HALOALKANES, HALOARENES, ALCOHOLS AND ETHERS(PART-1)

CONTENTS

Particulars			Page No.
Theory			**01 – 17**
Exercise - 1			**18 – 28**
Part - I	:	Subjective Questions	
Part - II	:	Only One Option Correct Type	
Part - III	:	Match the Columns	
Exercise - 2			**29 – 37**
Part - I	:	Only One Option Correct Type	
Part - II	:	Numerical Type Questions	
Part - III	:	One or More Than One Options Correct Type	
Part - IV	:	Comprehensions	
Exercise - 3			**38 – 46**
Part - I	:	JEE(ADVANCED) / IIT-JEE Problems (Previous Years)	
Part - II	:	JEE(MAIN) / AIEEE Problems (Previous Years)	
Answer Key			**47 – 50**
Reliable Ranker Problems (RRP)			**51 – 64**
Part - I	:	PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))	
Part - II	:	PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))	
Part - III	:	OLYMPIAD Problems (Previous Years)	
RRP Answer Key			**65**
RRP Solutions			**65 – 69**

JEE(ADVANCED) SYLLABUS

JEE(MAIN) SYLLABUS

Introduction :

Compounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding number of halogen atoms are known as halogen derivatives.

Alcohols are formed when one or more hydrogen atoms in an aliphatic hydrocarbon is replaced by –OH group.

The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R–O/Ar-O) yields another class of compounds known as ethers.

1. Physical properties

(a) Haloalkanes & Haloarenes

(1) Lower members like methyl chloride, methyl bromide etc are gases at room temperature whereas higher members are liquids or solids.

(2) Boiling point :

(i) Boiling point $\propto$ Polarity of molecule

For same alkyl group, boiling point order : RI > RBr > RCl > RF

(ii) Boiling point $\propto$ Molecular weight

If molecular weight is same, then Boiling point $\propto \frac{1}{\text{Branching}}$

e.g. $CH_3CH_2CH_2CH_2Br > CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 > CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$

(b) Alcohols

(1) C_1 to C_{11} are colourless liquids and higher alcohols are solids.

(2) Density of monohydric alcohol is less than H_2O.

(3) Density $\propto$ mol. wt. (for monohydric alcohol).

(4) **Solubility :** C_1 to C_3 and t-butyl alcohol is completely soluble in H_2O due to H–bonding.

$$\text{solubility} \propto \text{No. of side chain} \propto \frac{1}{\text{molecular weight}}$$

Order of solubility :

C_4H_9OH > $C_5H_{11}OH$ > $C_6H_{13}OH$

$CH_3CH_2CH_2CH_2OH$ < $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-OH$ < $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

$\underset{\underset{OH}{|}}{CH_3CH_2CH_2}$ < $CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$ < $\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$

[Number of —OH increases, H-bonding increases]

(5) **Boiling points :** B.P. $\propto$ molecular weight

If molecular weight is same then $\text{B.P.} \propto \frac{1}{\text{branching}}$

Order of BP : C_4H_9OH < $C_5H_{11}OH$ < $C_6H_{13}OH$

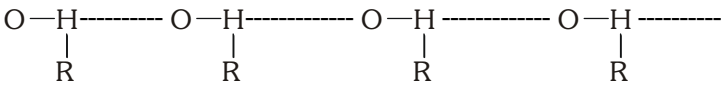
$CH_3CH_2CH_2CH_2OH$ > $CH_3CH_2CH(CH_3)OH$ > $(CH_3)_3COH$

$CH_3CH_2CH_2OH$ < $CH_3CH(OH)CH_2OH$ < $CH_2(OH)CH(OH)CH_2OH$

[Number of OH increases, H-bonding increases]

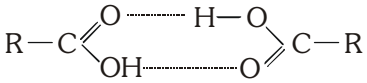
Que. Boiling point of alcohol is more than corresponding ether. Why ?

Ans. H-bonding in alcohol molecules



Que. Boiling point of alcohol is less than corresponding carboxylic acid. Why ?

Ans. Dimer formation in carboxylic acid.



(c) Ethers:

(1) CH_3OCH_3 , $CH_3OCH_2CH_3$ are gases and higher are volatile liquids.

(2) Ether are less polar [μ=1.18D].

(3) Ethers are less soluble in H_2O.

(4) Ethers have less BP than corresponding alcohol.

Que. Ethers are less soluble in H_2O. Why ?

Ans. Due to less polarity, it forms weaker H–Bonding with H_2O.

Que. Ethers have less B.P. than corresponding alcohol. Why ?

Ans. No H–Bonding in ether molecules.

2. Preparation

(a) Haloalkanes & Haloarenes

(1) From alcohols

$R–OH + HX \xrightarrow{ZnCl_2} R–X + H_2O$

$R–OH + NaBr + H_2SO_4 \longrightarrow R–Br + NaHSO_4 + H_2O$

$3R–OH + PX_3 \longrightarrow 3R–X + H_3PO_3$ (X = Cl, Br)

$R–OH \xrightarrow[X_2=Br_2,I_2]{red\ P/X_2} R\text{-}X$

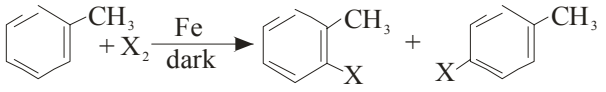
$R–OH + SOCl_2 \longrightarrow R–Cl + SO_2 + HCl$

(2) From hydrocarbons

(i) Free radical halogenation

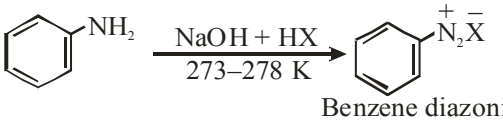
$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/UV\ light} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

(ii) By electrophilic substitution

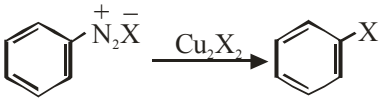


o-Halotoluene p-Halotoluene

(iii) Sandmeyer's reaction



Benzene diazonium halide



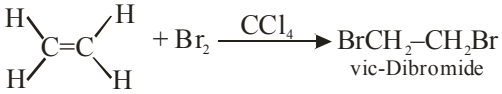
Aryl halide X =Cl, Br

(3) From alkenes

(i) Addition of hydrogen halides :

$$CH_3CH=CH_2 + HI \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

(ii) Addition of halogens : In the laboratory,



vic-Dibromide

(4) Halogen Exchange

$$R–X + NaI \longrightarrow R–I + NaX$$

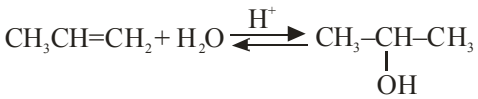
X=Cl, Br

$$H_3C–Br + AgF \longrightarrow H_3C–F + AgBr$$

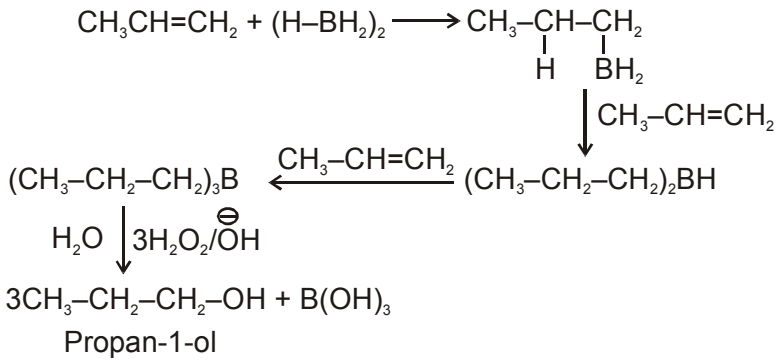
(b) Alcohols

(1) From alkenes

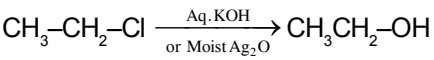
(i) By acid catalysed hydration :



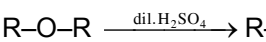
(ii) By hydroboration-oxidation :

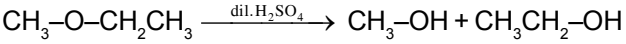


(2) From alkyl halides (By hydrolysis) :



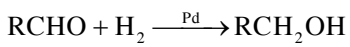
(3) From ethers :

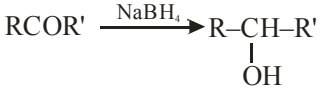




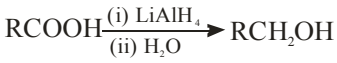
(4) From carbonyl compounds :

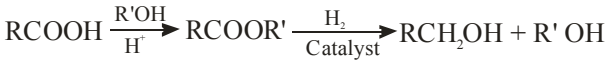
(i) By reduction of aldehydes and ketones :



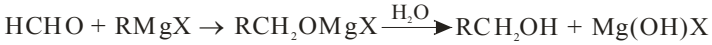


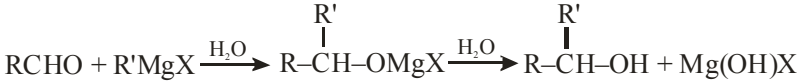
(ii) By reduction of carboxylic acids and esters:

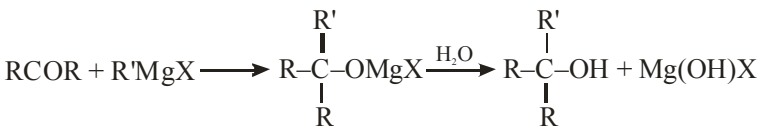




(5) From Grignard reagents

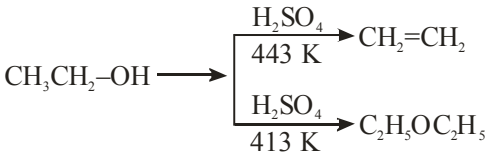






(c) Ethers

(1) By dehydration of alcohols



(2) Williamson synthesis : In this method, an alkyl halide is allowed to react with sodium alkoxide.

(3) Reaction with Dry Ag_2O

$2RX + Ag_2O \xrightarrow{\Delta} R–O–R + 2AgX$

e.g. $2CH_3–CH_2–Cl + Ag_2O \xrightarrow{\Delta} CH_3CH_2OCH_2CH_3 + 2AgCl$

3. Nucleophilic substitution reaction (S_N)

Replacement (displacement) of an atom or group by an other atom or group in a molecule is known as substitution reaction. If substitution reaction is brought about by a nucleophile then it is known as nucleophilic substitution reaction. Generally substitution takes place at sp^3 carbon.

$$R–\ell g + Nu^- \longrightarrow R – Nu + \ell g^-$$

Type of nucleophilic substitution reaction :

(I) S_N1 (II) S_N2 (III) S_Ni

3.1 Unimolecular nucleophilic substitution (S_N1) reaction :

Nucleophilic substitution which involves two step process

(a) First step : - Slow step involves ionisation to form carbocation

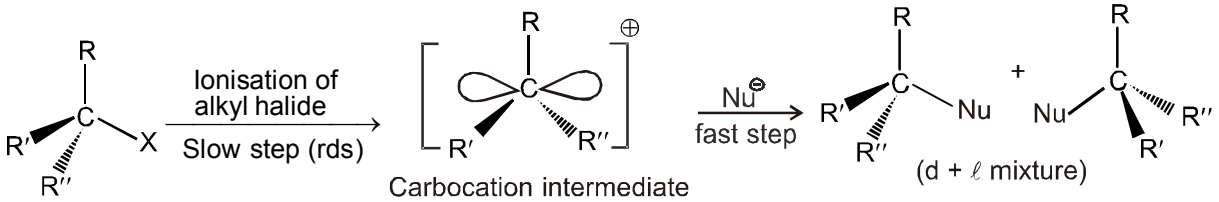
$$R–\ell g \longrightarrow R^+ + \ell g^-$$

(b) Second step : - Fast attack of nucleophile on carbocation to result into product .

$$R^+ + Nu^- \longrightarrow R–Nu$$

(a) S_N1 Reaction of Alkyl halide

Mechanism :



Characteristics of S_N1 reactions :

1. It is unimolecular, two step process.

2. Carbocation intermediate is formed so rearrangement is possible in S_N1 reaction.

3. It is first order reaction

4. Kinetics of the reaction Rate $\propto$ [Alkyl halide]

Rate of S_N1 reaction is independent of concentration and reactivity of nucleophile.

5. Energetics of the S_N1

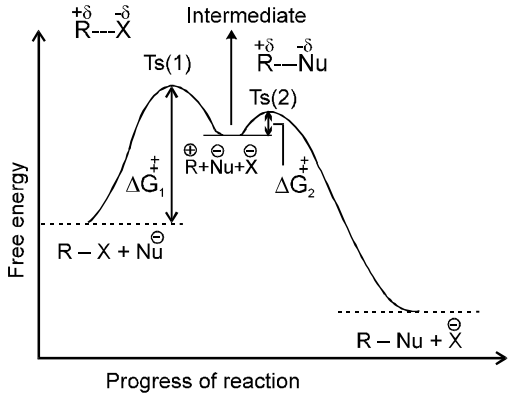


Figure : Free energy diagram for the S_N1 reaction.

6. Factors affecting the rates of S_N1

(i) The structure of the substrate : The rds of the S_N1 reaction is ionization step, a carbocation is formed in this step. This ionisation is strongly endothermic process, rate of S_N1 reaction depends strongly on carbocation stability because carbocation is the intermediate of S_N1 reaction which determines the energy of activation of the reaction.

Reactivity of $S_N1 \propto$ stability of carbocation.

S_N1 reactivity : $3° > 2° > 1° > CH_3 – X$

(ii) Concentration and reactivity of the nucleophile → The rate of S_N1 reaction is unaffected by the concentration and nature of the nucleophile

Weak, neutral, mostly solvents (protic) itself functions as nucleophiles in S_N^1 reaction. So S_N^1 reaction is termed as solvolysis reaction.

water → hydrolysis ; C_2H_5OH → ethanolysis

CH_3COOH → acetolysis ; NH_3 → ammonolysis

(iii) Effect of the solvent : (Ionising ability of the solvent)

The use of a polar protic solvent will greatly increase the rate of ionisation of an alkyl halide in any S_N1 reaction because it solvate cations and anions so effectively and stabilises the transition state leading to the intermediate carbocation and halide ion, thus the energy of activation is lower.

$R – X \rightleftharpoons \overset{\oplus}{R} + \overset{\ominus}{X}$ (Solvolysis)

Solvated ions

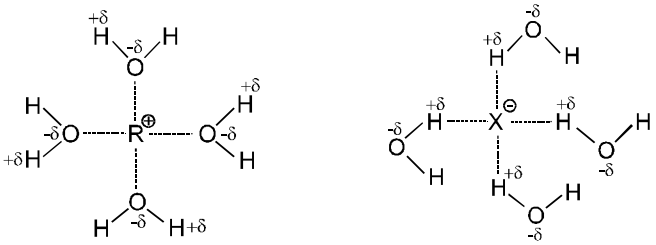


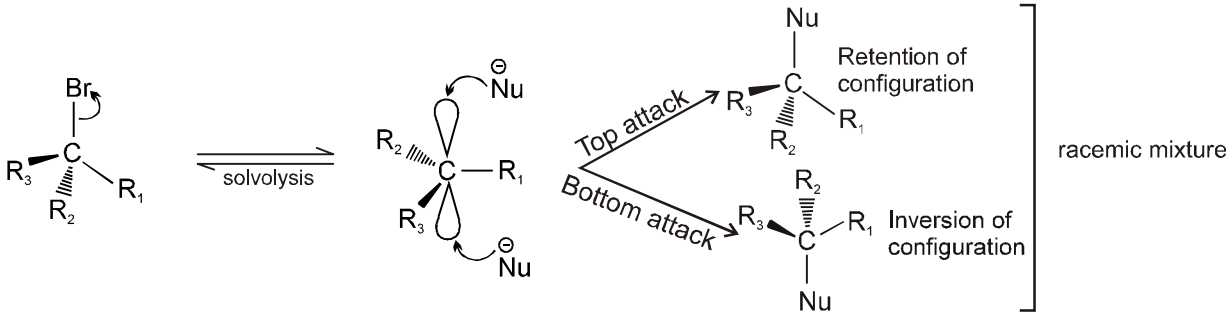
Table - : Dielectric constants ($\in$) and ionisation rates of t-Butylchloride in few common solvents

Solvent	$\in$	Relative rate
H_2O	80	8000
CH_3OH	33	1000
C_2H_5OH	24	200
$(CH_3)_2CO$	21	1
CH_3CO_2H	6	–

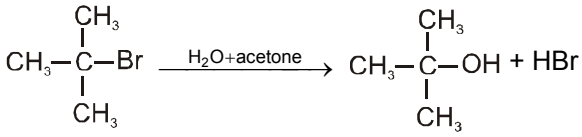
(iv) The nature of the leaving group → In the S_N1 reaction the leaving group begins to acquire a negative charge as the transition state is reached` stabilisation of this developing negative charge at the leaving group stabilises the transition state and this lowers the free energy of activation and there by increases the rate of reaction. Leaving ability of halogen is $F^- < Cl^- < Br^- < I^-$

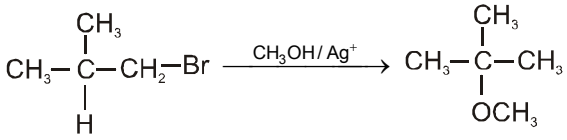
7. Stereochemistry of S_N1 reactions → In the S_N1 mechanism, the carbocation intermediate is sp^2 hybridized and planar, A nucleophile can attack on the carbocation from either face, if reactant is chiral than after attack of nucleophile from both faces gives both enantiomers as the product, which is called racemisation.

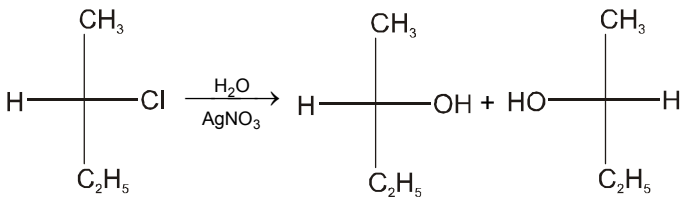
Mechanism of racemisation (S_N1) →



Reagents for alkyl halide are : H_2O , RCOOH , ROH & RSH

e.g.  (3° alkyl halide hence no S_{N^2} reaction)

e.g.  (carbocation rearrangement)

e.g.  (Racemic product)

(b) S_N1 Reaction of Alcohols

(i) Reaction with hydrogen halides

A common method is to treat the alcohol with a hydrohalic acid, usually HI or HBr. These acids are used to convert alcohols into the corresponding alkyl halides.

(i) In acidic solution, an alcohol is in equilibrium with its protonated form. Protonation converts the hydroxy group from a poor leaving group $(OH)^{\ominus}$ into a good leaving group (H_2O). If the alcohol is protonated all the usual substitution and elimination reactions are feasible, depending on the structure (1°, 2°, 3°) of the alcohol.

(ii) Halides are anions of strong acids, so they are weak bases. Solutions of HBr and HI contain nucleophilic $Br^{\ominus}$ and $I^{\ominus}$ ions.

(iii) Concentrated hydrobromic acid rapidly converts t-Butyl alcohol to t-Butyl bromide. The strong acid protonates the hydroxyl group, converting it into a good leaving group. The hindered tertiary carbon atom cannot undergo S_N2 displacement, but it can ionise to a tertiary carbocation. Attack by bromide ion gives the alkyl bromide. The mechanism is similar to S_N1 mechanism.

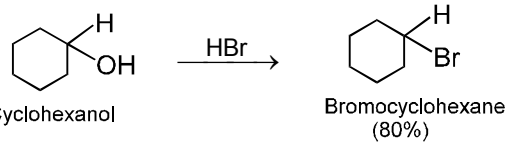
(iv) 1-Butanol reacts with sodium bromide in concentrated sulfuric acid to give 1-Bromobutane by an S_N2 displacement.

$$\underset{1-\text{butanol}}{CH_3(CH_2)_2-CH_2OH} \xrightarrow{NaBr,\ H_2SO_4} \underset{\substack{1-\text{bromobutane}\\(90\%)}}{CH_3(CH_2)_2-CH_2Br}$$

Protonation converts the hydroxy group to a good leaving group, but ionization to a primary carbocation is unfavourable. The protonated unbranched primary alcohol is well suited for the S_N2 displacement.

(v) Secondary alcohols also react with HBr to form alkyl bromides usually by the S_N1 mechanism.

e.g.



Cyclohexanol — Bromocyclohexane (80%)

(vi) HCl (Hydrochloric acid) reacts with alcohols in much the same way that as the hydrobromic acid.

(vii) Chloride ion is a weaker nucleophlile than bromide ion because it is smaller and less polarizable. Lewis acid, such as $ZnCl_2$, is sometimes necessary to promote the reaction of HCl with primary and secondary alcohols.

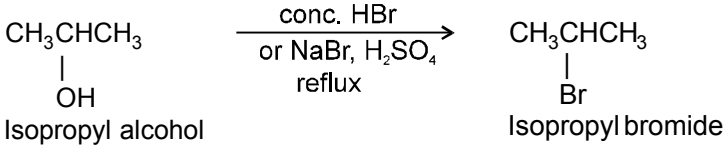
Mechanism :

$$R-OH \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} R-\overset{\oplus}{O}H_2 \xrightarrow[-H_2O]{RDS} \overset{\oplus}{R} \xrightarrow{X^{\ominus},\ Fast} R-X$$

Reactivity of HX : HI > HBr > HCl

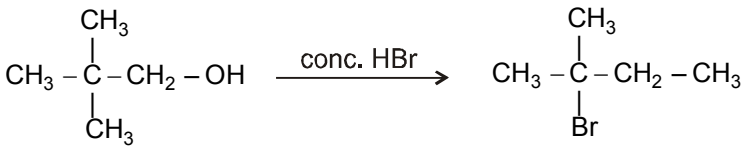
Reactivity of ROH : 3° > 2° > 1°

e.g.



Isopropyl alcohol — Isopropyl bromide

e.g.



Lucas reagent

(i) A mixture of concentrated hydrochloric acid and zinc chloride is called the Lucas reagent.

(ii) Whether an alcohol is primary, secondary or tertiary is identified by the Lucas test, which is based upon the difference in reactivity of the three classes of alcohol towards hydrogen halides.

(iii) Alcohol (of not more than six carbons in their molecule) are soluble in the Lucas reagent. The corresponding alkyl chlorides are insoluble.

(iv) Formation of a chloride from an alcohol is indicated by the cloudiness that appears when the chloride separates from the solution hence, the time required for cloudiness to appear is a measure of the reactivity of the alcohol.

(v) A tertiary alcohol reacts immediately with the Lucas reagent, a secondary alcohol reacts within five minutes and a primary alcohol does not react appreciably at room temperature.

e.g. $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \xrightarrow{\text{anhy. } ZnCl_2 / HCl} CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3$

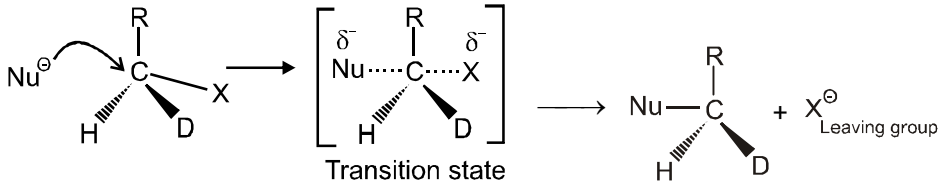
3 – Chloropentane

3.2 Bimolecular nucleophilic substitution (S_N2) reaction

Nucleophilic substitution in which incoming group replaces leaving group in one step only.

(a) S_N2 Reaction of Alkyl halide

Mechanism :



Characterstics of S_N2

1. It is bimolecular, one step concerted process

2. It is second order reaction because in the rds both species are involved

3. Kinetics of the reaction : rate $\propto$ [alkyl halide] [nucleophile]

rate = k[alkyl halide] [nucleophile]

If the concentration of alkyl halide in the reaction mixture is doubled, the rate of the nucleophilic substitution reaction is double. If the concentration of nucleophile is doubled the rate of reaction is also double. If the concentration of both are doubled then the rate of the reaction quadriples.

4. Energetics of the reaction :

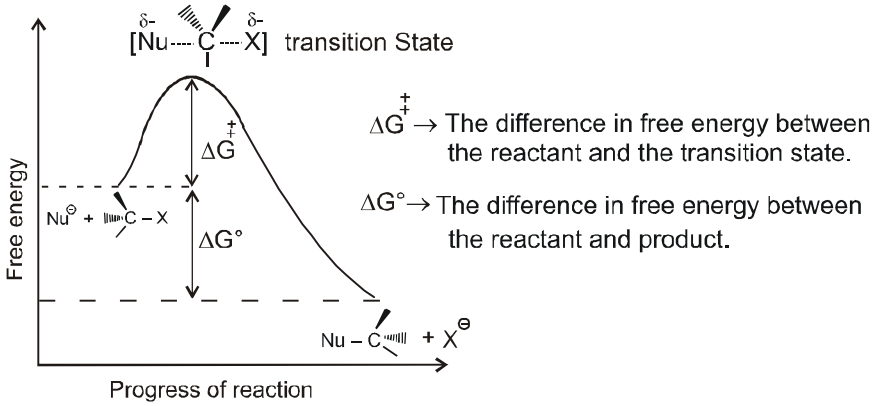
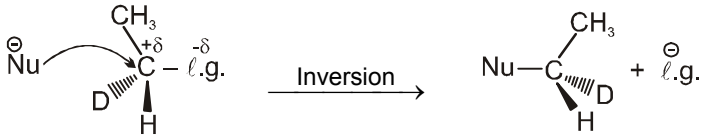


Figure : A free energy diagrams for S_N2 reaction

5. No intermediates are formed in the S_N2 reaction, the reaction proceeds through the formation of an unstable arrangement of atoms or group called transition state.

6. The stereochemistry of S_N2 reactions → As we seen earlier, in an S_N2 mechanism the nucleophile attacks from the back side, that is from the side directly opposite to the leaving group. This mode of attack causes an inversion of configuration at the carbon atom that is the target of nucleophilic attack. This inversion is also known as **Walden inversion**.



7. Factors affecting the rate of S_N2 reaction : Number of factors affect the relative rate of S_N2 reaction, the most important factors are

(i) Effect of the structure of the substrate :

S_N2 reactivity CH_3 > 1° > 2° >> 3° (unreactive)

The important reason behind this order of reactivity is a steric effect. Very large and bulky groups can often hinder the formation of the required transition state and crowding raises the energy of the transition state and slows down reaction.

Table : Relative rate of reactions of alkyl halide in S_N2 reaction.

Substituent	Compound	Relative rate
Methyl	CH_3X	30
1°	CH_3CH_2X	1
2°	$(CH_3)_2CHX$	0.02
Neopentyl	$(CH_3)_3CCH_2X$	0.00001
3°	$(CH_3)_3CX$	~ 0

(ii) Concentration and reactivity of the nucleophile

– As nucleophilicity of nucleophile increases rate of S_N2 increases.

– Anionic nucleophiles mostly give S_N2 reaction

– A stronger nucleophile attacks upon α-carbon with faster rate than the rate of departing of leaving group.

(iii) The effect of the solvent: Polar aprotic solvent have crowded positive centre, so they do not solvate the anion appreciably therefore the rate of S_N2 reaction is increased when they are carried out in polar aprotic solvent.

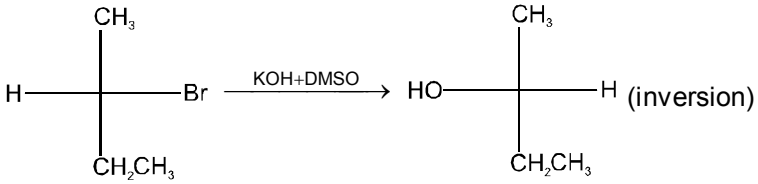
(iv) The nature of the leaving group : Weaker bases are good leaving groups. A good leaving group always stabilise the transition state and lowers its free energy of activation and there by increases the rate of the reaction. Order of leaving ability of halide ion $F^- < Cl^- < Br^- < I^-$

Reagents for alkyl halide are : OH^- , SH^- , I^- ,CN^-, NH_3 ..... (**strong anionic nucleophile)**

e.g. $CH_3–Cl \xrightarrow[(:OH^-)\text{strong nucleophil e}]{\text{aq.KOH}} CH_3–OH + Cl^-$

e.g. $CH_3–CH_2–CH_2–Br \xrightarrow{NaOH+DMF} CH_3–CH_2–CH_2–OH + Br^-$

e.g.



(inversion)

(b) S_N2 Reaction of Alcohol

(i) Reaction with HX

The protonated β unbranched primary alcohol is well suited for the S_N2 reaction.

Mechanism :

$$R\text{–}OH \overset{H^{\oplus}}{\rightleftharpoons} R\text{–}\overset{\oplus}{O}H_2 \xrightarrow{X^{\ominus}} R\text{–}X + H_2O$$

(ii) Reaction with phosphorus trihalides

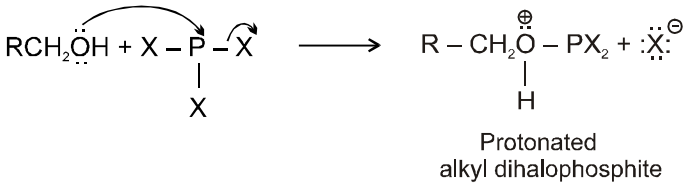
Several phosphorus halides are useful for converting alcohols to alkyl halides. PBr_3, PCl_3, & PCl_5 work well and are commercially available.

Phosphorus halides produce good yields of most primary and secondary alkyl halides, but none works well with tertiary alcohols. The two phosphorus halides used most often are PBr_3 and the P_4/I_2 combination.

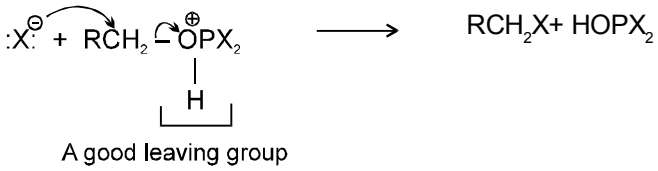
$$3R\text{–}OH + PX_3 \xrightarrow{(PX_3 = PCl_3, PBr_3, PI_3)} 3R\text{–}X + H_3PO_3$$

Mechanism :

Step : 1



Step : 2



Remarks

The mechanism for the reaction involves attack of the alcohol group on the phosphorus atom, displacing a halide ion and forming a protonated alkyl dihalophosphite

In second step a halide ion acts as nucleophile to displace $HOPX_2$, a good leaving group due to the electronegative atoms bonded to the phosphorus.

(iii) Reaction with PCl_5

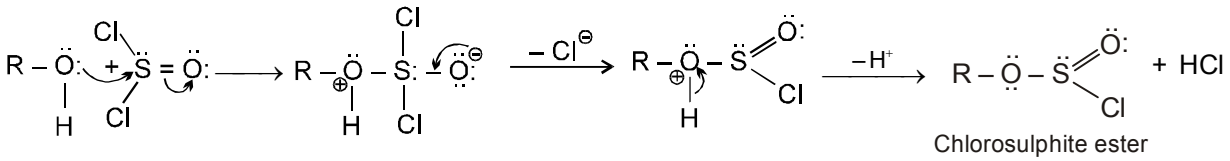
$$R\text{–}OH + PCl_5 \xrightarrow{S_N2} R\text{–}Cl + HCl + POCl_3$$

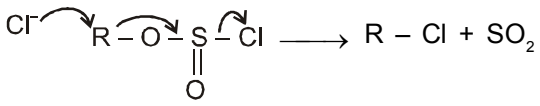
(iv) Reaction with thionyl chloride in presence of pyridine

Thionyl chloride ($SOCl_2$) is often the best reagent for converting an alcohol to an alkyl chloride. The by products (gaseous SO_2 and HCl) leave the reaction mixture and ensure that there can be no reverse reaction.

$$R\text{–}OH + Cl\text{–}\overset{\overset{O}{\|}}{S}\text{–}Cl \xrightarrow[\text{Heat}]{\text{Pyridine}} R\text{–}Cl + SO_2 + HCl$$

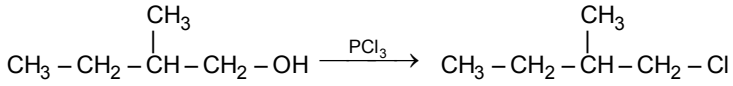
Mechanism :

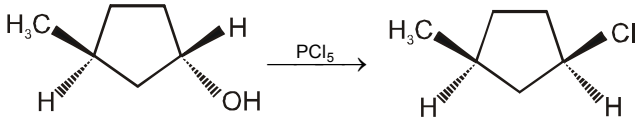


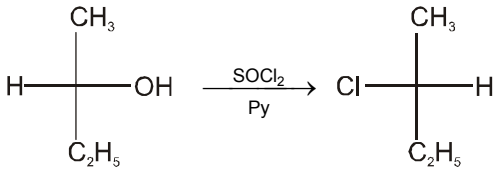


In the first step, the nonbonding electrons of the hydroxy oxygen atom attack the electrophilic sulphur atom of thionyl chloride. A chloride ion is expelled a proton and gives test of chloro sulphite ester. Second step is an S_N2 mechanism.

e.g. $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{HCl / ZnCl_2} CH_3CH_2CH_2CH_2CH_2Cl$
n – Pentyl alcohol — n – Pentyl chloride

e.g. 

e.g. 

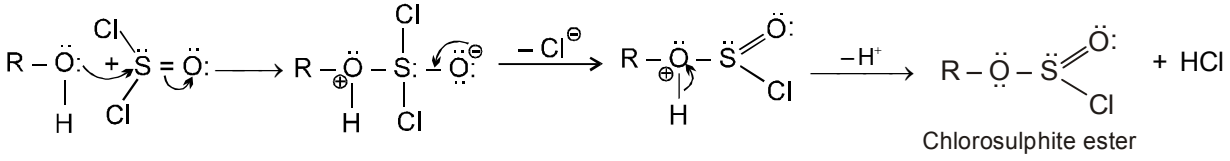
e.g. 

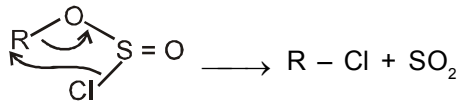
3.3 S_Ni Reaction

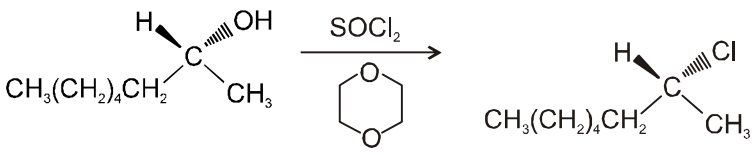
In S_Ni mechanism an internal nucleophile attacks from the same side of leaving group, means retention of configuration. It is an S_Ni mechanism, where i means internal

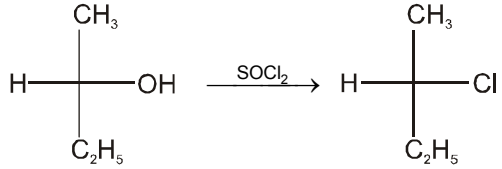
$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

Mechanism :



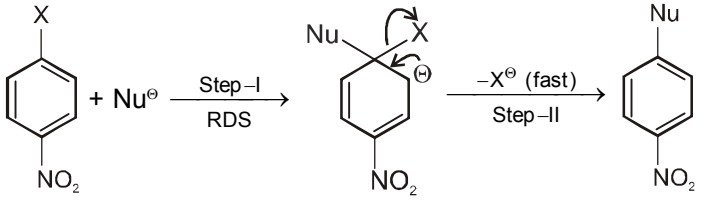


e.g. 

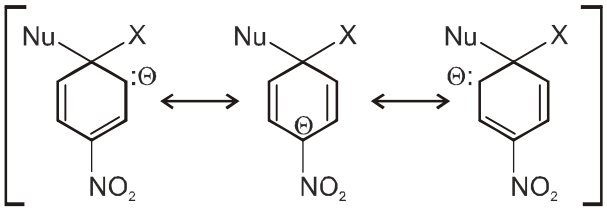
e.g. 

3.4 Bimolecular nucleophilic substitution in aromatic compound (S_N2 Ar) Reaction

This is the characteristic reaction of arylhalides with ortho or para electron withdrawing substituent. The reaction mechanism can be visualised as :

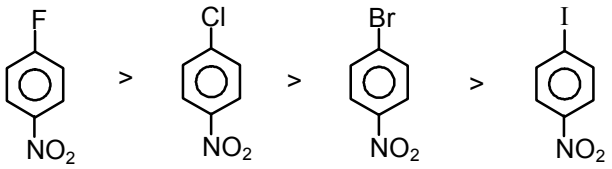


Intermediate ion is stabilized by resonance.

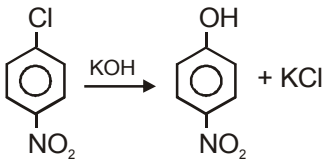


EWG ↑ Rate of reaction ↑

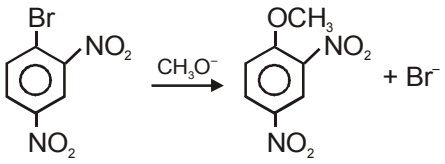
Reactivity order towards (S_N2Ar)



e.g.



e.g.



3.5 Nucleophilic Substitution Reaction of Ethers

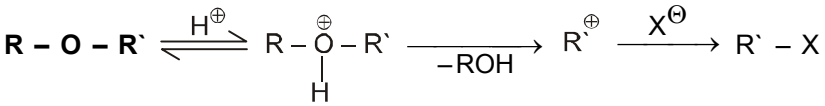
(a) S_N1 Reaction of Ethers

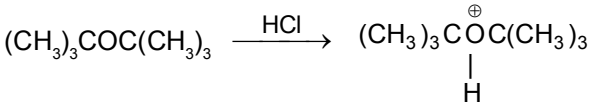
(i) Reaction with HX

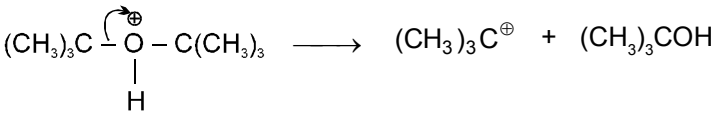
Ethers are unreactive towards most bases, but they can react under acidic conditions. A protonated ether can undergo substitution or elimination with the expulsion of an alcohol. Ethers react with conc. HBr and HI because these reagents are sufficiently acidic to protonate the ether, while bromide and iodide are good nucleophiles for the substitution.

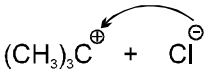
If R or R' is 3º then mechanism will be S_N1 otherwise S_N2 .

Mechanism :

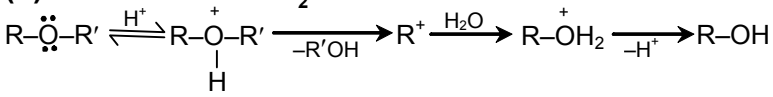


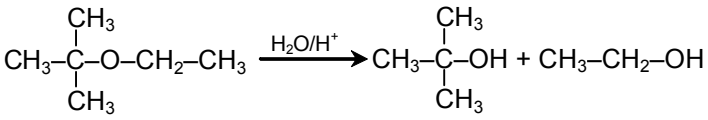






(ii) Reaction with H_2O/H^+



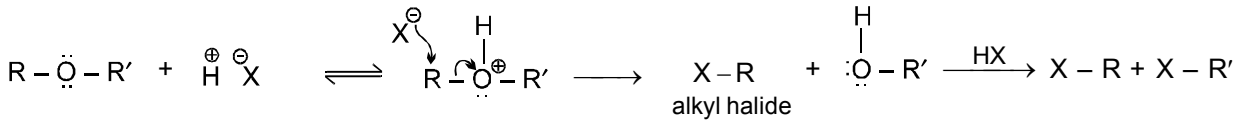


(b) S_N2 Reaction of Ethers

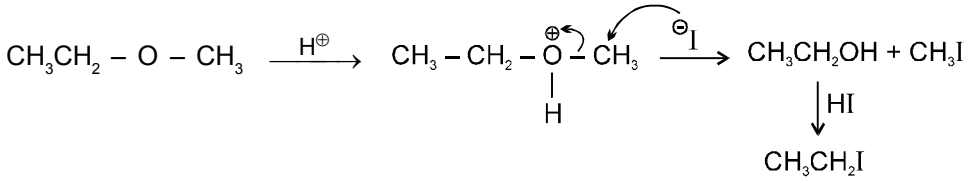
(i) Reaction with HX

A protonated ether can undergo substitution reaction. Ether react with conc. HBr and HI because these reagents are sufficiently acidic to protonate the ether. If R or R' is 3° then mechanism will be S_N1 otherwise S_N2.

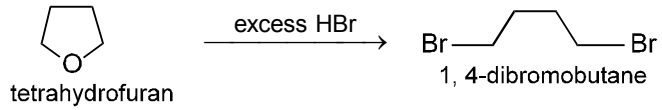
Mechanism :



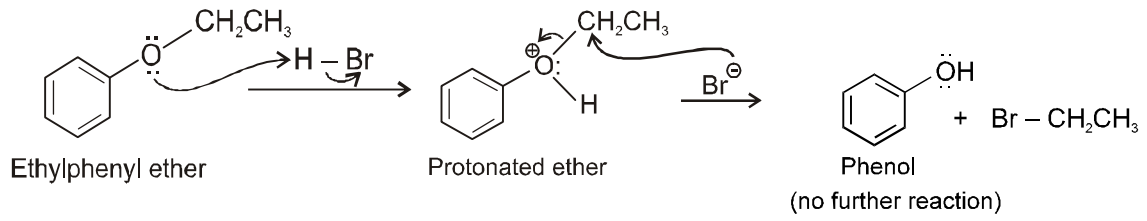
1.



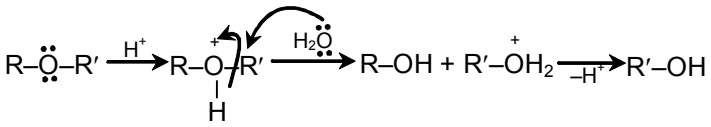
2.



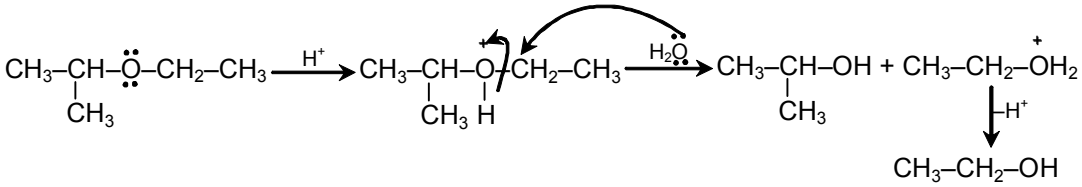
3.



(ii) Reaction with H_2O/H^+



(Steric crowding R > R′)



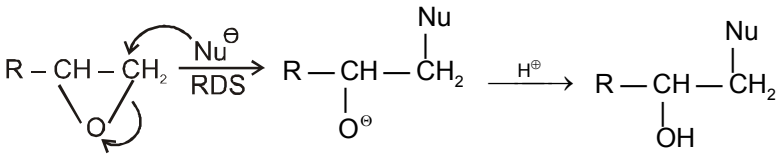
3.6 Nucleophilic Substitution Reaction of Epoxide :

Epoxides are much more reactive than ether because of angle strain in three membered ring therefore epoxide readily undergo nucleophilic substitution reaction.

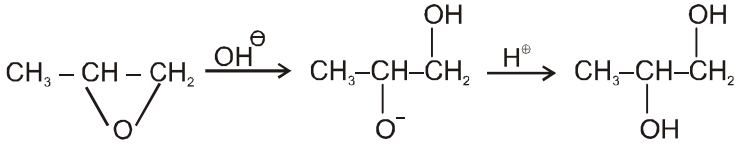
In basic medium mechanism is S_N2. Nucleophile attacks on less hindered carbon.

Mechanism :

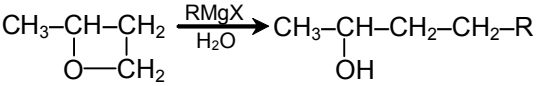
e.g.



e.g.

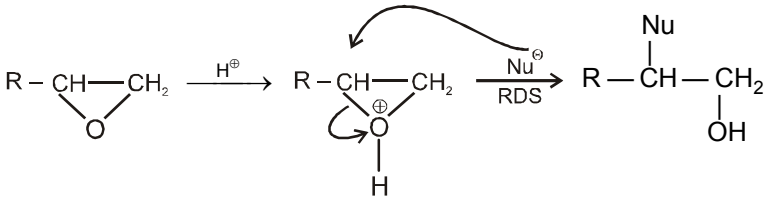


e.g.

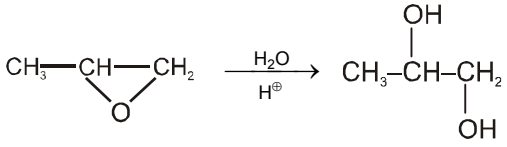


In acidic medium mechanism is S_N1 type. Nucleophilic attacks on more substituted carbon.

Mechanism :



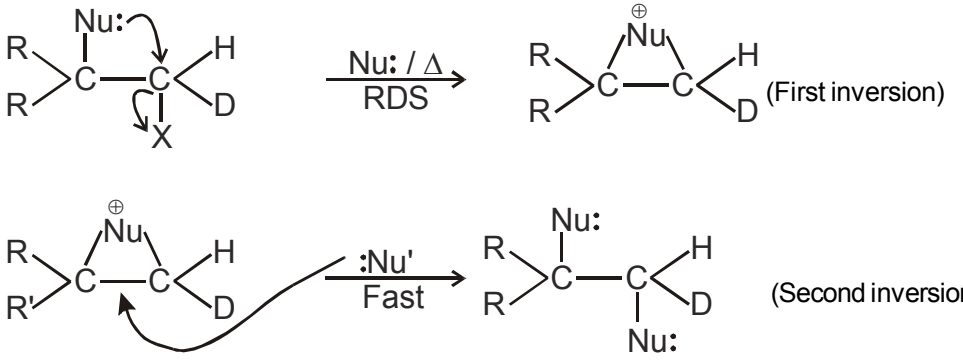
e.g.



3.7 Neighbouring Group Participation in S_N reaction [Anchimeric assistance]

It is occasionally found with certain substrates the rate of reaction is greater than expected, and the configuration at a chiral carbon is retained and not inverted or racemized. In these cases there is usually a group with an unshared pair of electrons. β to the leaving group (or sometimes farther away). The mechanism operating in such cases is called the Neighbouring Group Participation (NGP) mechanism.

General Reaction :



Characteristics of reaction :

- In an alkyl hilide (or in some other compounds) if an internal nucleophile is present at β -carbon, then the nucleophilic substitution takes places with NGP (or anchimeric assistance)
- In I step, under the reaction conditions (like Δ) the nucleophile gives intramolecular S_N2 at α -carbon (1st inversion)
- In II step, the external nucleophile attacks at α -carbon and 2nd S_N2 reaction takes place. (2nd inversion)

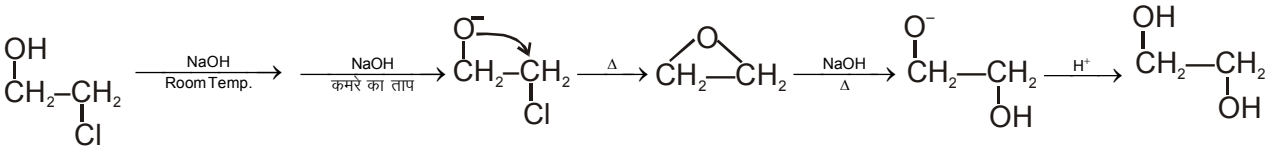
Evidences of NGP

- rate of reaction becomes very fast.
- retention of configuration at α -carbon

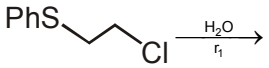
** The internal nucleophile can be –OH, –COOH, –SH, $–O^-$, $–COO^-$, $–S^-$, –SR, –NR, –Ph or $–CH=CH_2$.

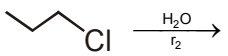
e.g. 1 Reaction of 2-Chloroethanol with NaOH

Mech.



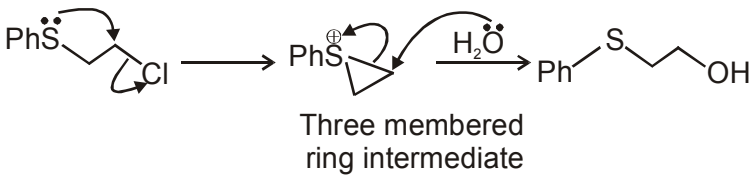
e.g. 2



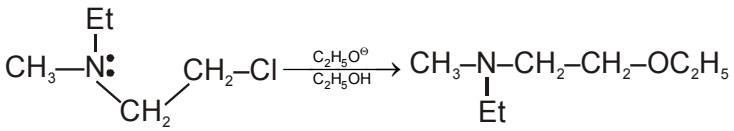


$(r_1 > r_2)$

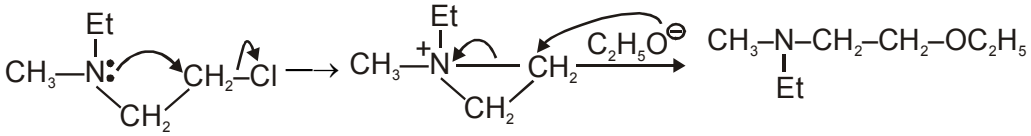
Mech.



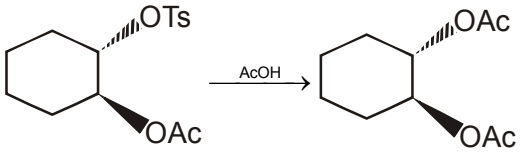
e.g. 3



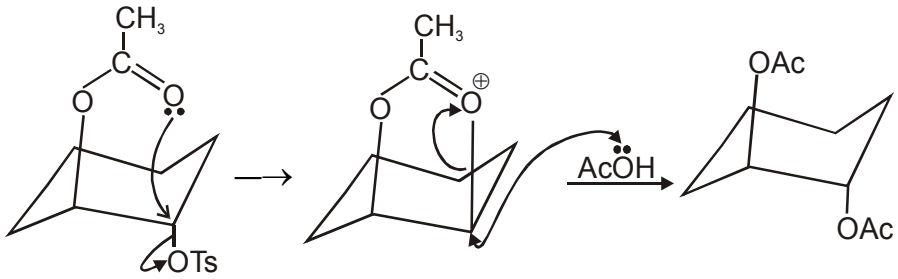
Mech.



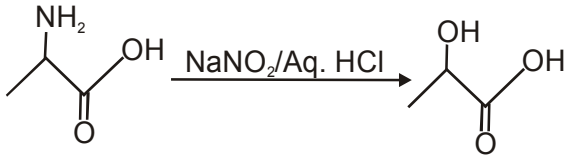
e.g. 4



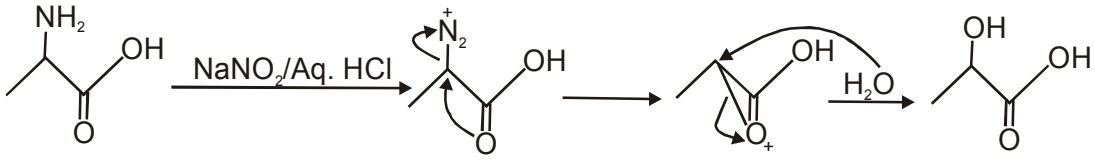
Mech.



e.g. 5.



Mech.

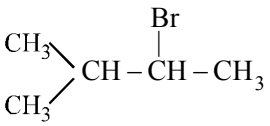
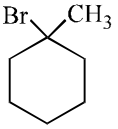
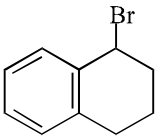


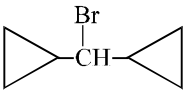
Exercise-1

PART - I : SUBJECTIVE QUESTIONS

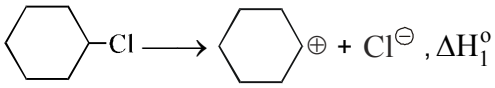
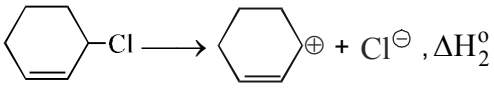
Section (A) : Unimolecular Nucleophilic Substitution Reaction (S_N1)

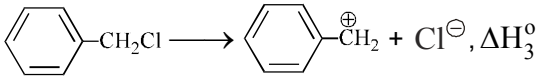
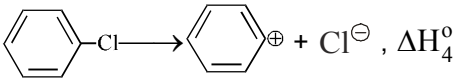
A-1. Arrange the following compounds in decreasing order of their reactivity for hydrolysis reaction.

(a) : (I)  (II)  (III) $C_6H_5-CH(Br)-C_6H_5$ (IV) 

(b) : (I) C_6H_5–CH_2–Br (II) $C_6H_5-CH(Br)-C_2H_5$ (III)  (IV) 

A-2. For the reactions

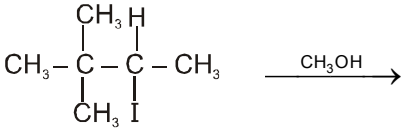
(I)  (II) 

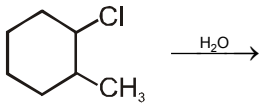
(III)  (IV) 

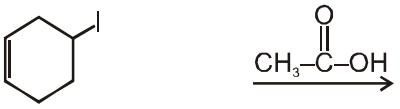
Write the correct decreasing order of enthalpies of reaction for producing carbocation :

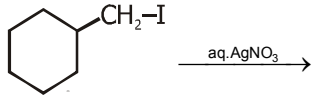
A-3. What effect do you expect due to following changes in S_N1 reaction of $(CH_3)_3CBr$ with CH_3OH ?
(a) The concentration of $(CH_3)_3CBr$ is doubled and that of CH_3OH is halved.
(b) The concentration of both $(CH_3)_3CBr$ and CH_3OH are tripled.

A-4. For each of the following solvolysis reaction give the products (major as well as minor).

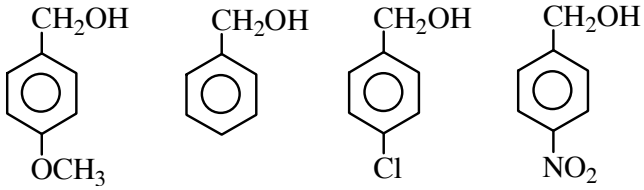
(a) 

(b) 

(c) 

(d) 

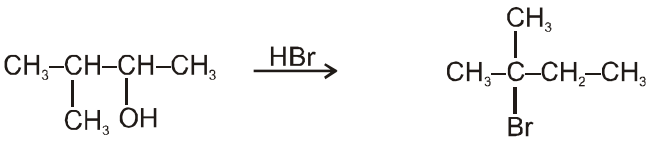
A-5. Observe the following compounds

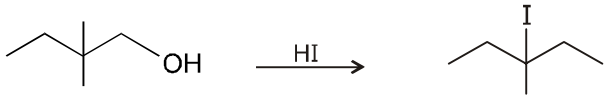


(1) (2) (3) (4)

X : The number which indicate more reactive compound with HX
Y : The number which indicate less reactive compound with HX
Find the sum of X + Y

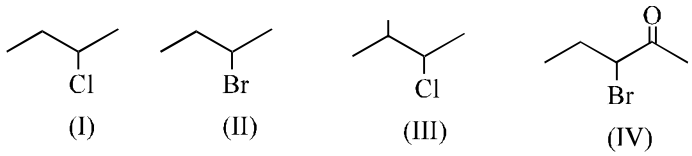
A-6. Write the mechanism of the following reaction and mention the rate determining step.

(a) 

(b) 

Section (B) : Bimolecular Nucleophilic Substitution Reaction (S_N2 & S_Ni)

B-1. Arrange the compounds of each set in order of reactivity towards S_N2 displacement.
(a) (I) 2-Bromo-2-methylbutane, (II) 1-Bromopentane, (III) 2-Bromopentane

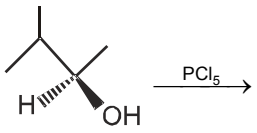
(b) 

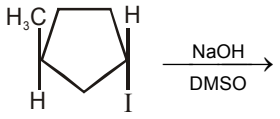
B-2. In how many compounds, S_N2 will be negligible?

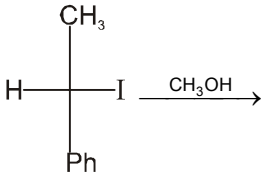
B-3. Which reacts faster?
(a) $PhCH_2Br$ and $PhCMe_2Br$ (H_2O / C_2H_5OH)
(b) $PhCH_2CH_2Br$ and $PhCMe_2Br$ (NaI / Acetone)

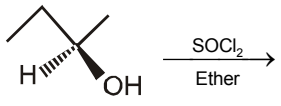
B-4. In S_N2 reaction of alkyl halide if we doubled the concentration of both reactant and nucleophile the rate of S_N2 reaction increases by..... times :

B-5. What will be the major product of the following reaction ?

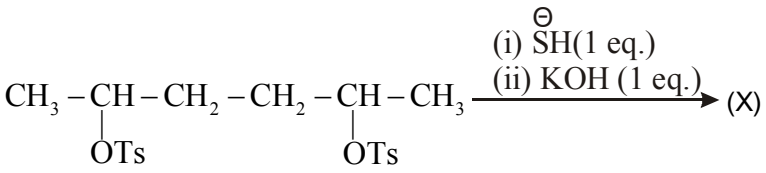
(a) 

(b) 

(c) 

(d) 

B-6. In the given reaction



How many statements are correct for given reaction?

S_1 : X is hetrocylic compound.

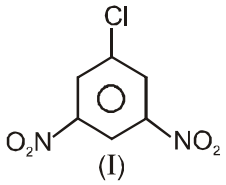
S_2 : OTs is a poor leaving group.

S_3 : One step is acid base reaction in given reaction.

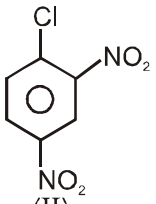
S_4 : Two times S_N2 involved in given reaction.

Section (C) : Aromatic Nucleophilic Substitution Reaction of aryl halide (S_N2Ar)

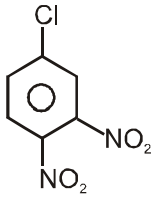
C-1. Write the correct reactivity order with NaOH for the following compounds.



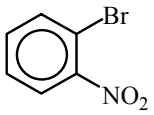
(I)

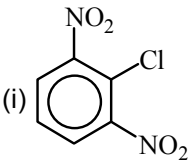


(II)

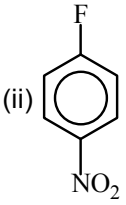


(III)

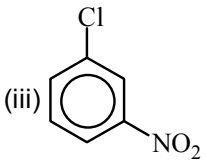
C-2. Number of compounds which can show faster rate of nucleophilic substitution of halogen than  are ?



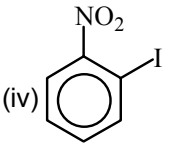
(i)



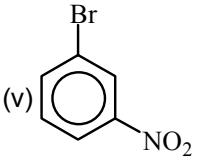
(ii)



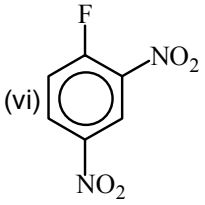
(iii)



(iv)

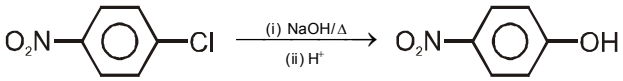


(v)

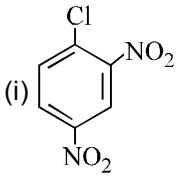


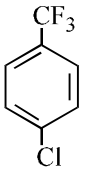
(vi)

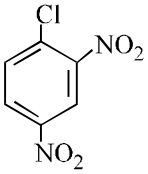
C-3. Write the mechanism of following reaction :

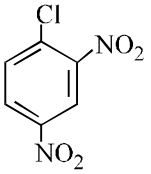


C-4. Write the principal organic product in each of the following reactions:

(i)  $\xrightarrow[\text{triethylene glycol}]{H_2NNH_2}$ B

(ii)  $\xrightarrow[(ii)\ NaOCH_3, CH_3OH]{(i)\ HNO_3, H_2SO_4}$ C

(iii)  $+ CH_3CH_2ONa \longrightarrow$ D

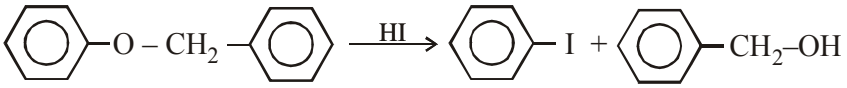
(iv)  $+ C_6H_5CH_2SNa \longrightarrow$ E

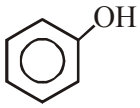
Section (D) : Nucleophilic Substitution Reaction of Ethers & Epoxides

D-1. How many reactions represent incorrect major products?

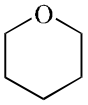
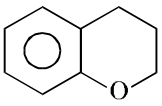
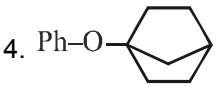
(a) $Me_3C–O–CH_3 \xrightarrow{HI} Me_3C–OH + CH_3I$

(b) $H_3C–O–CH_2–CH_3 \xrightarrow{HI} CH_3OH + ICH_2CH_3$

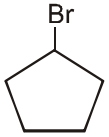
(c) 

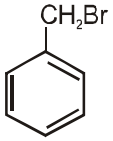
(d) Anisole $\xrightarrow{HI}$  $+ CH_3I$

D-2. Write the number of that compound which forms di-iodide on reaction with HI (excess)?

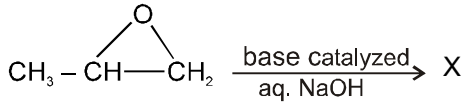
1.  2.  3. Ph–O–Ph 4. 

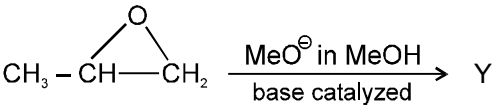
D-3. Few dialkyl ethers & cyclic ethers were allowed to react with excess of HBr with the following results. Identify the ether in each case.

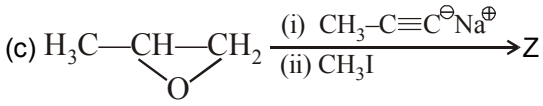
(a) $\xrightarrow[\text{excess}]{HBr}$  $+ \quad CH_3 – CH_2 – CH_2 – CH_2 – Br$

(b) $\xrightarrow[\text{excess}]{HBr}$ 

D-4. Give the products of the following reactions

(a)  X

(b)  Y

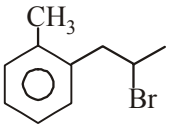
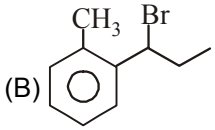
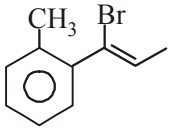
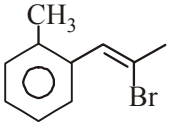
(c)  Z

PART - II : ONLY ONE OPTION CORRECT TYPE

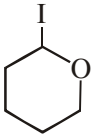
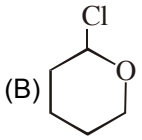
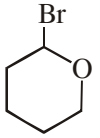
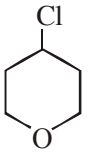
Section (A) : Unimolecular Nucleophilic Substitution Reaction (S_N1)

A-1. S_N1 reactions occur through the formation of intermediate :
(A) Carbocation (B) Carbanion (C) Free radical (D) Carbene

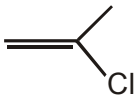
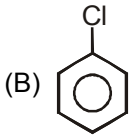
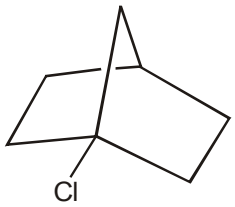
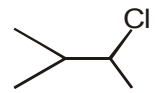
A-2. Which compound undergoes hydrolysis by the S_N1 mechanism at the fastest rate?

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

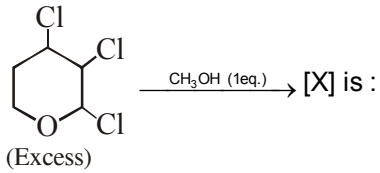
A-3. Which one of the following compounds will be most reactive for S_N1 reactions ?

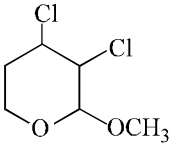
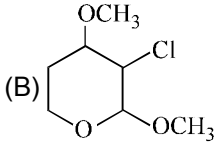
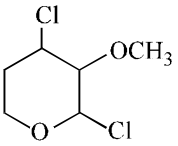
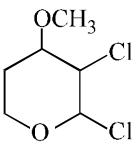
(A) 
(B) 
(C) 
(D) 

A-4. Which of the following compound can show S_N1 reaction?

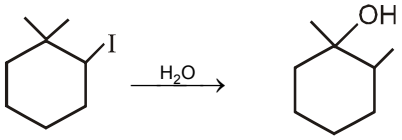
(A) 
(B) 
(C) 
(D) 

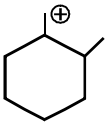
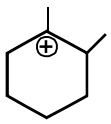
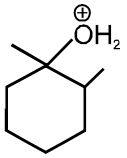
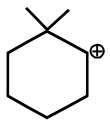
A-5. In the given reaction:


(Excess)

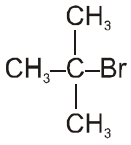
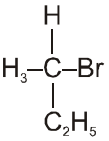
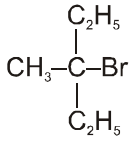
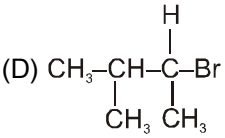
(A) 
(B) 
(C) 
(D) 

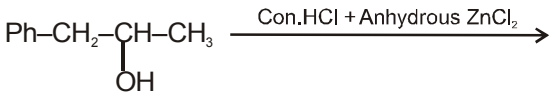
A-6. Which of the following is not expected to be intermediate of the following reaction ?



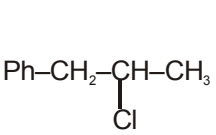
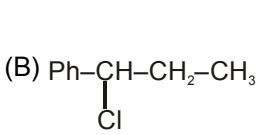
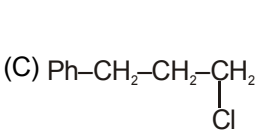
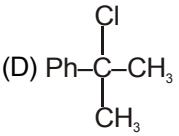
(A)  (B)  (C)  (D) 

A-7. Which one of the following compounds will give (d) and (ℓ) form in S_N1 reaction (as major product)?

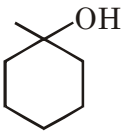
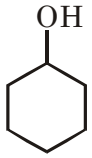
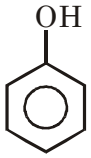
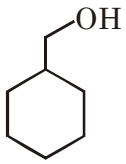
(A)  (B)  (C)  (D) 

A-8. 

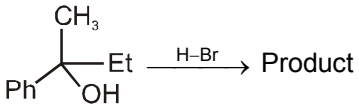
X is :

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

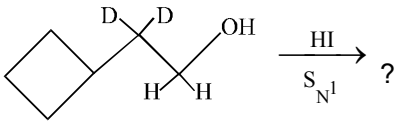
A-9. Which of the following alcohol gives immediate turbidity with Lucas reagent?

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

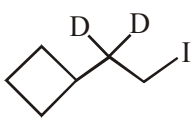
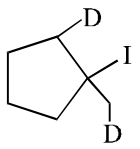
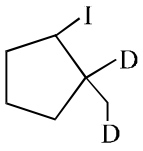
A-10. Which describes the best stereochemical aspects of the following reaction ?



(A) Inversion of configuration occurs at the carbon undergoing substitution.
(B) Retention of configuration occurs at the carbon undergoing substitution.
(C) Racemization occurs at the carbon undergoing substitution.
(D) The carbon undergoing substitution is not stereogenic.

A-11. 

Major product is:

(A)  (B)  (C)  (D) None of these

Section (B) : Bimolecular Nucleophilic Substitution Reaction (S_N2 & S_Ni)

B-1. S_N2 mechanism proceeds through intervention of :

(A) Carbonium ion (B) Transition state (C) Free radical (D) Carbanion

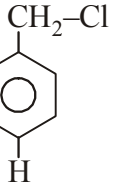
B-2. For reaction $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

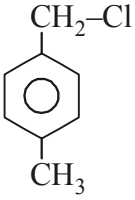
the rate of reaction is given by the expression :

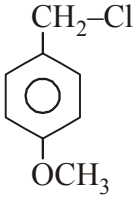
(A) Rate = k $[CH_3Br]$ (B) Rate = k $[OH^-]$

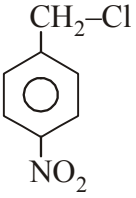
(C) Rate = k $[CH_3Br][OH^-]$ (D) Rate = k $[CH_3Br]$ $[H_2O]$

B-3. Which of the following is most reactive toward S_N2?

(A) 

(B) 

(C) 

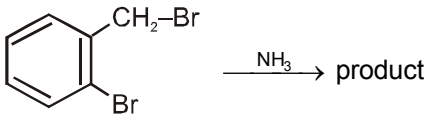
(D) 

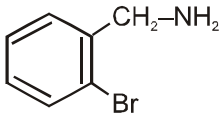
B-4. The given compound $CH_3–O–CH_2–Br$ gives which one of the following reaction ?

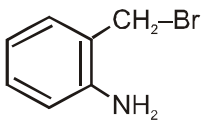
(A) Only S_N1 (B) Only S_N2

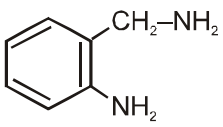
(C) S_N1 as well as S_N2 (D) None

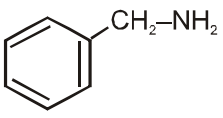
B-5. What is the major product obtained in the following reaction ?



(A) 

(B) 

(C) 

(D) 

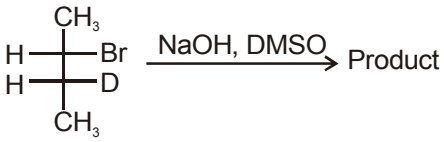
B-6. Identify the reactants (X) and (Y) for the following reaction, respectively.

(X) + (Y) $\xrightarrow{NaNH_2}$ 4– Decyne

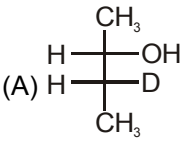
Alkyl halide Alkyne

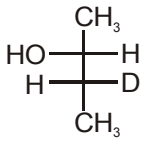
(A) $CH_3(CH_2)_4CH_2–Cl$ + $CH_3–C\equiv CH$ (B) $CH_3(CH_2)_2CH_2–Cl$ + $CH_3–(CH_2)_2–C\equiv CH$

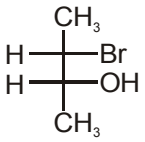
(C) $CH_3(CH_2)_2CH_2–Cl$ + $CH_3(CH_2)_3–C\equiv CH$ (D) $CH_3–CH_2–CH_2–Cl$ + $CH_3(CH_2)_4–C\equiv CH$

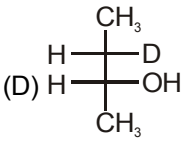
B-7. 

Product is :

(A) 

(B) 

(C) 

(D) 

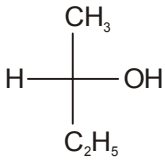
B-8. $CH_3(CH_2)_2CH_2OH \xrightarrow{HBr} X$,

1 – butanol

Identify X and the mechanism of the reaction

(A) $CH_3 - CH_2 - CH_2 - CH_2 - Br$ & S_N1 (B) $CH_3 - CH_2 - CH_2 - CH_2 - Br$ & S_N2

(C) $CH_3 - \underset{\underset{Br}{|}}{CH} - CH_2 - CH_3$ & S_N1 (D) $CH_3 - \underset{\underset{Br}{|}}{CH} - CH_2 - CH_3$ & S_N2

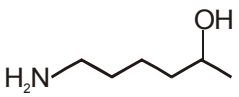
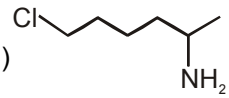
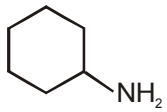
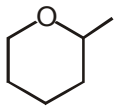
B-9.  $\xrightarrow{PCl_5}$ X ; (X) is

(D-2-Butanol)

(A) S-2-Chlorobutane (B) R - 2-Chlorobutane

(C) Mixture of R and S 2-Chlorobutane (D) 1-Chlorobutane

B-10. 6-Chlorohexan-2-ol $\xrightarrow[\Delta]{NaNH_2}$ major product is

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

B-11. Consider the following reaction.

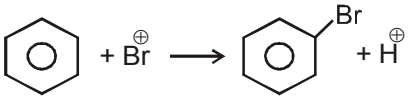
$$CH_3 - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_3 \xrightarrow[ether]{SOCl_2} CH_3 - CH_2 - \underset{\underset{Cl}{|}}{CH} - CH_3$$

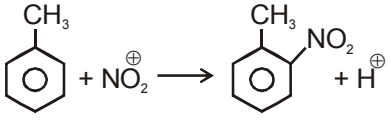
In the above reaction which phenomenon will take place :

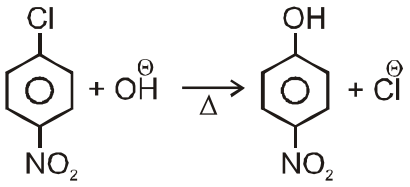
(A) Inversion (B) Retention (C) Racemisation (D) Isomerisation

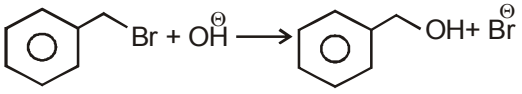
Section (C) : Aromatic Nucleophilic Substitution Reaction of Aryl halide (S_N2Ar)

C-1. Which of the following reaction is S_N2Ar reaction ?

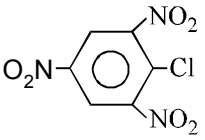
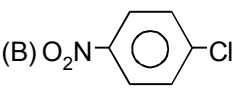
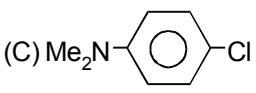
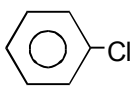
(A) 

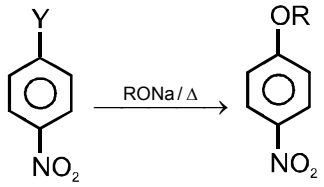
(B) 

(C) 

(D) 

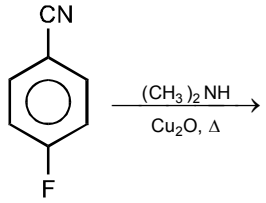
C-2. Which chloroderivative of benzene among the following would undergo-hydrolysis most readily with NaOH to furnish the corresponding hydroxy derivative?

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

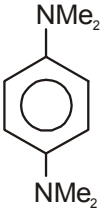
C-3. 

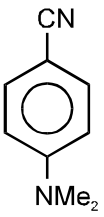
Above reaction has maximum rate when :

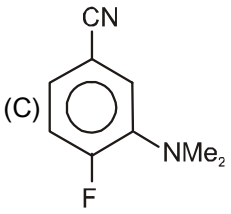
(A) Y = – I (B) Y = – Br (C) Y = – Cl (D) Y = – F

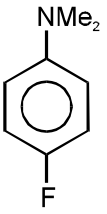
C-4. 

The product is

(A) 

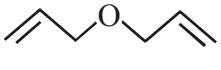
(B) 

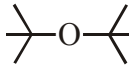
(C) 

(D) 

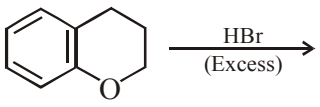
Section (D) : Nucleophilic Substitution Reactions of Ethers & Epoxides

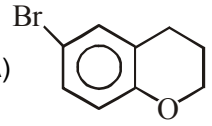
D-1. Which of the following ethers is the least reactive to cleavage with conc. HBr ?

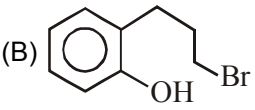
(A) Ph—CH_2—O—CH_3 (B) Ph—O—Ph (C) 

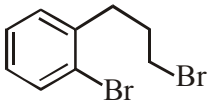
(D) 

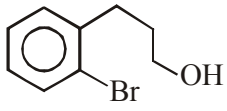
D-2. Find out correct product of reaction :

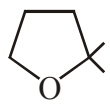


(A) 

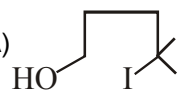
(B) 

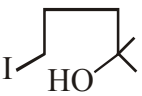
(C) 

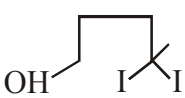
(D) 

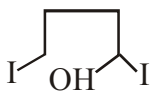
D-3. 

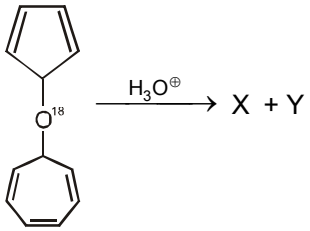
+ HI (1 eq.) ⟶ Product, Product is :

(A) 

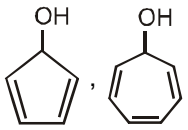
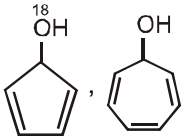
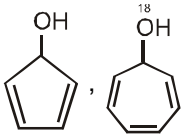
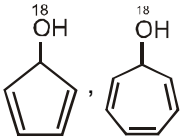
(B) 

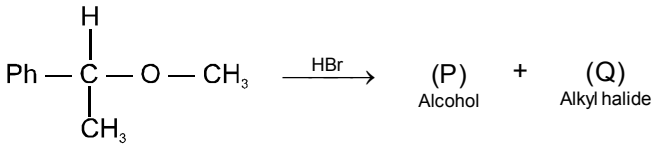
(C) 

(D) 

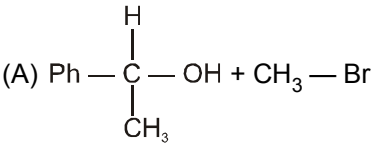
D-4. 

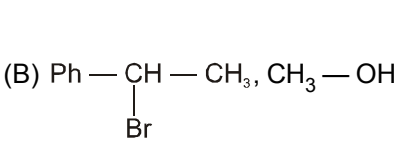
The products X and Y are

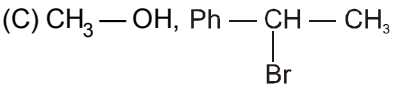
(A)  (B)  (C)  (D) 

D-5. 

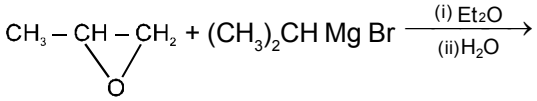
(P) and (Q) are respectively.

(A) 

(B) 

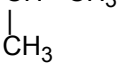
(C) 

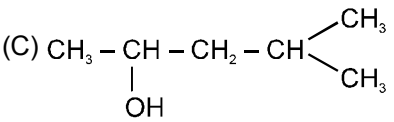
(D) $CH_3 — OH + PH — CH_3 — CH_2 — Br$

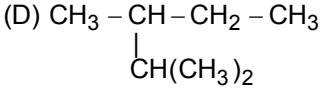
D-6. 

What will be the product :

(A) $CH_3 – (CH_2)_4 – CH_2 – OH$

(B) 

(C) 

(D) 

PART - III : MATCH THE COLUMN

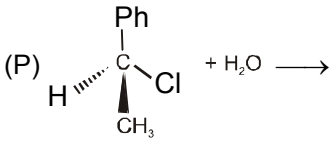
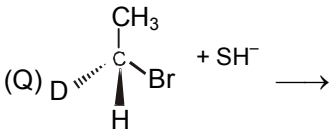
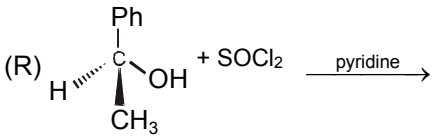
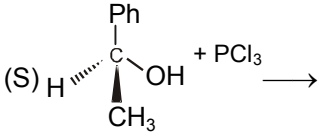
1. Match List I with List II and select the correct answer from the codes given below:

List I (Reactions)	**List II (Products)**
(P) $CH_3–O–SO_2CH_3 + C_2H_5\overset{\ominus}{O}$	(1) $CH_3–CH_2–PH_2$
(Q) $CH_3–CH_2–I + PH_3$	(2) $CH_3–O–C_2H_5$
(R) $HC\equiv\overset{\ominus}{C}\overset{\oplus}{N}a + CH_3–CH_2–Br$	(3) $CH_3–O–CH_3$
(S) $CH_3–Cl + CH_3–\overset{\ominus}{O}$	(4) $CH\equiv C–CH_2–CH_3$

(A) P–2 ; Q–1 ; R–4 ; S–3 (B) P–2 ; Q–1 ; R–3 ; S–4

(C) P–4 ; Q–2 ; R–3 ; S–1 (D) P–1 ; Q–2 ; R–4 ; S–3

2. Match column I with column II and select the correct answer from the codes given below:

Column-I Substrate	**Column-II Stereochemistry of product**
(P) 	(1) Retention
(Q) 	(2) Racemisation
(R) 	(3) Inversion
(S) 	(4) Intermediate is carbocation

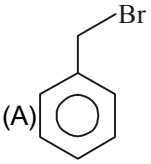
(A) P–2 ; Q–1 ; R–4 ; S–3 (B) P–2,4 ; Q–3 ; R–1 ; S–3

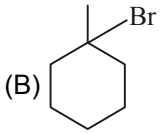
(C) P–4 ; Q–2 ; R–3 ; S–1 (D) P–1 ; Q–2 ; R–4 ; S–3

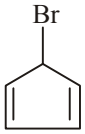
Exercise-2

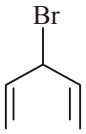
PART - I : ONLY ONE OPTION CORRECT TYPE

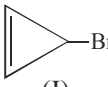
1. Which of the following can not give S_N1 reaction easily?

(A) 

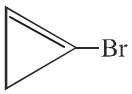
(B) 

(C) 

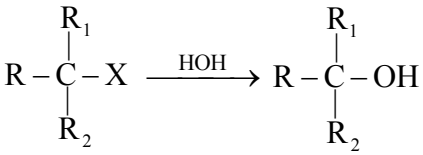
(D) 

2. For  , which is not the correct statement ?

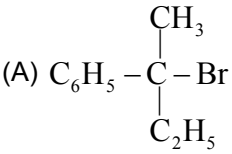
(I)

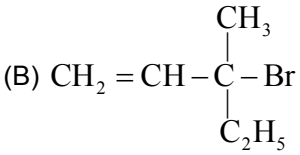
(A) I is more soluble in water than bromocyclopropane.
(B) I gives pale yellow ppt. on addition with aq. $AgNO_3$.
(C) I is aromatic compound.
(D) I is more ionic than 

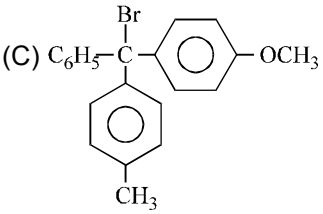
3. For the given reaction

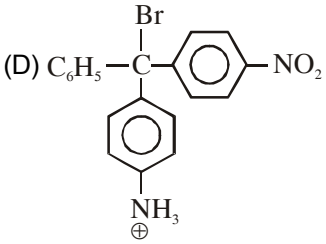


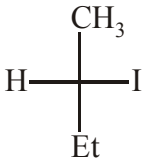
Which substrate will give maximum racemisation?

(A) 

(B) 

(C) 

(D) 

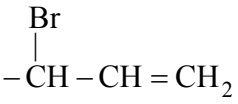
4.  Products. (If 96% racemisation takes place) :

Find out the correct statement about the reaction.
(A) Among the products 48% S and 48% R configuration containing molecules are present.
(B) Among the products 50% S and 50% R configuration containing molecules are present.
(C) Among the products 48% S and 52% R configuration containing molecules are present.
(D) Among the products 52% S and 48% R configuration containing molecules are present.

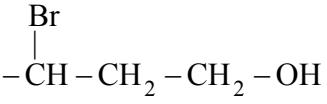
5. In the given reaction the product [P] can be :

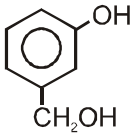
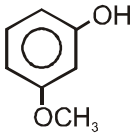
$CH_3–CH=CH–CH_2–OH \xrightarrow[S_N1']{HBr} [P]$

(A) $CH_3–CH=CH–CH_2–CH_2–Br$

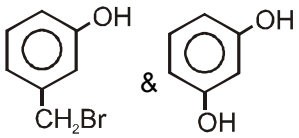
(B) 

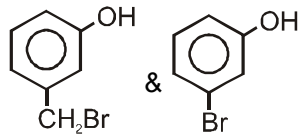
(C) $CH_2=CH–CH=CH_2$

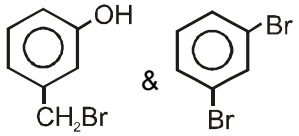
(D) 

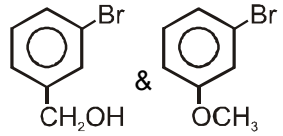
6.  $\xrightarrow[\Delta]{HBr}$ (A) ,  $\xrightarrow[\Delta]{HBr}$ (B)

The product (A) and (B) are respectively :

(A) 

(B) 

(C) 

(D) 

7. Select suitable reason for non-occurence of the following reaction :

$Br^- + CH_3OH \longrightarrow BrCH_3 + OH^-$

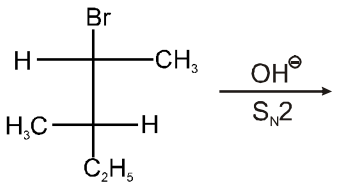
(A) Attacking nucleophile is stronger one.

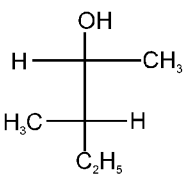
(B) Leaving group is a stronger base than nucleophile.

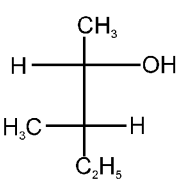
(C) Alcohols are not good substrate for S_N reaction.

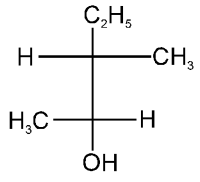
(D) Hydroxide ions are weak bases.

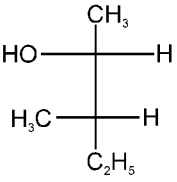
8. In the following reaction the most probable product will be :

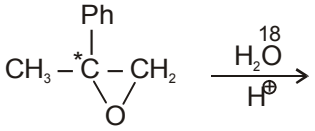


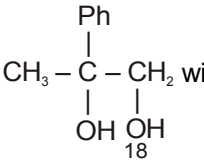
(A) 

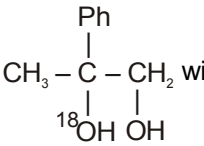
(B) 

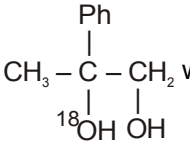
(C) 

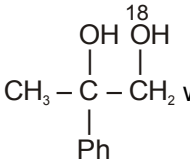
(D) 

9.  , The major product is ?

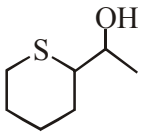
(A)  with retention, optically active

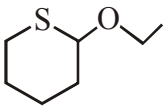
(B)  with racemisation

(C)  with 100% inversion, optically active

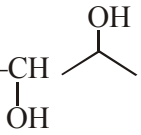
(D)  with racemisation

10. The product of the reaction is :

(A) 

(B) 

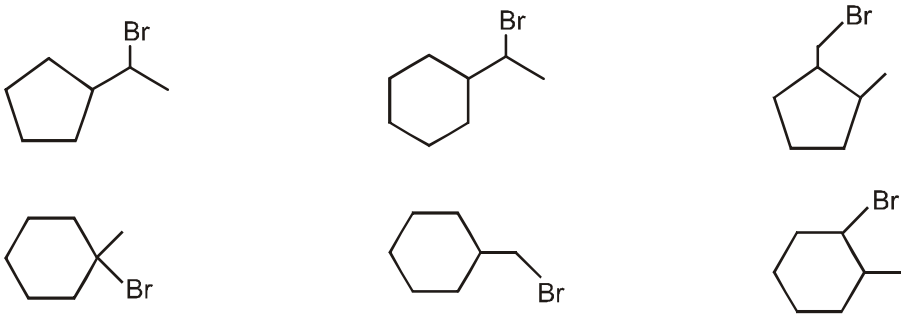
(C) HS–$(CH_2)_5$–O–Et

(D) 

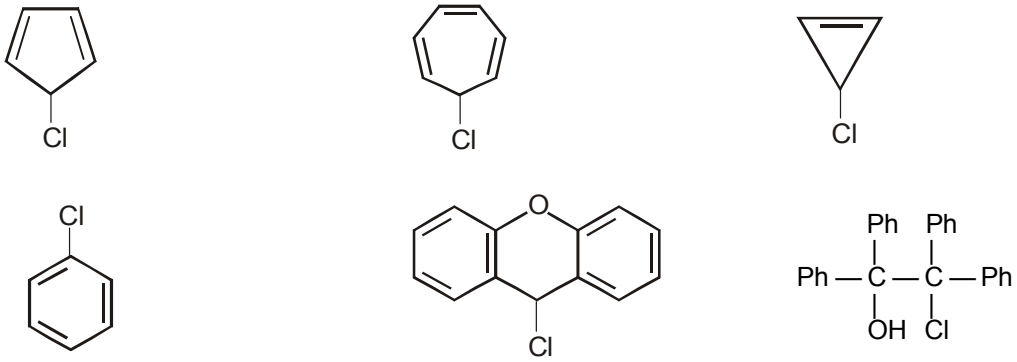
11. Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to
(A) The formation of less stable carbanion
(B) Longer carbon halogen bond
(C) The inductive effect
(D) sp^2–hybridized carbon attached to the halogen

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. Among the 6, how many cyclic isomers of molecular formula $C_7H_{13}Br$ can form 1-methylcyclohexan-1-ol on reaction with H_2O/acetone/Ag^+?



2. How many of the following compounds will give white precipitate with aqueous $AgNO_3$?



3. S_N1 reaction undergoes through a carbocation intermediate as follows : -

$$R\text{–}X\ (aq.) \underset{}{\overset{Slow}{\rightleftharpoons}} R^+(aq.) + X^-(aq.) \xrightarrow[fast]{H_2O} ROH(aq.) + H^+(aq.)$$

[R = t-Bu, iso-Pr, Et, Me] (X = Cl, Br, I)

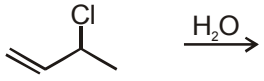
How many statements are correct?

S_1. The decreasing order of rate of S_N1 reaction is t-BuX > iso-PrX > EtX > MeX

S_2. The decreasing order of ionisation energy is MeX > EtX > iso-PrX > t-BuX

S_3. The decreasing order of energy of activation is t-BuX > iso-PrX >EtX > MeX

4.

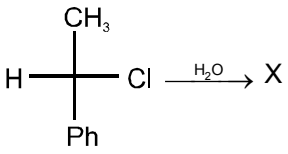


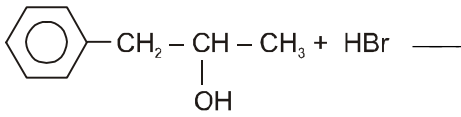
(R)
optically active

$\xrightarrow{H_2O}$

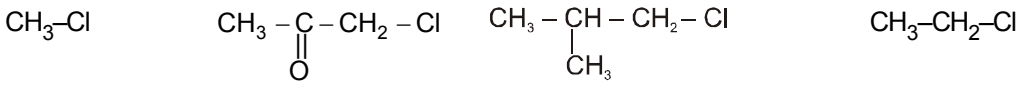
How many organic products are formed in the above reaction ?

5. Find the total number of isomeric products obtained in these reactions and report your answer as | X | Y | :



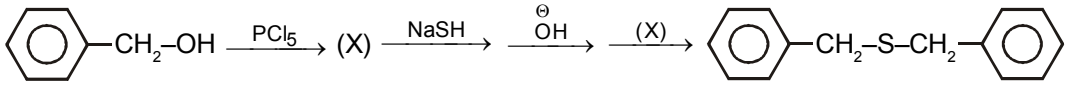
6.  Number of possible isomeric products including stereoisomers will be :

7. Which number compound is most reactive for S_N2 reaction ?



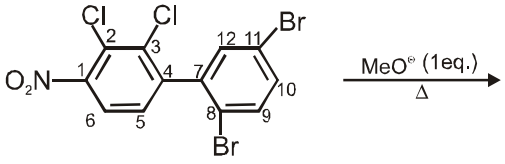
(1) (2) (3) (4)

8. When the concentration of alkyl halide is tripled and the concentration of $\overset{\ominus}{OH}$ ion is reduced to half, the rate of S_N2 reaction increases by X times. Report your answer as 10 X.

9. 

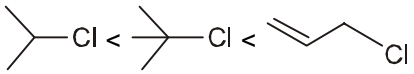
The number of times S_N2 reaction has taken place is .....

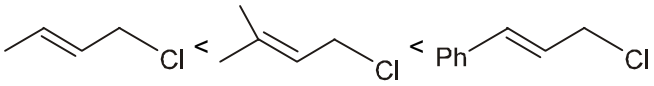
10. In the following reaction the nucleophile ($MeO^{\ominus}$) will displace which of the halogen atom most readily?

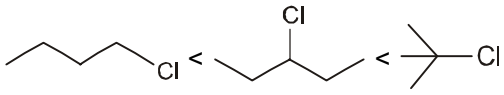


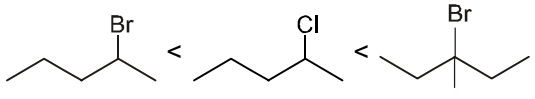
PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Which of the following order is/are correct for the solvolysis in 50% aqueous ethanol at 44.6°C?

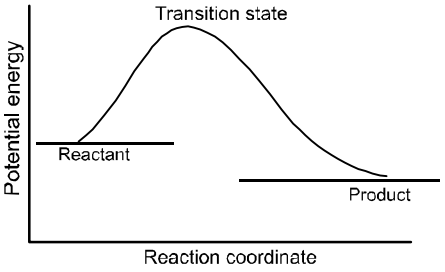
(A) 

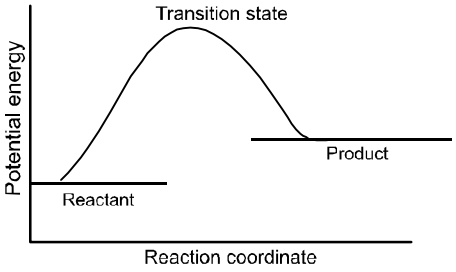
(B) 

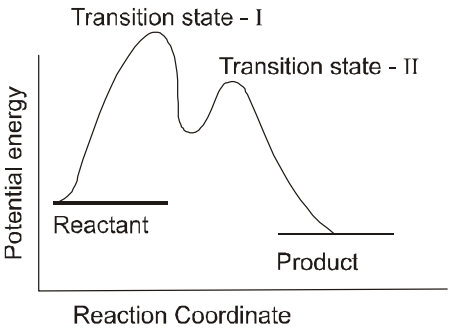
(C) 

(D) 

2. Following are the curves for nucleophilic substitution reaction?

(I)


(II)


(III)


The correct statement (s) is/(are)
(A) 'I' is potential energy diagram for S_N2 reaction that takes place with a negative potential energy change.
(B) 'II' is potential energy diagram for S_N2 reaction with a positive potential energy change.
(C) 'III' shows potential energy diagram for S_N1 reaction with large energy of activation for first.
(D) 'III' shows potential energy diagram for S_N1 reaction and first step is RDS for forward reaction.

3. Rate of S_N2 depends on :

(A) Conc of Nucleophile (B) Conc of substrate

(C) Nature of leaving group (D) Nature of solvent

4. Which of the following statements is / are true?

(A) $CH_3–CH_2–CH_2–I$ will react more readily than $(CH_3)_2$ CHI for S_N2 reactions.

(B) $CH_3–CH_2–CH_2–Cl$ will react more readily than $CH_3–CH_2–CH_2–Br$ for S_N2 reaction.

(C) $CH_3–CH_2–CH_2–CH_2–Br$ will react more readily than $(CH_3)_3C–CH_2–Br$ for S_N2 reactions.

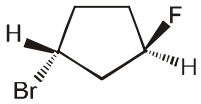
(D) $CH_3–O–C_6H_4–CH_2Br$ will react more readily than $NO_2–C_6H_4–CH_2Br$ for S_N2 reaction.

5. Observe the following reaction I and II k_1 k_1', k_2 k_2' are rate constants. Select the correct option(s).

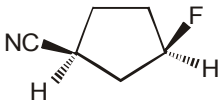
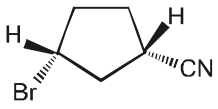
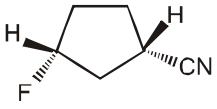
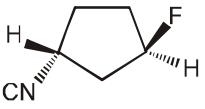
(I) $\xleftarrow[[k_1']]{(CH_3CH_2)_3N:}$ $CH_3 - I$ $\xrightarrow[(k_1)]{N:}$

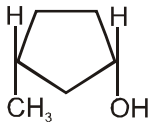
(II) $\xleftarrow[[k_2']]{(CH_3CH_2)_3N:}$ $CH_3 - \underset{\underset{I}{|}}{CH} - CH_3$ $\xrightarrow[(k_2)]{N:}$

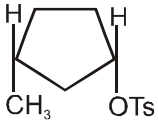
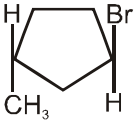
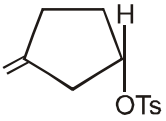
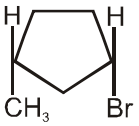
(A) $k_1 > k_1'$ (B) $k_1 > k_2$ (C) $k_2' > k_2$ (D) $k_2' > k_1'$

6.  + NaCN (1 mole) $\longrightarrow$ A (Major)

major product of this reaction is.

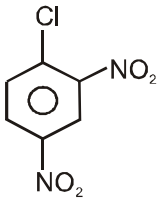
(A)  (B)  (C)  (D) 

7.  $\xrightarrow[\text{Pyridine}]{\text{TsCl}}$ X $\xrightarrow{\text{NaBr}}$ Y. X and Y are :

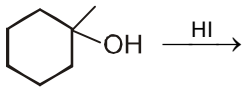
(A) X =  (B) Y =  (C) X =  (D) Y = 

8. Which of the following reactions are nucleophilic substitution reactions ?

(A) $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-Ph \xrightarrow{PCl_5}$

(B)  $\xrightarrow[\Delta]{C_6H_5-CH_2-SNa}$

(C) $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{SOCl_2}$

(D) 

9. Identify correct steps representing S_N1 mechanism for the cleavage of ether with HI

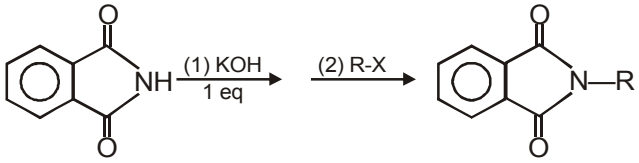
$$R-O-R' + HI \longrightarrow R-\overset{\oplus}{\underset{\underset{H}{|}}{O}}-R' + \overset{\ominus}{I}$$

(A) $\overset{\ominus}{I} + R-\overset{\overset{H}{|}}{\underset{\oplus}{O}}-R' \xrightarrow[(rds)]{slow} RI + HOR'$ (R is 1°)

(B) $R-\overset{\overset{H}{|}}{\underset{\oplus}{O}}-R' \xrightarrow[(rds)]{slow} R^{\oplus}$ (R is 3°) + R′OH

(C) $R^{\oplus} + \overset{\ominus}{I} \xrightarrow{fast} RI$

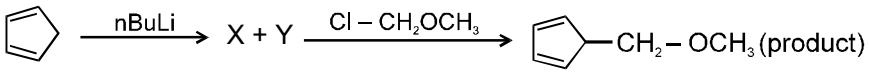
(D) $R^{\oplus} + \overset{\ominus}{I} \xrightarrow[(rds)]{slow} R-I$

10. 

In which option correct rate for step 2 is given for the different R–X?

(A) $CH_3–CH_2–Br < CH_3—\underset{\underset{Br}{|}}{CH}—CH_3$ (B) $Ph–Cl > CH_3–Cl$

(C) $Ph–CH_2–Br > Ph—\underset{\underset{Br}{|}}{CH}—CH_3$ (D) $CH_2=CH–CH_2–Cl > CH_3–CH_2–CH_2–Cl$

11. 

In the above reaction which of the following are correct?

(A) step-1 is an acid-base reaction (B) step-2 is an S_N2 reaction

(C) X = n-Butane ; Y = aromatic compound (D) the nucleophile in 2nd reaction is $:Bu^{\ominus}$

12. $CH_3Br + NH_3 \xrightarrow{\Delta} [(CH_3)_4N^{\oplus}]Br^{\ominus}$

excess salt

About the salt obtained, which statements are correct?

(A) Obtained by S_N2 mechanism. (B) NH_3 is nucleophile.

(C) Reaction is through S_N1 mechanism (D) 4 equivalent of NH_3 is used during reaction.

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

Groups like CN & $[-O-\ddot{N}=O]$ possess two nucleophilic centres and are called ambident nucleophiles. Actually cyanide group is hybrid of two contributing structures and therefore can act as nucleophile in two different ways $[\overset{\ominus}{C}\equiv N \longleftrightarrow :C=N^{\ominus}]$. Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage $[O-\ddot{N}=O]$.

1. Correct option among the following is :

(A) $\underset{\text{Haloalkane}}{R-X} \xrightarrow{KCN} \underset{\text{Major product}}{RNC}$ (B) $R-X \xrightarrow{AgCN} \underset{\text{Major}}{R–CN}$

(C) $R-X \xrightarrow{KNO_2} \underset{\text{Major}}{R-O-N=O}$ (D) $R-X \xrightarrow{AgNO_2} \underset{\text{Major product}}{R-O-N=O}$

2. Incorrect statement is :

$$R-X \xrightarrow[AgCN]{KCN}$$

(A) KCN is predominentely ionic in nature (B) AgCN is mainly covalent in nature

(C) In AgCN, carbon is the donor atom (D) In AgCN nitrogen is the donor atom

Comprehension # 2

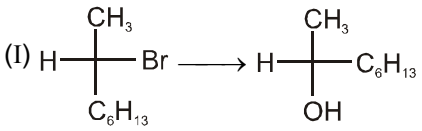
One of the most interesting and useful aspects of stereochemistry is the study of what happens to optically acitive molecules when they react. The product isolated from the reaction of the chiral starting material can tell us a great deal about the reaction mechanism . We observe

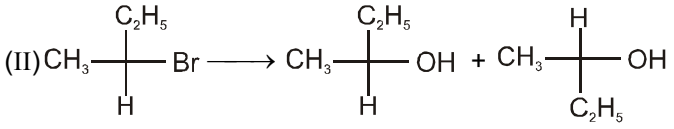
$S_N2 \longrightarrow$ Inversion of configuration

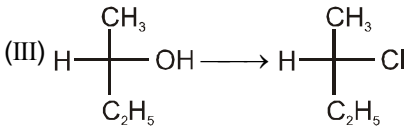
$S_N1 \longrightarrow$ Racemisation

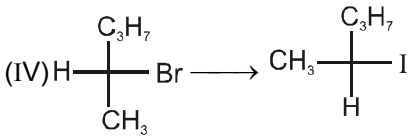
$S_Ni \longrightarrow$ Retention of configuration

3. In the given reactions, mention reaction mechanism respectively.





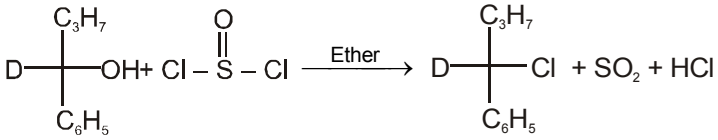




(A) S_N2 , S_N1 , S_N2 , S_Ni (B) S_N2 , S_N1 , S_Ni , S_N2

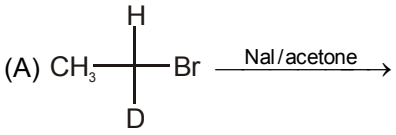
(C) S_N1 , S_N2 , S_Ni , S_N1 (D) S_N2 , S_Ni , S_N1 , S_N2

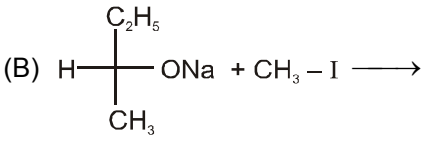
4. The given reaction is an example of which type of mechanism ?

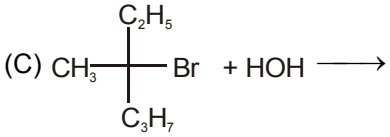


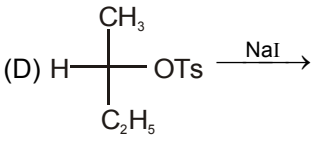
(A) S_N^2 (B) S_N^1 (C) S_N^i (D) None

5. In which of the following reaction retention of configuration is observed ?





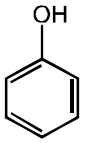




Exercise-3

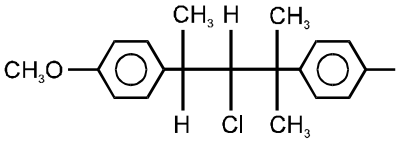
PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

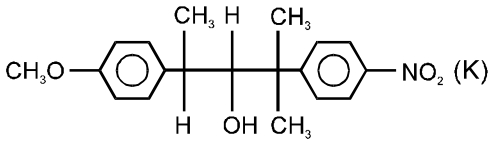
*** Marked Questions may have more than one correct option.**

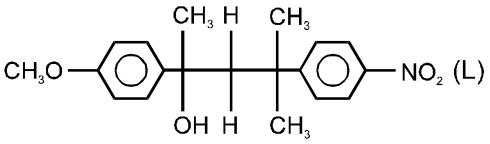
1.  $+ C_2H_5I \xrightarrow[\text{Anhydrous } (C_2H_5OH)]{\bar{O}C_2H_5 \text{ (excess)}}$ product, major product is **[JEE-2003]**

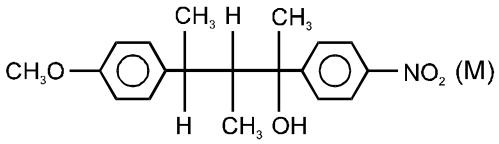
(A) $C_6H_5OC_2H_5$ (B) $C_2H_5OC_2H_5$ (C) $C_6H_5OC_6H_5$ (D) C_6H_5I

2. Explain why 7-bromo-1, 3, 5-cycloheptatriene exist as an ion while 5-Bromo-1, 3-cyclopentadiene does not form any ion even in the presence of Ag^+ . Explain why ? **[JEE 2004, 4/60]**

3. Compound (X)  is reacted with aqueous acetone it gives following products. **[JEE(s)2005, 3/144]**

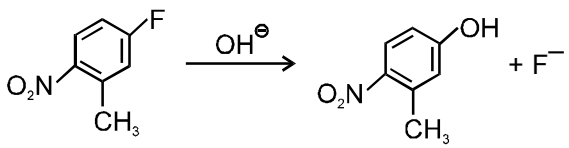


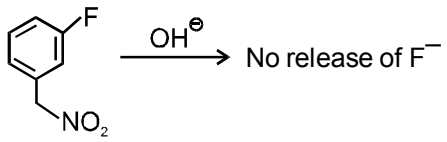




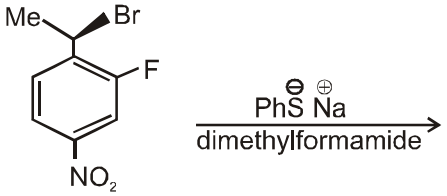
(A) K, L (B) K, M (C) L only (D) M only

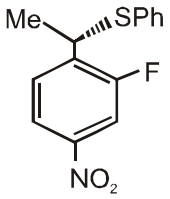
4. Explain the following observations : **[JEE 2005, 4/84]**

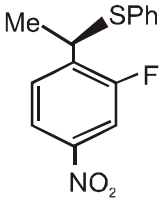


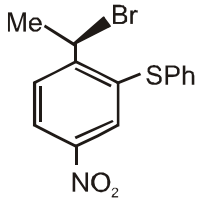


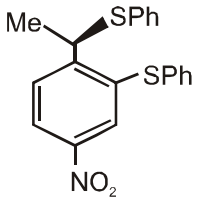
5. The major product of the following reaction is **[JEE-2008, 3/163]**

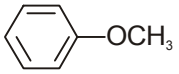


(A) 

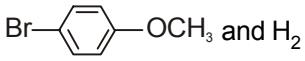
(B) 

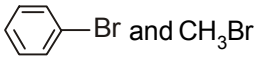
(C) 

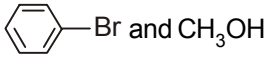
(D) 

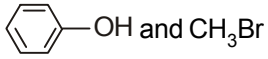
6. In the reaction 

the products are : **[JEE-2010, 3/163]**

(A) 

(B) 

(C) 

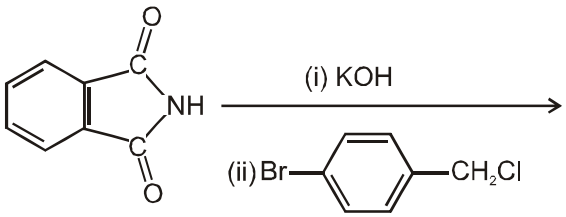
(D) 

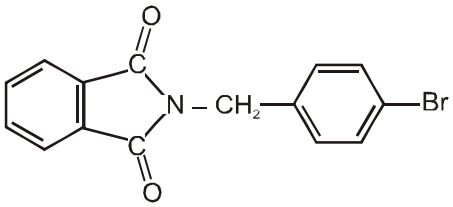
7. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are : **[JEE-2010, 3/163]**

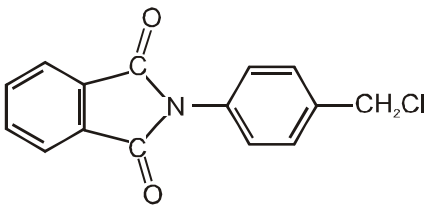
(A) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$ (B) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C\equiv CH$

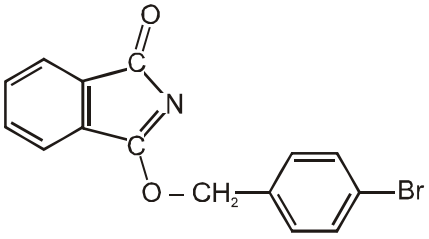
(C) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C\equiv CH$ (D) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$

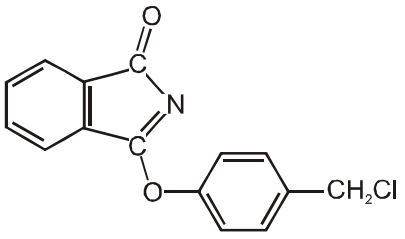
8. The major product of the following reaction is : **[JEE-2011, 3/160]**



(A) 

(B) 

(C) 

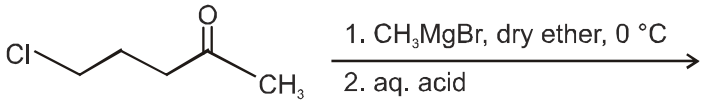
(D) 

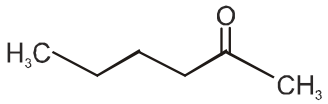
9. KI in acetone, undergoes S_N2 reaction with each P, Q, R and S. The rates of the reaction vary as **[JEE-2013, 2/120]**

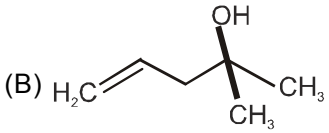
P **Q** **R** **S**

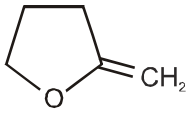
(A) P > Q > R > S (B) S > P > R > Q (C) P > R > Q > S (D) R > P > S > Q

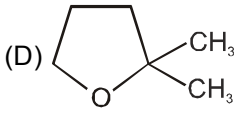
10. The major product in the following reaction is : **[JEE(Adv.)-2014, 3/120]**



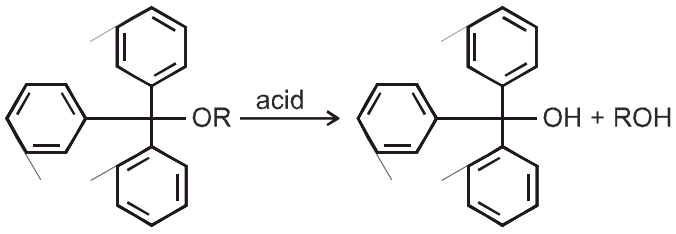
(A) 

(B) 

(C) 

(D) 

11. The acidic hydrolysis of ether (X) shown below is fastest when : **[JEE(Advanced)-2014, 3/120]**

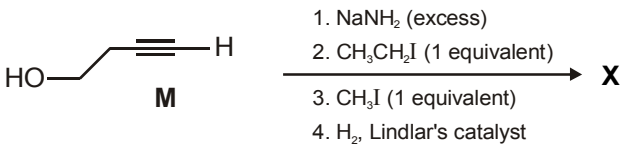


[X]

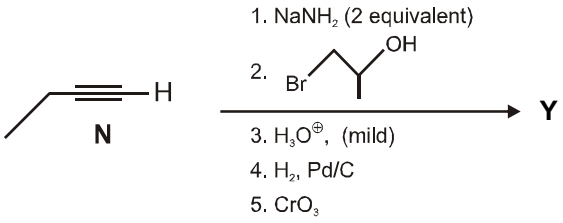
(A) one phenyl group is replaced by a methyl group.
(B) one phenyl group is replaced by a para-methoxyphenyl group.
(C) two phenyl groups are replaced by two para-methoxyphenyl groups.
(D) no structural change is made to X.

Paragraph for questions 12 and 13

Schemes **1** and **2** describe sequential transformation of alkynes **M** and **N**. Consider only the **major products** formed in each step for both the schemes.

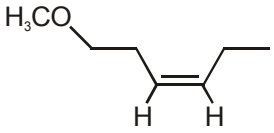


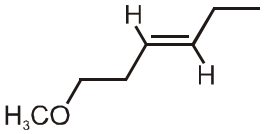
M **X** **Scheme-1**

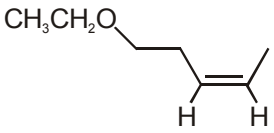


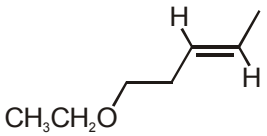
Scheme-2

12. The product **X** is : **[JEE(Advanced)-2014, 3/120]**

(A) 

(B) 

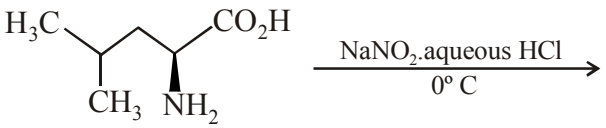
(C) 

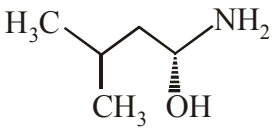
(D) 

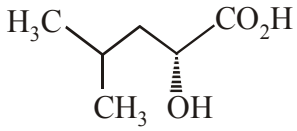
13. The correct statement with respect to product **Y** is **[JEE(Advanced)-2014, 3/120]**

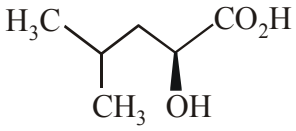
(A) It gives a positive Tollens test and is a functional isomer of **X**.
(B) It gives a positive Tollens test and is a geometrical isomer of **X**.
(C) It gives a positive iodoform test and is a functional isomer of **X**.
(D) It gives a positive iodoform test and is a geometrical isomer of **X**.

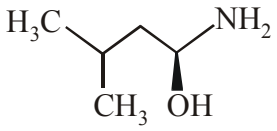
14. The major product of the reaction is : **[JEE(Advanced)-2015, 4/120]**



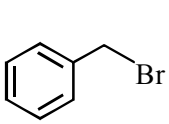
(A) 

(B) 

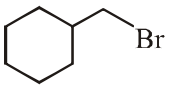
(C) 

(D) 

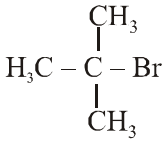
15. For the following compounds, the correct statement(s) with respect of nucleophilic substitution reactions is(are); **[JEE(Advanced)-2017, 4/120]**



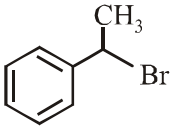
(I)



(II)



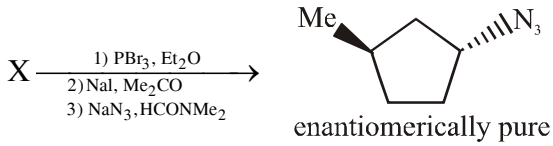
(III)



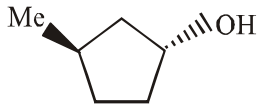
(IV)

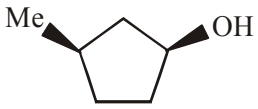
(A) Compound IV undergoes inversion of configuration.
(B) The order of reactivity for I, III and IV is : IV > I > III.
(C) I and III follow S_N1 mechanism.
(D) I and II follow S_N2 mechanism.

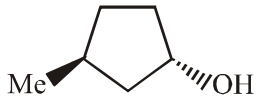
16. In the following reaction sequence, the correct structure(s) of X is (are)

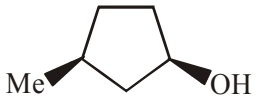


[JEE(Advanced)-2017, 4/120]

(A) 

(B) 

(C) 

(D) 

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

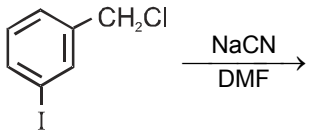
1. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in a test tube and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment ? **[AIEEE-2003]**

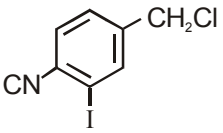
(1) A was C_6H_5I (2) A was $C_6H_5CH_2I$
(3) B was C_6H_5I (4) Addition of HNO_3 was unnecessary

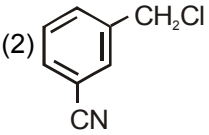
2. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of : **[AIEEE-2005]**

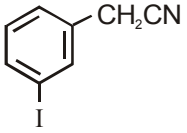
(1) steric hinderance (2) inductive effect (3) instability (4) insolubility

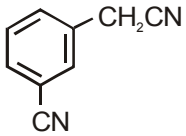
3. The structure of the major product formed in the following reaction is : **[AIEEE-2006]**



(1) 

(2) 

(3) 

(4) 

4. Which of the following is the correct order of decreasing S_N2 reactivity ? **[AIEEE-2007, 3/120]**

(1) $RCH_2X > R_3CX > R_2CHX$ (2) $RCH_2X > R_2CHX > R_3CX$
(3) $R_3CX > R_2CHX > RCH_2X$ (4) $R_2CHX > R_3CX > RCH_2X$

5. The organic chloro compound, which shows complete stereochemical inversion during an S_N2 reaction, is: **[AIEEE-2008, 3/105]**

(1) $(CH_3)_3CCl$ (2) $(CH_3)_2CHCl$ (3) CH_3Cl (4) $(C_2H_5)_2CHCl$

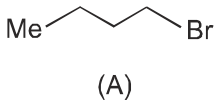
6. Which of the following on heating with aqueous KOH, produces acetaldehyde ? **[AIEEE-2009, 4/144]**

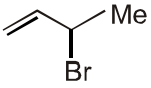
(1) CH_3CH_2Cl (2) CH_2ClCH_2Cl (3) CH_3CHCl_2 (4) CH_3COCl

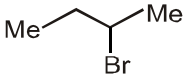
7. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is **[AIEEE-2010, 4/144]**

(1) 2-Butanol (2) 2-Methylpropan-2-ol (3) 2-Methylpropanol (4) 1-Butanol

8. Consider the following bromides : **[AIEEE-2010, 4/144]**


(A)


(B)


(C)

The correct, order of S_N1 reactivity is :

(1) B > C > A (2) B > A > C (3) C > B > A (4) A > B > C

9. A solution of (–)-1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of : **[JEE(Main) 2013, 4/120]**

(1) carbanion (2) carbene (3) carbocation (4) free radical

10. An unknown alochol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism : **[JEE(Main) 2013, 4/120]**

(1) secondary alcohol by S_N1 (2) tertiary alcohol by S_N1

(3) secondary alcohol by S_N2 (4) tertiary alcohol by S_N2

11. In S_N2 reactions, the correct order of reactivity for the following compounds : CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is : **[JEE(Main) 2014, 4/120]**

(1) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(2) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(3) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

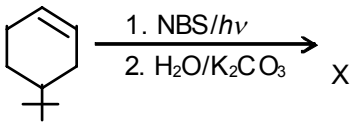
(4) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

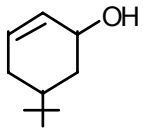
12. The synthesis of alkyl fluorides is best accomplished by : **[JEE(Main) 2015, 4/120]**

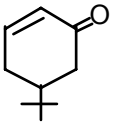
(1) Free radical fluorination (2) Sandmeyer's reaction

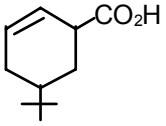
(3) Finkelstein reaction (4) Swarts reaction

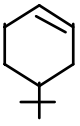
13. The product of the reaction give below is : **[JEE(Main) 2016, 4/120]**



(1) 

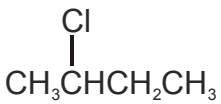
(2) 

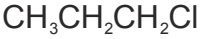
(3) 

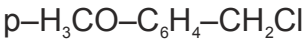
(4) 

14. The increasing order of the reactivity of the following halides for the S_N1 reaction is :

[JEE(Main) 2017, 4/120]

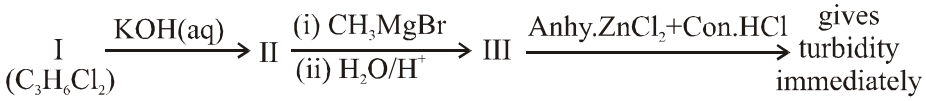

(I)

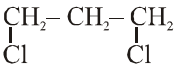

(II)

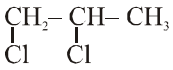

(III)

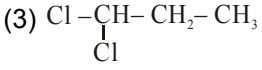
(1) (II) < (I) < (III) (2) (I) < (III) < (II) (3) (II) < (III) < (I) (4) (III) < (II) < (I)

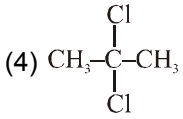
15. In the following reaction sequence,The compound I is : **[JEE(Main) 2017, 4/120]**



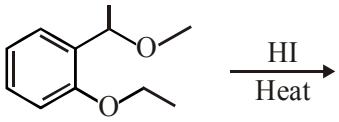
(1) 

(2) 

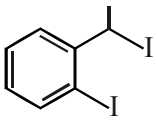
(3) 

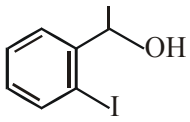
(4) 

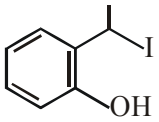
16. The major product formed in the following reaction is :

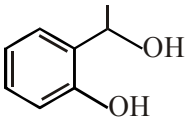


[JEE(Main) 2017, 4/120]

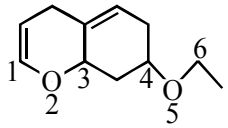
(1) 

(2) 

(3) 

(4) 

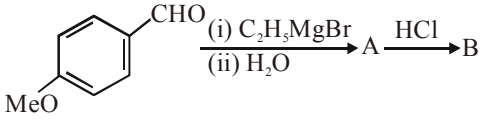
17. On treatment of the following compound with a strong acid, the most susceptible site for bond cleavage is :-



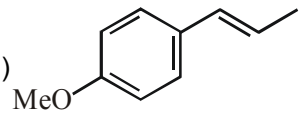
[JEE(Main) 2018, 4/120]

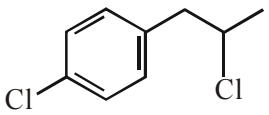
(1) C4 – O5 (2) O2 – C3 (3) O5 – C6 (4) C1 – O2

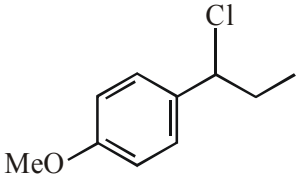
18. The major product B formed in the following reaction sequence is :

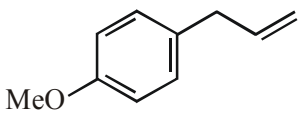


[JEE(Main) 2018, 4/120]

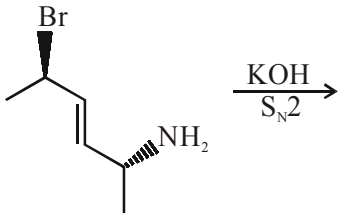
(1) 

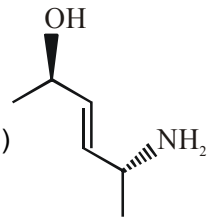
(2) 

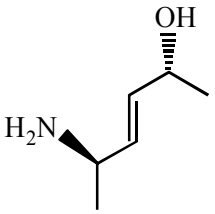
(3) 

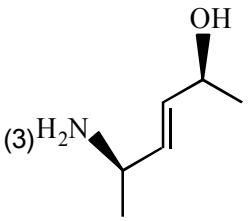
(4) 

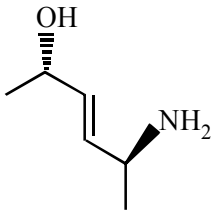
19. The major product of the following reaction is : **[JEE(Main) 2018, 4/120]**



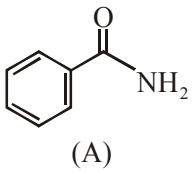
(1) 

(2) 

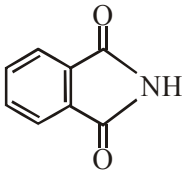
(3) 

(4) 

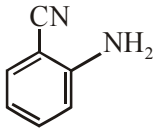
20. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is : **[JEE(Main) 2019, (Jan.) 4/120]**



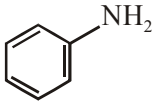
(A)



(B)



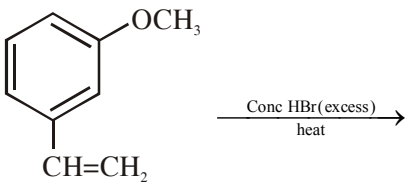
(C)

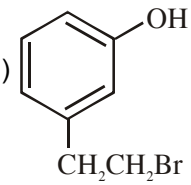


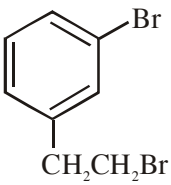
(D)

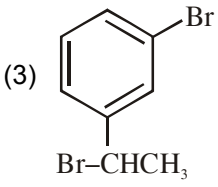
(1) (B) < (A) < (D) < (C)
(2) (B) < (A) < (C) < (D)
(3) (A) < (C) < (D) < (B)
(4) (A) < (B) < (C) < (D)

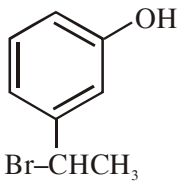
21. The major product of the following reactions: **[JEE(Main) 2019, (April) 4/120]**



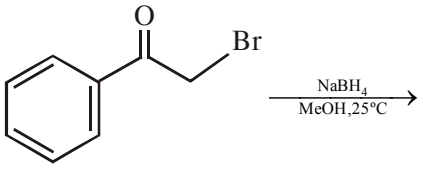
(1) 

(2) 

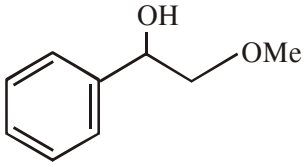
(3) 

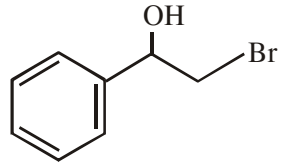
(4) 

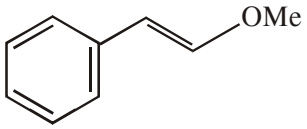
22. The major product of the following reaction is:

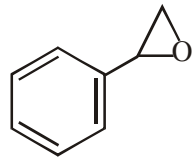


[JEE(Main) 2019, (April) 4/120]

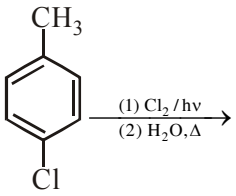
(1) 

(2) 

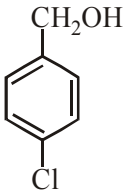
(3) 

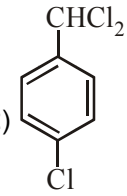
(4) 

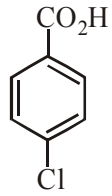
23. The major product of the following reaction is:

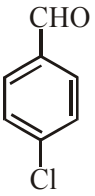


[JEE(Main) 2019, (April) 4/120]

(1) 

(2) 

(3) 

(4) 

ANSWER KEY

EXERCISE -1

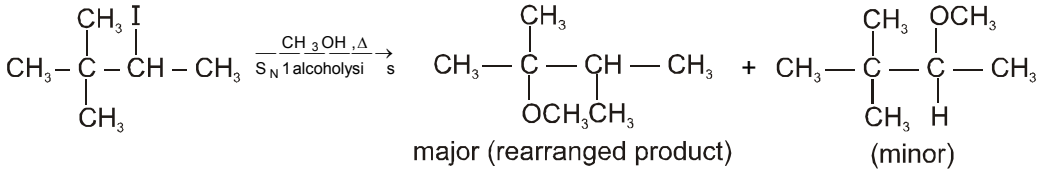
PART - I

A-1. (a) III > IV > II > I ; (b) IV > II > I > III

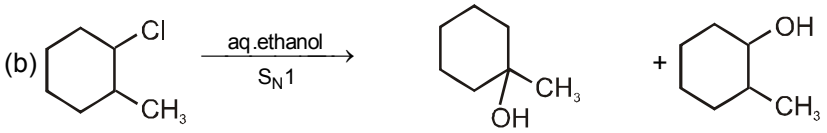
A-2. $\Delta H_4^o > \Delta H_1^o > \Delta H_2^o > \Delta H_3^o$

A-3. (a) Rate - doubled (b) Rate - tripled

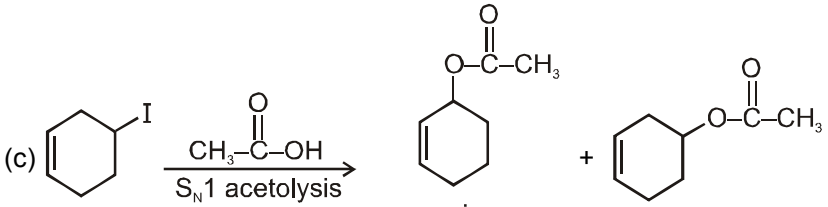
Sol. Rate of S_N1 does not depend upon concentration of nucleophile & solvent.

A-4. (a) 

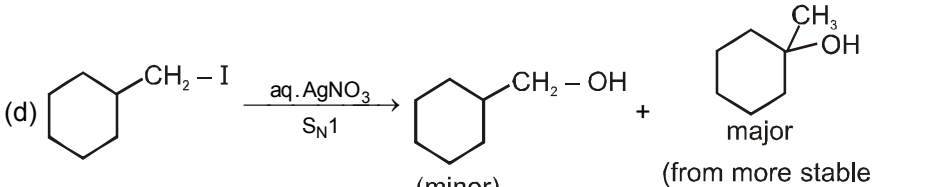
major (rearranged product) (minor)

(b) 

major (from rearranged 3° carbocation) (minor)

(c) 

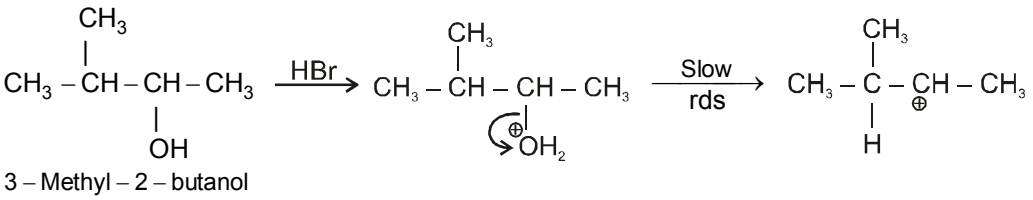
major (from rearranged allylic cation) minor

(d) 

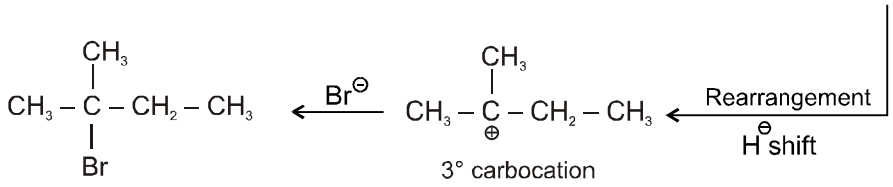
(minor) major (from more stable rearranged carbocation)

A-5. 5

Sol. X = 1, Y = 4

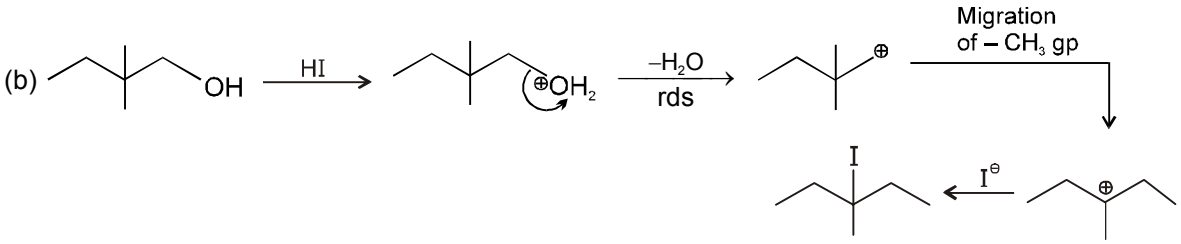
A-6. (a) 

3 – Methyl – 2 – butanol

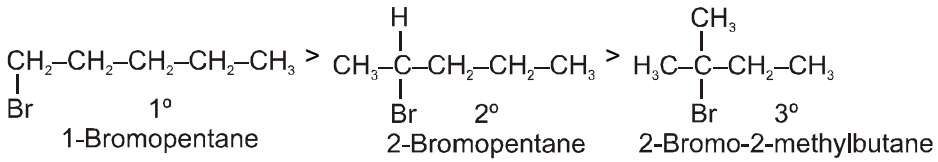


3° carbocation

2-Bromo-2-methylbutane

(b) 

B-1. (a) II > III > I, (b) IV > II > I > III

Sol. (a) 

1-Bromopentane 2-Bromopentane 2-Bromo-2-methylbutane

B-2. 3

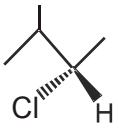
Sol. P,Q,R

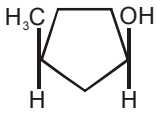
B-3. (a) $PhCMe_2Br$ (b) $PhCH_2CH_2Br$

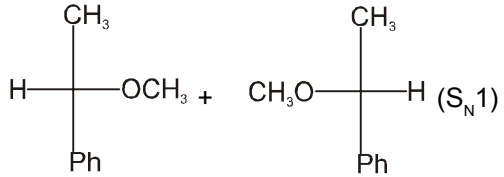
Sol. (a) Rate of S_N1 reaction $\propto$ stability of carbocation intermediate.

(b) Rate of S_N2 reaction $\propto \frac{1}{\text{steric crowding}}$

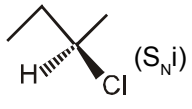
B-4. 4

B-5. (a) 

(b) 

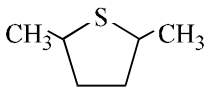
(c) 

(S_N1)

(d) 

(S_Ni)

B-6. 3 (S_1,S_3, S_4)

Sol. 

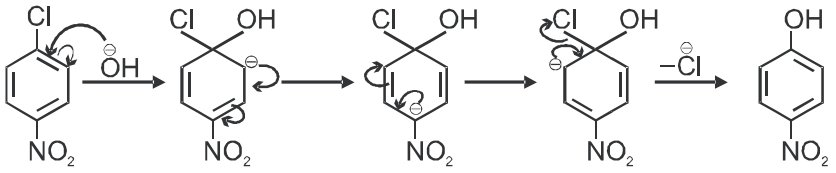
C-1. II > III > I

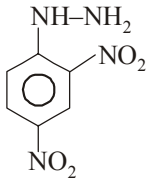
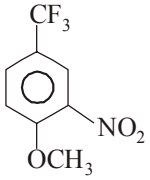
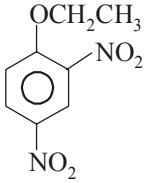
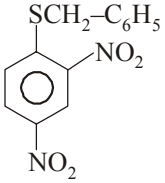
Sol. NO_2 group at ortho & para position to Cl group facilitate the nucleophilic attack for substitution reaction.

C-2. 3

Sol. (i), (ii), (vi)

C-3. **Mechanism**

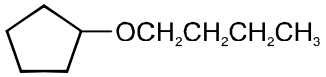
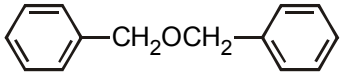


C-4. **(i)**  **(ii)**  **(iii)**  **(iv)** 

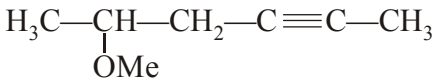
D-1. (3)

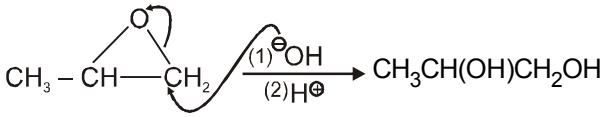
Sol. (a), (b), (c)

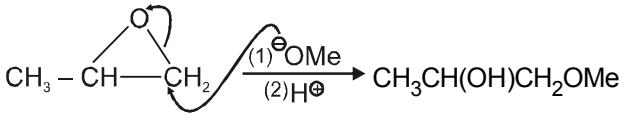
D-2. 1

D-3. a =  b = 

D-4. (a) X = $CH_3CH(OH)CH_2OH$ (b) Y = $CH_3CH(OH)CH_2OMe$

(c) 

Sol. (a) 

(b) 

PART - II

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

PART - III

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

EXERCISE -2

PART - I

1. (C) **2.** (C) **3.** (C) **4.** (C) **5.** (B) **6.** (A) **7.** (B)
8. (B) **9.** (C) **10.** (A) **11.** (D)

PART - II

1. 5 **2.** 4 **3.** **2** (S_1 & S_2) **4.** 4 **5.** 22 **6.** 4
7. 2 **8.** 15 **9.** 3. **10.** 2

PART - III

1. (BC) **2.** (ABCD) **3.** (ABCD) **4.** (AC) **5.** (AB) **6.** (AC) **7.** (AB)
8. (ABCD) **9.** (BC) **10.** (CD) **11.** (ABC) **12.** (AB)

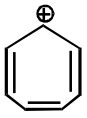
PART - IV

1. (C) **2.** (C) **3.** (B) **4.** (C) **5.** (B)

EXERCISE -3

PART - I

1. (B)

2. 7-bromo-1, 3, 5-cycloheptatriene on ionisation gives tropylium ion  which is aromatic & highly stable, but ionisation of 5-bromo-1, 3-cyclopentadiene gives 1, 3-cyclopentadienyl cation  which is anti aromatic & unstable. (non existent)

3. (A)

4. (A) Due to presence of p-NO_2 group, (– I, -m group) the S_N2 Ar reaction is accelerated (due to stabilization of intermediate carbanion). In the second case NO_2 can not exert its – m effect to stabilize the carbanion.

5. (A) **6.** (D) **7.** (D) **8.** (A) **9.** (B) **10.** (D) **11.** (C)
12. (A) **13.** (C) **14.** (C) **15.** **(A,C,D)** **16.** **(B)**

PART - II

1. (1) **2.** (1) **3.** (3) **4.** (2) **5.** (3) **6.** (3) **7.** (2)
8. (1) **9.** (3) **10.** (2) **11.** (2) **12.** (4) **13.** (1) **14.** (1)
15. (4) **16.** (3) **17.** (2) **18.** (3) **19.** (3) **20.** (2) **21.** (4)
22. (4) **23.** (4)

✍ **Marked Questions may have for Revision Questions.**

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

Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

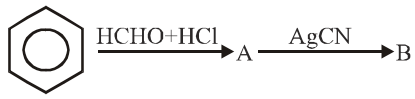
SECTION–I : (Maximum Marks : 80)

- 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 : +4If 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 of the following compounds is most rapidly hydrolysed by S_N1 mechanism ?

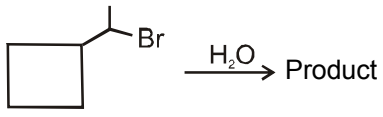
(A) C_6H_5Cl (B) $Cl–CH_2–CH=CH_2$ (C) $(C_6H_5)_3CCl$ (D) $C_6H_5CH_2Cl$

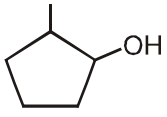
2. The compound A and B in the following reaction are, respectively :

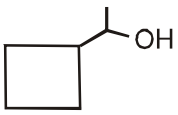


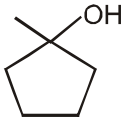
(A) A-Benzyl alcohol, B-Benzyl isocyanide
(B) A-Benzyl chloride, B-Benzyl cyanide
(C) A-Benzyl chloride, B-Benzyl isocyanide
(D) A-Benzyl alcohol, B-Benzyl cyanide

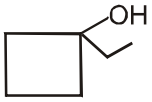
3. What will be the major product of the following reaction



(A) 

(B) 

(C) 

(D) 

4. In an S_N1 reaction on chiral centres there is :
(A) 100 % racemization
(B) inversion more than retention leading to partial racemization
(C) 100 % retention
(D) 100 % inversion

5. What is the correct order of reactivity of alcohols in the following reaction?

$R–OH + HCl + ZnCl_2 \rightarrow R–Cl + H_2O$

(A) Ethanol > Propan-1-ol > Butan-2-ol

(B) Butan-1-ol > Propan-1-ol > Butan-2-ol

(C) Neopentyl alcohol > t-Butyl alcohol > Methanol

(D) t-Butyl alcohol > Butan-2-ol > Propan-1-ol

6. $CH_3–CH_2–\underset{\underset{OH}{|}}{CH}–CH_3 \xrightarrow{HCl/\,ZnCl_2} [X]$

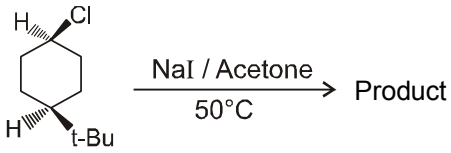
Identify product X and the mechanism of the reaction.

(A) $CH_3 – CH_2 – CH_2 – CH_2 – Cl$ & S_N1

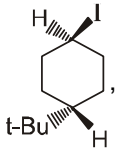
(B) $CH_3 – CH_2 – CH_2 – CH_2 – Cl$ & S_N2

(C) $CH_3 – \underset{\underset{Cl}{|}}{CH} – CH_2 – CH_3$ & S_N1

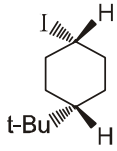
(D) $CH_3 – \underset{\underset{Cl}{|}}{CH} – CH_2 – CH_3$ & S_N2

7. 

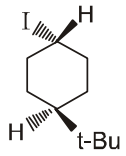
Product and mechanism are respectively

(A) 

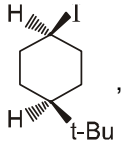
, S_N1

(B) 

, S_N2

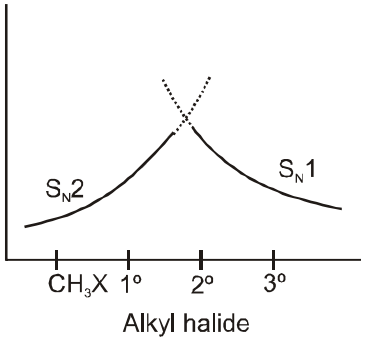
(C) 

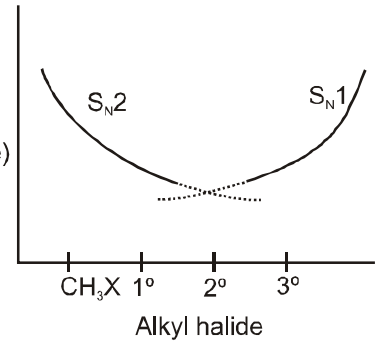
, S_N2

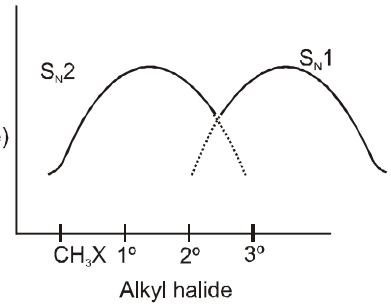
(D) 

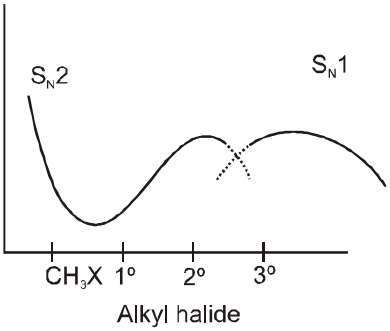
, S_N1

8. Which of the following curves correctly represents S_N1 vs S_N2 reactions ?

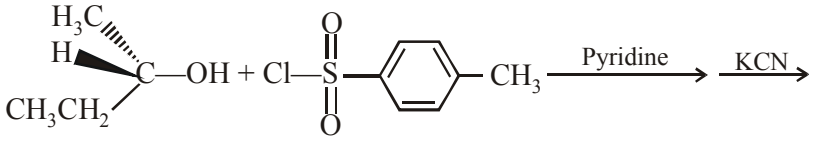
(A) 

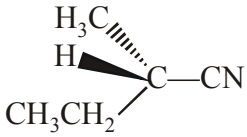
(B) 

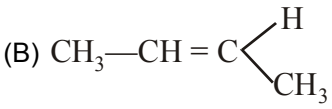
(C) 

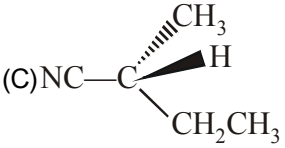
(D) 

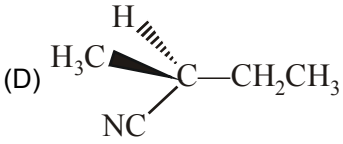
9. Find the major product of following reaction :



(A) 

(B) 

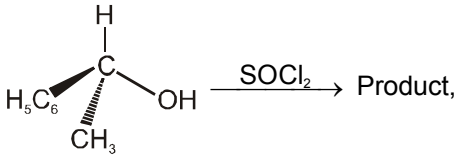
(C) 

(D) 

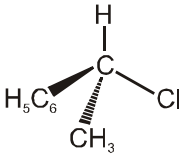
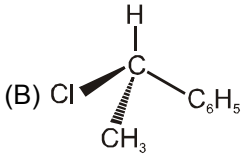
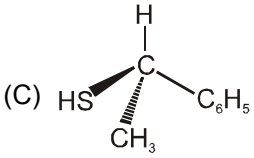
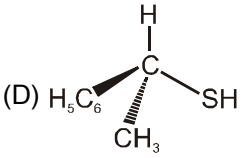
10. When 2-chloroethanol is warmed slightly with dilute NaOH, the major product formed is :

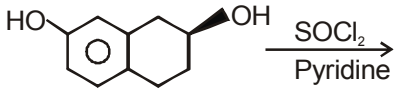
(A) $CH_3–CH_2–CH_2–O–CH_2–CH_2–Cl$ (B) $HO–CH_2–CH_2–CH_2–CH_2–OH$

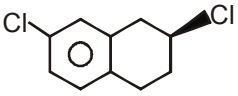
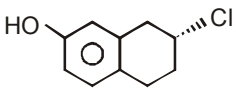
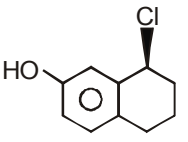
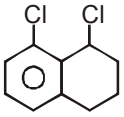
(C) $HO–CH_2–CH_2–OH$ (D) 

11. 

Identify the product

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

12. 

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

13. Which of the following statement is not true ?

(A) Nucleophiles possess unshared pairs of electron which are utillized in forming bonds with electrophilic substrate.

(B) The cyanide ion is an ambident nucleophile and causes nucleophilic substitution of alkyl halide by either of its carbon atom or nitrogen atom.

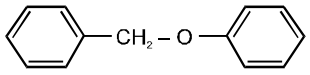
(C) The nitrite ion is an ambident nucleophile and causes nucleophilic substitution of alkyl halide by either of its oxygen atoms or nitrogen atom.

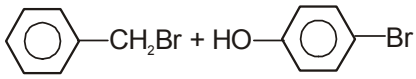
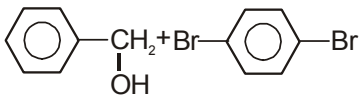
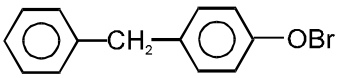
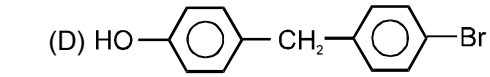
(D) Strength of nucleophile generally decreases on going down a group in the periodic table.

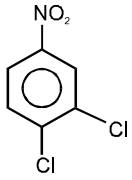
14. Which of the following statements are correct for the given alcohol ?

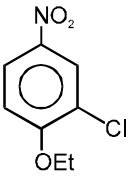
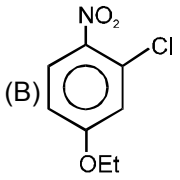
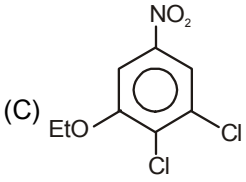
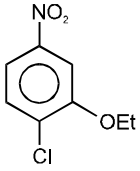
$R-OH \xrightarrow{X^{\ominus}} R-X + \overset{\ominus}{O}H$

(A) Reaction will not take place because $\overset{\ominus}{O}H$ is poor leaving group ; $X^{\ominus}$ is weak base and $\overset{\ominus}{O}H$ is strong base
(B) Reaction will not take place because $\overset{\ominus}{O}H$ is poor leaving group ; $X^{\ominus}$ is strong base and $\overset{\ominus}{O}H$ is weak base.
(C) Reaction will not take place because $\overset{\ominus}{O}H$ is good leaving group ; $X^{\ominus}$ is strong base and $\overset{\ominus}{O}H$ is weak base.
(D) Reaction will not take place because $\overset{\ominus}{O}H$ is good leaving group ; $X^{\ominus}$ is weak base and $\overset{\ominus}{O}H$ is strong base.

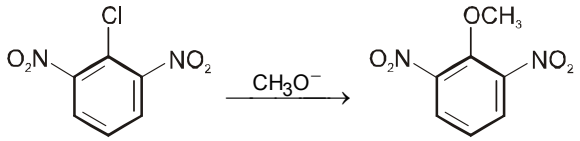
15.  $\xrightarrow{Br_2 / Fe}$ $\xrightarrow[\Delta]{\text{Conc. HBr}}$ $\xrightarrow[\Delta]{\text{सान्द्र. HBr}}$ product is -

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

16.  $\xrightarrow[\Delta]{\text{EtONa (1 mol)}}$ The product is ?

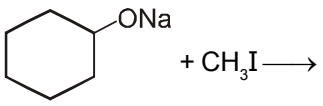
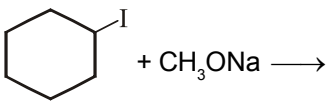
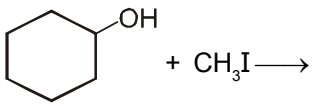
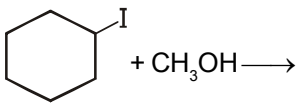
(A) 
(B) 
(C) 
(D) 

17. The reaction most likely occurs by which of the following mechanism ?



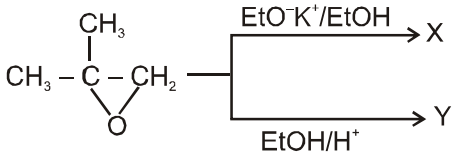
(A) Addition-elimination
(B) addition only
(C) Elimination-addition
(D) Neither of these

18. Which of the following reaction is the best choice for preparing methyl cyclohexyl ether ?

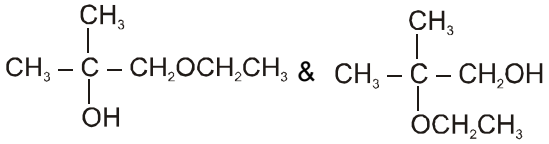
(A) 
(B) 
(C) 
(D) 

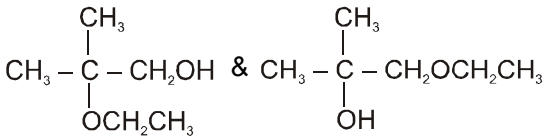
19. $(CH_3)_3C-O-CH_2-C_6H_5$ can be prepared from Williamsons synthesis, using :
(A) $(CH_3)_3C-Cl$ and $C_6H_5CH_2ONa$
(B) $C_6H_5CH_2Cl$ and $(CH_3)_3C-ONa$
(C) $(CH_3)_3C-O-CH_2-Cl$ and C_6H_5ONa
(D) All of these

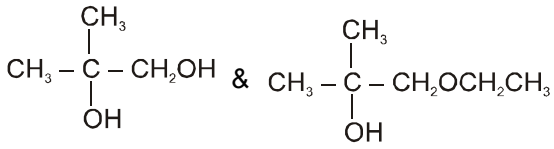
20.

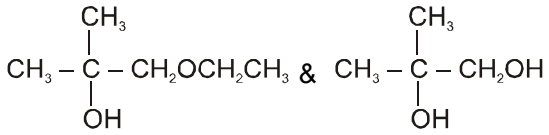


The product X and Y are respectively :

(A) 

(B) 

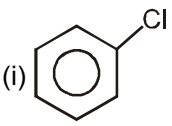
(C) 

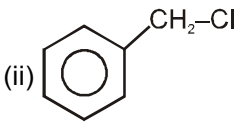
(D) 

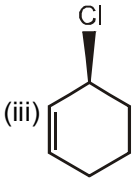
SECTION-II : (Maximum Marks: 20)

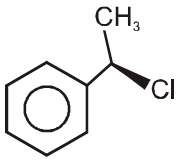
- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 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.

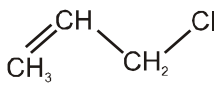
21. Number of compounds which slowly racemises on addition of $SbCl_5$?

(i) 

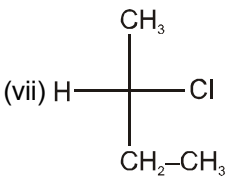
(ii) 

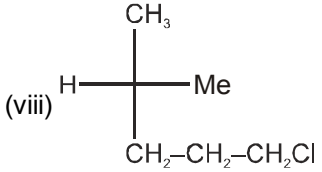
(iii) 

(iv) 

(v) 

(vi) $CH_2 = CH - Cl$

(vii) 

(viii) 

22. $C_2H_5 - \underset{\displaystyle CH_3}{\overset{|}{C}} = CH - CH_2 - Br \xrightarrow{H_2O\,/\,Acetone}$

How many total substitution products are formed including stereoisomers in the above reaction?

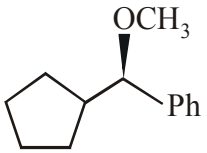
23. For the reaction : $R–X + OH^- \longrightarrow R–OH + X^-$; the rate expression is given as rate = 6.0×10^{-5} [R–X][OH^-] + 2×10^{-7} [R–X]. what percentage of R–X react by the S_N2 mechanism when [OH^-] = 0.01 molar ?

24. In the given reaction, the percentage of (-) enantiomer formed is :

$CH_3–\overset{*}{C}HI–CH_2–CH_3 \xrightarrow{I^\ominus} CH_3–\overset{*}{C}HI–CH_2CH_3$

$(\alpha)_{obs} = –15.90°$ $(\alpha)_{obs} = –15.26°$

25. How many total alcohols are formed by acidic hydrolysis of following ether?



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 :

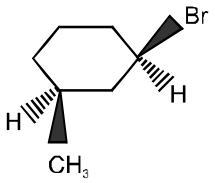
Full Marks	:	+3	If only the bubble corresponding to the correct option is darkened.
Zero Marks	:	0	If none of the bubbles is darkened.
Negative Marks	:	–1	In all other cases

1. Consider the following reactions, which are carried out at the same temperature.

$CH_3 – Br + OH^\ominus \xrightarrow{Et\,OH} CH_3 – OH + Br^\ominus$ ....(i)

$CH_3 – Br + OH^\ominus \xrightarrow{DMSO} CH_3 – OH + Br^\ominus$ ....(ii)

Which of the following statement is correct about these reactions.
(A) Both the reactions take place at the same rate
(B) The first reaction takes place faster than second reaction.
(C) The second reaction takes place faster than first reaction.
(D) Both the reactions take place by S_N1 mechanism

2. 

+ KOH $\xrightarrow{acetone}$ Product

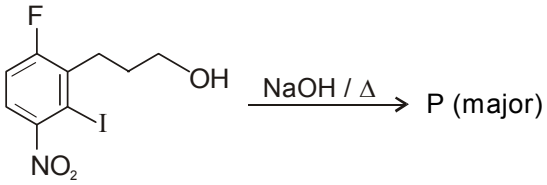
(1R, 3S)–Cis–1–Bromo–3–methylcyclohexane.
The product formed in the reaction is

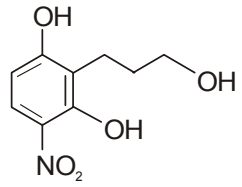
(A) (1R, 3S)–Cis–3–methyl cyclohexanol (B) (1S, 3S)–Cis–3– methyl cyclohexanol
(C) (1S, 3S)–Trans–3–methyl cyclohexanol (D) (1R, 3R)–Trans–3–methyl cyclohexanol

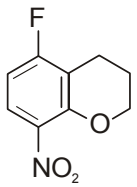
3. An optically active, pure, four carbon containing saturated alcohol X when reacted with NaH followed by $CH_3 - I$ gives a compound M. Same alcohol (X) when treated with TsCl followed by sodium methoxide gives M′. M and M′ are

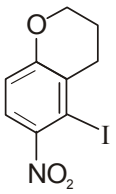
(A) Identical (B) Enantiomer (C) Diastereomer (D) Geometrical isomers

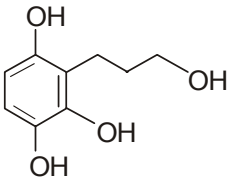
4. The product 'P' is



(A) 

(B) 

(C) 

(D) 

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 relative rates of nucleophilic substitution for the given substrates are as follows

Compoud	**Approx. Relative rate**
CH_3CH_2Br	1.0
$CH_3CH_2CH_2Br$	0.28
$(CH_3)_2CHCH_2Br$	0.030
$(CH_3)_3\,CCH_2Br$	0.00000042

The correct statement (s) is/are :

(A) Each of the above reactions is likely to be S_N2

(B) Each of the above reactions is likely to be S_N1

(C) First two reactions follow S_N2 and next two reactions follow S_N1 pathway

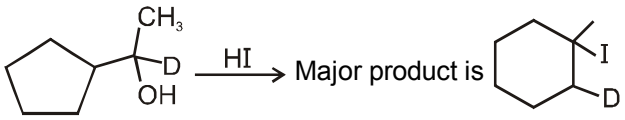
(D) The important factor behind this order of reactivity is “steric effect”

6. Select the correct options

(A) Solvolysis of $(CH_3)_2C=CH-CH_2-Cl$ in ethanol at 25°C is more faster than primary alkyl chloride.

(B) $CH_3-CH=CH-CH_2-OH$ when reacts with HBr give a mixture of 1–bromo–2–butene and 3–bromo 1–butene.

(C) When solution of 3–buten–2–ol in aqueous sulphuric acid is allowed to stand for one week, it was found to contain both 3–buten–2–ol and 2–buten–1–ol

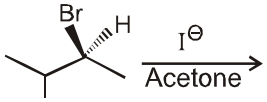
(D)  Major product is

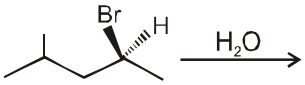
7. Which of the following are favourable conditions for S_N2 mechanism in alkyl halides ?

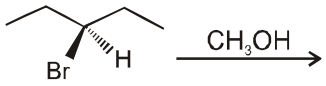
(A) Strong nucleophile (B) High conc. of nucleophile

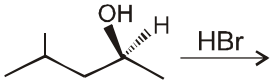
(C) 3° alkyl halide (D) Polar protic solvent

8. Which reaction results in the formation of a pair of enantiomers ?

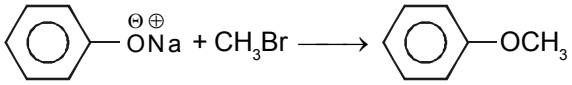
(A) 

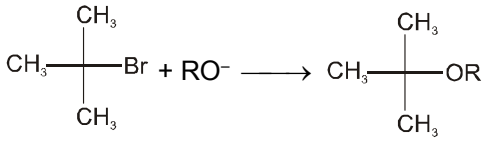
(B) 

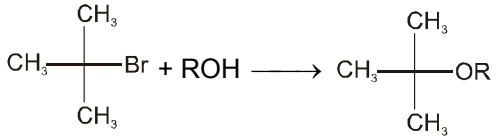
(C) 

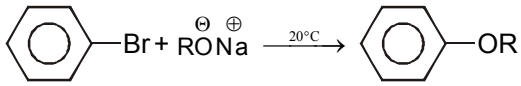
(D) 

9. Which of the following reaction are not feasible ?

(A) 

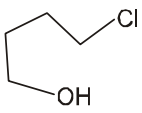
(B) 

(C) 

(D) 

10. Which of the following reactions take place by S_N2 mechanism ?

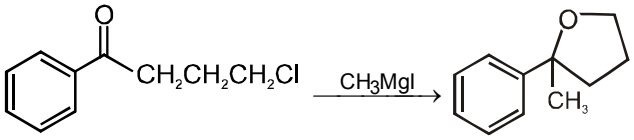
(A) $CH_3-CH_2-ONa + CH_3-CH_2-Cl \longrightarrow$

(B)  $+ NaOH \longrightarrow$

(C) $(CH_3)_3C-CH_2-CH_2-Br$ + excess $NH_3 \longrightarrow$

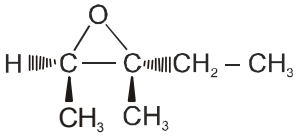
(D) $CH_3-CH_2-OH + HBr \longrightarrow$

11. Which of the following are correct regarding the given reaction ?



(A) Nucleophilic substitution
(B) Intramolecular nucleophilic attack
(C) Dehydration
(D) Nucleophilic addition

12. When Cis-3-Methyl- 2,3 -epoxypentane treated with aqueous acid then.



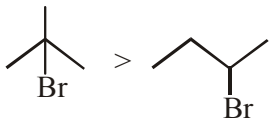
Cis-3-Methyl- 2,3 -epoxypentane

(A) Ring opeing takes palce.
(B) The product is chiral.
(C) The product is achiral.
(D) Protonation takes place initially.

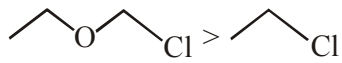
SECTION-III : (Maximum Marks: 18)

- 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.

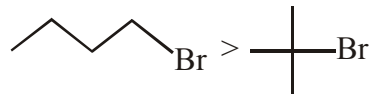
13. How many orders are correct ?

(P) 

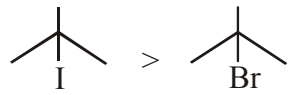
(Reactivity order towards S_N1-reaction)

(Q) 

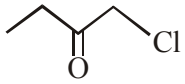
(Reactivity order towards S_N2-reaction)

(R) 

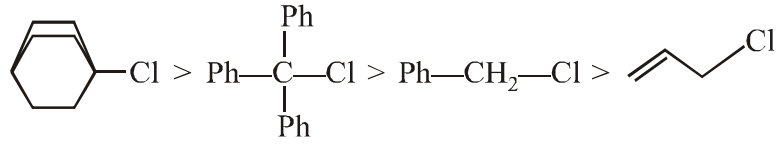
(Reactivity order towards S_N2-reaction)

(S) 

(Reactivity order towards S_N1-reaction)

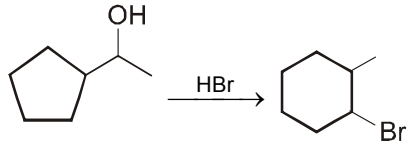
(T) 

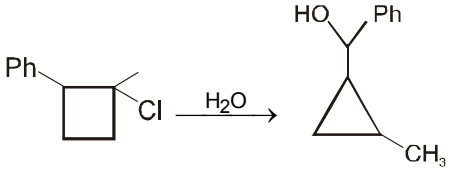
$> H_3C–Cl > H_3C–CH_2–Cl$
(Reactivity order towards S_N2-reaction)

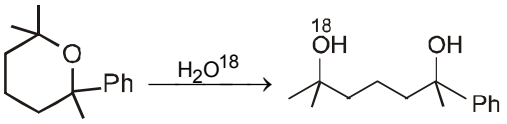
(U) 

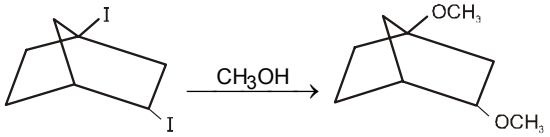
(Reactivity order towards S_N1-reaction)

14. How many reactions are not representing the correct major product ?

M : 

N : 

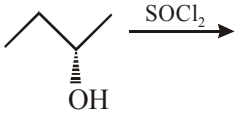
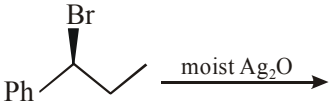
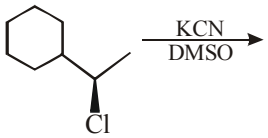
Y : 

Z : 

15. Which number indicate least reactivity towards KCN ?

(1) Benzyl chloride (2) Chlorobenzene (3) Ethyl chloride (4) Allylchloride

16.

List -I	**List-II**
Reaction	**Mechanism for the formation of major product**
(P) 	(1) S_N1
(Q) 	(2) S_Ni
(R) 	(3) S_N2

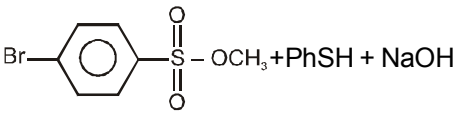
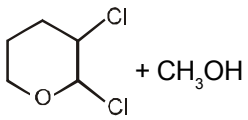
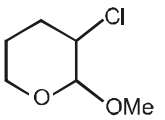
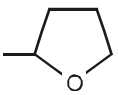
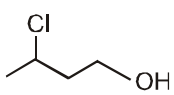
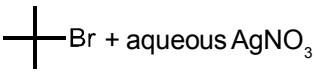
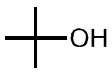
P $\rightarrow$X; Q $\rightarrow$ Y; R $\rightarrow$ Z

Write the value of (Y + Z –X) = ?

17. $Me_2CHCH_2OH \xrightarrow{Na} A \xrightarrow{MeI} B$

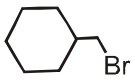
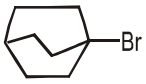
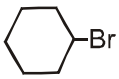
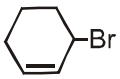
Molecular weight of B.

18. Write the number of reactant(s) which represent correct product and type of reaction.

Reactant	**Product**	**Type of reaction**
(1) 	PhSMe	S_N1
(2) 		S_N2
(3) 		S_N2
(4) 		S_N1

PART - 3 : OLYMPIAD (PREVIOUS YEARS)

1. The compound which undergoes S_N1 reaction most rapidly is **[NSEC-2003]**

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

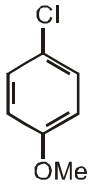
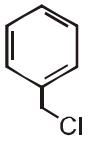
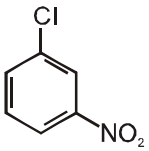
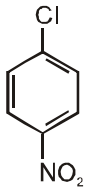
2. The aprotic polar solvent is **[NSEC-2003]**

(A) isopropanol (B) 1,2 -dichloroethane (C) nitrobenzene (D) chloroform.

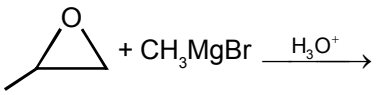
3. The reagent wihch can react with 1 -chlorobutane to give substitution reaction is **[NSEC-2003]**

(A) $AlCl_3$ (B) KOH - MeOH (C) NaCN (D) Mg - ether

4. Compound which undergoes nucleophilic substitution reactions most readily is **[NSEC-2003]**

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

5. The following sequence of reactions gives **[NSEC-2004]**

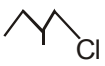
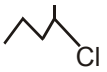


(A) 1 -butanol (B) 2-butanol
(C) 3,4-hexanediol (D) 3-methyl-3-pentanol.

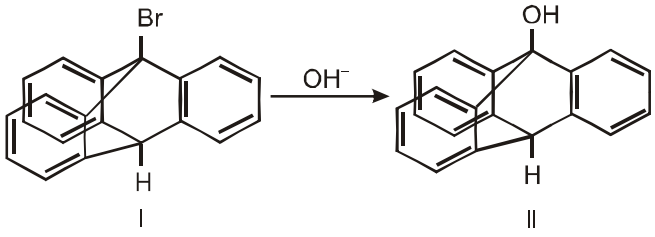
6. The reagent which can react with 2-bromopropane to give mainly a substitution product is **[NSEC-2004]**

(A) sodium sulphate (B) sodium cyanide (C) sodium chloride (D) sodium ethoxide.

7. Arrange in order of decrease in rates in S_N2 reaction. **[NSEC-2005]**

I.  II. CH_3Cl III.  IV. 

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

8.  **[NSEC-2006]**

I II

Conversion of I to II

(A) takes place by S_N1 (B) takes place by S_N2
(C) takes place by E1 (D) does not take place.

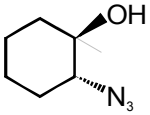
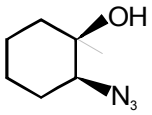
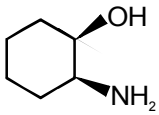
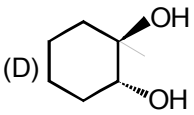
9. In a nucleophilic substitution reaction, the least reactive compound is **[NSEC-2006]**

(A) CH_3CH_2Cl (B) $(CH_3)_3CCl$ (C) $CH_2 = CHCl$ (D) $CH_2 = CHCH_2Cl$.

10. The product obtained on reaction of alkyl halide with $AgNO_3$ is **[NSEC-2006]**

(A) alkyl nitrate (B) nitroalkane (C) alkyl nitrite (D) nitrosoalkane.

11. The reaction of cyclohexane epoxide with NaN_3 in aqueous dioxane would give **[NSEC-2006]**

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

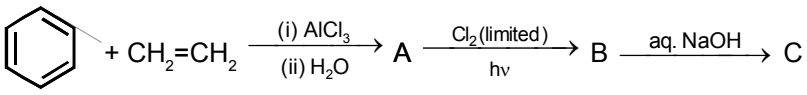
12. The major product of the following reaction is **[NSEC-2010]**

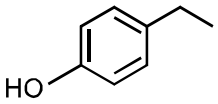
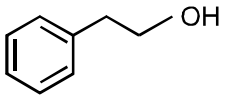
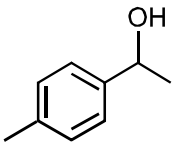
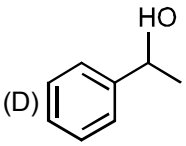
$$CH_3-CH_2-C\equiv CH \xrightarrow{(i)\ NaNH_2,\ (ii)\ CH_3CH_2Br}$$

(A) $CH_3-CH_2-C\equiv C-CH_2-CH_3$ (B) $CH_3-\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}-C\equiv CH$

(C) $CH_3-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$ (D) $CH_3-CH_2-C\equiv C-NH_2$

13. The product (C) of the following sequence of reactions is : **[NSEC-2011]**

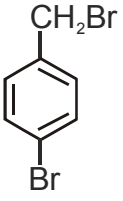
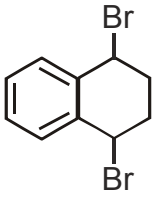
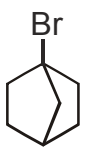
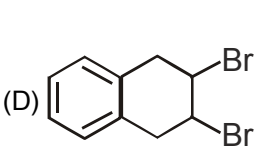


(A)  (B)  (C)  (D) 

14. (i) chlorobenzene is mono-nitrated to M **[NSEC-2014]**
(ii) nitrobenzene is mono-chlorinated to N
(iii) anisole is mono-nitrated to P
(iv) 2-nitrochlorobenzene is mono-nitrated to Q
Out of M, N, P and Q the compound that undergoes reaction with aq. NaOH **fastest** is
(A) M (B) N (C) P (D) Q

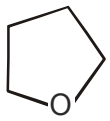
15. The appropriate sequence of reactions for obtaining 2-phenylbutanoic acid from benzene is **[NSEC-2015]**
(A) (i) 1-chlorobutane/$AlCl_3$ (ii) limited Cl_2, light (iii) aq NaCN (iv) H^+, H_2O, heat
(B) (i) 2-chlorobutane/$AlCl_3$ (ii) $K_2Cr_2O_7/H_2SO_4$
(C) (i) propanoyl chloride/$AlCl_3$ (ii) Zn-Hg/HCl (iii) limited Cl_2(g), light (iv) aq. NaCN (v) H^+, H_2O, heat
(D) (i) butanoyl chloride/$AlCl_3$ (ii) $NaBH_4$ (iii) CuCN (iv) H^+, H_2O, heat

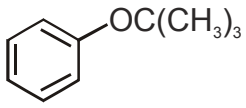
16. The compound that reacts fastest with methylamine is **[NSEC - 2016]**

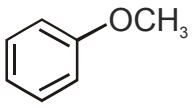
(A)  (B)  (C)  (D) 

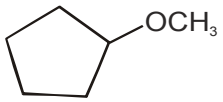
17. One mole of 4-nitrocatechol (4-nitro-1,2-dihydroxybenzene) on treatment with an excess of NaH followed by one mole of methyl iodide gives ? **[NSEC - 2017]**
(A) 4-nitro-1,2-dimethoxybenzene (B) 4-nitro-5-methyl-1,2-dimethoxybenzene
(C) 2-methoxy-5-nitrophenol (D) 2-methoxy-4-nitrophenol

18. Which of the following ethers cannot be prepared by Williamson synthesis ? **[NSEC - 2017]**

(A) 

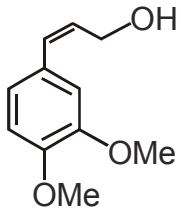
(B) 

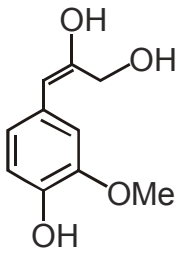
(C) 

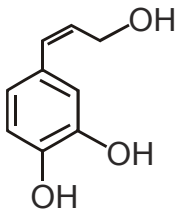
(D) 

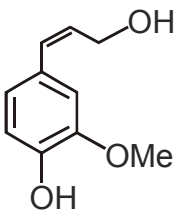
19. Coniferyl alcohol obtained from pine trees. The following observations were made about this alcohol . **[NSEC - 2017]**

I. It forms methylated product with MeI in presence of base.
II. One equivalent of coniferyl alcohol reacts with two equivalents of benzoyl chloride.
III. Upon ozonolysis, coniferyl alcohol gives a product 'Y' (M.F. $C_2H_4O_2$).

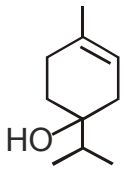
(A) 

(B) 

(C) 

(D) 

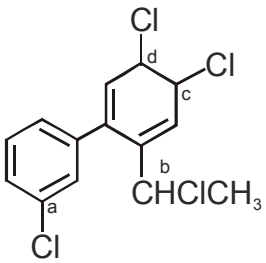
20. Terpinen-4-ol is an active ingredient in tea tree oil has the following structure. **[NSEC - 2017]**



The correct observations for terpinen-4-ol is/are.
I. It rotates the plane of plane polarized light.
II. It reacts with Baeyer's reagent to form a triol.
III. On reaction with NaBr and H_2SO_4 , it gives a dibromo compound.
IV. On ozonolysis it gives a compound with molecular formula $C_{10}H_{18}O_3$.

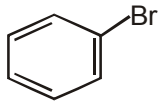
(A) I, II, III and IV (B) I, III and IV (C) II and III (D) III and IV

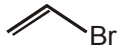
21. The decreasing reactivity of the sites (a-d) in the following compounds in S_N1 reaction is. **[NSEC - 2017]**



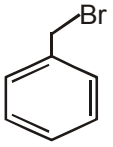
(A) d > b > c > a (B) d > c > a > b (C) d > c > b > a (D) c > d > b > a

22. The compound which would undergo a reaction with ammonia by S_N1 mechanism is. **[NSEC - 2018]**

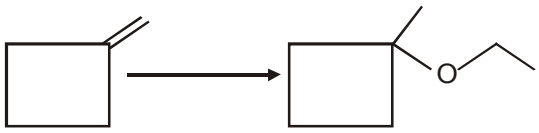
(A) 

(B) 

(C) 

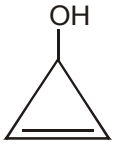
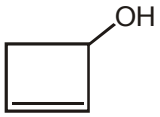
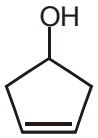
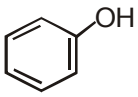
(D) 

23. The sequence of reagents required for the following conversion is **[NSEC - 2018]**

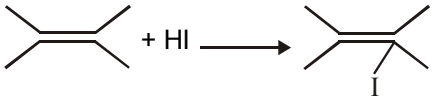


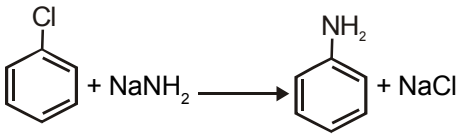
(A) (i) $B_2H_6/H_2O_2/OH^-$ (ii) Na (iii) C_2H_5I
(B) (i) HCl (ii) C_2H_5ONa
(C) (i) H_3O^+ (ii) Na (iii) C_2H_5OH
(D) (i) H_3O^+ (ii) Na (iii) C_2H_5Cl

24. The compound most likely to lose water on protonation is **[NSEC - 2018]**

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

25. The reactions from those given below that involve a carbocation intermediate are **[NSEC - 2019]**

(i) 

(ii) 

(iii) 

(A) i, ii and iii
(B) i and ii
(C) i and iii
(D) ii and iii

RRP ANSWER KEY

PART- 1

1.	(C)	**2.**	(C)	**3.**	(C)	**4.**	(B)	**5.**	(D)	**6.**	(C)	**7.**	(C)
8.	(B)	**9.**	(C)	**10.**	(D)	**11.**	(A)	**12.**	(B)	**13.**	(D)	**14.**	(A)
15.	(A)	**16.**	(A)	**17.**	(A)	**18.**	(A)	**19.**	(B)	**20.**	(A)	**21.**	3
22.	4	**23.**	75%	**24.**	98%	**25.**	8						

PART 2

1.	(C)	**2.**	(C)	**3.**	(B)	**4.**	(C)	**5.**	(AD)	**6.**	(ABCD)	**7.**	(AB)
8.	(BD)	**9.**	(BD)	**10.**	(ABCD)	**11.**	(ABD)	**12.**	(ABD)	**13.**	**5**	**14.**	4
15.	(2)	**16.**	**2**	**17.**	(088)	**18.**	(4)						

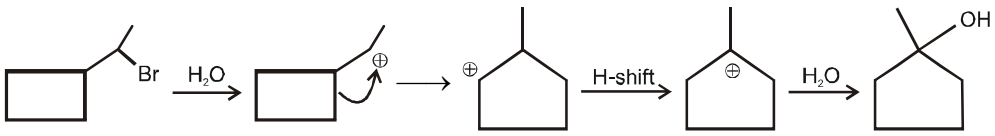
PART - 3

1.	(D)	**2.**	(C)	**3.**	(C)	**4.**	(B)	**5.**	(B)	**6.**	(B)	**7.**	(C)
8.	(D)	**9.**	(C)	**10.**	(A)	**11.**	(A)	**12.**	(A)	**13.**	(D)	**14.**	(D)
15.	(C)	**16.**	(A)	**17.**	(D)	**18.**	(B)	**19.**	(D)	**20.**	(A)	**21.**	(C)
22.	(D)	**23.**	(D)	**24.**	(A)	**25.**	(C)						

RRP SOLUTIONS

PART- 1

3.



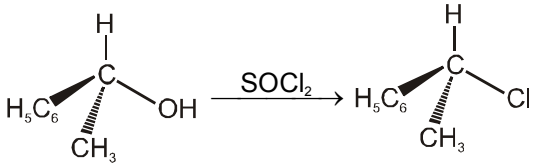
4. Inversion product will be more than retention product due to close ion pair formation.

5. Rate of reaction $\propto$ stability of carbocation intermediate

7. Strong anionic nucleophile so mechanism is S_N2.

8. 1° R-X gives S_N2 reaction fastest and 3° R-X gives S_N1 reaction fastest.

11.

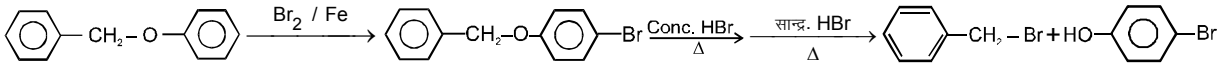


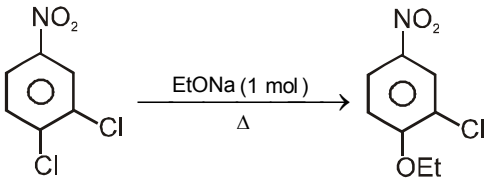
This reaction follows S_Ni mechanism, so retention of configuration takes place.

12. It is a S_N2 reaction, so inversion takes place at sp^3 carbon .

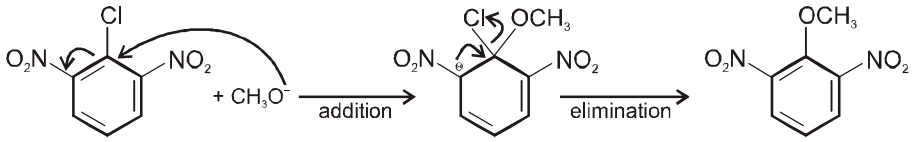
13. Strength of Nucleophile generally increases on going down a group in the periodic table, so (4) is not true.

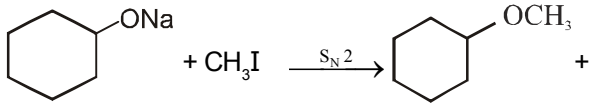
14. Nucleophilic substitution of alcohol is acid catalysed reaction.

15. 

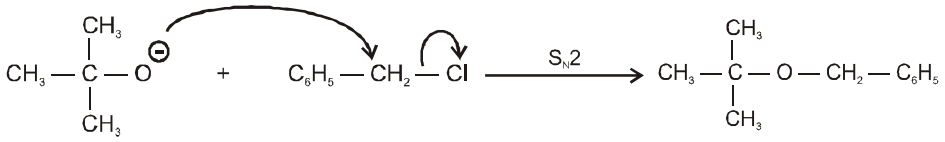
16. 

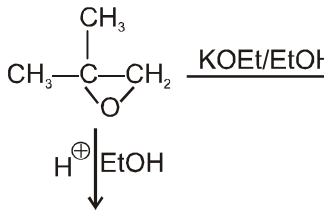
[– M effect of $-NO_2$ group at para position]

17. 

18. 

Strong anionic nucleophile and 1° alkyl halide favours S_N2 mechansim.

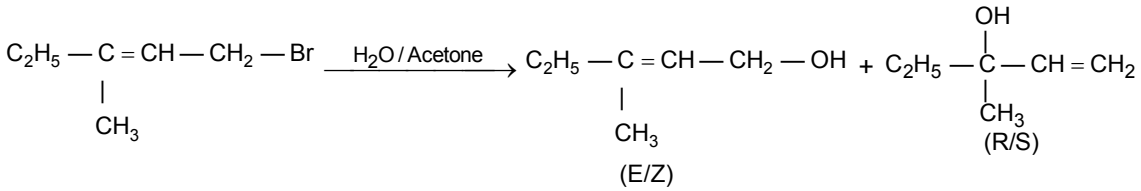
19. 

20. 

In basic medium S_N2 product $Nu^{\ominus}$ attack from less crowded side.

In acidic medium S_N1 type product, $Nu^{\ominus}$ attack from crowded side.

21. (iii), (iv) & (vii)

22. 

23. The rate is made up of two parts S_N1 and S_N2 rate
$= 6.0 \times 10^{-5}\,[RX][OH^-] + 2 \times 10^{-7}\,[RX]$

$$\text{Thus } \%\ S_N2 = \left[\frac{S_N2}{S_N2 + S_N1}\right] \times 100 = \left[\frac{6.0\times10^{-5}\,[RX][OH^-]}{6.0\times10^{-5}\,[RX][OH^-] + 2\times10^{-7}\,[RX]}\right] \times 100$$

$= 75\%$

24. $CH_3 - \underset{\underset{I}{|}}{CH} - CH_2 - CH_3 \xrightarrow{I^-} CH_3 - \underset{\underset{I}{|}}{CH} - CH_2 - CH_3$

$[\alpha]_{obs} = -15.90^\circ$ $[\alpha]_{obs} = -15.26^\circ$

$$\% \text{ of } (-) \text{ enantiomers} = \frac{-15.26}{15.96} \times 100$$

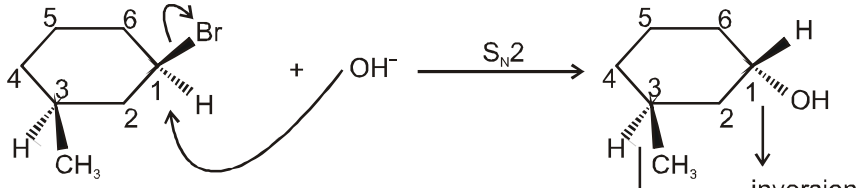
$$= 96\ \%$$

Racemic mixture = (100 – 96) = 4%
Racemic mixture = 2% (+) + 2% (–)
(+) enantiomer = 2%
Total (–) enantiomer = 96 + 2 = 98 %

PART 2

1. Polar aprotic solvent favours S_N2 mechanism.

2.



(1R, 3S) – Cis – 1 – Bromo –3 – methyl cyclohexane

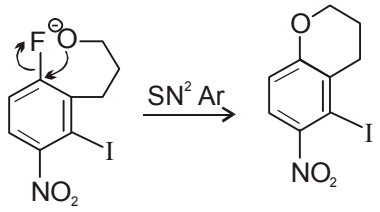
(1S, 3S) – trans – 3 – methyl cyclohexanol

3. $CH_3-CH_2-\underset{\text{Optically active}}{\underset{|}{\overset{CH_3}{CH}}}-OH \xrightarrow[\text{Acid Base}]{NaH} CH_3-CH_2-\underset{|}{\overset{CH_3}{CH}}-ONa \xrightarrow[S_N2]{CH_3I} CH_3-CH_2-\underset{|}{\overset{CH_3}{CH}}-OCH_3$ Retention in product.

$CH_3-CH_2-\underset{\text{Optically active}}{\underset{|}{\overset{CH_3}{CH}}}-OH + TsCl \longrightarrow CH_3-CH_2-\underset{|}{\overset{CH_3}{CH}}-OTs \xrightarrow[S_N2]{CH_3ONa} CH_3-CH_2-\underset{|}{\overset{CH_3}{CH}}-OCH_3$ inverstion take place.

M = Retention product and M′ = inversion product, so they are enantiomers.

4.

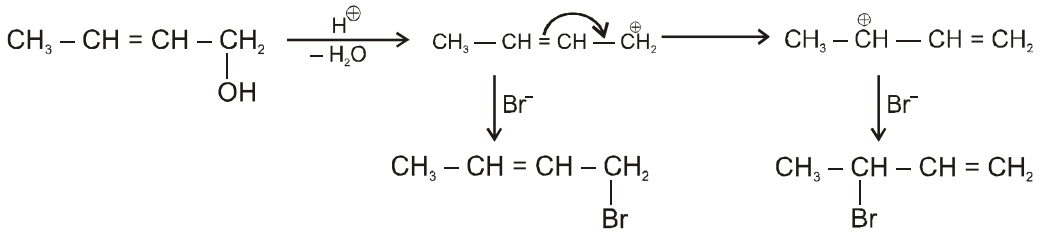


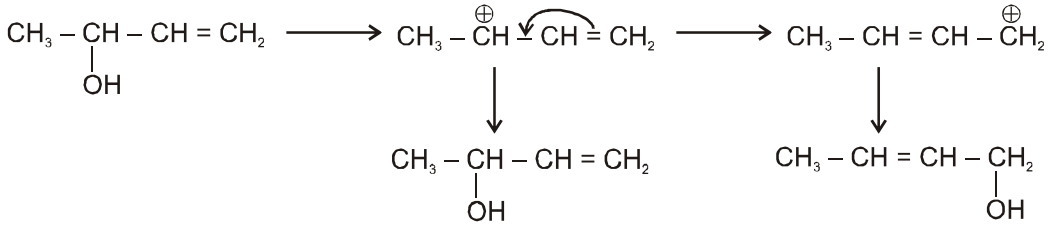
5. Due to steric effect.

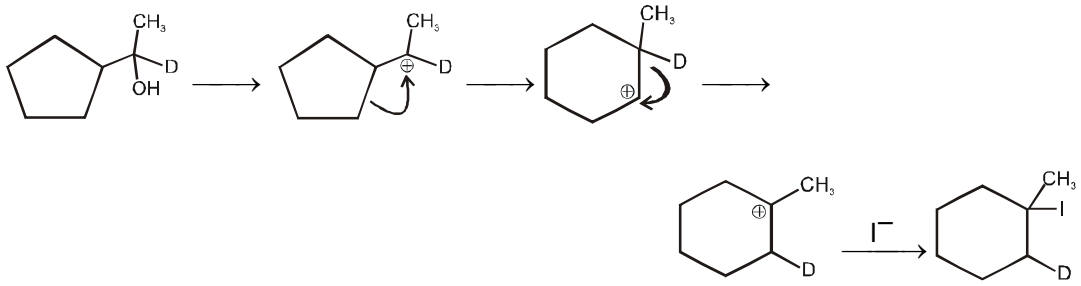
6. (A) $\underset{CH_3}{\overset{CH_3}{\diagdown}}C = CH - CH_2 - Cl \xrightarrow[S_N1 \text{ Reaction}]{C_2H_5OH} \underset{CH_3}{\overset{CH_3}{\diagdown}}C = CH - \overset{\oplus}{C}H_2 \longleftrightarrow CH_3 - \underset{CH_3}{\overset{\oplus}{C}} - CH = CH_2$

$R - X \xrightarrow{S_N}$ No stable carbocation

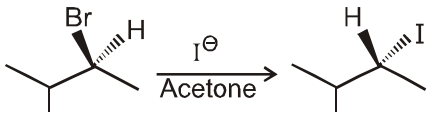
(1° R – X)

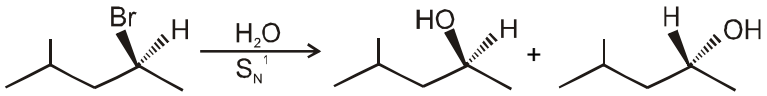
(B) 

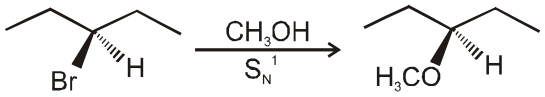
(C) 

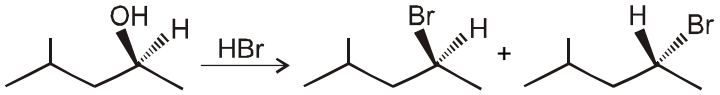
(D) 

7. S_N2 Reaction ⟶ High conc. of Nucleophile
⟶ Strong Nucleophile
⟶ Polar Aprotic solvent
⟶ Rate of reaction = 3° RX < 2° RX < 1° RX < CH_3–X

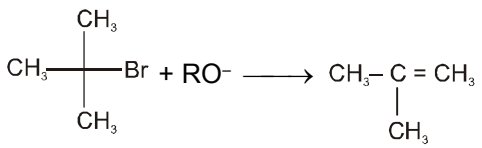
8.  [Only one product]

 [Enantiomeric pair]

 [Only one product]

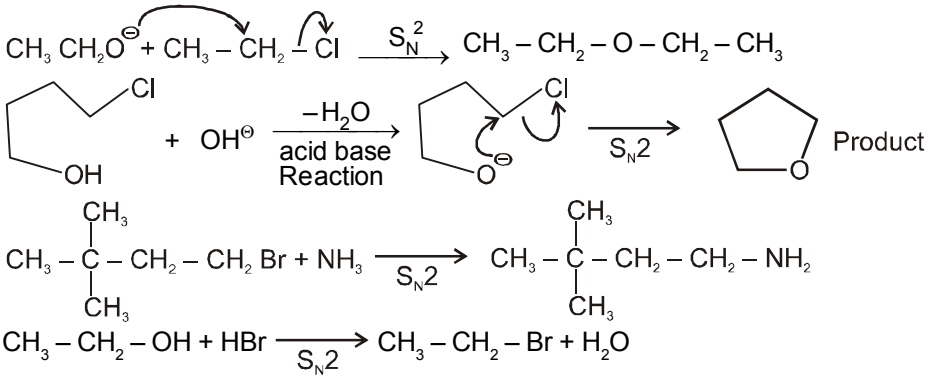
 [Enantiomeric pair]

9. Correct product for (B) option.

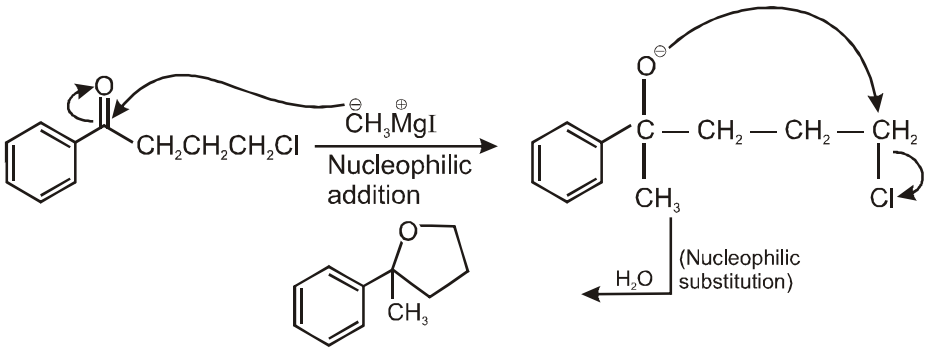


Option (D) is also not feasible because aromatic halide do not give SN reaction in normal condition.

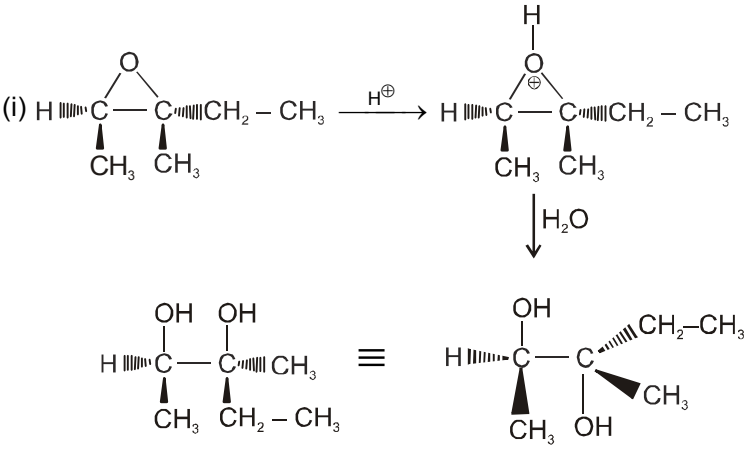
10.



11.



12.

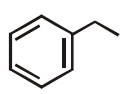
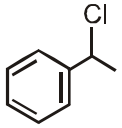
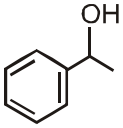


13. (P), (Q), (R), (S), (T) are correct

16. P $\rightarrow$2; Q $\rightarrow$ 1; R $\rightarrow$ 3

PART 3

12. $CH_3 - CH_2 - C \equiv C - H \xrightarrow{NaNH_2} CH_3 - CH_2 - C \equiv \overset{-}{C}\overset{+}{N}a \xrightarrow[S_N2]{CH_3CH_2Br} CH_3–CH_2–C\equiv C–CH_2–CH_3$

13. A =  B =  C = 

but official answer given A.