Exercise-1

✍ **Marked questions are recommended for Revision.**

PART - I : SUBJECTIVE QUESTIONS

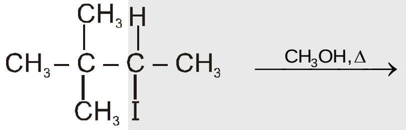
Section (A) : Unimolecular nucleophilic substitution reaction (S_N1)

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.

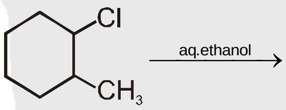
A-2.✍ What effect do you expect due to following changes in S_N1 reaction of $(CH_3)_3CBr$ with CH_3OH ?
(a) The concentration of $(CH_3)_3CBr$ is doubled and that of CH_3OH is halved.
(b) The concentration of both $(CH_3)_3CBr$ and CH_3OH are tripled.

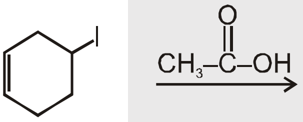
A-3.✍ Why 3-Chlorocyclopropene is solvolyzed in methanol at much higher rate than 5-Chlorocyclopenta-1,3-diene ?

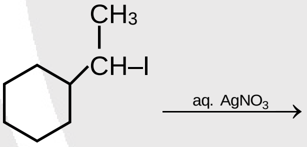
A-4.^✍ For each of the following solvolysis reaction give the products (major as well as minor)

(a) 

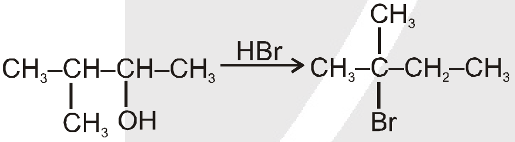
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{I}{C}}-CH_3 \xrightarrow{CH_3OH,\Delta}$

(b) 

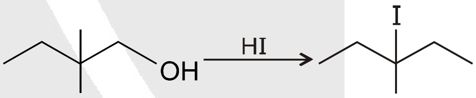
(c) 

(d) 

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

(a) 

$CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_3 \xrightarrow{HBr} CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$

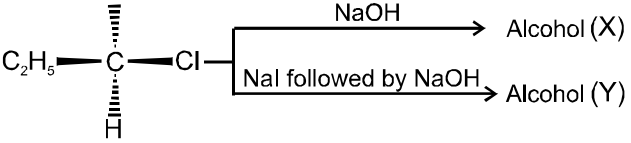
(b) 

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

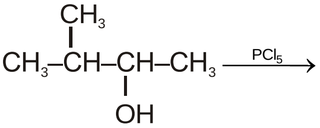
B-1.✍ Arrange the compounds of each set in order of decreasing reactivity towards S_N2 displacement.
(a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
(b) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane

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)

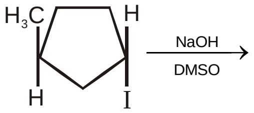
B-3.✍ Work out the stereochemistry of following reaction



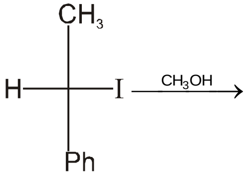
B-4. What will be the major product of the following reaction ?

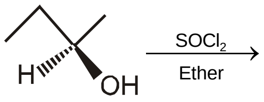
(a) 

$CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_3 \xrightarrow{PCl_5}$

(b) 

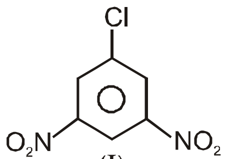
B-5. Write the product of the following reaction with proper stereochemistry.

(a) 

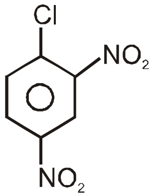
(b) 

Section (C) : Bimolecular aromatic nucleophilic substitution reaction (SN2 Ar)

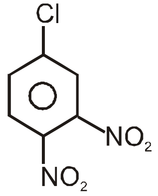
C-1. Write the correct reactivity order with NaOH for the following compounds.



(I)

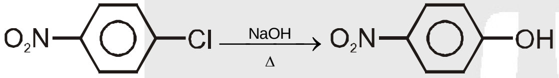


(II)

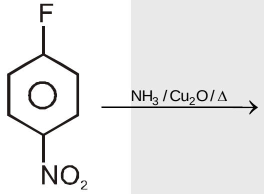


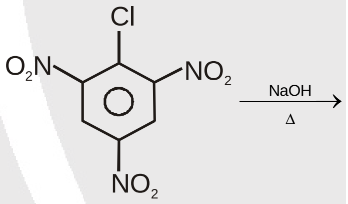
(III)

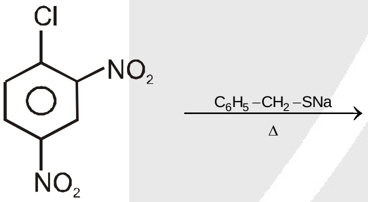
C-2. Write the mechanism of following reaction :

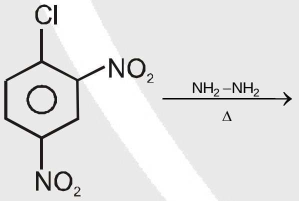


C-3. Give the products in following reactions :

(a) 

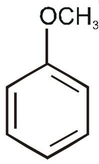
(b) 

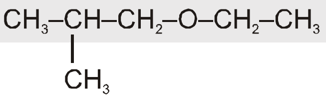
(c) 

(d) 

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

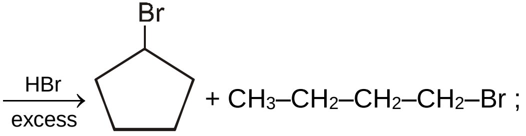
D-1. Predict the product of the following reactions using one equivalent of HI.

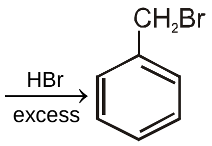
(a) 

(b) 

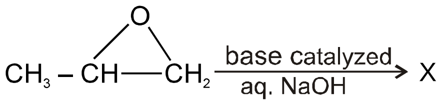
$CH_3–\underset{\displaystyle CH_3}{\underset{|}{C}H}–CH_2–O–CH_2–CH_3$

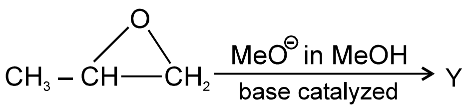
D-2. Few dialkyl ethers & cyclic ethers were allowed to react with excess of HBr with the following results. Identify the ether in each case.

(P) 

(Q) 

D-3. Give the products of the following reactions

(i) 

(ii) 

PART - II : ONLY ONE OPTION CORRECT TYPE

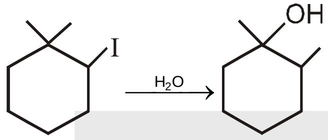
Section (A) : Unimolecular nucleophilic substitution reaction (S_N1)

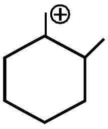
A-1. S_N1 reaction occurs through the formation of intermediate :
(A) Carbocation (B) Carbanion (C) Free radical (D) Carbene

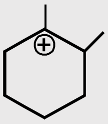
A-2.^✍ In an S_N1 reaction, the configuration of the product undergoes :
(A) inversion (B) racemization (C) retention (D) None of these

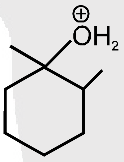
A-3.✍ When the concentration of alkyl halide is doubled and the amount of H_2O taken as solvent is reduced to half, the rate of S_N1 reaction increases by:
(A) 3 times (B) 2 times (C) 1.5 times (D) 6 times

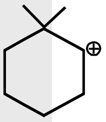
A-4.✍ Which of the following is not expected to be intermediate of the following reaction ?



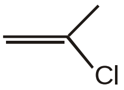
(A) 

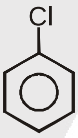
(B) 

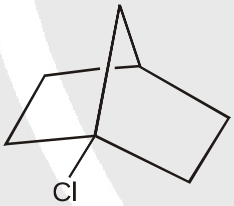
(C) 

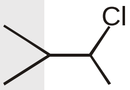
(D) 

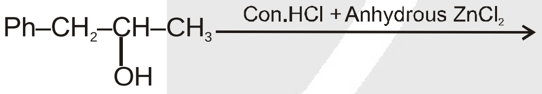
A-5. Which of the following compound can show S_N1 reaction :

(A) 

(B) 

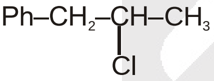
(C) 

(D) 

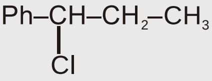
A-6. 

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

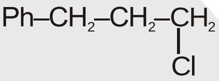
X is :

(A) 

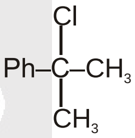
$Ph{-}CH_2{-}\underset{Cl}{CH}{-}CH_3$

(B) 

$Ph{-}\underset{Cl}{CH}{-}CH_2{-}CH_3$

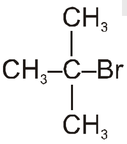
(C) 

$Ph{-}CH_2{-}CH_2{-}\underset{Cl}{CH_2}$

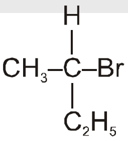
(D) 

$Ph{-}\overset{Cl}{\underset{CH_3}{C}}{-}CH_3$

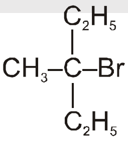
A-7.✍ Which one of the following compound will give (d) and (ℓ) form in S_N1 reaction (as major product)

(A) 

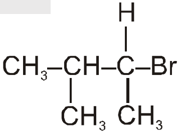
$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Br$

(B) 

$CH_3{-}\overset{H}{\underset{C_2H_5}{C}}{-}Br$

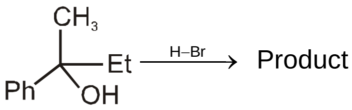
(C) 

$CH_3{-}\overset{C_2H_5}{\underset{C_2H_5}{C}}{-}Br$

(D) 

$CH_3{-}\underset{CH_3}{CH}{-}\overset{H}{\underset{CH_3}{C}}{-}Br$

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



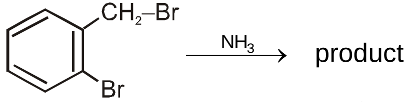
(A) Inversion of configuration occurs at the carbon undergoing substitution.
(B) Retention of configuration occurs at the carbon undergoing substitution.
(C) Racemization occurs at the carbon undergoing substitution.
(D) The carbon undergoing substitution is not stereogenic.

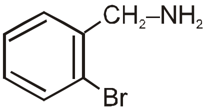
Section (B) : Bimolecular nucleophilic substitution reaction (S_N2 & S_Ni)

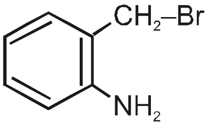
B-1. S_N2 mechanism proceeds through intervention of :
(A) Carbonium ion (B) Transition state (C) Free radical (D) Carbanion

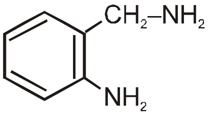
B-2. In S_N2 reaction if we doubled the concentration of reactant and nucleophile the rate of S_N2 reaction increases by :
(A) 2 times (B) 4 times (C) 8 times (D) No change

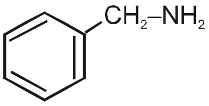
B-3. What is the major product obtained in the following reaction ?



(A) 

(B) 

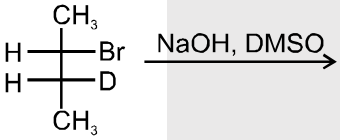
(C) 

(D) 

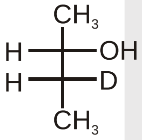
B-4. Identify the reactants (X) and (Y) for the following reaction, respectively.

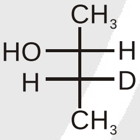
$$\underset{\text{Alkyl halide}}{(X)} + \underset{\text{Alkyne}}{(Y)} \xrightarrow{NaNH_2} \text{4-Decyne}$$

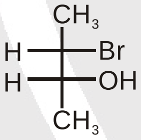
(A) $CH_3(CH_2)_4CH_2–Cl + CH_3–C{\equiv}CH$ (B) $CH_3(CH_2)_2CH_2–Cl + CH_3–(CH_2)_2–C{\equiv}CH$
(C) $CH_3(CH_2)_2CH_2–Cl + CH_3(CH_2)_3–C{\equiv}CH$ (D) $CH_3–CH_2–CH_2–Cl + CH_3(CH_2)_4–C{\equiv}CH$

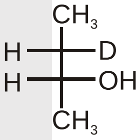
B-5. 

Product, Product is :

(A) 

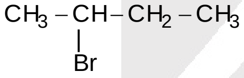
(B) 

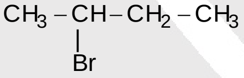
(C) 

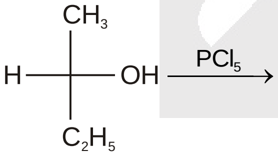
(D) 

B-6. $$\underset{\text{1-butanol}}{CH_3(CH_2)_2CH_2OH} \xrightarrow{HBr} X,$$

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)  $\underset{\displaystyle Br}{CH_3-\underset{|}{CH}-CH_2-CH_3}$ & S_N1

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

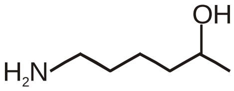
B-7. 

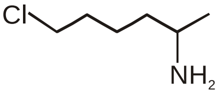
X ; (X) is

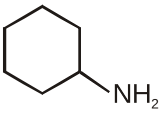
(D-2-Butanol)

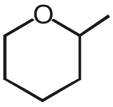
(A) S-2-Chlorobutane
(B) R-2-Chlorobutane
(C) Mixture of R and S, 2-Chlorobutane
(D) 1-Chlorobutane

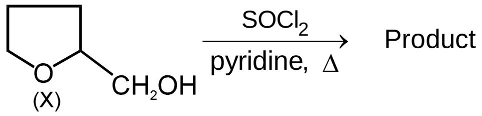
B-8. 6-Chlorohexan-2-ol $\xrightarrow[\Delta]{NaNH_2}$ major product is

(A) 

(B) 

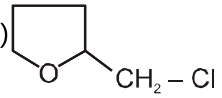
(C) 

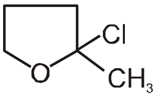
(D) 

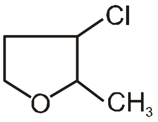
B-9. 

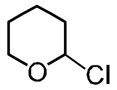
(X)

Product of the above reaction is :

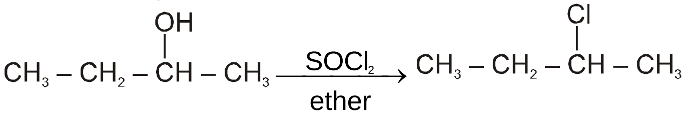
(A) 

(B) 

(C) 

(D) 

B-10. Consider the following reaction.



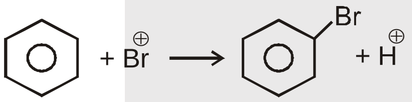
$$CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow[\text{ether}]{SOCl_2} CH_3-CH_2-\overset{Cl}{\overset{|}{CH}}-CH_3$$

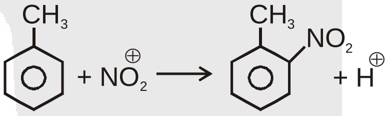
In the above reaction which phenomenon will take place :

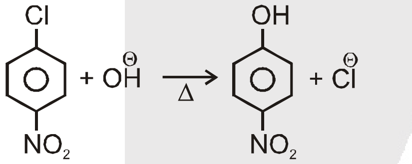
(A) Inversion (B) Retention (C) Racemisation (D) Isomerisation

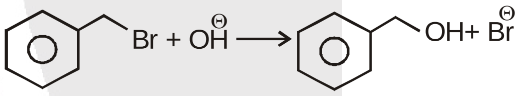
Section (C) : Bimolecular aromatic nucleophilic substitution reaction (SN2 Ar)

C-1. Which of the following reaction is SN2Ar reaction ?

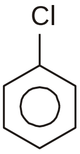
(A) 

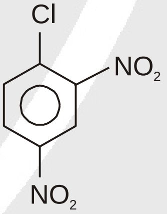
(B) 

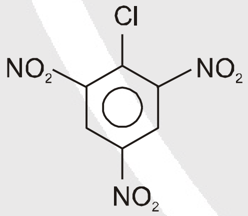
(C) 

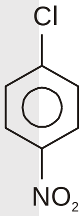
(D) 

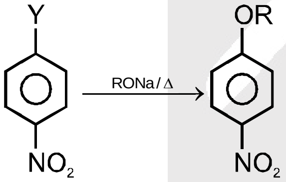
C-2. Which of the following compound gives fastest SN2 Ar reaction ?

(A) 

(B) 

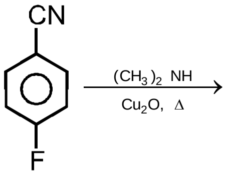
(C) 

(D) 

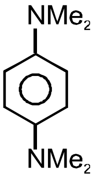
C-3. 

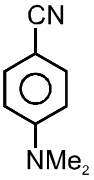
Above reaction has maximum rate when :

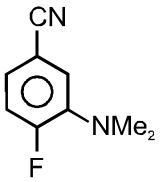
(A) Y = – I (B) Y = – Br (C) Y = – Cl (D) Y = – F

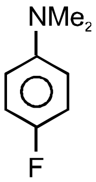
C-4. 

The product is :

(A) 

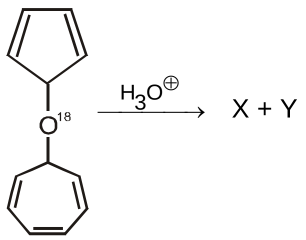
(B) 

(C) 

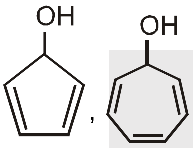
(D) 

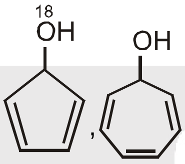
Section (D) : Nucleophilic substitution reaction of Ethers & Epoxides

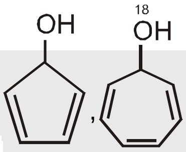
D-1. In the given reaction, $CH_3-CH_2-CH_2-O-CH_2-CH_3 \xrightarrow{HCl/\Delta} [X] + [Y]$
[X] and [Y] respectively will be :
(A) $CH_3-CH_2-CH_2OH$ & CH_3-CH_2-Cl (B) $CH_3-CH_2-CH_2-Cl$ & CH_3-CH_2-OH
(C) $CH_3-CH_2-CH_2-Cl$ & $CH_2=CH_2$ (D) $CH_3-CH=CH_2$ & $CH_2=CH_2$

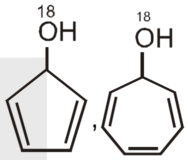
D-2. 

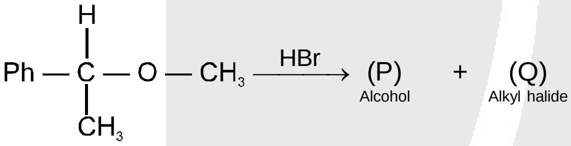
The products X and Y are

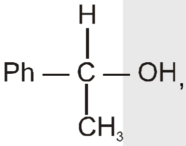
(A) 

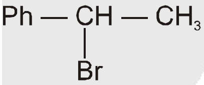
(B) 

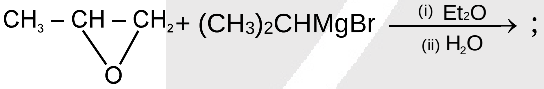
(C) 

(D) 

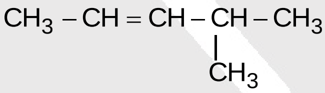
D-3. 
$\mathrm{Ph-\underset{CH_3}{\overset{H}{C}}-O-CH_3} \xrightarrow{HBr} \underset{\text{Alcohol}}{(P)} + \underset{\text{Alkyl halide}}{(Q)}$; (P) & (Q) respectively is :

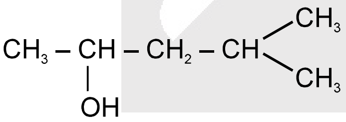
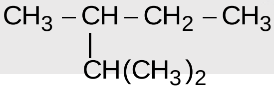
(A) 
$\mathrm{Ph-\underset{CH_3}{\overset{H}{C}}-OH}$, CH_3-Br (B) $Ph-CH_2-OH$, CH_3-CH_2-Br

(C) CH_3-OH, 
$\mathrm{Ph-\underset{Br}{CH}-CH_3}$ (D) CH_3-OH, $Ph-CH_3-CH_2-Br$

D-4. 

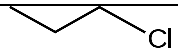
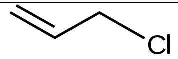
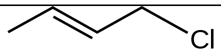
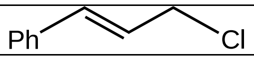
; What will be the product :

(A) $CH_3-(CH_2)_4-CH_2-OH$ (B) 
$\mathrm{CH_3-CH=CH-\underset{CH_3}{CH}-CH_3}$

(C) 
$\mathrm{CH_3-\underset{OH}{CH}-CH_2-CH(CH_3)_2}$ (D) 
$\mathrm{CH_3-\underset{CH(CH_3)_2}{CH}-CH_2-CH_3}$

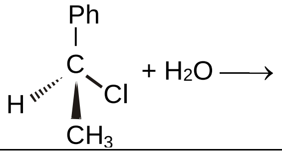
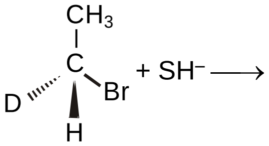
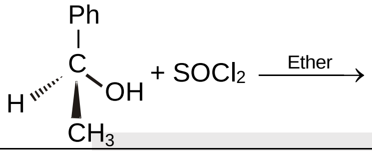
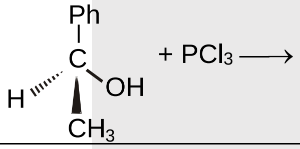
PART - III : MATCH THE COLUMN

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 :

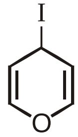
	Column-I		Column-II
	Substrate		**Stereochemistry of product**
(A)		(p)	Retention
(B)		(q)	Racemisation
(C)		(r)	Inversion
(D)		(s)	Intermediate is carbocation

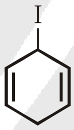
Exercise-2

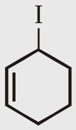
✍ **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

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

(i) 

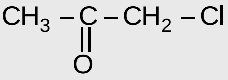
(ii) 

(iii) 

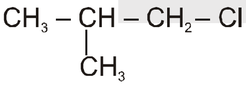
(A) ii > iii > i (B) i > ii > iii (C) iii < ii < i (D) i > iii > ii

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

(I) $CH_3–Cl$

(II) 

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-Cl$

(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

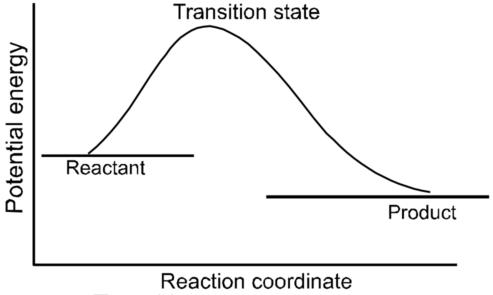
(B) inversion more than retention leading to partial racemization

(C) 100 % retention

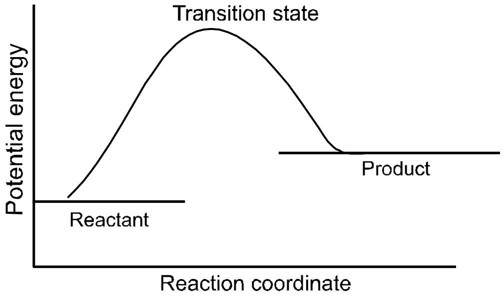
(D) 100 % inversion

4.✍ Following are the curves for nucleophilic substitution reaction.

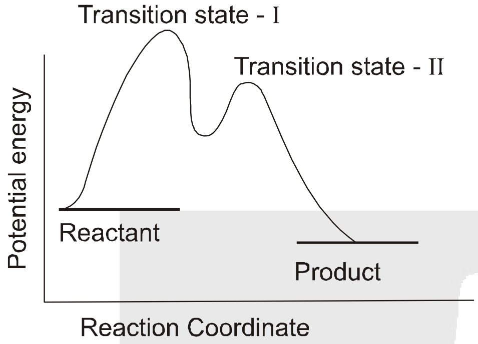
(I)



(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

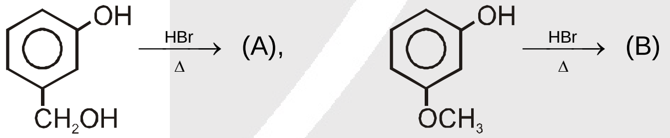
(D) All of the above

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

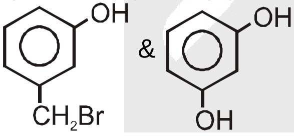
(C) The inductive effect (D) sp^2–hybridized carbon attached to the halogen

6.✍

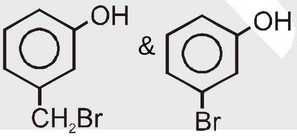


The product (A) and (B) are respectively :

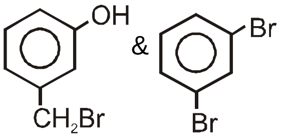
(A)



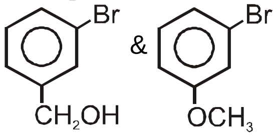
(B)



(C)



(D)



7.✍ S_N1 reaction underoges through a carbocation intermediate as follows :

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

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

The correct statements are

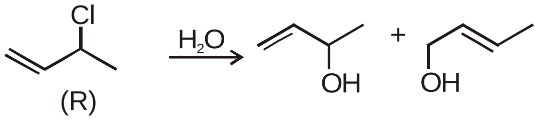
I. The decreasing order of rate of S_N1 reaction is t-BuX > iso-PrX > EtX > MeX

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.✍

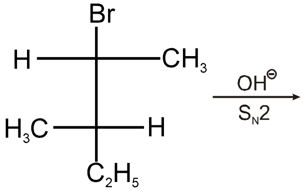


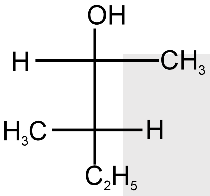
(R)
optically active

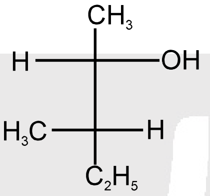
What is correct for the above reaction :

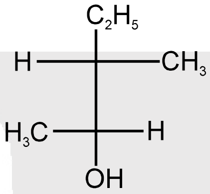
(A) Total three products are formed.
(B) Products mixture is optically active.
(C) Total two products are chiral.
(D) Intermediate carbocation is not formed in the reaction.

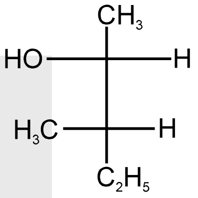
9.✍ In the following reaction the most probable product will be :



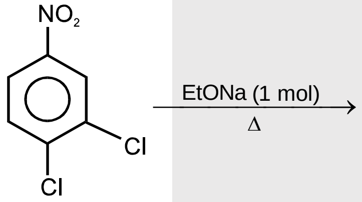
(A)


(B)


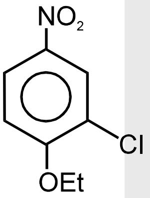
(C)


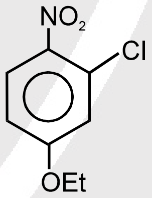
(D)


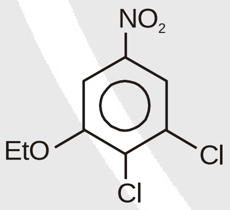
10.✍

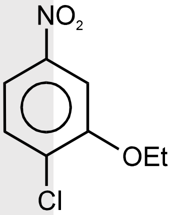


The product is :

(A)


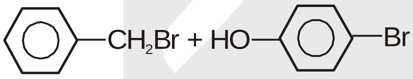
(B)


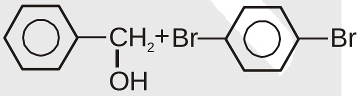
(C)


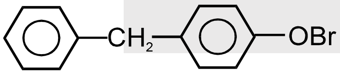
(D)


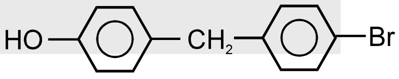
11.

product is -

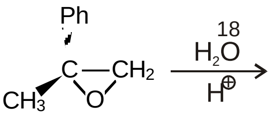
(A)


(B)


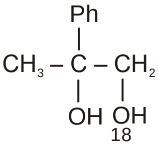
(C)


(D)


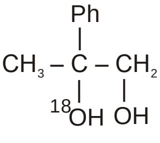
12.



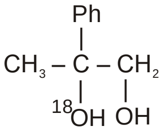
, The major product is

(A)


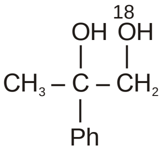
$CH_3-\overset{Ph}{\underset{OH}{C}}-\underset{\overset{}{O}H_{18}}{CH_2}$ with retention, optically active

(B)


$CH_3-\overset{Ph}{\underset{^{18}OH}{C}}-\underset{OH}{CH_2}$ with racemisation

(C)


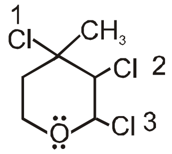
$CH_3-\overset{Ph}{\underset{^{18}OH}{C}}-\underset{OH}{CH_2}$ with inversion, optically active

(D)


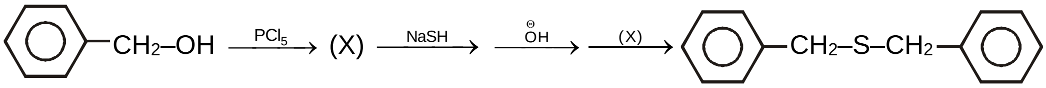
$CH_3-\overset{OH}{\underset{Ph}{C}}-\overset{\overset{18}{O}H}{CH_2}$ with racemisation

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. The most reactive chlorine towards H_2O is :

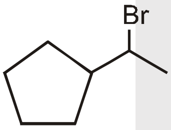


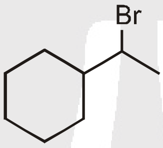
2. When the concentration of alkyl halide is tripled and the concentration of $\overset{\ominus}{OH}$ ion is reduced to half, the rate of S_N2 reaction increases by X times. Report your answer as 10 X.

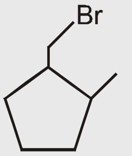
3.✍ 

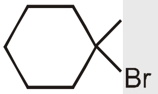
The number of times where S_N2 reaction taken place in above reaction sequence is

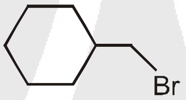
4. Among the 6, how many cyclic isomers of molecular formula $C_7H_{13}Br$ can form 1-methylcyclohexane-1-ol on reaction with H_2O/acetone/Ag^+.

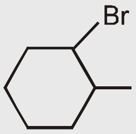
(i) 

(ii) 

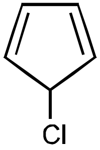
(iii) 

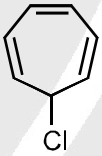
(iv) 

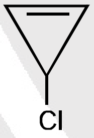
(v) 

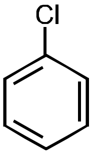
(vi) 

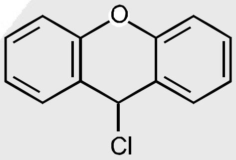
5.✍ How many of the following compounds will give white precipitate with aqueous $AgNO_3$.

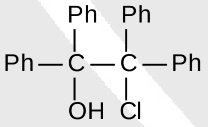
(i) 

(ii) 

(iii) 

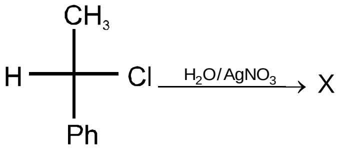
(iv) 

(v) 

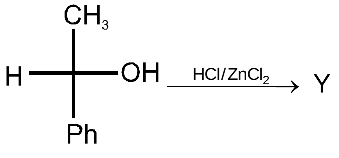
(vi) 

$Ph\text{—}\underset{OH}{\overset{Ph}{C}}\text{—}\underset{Cl}{\overset{Ph}{C}}\text{—}Ph$

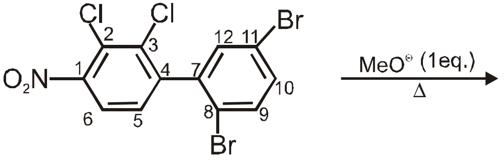
6.✍ Find the total number of isomeric products obtained in these reactions. Report your answer as $\boxed{X}\boxed{Y}$:



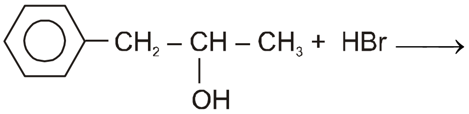
;



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



8.

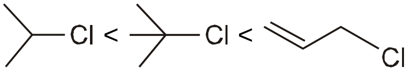


Number of possible isomeric products including stereoisomers will be :

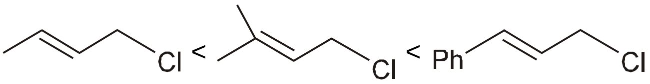
PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

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

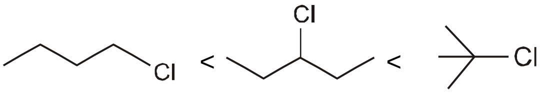
(A)



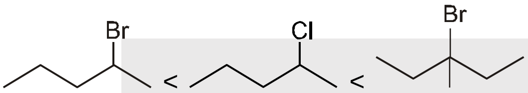
(B)



(C)

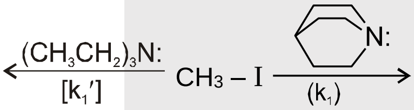


(D)

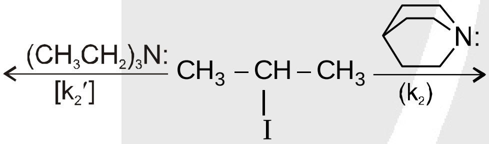


2. Observe the following reaction I and II $k_1 k_1'$, $k_2 k_2'$ are rate constants. Select the correct option(s).

(I)

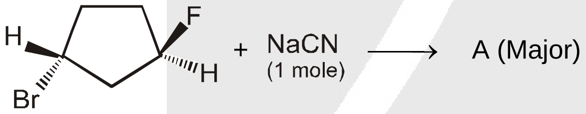


(II)



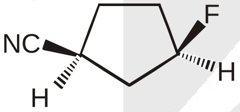
(A) $k_1 > k_1'$ (B) $k_1 > k_2$ (C) $k_2' > k_2$ (D) $k_2' > k_1'$

3.

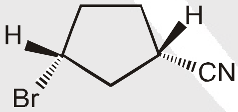


major product of this reaction is.

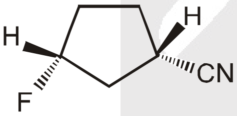
(A)



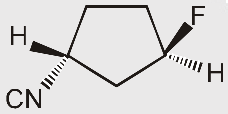
(B)



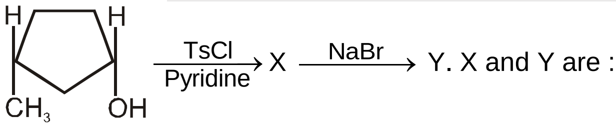
(C)



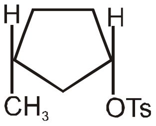
(D)



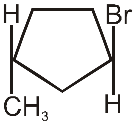
4.



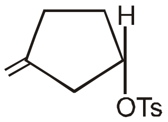
(A) X =



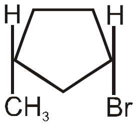
(B) Y =



(C) X =



(D) Y =

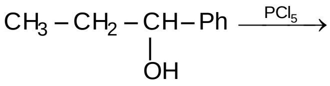


5.* Which of the following conditions are favour for S_N2 mechanism in alkyl halides ?

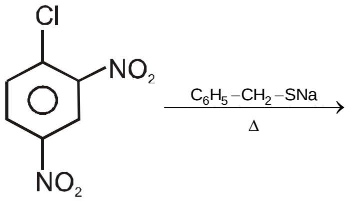
(A) Strong nucleophile (B) High conc. of nucleophile

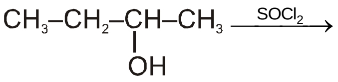
(C) 3° alkyl halide (D) Polar protic solvent

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

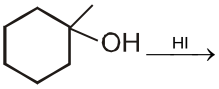
(A) 

$CH_3-CH_2-\underset{OH}{CH}-Ph \xrightarrow{PCl_5}$

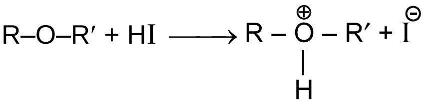
(B) 

(C) 

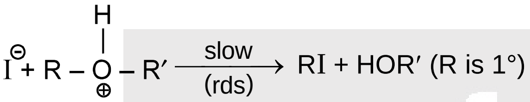
$CH_3-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{SOCl_2}$

(D) 

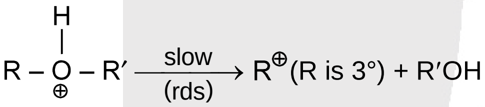
7. Identify correct steps representing S_N1 mechanism for the cleavage of ether with HI



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

(A) 

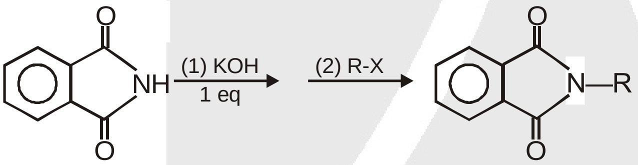
$I^{\ominus} + R-\underset{\oplus}{\overset{H}{O}}-R' \xrightarrow[\text{(rds)}]{\text{slow}} RI + HOR'$ (R is 1°)

(B) 

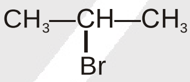
$R-\underset{\oplus}{\overset{H}{O}}-R' \xrightarrow[\text{(rds)}]{\text{slow}} R^{\oplus}$(R is 3°) + $R'OH$

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

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

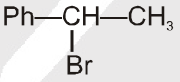
8.✍ 

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

(A) $CH_3–CH_2–Br <$ 

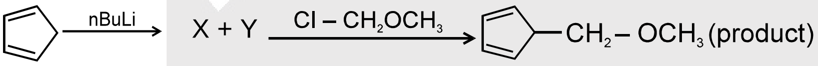
$CH_3-\underset{Br}{CH}-CH_3$

(B) $Ph–Cl > CH_3–Cl$

(C) $Ph–CH_2–Br >$ 

$Ph-\underset{Br}{CH}-CH_3$

(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

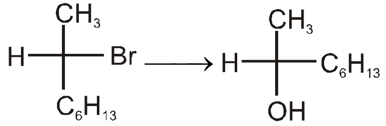
Read the following passage carefully and answer the questions.

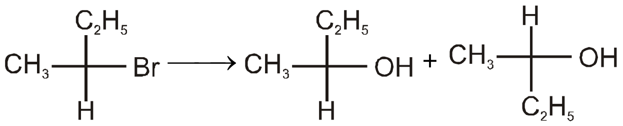
Comprehension # 1

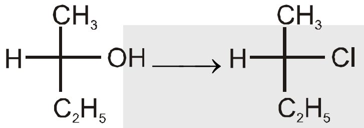
One of the most interesting and useful aspects of stereochemistry is the study of what happens to optically acitive molecules when they react. The product isolated from the reaction of the chiral material can tell us a great deal about the reaction mechanism. We observe

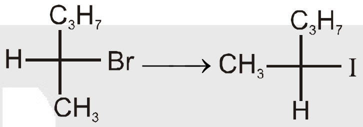
$S_N2 \longrightarrow$ Inversion of configuration
$S_N1 \longrightarrow$ Racemisation
$S_Ni \longrightarrow$ Retention of configuration

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

(I)


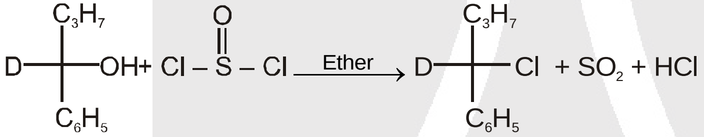
(II)


(III)


(IV)


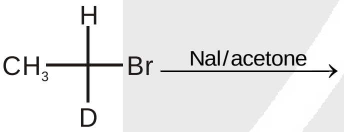
(A) S_N2, S_N1, S_N2, S_Ni (B) S_N2, S_N1, S_Ni, S_N2
(C) S_N1, S_N2, S_Ni, S_N1 (D) S_N2, S_Ni, S_N1, S_N2

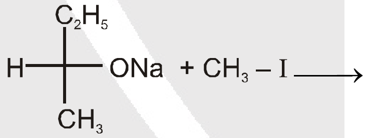
2. The given reaction is an example of which type of mechanism ?

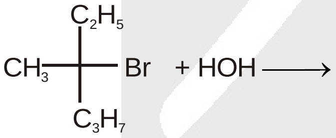


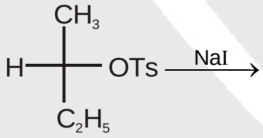
(A) S_N2 (B) S_N1 (C) S_Ni (D) None

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

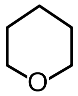
(A)


(B)


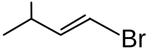
(C)


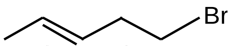
(D)


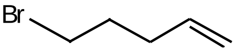
Comprehension # 2

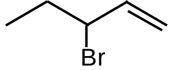
An organic compound 'A' has molecular formula C_5H_9Br decolorises brown colour of bromine water but does not rotate plane polarised light. 'A' on treatment with HBr/ROOR forms $C_5H_{10}Br_2$ which on further treatment with NaOH(aq) gives the cyclic ether


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

(A)


(B)


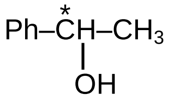
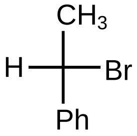
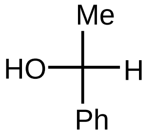
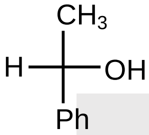
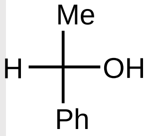
(C)


(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)	 $\underset{\text{OH}}{\text{Ph–}\overset{*}{\text{C}}\text{H–CH}_3}$ (±)
(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

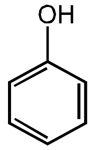
2. The compound that will react most readily with NaOH to form methanol is : **[IIT-JEE-2001(S), 1/135]**
(A) $(CH_3)_4N^+I^-$ (B) CH_3OCH_3 (C) $(CH_3)_3S^+I^-$ (D) $(CH_3)_3C$–Cl

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.

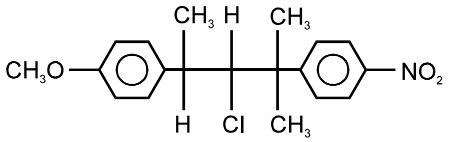
$$CH_3CH_2C{\equiv}C–H \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} X \xrightarrow{H_2\ /\ Pd\ .\ BaSO_4} Y \xrightarrow{\text{alkaline } KMnO_4} Z$$

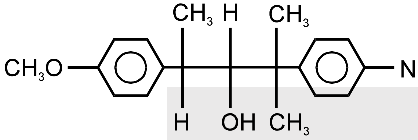
Is the compound Z optically active ? Justify your answer. **[IIT-JEE-2002(M), 5/150]**

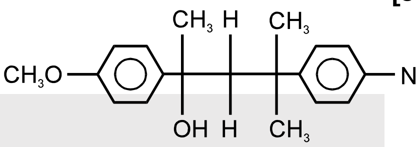
5.  + C_2H_5I $\xrightarrow[\text{Anhydrous}(C_2H_5OH)]{\overset{-}{O}C_2H_5\ \text{(excess)}}$ product, major product is **[JEE-2003(S), 3/144]**

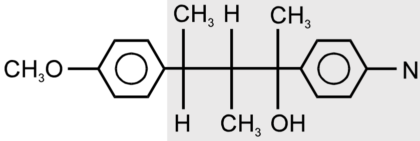
(A) $C_6H_5OC_2H_5$ (B) $C_2H_5OC_2H_5$ (C) $C_6H_5OC_6H_5$ (D) C_6H_5I

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]**

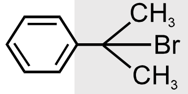

(K)

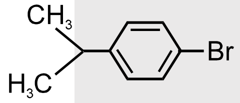

(L)

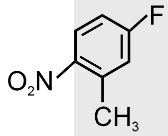
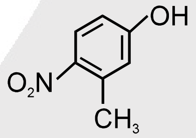

(M)

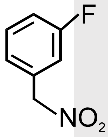
(A) K, L (B) K, M (C) L only (D) M only

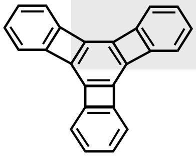
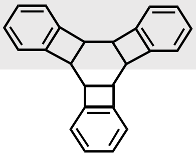
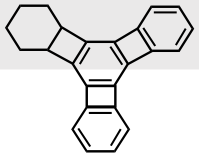
8. Explain the following observations : **[JEE 2005(M), 4/144]**

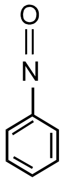
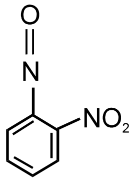
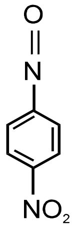
(A)  $\xrightarrow{\text{aqueous } C_2H_5OH}$ Acidic solution

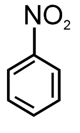
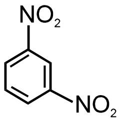
 $\xrightarrow{\text{aqueous } C_2H_5OH}$ Neutral solution

(B)  $\xrightarrow{OH^{\ominus}}$  + F^-

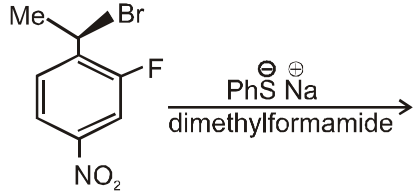
 $\xrightarrow{OH^{\ominus}}$ No release of F^-

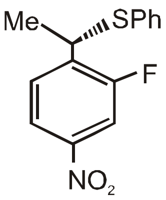
(C)  $\xrightarrow{3H_2\,/\,Pd/C}$  but not 

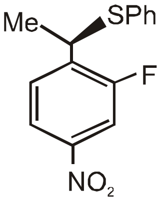
(D)  $\xrightarrow{\text{conc. } H_2SO_4 + \text{conc.}HNO_3}$  + 

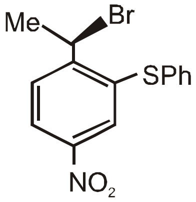
 $\xrightarrow{\text{conc. } H_2SO_4 + \text{conc.}HNO_3}$ 

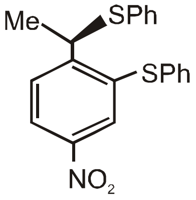
9. The major product of the following reaction is **[JEE-2008, 3/162]**

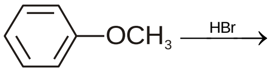


(A)


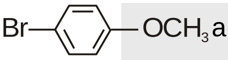
(B)


(C)


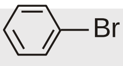
(D)


10. In the reaction


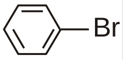
the products are : **[JEE-2010, 3/160]**

(A)


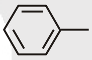
and H_2

(B)


and CH_3Br

(C)


and CH_3OH

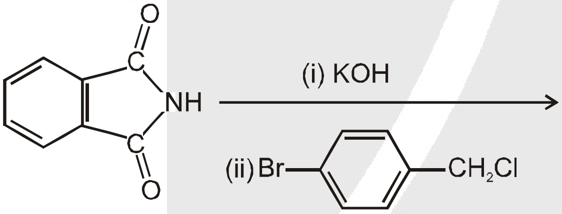
(D)


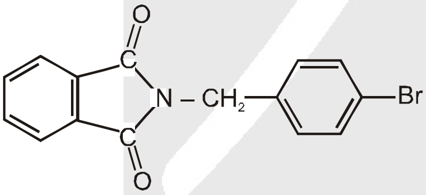
and CH_3Br

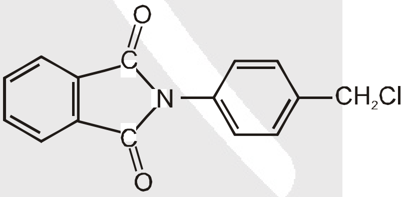
11. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are : **[JEE-2010, 3/160]**

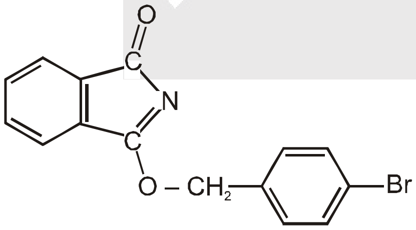
(A) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$
(B) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C{\equiv}CH$
(C) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C{\equiv}CH$
(D) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C{\equiv}CH$

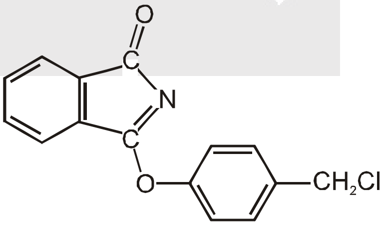
12. The major product of the following reaction is : **[JEE-2011, 3/163]**



(A)


(B)


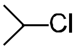
(C)


(D)


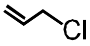
13. KI in acetone, undergoes S_N2 reaction with each P, Q, R and S. The rates of the reaction vary as **[JEE-2013, 2/126]**

$H_3C–Cl$

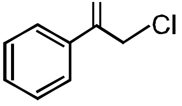
P



Q



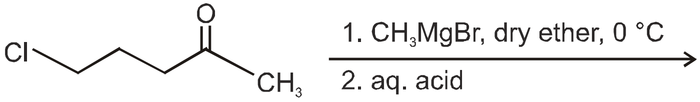
R

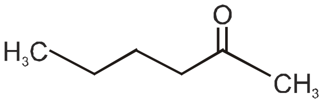


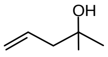
S

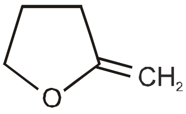
(A) P > Q > R > S (B) S > P > R > Q (C) P > R > Q > S (D) R > P > S > Q

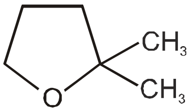
14. The major product in the following reaction is : **[JEE(Advanced)-2014, 3/120]**



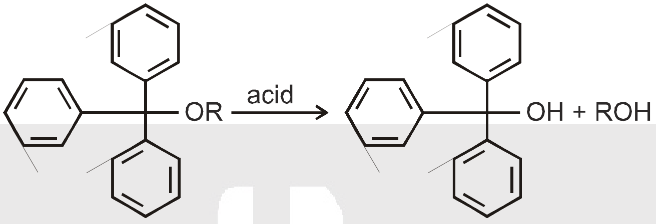
(A) 

(B) 

(C) 

(D) 

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

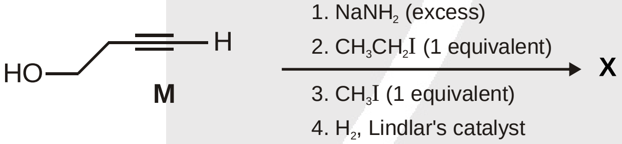


[X]

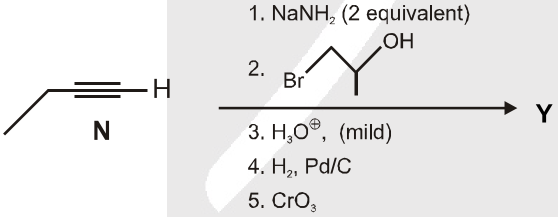
(A) one phenyl group is replaced by a methyl group.
(B) one phenyl group is replaced by a para-methoxyphenyl group.
(C) two phenyl groups are replaced by two para-methoxyphenyl groups.
(D) no structural change is made to X.

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.

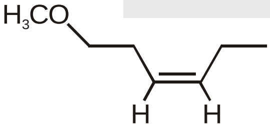


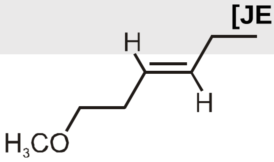
Scheme-1

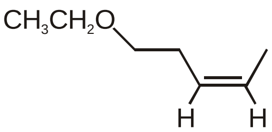


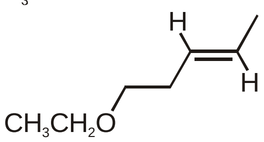
Scheme-2

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

(A) 

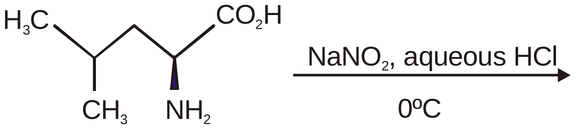
(B) 

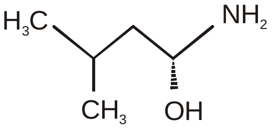
(C) 

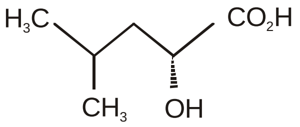
(D) 

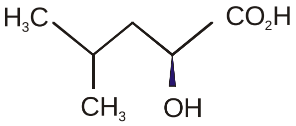
17. The correct statement with respect to product **Y** is **[JEE(Advanced)-2014, 3/120]**
(A) It gives a positive Tollens test and is a functional isomer of **X**.
(B) It gives a positive Tollens test and is a geometrical isomer of **X**.
(C) It gives a positive iodoform test and is a functional isomer of **X**.
(D) It gives a positive iodoform test and is a geometrical isomer of **X**.

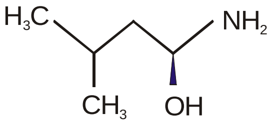
18. The major product of the reaction is **[JEE(Advanced)-2015, 4/120]**



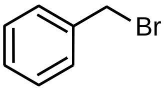
(A)


(B)


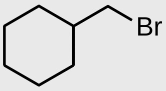
(C)


(D)


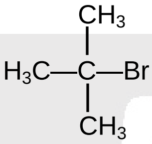
19.* For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is (are) **[JEE(Advanced)-2017, 4/122]**



I

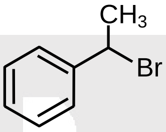


II



$(CH_3)_3C-Br$

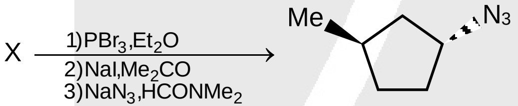
III



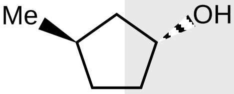
IV

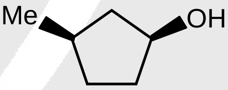
(A) Compound **IV** undergoes inversion of configuration
(B) The order of reactivity for **I**, **III** and **IV** is : **IV > I >III**
(C) **I** and **III** follow S_N1 mechanism
(D) **I** and **II** follow S_N2 mechanism

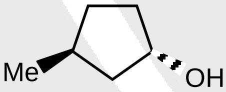
20.* In the following reaction sequence, the correct structure(s) of **X** is (are) **[JEE(Advanced)-2018, 4/120]**

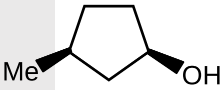


enantiomerically Pure

(A)


(B)


(C)


(D)


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

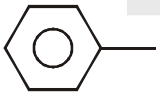
JEE(MAIN) OFFLINE PROBLEMS

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

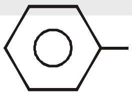
(1) $(CH_3)_3C-Cl + KOH \longrightarrow$

(2)


+ KOH ⟶

(3)


—Cl + KOH ⟶

(4)


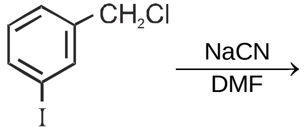
—$CH_2CH_2Cl + KOH \longrightarrow$

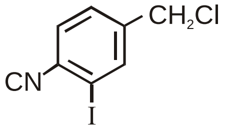
2. The reaction : $(CH_3)_3C-Br \xrightarrow{H_2O} (CH_3)_3C-OH$ is an example of - **[AIEEE-2002, 3/225]**
(1) elimination reaction.
(2) substitution reaction.
(3) free radical reaction.
(4) rearrangement reaction.

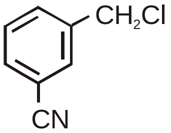
3. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in a test tube and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance 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

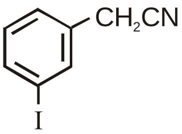
4. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of: **[AIEEE-2005, 3/225]**
(1) steric hinderance (2) inductive effect (3) instability (4) insolubility

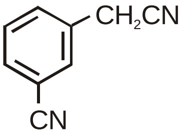
5. The structure of the major product formed in the following reaction is : **[AIEEE-2006, 3/165]**



(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

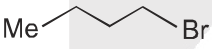
7. Which of the following is the correct order of decreasing S_N2 reactivity ? **[AIEEE-2007, 3/120]**
(1) $RCH_2X > R_3CX > R_2CHX$ (2) $RCH_2X > R_2CHX > R_3CX$
(3) $R_3CX > R_2CHX > RCH_2X$ (4) $R_2CHX > R_3CX > RCH_2X$

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) $(C_2H_5)_2CHCl$

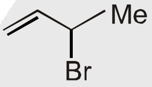
9. Which of the following on heating with aqueous KOH, produces acetaldehyde ? **[AIEEE-2009, 4/144]**
(1) CH_3CH_2Cl (2) CH_2ClCH_2Cl (3) CH_3CHCl_2 (4) CH_3COCl

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

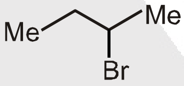
11. Consider the following bromides : **[AIEEE-2010, 4/144]**



(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

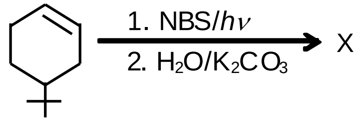
12. A solution of (–)-1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of : **[JEE(Main) 2013, 4/120]**
(1) carbanion (2) carbene (3) carbocation (4) free radical

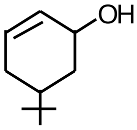
13. An unknown alochol is treated with the “Lucas reagent” to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism : **[JEE(Main) 2013, 4/120]**
(1) secondary alcohol by S_N1 (2) tertiary alcohol by S_N1
(3) secondary alcohol by S_N2 (4) tertiary alcohol by S_N2

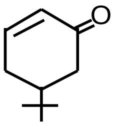
14. In S_N2 reactions, the correct order of reactivity for the following compounds: CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is : **[JEE(Main) 2014, 4/120]**
(1) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$
(2) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(3) $CH_3CH_2Cl > CH_3Cl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

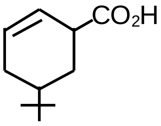
15. The synthesis of alkyl fluorides is best accomplished by : **[JEE(Main) 2015, 4/120]**
(1) Free radical fluorination (2) Sandmeyer's reaction
(3) Finkelstein reaction (4) Swarts reaction

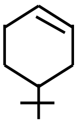
16. The product of the reaction give below is : **[JEE(Main) 2016, 4/120]**



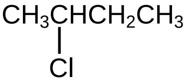
(1) 

(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]**


$CH_3\underset{\underset{Cl}{|}}{C}HCH_2CH_3$

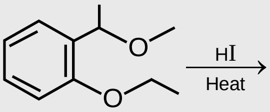
$CH_3CH_2CH_2Cl$

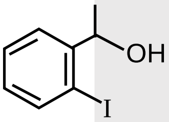
p–$H_3CO–C_6H_4–CH_2Cl$

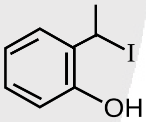
(I) (II) (III)

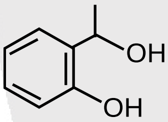
(1) (II) < (I) < (III)
(2) (I) < (III) < (II)
(3) (II) < (III) < (I)
(4) (III) < (II) < (I)

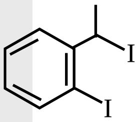
18. The major product formed in the following reaction is : **[JEE(Main) 2018, 4/120]**



(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

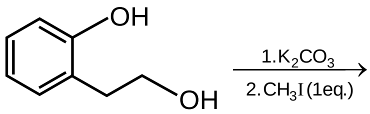
4. The final product formed when Methyl amine is treated with $NaNO_2$ and HCl is : **[JEE(Main) 2014 Online (19-04-14), 4/120]**

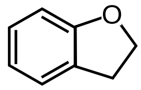
(1) Diazomethane
(2) Methylalcohol
(3) Methylcyanide
(4) Nitromethane

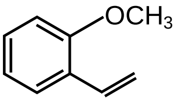
5. Williamson synthesis of ether is an example of : **[JEE(Main) 2014 Online (19-04-14), 4/120]**

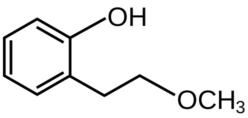
(1) Nucleophilic addition
(2) Electrophilic addition
(3) Electrophilic substitution
(4) Nucleophilic substitution

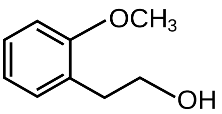
6. The major product of the following reaction is : **[JEE(Main) 2017 Online (08-04-17), 4/120]**



(1) 

(2) 

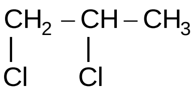
(3) 

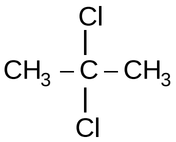
(4) 

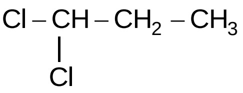
7. In the following reaction sequence :

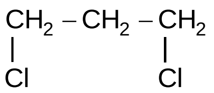
$$\underset{(C_3H_6Cl_2)}{\overset{I}{}} \xrightarrow{KOH(aq)} II \xrightarrow[(ii)H_2O/H^+]{(i)CH_3MgBr} III \xrightarrow{Anhy.\,ZnCl_2+Con.HCl} \text{gives turbidity immediately}$$

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

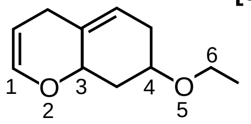
(1) 
$\underset{Cl}{CH_2}-\underset{Cl}{CH}-CH_3$

(2) 
$CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_3$

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

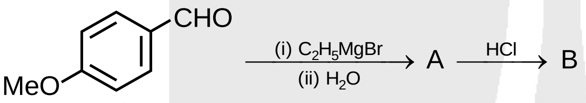
(4) 
$\underset{Cl}{CH_2}-CH_2-\underset{Cl}{CH_2}$

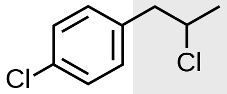
8. On treatment of the following compound with a strong acid, the most susceptible site for bond cleavage is : **[JEE(Main) 2018 Online (15-04-18), 4/120]**

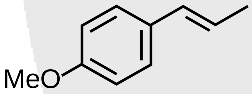


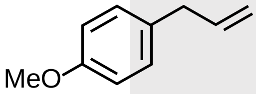
(1) $C_1 - O_2$ (2) $O_2 - C_3$ (3) $C_4 - O_5$ (4) $O_5 - C_6$

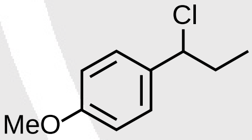
9. The major product B formed in the following reaction sequence is : **[JEE(Main) 2018 Online (16-04-18), 4/120]**



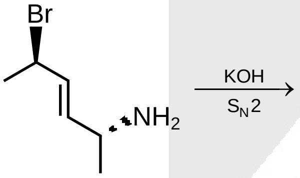
(1) 

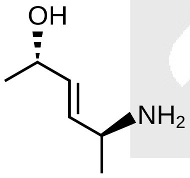
(2) 

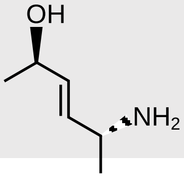
(3) 

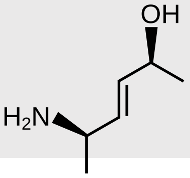
(4) 

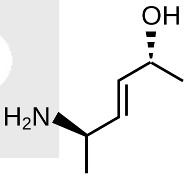
10. The major product of the following reaction is : **[JEE(Main) 2018 Online (16-04-18), 4/120]**



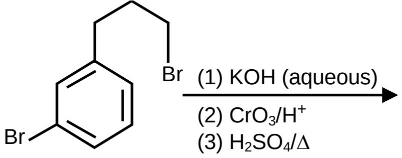
(1) 

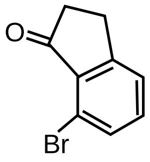
(2) 

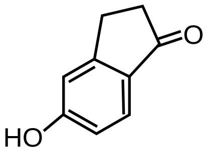
(3) 

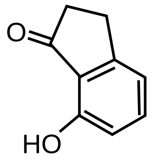
(4) 

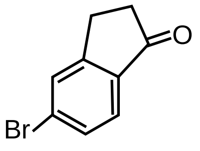
11. The major product of the following reaction is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**



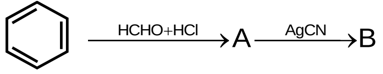
(1) 

(2) 

(3) 

(4) 

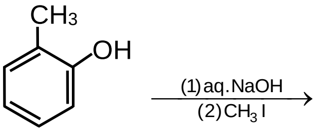
12. The compound A and B in the following reaction are, respectively :

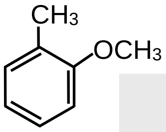


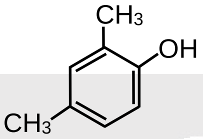
[JEE(Main) 2019 Online (09-01-19), 4/120]

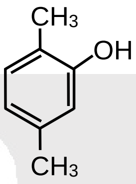
(1) A = Benzyl alcohol, B = Benzyl isocyanide
(2) A = Benzyl chloride, B = Benzyl cyanide
(3) A = Benzyl chloride, B = Benzyl isocyanide
(4) A = Benzyl alcohol, B = Benzyl cyanide

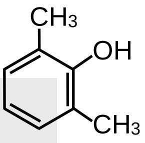
13. The major product of the following reaction: **[JEE(Main) 2019 Online (10-01-19), 4/120]**



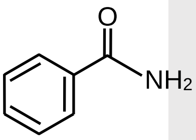
(1) 

(2) 

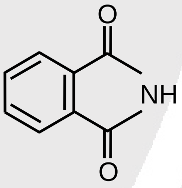
(3) 

(4) 

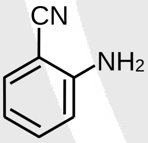
14. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is : **[JEE(Main) 2019 Online (12-01-19), 4/120]**



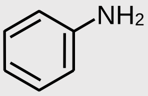
(A)



(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

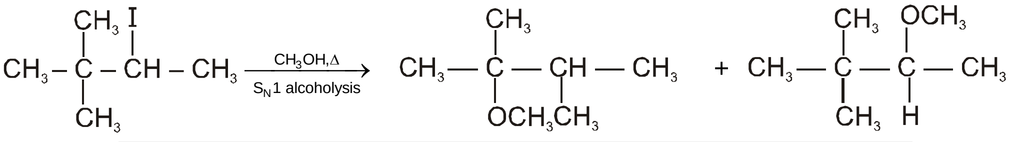
PART – I

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

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

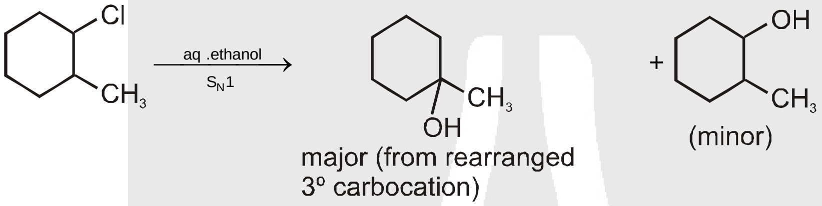
A-3. 3-Chlorocyclopropene form aromatic carbocation while 5-Chlorocyclopenta-1,3-diene form antiaromatic carbocation.

A-4. (a)

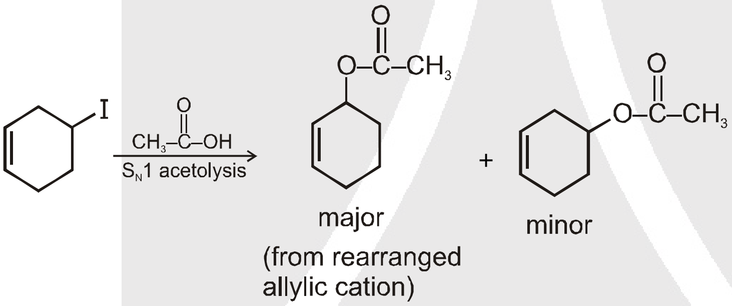


major (rearranged product) (minor)

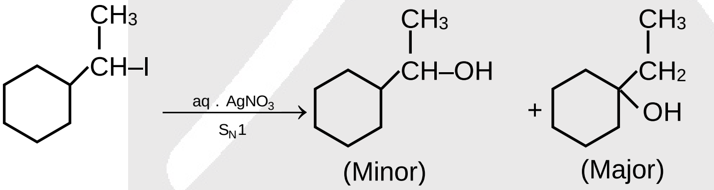
(b)



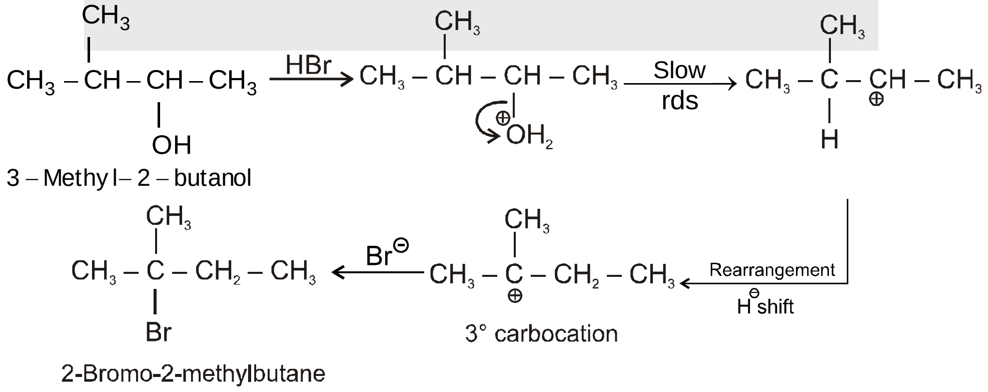
(c)

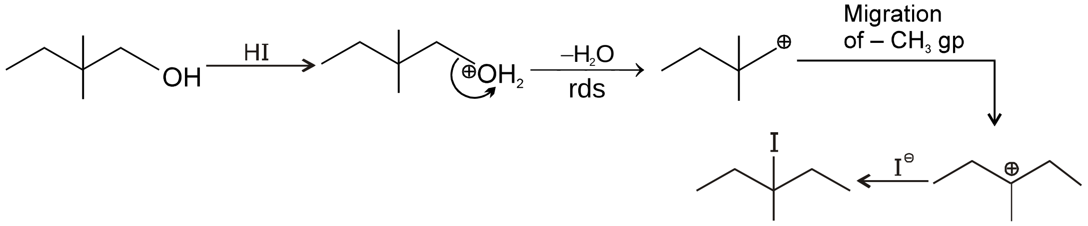


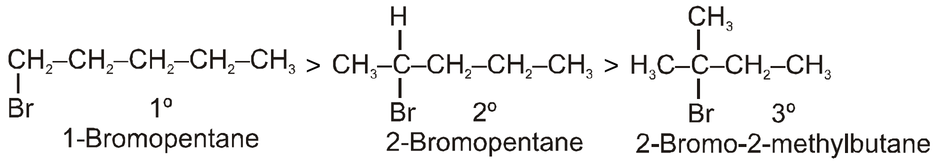
(d)



A-5. (a)



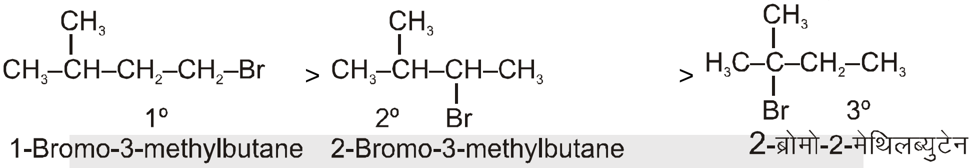
(b) 

B-1. (a) 

$\underset{Br}{CH_2}-CH_2-CH_2-CH_2-CH_3 > CH_3-\overset{H}{\underset{Br}{C}}-CH_2-CH_2-CH_3 > H_3C-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$

1° 2° 3°

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

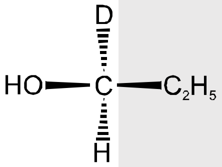
(b) 

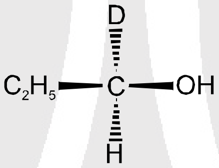
$CH_3-\overset{CH_3}{CH}-CH_2-CH_2-Br > CH_3-\overset{CH_3}{CH}-\underset{Br}{CH}-CH_3 > H_3C-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$

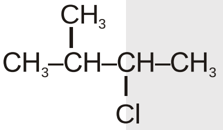
1° 2° 3°

1-Bromo-3-methylbutane 2-Bromo-3-methylbutane 2-ब्रोमो-2-मेथिलब्युटेन

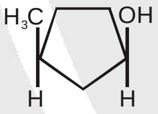
B-2. (a) $PhCMe_2Br$ (b) $PhCH_2CH_2Br$

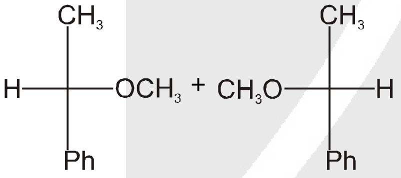
B-3. X = 

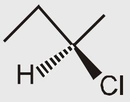
Y = 

B-4. (a) 

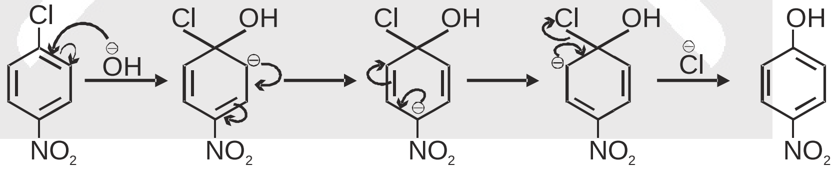
$CH_3-\overset{CH_3}{CH}-\underset{Cl}{CH}-CH_3$

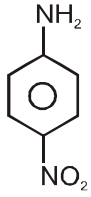
(b) 

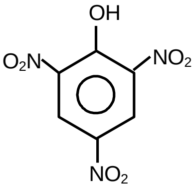
B-5. (a) 

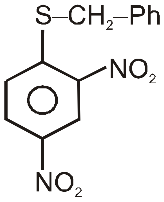
(b) 

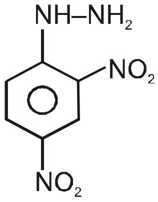
C-1. II > III > I

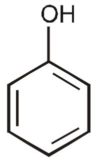
C-2. **Mechanism :** 

C-3. (a) 

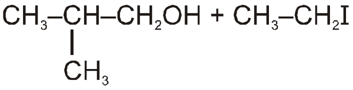
(b) 

(c) 

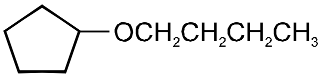
(d) 

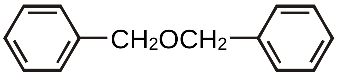
D-1. (a) 

+ CH_3I

(b) 

$CH_3-\underset{CH_3}{CH}-CH_2OH + CH_3-CH_2I$

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)

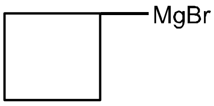
PART – IV

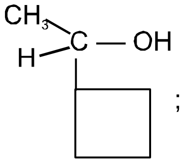
1.	(B)	**2.**	(C)	**3.**	(B)	**4.**	(C)	**5.**	(B)
6.	(B)	**7.**	(D)	**8.**	(D)				

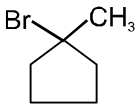
EXERCISE – 3

PART – I

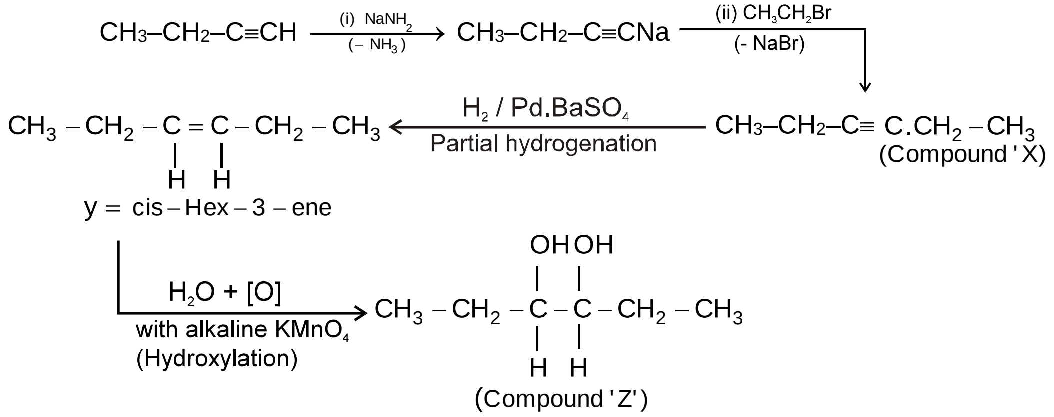
1. (D) **2.** (C)

3. (A) = 

; (B) = 

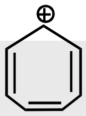
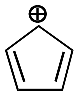
; (C) = 

4.



$CH_3–CH_2–C≡CH \xrightarrow[(-NH_3)]{(i)\ NaNH_2} CH_3–CH_2–C≡CNa \xrightarrow[(-NaBr)]{(ii)\ CH_3CH_2Br} CH_3–CH_2–C≡C.CH_2–CH_3$ (Compound 'X)

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)		