ORGANIC REACTION MECHANISMS-III

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JEE(Advanced) Syllabus

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Haloarenes : Nucleophilic aromatic substitution in haloarenes and substituted haloarenes (excluding Benzyne mechanism and Cine substitution).
Alcohols: Esterification, dehydration, reaction with sodium, phosphorus halides, $ZnCl_2$/concentrated HCl.
Ethers : Preparation by Williamson's Synthesis.

JEE(Main) Syllabus

Organic Reaction Mechanisms: Organic Compounds with functional groups Containing Halogens (x)
Alkyl halides: Nature of C–X bond in haloalkanes, physical and chemical properties, mechanism of substitution reactions, elimination reactions and rearrangement reactions, reactivity of C–X bond in haloalkanes.
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Organic compounds with functional groups containing oxygen
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Organic Reaction Mechanisms-III

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.

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

Types of nucleophilic substitution reaction :

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

Section (A) : Unimolecular nucleophilic substitution reaction (S_N1)

Nucleophilic substitution which involves two step process

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

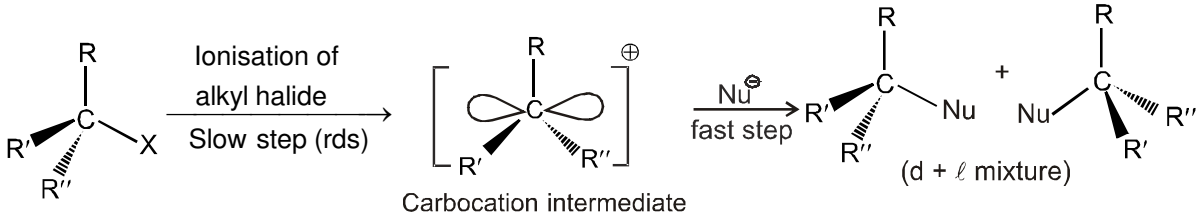
$$R–\ell g \longrightarrow R^+ + \ell g^-$$

(b) **Second step :** Fast attack of nucleophile on carbocation results into product.

$$R^+ + Nu^- \longrightarrow R–Nu$$

(1) 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 reaction :

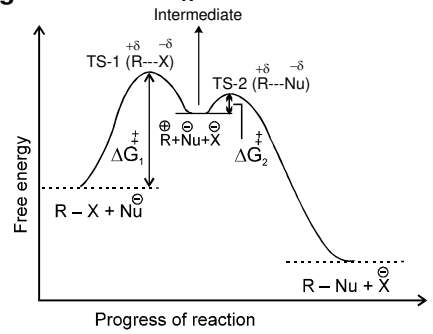


Figure : Free energy diagram for the S_N1 reaction.

6. Factors affecting the rate of S_N1 reaction :

(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.

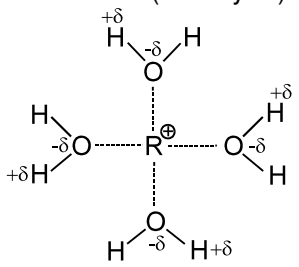
S_N1 reactivity : 3° > 2° > 1° > CH_3–X

(ii) Concentration and reactivity of the nucleophile : The rate of S_N1 reaction is unaffected by the concentration and nature of the nucleophile.
Weak and neutral nucleophile favours S_N1 reaction.
Mostly solvents (protic) itself functions as nucleophiles in S_N1 reaction, so S_N1 reaction is termed as solvolysis reaction.
water $\rightarrow$ hydrolysis ; $C_2H_5OH \rightarrow$ ethanolysis
$CH_3COOH \rightarrow$ acetolysis ; $NH_3 \rightarrow$ ammonolysis

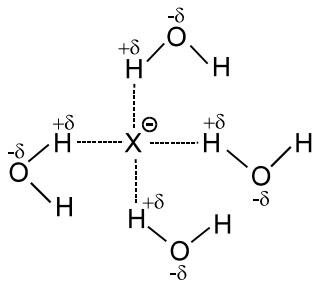
(iii) Effect of the solvent : (Ionising ability of the solvent)
The use of a polar protic solvent will greatly increase the rate of ionisation of an alkyl halide in any S_N1 reaction because it solvate cations and anions so effectively and stabilises the transition state leading to the intermediate carbocation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

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

Solvated ions



Solvolysis



Solvated ions

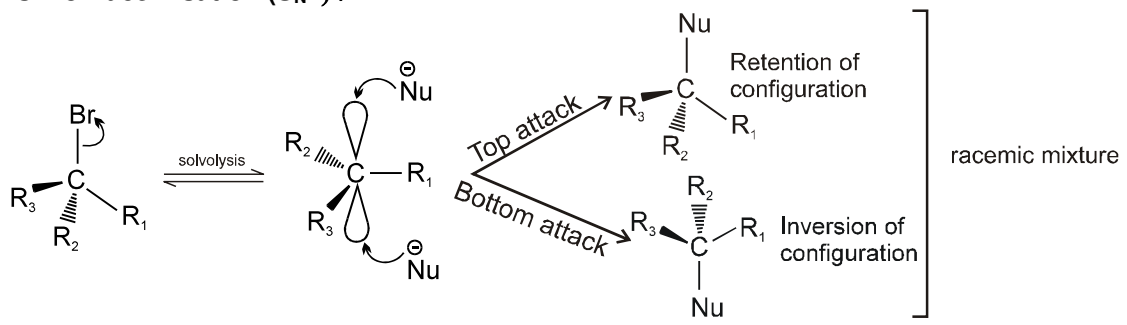
Table : Dielectric constants ($\in$) and ionisation rate of t-Butylchloride in few common solvents

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	–

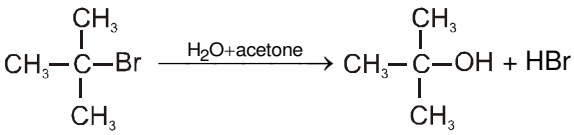
(iv) The nature of the leaving group : In the S_N1 reaction the leaving group begins to acquire a negative charge as the transition state is reached` stabilisation of this developing negative charge at the leaving group stabilises the transition state and this lowers the free energy of activation and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

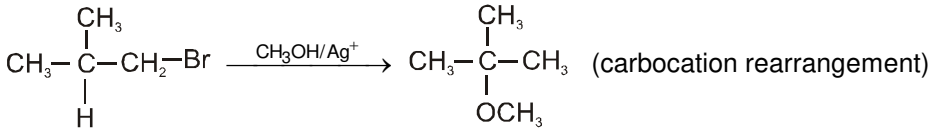
7. Stereochemistry of S_N1 reactions : In the S_N1 mechanism, the carbocation intermediate is sp^2 hybridized and planar, A nucleophile can attack on the carbocation from either face, if reactant is chiral then attack of nucleophile from both faces gives enantiomers as the product, which is called racemisation.

Mechanism of racemisation (S_N1) :

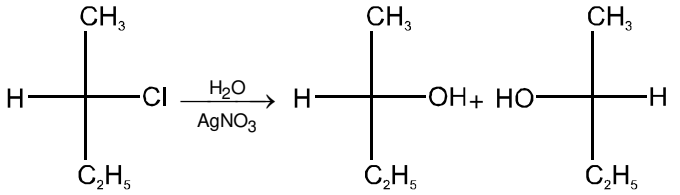


Reagents for alkyl halide are : H_2O , RCOOH , ROH & RSH

Ex-1.  (3° alkyl halide hence no S_N2 reaction)

Ex-2. 

(carbocation rearrangement)

Ex-3. 

(Racemic product)

(2) 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.

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

(90%)

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

Reactivity of HX : HI > HBr > HCl
Reactivity of ROH : 3° > 2° > 1°

e.g. CH_3CHCH_3 (OH) $\xrightarrow[\text{or NaBr, } H_2SO_4,\ \text{reflux}]{\text{conc. HBr}}$ CH_3CHCH_3 (Br)

Isopropyl alcohol → Isopropyl bromide

e.g. $CH_3-C(CH_3)_2-CH_2-OH \xrightarrow{\text{conc. HBr}} CH_3-C(CH_3)_2-CH_2-CH_3$ (Br)

Lucas Reagent

(i) A mixture of concentrated hydrochloric acid and anhydrous 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. $CH_3-CH_2-CH(OH)-CH_2-CH_3 \xrightarrow{\text{anhy. } ZnCl_2/HCl} CH_3-CH_2-CH(Cl)-CH_2-CH_3$

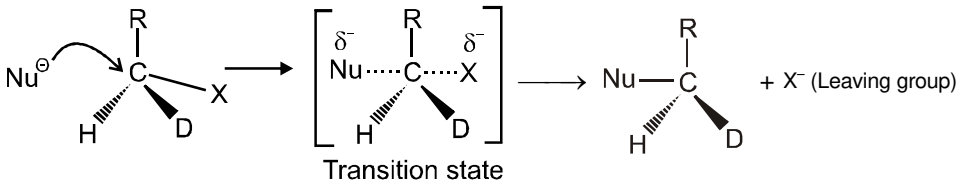
3 – Chloropentane

Section (B) : Bimolecular nucleophilic substitution reaction (S_N2)

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

(1) S_N2 Reaction of Alkyl halide :

Mechanism :



Characteristic 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 :

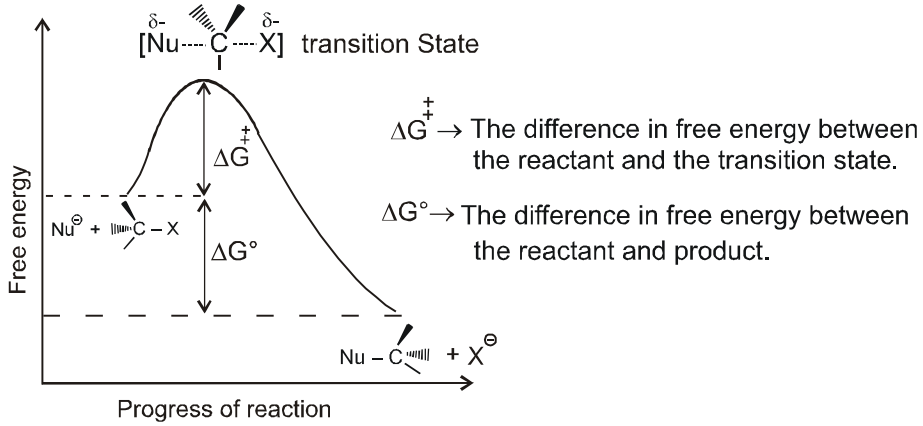
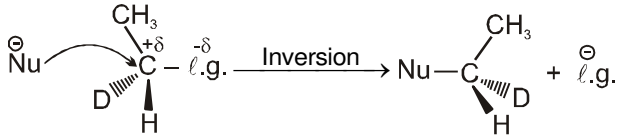


Figure : A free energy diagrams for S_N2 reaction

5. No intermediates are formed in the S_N2 reaction, the reaction proceed through the formation of an unstable arrangment of atoms or groups called transition state.

6. The stereochemistry of S_N2 reaction : 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. Factor's 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 slow down the rate of reaction.

Table : Relative rate of reaction of alkyl halides by S_N2 mechanism.

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 reactions increased when they are carried out in polar aprotic solvent.

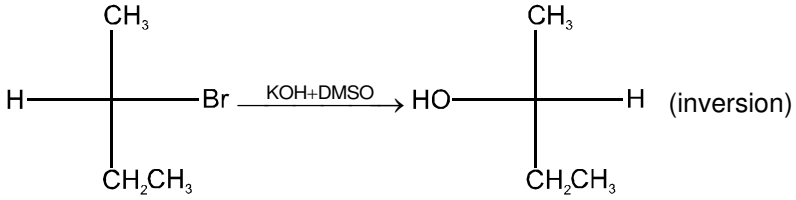
(iv) The nature of the leaving group : Weaker bases are good leaving groups. A good leaving group always stabilise the transition state and lowers its free energy of activation and there by increases the rate of the reaction. Order of leaving ability of halide ion $F^- < Cl^- < Br^- < I^-$

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

Ex-1. $CH_3–Cl \xrightarrow[(:OH^-)\text{strong nucleophile}]{\text{aq.KOH}} CH_3–OH + Cl^-$

Ex-2. $CH_3–CH_2–CH_2–Br \xrightarrow{NaOH+DMF} CH_3–CH_2–CH_2–OH + Br^-$

Ex-3.



(inversion)

(2) S_N2 Reaction of Alcohol :

(i) Reaction with HX : The protonated β unbranched primary alcohol is well suited for the S_N2 reaction.

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

(ii) Reaction with phosphorus trihalides

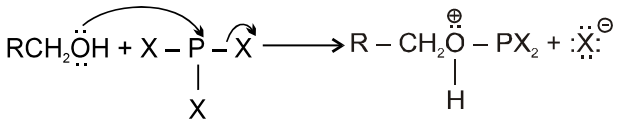
Several phosphorus halides are useful for converting alcohols to alkyl halides. PBr_3, PCl_3, & PCl_5 work well and are commercially available.

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.

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

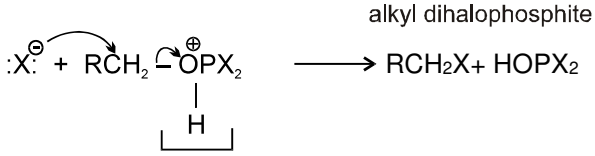
Mechanism :

Step-1 :



Protonated
alkyl dihalophosphite

Step-2 :



A good leaving group

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

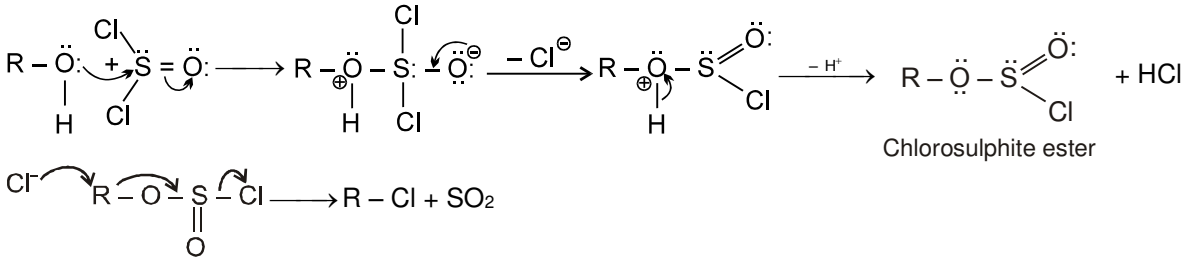
$$R–OH + PCl_5 \xrightarrow{S_N2} R–Cl + HCl + POCl_3$$

(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.

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

Mechanism :

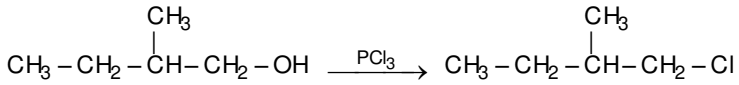


In the first step, the nonbonding electrons of the hydroxy oxygen atom attack the electrophilic sulphur atom of thionyl chloride. A chloride ion is expelled a proton and gives test of chloro sulphite ester. Second step is an S_N2 mechanism.

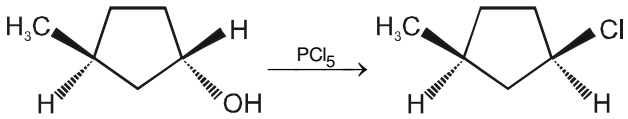
Ex-1. $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{HCl / ZnCl_2} CH_3CH_2CH_2CH_2CH_2Cl$

n – Pentyl alcohol — n – Pentyl chloride

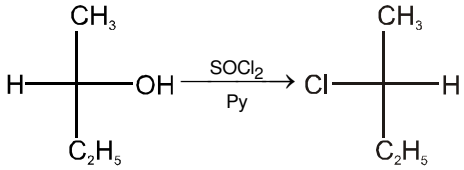
Ex-2.



Ex-3.



Ex-4.

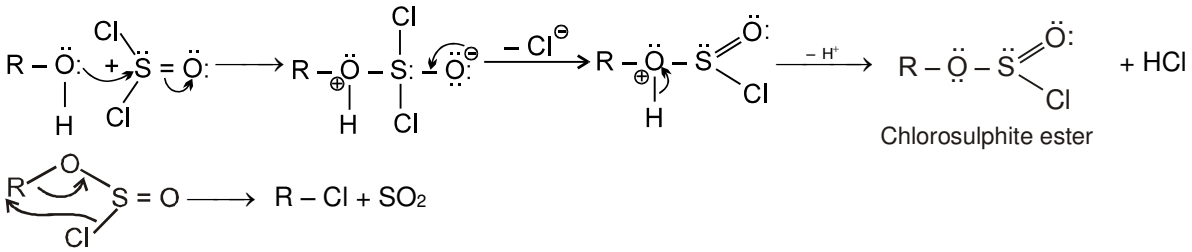


(3) S_Ni Reaction :

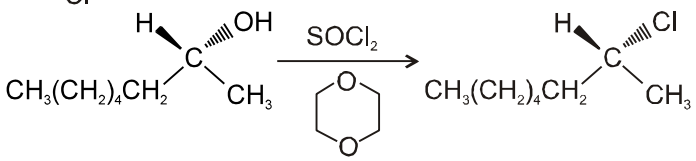
In S_Ni mechanism an internal nucleophile attacks from the same side of leaving group, means retension of configuration. It is an S_Ni mechanism, where i means internal

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

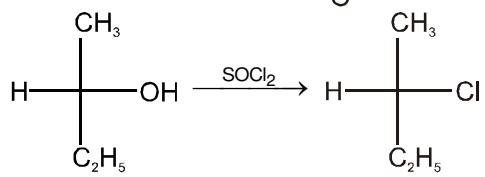
Mechanism :



Ex-1.

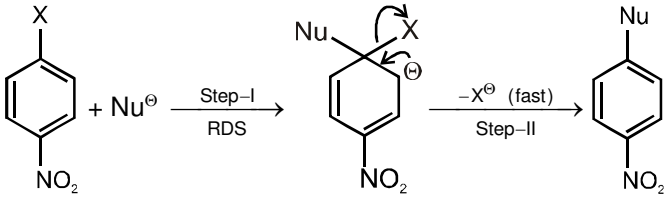


Ex-2.

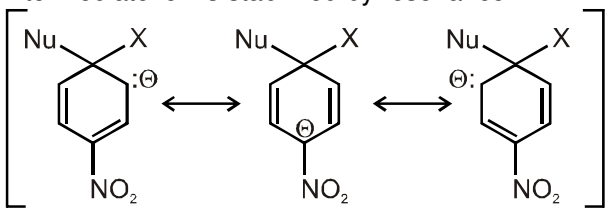


Section (C) : Bimolecular aromatic nucleophilic substitution reaction (S_N2 Ar)

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

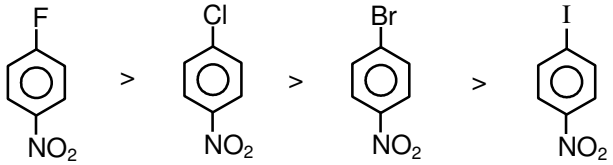


Intermediate ion is stabilized by resonance.

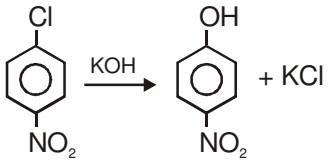


EWG ↑ ⇒ Rate of reaction ↑

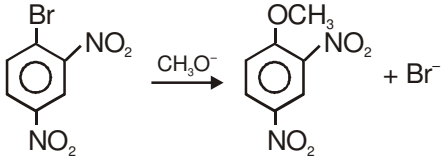
Reactivity order towards S_N2Ar :



Ex-1.



Ex-2.



Section (D) : Nucleophilic substitution reaction of Ethers & Epoxides

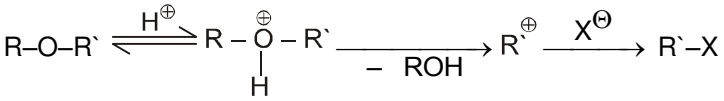
(1) S_N1 Reaction of Ethers

(i) Reaction with HX :

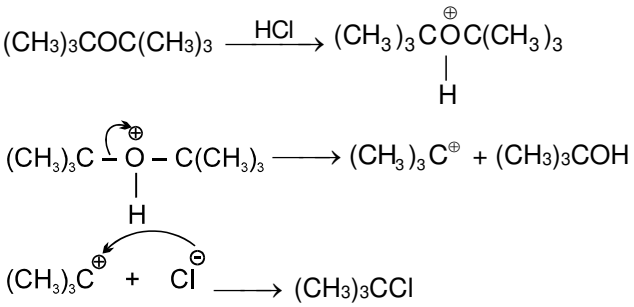
Ethers are unreactive towards most bases, but they can react under acidic conditions. A protonated ether can undergo substitution or elimination with the expulsion of an alcohol. Ethers react with conc. HBr and HI because these reagents are sufficiently acidic to protonate the ether, while bromide iodide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

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

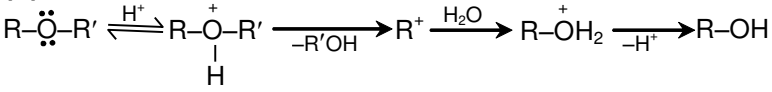
Mechanism :



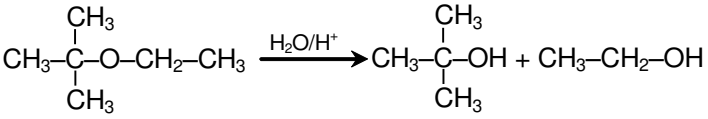
Ex.



(ii) Reaction with H_2O/H^+ :



Ex.

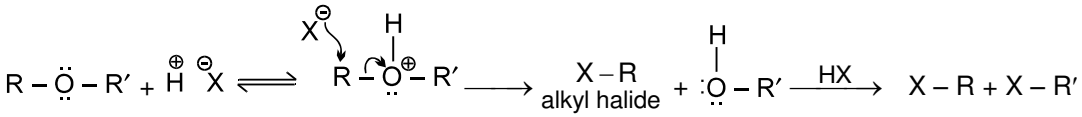


(2) S_N2 Reaction of Ethers

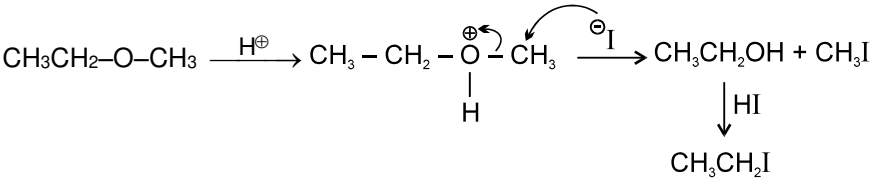
(i) Reaction with HX :

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 3º then mechanism will be S_N1 otherwise S_N2.

Mechanism :

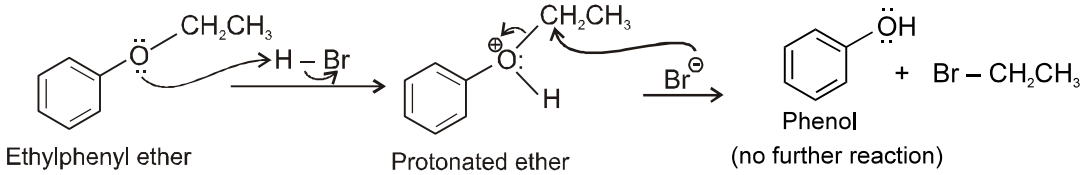


Ex.

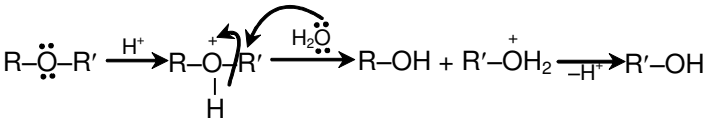


Ex.

Ex.

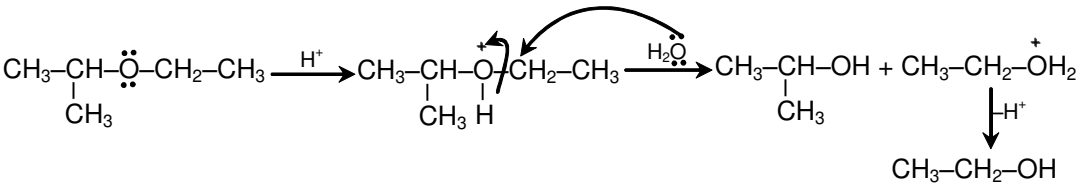


(ii) Reaction with H_2O/H^+ :



(Steric crowding R > R')

Ex.

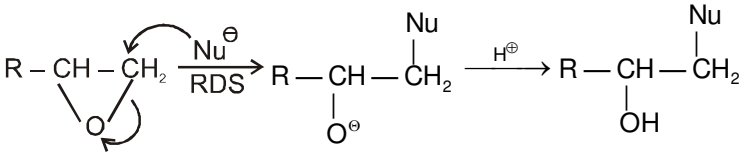


(3) Nucleophilic substitution reaction of Epoxide :

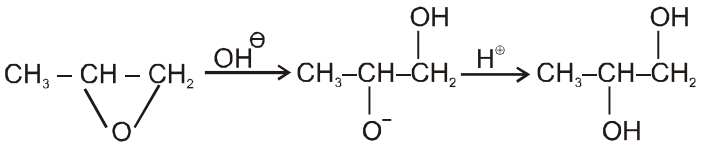
Epoxides are much more reactive than ether because of angle strain in three membered ring therefore epoxide readily undergo nucleophilic substitution reaction.

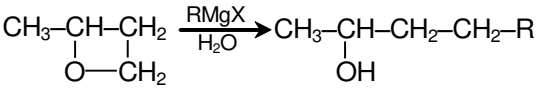
In basic medium mechanism is S_N2. Nucleophile atacks on less hindered carbon.

Mechanism :



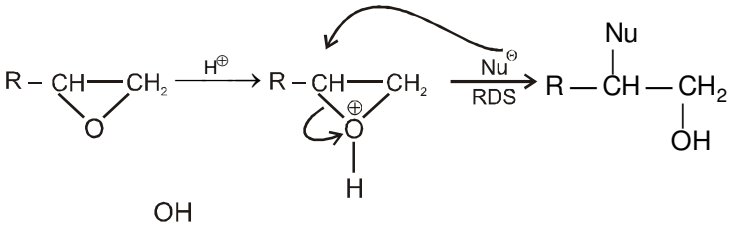
Ex.



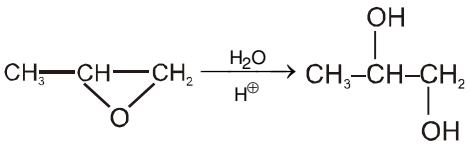


In acidic medium mechanism is S_N1 type. Nucleophile attacks on more substituted carbon.

Mechanism :



Ex.



Exercise-1

Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

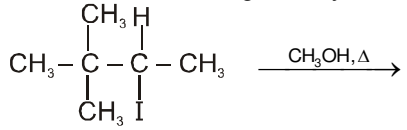
Section (A) : Unimolecular nucleophilic substitution reaction (S_N1)

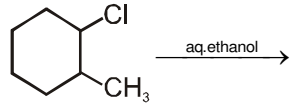
A-1. Which compound in the following couples will react faster in S_N1 reaction and why ?
(a) 1-Bromopentane or 2-Bromopentane
(b) 1-Bromo-2-methylbutane or 2-Bromo-2 methylbutane.

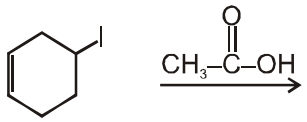
A-2. What effect do you expect due to following changes in S_N1 reaction of $(CH_3)_3CBr$ with CH_3OH ?
(a) The concentration of $(CH_3)_3CBr$ is doubled and that of CH_3OH is halved.
(b) The concentration of both $(CH_3)_3CBr$ and CH_3OH are tripled.

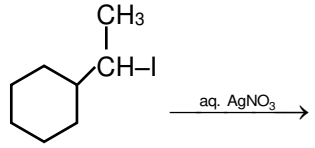
A-3. Why 3-Chlorocyclopropene is solvolyzed in methanol at much higher rate than 5-Chlorocyclopenta-1,3-diene ?

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

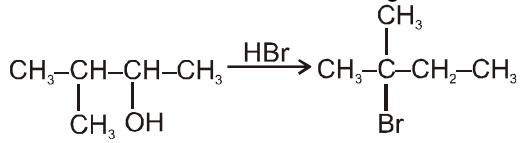
(a) 

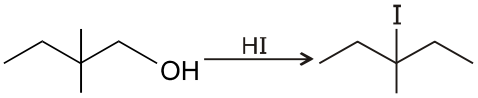
(b) 

(c) 

(d) 

A-5. Write the mechanism of the following reaction and mention the rate determining step.

(a) 

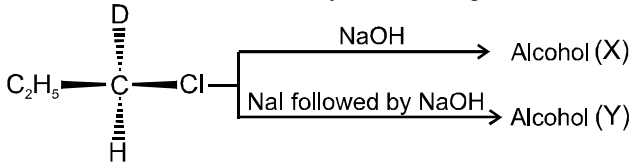
(b) 

Section (B) : Bimolecular nucleophilic substitution reaction (S_N2 & S_Ni)

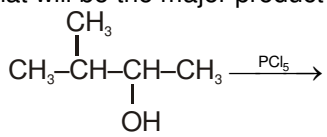
B-1. Arrange the compounds of each set in order of decreasing reactivity towards S_N2 displacement.
(a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
(b) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane

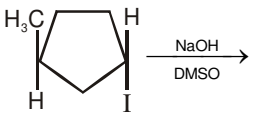
B-2. Which reacts faster
(a) $PhCH_2Br$ or $PhCMe_2Br$ (H_2O / C_2H_5OH)
(b) $PhCH_2CH_2Br$ or $PhCMe_2Br$ (NaI / Acetone)

B-3. Work out the stereochemistry of following reaction

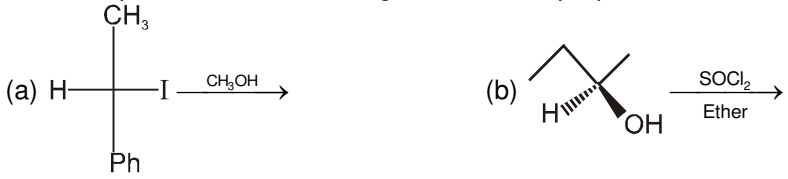


B-4. What will be the major product of the following reaction ?

(a) 

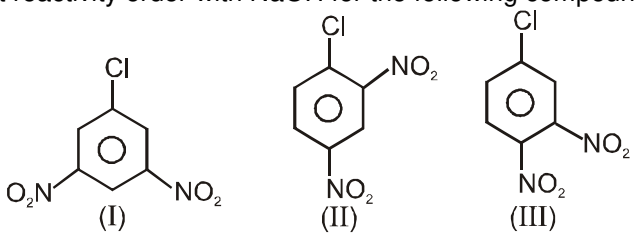
(b) 

B-5. Write the product of the following reaction with proper stereochemistry.

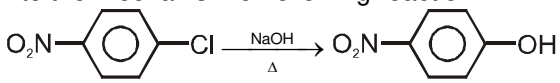


Section (C) : Bimolecular aromatic nucleophilic substitution reaction (S_N2 Ar)

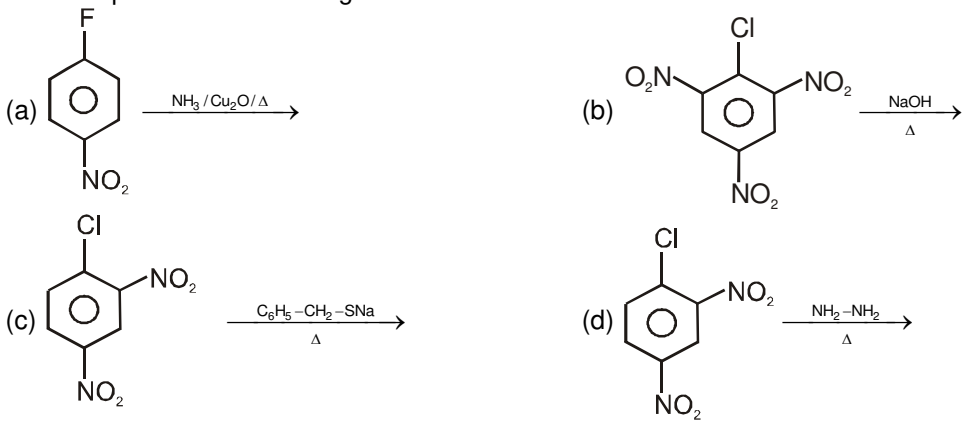
C-1. Write the correct reactivity order with NaOH for the following compounds.



C-2. Write the mechanism of following reaction :

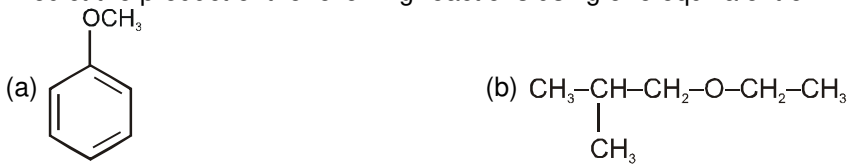


C-3. Give the products in following reactions :

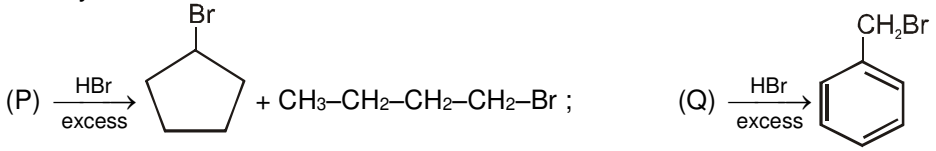


Section (D) : Nucleophilic substitution reaction of Ethers & Epoxides

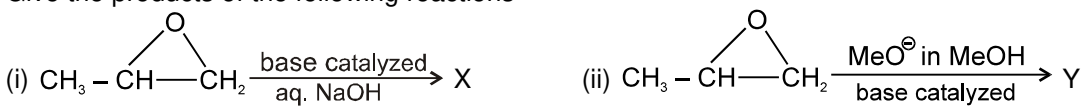
D-1. Predict the product of the following reactions using one equivalent of HI.



D-2. Few dialkyl ethers & cyclic ethers were allowed to react with excess of HBr with the following results. Identify the ether in each case.



D-3. Give the products of the following reactions



PART - II : ONLY ONE OPTION CORRECT TYPE

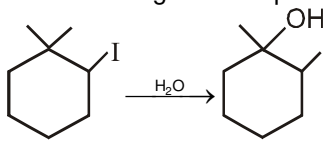
Section (A) : Unimolecular nucleophilic substitution reaction (S_N1)

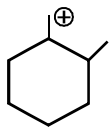
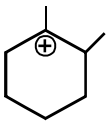
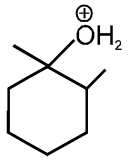
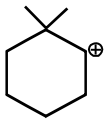
A-1. S_N1 reaction occurs through the formation of intermediate :
(A) Carbocation (B) Carbanion (C) Free radical (D) Carbene

A-2.^ In an S_N1 reaction, the configuration of the product undergoes :
(A) inversion (B) racemization (C) retention (D) None of these

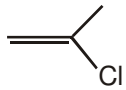
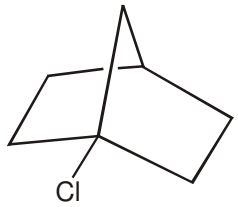
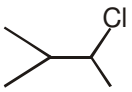
A-3. When the concentration of alkyl halide is doubled and the amount of H_2O taken as solvent is reduced to half, the rate of S_N1 reaction increases by:
(A) 3 times (B) 2 times (C) 1.5 times (D) 6 times

A-4. Which of the following is not expected to be intermediate of the following reaction ?



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

A-5. Which of the following compound can show S_N1 reaction :

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

A-6. $Ph-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow{Con.HCl + Anhydrous\ ZnCl_2}$ X (Major product)

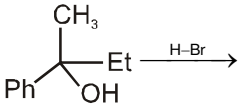
X is :

(A) $Ph-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$ (B) $Ph-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_3$ (C) $Ph-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH_2}}$ (D) $Ph-\underset{\displaystyle CH_3}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}-CH_3$

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

(A) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br$ (B) $CH_3-\underset{\displaystyle C_2H_5}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-Br$ (C) $CH_3-\underset{\displaystyle C_2H_5}{\overset{\displaystyle C_2H_5}{\overset{|}{\underset{|}{C}}}}-Br$ (D) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle H}{\overset{|}{CH}}}-\underset{\displaystyle CH_3}{\overset{\displaystyle Br}{\overset{|}{C}}}-CH_3$

A-8. Which describes the best stereochemical aspects of the following reaction ?



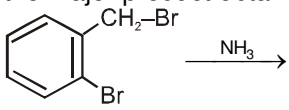
(A) Inversion of configuration occurs at the carbon undergoing substitution.
(B) Retention of configuration occurs at the carbon undergoing substitution.
(C) Racemization occurs at the carbon undergoing substitution.
(D) The carbon undergoing substitution is not stereogenic.

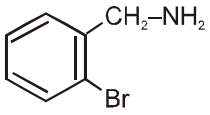
Section (B) : Bimolecular nucleophilic substitution reaction (S_N2 & S_Ni)

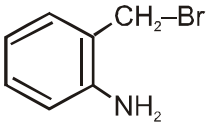
B-1. S_N2 mechanism proceeds through intervention of :
(A) Carbonium ion (B) Transition state (C) Free radical (D) Carbanion

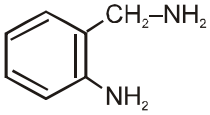
B-2. In S_N2 reaction if we doubled the concentration of reactant and nucleophile the rate of S_N2 reaction increases by :
(A) 2 times (B) 4 times (C) 8 times (D) No change

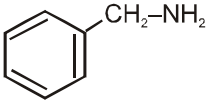
B-3. What is the major product obtained in the following reaction ?



(A) 

(B) 

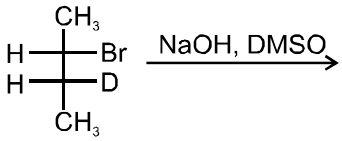
(C) 

(D) 

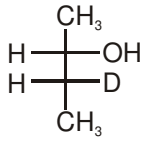
B-4. Identify the reactants (X) and (Y) for the following reaction, respectively.

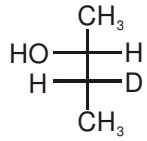
(X) + (Y) $\xrightarrow{NaNH_2}$ 4-Decyne
Alkyl halide Alkyne

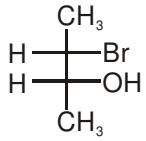
(A) $CH_3(CH_2)_4CH_2–Cl + CH_3–C\equiv CH$ (B) $CH_3(CH_2)_2CH_2–Cl + CH_3–(CH_2)_2–C\equiv CH$
(C) $CH_3(CH_2)_2CH_2–Cl + CH_3(CH_2)_3–C\equiv CH$ (D) $CH_3–CH_2–CH_2–Cl + CH_3(CH_2)_4–C\equiv CH$

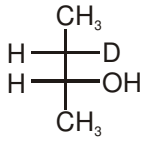
B-5. 

Product, Product is :

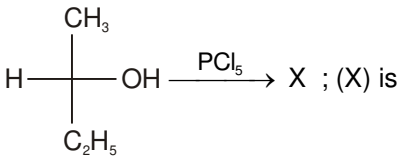
(A) 

(B) 

(C) 

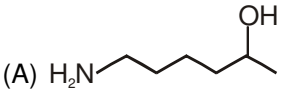
(D) 

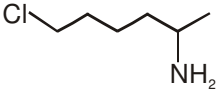
B-6. $CH_3(CH_2)_2CH_2OH \xrightarrow{HBr} X$,
1–butanol
Identify X and the type of mechanism of the reaction?
(A) $CH_3–CH_2–CH_2–CH_2–Br$ & S_N1 (B) $CH_3–CH_2–CH_2–CH_2–Br$ & S_N2
(C) $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-CH_3$ & S_N1 (D) $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-CH_3$ & S_N2

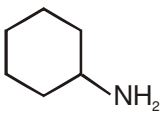
B-7. 

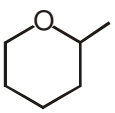
X ; (X) is
(D-2-Butanol)
(A) S-2-Chlorobutane
(B) R-2-Chlorobutane
(C) Mixture of R and S, 2-Chlorobutane
(D) 1-Chlorobutane

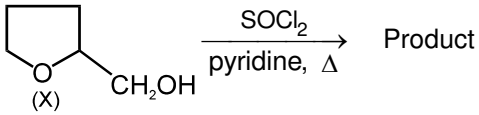
B-8. 6-Chlorohexan-2-ol $\xrightarrow[\Delta]{NaNH_2}$ major product is

(A) 

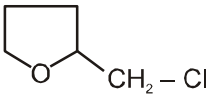
(B) 

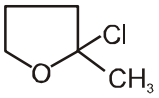
(C) 

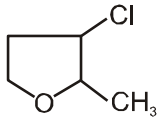
(D) 

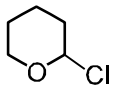
B-9. 

Product of the above reaction is :

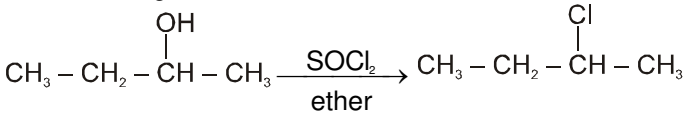
(A) 

(B) 

(C) 

(D) 

B-10. Consider the following reaction.

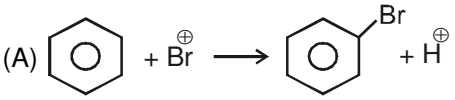


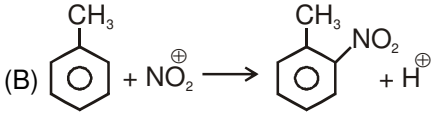
In the above reaction which phenomenon will take place :

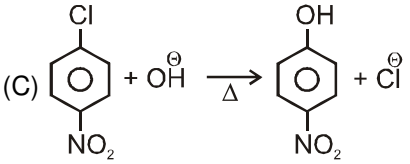
(A) Inversion (B) Retention (C) Racemisation (D) Isomerisation

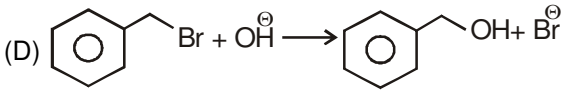
Section (C) : Bimolecular aromatic nucleophilic substitution reaction (S_N2 Ar)

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

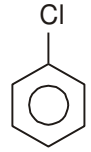
(A) 

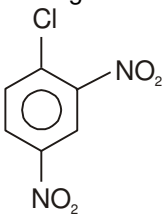
(B) 

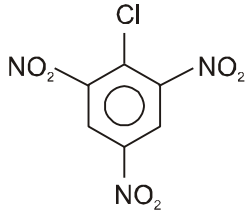
(C) 

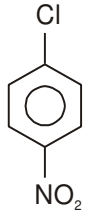
(D) 

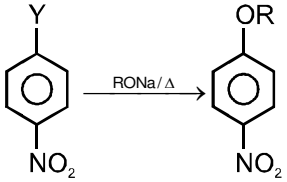
C-2. Which of the following compound gives fastest S_N2 Ar reaction ?

(A) 

(B) 

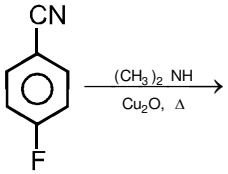
(C) 

(D) 

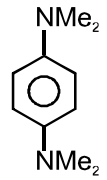
C-3. 

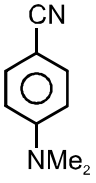
Above reaction has maximum rate when :

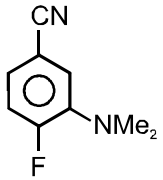
(A) Y = – I (B) Y = – Br (C) Y = – Cl (D) Y = – F

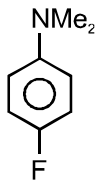
C-4. 

The product is :

(A) 

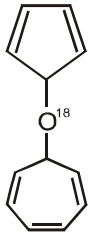
(B) 

(C) 

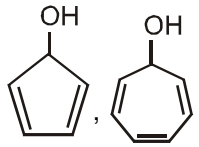
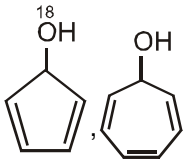
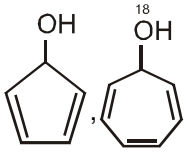
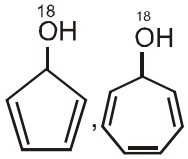
(D) 

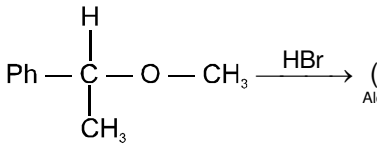
Section (D) : Nucleophilic substitution reaction of Ethers & Epoxides

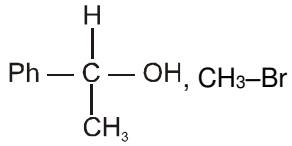
D-1. In the given reaction, $CH_3–CH_2–CH_2–O–CH_2–CH_3 \xrightarrow{HCl/\Delta}$ [X] + [Y]
[X] and [Y] respectively will be :
(A) $CH_3–CH_2–CH_2OH$ & $CH_3–CH_2–Cl$ (B) $CH_3–CH_2–CH_2–Cl$ & $CH_3–CH_2–OH$
(C) $CH_3–CH_2–CH_2–Cl$ & $CH_2=CH_2$ (D) $CH_3–CH=CH_2$ & $CH_2=CH_2$

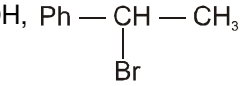
D-2.  $\xrightarrow{H_3O^{\oplus}}$ X + Y

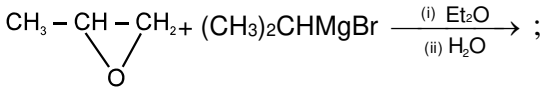
The products X and Y are

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

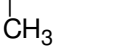
D-3.  ; (P) & (Q) respectively is :

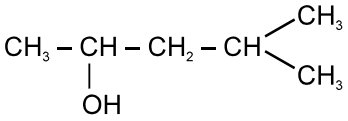
(A)  (B) $Ph–CH_2–OH$, $CH_3–CH_2–Br$

(C) $CH_3–OH$,  (D) $CH_3–OH$, $Ph–CH_3–CH_2–Br$

D-4.  ; What will be the product :

(A) $CH_3–(CH_2)_4–CH_2–OH$

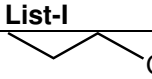
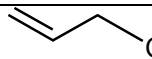
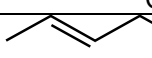
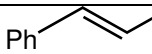
(B) 

(C) 

(D) 

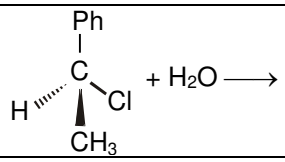
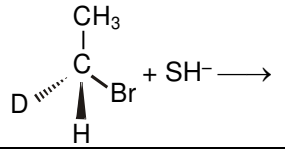
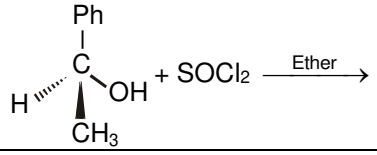
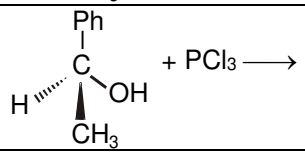
PART - III : MATCH THE COLUMN

1. Match List-I (Alkyl chloride) with List-II (Rates of solvolysis) and select the correct answer using the code given below the lists :

	List-I		List-II
(P)		(1)	1
(Q)		(2)	0.07
(R)		(3)	7700
(S)		(4)	91

Codes :
(A) P-2; Q-1; R-4; S-3 (B) P-2; Q-1; R-3; S-4 (C) P-1; Q-2; R-3; S-4 (D) P-1; Q-2; R-4; S-3

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

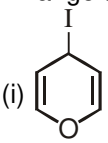
	Column-I		Column-II
	Substrate		**Stereochemistry of product**
(A)		(p)	Retention
(B)		(q)	Racemisation
(C)		(r)	Inversion
(D)		(s)	Intermediate is carbocation

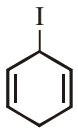
Exercise-2

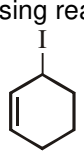
Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

1. Arrange the following compounds in order of decreasing reactivity towards S_N1 reaction.

(i) 

(ii) 

(iii) 

(A) ii > iii > i (B) i > ii > iii (C) iii < ii < i (D) i > iii > ii

2. The decreasing order of rate of S_N2 reaction for given compounds is :

(I) $CH_3–Cl$

(II) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-Cl$

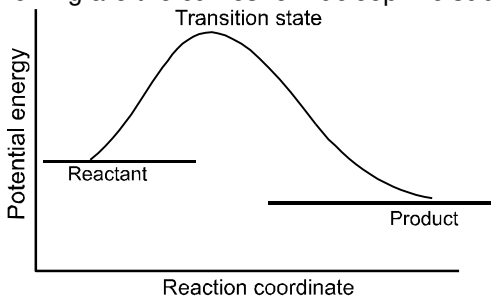
(III) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Cl$

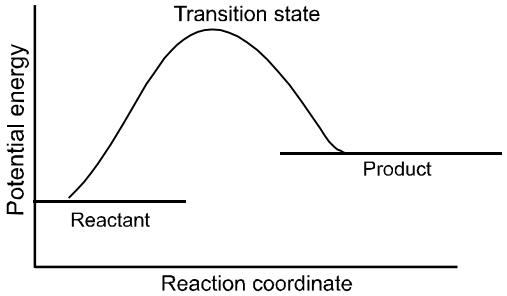
(IV) $CH_3–CH_2–Cl$

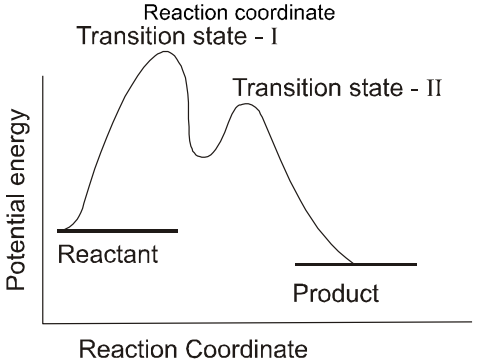
(A) IV > III > II > I (B) II > III > I > IV (C) II > I > IV > III (D) none

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

4. Following are the curves for nucleophilic substitution reaction.

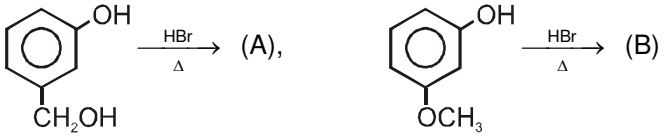
(I)


(II)


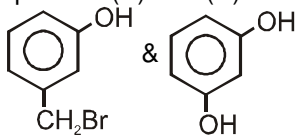
(III)


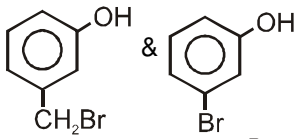
The correct statement is :
(A) 'I' is potential energy diagram for S_N2 reaction that takes place with a negative potential energy change.
(B) 'II' is potential energy diagram for S_N2 reaction with a positive potential energy change
(C) 'III' shows potential energy diagram for S_N1 reaction with large energy of activation for first (slowest) step
(D) All of the above

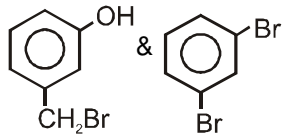
5. Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to
(A) The formation of less stable carbanion (B) Longer carbon halogen bond
(C) The inductive effect (D) sp^2–hybridized carbon attached to the halogen

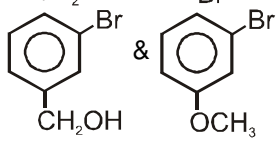
6. 

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

(A) 

(B) 

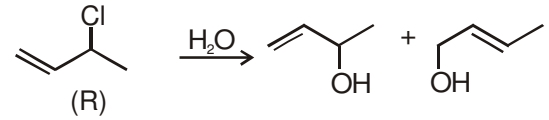
(C) 

(D) 

7. S_N1 reaction underoges 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)
The correct statements are
I. The decreasing order of rate of S_N1 reaction is t-BuX > iso-PrX > EtX > MeX
II. The decreasing order of ionisation energy is MeX > EtX > iso-PrX > t-BuX
III. The decreasing order of energy of activation is t-BuX > iso-PrX >EtX > MeX
(A) I & II are correct (B) I & III are correct (C) II and III are correct (D) I, II & III are correct

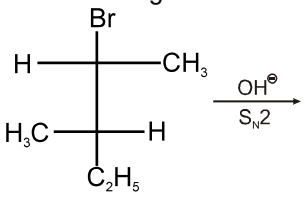
8. 

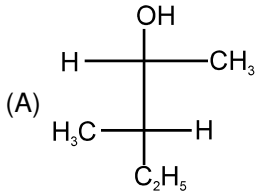
(R)
optically active

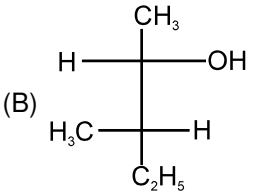
What is correct for the above reaction :

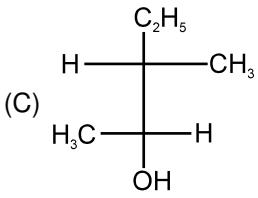
(A) Total three products are formed.
(B) Products mixture is optically active.
(C) Total two products are chiral.
(D) Intermediate carbocation is not formed in the reaction.

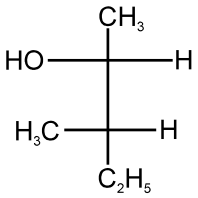
9. In the following reaction the most probable product will be :

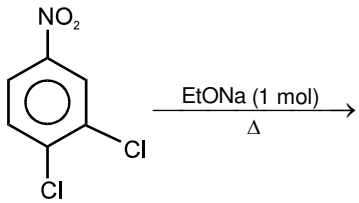


(A) 

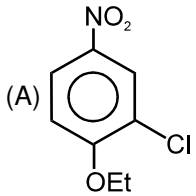
(B) 

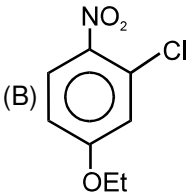
(C) 

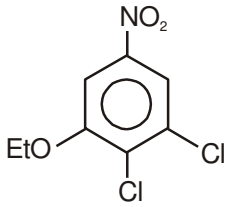
(D) 

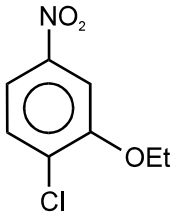
10. 

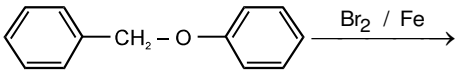
The product is :

(A) 

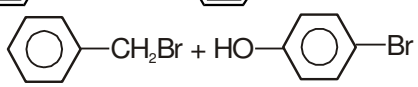
(B) 

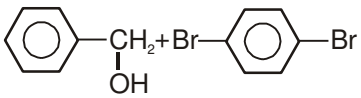
(C) 

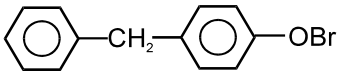
(D) 

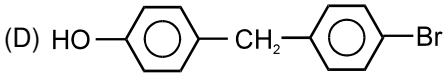
11. 

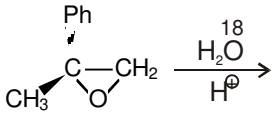
product is -

(A) 

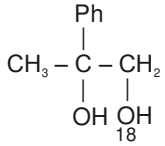
(B) 

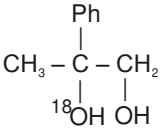
(C) 

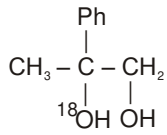
(D) 

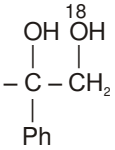
12. 

, The major product is

(A)  with retention, optically active

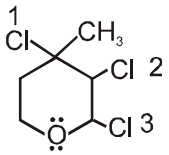
(B)  with racemisation

(C)  with inversion, optically active

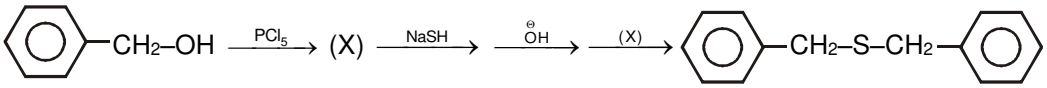
(D)  with racemisation

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. The most reactive chlorine towards H_2O is :

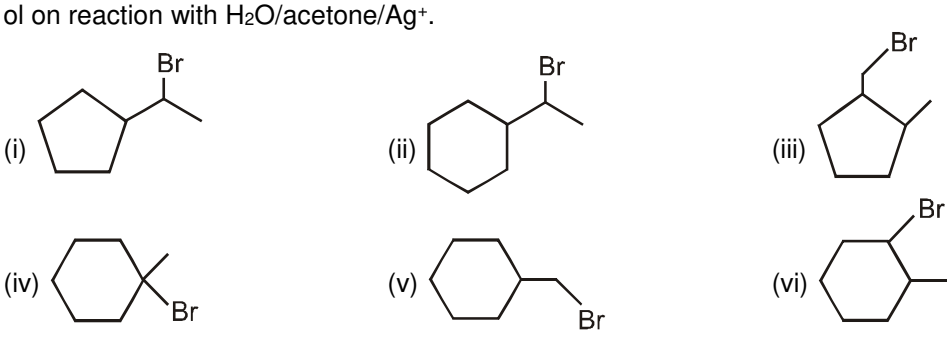


2. When the concentration of alkyl halide is tripled and the concentration of $\overset{\ominus}{OH}$ ion is reduced to half, the rate of S_N2 reaction increases by X times. Report your answer as 10 X.

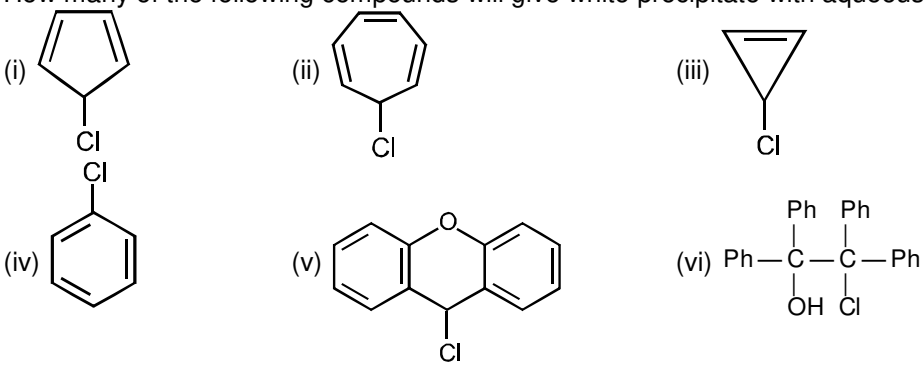
3. 

The number of times where S_N2 reaction taken place in above reaction sequence is

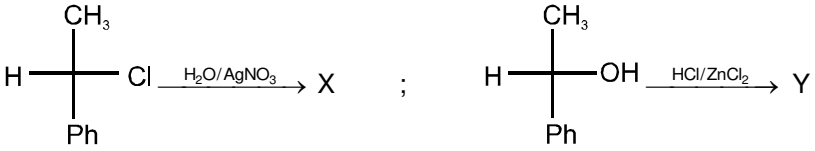
4. Among the 6, how many cyclic isomers of molecular formula $C_7H_{13}Br$ can form 1-methylcyclohexane-1-ol on reaction with H_2O/acetone/Ag^+.



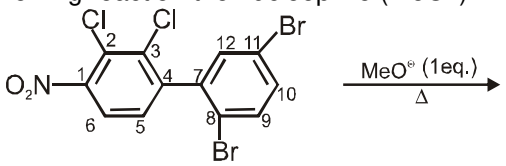
5. How many of the following compounds will give white precipitate with aqueous $AgNO_3$.

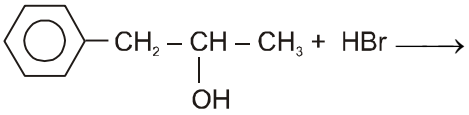


6. Find the total number of isomeric products obtained in these reactions. Report your answer as | X | Y | :



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

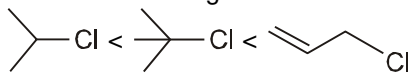


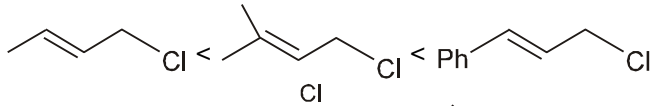
8. 

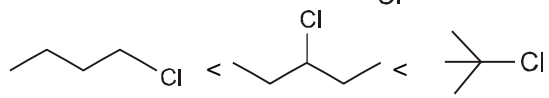
Number of possible isomeric products including stereoisomers will be :

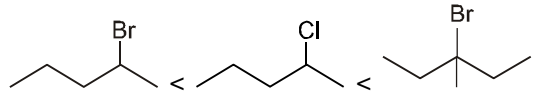
PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

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

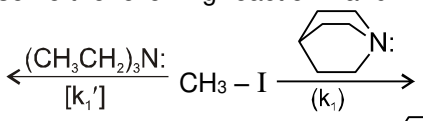
(A) 

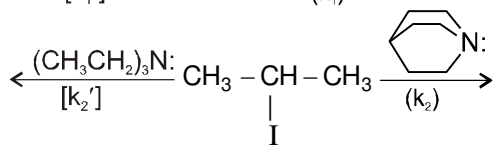
(B) 

(C) 

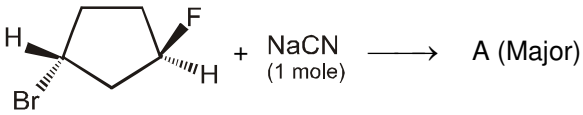
(D) 

2. Observe the following reaction I and II k_1k_1', k_2k_2' are rate constants. Select the correct option(s).

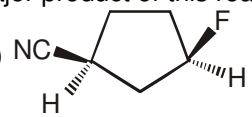
(I) 

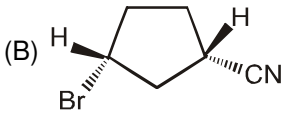
(II) 

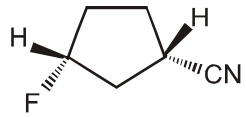
(A) $k_1 > k_1'$ (B) $k_1 > k_2$ (C) $k_2' > k_2$ (D) $k_2' > k_1'$

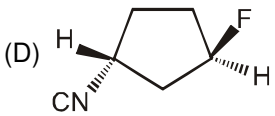
3. 

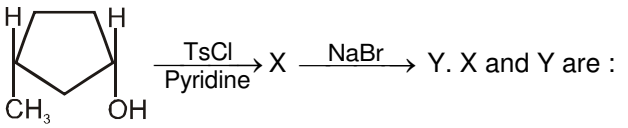
major product of this reaction is.

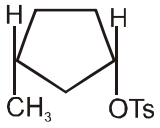
(A) 

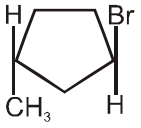
(B) 

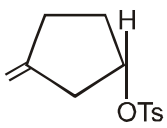
(C) 

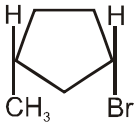
(D) 

4. 

(A) X = 

(B) Y = 

(C) X = 

(D) Y = 

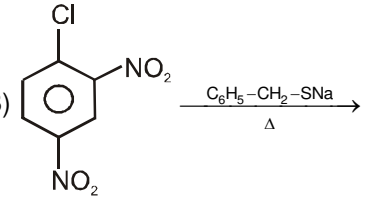
5.* Which of the following conditions are favour for S_N2 mechanism in alkyl halides ?

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

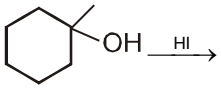
(C) 3º alkyl halide (D) Polar protic solvent

6. Which of the following reactions are nucleophilic substitution reaction ?

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

(B) 

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

(D) 

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

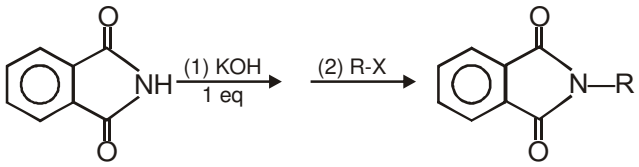
$R-O-R' + HI \longrightarrow R-\overset{\oplus}{\underset{\underset{H}{|}}{O}}-R' + \overset{\ominus}{I}$

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

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

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

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

8. 

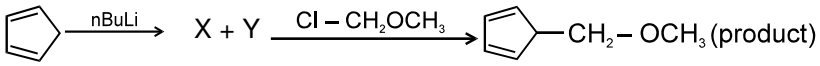
In which option correct rate for step-2 is given for the different R–X

(A) $CH_3-CH_2-Br < \underset{\underset{Br}{|}}{CH_3-CH-CH_3}$

(B) $Ph-Cl > CH_3-Cl$

(C) $Ph-CH_2-Br > \underset{\underset{Br}{|}}{Ph-CH-CH_3}$

(D) $CH_2=CH-CH_2-Cl > CH_3-CH_2-CH_2-Cl$

9. 

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 $:Bu^{\ominus}$

10. $CH_3Br + NH_3 \xrightarrow{\Delta} [(CH_3)_4]\ N^{\oplus}\ Br^{\ominus}$

excess salt

About the salt obtained which is true ?

(A) by S_N2 mechanism.

(B) NH_3 is nucleophile.

(C) by 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

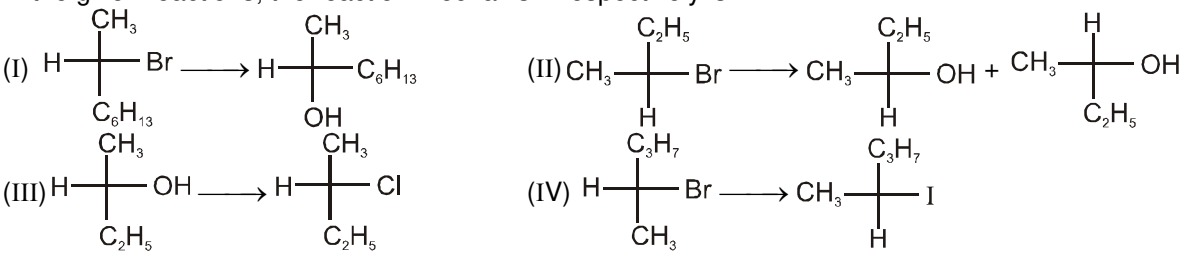
One of the most interesting and useful aspects of stereochemistry is the study of what happens to optically acitive molecules when they react. The product isolated from the reaction of the chiral material can tell us a great deal about the reaction mechanism. We observe

$S_N2 \longrightarrow$ Inversion of configuration

$S_N1 \longrightarrow$ Racemisation

$S_Ni \longrightarrow$ Retention of configuration

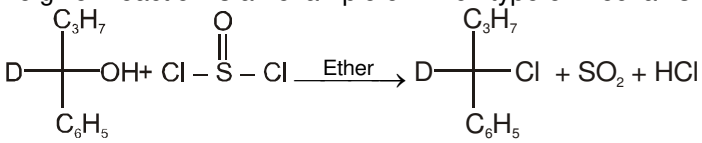
1. In the given reactions, the reaction mechanism respectively is :



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

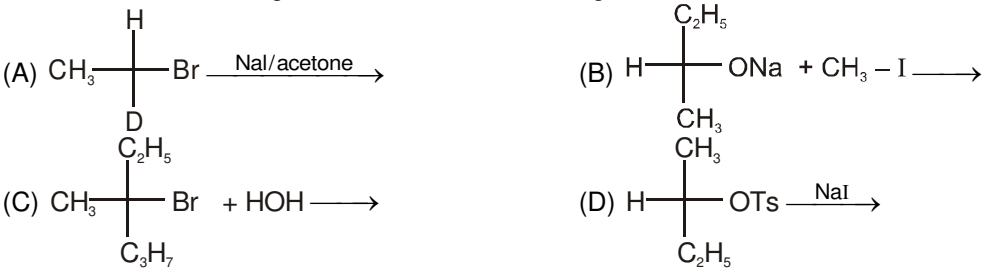
(C) S_N1, S_N2, S_Ni, S_N1 (D) S_N2, S_Ni, S_N1, S_N2

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



(A) S_N2 (B) S_N1 (C) S_Ni (D) None

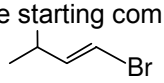
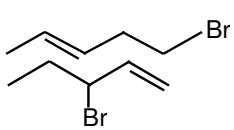
3. In which of the following reaction retention of configuration is observed ?

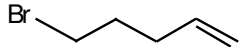


Comprehension # 2

An organic compound 'A' has molecular formula C_5H_9Br decolorises brown colour of bromine water but does not rotate plane polarised light. 'A' on treatment with HBr/ROOR forms $C_5H_{10}Br_2$ which on further treatment with NaOH(aq) gives the cyclic ether 

4. The starting compound 'A' most likely to be.

(A)  (B) 

(C)  (D)

5. Compound 'A' on treatment with HBr will produce

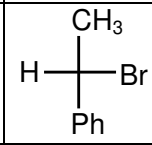
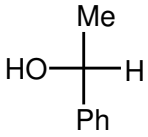
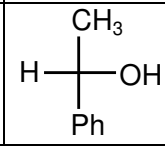
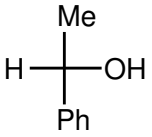
(A) An achiral dibromide (B) A racemic mixture

(C) A single pure enantiomer (D) A meso dibromide

Comprehension # 3

Answer Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.

Columns 1,2 and 3 contain reactants, reagents & products respectively.

Column-1		Column-2		Column-3	
(I)	$Ph–CH_2–CH_2–Br$	(i)	$NaOH/H_2O$	(P)	$Ph–\overset{*}{C}H(OH)–CH_3$ (±)
(II)		(ii)	HI, H_2O/acetone	(Q)	
(III)		(iii)	NaOH/DMSO	(R)	$Ph–CH_2–CH_2–OH$
(IV)	$Ph–CH_2–CH_2–OH$	(iv)	$SOCl_2$/Pyridine, (NaOH/DMF)	(S)	

6. $S_N1 + S_N2$ mixed mechanism is observed in the reaction :
(A) (I), (iii) (P) (B) (II) (i) (P) (C) (III) (iv) (Q) (D) (IV) (ii) (S)

7. Only S_N1 mechanism is observed in :
(A) (I), (i) (R) (B) (II) (iii) (P) (C) (IV) (ii) (S) (D) (III) (ii) (P)

8. S_N2 mechanism is observed in :
(A) (I), (iii) (R) (B) (IV) (iv) (R) (C) (II) (iii) (Q) (D) all

Exercise-3

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

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

1. An S_N2 reaction at an asymmetric carbon of a compound always gives : **[IIT-JEE-2001(S), 1/135]**
(A) an enantiomer of the substrate (B) a product with opposite optical rotation
(C) a mixture of diastereomers (D) a single stereoisomer

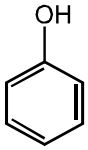
2. The compound that will react most readily with NaOH to form methanol is : **[IIT-JEE-2001(S), 1/135]**
(A) $(CH_3)_4N^+I^-$ (B) CH_3OCH_3 (C) $(CH_3)_3S^+I^-$ (D) $(CH_3)_3C–Cl$

3. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic (A) reacts with ethanal to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives1-bromo-1-methyl cyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B). **[IIT-JEE-2001(S), 5/135]**

4. Identify X, Y and Z in the following synthetic scheme and write their structures.

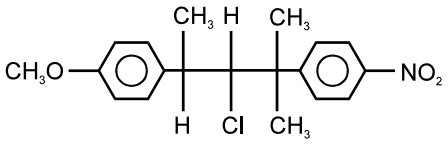
$$CH_3CH_2C{\equiv}C–H \xrightarrow[(ii)\ CH_3CH_2Br]{(i)\ NaNH_2} X \xrightarrow{H_2\ /\ Pd\ .\ BaSO_4} Y \xrightarrow{\text{alkaline } KMnO_4} Z$$

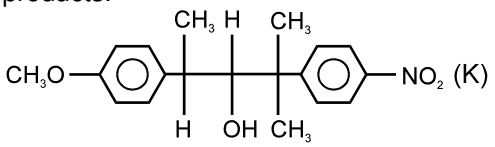
Is the compound Z optically active ? Justify your answer. **[IIT-JEE-2002(M), 5/150]**

5.  + C_2H_5I $\xrightarrow[\text{Anhydrous}(C_2H_5OH)]{\bar{O}C_2H_5\ (\text{excess})}$ product, major product is **[JEE-2003(S), 3/144]**

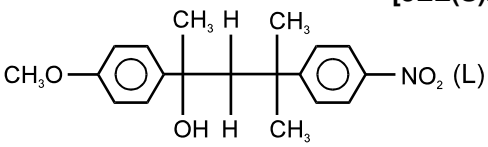
(A) $C_6H_5OC_2H_5$ (B) $C_2H_5OC_2H_5$ (C) $C_6H_5OC_6H_5$ (D) C_6H_5I

6. 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(S), 4/144]**

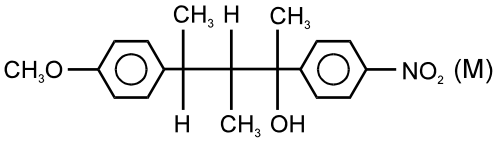
7. Compound (X)  is reacted with aqueous acetone it gives following products. **[JEE(S)2005, 3/144]**



(K)



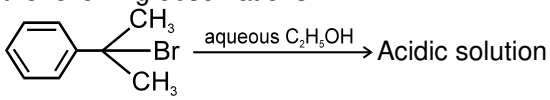
(L)

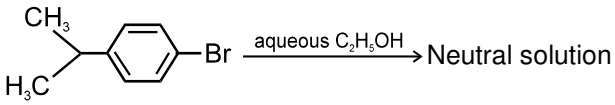


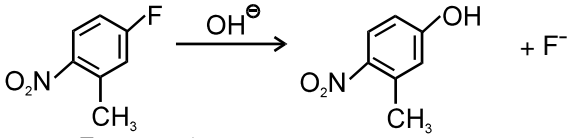
(M)

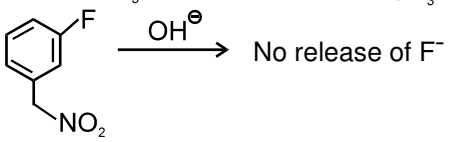
(A) K, L (B) K, M (C) L only (D) M only

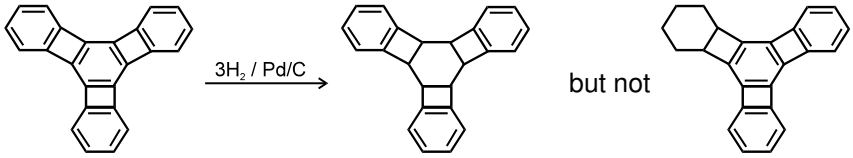
8. Explain the following observations : **[JEE 2005(M), 4/144]**

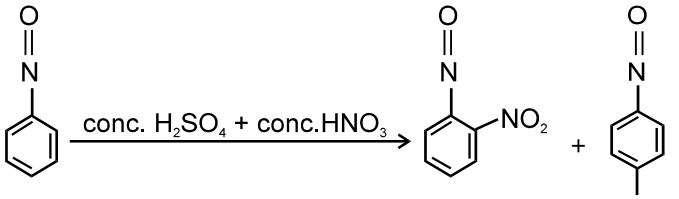
(A)  Acidic solution

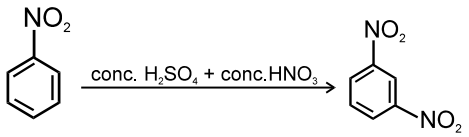
 Neutral solution

(B) 

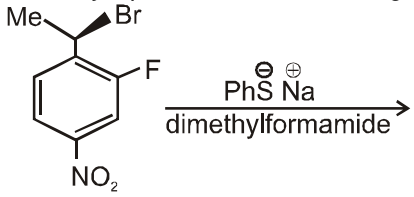


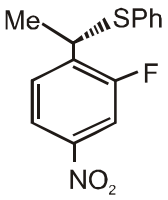
(C) 

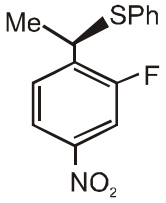
(D) 

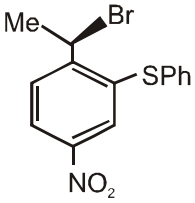


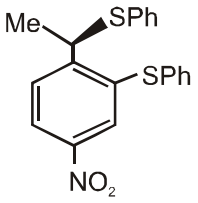
9. The major product of the following reaction is **[JEE-2008, 3/162]**



(A) 

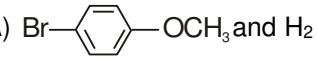
(B) 

(C) 

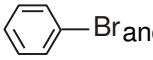
(D) 

10. In the reaction 

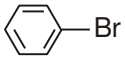
the products are : **[JEE-2010, 3/160]**

(A) 

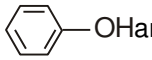
and H_2

(B) 

and CH_3Br

(C) 

and CH_3OH

(D) 

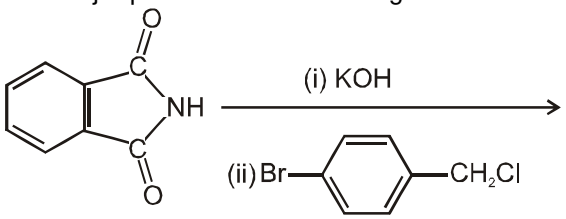
and CH_3Br

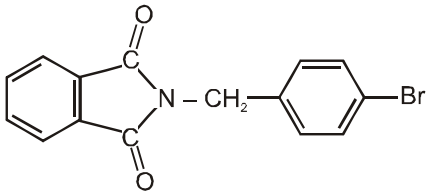
11. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are : **[JEE-2010, 3/160]**

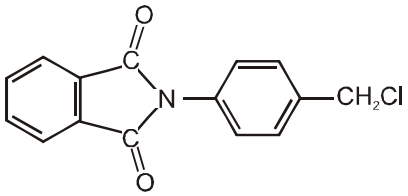
(A) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$ (B) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C{\equiv}CH$

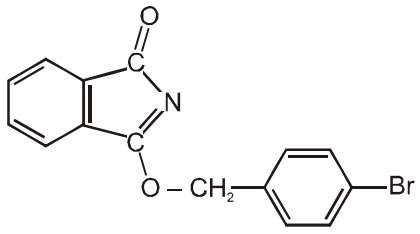
(C) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C{\equiv}CH$ (D) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$

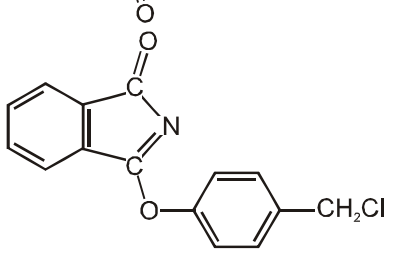
12. The major product of the following reaction is : **[JEE-2011, 3/163]**



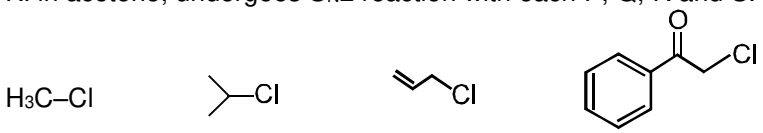
(A) 

(B) 

(C) 

(D) 

13. KI in acetone, undergoes S_N2 reaction with each P, Q, R and S. The rates of the reaction vary as

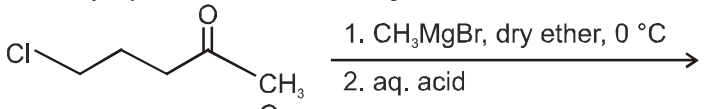


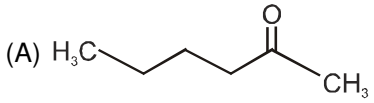
[JEE-2013, 2/126]

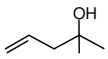
P **Q** **R** **S**

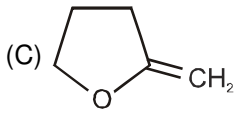
(A) P > Q > R > S (B) S > P > R > Q (C) P > R > Q > S (D) R > P > S > Q

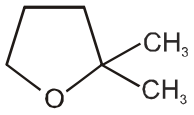
14. The major product in the following reaction is : **[JEE(Advanced)-2014, 3/120]**



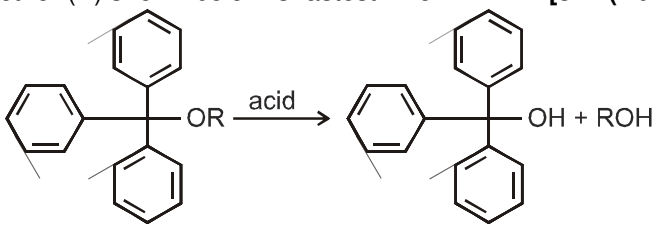
(A) 

(B) 

(C) 

(D) 

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

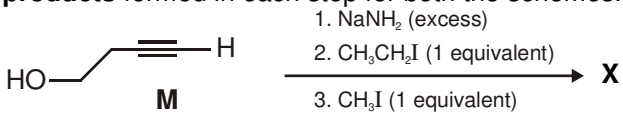


[X]

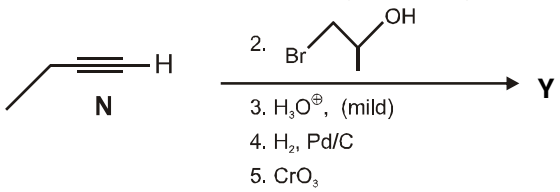
(A) one phenyl group is replaced by a methyl group.
(B) one phenyl group is replaced by a para-methoxyphenyl group.
(C) two phenyl groups are replaced by two para-methoxyphenyl groups.
(D) no structural change is made to X.

Paragraph for questions 16 and 17

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.

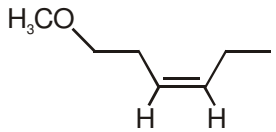


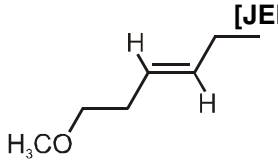
Scheme-1

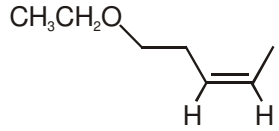


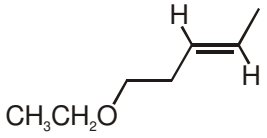
Scheme-2

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

(A) 

(B) 

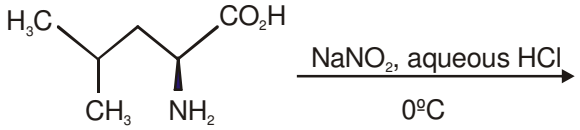
(C) 

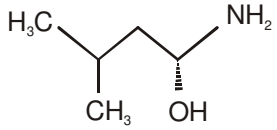
(D) 

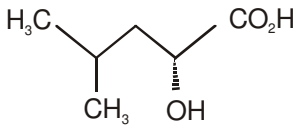
17. The correct statement with respect to product **Y** is **[JEE(Advanced)-2014, 3/120]**

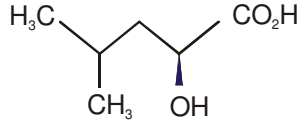
(A) It gives a positive Tollens test and is a functional isomer of **X**.
(B) It gives a positive Tollens test and is a geometrical isomer of **X**.
(C) It gives a positive iodoform test and is a functional isomer of **X**.
(D) It gives a positive iodoform test and is a geometrical isomer of **X**.

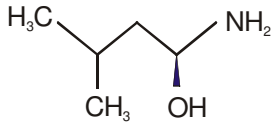
18. The major product of the reaction is **[JEE(Advanced)-2015, 4/120]**



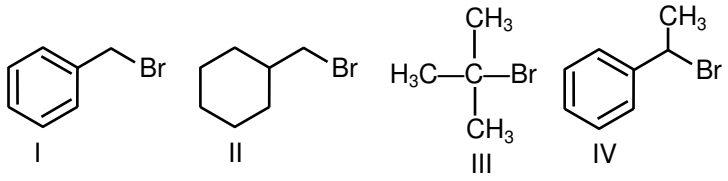
(A) 

(B) 

(C) 

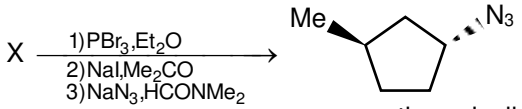
(D) 

19.* For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is (are) **[JEE(Advanced)-2017, 4/122]**

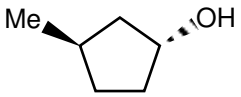


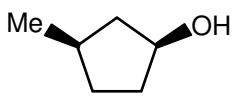
(A) Compound **IV** undergoes inversion of configuration
(B) The order of reactivity for **I**, **III** and **IV** is : **IV > I >III**
(C) **I** and **III** follow S_N1 mechanism
(D) **I** and **II** follow S_N2 mechanism

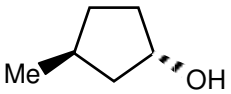
20.* In the following reaction sequence, the correct structure(s) of **X** is (are) **[JEE(Advanced)-2018, 4/120]**

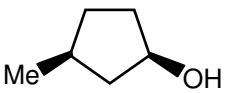


enantiomerically Pure

(A) 

(B) 

(C) 

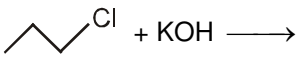
(D) 

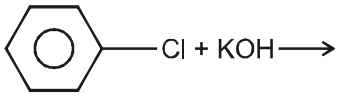
PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

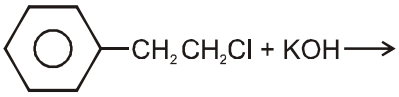
JEE(MAIN) OFFLINE PROBLEMS

1. S_N1 reaction is feasible in : **[AIEEE-2002, 3/225]**

(1) $(CH_3)_3C–Cl + KOH \longrightarrow$

(2) 

(3) 

(4) 

2. The reaction : $(CH_3)_3C–Br \xrightarrow{H_2O} (CH_3)_3C–OH$ is an example of - **[AIEEE-2002, 3/225]**

(1) elimination reaction.
(2) substitution reaction.
(3) free radical reaction.
(4) rearrangement reaction.

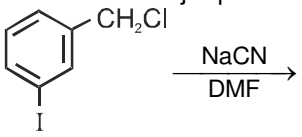
3. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in a test tube and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment ? **[AIEEE-2003, 3/225]**

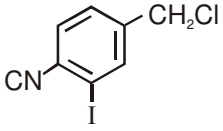
(1) A was C_6H_5I
(2) A was $C_6H_5CH_2I$
(3) B was C_6H_5I
(4) Addition of HNO_3 was unnecessary

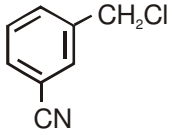
4. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of: **[AIEEE-2005, 3/225]**

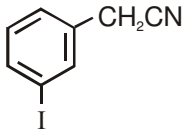
(1) steric hinderance (2) inductive effect (3) instability (4) insolubility

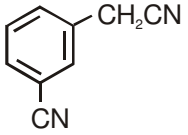
5. The structure of the major product formed in the following reaction is : **[AIEEE-2006, 3/165]**



(1) 

(2) 

(3) 

(4) 

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

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

[Nu^- = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O^-] **[AIEEE-2006, 3/165]**

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

7. 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) $R_2CHX > R_3CX > RCH_2X$

8. 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) $(C_2H_5)_2CHCl$

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

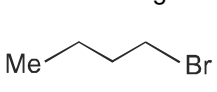
(1) CH_3CH_2Cl (2) CH_2ClCH_2Cl (3) CH_3CHCl_2 (4) CH_3COCl

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

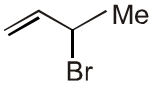
(1) 2-Butanol (2) 2-Methylpropan-2-ol

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

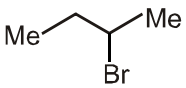
11. Consider the following bromides : **[AIEEE-2010, 4/144]**



(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

12. 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

13. 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

14. 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) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

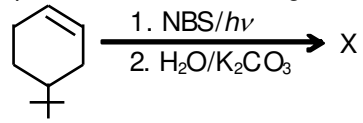
(4) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

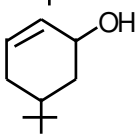
15. The synthesis of alkyl fluorides is best accomplished by : **[JEE(Main) 2015, 4/120]**

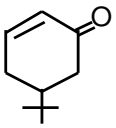
(1) Free radical fluorination (2) Sandmeyer's reaction

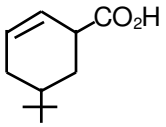
(3) Finkelstein reaction (4) Swarts reaction

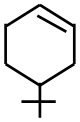
16. The product of the reaction give below is : **[JEE(Main) 2016, 4/120]**



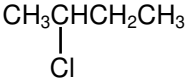
(1) 

(2) 

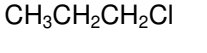
(3) 

(4) 

17. The increasing order of the reactivity of the following halides for the S_N1 reaction is : **[JEE(Main) 2017, 4/120]**



(I)



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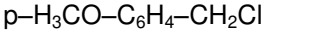
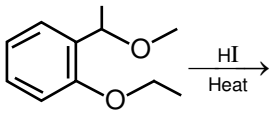
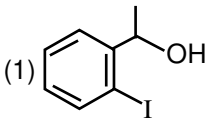


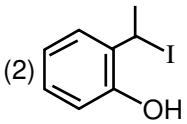
(III)

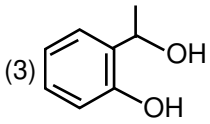
(1) (II) < (I) < (III) (2) (I) < (III) < (II) (3) (II) < (III) < (I) (4) (III) < (II) < (I)

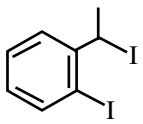
18. The major product formed in the following reaction is : **[JEE(Main) 2018, 4/120]**



(1) 

(2) 

(3) 

(4) 

JEE(MAIN) ONLINE PROBLEMS

1. Allyl phenyl ether can be prepared by heating : **[JEE(Main) 2014 Online (09-04-14), 4/120]**
(1) $C_6H_5Br + CH_2=CH-CH_2-ONa$ (2) $CH_2=CH-CH_2-Br + C_6H_5ONa$
(3) $C_6H_5-CH=CH-Br + CH_3-ONa$ (4) $CH_2=CH-Br + C_6H_5-CH_2-ONa$

2. In a nucleophilic substitution reaction :

$$R-Br + Cl^- \xrightarrow{DMF} R-Cl + Br^-$$

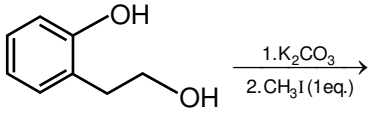
Which one of the following undergoes complete inversion of configuration ? **[JEE(Main) 2014 Online (09-04-14), 4/120]**
(1) $C_6H_5CHC_6H_5Br$ (2) $C_6H_5CH_2Br$
(3) $C_6H_5CHCH_3Br$ (4) $C_6H_5CCH_3C_6H_5Br$

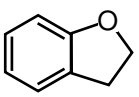
3. The major product formed when 1,1,1-trichloro-propane is treated with aqueous potassium hydroxide is: **[JEE(Main) 2014 Online (19-04-14), 4/120]**
(1) Propyne (2) 1-Propanol (3) 2-Propanol (4) Propionic acid

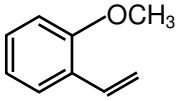
4. The final product formed when Methyl amine is treated with $NaNO_2$ and HCl is : **[JEE(Main) 2014 Online (19-04-14), 4/120]**
(1) Diazomethane (2) Methylalcohol (3) Methylcyanide (4) Nitromethane

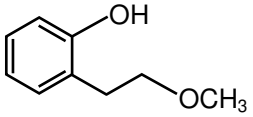
5. Williamson synthesis of ether is an example of : **[JEE(Main) 2014 Online (19-04-14), 4/120]**
(1) Nucleophilic addition (2) Electrophilic addition
(3) Electrophilic substitution (4) Nucleophilic substitution

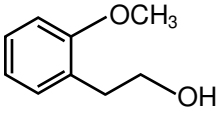
6. The major product of the following reaction is : **[JEE(Main) 2017 Online (08-04-17), 4/120]**



(1) 

(2) 

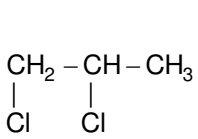
(3) 

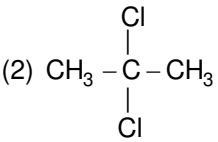
(4) 

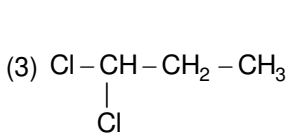
7. In the following reaction sequence :

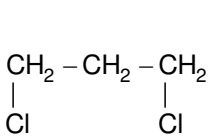
$$\underset{(C_3H_6Cl_2)}{\overset{I}{}} \xrightarrow{KOH(aq)} II \xrightarrow[(ii)\,H_2O/H^+]{(i)\,CH_3MgBr} III \xrightarrow{Anhy.\,ZnCl_2+Con.HCl} \text{gives turbidity immediately}$$

The compound I is : **[JEE(Main) 2017 Online (09-04-17), 4/120]**

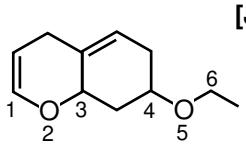
(1) 

(2) 

(3) 

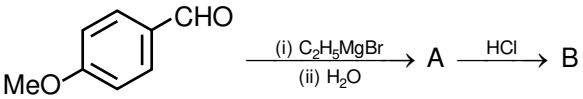
(4) 

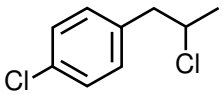
8. On treatment of the following compound with a strong acid, the most susceptible site for bond cleavage is : **[JEE(Main) 2018 Online (15-04-18), 4/120]**

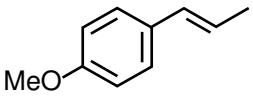


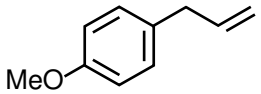
(1) $C_1 - O_2$ (2) $O_2 - C_3$ (3) $C_4 - O_5$ (4) $O_5 - C_6$

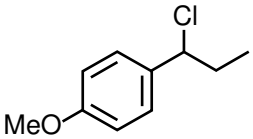
9. The major product B formed in the following reaction sequence is : **[JEE(Main) 2018 Online (16-04-18), 4/120]**



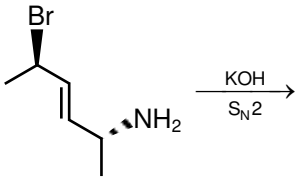
(1) 

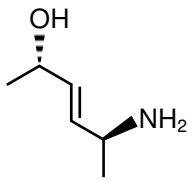
(2) 

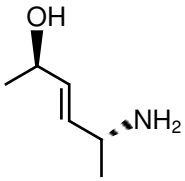
(3) 

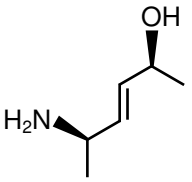
(4) 

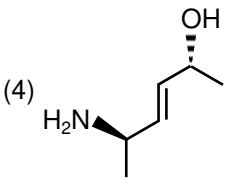
10. The major product of the following reaction is : **[JEE(Main) 2018 Online (16-04-18), 4/120]**



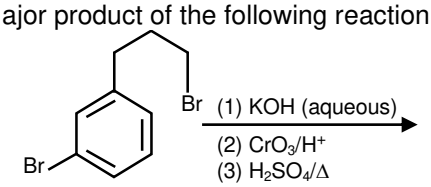
(1) 

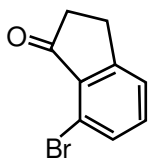
(2) 

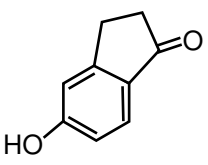
(3) 

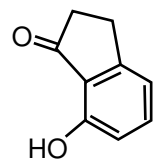
(4) 

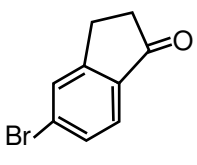
11. The major product of the following reaction is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**



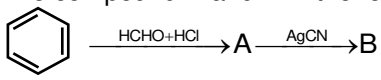
(1) 

(2) 

(3) 

(4) 

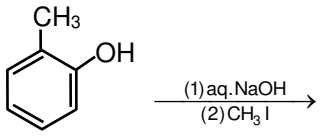
12. The compound A and B in the following reaction are, respectively :

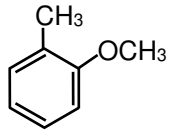


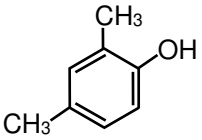
[JEE(Main) 2019 Online (09-01-19), 4/120]

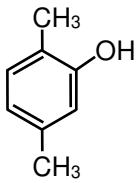
(1) A = Benzyl alcohol, B = Benzyl isocyanide
(2) A = Benzyl chloride, B = Benzyl cyanide
(3) A = Benzyl chloride, B = Benzyl isocyanide
(4) A = Benzyl alcohol, B = Benzyl cyanide

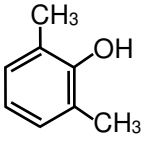
13. The major product of the following reaction: **[JEE(Main) 2019 Online (10-01-19), 4/120]**



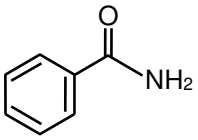
(1) 

(2) 

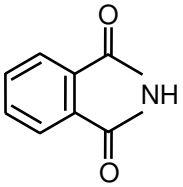
(3) 

(4) 

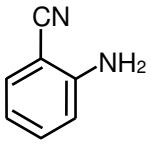
14. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is : **[JEE(Main) 2019 Online (12-01-19), 4/120]**



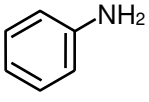
(A)



(B)



(C)



(D)

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

Answers

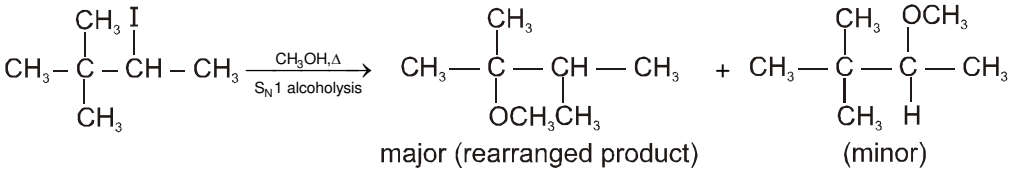
EXERCISE - 1

PART – I

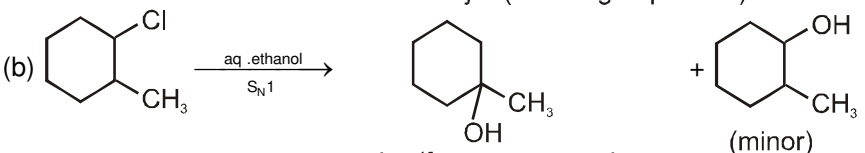
A-1. (a) 2-Bromopentane (b) 2-Bromo-2-methylbutane

A-2. (a) Rate-doubled (b) Rate-tripled

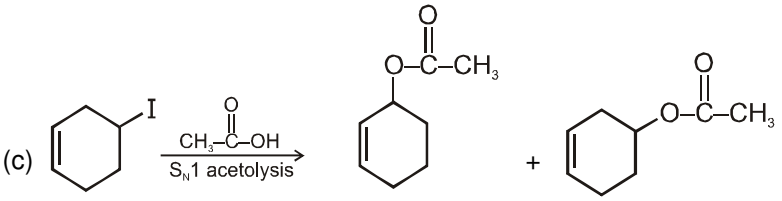
A-3. 3-Chlorocyclopropene form aromatic carbocation while 5-Chlorocyclopenta-1,3-diene form antiaromatic carbocation.

A-4. (a) 

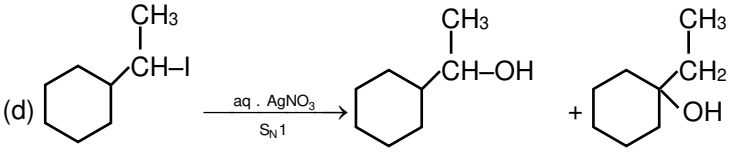
major (rearranged product) (minor)

(b) 

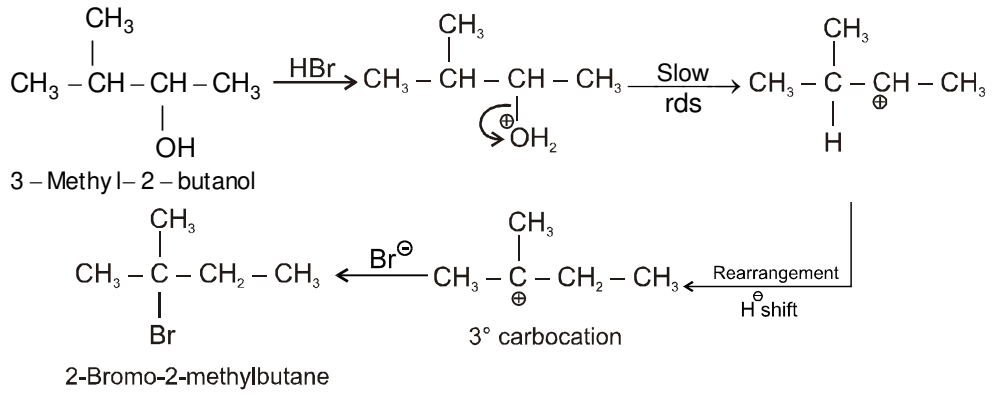
major (from rearranged 3° carbocation) (minor)

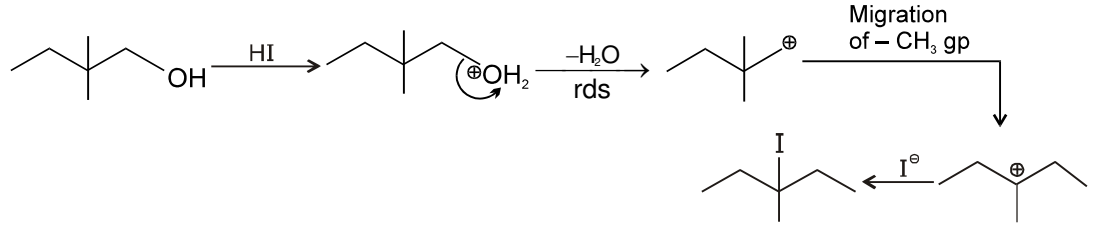
(c) 

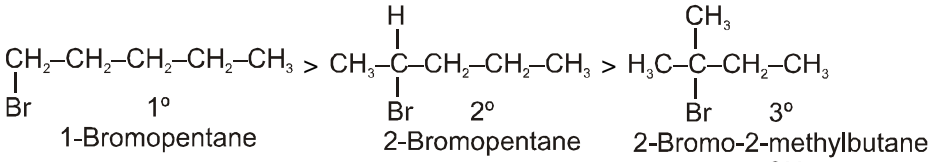
major (from rearranged allylic cation) minor

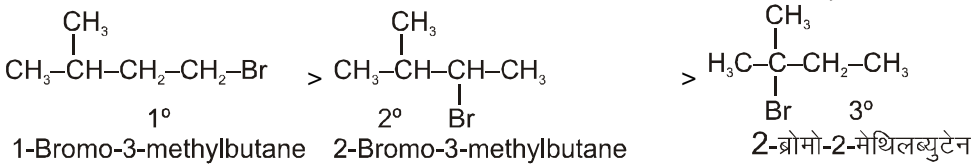
(d) 

(Minor) (Major)

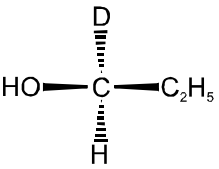
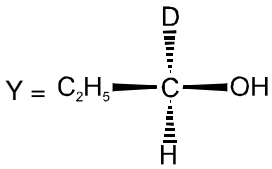
A-5. (a) 

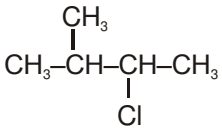
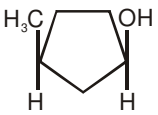
(b) 

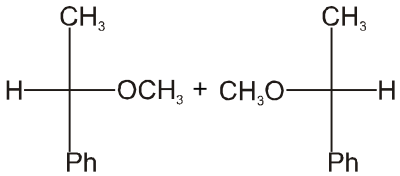
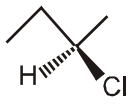
B-1. (a) 

(b) 

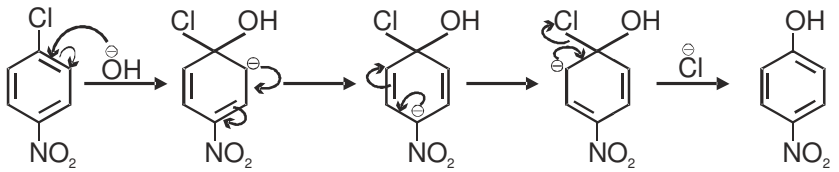
B-2. (a) $PhCMe_2Br$ (b) $PhCH_2CH_2Br$

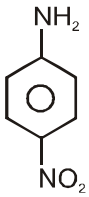
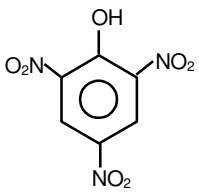
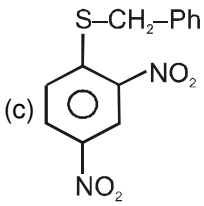
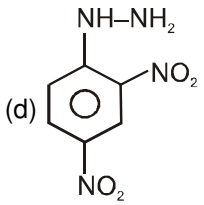
B-3. X =  Y = 

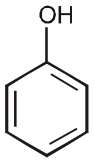
B-4. (a)  (b) 

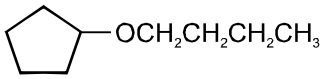
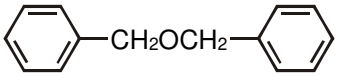
B-5. (a)  (b) 

C-1. II > III > I

C-2. **Mechanism :** 

C-3. (a)  (b)  (c)  (d) 

D-1. (a)  + CH_3I (b) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH + CH_3-CH_2I$

D-2. P =  Q = 

D-3. (i) X = $CH_3CH(OH)CH_2OH$ (ii) Y = $CH_3CH(OH)CH_2OMe$

PART – II

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

PART – III

1. (A) **2.** (A) → q,s ; (B) → r ; (C) → p ; (D) → r

EXERCISE – 2

PART – I

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

PART – II

1.	3	**2.**	15	**3.**	3	**4.**	5 (Except (ii))		
5.	4 (Except (i, iv))			**6.**	22	**7.**	2	**8.**	4

PART – III

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

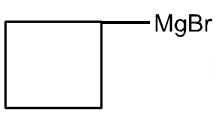
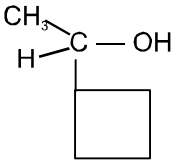
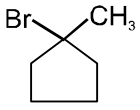
PART – IV

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

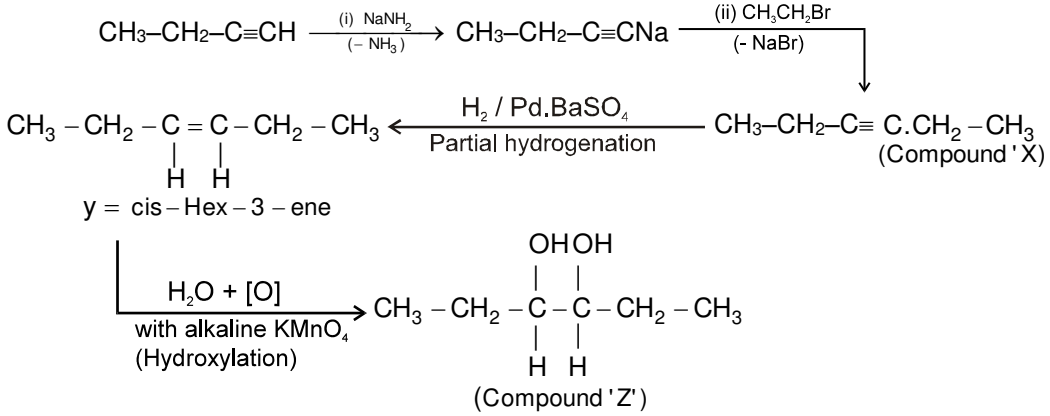
EXERCISE – 3

PART – I

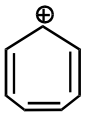
1. (D) **2.** (C)

3. (A) =  ; (B) =  ; (C) = 

4.



5. (B)

6. 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)

7. (A)

8. (A) In 1st SN^1 reaction is possible so by-product is HBr in 2nd SN^1 reaction is not possible.
(B) 1st can give SN^2 Ar but 2nd can not give because –m of $–NO_2$ is not opperating.
(C) 2nd product has two antiaromatic rings but 1st does not have antiaromatic system.
(D) $–NO_2$ is metadirecting but –N=O group is ortho-para directing due to +m of –N=O.

9.	(A)	**10.**	(D)	**11.**	(D)	**12.**	(A)	**13.**	(B)
14.	(D)	**15.**	(C)	**16.**	(A)	**17.**	(C)	**18.**	(C)
19.	(ACD)	**20.**	(B)						

PART – II

JEE(MAIN) OFFLINE PROBLEMS

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

JEE(MAIN) ONLINE PROBLEMS

1.	(2)	**2.**	(3)	**3.**	(4)	**4.**	(2)	**5.**	(4)
6.	(4)	**7.**	(2)	**8.**	(2)	**9.**	(4)	**10.**	(3)
11.	(4)	**12.**	(3)	**13.**	(1)	**14.**	(1)		

Additional Problems for Self Practice (APSP)

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

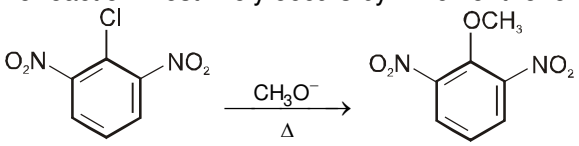
PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr. **Max. Marks : 120**

Important Instructions

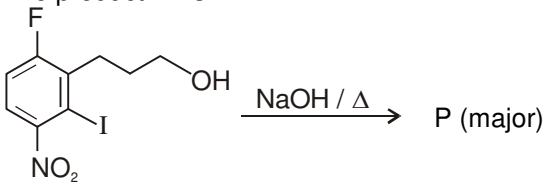
1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120.**
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. ¼ **(one fourth)** marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
5. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

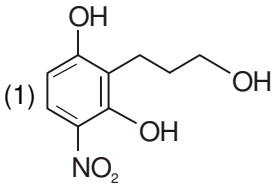
1. The reaction most likely occurs by which of the following mechanism ?

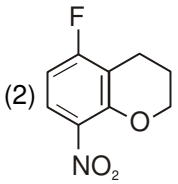


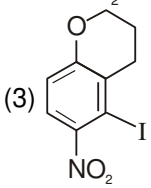
(1) Addition-elimination (2) addition only
(3) Elimination-addition (4) Neither of these

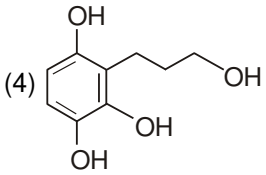
2. The product 'P' is



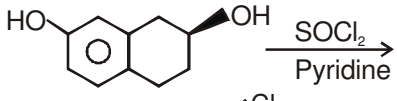


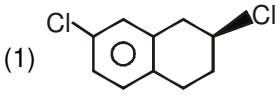


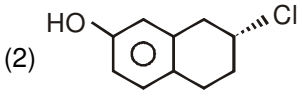


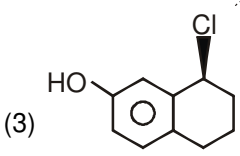


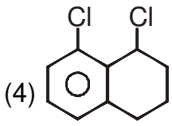
3.

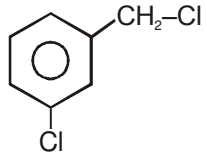


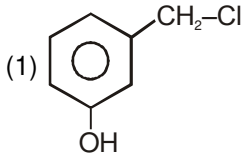
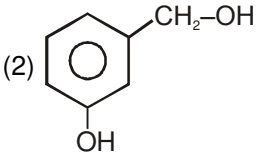
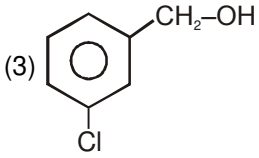
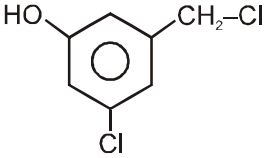


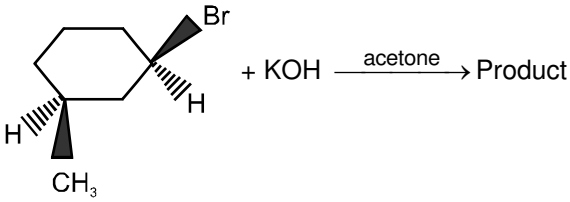






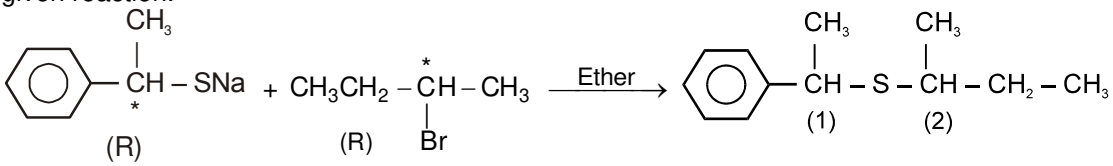
4.  Product is :

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

5. 

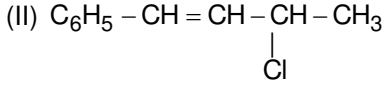
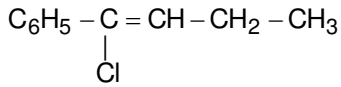
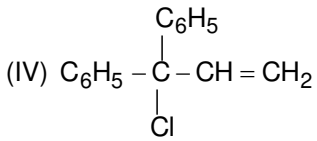
(1R, 3S)–Cis–1–Bromo–3–methylcyclohexane.
The product formed in the reaction is
(1) (1R, 3S)-Cis-3-methyl cyclohexanol
(2) (1S, 3S)-Cis-3- methyl cyclohexanol
(3) (1S, 3S)-Trans-3-methyl cyclohexanol
(4) (1R, 3R)-Trans-3-methyl cyclohexanol

6. Which configuation will be adopted by the poduct at cabon atoms marked (1) and (2) respectively in the given reaction.

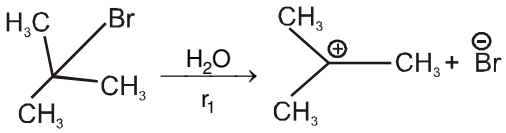
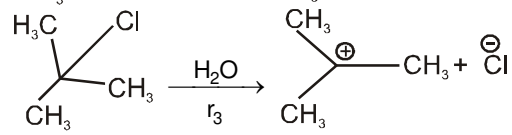
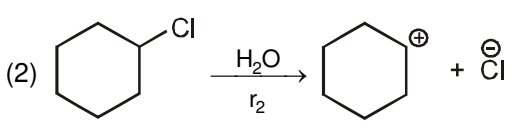


(1) R, R
(2) R, S
(3) S, S
(4) S, R

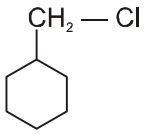
7. What is the correct order of reactivity of alcohols in the following reaction?
$R–OH + HCl + ZnCl_2 \rightarrow R–Cl + H_2O$
(1) Ethanol > Propan-1-ol > Butan-2-ol
(2) Butan-1-ol > Propan-1-ol > Butan-2-ol
(3) Neopentyl alcohol > t-Butyl alcohol > Methanol
(4) t-Butyl alcohol > Butan-2-ol > Propan-1-ol

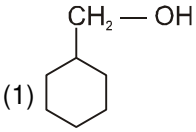
8. The increasing order of reactivity of the following isomeric halides with $AgNO_3$ (H_2O + alcohol) is :
(I) $C_6H_5–CH=CH–CH_2–CH_2–Cl$
(II) 
(III) 
(IV) 

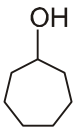
(1) III < IV < II < I
(2) I < III < IV < II
(3) III < I < II < IV
(4) I < II < IV < III

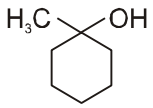
9. (1) 
(3) 
(2) 

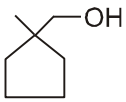
the rates r_1, r_2 and r_3 are in the order :
(1) $r_1 > r_2 > r_3$
(2) $r_3 > r_1 > r_2$
(3) $r_1 > r_3 > r_2$
(4) $r_2 > r_1 > r_3$

10.  $\xrightarrow[AgNO_3]{H_2O}$ 'Y' Product :

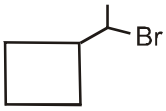
(1) 

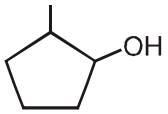
(2) 

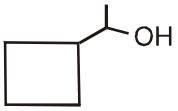
(3) 

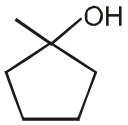
(4) 

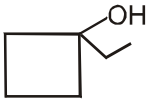
11. What will be the major product of the following reaction

 $\xrightarrow{H_2O}$ Product

(1) 

(2) 

(3) 

(4) 

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

Identify product X and the mechanism of the reaction.

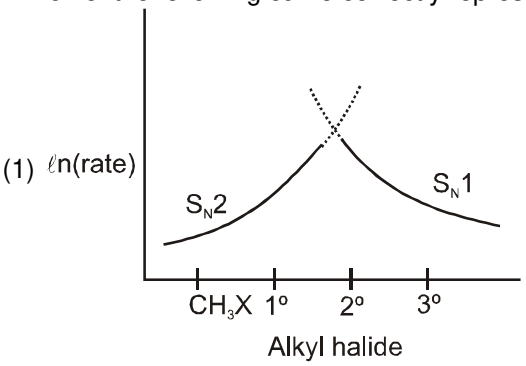
(1) $CH_3–CH_2–CH_2–CH_2–Cl$ & S_N1

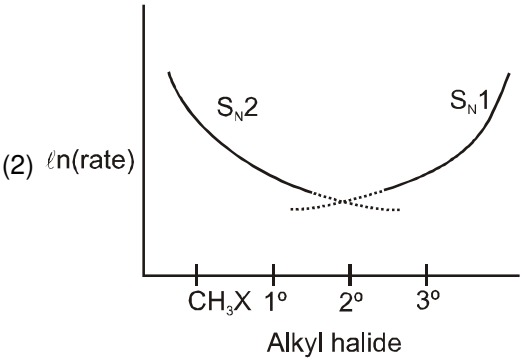
(2) $CH_3–CH_2–CH_2–CH_2–Cl$ & S_N2

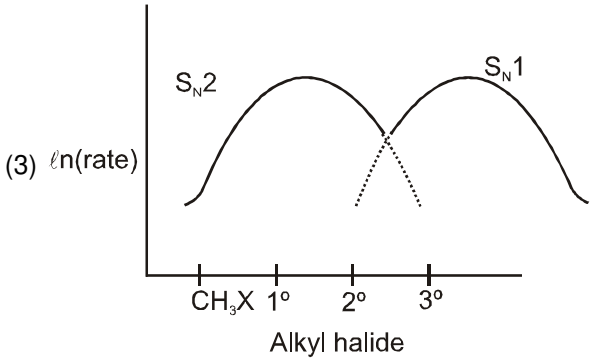
(3) $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3$ & S_N1

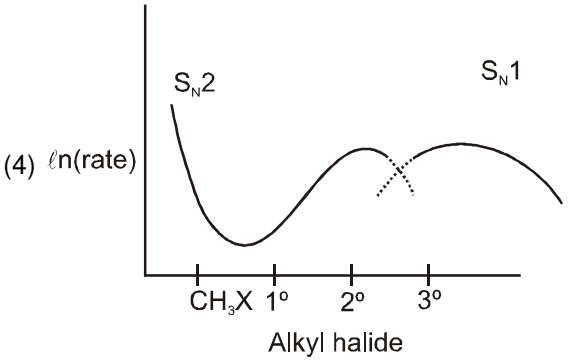
(4) $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3$ & S_N2

13. Which of the following curve correctly represents S_N1 vs S_N2

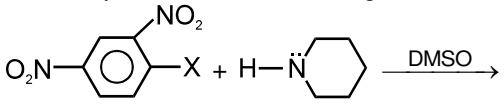
(1) 

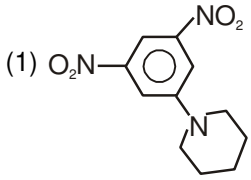
(2) 

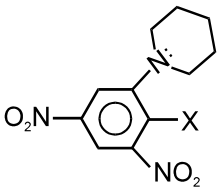
(3) 

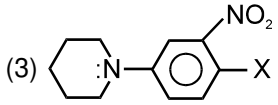
(4) 

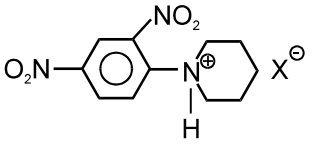
14. The final product of the following reaction is :

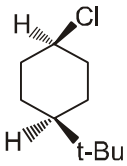


(1) 

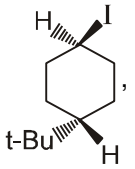
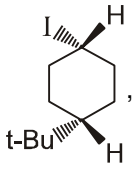
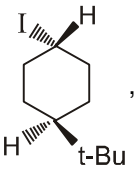
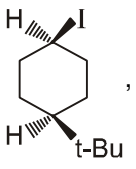
(2) 

(3) 

(4) 

15.  $\xrightarrow[50°C]{NaI\ /\ Acetone}$ Product

Product and mechanism of the reaction respectively is :

(1)  , S_N1 (2)  , S_N2 (3)  , S_N2 (4)  , S_N1

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

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

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

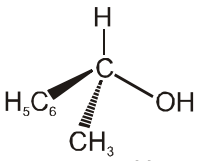
Which of the following statement is correct about these reactions.

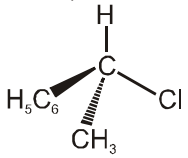
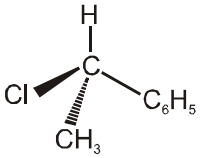
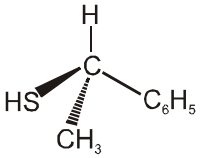
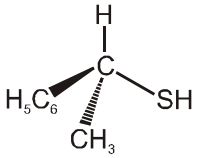
(1) Both the reactions take place at the same rate

(2) The first reaction takes place faster than second reaction.

(3) The second reaction takes place faster than first reaction.

(4) Both the reactions take place by S_N1 mechanism

17.  $\xrightarrow{SOCl_2}$ Product, Identify the product

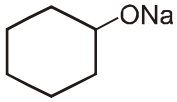
(1)  (2)  (3)  (4) 

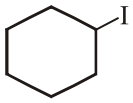
18. $Cl–CH_2CH_2CH_2CH_2OH \xrightarrow{NaOH(aq.)}$ A, the product A is

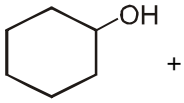
(1) $HO–CH_2CH_2CH_2CH_2OH$ (2) 

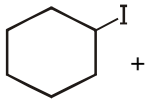
(3) (4) $ClCH_2CH_2CH_2CH_2ONa$

19. Which of the following reactions is the best choice for preparing methyl cyclohexyl ether ?

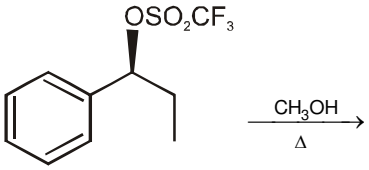
(1)  + $CH_3I \longrightarrow$

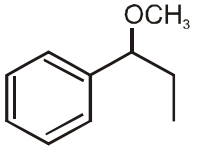
(2)  + $CH_3ONa \longrightarrow$

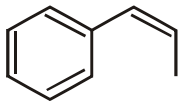
(3)  + $CH_3I \longrightarrow$

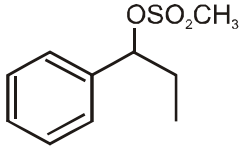
(4)  + $CH_3OH \longrightarrow$

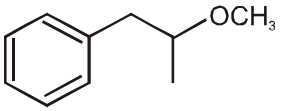
20. Which product would be expected to predominate in the given reaction ?



(1) 

(2) 

(3) 

(4) 

21. Select correct statement

(1) Solvolysis of $(CH_3)_2C{=}CH{-}CH_2{-}Cl$ in ethanol is faster than primary alkyl chloride (25°C)

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

(3) 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

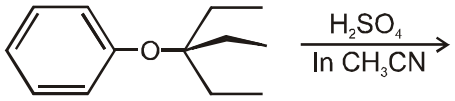
(4) All of these

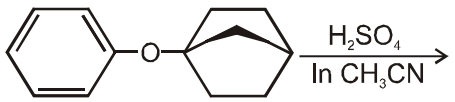
22. $(CH_3)_3C{-}O{-}CH_2{-}C_6H_5$ can be prepared from Williamsons synthesis, using :

(1) $(CH_3)_3C{-}Cl$ and $C_6H_5CH_2ONa$ (2) $C_6H_5CH_2Cl$ and $(CH_3)_3C{-}ONa$

(3) $(CH_3)_3C{-}O{-}CH_2{-}Cl$ and C_6H_5ONa (4) All of these

23. Consider the following reactions carried out at the same temperature.

(I) 

(II) 

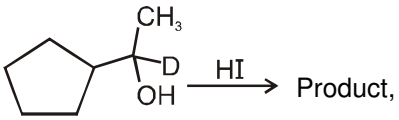
Which of the following statement is correct about these reaction.

(1) Both the reactions take place at the same rate

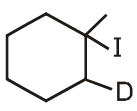
(2) The first reaction takes place faster than second reaction.

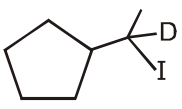
(3) The second reaction takes place faster than first reaction.

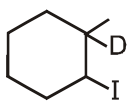
(4) Both the reactions take place by S_N1 mechanism

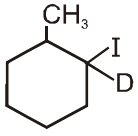
24.  Product,

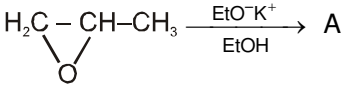
Identify the major product :

(1) 

(2) 

(3) 

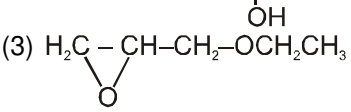
(4) 

25. 

The product A is :

(1) $CH_3CH_2O–CH_2–\underset{\displaystyle OH}{\underset{|}{CH}}–CH_3$

(2) $\underset{\displaystyle OH}{\underset{|}{CH_2}}–\underset{\displaystyle CH_3}{\underset{|}{CH}}–OCH_2CH_3$

(3) 

(4) $CH_3CH_2O–CH_2–\underset{\displaystyle OH}{\underset{|}{CH}}–OCH_2CH_3$

26. Which of the following statement is not true ?

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

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

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

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

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

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

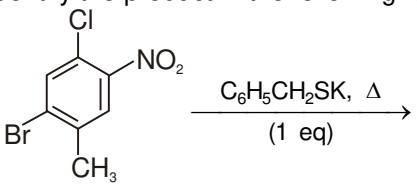
(1) Reaction will not take place because $\overset{\ominus}{O}H$ is poor leaving group; $\overset{\ominus}{X}$ is weak base and $\overset{\ominus}{O}H$ is strong base

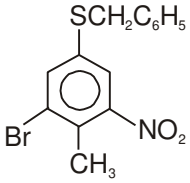
(2) Reaction will not take place because $\overset{\ominus}{O}H$ is poor leaving group; $\overset{\ominus}{X}$ is strong base and $\overset{\ominus}{O}H$ is weak base.

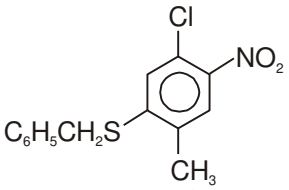
(3) Reaction will not take place because $\overset{\ominus}{O}H$ is strong leaving group; $\overset{\ominus}{X}$ is strong base and $\overset{\ominus}{O}H$ is weak base.

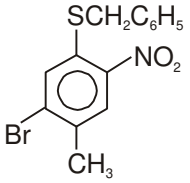
(4) Reaction will not take place because $\overset{\ominus}{O}H$ is good leaving group; $\overset{\ominus}{X}$ is weak base $\overset{\ominus}{O}H$ and is strong base.

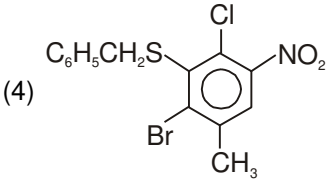
28. Identify the product in the following reaction ?



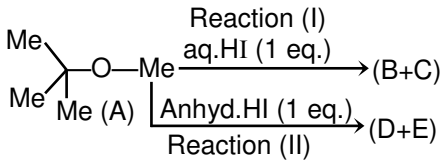
(1) 

(2) 

(3) 

(4) 

29.



Which of the following statements is correct ?
(i) The compounds (B) and (C) are Me_3C—I and MeOH and reaction (I) proceeds by S_N1 mechanism.
(ii) The compound (B) and (C) are Me_3C–OH and MeI and reaction (I) proceeds by S_N2 mechanism.
(iii) The compound (E) and (D) are Me_3C—I and MeOH and reaction (II) proceeds by S_N1 mechanism.
(iv) The compound (E) and (D) are Me_3C—OH and MeI and reaction (II) proceeds by S_N2 mechanism.
(1) (i) and (iii) (2) (ii) and (iii) (3) (i) and (iv) (4) (ii) and (iv)

30. Which of the following compound is least reactive in the nucleophilic aromatic substitution reaction with NaOH?
(1) p-nitrofluorobenzene (2) p-nitrochlorobenzene
(3) p-nitrobromobenzene (4) p-nitroiodobenzene

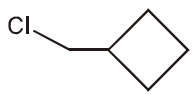
Practice Test-1 (IIT-JEE (Main Pattern))

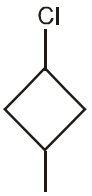
OBJECTIVE RESPONSE SHEET (ORS)

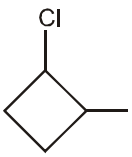
Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

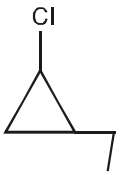
PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. A compound A has the molecular formula C_5H_9Cl. It does not react with bromine in carbon tetrachloride. On treatment with a strong base it produces a single compound B. B has a molecular formula C_5H_8 and reacts with bromine in carbon tetrachloride. Ozonolysis of B produces a compound C which has a molecular formula $C_5H_8O_2$. Which of the following structures is that of A ? **[NSEC-2000]**

(A) 

(B) 

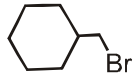
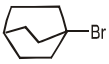
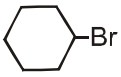
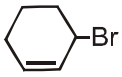
(C) 

(D) 

2. Find the identity of compound B in the following reaction sequence **[NSEC-2000]**
$CH \equiv CNa + CH_3CH_2CH_2CH_2Br \rightarrow A$
$A + Cl_2 \rightarrow B$
1 mol 1 mol
(A) trans-1,2-dichloro-1-hexene (B) cis-1,2-dichloro-1-hexene
(C) cis-1,2-dichlorobutane (D) trans-2,3-dichloro-2-hexene

3. What is the effect of doubling the concentration of HCl on the rate of reaction between t-butyl alcohol and HCl ? **[NSEC-2000]**
(A) It has no effect on the rate of reaction
(B) It halves the rate of reaction
(C) It doubles the rate of reaction
(D) It is not possible to predict its effect on the reaction.

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

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

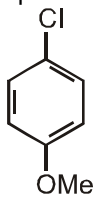
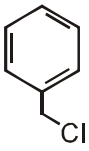
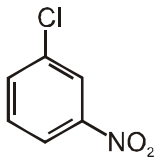
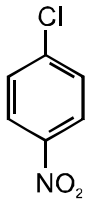
5. The aprotic polar solvent is **[NSEC-2003]**

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

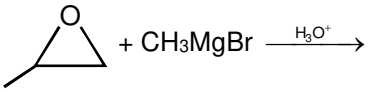
6. The reagent wihch can react with 1-chlorobutane to give substitution reaction is **[NSEC-2003]**

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

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

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

8. The following sequence of reactions give **[NSEC-2004]**

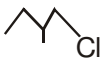
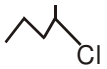


(A) 1-butanol (B) 2-butanol (C) 3,4-hexanediol (D) 3-methyl-3-pentanol.

9. 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.

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

I.  II. CH_3Cl III.  IV. 

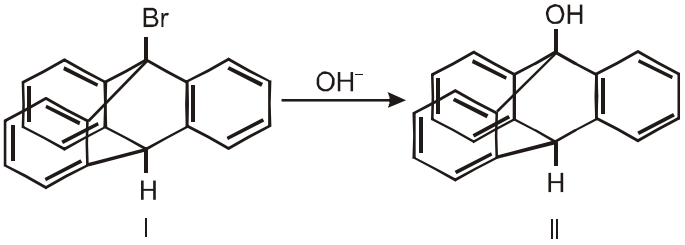
(A) I > II > III >IV (B) VI > II > I > III (C) II > I > III > IV (D) III > II > IV >I.

11. In the reactions given below:

$RCl \xrightarrow{\text{(i) KCN, (ii) } LiAlH_4}$ product A ; $RCl \xrightarrow{\text{(i) AgCN, (ii) } LiAlH_4}$ product B

the compounds A and B are : **[NSEC-2006]**

(A) chain isomers (B) position isomers (C) functional isomers (D) metamers.

12. 

I II

Conversion of I to II : **[NSEC-2006]**

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

13. 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) $CH_2 = CHCH_2Cl$.

14. In the following sequence:

$CH_3CH_2Cl \xrightarrow{NaCN}$ (i)

(i) $\xrightarrow{Ni/H_2}$ (ii)

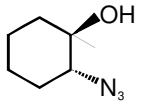
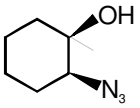
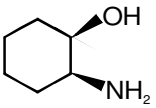
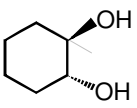
(ii) $\xrightarrow{\text{acetic anhydride}}$ (iii)

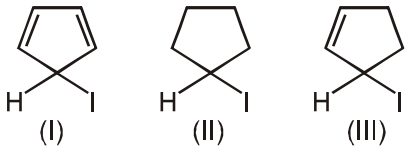
Product (iii) is : **[NSEC-2006]**

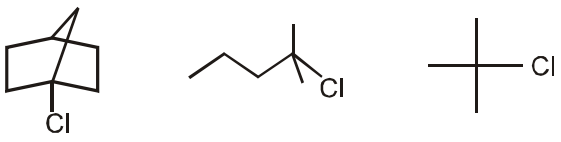
(A) $CH_3CH_2CH_2NH_2$ (B) $CH_3CH_2CH_2CONHCH_3$

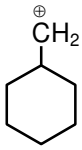
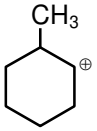
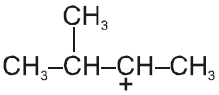
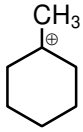
(C) $CH_3CH_2CH_2NHCOCH_3$ (D) $CH_3CH_2CH_2CONHCOCH_3$

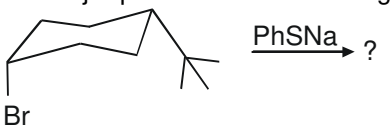
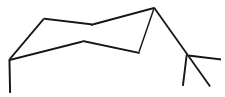
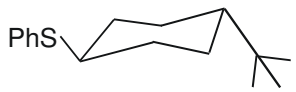
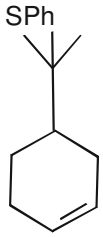
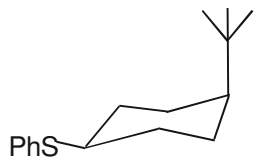
15. The product obtained on reaction of alkyl halide with $AgNO_3$ is **[NSEC-2006]**
(A) alkyl nitrate (B) nitroalkane (C) alkyl nitrite (D) nitrosoalkane.

16. The reaction of cyclohexane epoxide with NaN_3 in aqueous dioxane would give **[NSEC-2006]**
(A)  (B)  (C)  (D) 

17. The order of the rate of formation of carbocations from the following iodo compounds is : **[NSEC-2007]**

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

18. Indicate the order of reactivity of the following compounds in nucleophilic substitution (unimolecular) reaction **[NSEC-2007]**

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

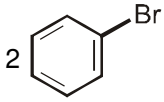
19. Which one of the following carbocations will not rearrange ? **[NSEC-2008]**
(A)  (B) 
(C)  (D) 

20. The major product in the following reaction is : **[NSEC-2008]**

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

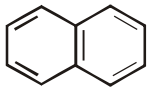
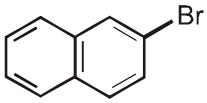
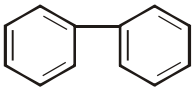
21. S_N1 reactivity of the following halides, **[NSEC-2009]**
(i) $(CH_3)_3CBr$ (ii) $(C_6H_5)_2CHBr$ (iii) $(C_6H_5)_2C(CH_3)Br$ (iv) $(CH_3)_2CHBr$
(A) iv > i > ii > iii (B) ii > i > iii > iv (C) i > iii > ii > iv (D) iii > ii > i > iv

22. The substances used for the preparation of ether by Williamson's synthesis are : **[NSEC-2009]**
(A) $(CH_3)_3CBr$ and CH_3ONa (B) $(CH_3)_3CBr$ and CH_3OH
(C) CH_3Br and $(CH_3)_3CONa$ (D) CH_3Br and $(CH_3)_3COH$

23. The compound A in the reaction is :



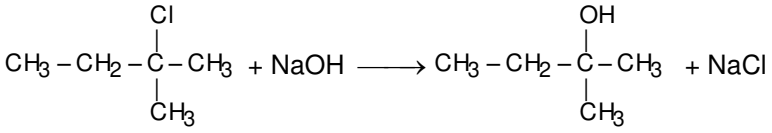
+ 2Na $\xrightarrow{\text{dry ether}}$ A + 2NaBr is : **[NSEC-2009]**

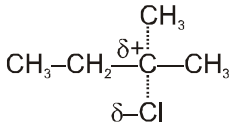
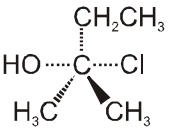
(A)  (B)  (C) 2  (D) 

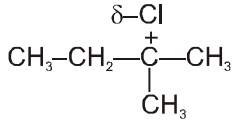
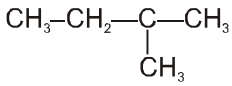
24. Among the following isomeric chloro compounds, the compound which will undergo S_N2 reaction readily is : **[NSEC-2009]**

(A) 4-chloro-1-butene (B) 1-chloro-1-butene (C) 1-chloro-2-butene (D) 2-chloro-1-butene

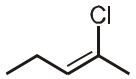
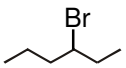
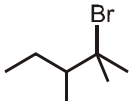
25. The intermediate formed in the following reaction is : **[NSEC-2010]**



(A)  (B) 

(C)  (D) 

26. The compound which would undergo S_N2 reaction fastest is : **[NSEC-2010]**

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

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

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

(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) $CH_3–CH_2–C\equiv C–NH_2$

28. The number of transition state/s and intermediate/s in a unimolecular nucleophilic substitution reaction are respectively- **[NSEC-2010]**

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

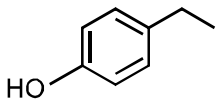
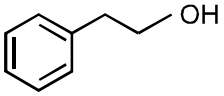
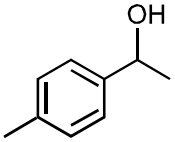
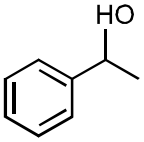
29. Ethyl phenyl ether is treated with conc. HI at 0°C and the rnixture of products is treated with thionyl chloride. The products formed are- **[NSEC-2010]**

(A) Ethanol + Chlorobenzene (B) Phenol + lodoethane

(C) lodoethane + Chlorobenzene (D) Chloroethane + Phenol

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

 + $CH_2=CH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlCl_3}$ A $\xrightarrow[h\nu]{Cl_2\text{(limited)}}$ B $\xrightarrow{\text{aq. NaOH}}$ C

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

31. The order of reactivity of ammonia with the following compound is : **[NSEC-2011]**

(I) CH_2=CHBr (II) CH_3–CH_2–COCl (III) CH_3–CH_2–CH_2–Cl (IV) $C(CH_3)_3C$-Br

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

32. The number of transition states in a unimolecular nucleophilic substitution (S_N1) reaction is **[NSEC-2012]**

(A) 0 (B) 1 (C) 2 (D) 3

33. The sequence of steps involved in aromatic nucleophilic substitution involving a benzyne intermediate is :

(A) Addition-elimination (B) Elimination-addition **[NSEC-2012]**

(C) Addition-rearrangement (D) Elimination-rearrangement

34. Select the most correct statement among the following : **[NSEC-2013]**

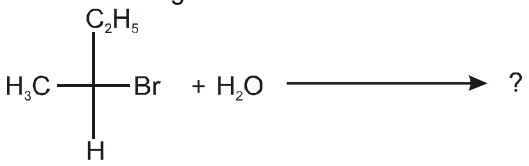
(A) S_N1 mechanism takes place in non-polar solvents

(B) S_N2 mechanism in chiral substrates gives racemic mixtures as products

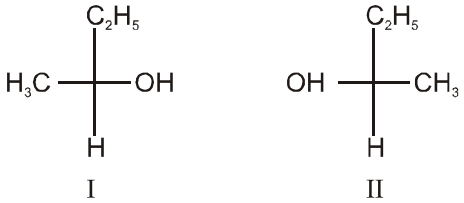
(C) S_N1 mechanism is encouraged by polar solvents

(D) The solvent never influences the mechanism

35. In the reaction given below :



the product obtained will contain : **[NSEC-2013]**



I II

(A) Only Compound I (B) Only Compound II

(C) Both compound I and II (D) this substitution cannot take place

36. The compound which undergoes hydrolysis on just warming with water and forms the corresponding hydroxyl derivative is **[NSEC-2014]**

(A) 2,4,6-trinitrochlorobenzene (B) 2-chloro-1-butene

(C) 2-chloro-2-methylbutane (D) 2, 4-dimethoxychlorobenzene

37. The best sequence of reactions to prepare 2-heptanone is **[NSEC-2014]**

(A) Propyne $\xrightarrow{NaNH_2} X \xrightarrow{n-C_4H_9Br_4} Y \xrightarrow[H_2SO_4]{H_2O,\ Hg^{2+}}$

(B) Ethyne $\xrightarrow{NaNH_2} X \xrightarrow{n-C_5H_{11}Br} Y \xrightarrow[H_2SO_4]{H_2O,\ Hg^{2+}}$

(C) 1-hexyne $\xrightarrow{NaNH_2} X \xrightarrow{CH_3Br} Y \xrightarrow[H_2SO_4]{H_2O,\ Hg^{2+}}$

(D) 1-pentyne $\xrightarrow{NaNH_2} X \xrightarrow{C_2H_5Br} Y \xrightarrow[H_2SO_4]{H_2O,\ Hg^{2+}}$

38. 1-Phenoxypropane is treated with excess of conc. HI at 0°C and the mixture of products is treated with thionyl chloride. The products formed are **[NSEC-2014]**

(A) n-propanol + Chlorobenzene (B) Phenol + n-propyl chloride

(C) n-propyl chloride + Chlorobenzene (D) n-propyl chloride + Phenol

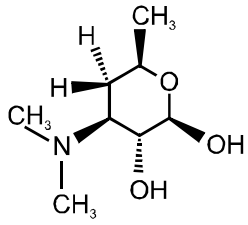
39. (i) chlorobenzene is mono-nitrated to M (ii) nitrobenzene is mono-chlorinated to N

(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: **[NSEC-2014]**

(A) M (B) N (C) P (D) Q

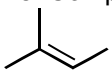
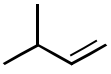
40. Desosamine has the following structure



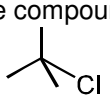
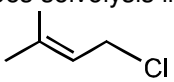
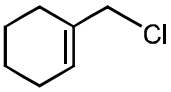
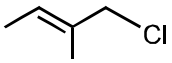
The number of functional groups which react with hydroiodic acid, the number of chiral centers, and the number of stereoisomer's possible respectively are **[NSEC-2015]**

(A) 4, 5, 8 (B) 3, 4, 16 (C) 3, 4, 8 (D) 4, 4, 16

41. Compound "X" reacts with diborane followed by alkaline hydrogen peroxide to form compound "Y". "Y" on reaction with a mixture of sodium bromide in sulphuric acid followed by bromobenzene and sodium in ether gives n-pentylbenzene. Compound "X" is : **[NSEC-2015]**

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

42. The compound that undergoes solvolysis in aq. ethanol most easily is **[NSEC-2015]**

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

43. The best reaction sequence to convert 2-methyl-1-bromopropane into 4-methyl-2-bromopentane is

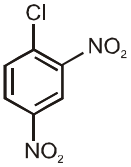
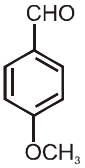
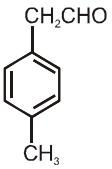
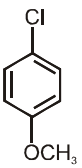
(A) (i) Mg in ether (ii) acetaldehyde (iii) H^+, H_2O (iv) Δ (v) HBr, H_2O_2 **[NSEC-2015]**

(B) (i) NaC≡CH in ether (ii) H_2, Lindlar catalyst (iii) HBr, no peroxide

(C) (i) alcoholic KOH (ii) CH_3COOOH (iii) H_2/Pt (iv) HBr, heat

(D) (i) NaC≡CH in ether (ii) H_3O^+ + $HgSO_4$ (iii) HBr, heat

44. The compound that will NOT react with hot concentrated aqueous alkali at atmospheric pressure is **[NSEC-2015]**

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

45. The appropriate sequence of reactions for obtaining 2-phenylbutanoic acid from benzene is

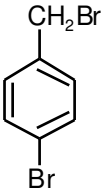
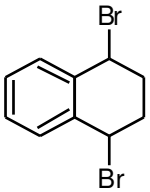
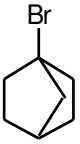
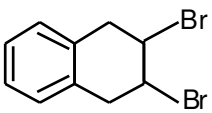
(A) (i) 1-chlorobutane/$AlCl_3$ (ii) limited Cl_2, light (iii) aq NaCN (iv) H^+, H_2O, heat **[NSEC-2015]**

(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

46. The compound that reacts fastest with methylamine is **[NCSE-2016]**

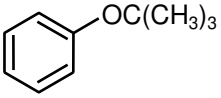
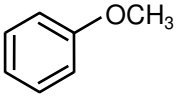
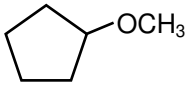
(A)  (B)  (C)  (D) 

47. One mode of 4-nitrocatechol (4-nitro-1,2-dhydroxybenzene) on treatment with an excess of NaH followed by one mole of methyl iodide gives- **[NCSE-2017]**

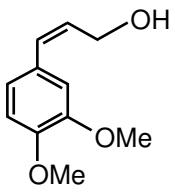
(A) 4-nitro-1, 2-diamethox ybenzene (B) 4-nitro-5methy-1, 2-dimethox ybenzene

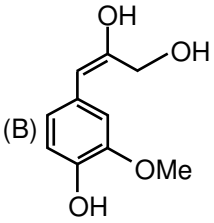
(C) 2-methox y-5 nitrophenol (D) 2-methoxy-4nitrophenol

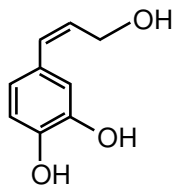
48. Which of the following ethers cannot be prepared by Williamson Synthesis ? **[NCSE-2017]**

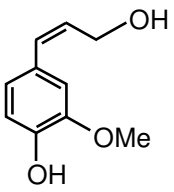
(A)  (B)  (C)  (D) 

49. Coniferyl alcohol is isolated from pine trees. The following observations were made about this alcohol.
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 $C_2H_4O_2$). **[NCSE-2017]**

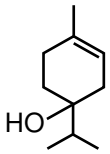
(A) 

(B) 

(C) 

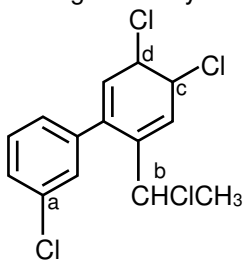
(D) 

50. Terpinen-4-ol is an active ingredient in tea tree oil has the following structure



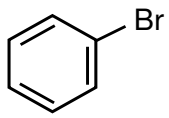
The correct observations for terpinen-4-ol is/are **[NCSE-2017]**
I. It rotates the plane of plane polarized light.
II. It reacts with Baeyer's reagent to form form a triol
III. On reaction with NaBr and H_2SO_4, it gives form a diobromo compound
IV. On ozonolysis it gives a compound with molecular formula $C_{10}H_{18}O_3$
(A) I, II, III and IV (B) I, III and IV (C) II and III (D) III and IV

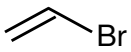
51. The increasing reactivity of the sites (a-d) in the following compound is S_N1 reaction is **[NCSE-2017]**

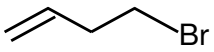


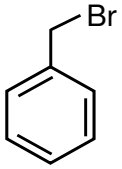
(A) d > b > c > a (B) d > c > a > b (C) d > c > b > a (D) c > d > b > a

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

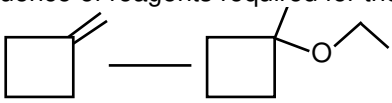
(A) 

(B) 

(C) 

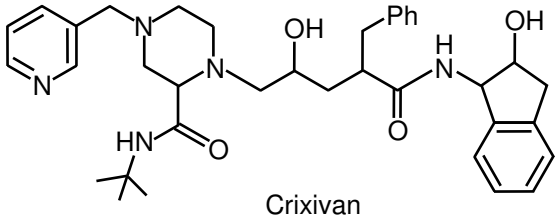
(D) 

53. The sequence of reagents required for the following conversion is **[NCSE-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

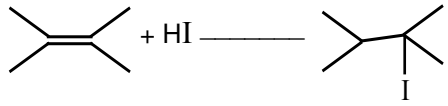
54. The maximum number of moles of CH_3I consumed by one mole of crixivan, a drug against AIDS is

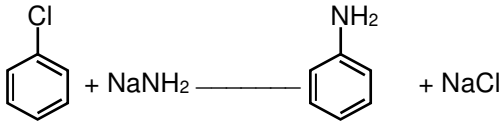


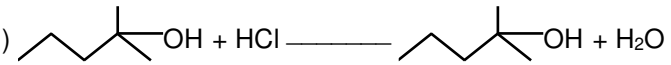
Crixivan **[NCSE-2018]**

(A) 2 (B) 3 (C) 5 (D) 7

55. The reactions from those given below that involve a carbocation intermediate are **[NCSE-2018]**

(i) 

(ii) 

(iii) 

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

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

Max. Time : 1 Hr. **Max. Marks : 66**

Important Instructions

A. General :

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

B. Question Paper Format

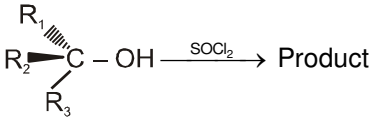
3. Each part consists of five sections.
4. Section-1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section-2 contains 6 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section 3 contains 4 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
7. Section 4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8. Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme

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

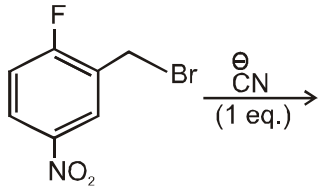
SECTION-1 : (Only One option correct Type)

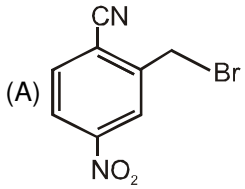
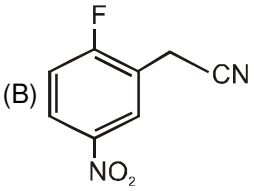
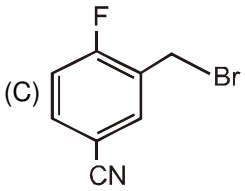
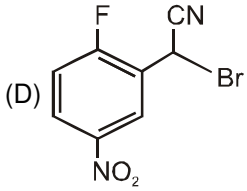
This section contains 8 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

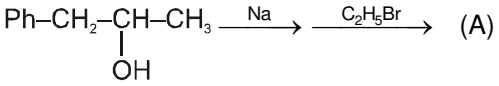
1. 

In the above reaction which phenomenon will take place :

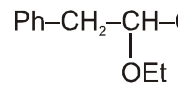
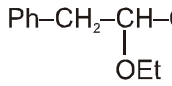
(A) Retention (B) Inversion (C) Racemisation (D) Partial racemisation

2.  A, Product (A) is

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

3. 

Product (A) in above reaction is

(A) 
(B) 
(C) 
(D) $Ph–CH=CH–CH_3$

4. 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

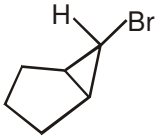
(A) Identical (B) Enantiomer (C) Diastereomer (D) Geometrical isomers

5. Replacement of chlorine from chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced because

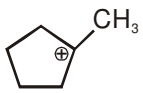
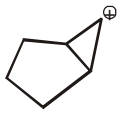
(A) NO_2 makes the ring electron rich at ortho- and para-positions.
(B) NO_2 withdraws electrons at meta position.
(C) NO_2 donates electrons at meta position.
(D) NO_2 withdraws electrons from ortho and para positions.

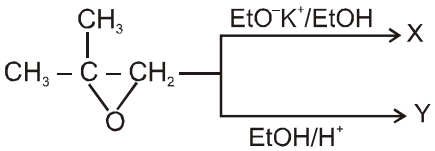
6. Which of the following statement is correct.

(A) Nucleophiles have an unshared electron pair and can make use of this to react with an electron rich species.
(B) $AgNO_3$ increases the rate of solvolysis in S_N1 reaction of alkyl halide.
(C) Inversion of configuration occurs at the carbon undergoing S_N1 reaction.
(D) Aryl halides are more reactive towards nucleophilc substitution reaction as compared to alkyl halide.

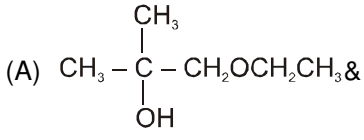
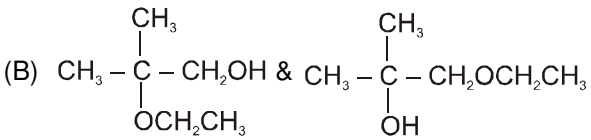
7.  $\xrightarrow{Ag^{\oplus}}$ Rearranged Carbocation + AgBr

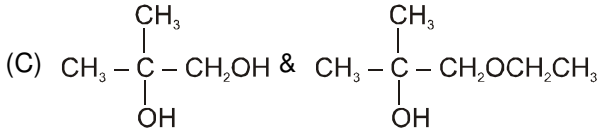
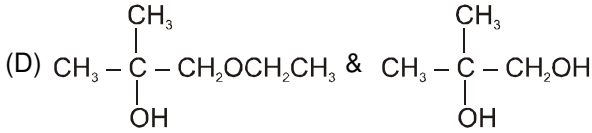
Rearranged carbocation is :

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

8. 

The product X and Y are respectively :

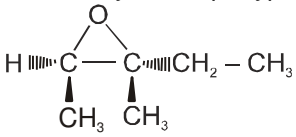
(A)  (B) 

(C)  (D) 

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

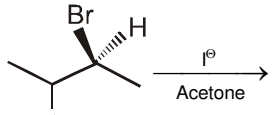
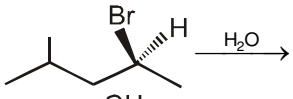
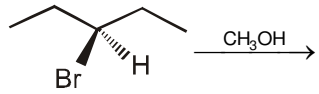
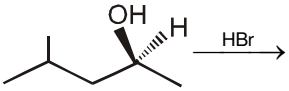
This section contains 6 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

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

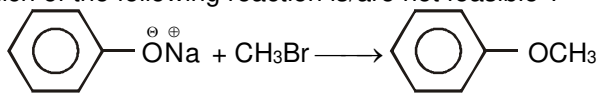
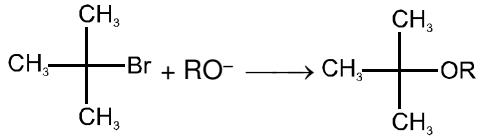
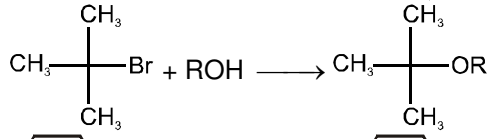
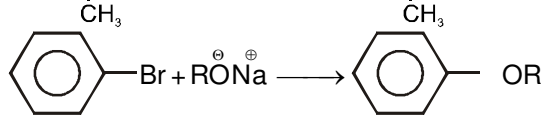
 Cis-3-Methyl-2,3-epoxypentane

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

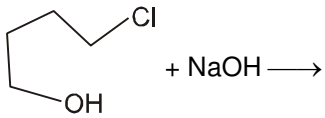
10. Which reaction results in the formation of a pair of enantiomers ?

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

11. Which of the following reaction is/are not feasible ?

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

12. Which of the following reactions take place by S_N2 mechanism :

(A) $CH_3–CH_2–ONa + CH_3–CH_2–Cl \longrightarrow$ (B) 

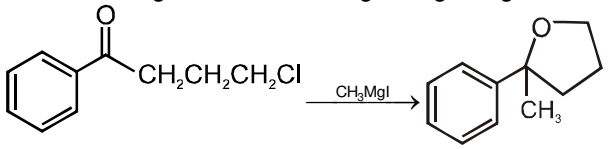
(C) $(CH_3)_3–C–CH_2–CH_2–Br$ + excess $NH_3 \longrightarrow$ (D) $CH_3–CH_2–OH + HBr \longrightarrow$

13. 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"

14. Which of the following is/are correct regarding the given reaction ?

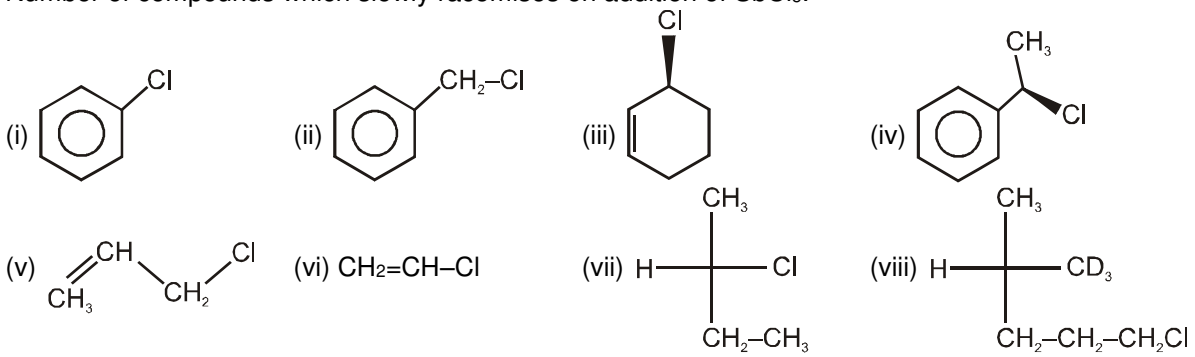


(A) Nucleophilic substitution
(B) Intramolecular nucleophilic attack
(C) Dehydration
(D) Nucleophilic addition

Section-3 : (One Integer Value Correct Type.)

This section contains 4 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

15. Number of compounds which slowly racemises on addition of $SbCl_5$.



16. $C_2H_5-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-Br \xrightarrow{H_2O/\text{Acetone}}$
(E)

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

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

$CH_3–HI–CH_2–\overset{*}{C}HCH_3 \xrightarrow{I^{\ominus}} CH_3–\overset{*}{C}HI–CH_2CH_3$

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

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

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

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

Paragraph for Questions 19 to 21

A kinetic distinction between the operation of S_N1 and S_N2 modes can be made by observing the effect on the overall reaction rate by adding a competing nucleophile. The total nucleophilic concentration is thus increased, so this will result in an increased reaction rate in S_N2 route. By contrast for S_N1 mode, the $[Nu:^{\ominus}]$ will not appear in the rate equation, the addition of competing nucleophile will fails significant effect on the observed reaction rate, though it will naturally influcence the composition of the products.

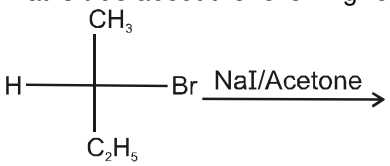
19. In which of the following reactions the overall reaction rate may increase by addition of NaN_3.

(i) $CH_3Cl + NaOH \longrightarrow$ (ii) $(CH_3)_3CCl + H_2O \longrightarrow$

(iii) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-Cl + NaI \longrightarrow$ (iv) $(CH_3)_2CH-OH + NaBr + H_2SO_4 \longrightarrow$

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

20. What is true about the following reaction



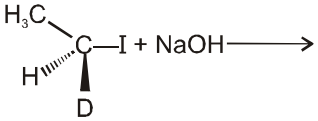
(A) If α–H is displaced by $-CD_3$ group walden inversion will be observed in the product.

(B) If NaN_3 is added the rate of decrease in concentration of reactant will slow down.

(C) On addition of KI the molecularity of reaction will be three.

(D) If KI is added rate of reaction will increase.

21. On addition of NaN_3 in the following reaction, the correct observation will be



$[\alpha] = + x^o$

(A) The rate of formation of alcohol will increase

(B) The rate of disappearance of alkyl halide will increase

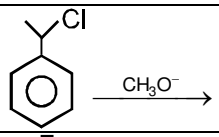
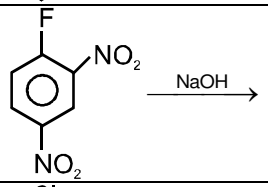
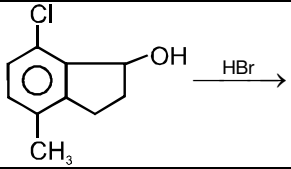
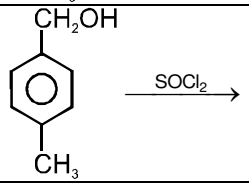
(C) The product alkyl azide will have optical rotation zero.

(D) The product mixture will have optical rotation $-x^o$.

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

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

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

	List I		**List II**
(P)		(1)	S_N1
(Q)		(2)	S_N2
(R)		(3)	S_Ni
(S)		(4)	S_N2 Ar

Codes :
(A) P–4 ; Q–1 ; R–2 ; S–3 (B) P–2 ; Q–1 ; R–3 ; S–4
(C) P–2 ; Q–4 ; R–1 ; S–3 (D) P–4 ; Q–2 ; R–1 ; S–3

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

OBJECTIVE RESPONSE SHEET (ORS)

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

Additional Problems for Self Practice (APSP)

PART - I

1.	(1)	**2.**	(3)	**3.**	(2)	**4.**	(3)	**5.**	(3)
6.	(2)	**7.**	(4)	**8.**	(3)	**9.**	(3)	**10.**	(3)
11.	(3)	**12.**	(3)	**13.**	(2)	**14.**	(4)	**15.**	(3)
16.	(3)	**17.**	(1)	**18.**	(2)	**19.**	(1)	**20.**	(1)
21.	(4)	**22.**	(2)	**23.**	(2)	**24.**	(1)	**25.**	(1)
26.	(4)	**27.**	(1)	**28.**	(3)	**29.**	(3)	**30.**	(4)

PART - II

1.	(B)	**2.**	(A)	**3.**	(A)	**4.**	(D)	**5.**	(C)
6.	(C)	**7.**	(B)	**8.**	(B)	**9.**	(B)	**10.**	(C)
11.	(C)	**12.**	(D)	**13.**	(C)	**14.**	(C)	**15.**	(A)
16.	(A)	**17.**	(C)	**18.**	(B)	**19.**	(D)	**20.**	(B)
21.	(D)	**22.**	(C)	**23.**	(D)	**24.**	(C)	**25.**	(C)
26.	(C)	**27.**	(A)	**28.**	(C)	**29.**	(D)	**30.**	(D)
31.	(B)	**32.**	(C)	**33.**	(B)	**34.**	(C)	**35.**	(C)
36.	(A)	**37.**	(B)	**38.**	(B)	**39.**	(D)	**40.**	(D)
41.	(D)	**42.**	(B)	**43.**	(B)	**44.**	(D)	**45.**	(C)
46.	(A)	**47.**	(D)	**48.**	(B)	**49.**	(D)	**50.**	(A)
51.	(C)	**52.**	(D)	**53.**	(D)	**54.**	(B)	**55.**	(B)

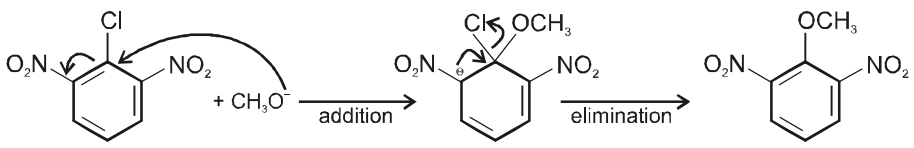
PART - III

1.	(A)	**2.**	(B)	**3.**	(B)	**4.**	(B)	**5.**	(D)
6.	(B)	**7.**	(B)	**8.**	(A)	**9.**	(ABD)	**10.**	(BD)
11.	(BD)	**12.**	(ABCD)	**13.**	(AD)	**14.**	(ABD)		
15.	3 (iii, iv, vii)	**16.**	4	**17.**	98%	**18.**	75%	**19.**	(B)
20.	(D)	**21.**	(B)	**22.**	(C)				

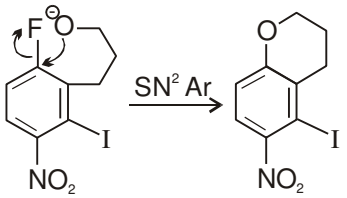
Additional Problems for Self Practice (APSP)

PART - I

1.

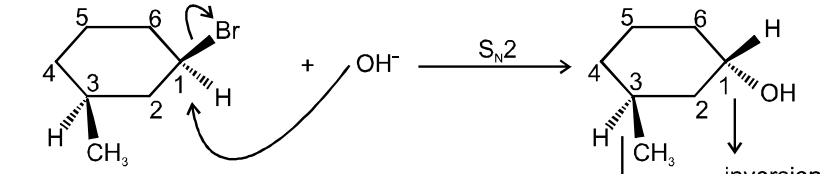


2.



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

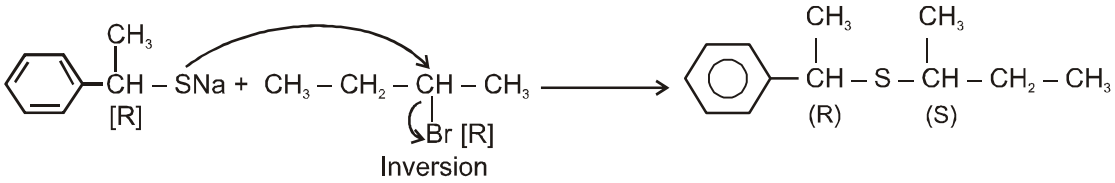
5.



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

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

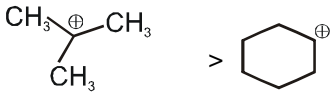
6.



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

8. On the basis of carbocation stability.

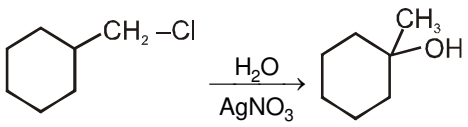
9. Carbocation Stability



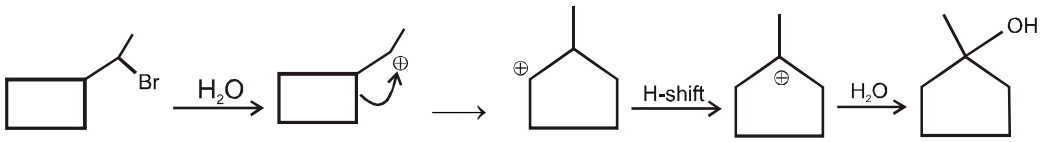
Leaving group ability is $Br^{\ominus} > Cl^{\ominus}$

Over all reaction order $r_1 > r_3 > r_2$

10.



11.



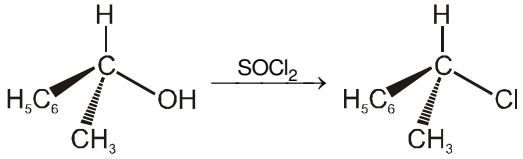
13. 1º R-X gives S_N2 reaction fastest and 3º R-X gives S_N1 reaction fastest.

14. It is a nucleophillc aromatic substitution reaction.

15. Strong anionic Nucleophile so mechanism is S_N2.

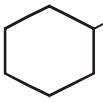
16. Polar aprotic solvent favours S_N2 mechanism.

17.



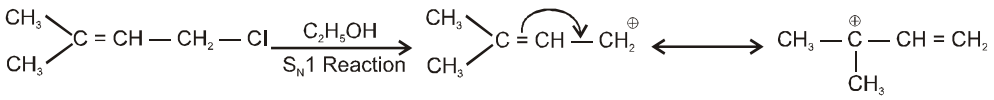
This reaction follows S_Ni mechanism, so retention of configuration takes place.

18. $Cl–CH_2–CH_2–CH_2–CH_2–OH \xrightarrow[-H_2O]{NaOH} Cl–CH_2–CH_2–CH_2–CH_2O^{\ominus}\,Na \longrightarrow$ 

19.  $+ CH_3I \longrightarrow$

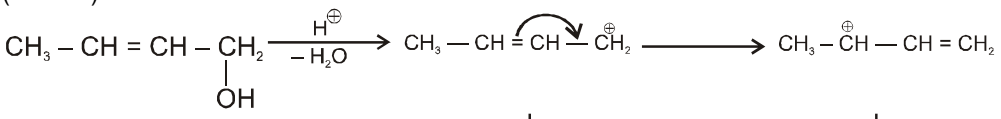
strong anionic nucleophile and 1º alkyl halide favours S_N2 mechansim.

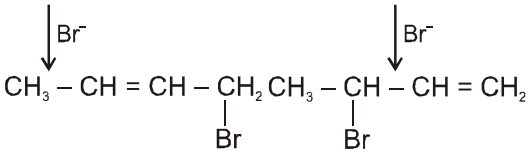
20. $-\overset{\ominus}{O}SO_2CF_3$ is better Leaving group and CH_3OH give S_N1 product as a major product.

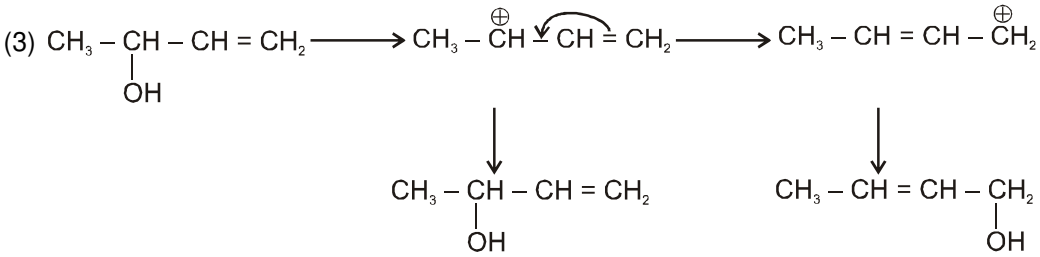
21. (1) 

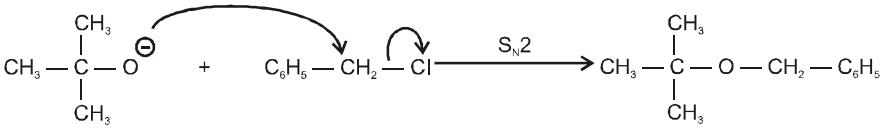
$R—X \xrightarrow{S_N}$ No stable carbocation

(1º R–X)

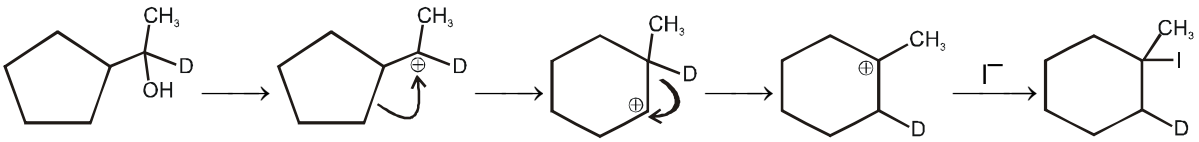
(2) 

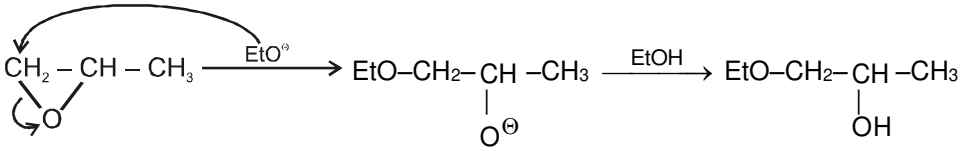


(3) 

22. 

23. Bridge head carbocation is not formed.

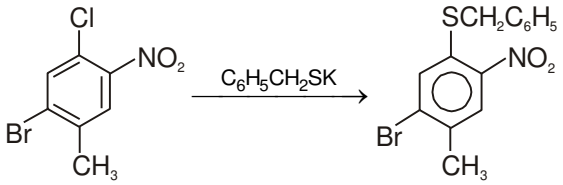
24. 

25. 

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

27. Nucleophilic substitution of alcohol is acid catalysed reaction.

28.

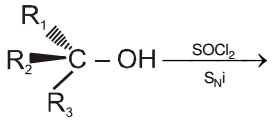


29. Product (B + C) by S_N1 Mech.
Product (D + E) by S_N2 Mech.

30. Because rate of S_N2 Ar is Ar–F > Ar–Cl > Ar–Br > Ar–I.

PART - III

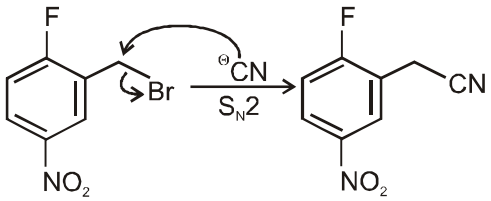
1.



Product (Retention)

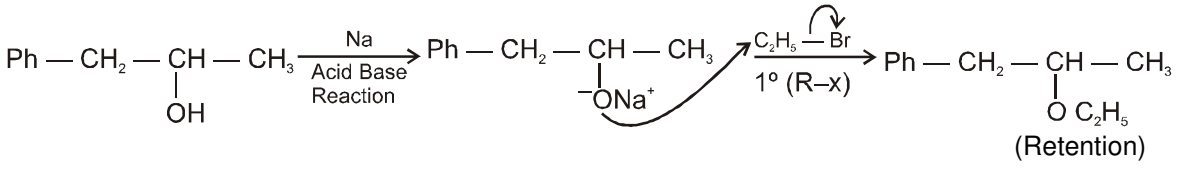
S_Ni Reaction condition follow retention of configuration.

2.



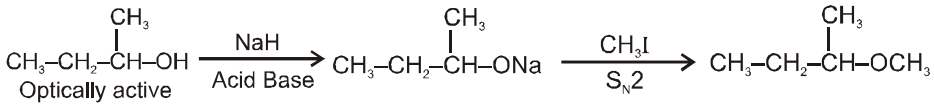
Aromatic halides do not give SN reaction in normal condition.

3.

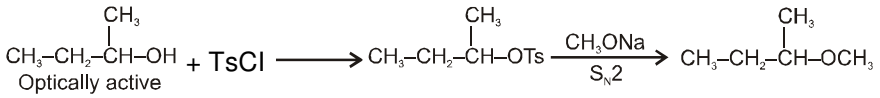


(Retention)

4.



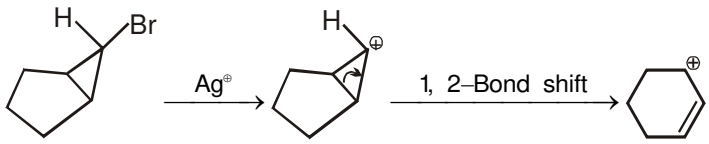
Retention of product.



Inverstion take place.

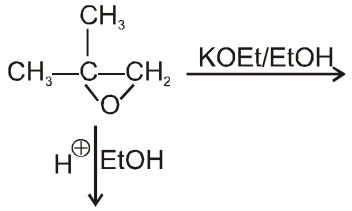
M = Retention product and M′ = inversion product, so they are enantiomers.

7.



(Rearranged carbocation)

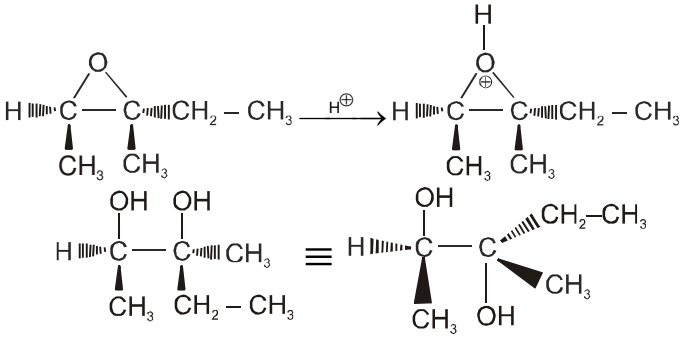
8.



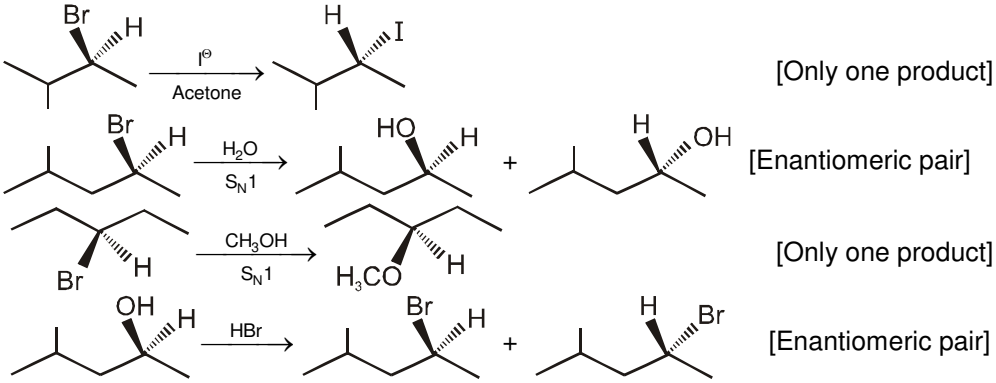
In basic medium S_N2 product $Nu^{\ominus}$ attack from less crowded side.

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

9. (i)



10.



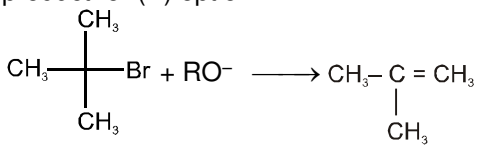
[Only one product]

[Enantiomeric pair]

[Only one product]

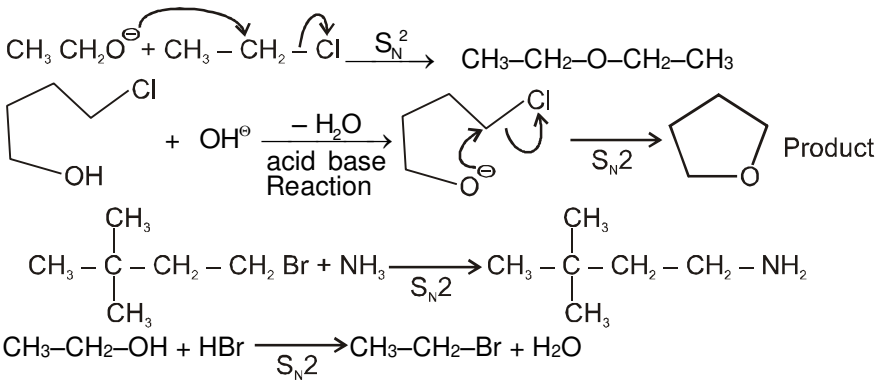
[Enantiomeric pair]

11. Correct product for (B) option.



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

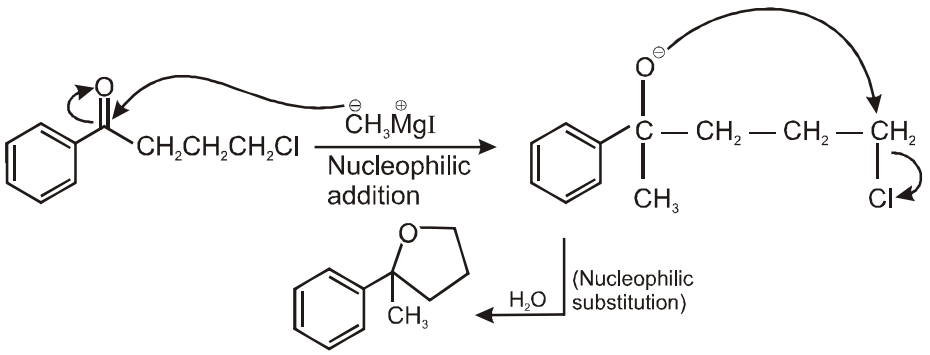
12.



Product

13. Due to steric effect.

14.



16. $C_2H_5-\underset{\underset{(E)}{CH_3}}{C}=CH-CH_2-Br \xrightarrow{H_2O/\text{Acetone}} C_2H_5-\underset{\underset{(E/Z)}{CH_3}}{C}=CH-CH_2-OH + C_2H_5-\underset{\underset{(R/S)}{CH_3}}{\overset{\overset{OH}{|}}{C}}-CH=CH_2$

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

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

% of (–) 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 %

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

Thus % $S_N2 = \left[\frac{S_N2}{S_N2 + S_N1}\right] \times 100 = \left[\frac{6.0 \times 10^{-5}\,[RX][OH^-]}{6.0 \times 10^{-5}\,[RX][OH^-] + 2 \times 10^{-7}[RX]}\right] \times 100 = 75\%$