GENERAL ORGANIC CHEMISTRY-III
&
GRIGNARD REAGENT

CONTENTS

JEE (Advanced) Syllabus

Common type of organic reactions - Substitution, Addition, Elimination and Rearrangement.
Electrophiles, Nucleophiles and Leaving groups.
Nucleophilic substitution reactions, Nucleophilic addition reactions and other reactions of Grignard reagent.

JEE (MAIN) Syllabus

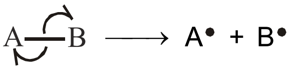
Common type of organic reactions - Substitution, Addition, Elimination and Rearrangement.
Electrophiles, Nucleophiles and Leaving groups.
Chemical reactions of Grignard reagent.

1. Types of bond dissociation

All chemical reactions are initiated with bond dissociation. There are two types of bond dissociation.

(a) Homolytic bond dissociation

A bond dissociation in which a bond pair electron is equally distributed to the bonding atoms.

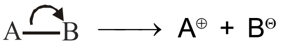


$$A{-}B \longrightarrow A^{\bullet} + B^{\bullet}$$

A homolytic bond dissociation generates radicals, these are generally neutral species.

(b) Hetrolytic bond dissociation

A bond dissociation in which a bond pair electron is shifted to one atom only.



$$A{-}B \longrightarrow A^{\oplus} + B^{\ominus}$$

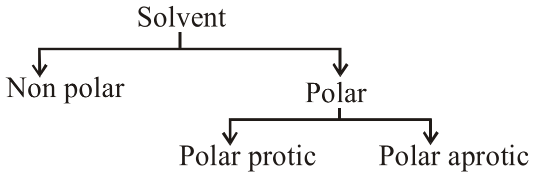
A hetrolytic bond dissociation always generate a cation and an anion.

An organic reaction can be represented as

$$\text{Reactant (substrate) + Reagent} \xrightarrow[\text{Catalyst Condition}]{\text{Solvent}} \text{Product + By-product}$$

2. Types of solvent

Solvent can be classified as :-



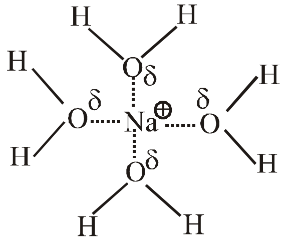
2.1 Polar Solvent : Polar solvent has some overall dipole moment. They are of two types

(a) Polar protic solvent

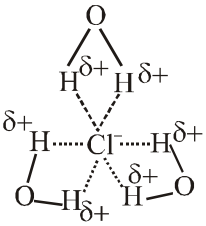
Solvents in which H atom is directly attched with highly electronegative atom. Polar protic solvents are capable of forming intermolecular hydrogen bonding.

e.g. H_2O, C_2H_5OH, CH_3COOH etc.

Polar protic solvent can solvate both cations as well as anions. Cations are solvated by ion dipole interaction with H_2O while anions are solvated by hydrogen bonding with H_2O. Solvation of NaCl in H_2O can be explained as



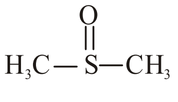
$Na^{\oplus}$ is solvated by ion-dipole interaction with H_2O



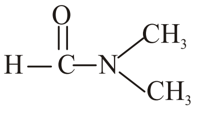
Cl^- is solvated by H-bonding with H_2O

(b) Polar aprotic solvents

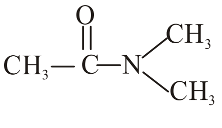
These are the solvents in which H is not attached with highly electro negative atom. These solvents can not give H^+ ions.



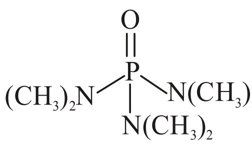
DMSO
(Dimethyl sulphoxide)



DMF
(Dimethyl formamide)

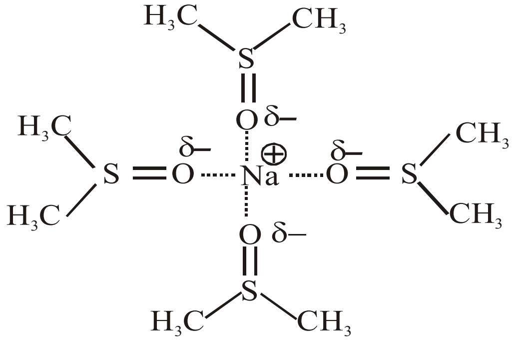


DMA
(Dimethyl acetamide)

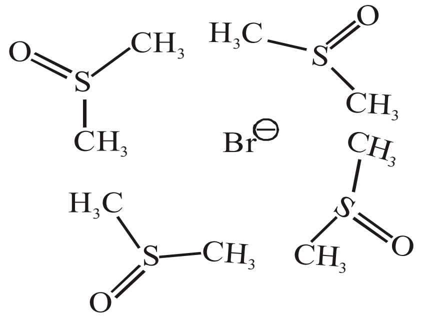


Hexamethylphosphoric triamide (HMPA)

Polar aprotic solvent can solvate cation very well, while anion is not solvated. When a salt is added then cation is trapped by ion dipole interaction, while anion is not well solvated.



Na$^{\oplus}$ is solvated by ion dipole interaction with DMSO

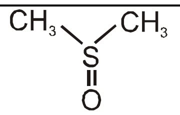
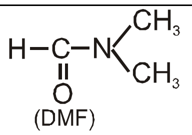
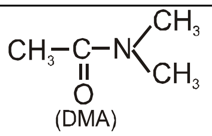
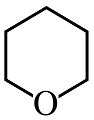


Br$^{\ominus}$ surrounded by solvent but not well solvated by DMSO

2.2 Non polar solvents

These solvents has overall zero or nearly zero dipole moment. CS_2, CCl_4, Benzene, Hexane etc.

Some common examples of solvents :

Solvents	**Polar protic**	**Polar aprotic**	**Non-Polar**
1. Benzene	×	×	✓
2. Toluene	×	×	✓
3. Water	✓	×	×
4. Alcohol	✓	×	×
5. H–COOH	✓	×	×
6. CH_3COOH	✓	×	×
7. NH_3	✓	×	×
8. Acetone	×	✓	×
9.  (DMSO)	×	✓	×
10.  (DMF)	×	✓	×
11.  (DMA)	×	✓	×
12.  (THP)	×	✓	×

3. Types of reagents

A reagent generates three types of attacking species generally.

(a) Electrophiles (b) Nucleophiles (c) Radicals

3.1 Electrophiles

An electrophile is a positively charged species or neutral molecule with electron deficient center. Electrophiles can act as Lewis acids.

Electrophiles are of following type :

(a) Positively charged electrophiles

H^+, Br^+, Cl^+, I^+, NO_2^+, R_3C^+, NO^+, Hg^{2+} etc

(b) Neutral electrophiles : In these electrophiles central atom has an incomplete octect and atleast one vacant orbital.

BF_3, BH_3, $AlCl_3$, $ZnCl_2$,PCl_5, $FeCl_3$, carbenes, nitrenes (Species with vacant p-orbital at central atom).

(c) Compounds having polar π bonds :

SO_3, SO_2, RCOCl, $(RCO)_2O$,Carbonyl compounds

3.2 Nucleophiles

It is an electron rich species which has atleast one lone pair of electrons. Nucleophile can be neutral or negativetely charged. Nucleophile is always act as Lewis base.

Nucleophile are of following types :

(a) Negatively charged nucleophiles :

$\bar{H}$, $\bar{O}H$, $\bar{O}–R$, $\bar{C}H_3$, $\bar{X}$, $\bar{S}H$, $R–\bar{S}$, $N\bar{O}_2$, $RCO\bar{O}$, $\bar{C}N$, $\bar{I}$, $\bar{B}r$, $\bar{N}_3$, $\bar{N}H_2$, etc

(b) Neutral nucleophiles : In these nucleophiles central atom has complete octet and atleast one lone pair of electron

$R-\ddot{N}H_2$, $\ddot{N}H_3$, $\ddot{N}H_2–\ddot{N}H_2$, $H-\underset{\bullet\bullet}{\ddot{O}}-H$ $R-\underset{\bullet\bullet}{\ddot{O}}-H$, $R-\ddot{O}-R$,

$H-\underset{\bullet\bullet}{\ddot{S}}-H$, $R-\underset{\bullet\bullet}{\ddot{S}}-H$, $R-\underset{\bullet\bullet}{\ddot{S}}-R$, $\ddot{P}H_3$, $\ddot{P}Ph_3$, 

(c) Organic compounds containing carbon-carbon double bonds can also behave as nucleophile.

$CH_2 = CH_2$, , $CH_2 = CH– CH= CH_2$, CH≡CH etc.

(d) Ambident nucleophiles : Species having two nucleophilic sites, but only one can donate lone pair of electron at a time, known as ambident nucleophiles.

CN^-, $O=N–O^-$, $S=C=N^-$ etc.

3.3 Radicals

It is an electron deficient specie with seven electrons around an atom in outer most shell.

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

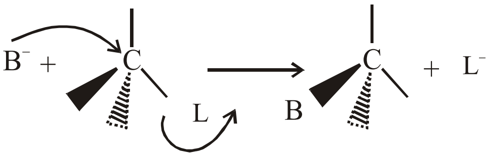
3.4 Nucleophilicity V/S Basicity

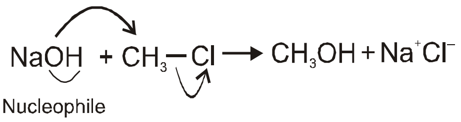
Nucleophiliticy is defined as the tendency of any species to give electron pair to an electron deficient center, while basicity is the ability of the species to remove H^+ ion, from an acid

Consider a species $B^–$

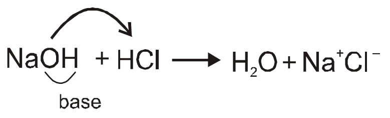
The nucleophilicity is determined by the kinetics of the reaction, which is reflected by its rate constant (k) while basicity is determined by the equilibrium constant, which is reflected by its K_b.

(i) It's functioning as a nucleophile is indicated as





(ii) It's functioning as base is indicated as $\bar{B} + H - A \rightleftharpoons B - H + A^-$



$\underset{\text{base}}{NaOH} + HCl \longrightarrow H_2O + Na^+Cl^-$

3.5 Criteria for nucleophilicity

The factors which increases electron density at donor atom increases nucleophilicity.

The more polarisable donor atom is a better nucleophile, therefore, size of donor atom increases nucleophilicity increases in a group.

(a) Periodicity :

(i) Nucleophilicity and basicity decreases from left to right in a period.

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

(ii) In a group, nucleophilicity increases from top to bottom due to increases in size of donor atom, but basicity decreases from top to bottom.

Acid strength : HI > HBr > HCl > HF

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

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

(b) Effect of the solvent

In polar protic solvent large nucleophiles are good, and the nucleophilicity of halide ions follows the order as :

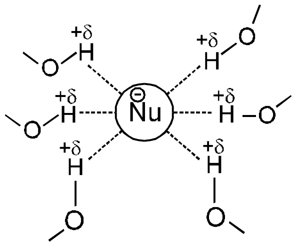
$$F^- < Cl^- < Br^- < I^-$$

In polar aprotic solvent (DMSO) the relative order of nucleophilicity of halide ions is

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

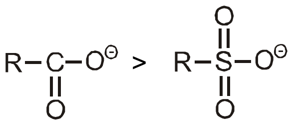
Also basic strength of halides follows the same order in DMSO but in polar protic solvent like H_2O they follow the reverse order of nucleophilicity.

This effect is related to the strength of the interaction between nucleophile and solvent molecules of polar protic solvent forms hydrogen bond to nucleophiles in the following manner :



Relative nucleophilicity in polar protic solvent

(i) $\overset{\ominus}{SH} > \overset{\ominus}{I} > \overset{\ominus}{OH} > \overset{\ominus}{N_3} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} > \overset{\ominus}{F} > H_2O$

(ii) 

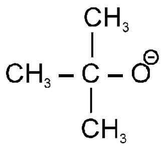
$R-\underset{\underset{O}{\|}}{C}-O^\ominus > R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^\ominus$

(iii) $HO^- > H_2O$

(iv) $NH_2^- > NH_3$

(v) $CF_3SO_3^- < PhCOO^- < PhO^- < RO^-$

(c) Steric effects on nucleophilicity

(i) 

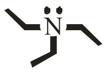
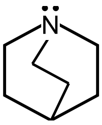
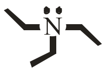
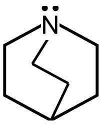
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\ominus}{O}$

t-butoxide

t–BuO$^-$ is strong base, yet weaker nucleophile (It cannot approach the carbon atom so easily.)

(ii) $CH_3-CH_2-\overset{\ominus}{O}$ (EtO$^-$ is strong base and strong nucleophile.)

ethoxide

S.No.	Nucleophilicity	Basicity	Remarks
1.	$CH_3^- > NH_2^- > OH^- > F^-$	$CH_3^- > NH_2^- > OH^- > F^-$	If donor atoms belong to same period, nuclephilicity and basicity order is same
2.	$SiH_3^- > PH_2^- > SH^- > Cl^-$	$SiH_3^- > PH_2^- > SH^- > Cl^-$	—//—
3.	$F^- < Cl^- < Br^- < I^-$	$F^- > Cl^- > Br^- > I^-$	In a group nucleophilicity increases while basicity decreases. on moving top to bottom.
4.	$OH^- < SH^-$	$OH^- > SH^-$	—//—
5.	$RO^- < RS^-$	$RO^- > RS^-$	—//—
6.	t-BuO$^-$ < EtO$^-$	t-BuO$^-$ > EtO$^-$	Steric reason
7.	 < 	 < 	—//—

Golden key points

(1) Nucleophilicity depends on the nature of solvent.

(2) Anions are better nucleophile than their neutral molecule.

(3) Nucleophilicity increases if adjacent atom of nucleophilic side has lone pair, because lone pairs repels each other. Example $\ddot{N}H_2-\ddot{N}H_2$.

(4) Strong base but weak nuecleophiles → t-BuO$^-$, NEt$_3$, LDA

(5) Strong nuecleophiles but very weak bases → I$^-$, Br$^-$, Cl$^-$, SeH$^-$

(6) Strong nuecleophiles but moderate bases → SH$^-$, N_2H_4

4. Leaving group and leaving ability (Nucleofugality)

Good leaving groups are those that become the most stable ion after they leave, because leaving group generally leave as a negative ion, so those leaving groups are good, which stabilise negative charge most effectively. Weaker base does this best, **so weaker is the base better is the leaving group.**

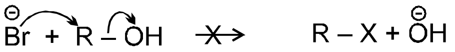
– The leaving group should have lower bond energy with carbon.

– Negative charge should be more stable either by dispersal or delocalization.

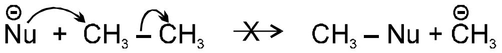
$Nu^- + CH_3CH_2–I \rightarrow CH_3CH_2–Nu + I^-$(leaving group)

$Nu^- + CH_3CH_2–OTs \rightarrow CH_3CH_2–Nu + OTs^-$(leaving group)

Strongly basic ions rarely act as leaving group.



$\overset{\ominus}{Br} + R-OH \not\rightarrow R-X + \overset{\ominus}{O}H$ (strong base / poor leaving group)



$\overset{\ominus}{Nu} + CH_3-CH_3 \not\rightarrow CH_3-Nu + \overset{\ominus}{C}H_3$ (It is not a leaving group)

Order of leaving ability of some groups -

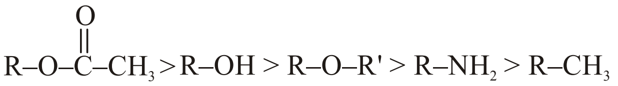
(i) $I^- > Br^- > Cl^- > F^-$

(ii) $HS^- > HO^-$

(iii) $CH_3^- < NH_2^- < OH^- < F^-$

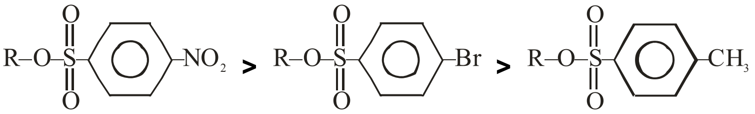
(iv) $R–COO^- > PhO^- > HO^- > RO^-$

(v)



$R–O–\overset{\overset{\displaystyle O}{||}}{C}–CH_3 > R–OH > R–O–R' > R–NH_2 > R–CH_3$

(vi)



(Where group attached with R is the leaving group)

5. Types of organic reactions

5.1 Acid-Base reaction

Compounds having reactive or acidic hydrogen atoms give acid base reaction.

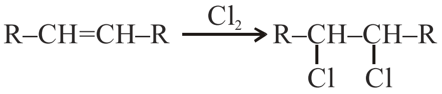
$R–COOH + NaOH \longrightarrow RCOONa + H_2O$

$C_2H_5OH + CH_3Li \longrightarrow C_2H_5OLi + CH_4$

5.2 Addition reaction

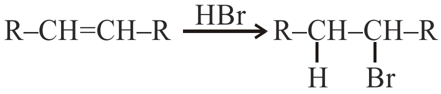
Where two or more molecules combine to form a larger one (the adduct). Addition reaction include such reactions as **halogenation, hydrohalogenation, hydration etc.**

(i)



$R–CH=CH–R \xrightarrow{Cl_2} R–\underset{Cl}{\underset{|}{C}H}–\underset{Cl}{\underset{|}{C}H}–R$

(ii)



$R–CH=CH–R \xrightarrow{HBr} R–\underset{H}{\underset{|}{C}H}–\underset{Br}{\underset{|}{C}H}–R$

(iii)

5.3 Substitution reaction

In which one group in a chemical compound is replaced by another group. Such reaction follows free radial subsitution, aromatic electrophilic substitution (Sc), nucleophilic subsititution (S_N1, S_N2, S_Ni, S_N2Th) etc.

(i) $R–L \xrightarrow{Y} R–Y + L$

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

(iii) $Ph–H \xrightarrow{Br^+} Ph–Br + H^+$

(iv) $R–CO–Cl \xrightarrow{EtO^-, EtOH} R–CO–OEt + Cl^-$

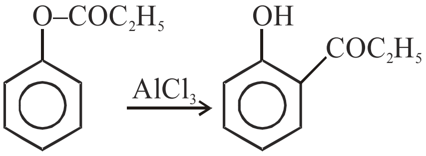
5.4 Elimination reaction

In which two substituent groups or atoms are removed from a molecule either in a one or more than one - steps mechanism. Such reactions include dehydration, dehalogenation etc.

$$R–\underset{X}{\underset{|}{C}}H–\underset{Y}{\underset{|}{C}}H–R \xrightarrow{\text{Reagent}} R–CH=CH–R$$

5.5 Rearrangement reaction

In many reactions atom or a group of atoms rearrange intramolecularly with in a molecule.



It is Fries rearrangement reaction.

6. Organometallic compounds

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

$\overset{\ominus}{C}$ $\overset{\oplus}{M}$ [RLi, RNa, RMgX, R_2Zn, R_2Cd, R_2CuLi]

Note : (1) If the metal atom is attached to oxygen, nitrogen. sulphur, etc., then such an organic compound is not regarded as an organometallic compound. The following structural formula do not belong to the family of organometallic compounds.

RONa (Sodium alkoxide). CH_3COONa (Sodium acetate), CH_3COOAg(Silveracetate),RSK (Potassium mercaptide) RNHK (N-Alkylpotassamide), $(CH_3COO)_4Pb$ (Lead tetraacetate) etc.

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

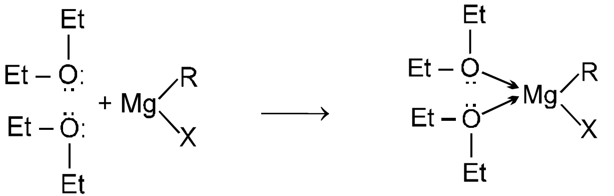
(3) Most important examples of organometallic compounds are Grignard reagents. In Grignard reagent, the carbon and magnesium atoms are bonded with each other through polar covalent bond (approx 35% ionic character) and magnesium atom is attached to halogen by ionic bond.

6.1 Grignard reagent

(a) Preparation of Grignard reagent

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

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



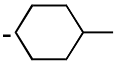
Alkylmagnesium halide dietherate

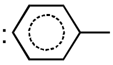
Note : Except halogens all other functional groups which can react with Grignard reagent [including –Acidic H, NO_2, –CN, CHO etc.] must be absent in the alkyl group otherwise Grignard reagent will be destroyed by internal reactions.

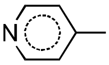
(b) Some examples of different Grignard reagent

(i) Aliphatic Grignard reagent :- $CH_3 - MgI$ (Methylmagnesium iodide)

(ii) Alkenyl Grignard reagent : - $CH_2 = CH - CH_2 - MgX$ (Allylmagnesium halide)

(iii) Alicyclic Grignard reagent : -  MgX (Cyclohexylmagnesium halide)

(iv) Aromatic Grignard reagent :  MgX (Phenylmagnesium halide)

(v) Heterocyclic aromatic Grignard reagent :-  MgX (Pyridine-4-magnesium halide)

(c) Reactivity of Grignard reagent

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

* Reactivity order with different alkyl part is
RMgX : ($R = 3^\circ > 2^\circ > 1^\circ > CH_3 > C{=}C > C{\equiv}C$)

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

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

6.2 Synthetic importance and chemical reaction of Grignard reagents

6.2.1 Synthesis of other organometallic compounds from Grignard reagent

$R{-}Mg{-}X + ZnCl_2 \longrightarrow R_2Zn + MgX(Cl)$

$R{-}Mg{-}X + HgCl_2 \longrightarrow R_2Hg + MgX(Cl)$

$R{-}Mg{-}X + SnCl_2 \longrightarrow R_2Sn + MgX(Cl)$

$R{-}Mg{-}X + PbCl_2 \longrightarrow R_2Pb + MgX(Cl)$

$R{-}Mg{-}X + CdCl_2 \longrightarrow R_2Cd + MgX(Cl)$

$4R - MgCl + 2PbCl_2 \longrightarrow R_4Pb + Pb + 4MgCl_2$

Two important antiknocking compounds, tetraethyllead (T.E.L.) and tetramethyllead (T.M.L.) are manufactured by the above reaction.

6.2.2 Synthesis of hydrocarbon by acid base reactions

General reaction : $R - MgX + H - Z \longrightarrow R - H + ZMgX$

$CH_3 - MgX + H - OH \longrightarrow CH_3 - H + Mg(OH)X$

$C_2H_5 - MgX + H - OR \longrightarrow C_2H_5 - H + Mg(OR)X$

$C_3H_7 - MgX + H - OC_6H_5 \longrightarrow C_3H_7 - H + Mg(OC_6H_5)X$

$C_2H_5 - MgX + H - NH_2 \longrightarrow C_2H_5 - H + Mg(NH_2)X$

$C_2H_5 - MgX + H - NR_2 \longrightarrow C_2H_5 - H + Mg(NR_2)X$

$CH_3 - MgX + H - NHC_6H_5 \longrightarrow CH_3 - H + Mg(NHC_6H_5)X$

$C_2H_5 - MgX + H - SR \longrightarrow C_2H_5 - H + Mg(SR)X$

$CH_3 - MgX + H - C \equiv N \longrightarrow CH_3 - H + Mg(CN)X$

$CH_3 - MgX + H - C \equiv CR \longrightarrow CH_3 - H + R - C \equiv C - MgX$ (Alkynylmagnesium halide)

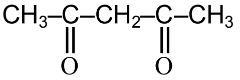
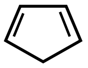
Methane gas is released on reacting methylmagnesium iodide with a compound containing reactive hydrogen atom. The reaction is used for estimation of reactive hydrogen atoms present in a molecule. This method is called **Zerewitinoff** method of estimation of reactive hydrogen atoms.

Worksheet - (A)

Mark E or Y or N for the given acid base reactions in the table. Where *(E = Equilibrium, Y = Yes, N = No)

Bases \ Acids	Ph–SH	Ph–OH	C_2H_5OH	$CH_3C{\equiv}CH$	NH_3	$C_2H_5NH_2$
1. $RCOO^-$ (Weak base in water)						
2. $Ph{-}O^-$ (Weak base in water)						
3. OH^- (Strong base in water)						
4. $C_2H_5O^-(EtO^-)$ (Strong base)						
5. $CH_3{-}C{\equiv}C^-$ (Strong base)						
6. H^- (Very strong base)						
7. NH_2^- (Very strong base)						
8. R^- (Strongest base)						

Worksheet - (B)

Bases / **Acids**	**$PhSO_3H$**	**RCOOH**	**H_2CO_3**	 $CH_3-\underset{\overset{\|}{O}}{C}-CH_2-\underset{\overset{\|}{O}}{C}-CH_3$	**H_2O**	
9. $RCOO^-$ (Weak base in water)						
10. $Ph-O^-$ (Weak base in water)						
11. OH^- (Strong base in water)						
12. $C_2H_5O^-(EtO^-)$ (Strong base)						
13. $CH_3-C\equiv C^-$ (Strong base)						
14. H^- (Very strong base)						
15. NH_2^- (Very strong base)						
16. R^- (Strongest base)						

Ans. **Worksheet - (A)**

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 - (B)

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

6.2.3 Synthesis of hydrocarbon by nucleophilic substitution reactions

(a) With alkyl halide (coupling) :

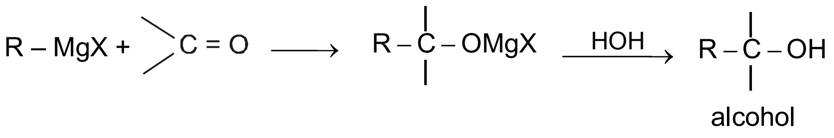
$$R-MgX + X'-R' \longrightarrow R-R' + MgXX'$$

$$R-MgX + \underset{\text{Allyl halide}}{X'-CH_2-CH=CH_2} \longrightarrow R-CH_2-CH=CH_2 + MgXX'$$

(b) Synthesis of higher alkynes

$$R'C\equiv C-H \xrightarrow[\text{- RH}]{\text{RMgX}} R'-C\equiv CMgX \xrightarrow[-\,MgX_2]{R''X} R'-C\equiv C-R''$$

6.2.4 Synthesis of alcohols by nucleophilic addition reaction of carbonyls

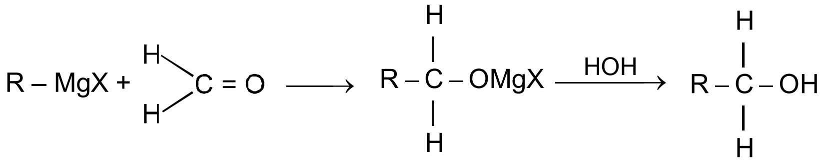


$$R-MgX + \rangle C=O \longrightarrow R-\underset{|}{\overset{|}{C}}-OMgX \xrightarrow{HOH} \underset{\text{alcohol}}{R-\underset{|}{\overset{|}{C}}-OH}$$

This is nucleophilic addition reaction

(a) Primary or 1° alcohols

Primary alcohols are formed on taking formaldehyde

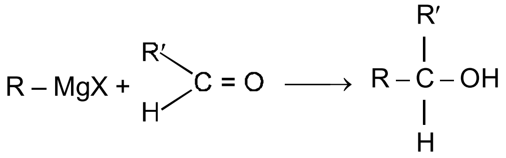


$$R-MgX + H_2C=O \longrightarrow R-CH_2-OMgX \xrightarrow{HOH} R-CH_2-OH$$

1° Alcohol

(b) Secondary or 2° alcohols

Secondary alcohols are formed by the reaction of any aldehyde other than formaldehyde.

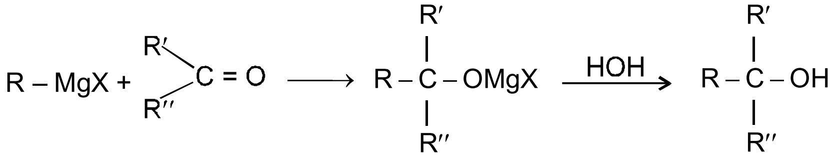


$$R-MgX + R'(H)C=O \longrightarrow R-CH(R')-OH$$

2° Alcohol

(c) Tertiary or 3° alcohols

Tertiary alcohols are formed by taking any ketone

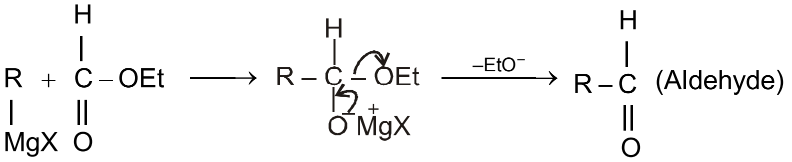


$$R-MgX + R'(R'')C=O \longrightarrow R-C(R')(R'')-OMgX \xrightarrow{HOH} R-C(R')(R'')-OH$$

3° Alcohol

6.2.5 Synthesis of aldehydes and ketones from acid derivatives

(i) Corresponding aldehyde is obtained by reacting formic ester and Grignard reagent in equimolar ratio.

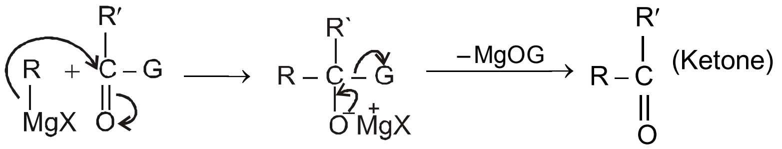


$$\underset{MgX}{R} + H-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow R-\underset{\overset{-}{O}\overset{+}{M}gX}{C}(H)-OEt \xrightarrow{-EtO^-} R-\overset{O}{\overset{\|}{C}}-H \text{ (Aldehyde)}$$

Tetrahedral intermediate

In this reaction tetrahedral intermediate is fromed so this mechanism is called **S_N2 Th mechanism.**

(ii) Other esters and acid derivatives give ketone with one equivalent of Grignard reagent.

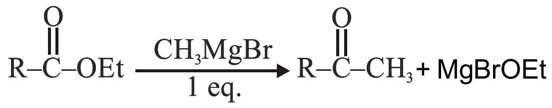


$$\underset{MgX}{R} + R'-\overset{O}{\overset{\|}{C}}-G \longrightarrow R-\underset{\overset{-}{O}\overset{+}{M}gX}{C}(R')-G \xrightarrow{-MgOG} R-\overset{O}{\overset{\|}{C}}-R' \text{ (Ketone)}$$

Where G = -OEt, – Cl, OCOR

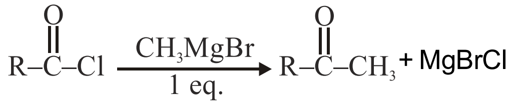
The above reaction sequence can be simplified as follows for convenience.

(iii)



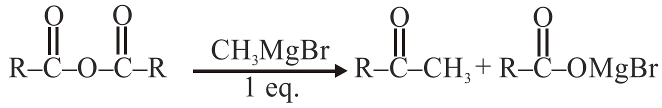
$$R-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[1\text{ eq.}]{CH_3MgBr} R-\overset{O}{\overset{\|}{C}}-CH_3 + MgBrOEt$$

(iv)



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[1\text{ eq.}]{CH_3MgBr} R-\overset{O}{\overset{\|}{C}}-CH_3 + MgBrCl$$

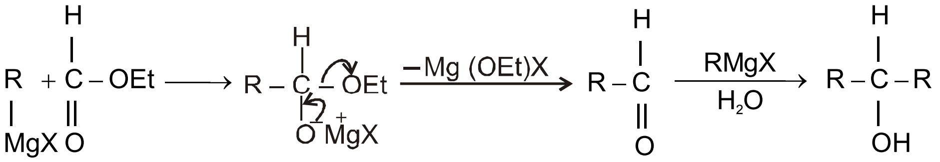
(v)



$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow[1\text{ eq.}]{CH_3MgBr} R-\overset{O}{\overset{\|}{C}}-CH_3 + R-\overset{O}{\overset{\|}{C}}-OMgBr$$

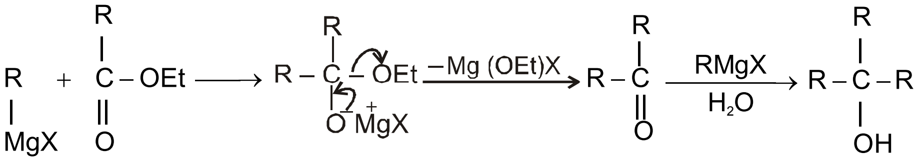
6.2.6 Synthesis of alcohols by reaction with acid derivatives

(a) From formic ester : Secondary alcohols are obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and adding formic ester to it.



$$\underset{\text{MgX}}{\text{R}} + \text{H}-\underset{\text{O}}{\overset{\|}{\text{C}}}-\text{OEt} \longrightarrow \text{R}-\overset{\text{H}}{\underset{\text{O}^{-}\overset{+}{\text{MgX}}}{\text{C}}}-\text{OEt} \xrightarrow{-\text{Mg (OEt)X}} \text{R}-\overset{\text{H}}{\underset{\text{O}}{\overset{|}{\text{C}}}} \xrightarrow[\text{H}_2\text{O}]{\text{RMgX}} \text{R}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{R}$$

(b) Tertiary alcohols are obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and an ester, acid anhydride of a higher homologue of formic acid.



$$\underset{\text{MgX}}{\text{R}} + \text{R}-\underset{\text{O}}{\overset{\|}{\text{C}}}-\text{OEt} \longrightarrow \text{R}-\overset{\text{R}}{\underset{\text{O}^{-}\overset{+}{\text{MgX}}}{\text{C}}}-\text{OEt} \xrightarrow{-\text{Mg (OEt)X}} \text{R}-\overset{\text{R}}{\underset{\text{O}}{\overset{|}{\text{C}}}} \xrightarrow[\text{H}_2\text{O}]{\text{RMgX}} \text{R}-\overset{\text{R}}{\underset{\text{OH}}{\text{C}}}-\text{R}$$

Various alcohols can be prepared by changing R in the above synthesis.

6.2.7 Other reactions of Grignard reagent

(a) Synthesis of alcohols

$R-MgX + O=O \longrightarrow R-O-O-MgX$

$R-O-O-MgX + R-MgX \longrightarrow 2R-O-MgX$

$R-O-MgX + HOH \longrightarrow R-O-H + Mg(OH)X$

Primary, secondary and tertiary alcohols can be obtained by above reaction

(b) Synthesis of phenols

Phenol is obtained on hydrolysis of the product obtained by reaction of arylmagnesium bromide with oxygen.

$$C_6H_5MgBr + O_2 \xrightarrow[\text{(ii) H}^+]{\text{(i) Ether}} C_6H_5OH + MgBr(OH)$$

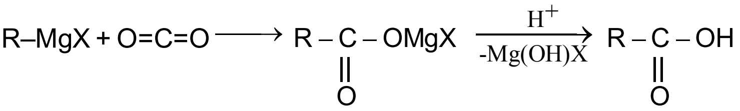
(c) Synthesis of ketones by alkyl cyanides

A ketimine is formed on hydrolysis of the adduct obtained by the reaction of Grignard reagent and an alkyl cyanide, which gives ketone on further hydrolysis.

$$RMgX + RCN \longrightarrow R_2C=NMgX \xrightarrow{HOH} \underset{\text{Ketimine}}{R_2C=NH} \xrightarrow{HOH} \underset{\text{Ketone}}{R_2C=O}$$

(d) Synthesis of carboxylic acids

A carboxylic acid is formed on acidification of the adduct formed by passing carbon dioxide in the ethereal solution of a Grignard reagent.



$$\text{R–MgX} + \text{O=C=O} \longrightarrow \text{R}-\underset{\text{O}}{\overset{\|}{\text{C}}}-\text{OMgX} \xrightarrow[\text{-Mg(OH)X}]{\text{H}^+} \text{R}-\underset{\text{O}}{\overset{\|}{\text{C}}}-\text{OH}$$

(e) Synthesis of carboxylic acid esters

Esters are formed on reacting the ethylchloroformate with Grignard reagent.

$RMgCl + ClCOOEt \longrightarrow RCOOEt + MgCl_2$

(f) Synthesis of ethers

Higher ethers can be synthesised by reacting a lower chlorinated ether with Grignard reagent.

$R-MgCl + Cl-CH_2-O-R \longrightarrow R-CH_2-O-R + MgCl_2$

$$CH_3MgCl + \underset{\text{Chloromethyl ethyl ether}}{Cl-CH_2-O-C_2H_5} \longrightarrow \underset{\text{Diethyl ether}}{CH_3-CH_2-O-C_2H_5}$$

(g) Synthesis of mercaptans

Alkanethiols, i.e. mercaptan is formed on hydrolysis of the product obtained by adding sulphur to the ethereal solution of Grignard reagent.

$$R–MgCl + S \longrightarrow R–S–MgCl \xrightarrow{HOH} R–S–H + Mg(OH)Cl$$

7. Application 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.

7.1 Rate of chemical reaction

The rate of change of concentration with time of different chemical species taking part in a chemical reaction is known as **rate of reaction of that species.**

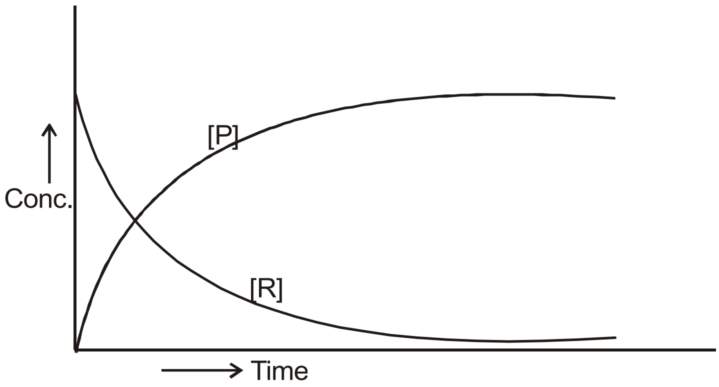
$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol/lit.}}{\text{sec}} = \text{mol lit}^{-1}\ \text{time}^{-1} = \text{mol dm}^{-3}\ \text{time}^{-1}$$

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

For a reaction

$$R \longrightarrow P$$

$$\text{Rate} = \frac{\text{Total change in concentration}}{\text{Total time taken}} = \frac{\Delta c}{\Delta t} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$



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

We very well know that the rate of reaction of all the species taking part in a chemical reaction are not equal as evident from their stochiometric coefficients. The following example will make it clear

eg. $N_2 + 3H_2 \rightarrow 2NH_3$

rate of reacton of $N_2 = \frac{-d[N_2]}{dt}$

rate of reaction of $H_2 = \frac{-d[H_2]}{dt}$

rate of reaction of $NH_3 = \frac{d[NH_3]}{dt}$

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

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

The value of above expressions is also written as rate of the given reaction.

* **Remember that "Rate of Reaction" phrase** has no meaning if a balanced equation is not given. Hence rate of reaction phrase is always used with a balanced chemical equation,

And for balanced chemical equation as given below, $aA + bB \rightarrow cC + dD$

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

7.2 Rate law

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law. It can only be established by experiments.

Rate $\propto$ (conc.)$^{\text{order}}$

Rate = k (conc.)$^{\text{order}}$ Where k= Rate constant

Note : Value of k is a constant for a given reaction, depends only on temperature.

Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of intermediates.

7.3 Order of reaction

Let there be a reaction $n_1A + n_2B \longrightarrow$ products.

Now, if on the basis of experiment, we find that

$R \propto [A]^p [B]^q$ Where p may or may not be equal to n_1 and similarly q may or may not be equal to 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.

7.4 Molecularity

The number of molecules that react in an elementary step is the molecularity of the elementary reaction. Molecularity is defined only for the elementary reactions which is equal to number of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy. No elementary reactions involving more than three molecules are known, because of very low probability of near-simultaneous collision of more than three molecules.

The rate law for the elementary reaction

$aA + bB \longrightarrow$ products rate = $k[A]^a[B]^b$, where a + b = 1, 2 or 3.

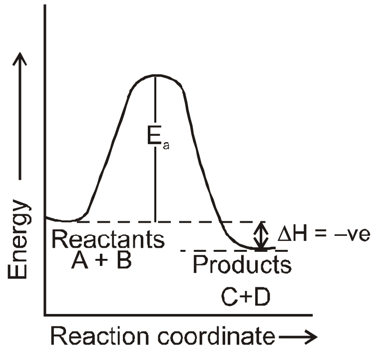
The mechanism of any complex reaction is always written in terms of elementary steps, so molecularity of each of these steps will be defined but net molecularity of complex reaction has no meaning.

Comparison between molecularity and order of reaction

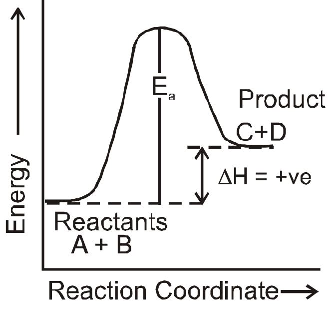
Molecularity of reaction	Order of reaction
1. It is defined as the no. of molecules of reactant taking part in particular step.	1. It is defined as the sum of the power of concentration terms that appear in the law.
2. It is always a whole number. It is can neither be zero nor fractional.	2. It may be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

7.5 Reaction profile

The energy of the reacting system as a function of the progress of the reaciton is known as reaciton profile or energy diagram.



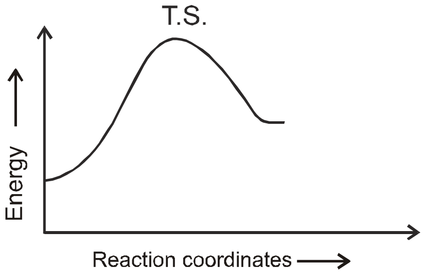
(Exothermic)



(Endothermic)

(a) Elementary reactions

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

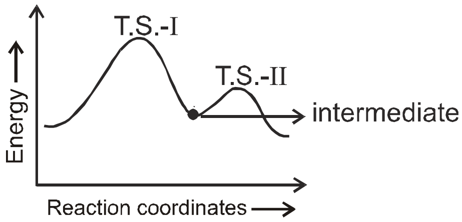


T.S. = Transition state

An elementary reaction the sum of stoichiometric coefficients is equal to order of the reactions.

(b) Complex reactions

Reaction which proceed in more than one steps. or having some mechanism. Complex reaction takes places in a sequence of a number of elementary reactions.



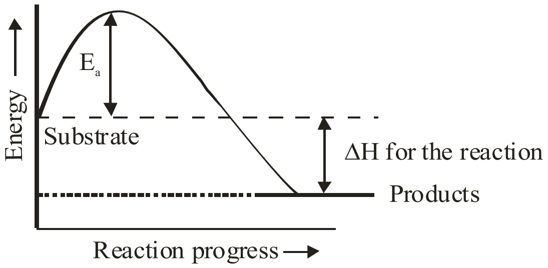
For complex reactions order is to be experimentally calculated

Order of complex reaction can be zero, fractions, whole no., even negative w.r.t. some species.

7.6 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.

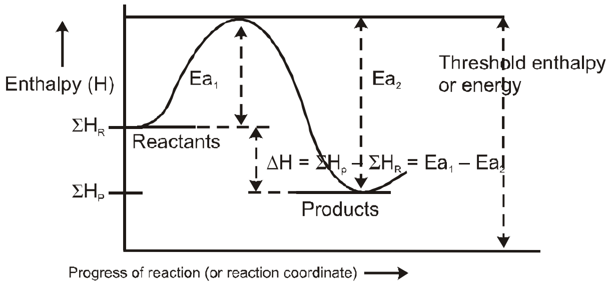
In equation : $S \rightarrow X \rightarrow P$,

X is the transition state, which is located at the peak of the curve on the energy graph.

7.7 Activation energy

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

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



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

Threshold energy

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

E_a = Threshold energy – Actual average energy

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

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

7.8 Factors affecting rate of chemical reaction

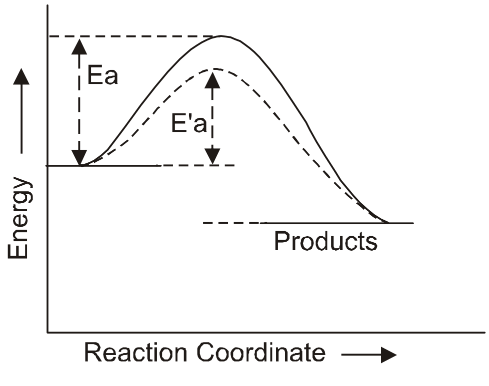
1. Effect of concentration : It is seen by rate law which is experimental data.

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

2. Chemical nature of reactants : This is the point of detailed study in organic chemistry

In general rate of reaction : Gaseous > Liquid > Solid medium.

3. Effect of Catalyst : Presence of positive catalyst lower down the activation energy hence increases the rate of reaction.



4. Effect of temperature : Rate of reaction is generally increases with temperature.

7.9 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.)

Exercise # 1

PART-I : SUBJECTIVE QUESTIONS

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

A-1. Define electrophile and nucleophile with examples.

A-2. What is nucleophilicity? Write the factors affecting nucleophilicity.

A-3. What is leaving groups (Nucleofuse)? Write about leaving group ability.

A-4. Which of the followings are electrophile ?

(a) CN^- (b) H^+ (c) Br^+ (d) $AlCl_3$

(e) BH_3 (f) $CH_3-\overset{\oplus}{C}=O$ (g) NH_3 (h) $\overset{\oplus}{N}O_2$

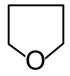
A-5. Which of the followings are nucleophile ?

(a) HS^- (b) BF_3 (c) C_2H_5-OH (d) $(CH_3)_3\ddot{N}$

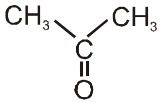
(e) $:CH_2$ (f) $:\ddot{N}H$

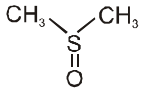
A-6. Define ambident nucleophile with an example:

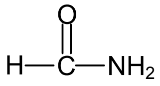
A-7. Label each of the following solvent as protic or aprotic.

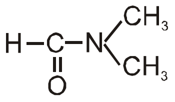
(a) 
(Tetrahydrofuran)

(b) Acetonitrile (c) Acetic acid

(d) 
(acetone)

(e) 
(DMSO)

(f) 
$H-\overset{O}{\overset{\|}{C}}-NH_2$
(Formamide)

(g) 
(DMF)

(h) Cyclohexane (i) Ammonia

Section (B) : Types of organic reactions and reactions of Grignard reagent.

B-1. Write the condition for feasibility of acid base reaction.

B-2. Write the method of preparation of Grignard reagent. Write a reaction of Grignard reagent as a base.

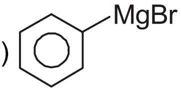
B-3. Write the product when Grignard reagent reacts with carbonyl compound followed by acidification.

B-4. 1 mole of an organic compound which have molecular formula $C_4H_4O_3$, gives 3 moles of gas on treatment with methyl magnesium bromide. Give structure of the compound.

B-5. Predict the product of the following reactions

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

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

(c)  + $DOCH_3 \longrightarrow$

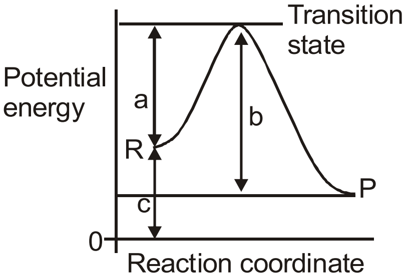
Section (C) : Chemical kinetics in Organic reactions

C-1. Consider the chemical reaction, $2A + B \longrightarrow C$

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

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

C-3. The potential energy diagram for a reaction $R \longrightarrow P$ is given below



Give answer of the following questions -
(i) Activation energy of forward reaction
(ii) Activation energy of backward reaction
(iii) Enthalpy of (ΔH°) of reaction
(iv) Threshold energy
(v) Reaction is exothermic or endothermic

PART-II : OBJECTIVE QUESTIONS

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

A-1. Which of the following is protic solvent ?
(A) Acetone (B) Ethanol (C) DMF (D) Ether

A-2. Which of the following is aprotic solvent ?
(A) DMSO (B) NH_3 (C) H_2O (D) CH_3COOH

A-3. Which among the following species is an ambident nucleophile ?
(A) Ethene (B) Benzene
(C) Nitrite ion (D) Acetone

A-4. A nucleophile is :
(A) electron-rich species (B) electron-deficient species
(C) a Lewis acid (D) positively charged species

A-5. Correct arrangement of the following nucleophiles in the order of their nucleophilic strength is :

(A) $C_6H_5O^- < CH_3O^- < CH_3COO^- < OH^-$ (B) $CH_3COO^- < C_6H_5O^- < CH_3O^- < OH^-$

(C) $C_6H_5O^- < CH_3COO^- < CH_3O^- < OH^-$ (D) $CH_3COO^- < C_6H_5O^- < OH^- < CH_3O^-$

A-6. Which one of the following has maximum nucleophilicity ?

(A) $CH_3S^\ominus$ (B) $C_6H_5\text{–}\overset{\ominus}{O}$ (C) Et_3N (D) $F^\ominus$

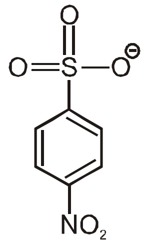
A-7. Which of the following is an electrophilic reagent ?

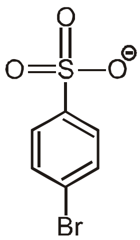
(A) H_2O (B) OH^- (C) NO_2^+ (D) None

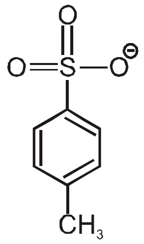
A-8. Out of the followings best leaving group is :

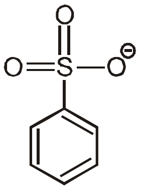
(A) F^- (B) Cl^- (C) Br^- (D) I^-

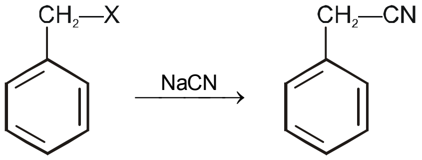
A-9. The best leaving group is :

(A) 

(B) 

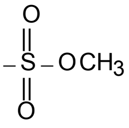
(C) 

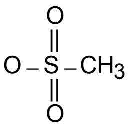
(D) 

A-10. 

In the above reaction rate is the fastest, when (X) is (Hints : rate depends upon leaving ability in this reaction):

(A) –OH (B) $\text{–}NH_2$

(C) 
$-\overset{\overset{\large O}{\|}}{\underset{\underset{\large O}{\|}}{S}}-OCH_3$

(D) 
$-O-\overset{\overset{\large O}{\|}}{\underset{\underset{\large O}{\|}}{S}}-CH_3$

Section (B) : Types of organic reactions and reactions of Grignard reagent

B-1. Substitution reactions involve :

(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.

B-2. Addition reactions involves

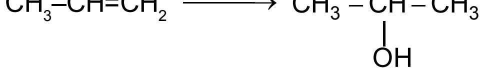
(A) Cleavage of a σ-bond and formation of a new σ-bond.

(B) Cleavage of two σ-bonds and formation of a new π-bond.

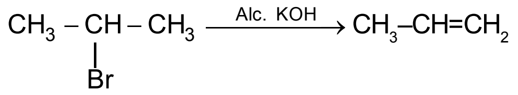
(C) Cleavage of a π-bond and formation of two new σ-bonds.

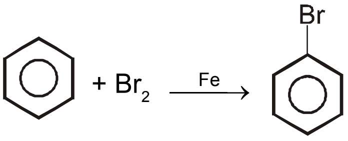
(D) None of these.

B-3. Which of the following reaction is an example of elimination reaction ?

(A) 
$CH_3\text{–}CH{=}CH_2 \xrightarrow{H_2O} CH_3-\underset{\underset{\large OH}{|}}{CH}-CH_3$

(B) $CH_3\text{–}CH_2\text{–}Br \xrightarrow{NaOH} CH_3\text{–}CH_2\text{–}OH$

(C) 
$CH_3-\underset{\underset{\large Br}{|}}{CH}-CH_3 \xrightarrow{\text{Alc. KOH}} CH_3\text{–}CH{=}CH_2$

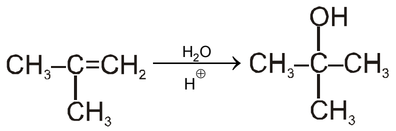
(D) 

B-4. The following reaction is an example of :

$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

(A) Acid - base reaction (B) Substitution reaction
(C) Addition reaction (D) Elimination reaction

B-5. The following reaction is an example of



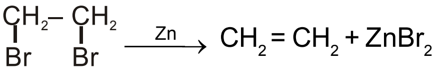
$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2 \xrightarrow[H^{\oplus}]{H_2O} CH_3-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

(A) Acid - base reaction (B) Substitution reaction
(C) Addition reaction (D) Elimination reaction

B-6. Which of the following reaction is a substitution reaction ?

(A) $CH_2 = CH_2 \xrightarrow{Ni/H_2} CH_3-CH_3$

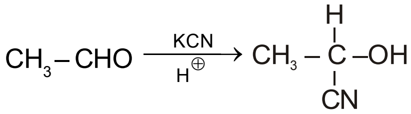
(B)



$\underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}} \xrightarrow{Zn} CH_2 = CH_2 + ZnBr_2$

(C) $CH_3 - I + \overset{\ominus}{OH} \longrightarrow CH_3OH + \overset{\ominus}{I}$

(D)



$CH_3-CHO \xrightarrow[H^{\oplus}]{KCN} CH_3-\overset{H}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-OH$

B-7. $C_6H_5COOH + CH_3MgI \longrightarrow$?

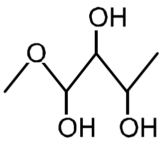
(A) $C_6H_5COOMgI$ (B) CH_4 (C) Both A & B (D) $C_6H_5COOCH_3$

B-8. $(CH_3)_3CMgCl$ on reaction with D_2O produces :

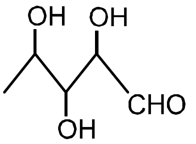
(A) $(CH_3)_3CD$ (B) $(CH_3)_3COD$ (C) $(CD_3)_3CD$ (D) $(CD_3)_3COD$

B-9. 1 mole of a compound X ($C_5H_{12}O_4$) upon treatment with CH_3MgX gives 4 mole of methane. Identify the structure of (X).

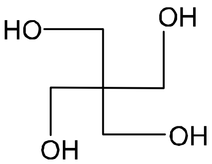
(A)



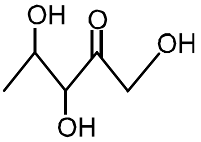
(B)



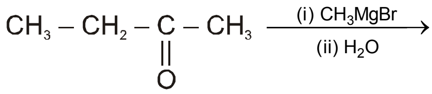
(C)



(D)

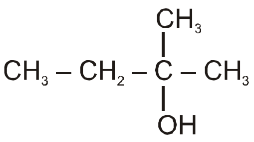


B-10.



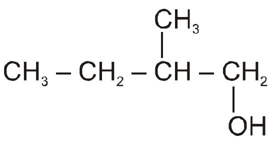
$CH_3-CH_2-\underset{O}{\underset{||}{C}}-CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr}$ Product is :

(A)



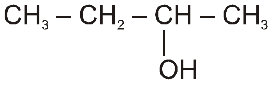
$CH_3-CH_2-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$

(B)



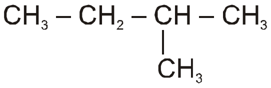
$CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

(C)



$CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$

(D)



$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

Section (C) : Chemical Kinetics in Organic reactions

C-1. For an elementary process $2X + Y \rightarrow Z + W$, the molecularity is :

(A) 2 (B) 1 (C) 3 (D) Unpredictable

C-2. What is the order of a reaction which has a rate expression = $k\,[A]^{3/2}[B]^{-1}$?

(A) 3/2 (B) 1/2 (C) 0 (D) None of these

C-3. The minimum energy for molecules to enter into chemical reaction is called ?

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

C-4. Catalyst increases the rate of reaction because :

(A) it decreases ΔH (B) it increases ΔH

(C) it decreases activation energy (D) it increases activation energy

C-5. Activation energy of a reaction is :

(A) The energy released during the reaction.

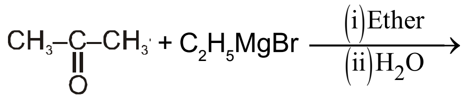
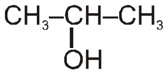
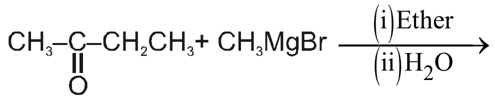
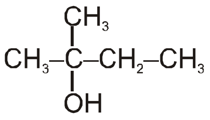
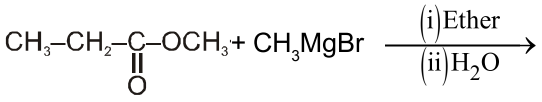
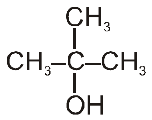
(B) The energy evolved when activated complex is formed.

(C) Minimum amount of energy needed to overcome the potential barrier of reaction.

(D) The energy needed to form one mole of the product.

PART-III : MATCH THE COLUMN

1. Match List I (Reaction) with List II (Product) and select the correct answer using the code given below the lists :

List-I	**List-II**
(A) $CH_3COCH_3 + CH_3MgBr \xrightarrow[(ii)H_2O]{(i)Ether}$	(p) CH_3-OH
(B)  $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + C_2H_5MgBr \xrightarrow[(ii)H_2O]{(i)Ether}$	(q)  $CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_3$
(C)  $CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_3 + CH_3MgBr \xrightarrow[(ii)H_2O]{(i)Ether}$	(r)  $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-CH_2-CH_3$
(D)  $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OCH_3 + CH_3MgBr \xrightarrow[(ii)H_2O]{(i)Ether}$	(s)  $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-CH_3$

2. Match the column-I with column-II :

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

Exercise # 2

PART - I : OBJECTIVE QUESTIONS

1. Identify set of electrophiles :

(A) CO_2, $\overset{\oplus}{C}H_3$, $:CH_2$, $Br^{\oplus}$

(B) HOH, SO_3, $:CCl_2$, $Cl^{\oplus}$

(C) SO_2, $CH_3-\underset{\cdot\cdot}{\ddot{O}}H$, $\overset{\oplus}{N}O_2$, $:CFCl$

(D) $H-\overset{\oplus}{C}=O$, $\overset{\oplus}{N}=O$, $Ph-\overset{\oplus}{C}H_2$, $\ddot{N}H_3$

2. Which of the following reactions is not feasible ?

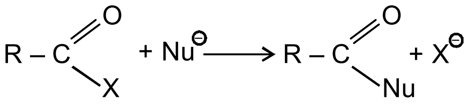
(A) $PhSO_3H + NaHCO_3 \longrightarrow$

(B) $Ph–OH + NaNH_2 \longrightarrow$

(C) $CH_3–NH_2 + NaOH \longrightarrow$

(D) $Ph–C\equiv CH + NaH \longrightarrow$

3. The reaction



is slowest when X is :

(A) Cl (B) NH_2 (C) OC_2H_5 (D) $OCOCH_3$

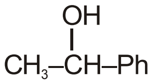
4. Consider the following groups :

(I) –OAc (II) –OMe (III) $–OSO_2Me$ (IV) $–OSO_2CF_3$

The order of leaving group nature is:

(A) I > II > III > IV (B) IV > III > I > II (C) III > II > I > IV (D) II > III > IV > I

5.



$$P \xrightarrow{PhMgBr} \xrightarrow{H_2O} CH_3–\underset{}{\overset{OH}{\overset{|}{C}}}H–Ph \quad (d+\ell)$$

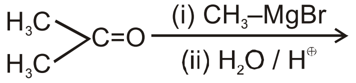
P can be :

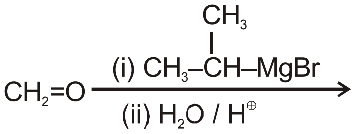
(A) CH_3COOH (B) $H–COOCH_3$ (C) $CH_3–COCl$ (D) $CH_3–CH=O$

6. Butan-2-ol is obtained by using carbonyl compound and Grignard reagent as :

(A) $CH_3–CH=O \xrightarrow[(ii)\ H_2O\ /\ H^{\oplus}]{(i)\ CH_3–CH_2–MgBr}$

(B) $CH_3–(CH_2)_2–CH=O \xrightarrow[(ii)\ H_2O\ /\ H^{\oplus}]{(i)\ CH_3–MgBr}$

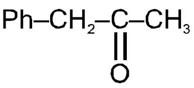
(C) 

(D) 

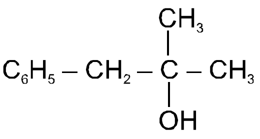
$CH_2=O \xrightarrow[(ii)\ H_2O\ /\ H^{\oplus}]{(i)\ CH_3–\overset{CH_3}{\overset{|}{C}}H–MgBr}$

7. Predict the major product in the following reaction:

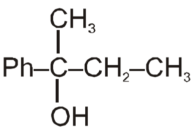
$$C_6H_5CH_2CO_2CH_3 \xrightarrow[2.\ H^+]{1.\ CH_3MgBr\ (excess)}$$

(A) 

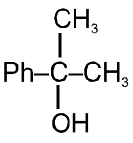
$Ph–CH_2–\underset{O}{\underset{||}{C}}–CH_3$

(B) 

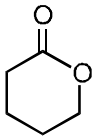
$C_6H_5 – CH_2 – \overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}} – CH_3$

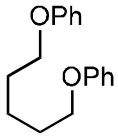
(C) 

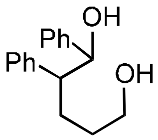
$Ph–\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}–CH_2–CH_3$

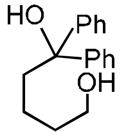
(D) 

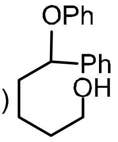
$Ph–\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}–CH_3$

8.  $\xrightarrow[\text{(2) } H_2O]{\text{(1) excess PhMgBr}}$ X, X is

(A) 

(B) 

(C) 

(D) 

9. The differential rate law equation for the elementary reaction A + 2B $\xrightarrow{K}$ 3C, is :

(A) $-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k\,[A]\,[B]^2$

(B) $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k\,[A]^2\,[B]$

(C) $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k\,[A]\,[B]^2$

(D) None of these

10. Following mechanism has been proposed for a reaction 2A + B → D + E
Step-1 A + B → C + D (slow step)
Step-2 A + C → E (fast step)
The rate law expression for the reaction is :
(A) rate = $K[A]^2\,[B]$
(B) rate = $K\,[A]\,[B]$
(C) rate = $K\,[A]^2$
(D) rate = $K[A][C]$

PART - II : NUMERICAL TYPE QUESTIONS

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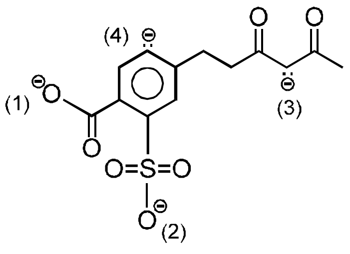
1. Among the following X is the number of electrophiles and Y is the number of nucleophiles. Report your answer as $\boxed{X \mid Y}$.

(i) $CH_3^{\oplus}$
(ii) $I^{\ominus}$
(iii) $NO_2^{\oplus}$
(iv) $\overset{\ominus}{C}H_3$
(v) $\ddot{N}H_3$
(vi) $Br^{\oplus}$
(vii) $\overset{\ominus}{Cl}$
(viii) H^+
(ix) $AlCl_3$
(x) CH_3OH
(xi) $CH_3-\overset{\oplus}{C}=O$
(xii) BH_3

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



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

4. How many compounds out of following will give secondary alcohol on treatment with Grignard reagent ?

(a) Ph–CO–CH_3 (b) Ph–CHO (c) HCHO (d) CH_3CH_2CHO

(e) CH_3CHO (f) Ph–CO–Ph (g) HCOOEt (h) $CH_3COOC_2H_5$

5. For the reaction A + B → 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 :

6. Find the moleculer weight of a carbonyl compound which react with methyl magnesium bromide to give primary alcohol ?

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

(1) PhO^- (2) $C_2H_5O^-$ (3) HS^- (4) Ph^-

(5) CH_3COO^- (6) $CH_3SO_3^-$ (7) PhS^- (8) CH_3OH

(9) NH_3 (10) CH_3^-

8. How many of the following are non-polar solvent ?

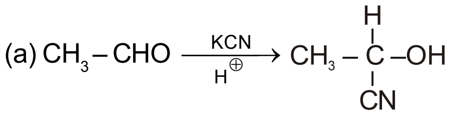
(a) DMS (b) CCl_4 (c) $CHCl_3$ (d) Acetone

(e) Ethyl alcohol (f) Dimethylacetamide (g) Benzene (h) Tetrahydrofuran

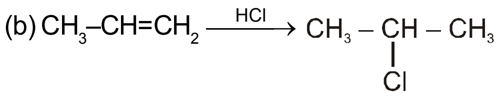
9. Complete the following reaction and calculate the number of sp^2 hybrid carbon atoms in the final product ?

$$\text{Ph–CHO} \xrightarrow[\text{(ii)}H_2O]{\text{(i)PhMgBr}}$$

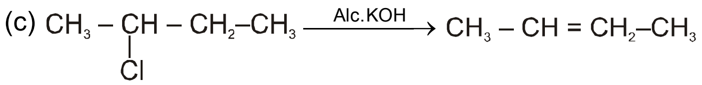
10. How many of the following reactions are addition reaction ?



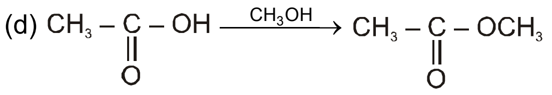
(a) $CH_3-CHO \xrightarrow[H^{\oplus}]{KCN} CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}-OH$



(b) $CH_3\text{–}CH{=}CH_2 \xrightarrow{HCl} CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3$

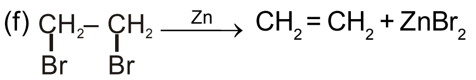


(c) $CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_2\text{–}CH_3 \xrightarrow{\text{Alc.KOH}} CH_3-CH=CH_2\text{–}CH_3$

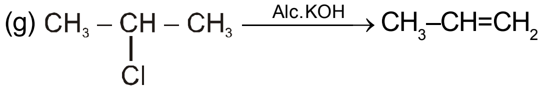


(d) $CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-OH \xrightarrow{CH_3OH} CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-OCH_3$

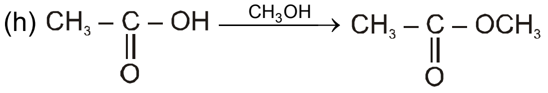
(e) $CH_3\text{–}CH_2\text{–}CH_2\text{–}OH \xrightarrow{PCl_5} CH_3\text{–}CH_2\text{–}CH_2\text{–}Cl$



(f) $\underset{\underset{\displaystyle Br}{|}}{CH_2}-\underset{\underset{\displaystyle Br}{|}}{CH_2} \xrightarrow{Zn} CH_2=CH_2+ZnBr_2$



(g) $CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3 \xrightarrow{\text{Alc.KOH}} CH_3\text{–}CH{=}CH_2$



(h) $CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-OH \xrightarrow{CH_3OH} CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-OCH_3$

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

1. Electrophiles are

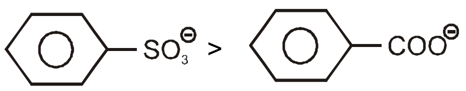
(A) electron deficent species (B) having atleast one pair of electron

(C) electron rich species (D) electron pair acceptor

2. Which of the following is/are ambident nucleophile(s) ?

(A) NO_2^- (B) $CN^{\ominus}$ (C) $NaHSO_3$ (D) SCN^-

3. The correct order of leaving group ability is/are :

(A) 

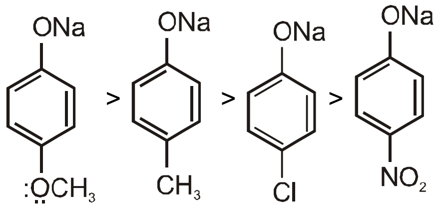
$C_6H_5SO_3^{\ominus} > C_6H_5COO^{\ominus}$

(B) $CF_3SO_3^{\ominus} > CCl_3SO_3^{\ominus}$

(C) $\overset{\ominus}{C}N > I^{\ominus}$ (D) $\overset{\ominus}{N}H_2 > \overset{\ominus}{O}H$

4. Which of the following given species in decreasing order of their nucleophilicity ?

(A) $I^{\ominus} > \overset{\ominus}{Br} > Cl^{\ominus} > H_2O$

(B) 

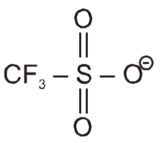
(C) $CH_3O^- > CH_3^-$ (D) $C_2H_5O^- > (CH_3)_3CO^-$

5. Identify set of nucleophiles :

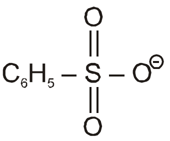
(A) $\overset{\ominus}{Cl}, \overset{\ominus}{O}H, \overset{\ominus}{R}, :CH_2$ (B) $CH_3COO^-, N_3^-, H_3O^+, HS^-$

(C) $CH_2{=}CH_2, CH_3NH_2, CH_3CH_2OH,$  (D) $H^-, CN^-, MeSH, PhNH_2$

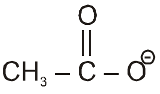
6. In nucleophilic substitution reactions the leaving ability is better than phenoxide ion for the following species is (when attached to the sp^3 hybridised carbon.)

(A) 

$CF_3-SO_2-O^{\ominus}$

(B) 

$C_6H_5-SO_2-O^{\ominus}$

(C) 

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus}$

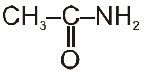
(D) $C_2H_5O^-$

7. Which of the following reactions yield benzene ?

(A) $PhMgBr + CH_3{-}Br$ (B) $PhMgBr + H_2O$ (C) $PhBr + H_2O$ (D) $PhMgBr + CH_3{-}C{\equiv}CH$

8. Which of the following liberate hydrogen gas with NaH?

(A) $CH_3{-}COOH$

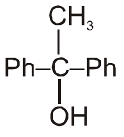
(B) 

$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-NH_2$

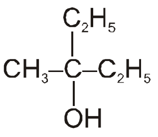
(C) $CH_3{-}C{\equiv}CH$ (D) $CH_3{-}CH_2{-}OH$

9. $$\text{X (an ethyl ester)} \xrightarrow[\text{(ii)}H_3O^{\oplus}]{\text{(i) Grignard's reagent (Y) (execess)}} \text{product}$$

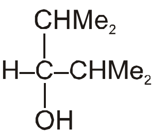
The product(s) may be :

(A) 

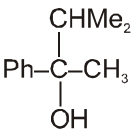
$Ph-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-Ph$

(B) 

$CH_3-\overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-C_2H_5$

(C) 

$H-\overset{\overset{\displaystyle CHMe_2}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CHMe_2$

(D) 

$Ph-\overset{\overset{\displaystyle CHMe_2}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3$

PART - IV : COMPREHENSION

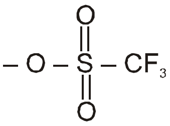
Comprehension # 1

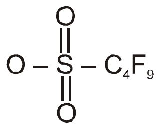
Nucleophilic aliphatic substitution reaction is given by those compounds which have electron rich groups as leaving groups. Less is the basicity of the leaving group, more is its leaving power.

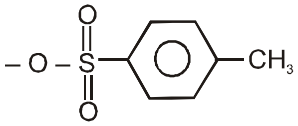
$$R-L+\overset{\ominus}{Nu}\longrightarrow R-Nu+\overset{\ominus}{L}$$

In the given reaction, L is the leaving group which leaves as nucleophile. $\overset{\ominus}{Nu}$ 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 ?

(A) 
$-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-CF_3$

(B) 
$-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-C_4F_9$

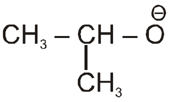
(C) 

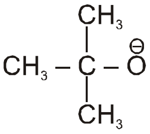
(D) $-\overset{\ominus}{Cl}$

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

(A) $\overset{\ominus}{CH_3}$

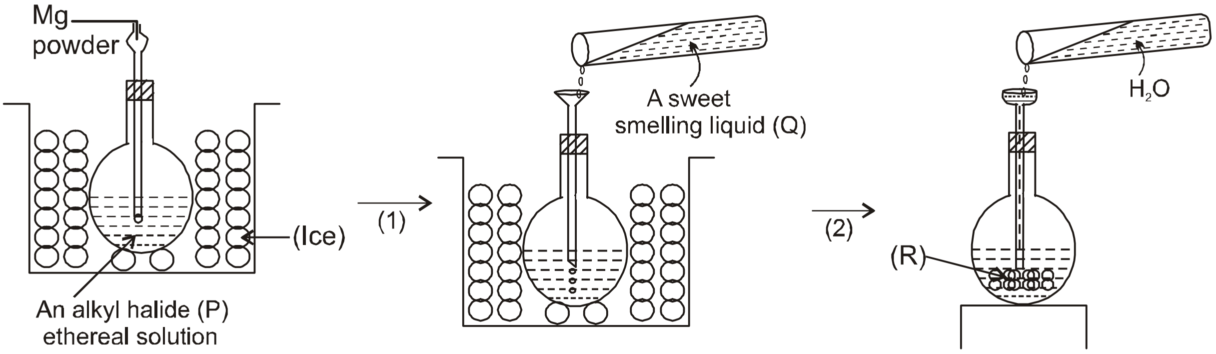
(B) $H\overset{\ominus}{O}$

(C) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{\ominus}{O}$

(D) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{\ominus}{O}$

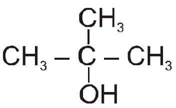
Comprehension-2

Observe the following experiment

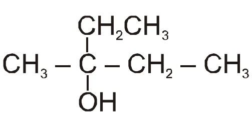


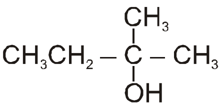
(I) (II) (III)

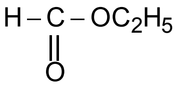
3. If the reactant 'P' is ethyl chloride then the product R can not be

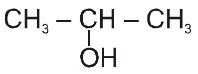
(A) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$

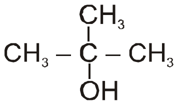
(B) $CH_3CH_2-O-CH_2CH_3$

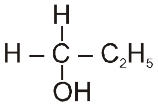
(C) 
$CH_3-\overset{CH_2CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2-CH_3$

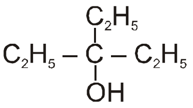
(D) 
$CH_3CH_2-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$

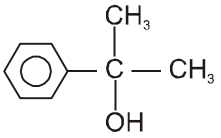
4. If the liquid Q is  $H-\underset{\underset{O}{\|}}{C}-OC_2H_5$ then the product R can be (P can be any other halide)

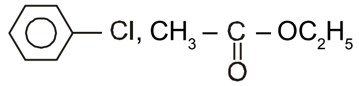
(A)  $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$

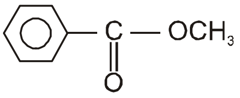
(B)  $CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$

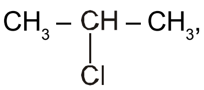
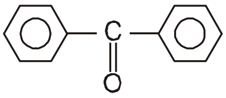
(C)  $H-\overset{H}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-C_2H_5$

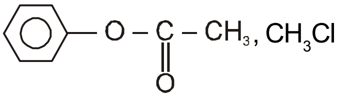
(D)  $C_2H_5-\overset{C_2H_5}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-C_2H_5$

5. If R is  then P and Q can be respectively.

(A) 

(B) CH_3-Cl, 

(C)  

(D) 

Exercise # 3

PART- I : JEE ADVANCE PROBLEMS (PREVIOUS YEARS)

1. Consider the chemical reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

The rate of this reaction can be expressed in terms of time derivatives of conc. of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst rate expressions : **[JEE-2002, 3/90]**

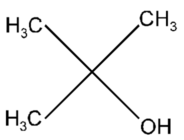
(A) Rate = $-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

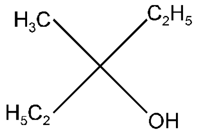
(B) Rate = $\frac{d[N_2]}{dt} = -3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$

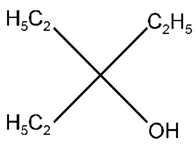
(C) Rate = $\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

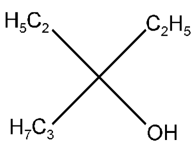
(D) Rate = $-\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

2. Ethylester $\xrightarrow[\text{excess}]{CH_3MgBr}$ P. The product P will be **[JEE-2003, 3/84]**

(A) 

(B) 

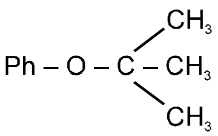
(C) 

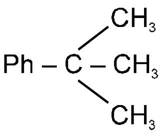
(D) 

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

(A) Ph – OH

(B) Ph – H

(C) 

(D) 

PART - II : JEE MAIN PROBLEMS (PREVIOUS YEARS)

1. Following reaction $(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$

is an example of : **[AIEEE-2002]**

(A) Elimination reaction (B) Free radical substitution

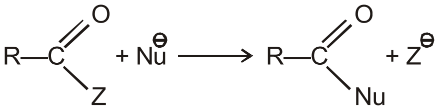
(C) Nucleophilic substitution (D) Electrophilic substitution

2. For the reaction A + 2B → C, rate is given by R = [A] $[B]^2$ then the order of the reaction is :

[AIEEE- 2002]

(A) 3 (B) 6 (C) 5 (D) 7

3. Rate of the reaction is fastest when Z is : **[AIEEE-2004]**



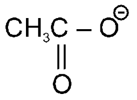
(A) Cl (B) $OCOCH_3$ (C) OC_2H_5 (D) NH_2

4. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives

[AIEEE-2004, 3/225]

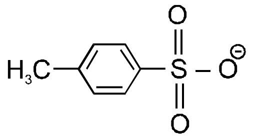
(A) Acetone (B) Acetamide (C) 2-Methyl-2-propanol (D) Acetyl iodide

5. The decreasing order of nucleophilicity among the following nucleophiles : **[AIEEE-2005, 3/225]**

(a) 
$CH_3\underset{\underset{O}{\|}}{C}-O^{\ominus}$

(b) $CH_3O^{\ominus}$

(c) $CN^{\ominus}$

(d) 

(A) (c), (b), (a), (d) (B) (b), (c), (a), (d) (C) (d), (c), (b), (a) (D) (a), (b), (c), (d)

6. $CH_3Br + Nu^- \longrightarrow CH_3 - Nu + Br^-$

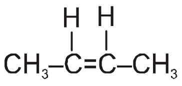
The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is :

[Nu^- = (A) → PhO^-, (B) → AcO^-, (C) → HO^-, (D) → CH_3O^-] **[AIEEE-2006]**

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

7. The treatment of CH_3MgX with $CH_3C{\equiv}C{-}H$ produces **[AIEEE-2008, 3/105]**

(A) $CH_3C{\equiv}C{-}CH_3$

(B) 
$CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_3$

(C) CH_4

(D) $CH_3{-}CH{=}CH_2$

8. For a reaction $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance of 'A' related to the rate of appearance of 'B' by the expression. **[AIEEE- 2008, 3/105]**

(A) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$ (B) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (C) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$ (D) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

9. Consider thiol anion ($RS^{\ominus}$) and alkoxy anion ($RO^{\ominus}$). Which of the following statement is correct ?

(A) $RS^{\ominus}$ is less basic but more nucleophilic than $RO^{\ominus}$. **[AIEEE-2011]**

(B) $RS^{\ominus}$ is more basic and more nucleophilic than $RO^{\ominus}$.

(C) $RS^{\ominus}$ is more basic but less nucleophilic than $RO^{\ominus}$.

(D) $RS^{\ominus}$ is less basic and less nucleophilic than $RO^{\ominus}$.

10. The increasing order of nucleophilicity of the following nucleophiles is : **[JEE(Main) 2019 Online (11-04-19)]**

(a) $CH_3CO_2^-$ (b) H_2O (c) $CH_3SO_3^-$ (d) OH^-

(A) (d) < (a) < (c) < (b) (B) (b) < (c) < (a) < (d)

(C) (a) < (d) < (c) < (b) (D) (b) < (c) < (d) < (a)

ANSWER KEY

Exercise # 1

PART - I

A-1. Electrophiles : Electrophiles are electron deficient species. Which can accept a pair of electron.

e.g. $\overset{\oplus}{H}$ $\overset{\oplus}{Cl}$,$\overset{\oplus}{Br}$,$\overset{\oplus}{NO_2}$, $\overset{\oplus}{CH_3}$ (positively charged species)

PCl_5, SO_2, SO_3 BH_3 (species with vacant orbital at central atom).

Nucleophiles : Nucleophiles are electron rich species having atleast one unshared pair of electron. It can be neutral or negativetely charged.

e.g. CN^-, OH^- Br^-, NH_2^-, NH_3, H_2O etc.

A-2. The tendency to give e- pair to an electron deficient carbon atom is defined as nucleophilicity.
Factors affecting nucleophilicity:
(i) Size: Nucleophilicity $\propto$ size (donor atom)
On going from top to bottom in periodic table nucleophilicity increases because of increasing in size.
(ii) Electronegativity: More is the electronegativity of the donor atom less is the nucleophilicity.
On going from left to right in periodic table nucleophilicity decreases because of electronegativity increases

$$\text{Nucliophilicity} \propto \frac{1}{EN}$$

(iii) Steric effect: Nucleophilicity is inversly proportional to steric hindrence
(iv) Nucleophilicity $\propto$ polarisability (distortion of e^- cloud)

A-3. The groups which depart from molecule during substitution reaction are known as leaving group. Leaving group ability directly proportional to stability of anion. It means that weaker bases are better leaving group because they are stable.

A-4. b, c, d, e, f, h
CN^- and NH_3 are nucleophile

A-5. a, c, d
BF_3, $:\ddot{N}H$ and $:CH_2$ can not act as nucleophiles because their p-orbitals are vacant.

A-6. **Ambident nucleophile :** The species which have more than one nucleophilic sites for reaction are called ambident nucleophiles.
For example, cyanide ion :

$:\bar{C}\equiv N: \rightleftharpoons :C=N:^{-}$

$CH_3Br + AgCN \longrightarrow CH_3NC + AgBr$

$CH_3Br + KCN \longrightarrow CH_3CN + KBr$

A-7.

Protic solvent	(c, f, i)
Aprotic solvent	(a, b, d, e, g, h)

B-1. Those acid base reactions are feasible which result in weak acid & weak base.

e.g. (i) $HCOOH + CH_3\text{-}COONa \longrightarrow HCOONa + CH_3COOH$ (feasible)

(ii) $Ph\text{-}COOH + Ph\text{-}ONa \longrightarrow Ph\ COONa + Ph\text{-}OH$ (feasible)

B-2. Preparation:

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

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.

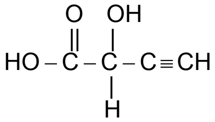
Following is the reaction of Grignard reagent as a base.

$$CH_3COOH + CH_3MgBr \longrightarrow CH_3COOMgBr + CH_4$$

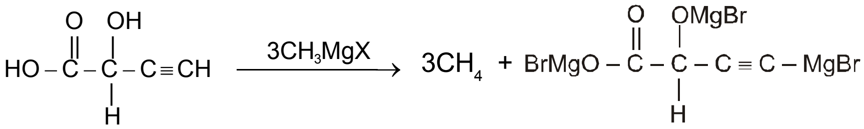
B-3. (a) When Grignard reagent reacts with formaldehyde followed by acidification 1° alcohol is formed.

(b) When Grignard reagent reacts with any other aldehyde followed by acidification 2° alcohol is formed.

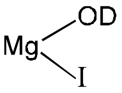
(c) When Grignard reagent reacts with any ketone followed by acidification 3° alcohol is formed.

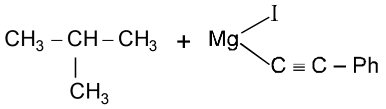
B-4. 

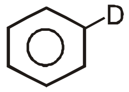
$$HO-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{OH}{C}}-C\equiv CH$$

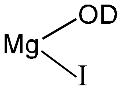


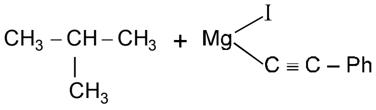
$$HO-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{OH}{C}}-C\equiv CH \xrightarrow{3CH_3MgX} 3CH_4 + BrMgO-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{OMgBr}{C}}-C\equiv C-MgBr$$

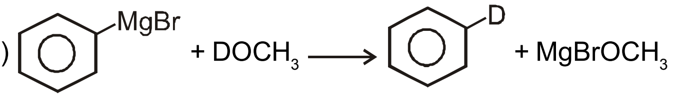
B-5. (a) CH_3-D + 

(b) 

(c) 

(a) $CH_3MgI + D_2O \longrightarrow CH_3-D$ + 

(b) $(CH_3)_2CH–CH_2MgI + Ph–C\equiv CH \longrightarrow$ 

(c) 

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

C-2. Rate = K $[A][B][C]^2$

C-3. (i) a (ii) b (iii) b – a (iv) a + c (v) Exothermic

PART - II

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

PART - III

1.	A–s, B–r, C–r, D–p, r	**2.**	A–p, r, s ; B–r, s ; C–r, s ; D–p, q

Exercise # 2

PART - I

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

PART - II

1.	75	**2.**	4	**3.**	88	**4.**	4	**5.**	8
6.	30	**7.**	**5**	**8.**	2	**9.**	**12**	**10.**	2

PART - III

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

PART - IV

1.	(B)	**2.**	(D)	**3.**	(B)	**4.**	(A)	**5.**	(B)

Exercise # 3

PART - I

1.	(A)	**2.**	(A)	**3.**	(B)

PART - II

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

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

Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

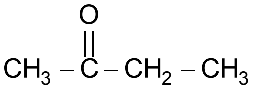
SECTION–I : (Maximum Marks : 80)

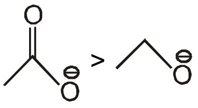
- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :
  Full Marks : +4 If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

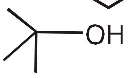
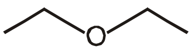
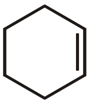
---

1. Which one of the following has minimum nucleophilicity ?
(A) $(CH_3)_3CLi$ (B) $NaNH_2$ (C) CH_3ONa (D) NaOH

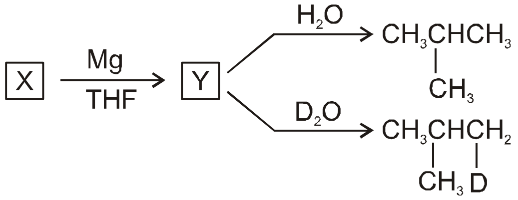
2. Which of the following is a nucleophile ?
(A) $\overset{\bullet}{C}H_3$ (B) $CH_2\mathbf{:}$ (C) $CH_3-\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}}$ (D) $CH_3-\overset{\bullet\bullet}{N}H_2$

3. Which of the following reactants will give only one organic product when reacted with NaCN / H_2SO_4 (small amounts) (No other isomer is obtained)
(A) CH_3CHO (B) HCHO (C) PhCHO (D) 
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

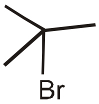
4. The correct order of leaving ability is :
(A) $\overset{\ominus}{O}H > H_2O$ (B) $\overset{\ominus}{O}H > \overset{\ominus}{S}H$ (C)  (D) $\overset{\ominus}{Cl} > \overset{\ominus}{I}$

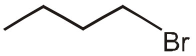
5. In which of reaction  will obtained as a product ?
(A) PhMgBr +  (B) PhMgBr + 
(C) PhMgBr + $CH_3–CH_2–CH_3$ (D) PhMgBr + 

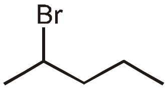
6.

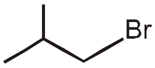


Give the structure of X.

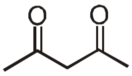
(A)


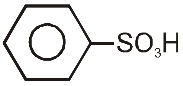
(B)


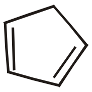
(C)


(D)


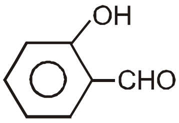
7. Which of the following compound give benzene on reaction with PhMgBr.

1.


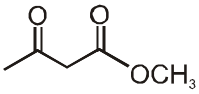
2.


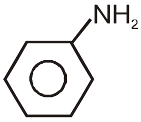
3.


4. $CH_3–C≡CH$

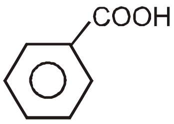
5.


6. CH_3NH_2 s

7.


8.


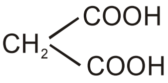
9. CH_3SH

10.


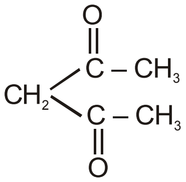
(A) 2,3,4,5 (B) 7,8,9 (C) 2,4,5,7,10 (D) All सभी

8. In which of the following reaction CH_4 will be obtained.

(i) $CH_3–MgBr + CH_3–C≡CH$

(ii) $CH_3 – MgBr + CH_2$

$CH_3-MgBr + CH_2(COOH)_2$

(iii) $CH_3–MgBr + HCN$

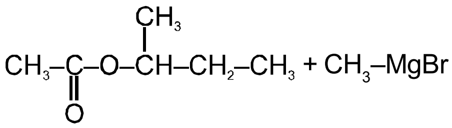
(iv) $CH_3 – MgBr + CH_2$

$CH_3-MgBr + CH_2(\overset{O}{\overset{\|}{C}}-CH_3)(\underset{O}{\underset{\|}{C}}-CH_3)$

(A) (i), (ii) & (iii) (B) (i), (ii), (iii) & (iv) (C) (iii) & (iv) (D) (iii) & (i), (iv)

9. Which of the following will not give 2° alcohol ?

(A) $CH_3–CH_2–CHO+ CH_3–MgBr$

(B) $CO_2 + CH_3–MgBr$

(C)

$CH_3–\underset{\underset{O}{\|}}{C}–O–\overset{\overset{CH_3}{|}}{C}H–CH_2–CH_3 + CH_3–MgBr$

(D) $HCHO \xrightarrow[Et_2O]{CH_3MgBr\,(excess)}$

10. Which of these statements is incorrect about nucleophiles ?

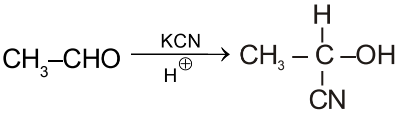
(A) Nucleophiles have an unshared electron pair and can make use of this to react with an electron deficient species.

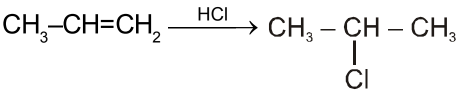
(B) The nucleophilicity of an element (as electron donor) generally increases on going down a group in the periodic table.

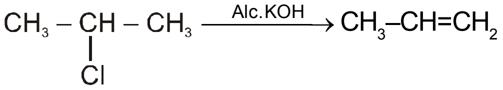
(C) A nucleophile is electron-deficient species.

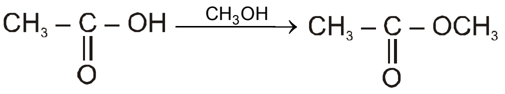
(D) All good nucleophiles are good bases when we deal across the period.

11. Which of the following reaction is substitution reaction ?

(A) 
$CH_3–CHO \xrightarrow[H^{\oplus}]{KCN} CH_3-\overset{H}{\underset{CN}{C}}-OH$

(B) 
$CH_3–CH=CH_2 \xrightarrow{HCl} CH_3-\underset{Cl}{CH}-CH_3$

(C) 
$CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow{Alc.KOH} CH_3–CH=CH_2$

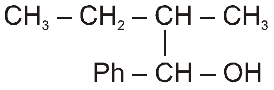
(D) 
$CH_3-\underset{O}{\overset{}{C}}-OH \xrightarrow{CH_3OH} CH_3-\underset{O}{C}-OCH_3$

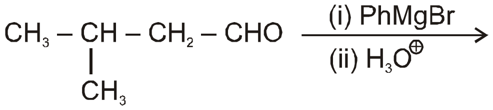
12. Which species will not be considered as an electrophile ?

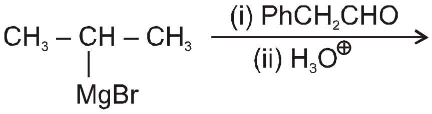
(A) $CH_3-CH_2^{\oplus}$ (B) $AlCl_3$ (C) NH_3 (D) SO_3

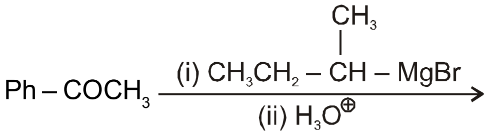
13. When Grignard reagent is treated with isopropyl formate followed by acid hydrolysis we get ?

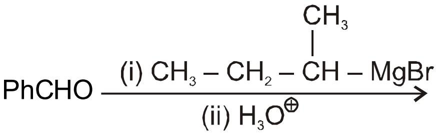
(A) Aldehyde (B) 2° alcohol (C) 3° alcohol (D) 1° alcohol

14. Compound 
$CH_3-CH_2-\underset{Ph-CH-OH}{CH}-CH_3$ can be prepared by :

(A) 
$CH_3-\underset{CH_3}{CH}-CH_2-CHO \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ PhMgBr}$

(B) 
$CH_3-\underset{MgBr}{CH}-CH_3 \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ PhCH_2CHO}$

(C) 
$Ph-COCH_3 \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ CH_3CH_2-\overset{CH_3}{CH}-MgBr}$

(D) 
$PhCHO \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ CH_3-CH_2-\overset{CH_3}{CH}-MgBr}$

15. Identify the correct set of aprotic solvent .

(A) Water, DMSO (B) DMSO, Acetone

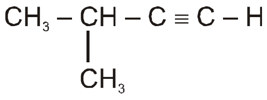
(C) Ethanol, Acetone (D) Diethylether, Methyl amine

16. Leaving group ability order amongst the following

(I) $C_6H_5O^-$ (II) p-$(CH_3)C_6H_4O^-$ (III) p-$(OCH_3)C_6H_4O^-$ (IV) p-$(NO_2)C_6H_4O^-$

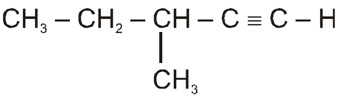
(A) I > II > III > IV (B) III > II > I > IV (C) IV > I > II > III (D) IV > III > II > I

17. 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

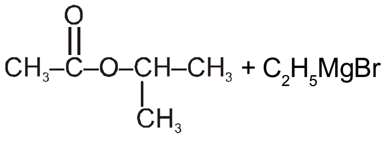
(A) 
$CH_3-\underset{CH_3}{CH}-C\equiv C-H$

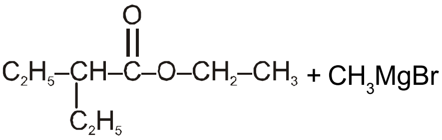
(B) $CH_3–C\equiv C–H$

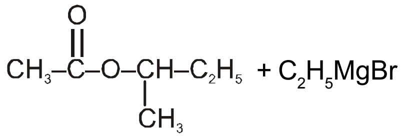
(C) $CH_3–CH_2–C\equiv C–H$

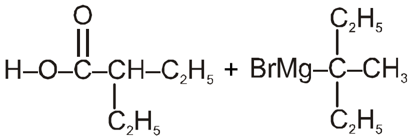
(D) 
$CH_3-CH_2-\underset{CH_3}{CH}-C\equiv C-H$

18. An ester on treatment with excess of Grignard reagent followed by acidification gives Butane-2-ol and 3-methylpentan-3-ol. Predict the reactant from the following :

(A) 
$CH_3–\overset{O}{C}–O–\underset{CH_3}{CH}–CH_3 + C_2H_5MgBr$

(B) 
$C_2H_5–\underset{C_2H_5}{CH}–\overset{O}{C}–O–CH_2–CH_3 + CH_3MgBr$

(C) 
$CH_3–\overset{O}{C}–O–\underset{CH_3}{CH}–C_2H_5 + C_2H_5MgBr$

(D) 
$H–O–\overset{O}{C}–\underset{C_2H_5}{CH}–C_2H_5 + BrMg–\overset{C_2H_5}{\underset{C_2H_5}{C}}–CH_3$

19. Decreasing order of relative nucleophilicity of the following nucleophiles in protic solvent is :

$\overset{\ominus}{\text{SH}}$, $\text{Ac}\overset{\ominus}{\text{O}}$, $\text{Ph}\overset{\ominus}{\text{O}}$, $\overset{\ominus}{\text{OH}}$, H_2O

(A) $\overset{\ominus}{\text{SH}} > \overset{\ominus}{\text{OH}} > H_2O > \text{Ac}\overset{\ominus}{\text{O}} > \text{Ph}\overset{\ominus}{\text{O}}$ (B) $\overset{\ominus}{\text{SH}} > \overset{\ominus}{\text{OH}} > \text{Ph}\overset{\ominus}{\text{O}} > \text{Ac}\overset{\ominus}{\text{O}} > H_2O$

(C) $\overset{\ominus}{\text{SH}} > \text{Ph}\overset{\ominus}{\text{O}} > \overset{\ominus}{\text{OH}} > H_2O > \text{Ac}\overset{\ominus}{\text{O}}$ (D) $\overset{\ominus}{\text{OH}} > \overset{\ominus}{\text{SH}} > \text{Ph}\overset{\ominus}{\text{O}} > \text{Ac}\overset{\ominus}{\text{O}} > H_2O$

20. Which of the following is not correct order for nucleophicity as well as basicity.
निम्न में से किसमें नाभिकस्नेहीता के साथ–साथ क्षारकता का सही क्रम नहीं हैं ?

(A) $HO^{\ominus} >> H_2O$ (B) $NH_2^{\ominus} >> NH_3$ (C) $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ (D) $MeO^{\ominus} > HO^{\ominus} > MeCOO^{\ominus}$

SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

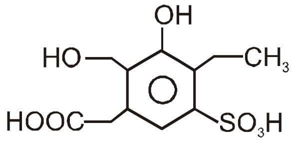
  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 If ONLY the correct numerical value is entered as answer.

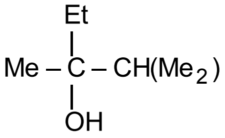
---

21. How many functional groups produced CH_4 gas by the reaction of compound (I) with CH_3MgBr.?
यौगिक (I) कि CH_3–Mg–Br के साथ अभिक्रिया कराने पर कितने क्रियात्मक समूह CH_4 गैस देते है?

(I)



22. How many types of Grignard reagent (RMgCl) can be used to prepare the following alcohol, by using different ketones ?



$$\text{Me}-\overset{\overset{\text{Et}}{|}}{\underset{\underset{\text{OH}}{|}}{\text{C}}}-\text{CH(Me}_2)$$

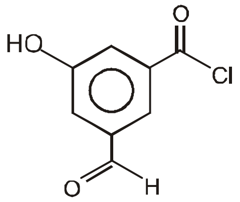
23. How many of the following reactions are examples of Acid-Base reaction?

(a) $CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3$ (b) $CH_3COOH + NaH \rightarrow CH_3COONa + H_2$
(c) $CH_3COCl + NaOH \rightarrow CH_3COOH + NaCl$ (d) $CH_3COCl + NH_3 \rightarrow CH_3CONH_2$

24. How many of the following solvent(s) is/are non-polar in nature ?

(a) CCl_4 (b) Dimethylacetamide (c) Benzene (d) Furan
(e) Toluene (f) Acetic acid (g) Carbondisulfide (h) Tetrahydropyrane

25.



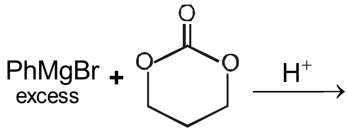
$\xrightarrow{\text{(x) RMgX}}$ Final product. X = Moles of RMgX consumed. value of X is :

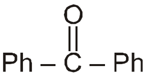
PART 2 : PAPER JEE (ADVANCED) PATTERN

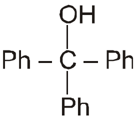
SECTION-I : (Maximum Marks : 12)

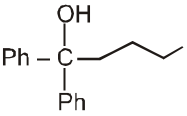
- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

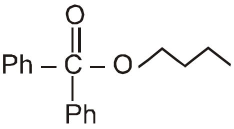
Full Marks : +3 If only the bubble corresponding to the correct option is darkened.
Zero Marks : 0 If none of the bubbles is darkened.
Negative Marks : –1 In all other cases

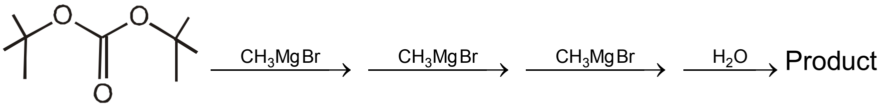
1.  (A) . Product (A) is :

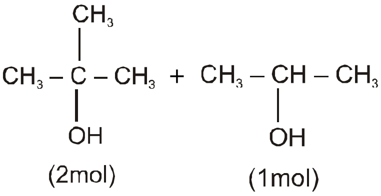
(A) 
$Ph-\overset{O}{\overset{\|}{C}}-Ph$

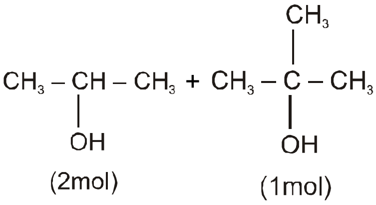
(B) 
$Ph-\underset{Ph}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-Ph$

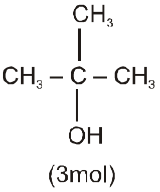
(C) 

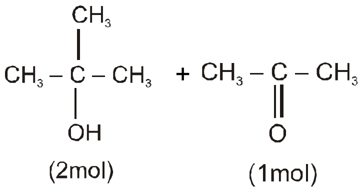
(D) 

2. 

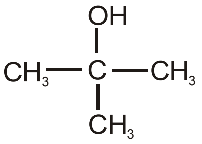
(A) 
$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 + CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$
(2mol) (1mol)

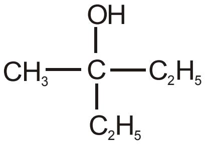
(B) 
$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 + CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$
(2mol) (1mol)

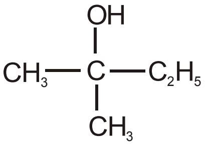
(C) 
$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$
(3mol)

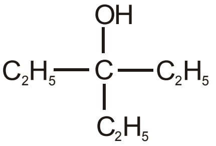
(D) 
$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 + CH_3-\underset{O}{\underset{\|}{C}}-CH_3$
(2mol) (1mol)

3. A sweet smelling compound(x) with molecular formula $C_8H_{16}O_2$ on reaction with excess of CH_3MgBr followed by acidification gives a single organic product(y), the structure of (y) can be :

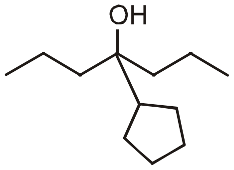
(A) 
$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3$

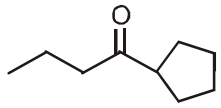
(B) 
$CH_3-\overset{OH}{\underset{C_2H_5}{C}}-C_2H_5$

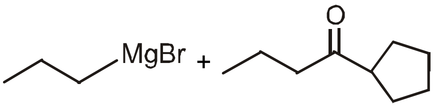
(C) 
$CH_3-\overset{OH}{\underset{CH_3}{C}}-C_2H_5$

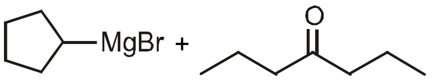
(D) 
$C_2H_5-\overset{OH}{\underset{C_2H_5}{C}}-C_2H_5$

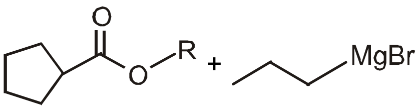
4. Which of the following combination of reactants can not be used to prepare the following compound ?



(A) CH_3MgBr (excess) + 

(B) 

(C) 

(D)  (excess)

SECTION - II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks	: +4	If only (all) the correct option(s) is (are) chosen.
Partial Marks	: +3	If all the four options are correct but ONLY three options are chosen.
Partial Marks	: +2	If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks	: +1	If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks	: 0	If none of the options is chosen (i.e. the question is unanswered).
Negative Marks	: –1	In all other cases.

- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

5. The correct nucleophilicity order(s) is/are :

(A) $CH_3O^{\ominus} > CH_3^{\ominus}$
(B) $CH_3S^{\ominus} > CH_3SH$
(C) $NH_3 > H_2O$
(D) $(CH_3CH_2)_3N > (CH_3CH_2)_3P$

6. Choose the correct order of nucleophilicity.

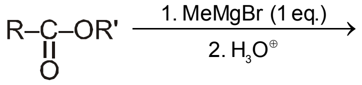
(A) $F^{\ominus}_{(DMSO)} > Cl^{\ominus}_{(DMSO)} > Br^{\ominus}_{(DMSO)} > I^{\ominus}_{(DMSO)}$
(B) $F^{\ominus}_{(aq)} > Cl^{\ominus}_{(aq)} > Br^{\ominus}_{(aq)} > I^{\ominus}_{(aq)}$
(C) $I^{\ominus}_{(aq)} > Br^{\ominus}_{(aq)} > Cl^{\ominus}_{(aq)} > F^{\ominus}_{(aq)}$
(D) $I^{\ominus}_{(DMSO)} > Br^{\ominus}_{(DMSO)} > Cl^{\ominus}_{(DMSO)} > F^{\ominus}_{(DMSO)}$

7. Which statement is/are correct for halogen

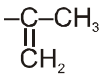
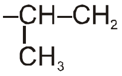
(A) Bond dissociation energy for $H-X$ follow $H-F > H-Cl > H-Br > H-I$
(B) Basicity order follows $F^- > Cl^- > Br^- > I^-$
(C) Nucleophilicity order follows $I^- > Br^- > Cl^- > F^-$
(D) Electronegativity order follows $F > Cl > Br > I$

8. Which of the following are nucleophiles ?

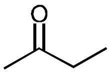
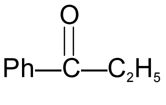
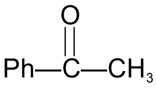
(A) NH_3
(B) N_3^-
(C) EtOH
(D) $[PCl_6]^-$

9. 
$\underset{\underset{O}{||}}{R-C-OR'} \xrightarrow[2.\ H_3O^{\oplus}]{1.\ MeMgBr\ (1\ eq.)}$ acetone as the sole organic product.

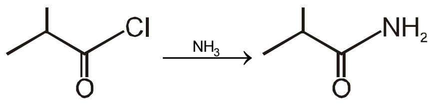
which is/are correctly matched with R and R′.

(A) R is – H
(B) R' is  $-\underset{\underset{CH_2}{||}}{C}-CH_3$
(C) R' is  $-\underset{\underset{CH_3}{|}}{CH}-CH_2$
(D) R is – CH_3

10. 2-Phenylbutan-2-ol can be prepared by :

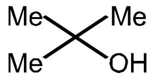
(A) PhMgBr +  $\xrightarrow{ether} \xrightarrow{H^{\oplus}}$
(B) CH_3MgBr +  $Ph-\overset{\overset{O}{||}}{C}-C_2H_5 \xrightarrow{ether} \xrightarrow{H^{\oplus}}$
(C) C_2H_5MgBr +  $Ph-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{ether} \xrightarrow{H^{\oplus}}$
(D) $CH_3CH_2CH_2MgBr + PhCHO \xrightarrow{ether} \xrightarrow{H^{\oplus}}$

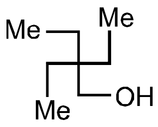
11. Which of the following reactions are substitution reaction ?

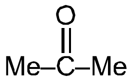
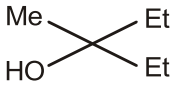
(A) $CH_2 = CH_2 \xrightarrow{HBr} CH_3-CH_2-Br$
(B) 

(C) $Ph-CH_3 + Cl_2 \xrightarrow{Sun\ light} Ph-CH_2Cl + HCl$
(D) $PhMgBr + H_2O \longrightarrow PhH + Mg(OH)Br$

12. When ethyl ethanoate is treated with excess of suitable Grignard reagent (RMgBr) followed by hydrolysis, the product(s) is/are :

(A) 

(B) 

(C)  $Me-\overset{\overset{O}{||}}{C}-Me$
(D) 

SECTION-III : (Maximum Marks: 18)

- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

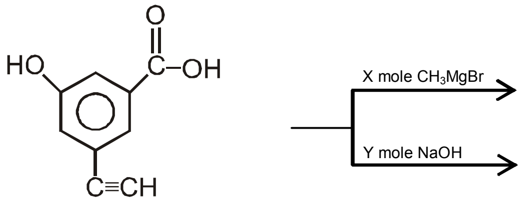
  Full Marks : +3 If ONLY the correct numerical value is entered as answer.

  Zero Marks : 0 In all other cases.

13. 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 is

14. On conversion into the Grignard reagent followed by treatement with water how many structural alkyl bromides would yield isopentane ?

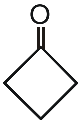
15.

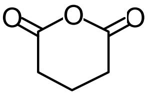


(1 mole)

Report your answer as $\boxed{X}\boxed{Y}$.

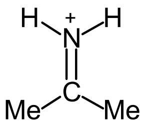
16. How many of the followings behave as electrophile ?

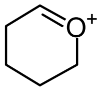
(i)


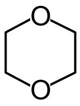
(ii)


(iii) SO_3

(iv) $NH_2–NH_2$

(v)


(vi)


(vii)


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

18. The activation energy for the forward reaction X $\rightarrow$ Y is 60 KJ mol^{-1} and ΔH is –20 KJ mol^{-1}. Calculate the activation energy (in KJ/mole) for the backard reaction Y $\rightarrow$ X.

PART - 3 : OLYMPIAD (PREVIOUS YEARS)

STAGE - I (NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC))

1. Which fo the following is NOT a nucleophile ? **[NSEC-2001]**

(A) H_2 (B) CH_3OH (C) H_2O (D) NH_3

2. 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 radical (C) H^+, BF_3, H_2O^+ (D) C_6H_6, CH_3^+, Cl_2

3. The non-nucleophilic base is **[NSEC-2004]**

(A) CN^- (B) $^-OC(Me)_3$ (C) HO^- (D) MeO^-

4. Identify the group in which the order of basicity is not correct ? **[NSEC-2005]**

(A) $OH^- > H_2O > H_3O^+$ (B) $S^{2-} > HS^- > H_2S$

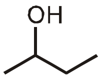
(C) $NH_3 > OH^- > H_2O$ (D) $Cl^- > Br > I^-$

5. The set that contains all nucleophiles is. **[NSEC-2010]**

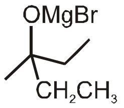
(A) H_2O, BF_3, Cl^-, NH_3 (B) $CH_3–NH_2$, H_2O, I^-, $CH_3–SH$

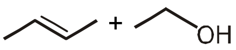
(C) $AlCl_3$, H^+, BF_3, I_2 (D) $AlCl_4^-$, OH^- , Br^-, H_2

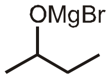
6. The product/s of the following reaction is/are **[NSEC-2010]**



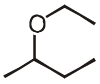
+ $CH_3CH_2MgBr \xrightarrow{\text{ether}} \xrightarrow{\text{ईथर}}$

(A) 

(B) 

(C) 

+ CH_3CH_3

(D) 

7. When a nucleophile attacks a carbonyl group to form an intermediate, the hybridisation of the carbon atom changes from **[NSEC-2014]**

(A) sp^3 to sp^2 (B) sp^2 to sp (C) sp to sp^2 (D) sp^2 to sp^3

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) $OCOC_2H_5 > OSO_3CF_3 > OC_2H_5 > OSO_2Me$

RRP ANSWER KEY

PART- 1

SECTION–I

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

SECTION-II

21.	4	**22.**	3	**23.**	1	**24.**	4	**25.**	4

PART 2

SECTION-I

1.	(B)	**2.**	(C)	**3.**	(C)	**4.**	(A)

SECTION-II

5.	(B,C)	**6.**	(A, C)	**7.**	(A, B, C, D)	**8.**	(A, B, C)	**9.**	(B, D)
10.	(A, B, C)	**11.**	(B, C)	**12.**	(A,D)				

SECTION-III

13.	60	**14.**	4	**15.**	32	**16.**	5	**17.**	13/12
18.	80								

PART - 3

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

RRP SOLUTIONS

PART - 1

SECTION - I

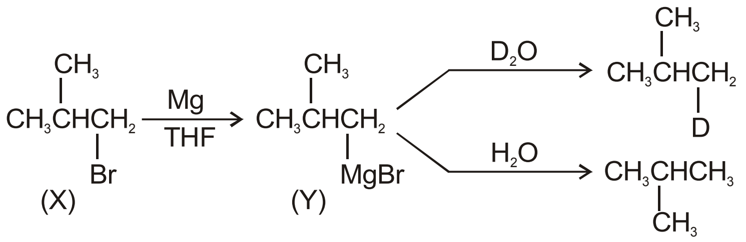
1. The nucleophilicity order is $R^{\ominus} > \overset{\ominus}{N}H_2 > CH_3O^{\ominus} > OH^{\ominus}$

2. The species with incomplete octet can not be a nucleophile.

3. Except HCHO all given carbonyl compound will give recemic mixture (±).

4. Weaker bases are better leaving group.

6.

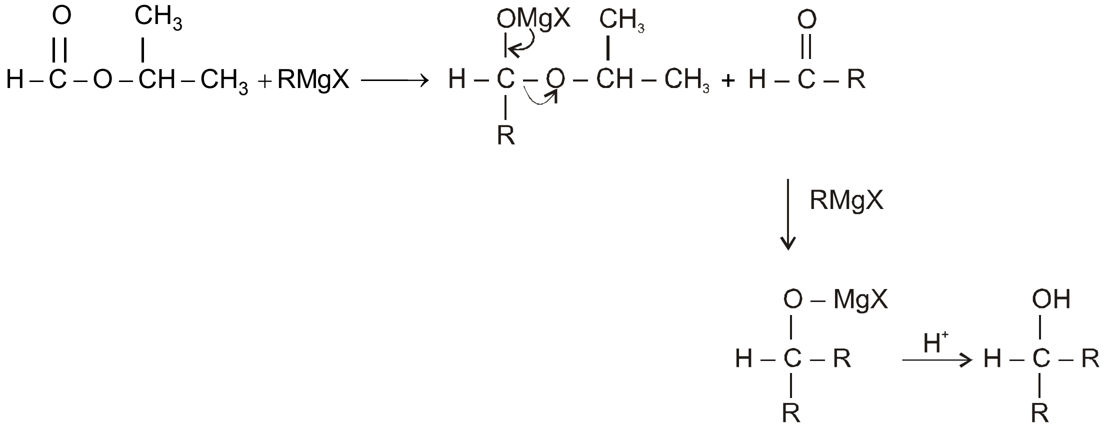


$$\underset{(X)}{CH_3\overset{CH_3}{\overset{|}{C}}HCH_2Br} \xrightarrow[THF]{Mg} \underset{(Y)}{CH_3\overset{CH_3}{\overset{|}{C}}HCH_2MgBr}\ \begin{cases}\xrightarrow{D_2O} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2D \\ \xrightarrow{H_2O} CH_3\underset{CH_3}{\underset{|}{C}}HCH_3\end{cases}$$

8. All of these reaction give CH_4.

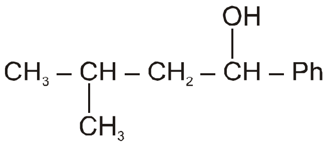
10. Nucleophiles are electron rich species.

13.



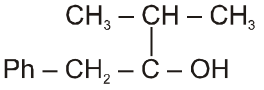
$$H-\overset{O}{\overset{||}{C}}-O-\overset{CH_3}{\overset{|}{C}H}-CH_3 + RMgX \longrightarrow H-\underset{R}{\underset{|}{\overset{OMgX}{\overset{|}{C}}}}-O-\overset{CH_3}{\overset{|}{C}H}-CH_3 + H-\overset{O}{\overset{||}{C}}-R \xrightarrow{RMgX} H-\underset{R}{\underset{|}{\overset{O-MgX}{\overset{|}{C}}}}-R \xrightarrow{H^+} H-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R$$

14. (A)



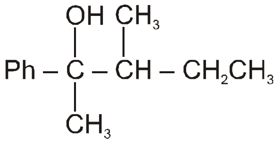
$$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_2-\overset{OH}{\overset{|}{C}H}-Ph$$

(B)



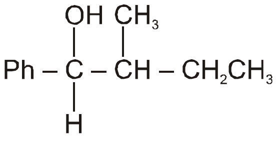
$$Ph-CH_2-\overset{CH_3-CH-CH_3}{\overset{|}{C}}-OH$$

(C)



$$Ph-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\overset{CH_3}{\overset{|}{C}H}-CH_2CH_3$$

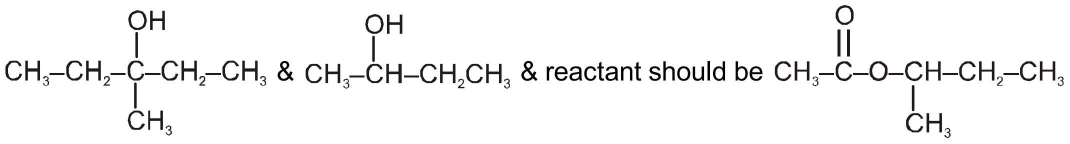
(D)



$$Ph-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\overset{CH_3}{\overset{|}{C}H}-CH_2CH_3$$

16. Conjugated base of strong acid is weak base and behave as better leaving group.

18. Alcohols obtained from reaction of ester with Grignard reagent will have two identical alkyl group which comes from Grignard reagent.



Therefore for $CH_3–CH_2–C(OH)(CH_3)–CH_2–CH_3$ & $CH_3–CH(OH)–CH_2CH_3$ & reactant should be $CH_3–C(=O)–O–CH(CH_3)–CH_2–CH_3$

and CH_3CH_2MgBr.

19. Nucleophilicity ∝ Size (in group)

SECTION - II

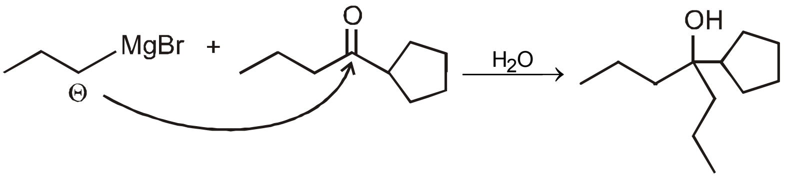
21. Active hydrogen containing functional group release CH_4 gas with CH_3MgBr. (i.e. OH, COOH, SO_3H)

24. a, c, e, g

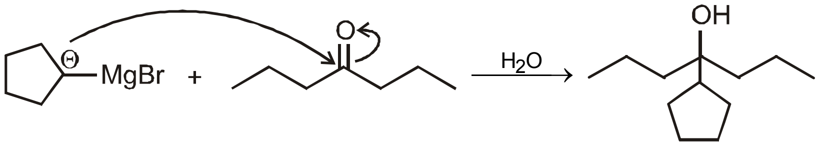
PART 2

SECTION-I

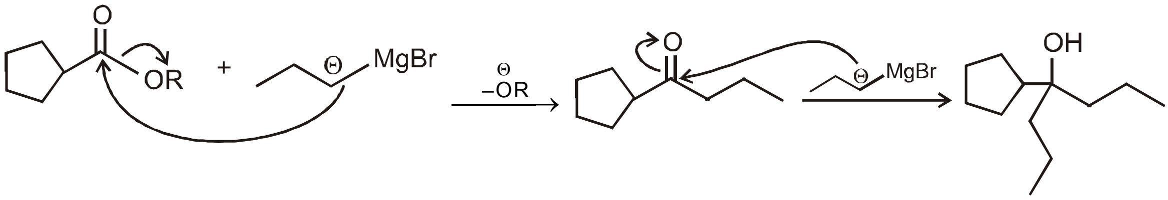
4. (B)



(C)



(D)

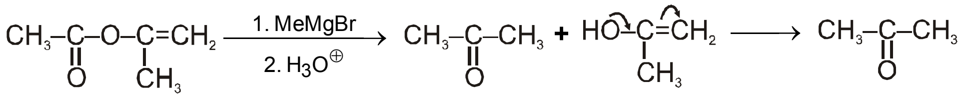


SECTION-II

5. Anionic nucleophiles are better nucleophile than their neutral species.

6. In aprotic solvent $Nu^{\ominus}$ increases, as compare to polar protic solvent.

9.



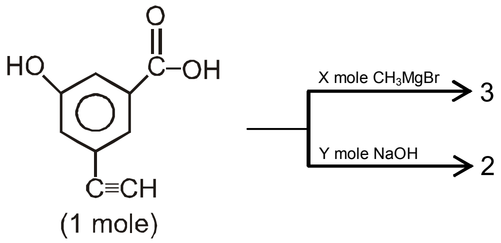
$$CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{C}=CH_2 \xrightarrow[2.\ H_3O^{\oplus}]{1.\ MeMgBr} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + HO-\underset{\underset{CH_3}{|}}{C}=CH_2 \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

SECTION-III

13. Number of millimoles of alcohol = $\dfrac{1.12\text{ ml}}{22.4\text{ ml/mmole}}$

molecular weight of alcohol = $\dfrac{\text{Wt of alcohol (mg)}}{\text{No. of milli moles of alcohol}} = \dfrac{3}{1.12/22.4} = 60.$

15.



A strogner acid displaces a weaker acid from the salt of the weaker acid.

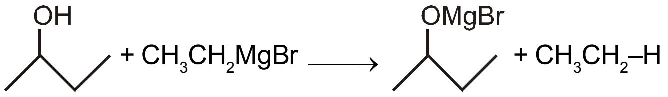
16. (i), (ii), (iii), (v) and (vi) are electrophiles.

17. Overall order = $\dfrac{1}{2}+\dfrac{1}{3}+\dfrac{1}{4}=\dfrac{13}{12}$.

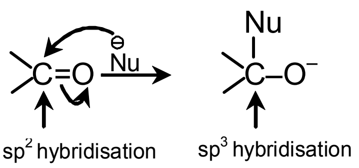
PART - 3

5. All other sets has electrophile like BF_3, $AlCl_3$ or H_2.

6. It is acid base reaction.



7.



8. $C_6H_5MgBr + CH_3OH \rightarrow$