) $-\text{O}-\text{SO}_2\text{CH}_3$

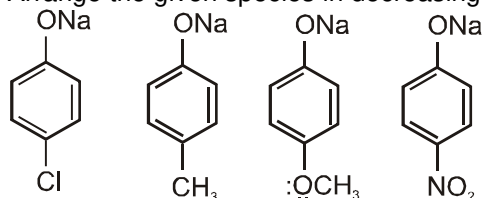
2. Correct arrangement of the following nucleophiles in the order of their nucleophilic strength is :

- (A) $\text{C}_6\text{H}_5\text{O}^- < \text{CH}_3\text{O}^- < \text{CH}_3\text{COO}^- < \text{OH}^-$
 (B) $\text{CH}_3\text{COO}^- < \text{C}_6\text{H}_5\text{O}^- < \text{CH}_3\text{O}^- < \text{OH}^-$
 (C) $\text{C}_6\text{H}_5\text{O}^- < \text{CH}_3\text{COO}^- < \text{CH}_3\text{O}^- < \text{OH}^-$
 (D) $\text{CH}_3\text{COO}^- < \text{C}_6\text{H}_5\text{O}^- < \text{OH}^- < \text{CH}_3\text{O}^-$

3. Which of the followings is not nucleophile ?

- (A) HS^- (B) $:\text{CH}_2$ (C) $\text{C}_2\text{H}_5\text{OH}$ (D) $(\text{CH}_3)_3\ddot{\text{N}}$

4. Arrange the given species in decreasing order of their nucleophilicity :



- (A) $2 > 1 > 3 > 4$ (B) $3 > 2 > 1 > 4$ (C) $4 > 1 > 2 > 3$ (D) $2 > 3 > 1 > 4$

5. Addition reactions involves

- (A) Cleavage of a σ -bond and formation of a new σ -bond.
 (B) Cleavage of two σ -bonds and formation of a new π -bond.
 (C) Cleavage of a π -bond and formation of two new σ -bonds.
 (D) None of these.

6. Following mechanism has been proposed for a reaction $2\text{A} + \text{B} \rightarrow \text{D} + \text{E}$

Step-1: $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ (slow)

Step-2: $\text{A} + \text{C} \rightarrow \text{E}$ (fast)

The rate law expression for the reaction is :

- (A) $\text{rate} = k[\text{A}]^2 [\text{B}]$ (B) $\text{rate} = k [\text{A}] [\text{B}]$ (C) $\text{rate} = k [\text{A}]^2$ (D) $\text{rate} = k[\text{A}][\text{C}]$

7. Differential rate law for the chemical reaction, $2\text{A}(\text{g}) \longrightarrow \text{B}(\text{g}) + 3\text{C}(\text{g})$ is-

- (A) $\text{Rate} = -\frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt} = \frac{d[\text{C}]}{dt}$ (B) $\text{Rate} = \frac{1}{2} \frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt} = \frac{1}{3} \frac{d[\text{C}]}{dt}$
 (C) $\text{Rate} = -\frac{1}{2} \frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt} = \frac{1}{3} \frac{d[\text{C}]}{dt}$ (D) $\text{Rate} = \frac{1}{2} \frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = -\frac{1}{3} \frac{d[\text{C}]}{dt}$

8. The total energy for molecules to enter into chemical reaction is called?

- (A) Kinetic energy (B) Potential energy
 (C) Threshold energy (D) Activation energy



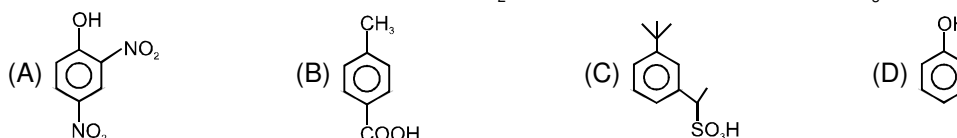
9. Activation energy of a reaction is:
 (A) The energy released during the reaction.
 (B) The energy evolved when activated complex is formed.
 (C) Minimum amount of energy needed to overcome the potential barrier of reaction.
 (D) The energy needed to form one mole of the product.

10. Which of the following reactions yield benzene?
 (A) $\text{PhMgBr} + \text{CH}_3\text{Br}$ (B) $\text{PhMgBr} + \text{CH}_2\text{O}$
 (C) $\text{PhBr} + \text{H}_2\text{O}$ (D) $\text{PhMgBr} + \text{CH}_3\text{C}\equiv\text{CH}$

11. $\text{C}_4\text{H}_{10}\text{O}$ (Y) + $\text{CH}_3\text{MgBr} \longrightarrow$ No Reaction, Y is :

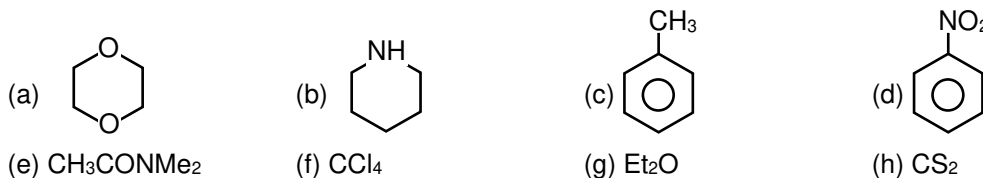


12. Which of the following will not release CO_2 gas after reaction with NaHCO_3 ?

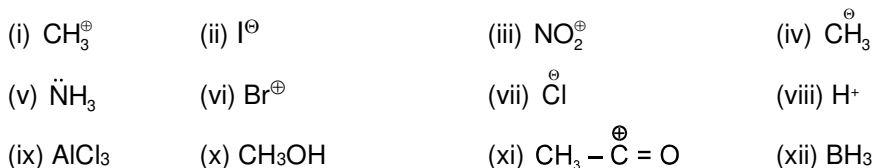


PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

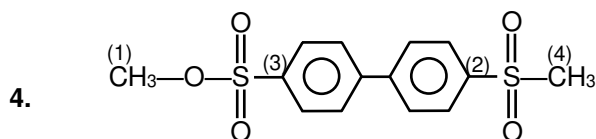
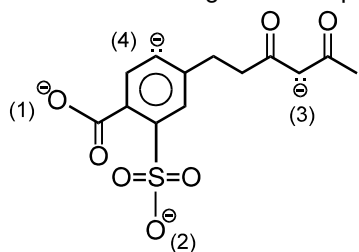
1. How many of the following are aprotic solvents?



2. Among the following X is the number of electrophiles and Y is the number of nucleophiles. Report your answer as X Y.



3. Which is the strongest nucleophilic site in the following species ?

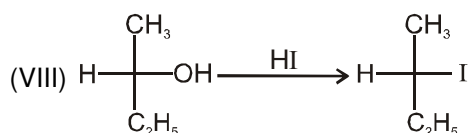
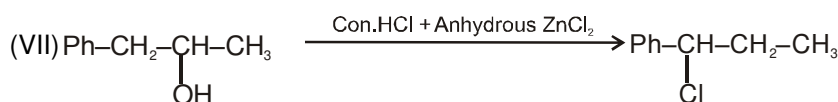
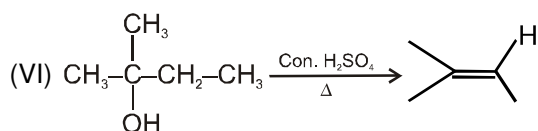
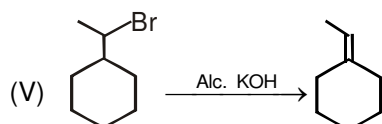
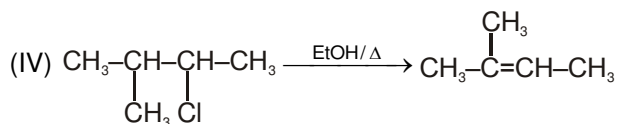
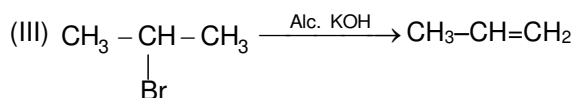
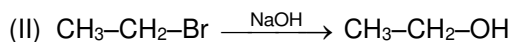
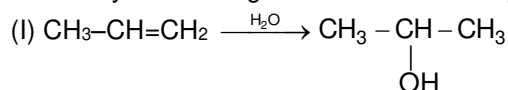


In the above structure which carbon atom is directly attached with a good leaving group?





5. How many reactions given below are examples of elimination reactions?



6. The rate of certain hypothetical reaction $\text{A} + \text{B} \rightarrow \text{products}$ is given by $r = \frac{-d[\text{A}]}{dt} = K [\text{A}]^{1/2} [\text{B}]^{3/2}$

The order of the reaction is :

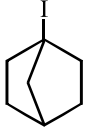
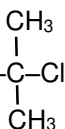
7. For the reaction $\text{A} + \text{B} \rightarrow \text{Products}$, it is found that the order of A is 2 and of B is 3 in the rate expression. When concentration of both is doubled the rate will increase by a factor of :

8. An alcohol (A), 0.22 g of this alcohol liberates 56 ml of CH_4 at STP on reaction with CH_3MgBr . Write the molecular weight of alcohol which satisfy these conditions.

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

- Electrophiles are
 (A) Electron deficient species (B) having atleast one pair of electron
 (C) Electron rich species (D) Electron pair acceptor
- Which of the following is/are ambident nucleophile(s) ?
 (A) NO_2^- (B) CN^- (C) SCN^- (D) PhO^-
- The correct order of leaving group ability is/are :
 (A) $\text{PhSO}_3^- > \text{PhCOO}^-$ (B) $\text{CF}_3\text{SO}_3^- > \text{CCl}_3\text{SO}_3^-$
 (C) $\text{CN}^- > \text{I}^-$ (D) $\text{NH}_2^- > \text{OH}^-$



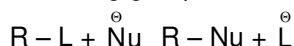
4. Which of the following liberate hydrogen gas with NaH?
 (A) CH_3COOH (B) $\text{CH}_3\text{C(=O)NH}_2$ (C) $\text{CH}_3\text{C}\equiv\text{CH}$ (D) $\text{CH}_3\text{CH}_2\text{OH}$
5. Which of the following are organometallic compounds ?
 (A) $\text{CH}_3\text{CH}_2\text{Na}$ (B) $(\text{CH}_3\text{CH}_2)_2\text{Zn}$ (C) Ph-MgBr (D) $\text{CH}_3\text{CH}_2\text{ONa}$
6. Which of the following alkyl halide(s) can form Grignard reagent after reaction with Mg in presence of dry ether?
 (A) $\text{CH}_3\text{C}\equiv\text{C-Br}$ (B) Ph-Cl (C)  (D) 
7. Which of the following(s) can be used as solvent for Grignard reagent preparation?
 (A) Diethyl ether (B) Acetone (C) Carbon tetrachloride (D) THF
8. Grignard reagents act as-
 (A) Strong Nucleophile (B) Electrophile
 (C) Strong base (D) Carbanion

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

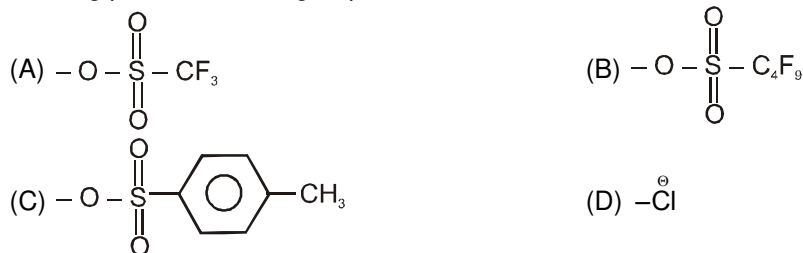
Comprehension # 1

Nucleophilic aliphatic substitution reaction is given by those compounds which have electron rich groups as leaving groups. Less is the basicity of the leaving group, more is its leaving power.

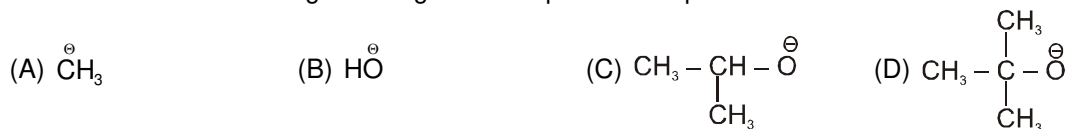


In the given reaction, L is the leaving group which leaves as nucleophile. Nu^- is the incoming group which is always nucleophilic in character. The reaction is nucleophilic substitution reaction which can be unimolecular or bimolecular reaction.

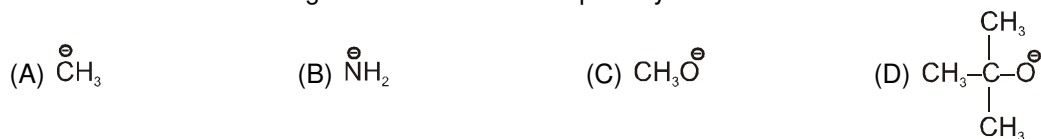
1. Leaving power of which group is maximum ?



2. Which one of the following is strong base but poor nucleophile ?



3. Which one of the following has maximum nucleophilicity ?

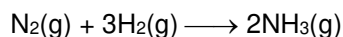




Exercise-3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Consider the chemical reaction,



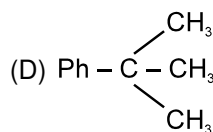
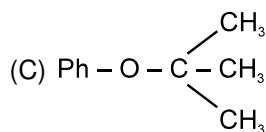
The rate of this reaction can be expressed in terms of time derivatives of conc. of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ or $\text{NH}_3(\text{g})$. Identify the correct relationship amongst rate expressions : [JEE-2002, 3/225]

- (A) $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$ (B) $\text{Rate} = \frac{d[\text{N}_2]}{dt} = -3 \frac{d[\text{H}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$
 (C) $\text{Rate} = \frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$ (D) $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$

2. Phenyl magnesium bromide reacting with t-Butyl alcohol gives [JEE-2005, 3/60]

(A) $\text{Ph}-\text{OH}$

(B) $\text{Ph}-\text{H}$



PART - II : JEE (MAIN) / AIEEE ONLINE PROBLEMS (PREVIOUS YEARS)

1. The increasing order of nucleophilicity of the following nucleophiles is :

(a) CH_3CO_2^-

(b) H_2O

(c) CH_3SO_3^-

(d) OH^-

[JEE(Main) 2019 Online (11-04-19)S2, 4/120]

(1) $(\text{d}) < (\text{a}) < (\text{c}) < (\text{b})$

(2) $(\text{b}) < (\text{c}) < (\text{a}) < (\text{d})$

(3) $(\text{a}) < (\text{d}) < (\text{c}) < (\text{b})$

(4) $(\text{b}) < (\text{c}) < (\text{d}) < (\text{a})$



Answers

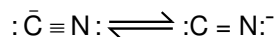
EXERCISE - 1

PART - I

A-1. Protic solvent (c, f, i) ; Aprotic solvent (a, b, d, e, g, h)

A-2. a, c, d

A-3. Ambident nucleophile: The species which have more than one nucleophilic site for reaction are called ambident nucleophiles. For example, cyanide ion:



A-4. I > II > IV > III

A-5. b, c, d, e, f, h

B-1. (b), (c)

B-2. (a), (b)

B-3. (b), (c)

C-1. $\text{Rate} = -\frac{1}{2} \frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = \frac{d[\text{C}]}{dt}$

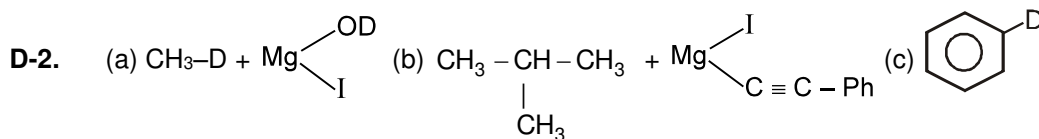
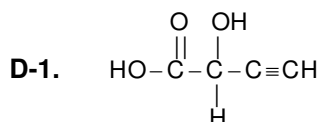
C-2. $\text{Rate} = k [\text{A}][\text{B}][\text{C}]^2$

C-3. 8

C-4. $\frac{13}{12}$

C-5. 80 KJ mol⁻¹

C-6. (i) a; (ii) b; (iii) a – b; (iv) a + c; (v) Exothermic



D-3.

1.	$\text{RC}\equiv\text{CNa} + \frac{1}{2}\text{H}_2 \uparrow$	6.	No reaction
2.	$\text{RNHNa} + \frac{1}{2}\text{H}_2 \uparrow$	7.	No reaction
3.	$\text{R}_2\text{NNa} + \frac{1}{2}\text{H}_2 \uparrow$	8.	p-Nitrophenoxide + CO ₂
4.	$\text{PhONa} + \text{NH}_3$	9.	$\text{Ph-C}\equiv\text{CNa} + \text{NH}_3 \uparrow$
5.		10.	No reaction



**PART - II**

- | | | | | |
|------------------|-----------------|-----------------|-----------------|------------------|
| A-1. (B) | A-2. (A) | A-3. (D) | A-4. (A) | A-5. (A) |
| A-6. (A) | A-7. (A) | A-8. (C) | A-9. (C) | A-10. (C) |
| B-1. (C) | B-2. (B) | B-3. (C) | C-1. (B) | C-2. (A) |
| C-3. (B) | C-4. (B) | C-5. (B) | C-6. (D) | C-7. (B) |
| C-8. (C) | D-1. (C) | D-2. (A) | D-3. (C) | D-4. (D) |
| D-5. (A) | D-6. (A) | D-7. (D) | D-8. (D) | D-9. (A) |
| D-10. (A) | | | | |

PART - III

1. (A) - p, r, s ; (B) - r, s ; (C) - r, s ; (D) - p, q

EXERCISE – 2**PART - I**

- | | | | | |
|----------------|----------------|---------------|---------------|----------------|
| 1. (D) | 2. (D) | 3. (B) | 4. (B) | 5. (C) |
| 6. (B) | 7. (C) | 8. (C) | 9. (C) | 10. (D) |
| 11. (D) | 12. (D) | | | |

PART - II

- | | | | |
|------------------------------|--------------|--------------|--------------|
| 1. 7 | 2. 75 | 3. 4 | 4. 1 |
| 5. 4 (III, IV, V, VI) | 6. 2 | 7. 32 | 8. 88 |

PART - III

- | | | | | |
|------------------|-----------------|-----------------|------------------|-----------------|
| 1. (AD) | 2. (ABC) | 3. (AB) | 4. (ABCD) | 5. (ABC) |
| 6. (ABCD) | 7. (AD) | 8. (ACD) | | |

PART - IV

- | | | |
|---------------|---------------|---------------|
| 1. (B) | 2. (D) | 3. (A) |
|---------------|---------------|---------------|

EXERCISE – 3**PART - I**

- | | |
|---------------|---------------|
| 1. (A) | 2. (B) |
|---------------|---------------|

PART - II

1. (2)



Additional Problems for Self Practice (APSP)

☞ Marked questions may have for revision questions.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Marks: 100

Max. Time : 1 Hour

Important Instructions:

A. General :

- The test paper is of 1 hour duration.
- The Test Paper consists of **25** questions and each questions carries **4** Marks. Test Paper consists of **Two** Sections.

B. Test Paper Format and its Marking Scheme:

- Section-1 contains **20** multiple choice questions. Each question has four choices (1), (2), (3) and (4) out of which **ONE** is correct. For each question in Section-1, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. In all other cases, minus one (**-1**) mark will be awarded.
- Section-2 contains **5** questions. The answer to each of the question is a **Numerical Value**. For each question in Section-2, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. No negative marks will be answered for incorrect answer in this section. In this section answer to each question is **NUMERICAL VALUE** with two digit integer and decimal upto two digit. If the numerical value has more than two decimal places **truncate/round-off** the value to **TWO** decimal placed.


SECTION-1

This section contains **20** multiple choice questions. Each questions has four choices (1), (2), (3) and (4) out of which Only **ONE** option is correct.

- Which of the following can act as nucleophile ?
(1) EtO^- (2) EtNH_2 (3) CN^- (4) All of these
- Which of the following has maximum nucleophilicity among them ?
(1) NaOH (2) NaI (3) NaSH (4) KCN
- The following reaction is an example of $\text{RCOOH} + \text{NaOH} \longrightarrow \text{RCOONa} + \text{H}_2\text{O}$
(1) Acid-base reaction (2) Substitution reaction
(3) Addition reaction (4) Elimination reaction
- Which of the following can not react with Grignard reagent?
(1) PhSH (2) $\text{CH}\equiv\text{CH}$ (3) PhCH_3 (4) PhNHCH_3
- Which of the following Grignard reagent is most reactive towards acidic H ?
(1) $\text{CH}_3\text{---CH}_2\text{MgBr}$ (2) $\text{CH}_3\text{---CHMgBr}$ (3) $\text{CH}_3\text{---}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{---MgBr}$ (4) $\text{CH}_2=\text{CHMgBr}$
- Which of the following Grignard reagent is most reactive ?
(1) $\text{CH}_3\text{---CH}_2\text{---MgCl}$ (2) $\text{CH}_3\text{---CH}_2\text{---MgBr}$
(3) $\text{CH}_3\text{---CH}_2\text{---MgI}$ (4) All have same reactivity
- Which solvent is non-polar solvent ?
(1) $\text{CH}_3\text{---CO---CH}_3$ (2) $\text{CH}_3\text{---SO---CH}_3$ (3) CH_3COOH (4) Cyclohexane





8. Which one of the following has minimum nucleophilicity ?
 (1) $(\text{CH}_3)_3\text{CLi}$ (2) NaNH_2 (3) CH_3ONa (4) NaOH
9. Which of the following is a nucleophile ?
 (1) $\cdot\text{CH}_3$ (2) $\text{CH}_2\cdot$ (3) $\text{CH}_3-\ddot{\text{N}}$ (4) $\text{CH}_3-\ddot{\text{N}}\text{H}_2$
10. The correct order of leaving ability is :
 (1) $\text{OH}^- > \text{H}_2\text{O}$ (2) $\text{OH}^- > \text{SH}^-$ (3) $\text{CH}_3\text{COO}^- > \text{CH}_3\text{CH}_2\text{O}^-$ (4) $\text{Cl}^- > \text{I}^-$
11. In which of reaction  will be obtained as a product ?
 (1) $\text{PhMgBr} + \text{CH}_3\text{C}(\text{CH}_3)_2\text{OH}$ (2) $\text{PhMgBr} + \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
 (3) $\text{PhMgBr} + \text{CH}_3\text{CH}_2\text{CH}_3$ (4) $\text{PhMgBr} + \text{Cyclohexene}$
12. In which of the following reaction CH_4 will be obtained?
 (i) $\text{CH}_3\text{MgBr} + \text{CH}_3\text{C}\equiv\text{CH}$ (ii) $\text{CH}_3\text{MgBr} + \text{CH}_2\text{C}(\text{COOH})_2$
 (iii) $\text{CH}_3\text{MgBr} + \text{HCN}$ (iv) $\text{CH}_3\text{MgBr} + \text{CH}_2\text{C}(\text{CH}_3)_2\text{C}(=\text{O})_2$
 (1) (i), (ii) & (iii) (2) (i), (ii), (iii) & (iv) (3) (iii) & (iv) (4) (iii) & (i), (iv)
13. Which of these statements is incorrect about nucleophiles ?
 (1) Nucleophiles have an unshared electron pair and can make use of this to react with an electron deficient species.
 (2) The nucleophilicity of an element (as electron donor) generally increases on going down a group in the periodic table.
 (3) A nucleophile is electron-deficient species
 (4) All good nucleophiles are good bases when we deal across the period.
14. Which species will not be considered as an electrophile ?
 (1) CH_3CH_2^+ (2) AlCl_3 (3) NH_3 (4) SO_3
15. Leaving group ability order amongst the following is
 (I) $\text{C}_6\text{H}_5\text{O}^-$ (II) $p\text{-(CH}_3\text{)}\text{C}_6\text{H}_4\text{O}^-$ (III) $p\text{-(OCH}_3\text{)}\text{C}_6\text{H}_4\text{O}^-$ (IV) $p\text{-(NO}_2\text{)}\text{C}_6\text{H}_4\text{O}^-$
 (1) $\text{I} > \text{II} > \text{III} > \text{IV}$ (2) $\text{III} > \text{II} > \text{I} > \text{IV}$
 (3) $\text{IV} > \text{I} > \text{II} > \text{III}$ (4) $\text{IV} > \text{III} > \text{II} > \text{I}$
16. $\text{H}-\text{C}(=\text{O})-\text{NH}-\text{H} + \text{NaH} \xrightarrow{\text{(excess)}} \text{X} + \text{H}_2 \uparrow$
 X is :
 (1) $\text{H}-\text{C}(=\text{O})-\text{NHNa}$ (2) $\text{H}-\text{C}(=\text{O})-\text{NNa}_2$ (3) $\text{Na}-\text{C}(=\text{O})-\text{NH}_2$ (4) $\text{H}-\text{C}(=\text{O})-\text{H}$
17. Consider an endothermic reaction $\text{X} \rightarrow \text{Y}$ with the activation energies E_b and E_f for the backward and forward reaction, respectively. In general.
 (1) $E_b < E_f$ (2) $E_b > E_f$ (3) $E_b = E_f$ (4) none of these

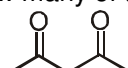
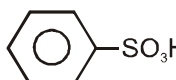

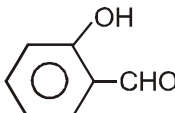
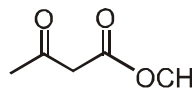
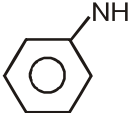
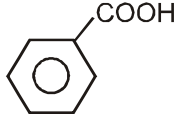
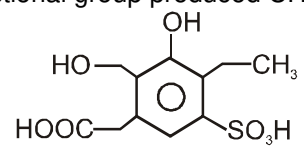




18. The differential rate law equation for the elementary reaction $A + 2B \xrightarrow{K} 3C$, is :
- (1) $-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A][B]^2$ (2) $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k[A]^2[B]$
- (3) $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k[A][B]^2$ (4) None of these
19. Which of the following is an organometallic compound?
- (1) $(CH_3)_4Si$ (2) $(CH_3COO)_4Pb$ (3) $(CH_3)_2Cd$ (4) CH_3-CH_2SK
20. CH_3-CH_2MgBr reacts most readily with-
- (1) CH_3-CH_2-OH (2) $H-C(=O)-H$ (3) $CH_3-C(=O)-O-R$ (4) CH_3-CH_2-Br

SECTION-2

This section contains 5 questions. Each question, when worked out will result in **Numerical Value**.

21. For an elementary process $2X + Y \rightarrow Z + W$, the molecularity is :
22. When 184 gm ethanol react with excess of CH_3MgCl then methane gas is evolved. Calculate mass of methane gas obtained.
23. How many of the following compound give benzene on reaction with $PhMgBr$?
- (1)  (2)  (3)  (4) $CH_3-C \equiv CH$
- (5)  (6) CH_3NH_2 (7)  (8) 
- (9) CH_3SH (10) 
24. How many functional group produced CH_4 gas by the reaction of compound (I) with CH_3MgBr ?
- (I) 
25. What is the order of a reaction, when rate expression is $= k[A]^{3/2}[B]^{-1}$?

Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25					
Ans.										



PART - II : JEE (MAIN) / AIEEE OFFLINE PROBLEMS (PREVIOUS YEARS)

- For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A][B]^2$ then the order of the reaction is:
 $A + 2B \rightarrow C$ $R = [A][B]^2$ [AIEEE- 2002, 3/225]
 (1) 3 (2) 6 (3) 5 (4) 7
- The differential rate law for the reaction $H_2 + I_2 \rightarrow 2HI$ is : [AIEEE- 2002,3/225]
 (1) $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$ (2) $\frac{d[H_2]}{dt} = \frac{d[I_2]}{dt} = \frac{1}{2} \frac{d[HI]}{dt}$
 (3) $\frac{1}{2} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$ (4) $-2 \frac{d[H_2]}{dt} = -2 \frac{d[I_2]}{dt} = + \frac{d[HI]}{dt}$
- Rate of the reaction is fastest when Z is : [AIEEE-2004, 3/225]

$$R-\overset{\overset{O}{\parallel}}{C}-Z + Nu^- \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-Nu + Z^-$$
 (1) Cl (2) $OCOCH_3$ (3) OC_2H_5 (4) NH_2
- A reaction involving two different reactants can never be: [AIEEE- 2005, 3/225]
 (1) unimolecular reaction (2) first order reaction
 (3) second order reaction (4) bimolecular reaction [AIEEE- 2005, 3/225]
- The treatment of CH_3MgX with $CH_3C \equiv C-H$ produces [AIEEE-2008, 3/105]
 (1) $CH_3C \equiv C-CH_3$ (2) $CH_3-\overset{\overset{H}{\mid}}{C}=\overset{\overset{H}{\mid}}{C}-CH_3$ (3) CH_4 (4) $CH_3-CH=CH_2$
- Phenyl magnesium bromide reacts with methanol to give - [AIEEE-2006, 3/165]
 (1) a mixture of anisole and $Mg(OH)Br$ (2) a mixture of benzene and $Mg(OMe)Br$
 (3) a mixture of toluene and $Mg(OMe)Br$ (4) a mixture of phenol and $Mg(Me)Br$
- For a reaction $\frac{1}{2}A \rightarrow 2B$, rate of disappearance of 'A' related to the rate of appearance of 'B' by the expression. [AIEEE- 2008, 3/105]
 (1) $-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$ (2) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (3) $-\frac{d[A]}{dt} = 4 \frac{d[B]}{dt}$ (4) $-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$

PART - III : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

- Which of the following is NOT a nucleophile ? [NSEC-2001]
 (A) H_2 (B) CH_3OH (C) H_2O (D) NH_3
- The group which contains a Lewis acid, a nucleophile and a radical is [NSEC-2003]
 (A) C_2H_6 , Br^+ , Cl atom (B) NH_3 , $AlCl_3$, H atom (C) H^+ , BF_3 , H_2O^+ (D) C_6H_6 , CH_3^+ , Cl_2
- The non-nucleophilic base is [NSEC-2004]
 (A) CN^- (B) $-OC(Me)_3$ (C) HO^- (D) MeO^-
- Which of the following series contains only nucleophiles ? [NSEC-2008]
 (A) NH_3 , H_2O , CN^- , I^- (B) $AlCl_3$, NH_3 , H_2O , I^-
 (C) $AlCl_3$, BF_3 , H_2O , NH_3 (D) $AlCl_3$, BF_3 , NO_2^+ , NH_3
- The best nucleophile among the following is : [NSEC-2011]
 (A) H_2O (B) CH_3SH (C) Cl^- (D) NH_3
- A catalyst accelerates a reaction primarily by stabilizing the [NSEC-2012]
 (A) substrate (B) product (C) intermediate (D) transition state



7. Which of the following information is not provided by a reaction mechanism? [NSEC-2012]
 (A) Which bonds are formed and which bonds are broken
 (B) Which intermediates and transition states are formed
 (C) Energy content of the reacting species
 (D) Which is the slowest step
8. The product X formed in the following reaction is [NSEC-2014]

$$C_6H_5MgBr + CH_3OH \rightarrow X$$
 (A) benzene (B) methoxybenzene (C) phenol (D) toluene
9. The correct order of the ability of the leaving group is [NSEC-2017]
 (A) $OCOC_2H_5 > OC_2H_5 > OSO_2Et > OSO_2CF_3$ (B) $OC_2H_5 > OCOC_2H_5 > OSO_2CF_3 > OSO_2Me$
 (C) $OSO_2CF_3 > OSO_2Me > OCOC_2H_5 > OC_2H_5$ (D) $OCOC_2H_5 > OSO_3CF_3 > OC_2H_5 > OSO_2Me$

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

Important Instructions

A. General :

- The test is of 1 hour duration.
- The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format

- Each part consists of five sections.
- Section 1 contains 6 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- Section 2 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- Section 3 contains 5 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
- Section 4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme :

- For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (-1) mark will be awarded.
- For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
- For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

This section contains 6 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

1. 0.34 g of hydrocarbon when treated with excess of CH_3MgI liberates 112 mL of CH_4 at STP the structure of hydrocarbon is
- (A) $CH_3 - \underset{\begin{array}{c} | \\ CH_3 \end{array}}{CH} - C \equiv C - H$ (B) $CH_3 - C \equiv C - H$
- (C) $CH_3 - CH_2 - C \equiv C - H$ (D) $CH_3 - CH_2 - \underset{\begin{array}{c} | \\ CH_3 \end{array}}{CH} - C \equiv C - H$



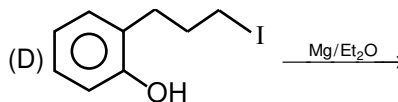
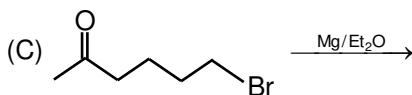
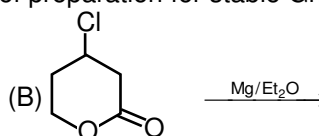
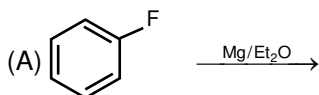


2. Decreasing order of relative nucleophilicity of the following nucleophiles in polar protic solvent is :
- $\text{SH}^\ominus, \text{AcO}^\ominus, \text{PhO}^\ominus, \text{OH}^\ominus, \text{H}_2\text{O}$
- (A) $\text{SH}^\ominus > \text{OH}^\ominus > \text{H}_2\text{O} > \text{AcO}^\ominus > \text{PhO}^\ominus$ (B) $\text{SH}^\ominus > \text{OH}^\ominus > \text{PhO}^\ominus > \text{AcO}^\ominus > \text{H}_2\text{O}$
 (C) $\text{SH}^\ominus > \text{PhO}^\ominus > \text{OH}^\ominus > \text{H}_2\text{O} > \text{AcO}^\ominus$ (D) $\text{OH}^\ominus > \text{SH}^\ominus > \text{PhO}^\ominus > \text{AcO}^\ominus > \text{H}_2\text{O}$
3. Which of the following is not nucleophile ?
 (A) OH^- (B) CN^- (C) BF_3 (D) NH_3
4. Which of the following is not correct order for nucleophilicity as well as basicity both ?
 (A) $\text{HO}^\ominus \gg \text{H}_2\text{O}$ (B) $\text{NH}_2^\ominus \gg \text{NH}_3$ (C) $\text{I}^\ominus > \text{Br}^\ominus > \text{Cl}^\ominus > \text{F}^\ominus$ (D) $\text{MeO}^\ominus > \text{HO}^\ominus > \text{MeCOO}^\ominus$
5. Catalyst increases the rate of reaction generally because:
 (A) it decreases ΔH (B) it increases ΔH
 (C) it decreases activation energy (D) it increases activation energy
6. A five carbon atoms alkyne forms a sodium salt and gives H_2 gas on treatment with sodamide. The alkyne may be
 (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ (B) $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$
 (C) $(\text{CH}_3)_2\text{CHC}\equiv\text{CH}$ (D) Either (A) or (C).

Section-2 : (One or More than one options correct Type)

This section contains 7 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

7. The correct nucleophilicity order(s) is/are :
 (A) $\text{CH}_3\text{O}^\ominus > \text{CH}_3^\ominus$ (B) $\text{CH}_3\text{S}^\ominus > \text{CH}_3\text{SH}$
 (C) $\text{NH}_3 > \text{H}_2\text{O}$ (D) $(\text{CH}_3\text{CH}_2)_3\text{N} > (\text{CH}_3\text{CH}_2)_3\text{P}$
8. Choose the correct order of nucleophilicity.
 (A) $\text{F}_{(\text{DMSO})}^\ominus > \text{Cl}_{(\text{DMSO})}^\ominus > \text{Br}_{(\text{DMSO})}^\ominus > \text{I}_{(\text{DMSO})}^\ominus$
 (B) $\text{F}_{(\text{aq})}^\ominus > \text{Cl}_{(\text{aq})}^\ominus > \text{Br}_{(\text{aq})}^\ominus > \text{I}_{(\text{aq})}^\ominus$
 (C) $\text{I}_{(\text{aq})}^\ominus > \text{Br}_{(\text{aq})}^\ominus > \text{Cl}_{(\text{aq})}^\ominus > \text{F}_{(\text{aq})}^\ominus$
 (D) $\text{I}_{(\text{DMSO})}^\ominus > \text{Br}_{(\text{DMSO})}^\ominus > \text{Cl}_{(\text{DMSO})}^\ominus > \text{F}_{(\text{DMSO})}^\ominus$
9. Which statement is/are correct for halogen
 (A) Bond dissociation energy for $\text{H}-\text{X}$ follow $\text{H}-\text{F} > \text{H}-\text{Cl} > \text{H}-\text{Br} > \text{H}-\text{I}$
 (B) Basicity order follows $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$
 (C) Nucleophilicity order follows $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
 (D) Electronegativity order follows $\text{F} > \text{Cl} > \text{Br} > \text{I}$
10. Which of the following is/are electrophile ?
 (A) CH_3^\oplus (B) $:\text{CCl}_2$ (C) NO^\oplus (D) $\text{CH}_2=\text{O}$
11. Which of the following is not the correct method of preparation for stable Grignard reagent ?





12. Which of the following orders is/are correct for the properties mentioned in brackets?

- (A) (Electrophilicity)
- (B) $\text{MeSO}_3^- > \text{MeCOO}^- > \text{CN}^- > \text{MeO}^-$ (leaving group ability)
- (C) $\text{MeI} > \text{Me-Br} > \text{Me-Cl} > \text{Me-F}$ (Reactivity towards magnesium, ether)
- (D) (Nucleophilicity)

13. Which of the following are nucleophiles?

- (A) $\ddot{\text{N}}\text{H}_3$ (B) N_3^- (C) EtOH (D) $[\text{PCl}_6]^-$

Section-3 : (Numerical Value Type.)

This section contains 5 questions. For each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places truncate/round-off the value to TWO decimal places.

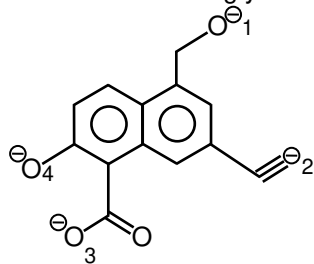
14. How many of following are electrophiles ?

- (1) $\text{CH}_3-\ddot{\text{C}}\text{H}$ (2) (3) (4) (5)
- (6) BF_3 (7) NO_2^+ (8) Cl^\oplus (9) Cl^\oplus (10) D^\oplus
- (11) SO_3 (12) CO_2 (13) AlCl_3 (14) (15) $\text{CH}_3-\text{C}^\oplus=\text{O}$
- (16) NO_2^\oplus (17) NO^\oplus (18) (19) (20)

15. How many of following are stronger nucleophiles than hydroxide ion in H_2O ?

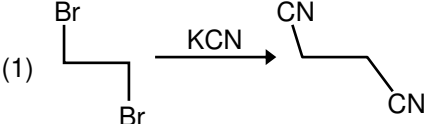
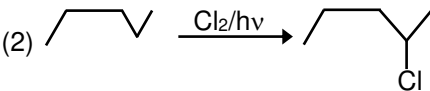
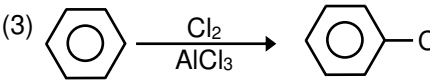
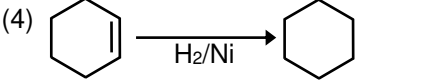
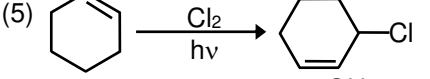
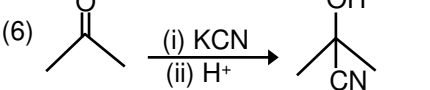
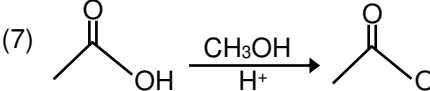
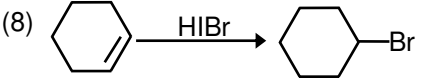
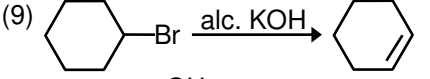
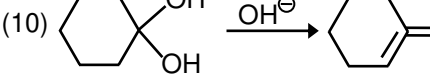
- (1) PhO^\ominus (2) $\text{OC}_2\text{H}_5^\ominus$ (3) OCH_3^\ominus (4) SH^\ominus (5)
- (6) (7) Ph-COO^\ominus (8) CH_3OH (9) NH_3 (10) CH_3^\ominus

16. Which site is strongly nucleophilic in the given structure?





17. How many of following reactions are correctly matched with their type of reaction?

- (1)  [Substitution reaction]
- (2)  [Addition reaction]
- (3)  [Elimination reaction]
- (4)  [Addition reaction]
- (5)  [Addition reaction]
- (6)  [Addition reaction]
- (7)  [Substitution reaction]
- (8)  [Addition reaction]
- (9)  [Substitution reaction]
- (10)  [Elimination reaction]

18. A sample of 3 mg of an unknown alcohol (ROH) is added to methyl magnesium iodide then 1.12 ml gas is evolved. What will be the molecular weight of alcohol ?

SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 19 to 21

Organometallic halides were discovered by the French chemist Victor Grignard in 1900.



: Rate of reaction for halides in the preparation of Grignard Reagents: $R-I > R-Br > R-Cl$

: Reactivity of Grignard Reagents with respect to different alkyl group $3^\circ > 2^\circ > 1^\circ$

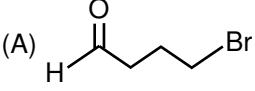
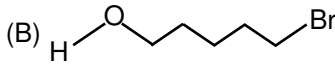
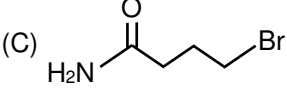
: Any reactive functional group with which Grignard Reagents can react, should not be present in the alkyl group of alkyl halide for the preparation of Grignard Reagents

Ex. $-OH, -NH_2, -CHO, -COR, -COX, -COOR, -CONH_2$

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 reagent (G.R.) by completing the octet of magnesium atom.

Answer the following on the basis of above information :

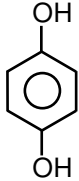
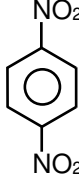
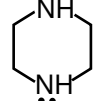


19. Which among the following alkyl halide will form most reactive Grignard Reagent?
- (A) $\text{H}_3\text{C}-\text{CH}_2-\text{Br}$ (B) $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Br}$ (C) $\text{CH}_2=\text{CH}-\text{Br}$ (D) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Br}$
20. Which among the following alkylhalide can be taken as preparation of Grignard reagent ?
- (A)  (B) 
 (C)  (D) $\text{CH}_3-\text{O}-\text{C}_6\text{H}_4-\text{CH}_2-\text{Br}$
21. Which among the following have fastest reaction with Grignard reagent ?
- (A) $\text{CH}_3-\text{CH}=\text{O}$ (B) $\text{H}_3\text{C}-\text{SH}$ (C) CH_3-NH_2 (D) $\text{CH}_3\text{CH}_2-\text{Br}$

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

22. Match the compound of column-I with their properties in column-II.

Column-I		Column-II	
(A)	CCl_4	(P)	Polar
(B)		(Q)	Non-polar
(C)		(R)	Protic
(D)		(S)	Aprotic

Practice Test-2 ((IIT-JEE (ADVANCED Pattern)))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22(A)	22(B)	22(C)	22(D)					
Ans.										



APSP Answers

PART - I

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (4) | 2. (3) | 3. (1) | 4. (3) | 5. (3) |
| 6. (3) | 7. (4) | 8. (4) | 9. (4) | 10. (3) |
| 11. (1) | 12. (2) | 13. (3) | 14. (3) | 15. (3) |
| 16. (1) | 17. (1) | 18. (3) | 19. (3) | 20. (1) |
| 21. 3 | 22. 64 | 23. 10 | 24. 4 | 25. 0.5 |

PART - II

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (1) | 2. (4) | 3. (1) | 4. (1) | 5. (3) |
| 6. (2) | 7. (1) | | | |

PART - III

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (A) | 2. (B) | 3. (B) | 4. (A) | 5. (C) |
| 6. (D) | 7. (C) | 8. (A) | 9. (C) | |

PART - IV

- | | | | | |
|------------|---|-----------|-----------|------------|
| 1. (A) | 2. (B) | 3. (C) | 4. (C) | 5. (C) |
| 6. (D) | 7. (BC) | 8. (AC) | 9. (ABCD) | 10. (ABCD) |
| 11. (ABCD) | 12. (ABCD) | 13. (ABC) | 14. 15 | 15. 4 |
| 16. 2 | 17. 6 | 18. 60 | 19. (B) | 20. (D) |
| 21. (B) | 22. $A \rightarrow Q, S$; $B \rightarrow P, R$, $C \rightarrow Q, S$; $D \rightarrow P, R$ | | | |

APSP Solutions

PART - I

8. The nucleophilicity order is $R^- > NH_2^- > CH_3O^- > OH^-$
9. The species with incomplete octet can not be a nucleophile.
10. Weaker bases are better leaving group.
12. All of these reaction give CH_4 .
13. Nucleophiles are electron rich species.
15. Conjugated base of strong acid is weak base and behave as better leaving group.
17. For endothermic reaction, $\Delta H = ve$
 $\Delta H = E_f - E_b$, it means $E_b < E_f$.
18. $A + 2B \xrightarrow{k} 3C$ (elementary reaction)

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = k [A] [B]^2$$
24. Active hydrogen containing functional group release CH_4 gas with CH_3MgBr . (i.e. OH , $COOH$, SO_3H)
25. Order of reaction = $\frac{3}{2} + (-1) = 0.5$.

PART - II

1. Order is the sum of the power of the concentrations terms in rate law expression. $R = [A].[B]^2$.
 Thus, order of reaction = $1 + 2 = 3$.
 $R = [A].[B]^2 = 3$





2. $H_2 + I_2 \rightarrow 2HI$
When 1 mole of H_2 and 1 mole of I_2 reacts, 2 moles of HI are formed in the same time interval.
Thus the rate may be expressed as :

$$\frac{-\Delta[H_2]}{\Delta t} = \frac{-\Delta[I_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[HI]}{\Delta t}$$
 The negative sign signifies a decrease in concentration of the reactant with increase of time.
3. Among the given option Cl^- is the best leaving group hence the rate of reaction will be fastest in case of $RCOCl$.
4. Generally, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation. Thus, a reaction involving two different reactants can never be unimolecular.
5. $CH_3MgX + CH_3 - C \equiv CH \longrightarrow CH_4 + CH_3 - C \equiv C - MgX$
6. $CH_3OH + C_6H_5MgBr \longrightarrow C_6H_6 + Mg(OCH_3)Br$
 methanol phenylmagnesium bromide benzene
7. $\frac{1}{2}A \rightarrow 2B \Rightarrow -\frac{1}{1/2} \frac{d(A)}{dt} = \frac{1}{2} \frac{d(B)}{dt}$

$$\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$$

PART – IV

2. Nucleophilicity \propto Size (in group)
5. $K = Ae^{-E/RT}$
7. Anionic nucleophiles are better nucleophile than their neutral species.
8. In aprotic solvent Nu^\ominus increases, as compare to polar protic solvent.
9. Self understood
11. Stable Grignard reagent's can't be synthesized with fluorides and with the presence of functional groups in halide reactants with functional groups which are reactive towards Grignard reagents.
12. (A) Electrophilicity is inversely proportional to stability of electrophiles.
 (B) Fact
 (C) Fact
 (D) Nucleophilicity is inversely proportional to steric crowding in same degree amines and inversely proportional to stability of lone pairs.
14. 2, 3, 8, 16 and 20 are nucleophiles.
15. 2, 3, 4 and 10 are stronger nucleophiles than OH^\ominus ion.
16. $C \equiv C - R$ is strongly nucleophilic site.
17. 1, 4, 6, 7, 8, 10
18. Number of millimoles of alcohol = $\frac{1.12 \text{ ml}}{22.4 \text{ ml/mole}}$
 molecular weight of alcohol = $\frac{\text{Wt of alcohol (mg)}}{\text{No. of milli moles of alcohol}} = \frac{3}{1.12/22.4} = 60.$