SOLVED EXAMPLES

Ex. 1 Which of the following is used as insecticide :

(A) D.D.T. **(B)** Chloritone **(C)** Chloropicrin **(D)** **(A)** and **(C)** both

Ans. **(D)**

Ex. 2 The product in the following reaction is :

$$Ph - Cl + Fe / Br_2 \longrightarrow Product$$

(A) o– bromo-chloro benzene **(B)** p– bromo-chloro benzene

(C) **(A)** and **(B)** both **(D)** 2, 4, 6-tribromo chloro benzene

Ans. **(C)**

Sol. Since – Cl group is deactivating and o/p directing group so only o– and p– products are formed.

Ex. 3 The most reactive towards SN^1 is :

(A) $PhCH_2Cl$ **(B)** Ph–Cl **(C)** $CH_3CHCl(CH_3)$ **(D)** p–NO_2—Ph—CH_2—Cl

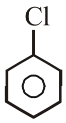
Ans. **(A)**

Sol. S_{N^1} the intermediate carbocation is formed.

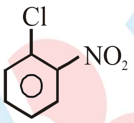
$C_6H_5—CH_2Cl \longrightarrow C_6H_5\overset{\oplus}{C}H_2$ is maximum stable due to resonance.

Ex. 4 Which of the following undergoes Hydrolysis most easily :

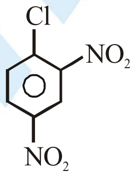
(A)



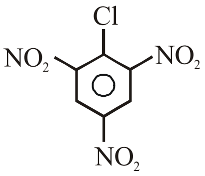
(B)



(C)



(D)



Ans. **(D)**

Sol. If there is more m-directing group then there will be more nuclephilic substitution reaction.

Exercise # 1

[Single Correct Choice Type Questions]

1. Consider the following reaction sequence,

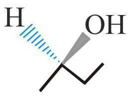
$$CH_3C\equiv CH \xrightarrow[HgSO_4]{aq.H_2SO_4} A \xrightarrow[Heat]{PCl_5} B.$$

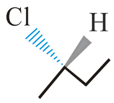
The products **(A)** and **(B)** are, respectively,

(A) CH_3COCH_3 and $CH_3CCl_2CH_3$
(B) CH_3CH_2CHO and $CH_3CH_2CHCl_2$
(C) $CH_3CHOHCH_3$ and $CH_3CHClCH_3$
(D) $CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2Cl$

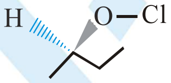
2. Which of the following has highest dipole moment:
(A) CH_3Cl **(B)** CH_3F **(C)** CH_3Br **(D)** CH_3I

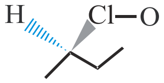
3. In S_{N^1} the first step involves the formation of
(A) free radical **(B)** carbanion **(C)** carbocation **(D)** final product

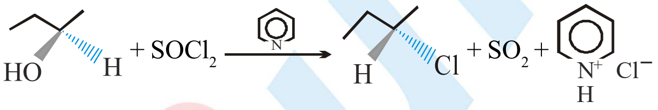
4. The product formed in the reaction  $+ SOCl_2 \rightarrow$ is-

(A) 

(B) 

(C) 

(D) 

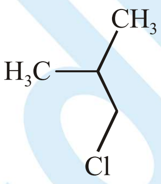
5. The reaction 

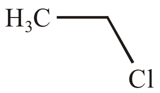
proceeds by the mechanism
(A) S_{N^1} **(B)** S_{N^2} **(C)** S_Ni **(D)** S_{E^2}

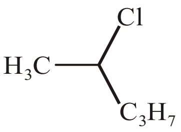
6. 1, 3- Dibromopropane reacts with metallic zinc to form
(A) propene **(B)** cyclopropane **(C)** propane **(D)** hexane

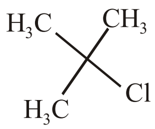
7. To form alkane isonitrile, alkyl halide is reacted with:
(A) KCN **(B)** AgCN **(C)** HCN **(D)** NH_4CN

8. Which one of the following compounds most readily undergoes substitution by S_N2 mechanism ?

(A) 

(B) 

(C) 

(D) 

9. Sec. Butyl chloride undergo alkaline hydrolysis in the polar solvent by
(A) S_{N^2} **(B)** S_{N^1} **(C)** S_{N^1} and S_{N^2} **(D)** none of these

10. The products of reaction of alcoholic silver nitrite with ethyl bromide are
(A) Ethane **(B)** Ethene **(C)** Ethyl alcohol **(D)** Nitro ethane

11. The reaction ,$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$ obeys the mechanism

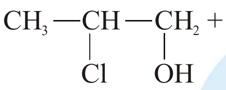
(A) S_{N^1} **(B)** S_{N^2} **(C)** E_1 **(D)** E_2

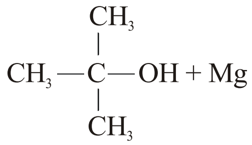
12. Ethylidene chloride can be prepared by the reaction of HCl and

(A) Ethane **(B)** Ethylene **(C)** Acetylene **(D)** Ethylene glycol

13. Grignard reagent can be prepared by

(A) $CH_3—CH_2—Cl + Mg \xrightarrow[ether]{dry}$

(B) 
$CH_3—\underset{Cl}{CH}—\underset{OH}{CH_2} + Mg \xrightarrow[ether]{dry}$

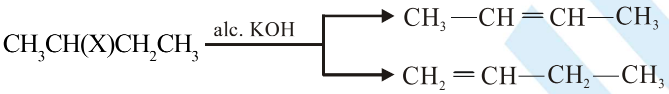
(C) 
$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—OH + Mg \xrightarrow[ether]{dry}$

(D) All of them

14. Most stable carbocation formed from $(CH_3)_3C–Br$, $(C_6H_5)_3CBr$,$(C_6H_5)_2CHBr$ and $C_6H_5CH_2Br$ would be

(A) $C_6H_5\overset{\oplus}{C}H_2$ **(B)** $(CH_3)_3\overset{\oplus}{C}$ **(C)** $(C_6H_5)_3\overset{\oplus}{C}$ **(D)** $(C_6H_5)_2\overset{\oplus}{C}H$

15. For the reaction



(A) $CH_3—CH=CH—CH_3$ predominates **(B)** $CH_2=CH—CH_2—CH_3$ predominates
(C) Both are formed in equal amounts **(D)** The product ratio depends on the halogen

16. 1–phenyl–2–chloropropane on treating with alc. KOH gives mainly

(A) 1–phenylpropene **(B)** 2–phenylpropene
(C) 1–phenylpropane–2–ol **(D)** 1–phenylpropan–1–ol

17. Grignard reagent is obtained when magnesium is treated with

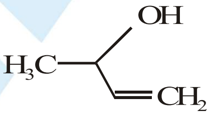
(A) Alkyl halide in presence of alcohol **(B)** Alkyl halide in presence of phenol
(C) Alkyl halide in presence of dry ether **(D)** Alkyl halide in presence of alcoholated ether

18. Ethylene reacts with bromine to form -

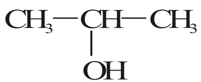
(A) Chloroethane **(B)** Ethylene dibromide **(C)** Cyclohexane **(D)** 1-bromo propane

19. The correct reactivity order of alcohols towards H–X will be

(I) $CH_2=CH—OH$

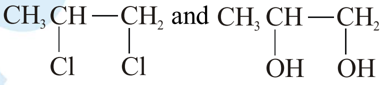
(II) 

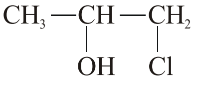
(III) $CH_3—CH_2—OH$

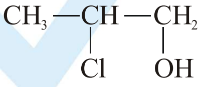
(IV) 
$CH_3—\underset{OH}{CH}—CH_3$

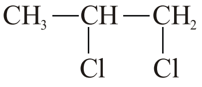
(A) II > I > III > IV **(B)** IV > III > II > I **(C)** II > IV > I > III **(D)** II > IV > III > I

20. Identify 'Z' in the following reaction series, $CH_3.CH_2CH_2Br \xrightarrow{aq.NaOH} (X) \xrightarrow[Heat]{Al_2O_3} (Y) \xrightarrow{HOCl} (Z)$:

(A) Mixture of 
$CH_3\underset{Cl}{CH}—\underset{Cl}{CH_2}$ and $CH_3\underset{OH}{CH}—\underset{OH}{CH_2}$

(B) 
$CH_3—\underset{OH}{CH}—\underset{Cl}{CH_2}$

(C) 
$CH_3—\underset{Cl}{CH}—\underset{OH}{CH_2}$

(D) 
$CH_3—\underset{Cl}{CH}—\underset{Cl}{CH_2}$

21. For the reaction,

$C_2H_5OH + HX \xrightarrow{ZnX_2} C_2H_5X$, the order of reactivity is

(A) HI > HCl > HBr **(B)** HI > HBr > HCl

(C) HCl > HBr > HI **(D)** HBr > HI > HCl

22. $C_2H_4 \xrightarrow{Br_2} X \xrightarrow{KCN} Y$; Y is

(A) CH_3CH_2CN **(B)** $NC—CH_2—CH_2—CN$

(C) $Br—CH_2—CH_2CN$ **(D)** $Br—CH{=}CHCN$

23. Reactivity order of halides for dehydrohalogenation is

(A) R – F > R – Cl > R – Br > R – I **(B)** R – I > R – Br > R – Cl > R – F

(C) R – I > R – Cl > R – Br > R – F **(D)** R – F > R – I > R – Br > R – Cl

24. Which of the following is least reactive in a nucleophilic substitution reaction

(A) $CH_2{=}CHCl$ **(B)** CH_3CH_2Cl

(C) $CH_2{=}CHCH_2Cl$ **(D)** $(CH_3)_3C–Cl$

25. Ethyl alcohol reacts at a faster rate with HI than with HCl in forming the corresponding ethyl halides under identical conditions mainly because -

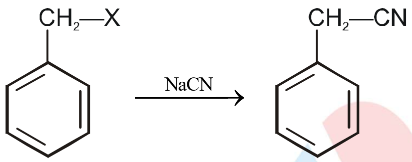
(A) HI, being a stronger acid, protonates ethyl alcohol at oxygen much better and helps substitution

(B) the bond length in HI is much shorter than that in HCl

(C) I^- is a much better leaving group

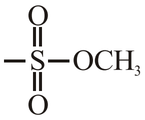
(D) I^- is a much better nucleophile than Cl^-

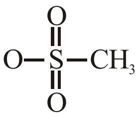
26.



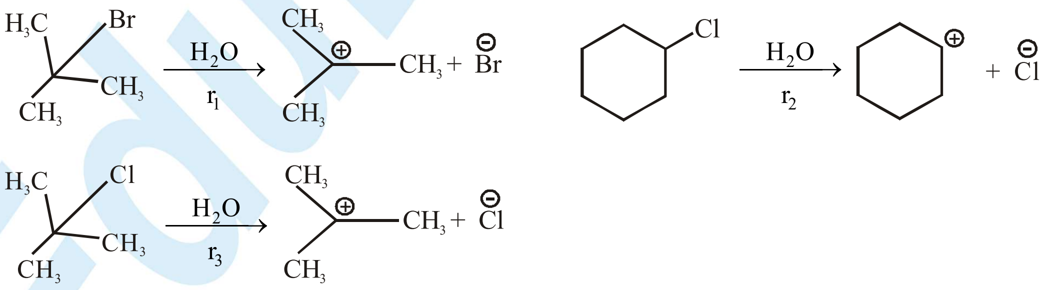
In the given reaction rate is fastest, when (X) is :

(A) –OH **(B)** $–NH_2$

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

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

27.



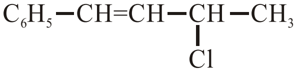
the rates r_1 , r_2 and r_3 are in the order :

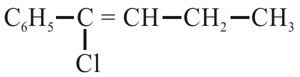
(A) $r_1 > r_2 > r_3$ **(B)** $r_3 > r_1 > r_2$

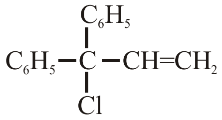
(C) $r_1 > r_3 > r_2$ **(D)** $r_2 > r_1 > r_3$

28. The increasing order of reactivity of the following isomeric halides with $AgNO_3$ (H_2O + alcohol) is :

(I) $C_6H_5-CH=CH-CH_2-CH_2-Cl$

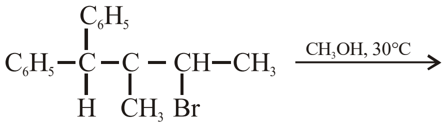
(II) 
$C_6H_5-CH=CH-\underset{Cl}{CH}-CH_3$

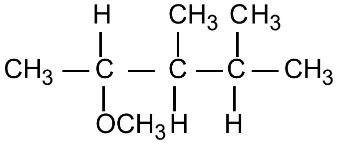
(III) 
$C_6H_5-\underset{Cl}{C}=CH-CH_2-CH_3$

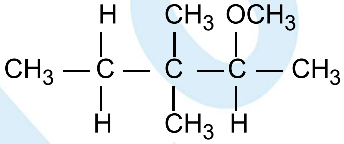
(IV) 
$C_6H_5-\underset{Cl}{\overset{C_6H_5}{C}}-CH=CH_2$

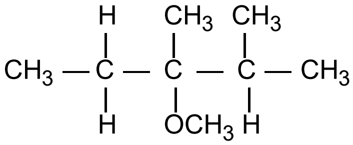
(A) III < IV < II < I **(B)** I < III < IV < II **(C)** III < I < II < IV **(D)** I < II < IV < III

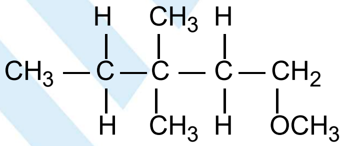
29. What will be the major product of the following reaction ?


$C_6H_5-\underset{H}{\overset{C_6H_5}{C}}-\underset{CH_3}{C}-\underset{Br}{CH}-CH_3 \xrightarrow{CH_3OH,\ 30°C}$

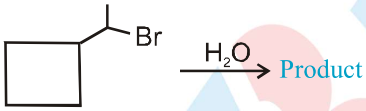
(A) 
$CH_3-\underset{OCH_3}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_3$

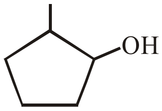
(B) 
$CH_3-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{OCH_3}{C}}-CH_3$

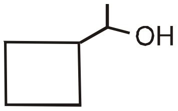
(C) 
$CH_3-\underset{H}{\overset{H}{C}}-\underset{OCH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_3$

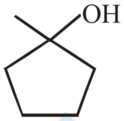
(D) 
$CH_3-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-\underset{OCH_3}{CH_2}$

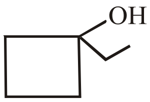
30. What will be the major product of the following reaction



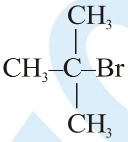
(A) 

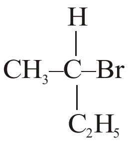
(B) 

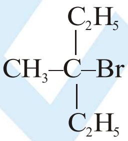
(C) 

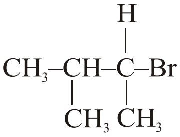
(D) 

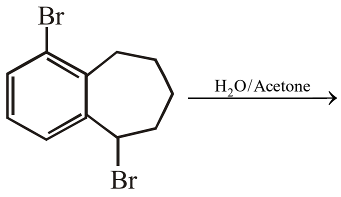
31. Which one of the following compounds will give (D) and (●) form in S_N1 reaction (as major product)

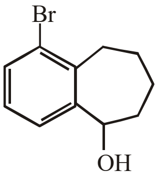
(A) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$

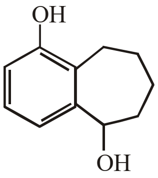
(B) 
$CH_3-\underset{C_2H_5}{\overset{H}{C}}-Br$

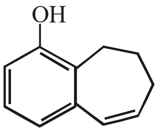
(C) 
$CH_3-\underset{C_2H_5}{\overset{C_2H_5}{C}}-Br$

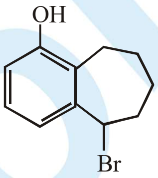
(D) 
$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{\overset{H}{C}}-Br$

32.  (A) ; Product (A) is :

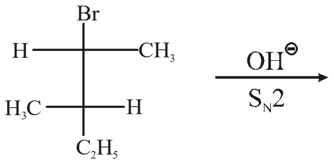
(A) 

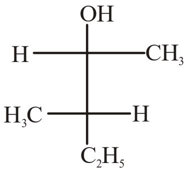
(B) 

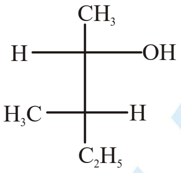
(C) 

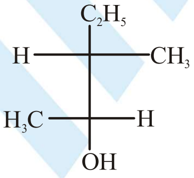
(D) 

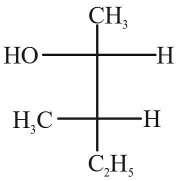
33. In the following reaction the most probable product will be :



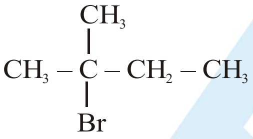
(A) 

(B) 

(C) 

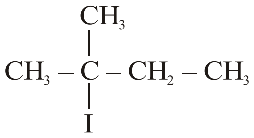
(D) 

34. Which one of the following compounds undergoes E1 reaction most readily ?

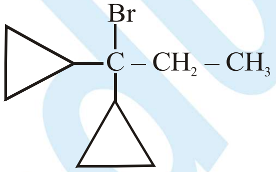
(A) 
$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_2-CH_3}$

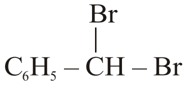
(B) $\mathrm{CH_3-CH_2-CH_2-Br}$

(C) $\mathrm{CH_3-CH_2-CH_2-I}$

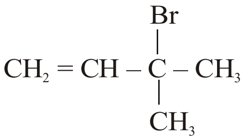
(D) 
$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{I}{|}}{C}}-CH_2-CH_3}$

35. Which of the following will be most reactive for E1 reaction ?

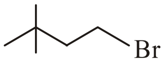
(A) 

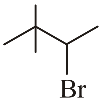
(B) 
$\mathrm{C_6H_5-\overset{\overset{Br}{|}}{CH}-Br}$

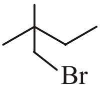
(C) 
$\mathrm{CH_2=CH-\overset{\overset{Br}{|}}{CH}-CH_3}$

(D) 
$\mathrm{CH_2=CH-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$

36. Which of the following cannot undergo E2 reaction ?

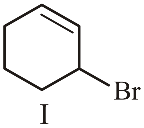
(A) 

(B) 

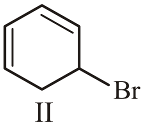
(C) 

(D) none of these

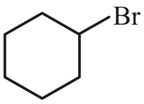
37. Arrange the following in decreasing order of stability of their transition state during elimination by strong base



I



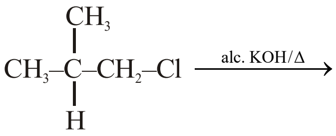
II



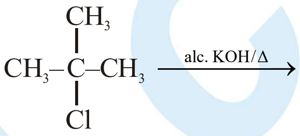
III

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

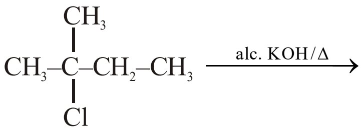
38. In which of the following reaction, regioselectivity can be observed.

(A) 

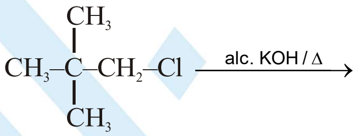
$$\mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}{-}CH_2{-}Cl} \xrightarrow{\text{alc. KOH}/\Delta}$$

(B) 

$$\mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}{-}CH_3} \xrightarrow{\text{alc. KOH}/\Delta}$$

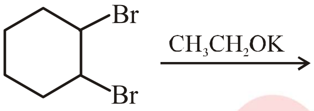
(C) 

$$\mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}{-}CH_2{-}CH_3} \xrightarrow{\text{alc. KOH}/\Delta}$$

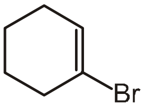
(D) 

$$\mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CH_2{-}Cl} \xrightarrow{\text{alc. KOH}/\Delta}$$

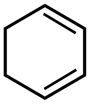
39. The most probable product in the following reaction is :

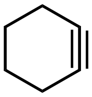


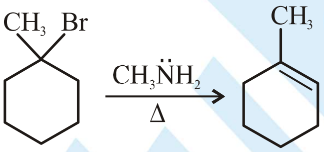
Trans

(A) 

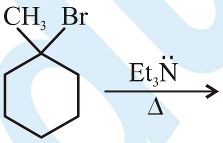
(B) 

(C) 

(D) 

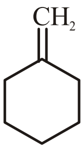
40. If 

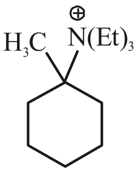
; Then what will be the major product of the following reaction



major product

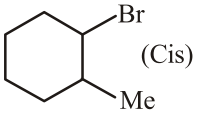
(A) 

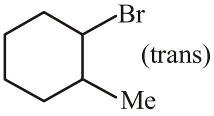
(B) 

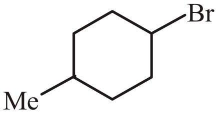
(C) 

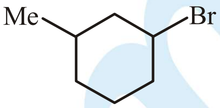
(D) B & C both

41. Which of the following will undergo fastest elimination reaction with alcoholic KOH.

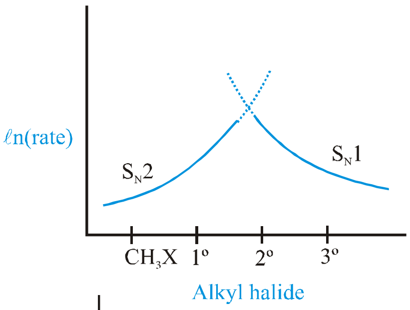
(A) 

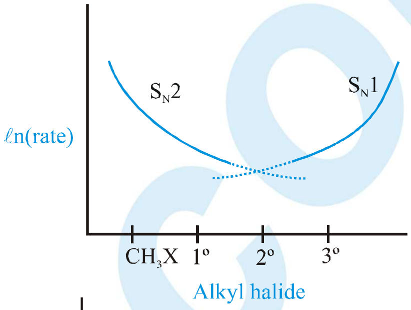
(B) 

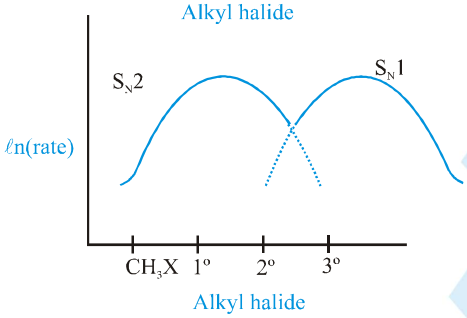
(C) 

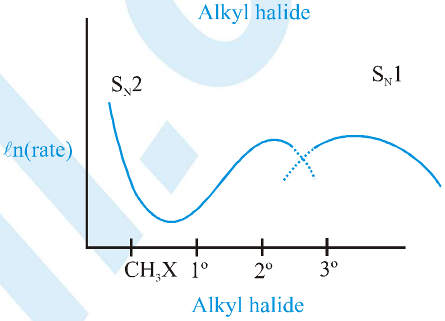
(D) 

42. Which of the following curves correctly represents S_N1 vs S_N2

(A) 

(B) 

(C) 

(D) 

43. Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to

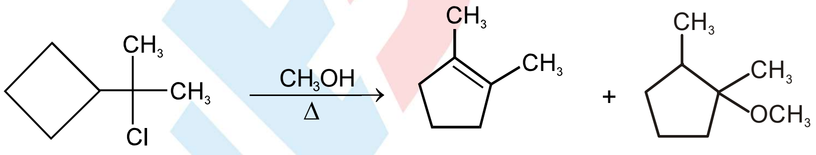
(A) The formation of less stable carbanion

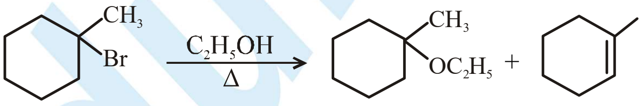
(B) Longer carbon halogen bond

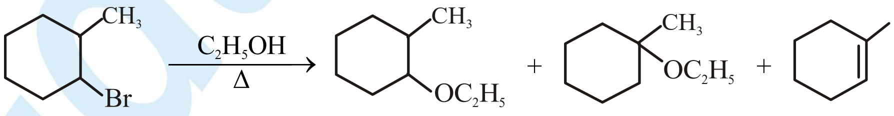
(C) The inductive effect

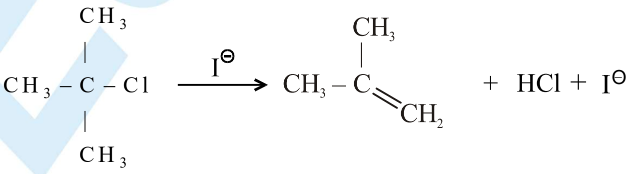
(D) sp^2–hybridized carbon attached to the halogen

44. Which of the following reaction is not feasible.

(A) 

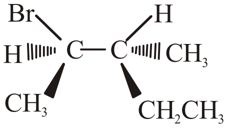
(B) 

(C) 

(D) 

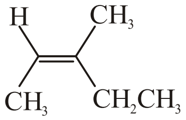
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl \xrightarrow{I^{\ominus}} CH_3-\overset{\displaystyle CH_3}{C}=CH_2 + HCl + I^{\ominus}$$

45. Select the formula representing the major product of the following reaction

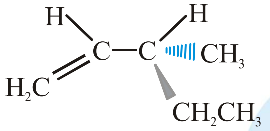


$$\xrightarrow[\Delta]{CH_3CH_2OK/CH_3CH_2OH}$$

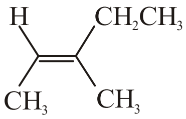
(A)



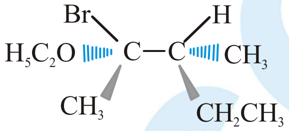
(B)



(C)

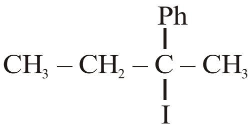


(D)



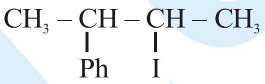
46. The correct order of S_N2 / E2 ratio for the % yield of product of the following halide is

(P)



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

(Q)



$CH_3-\underset{\underset{Ph}{|}}{CH}-\underset{\underset{I}{|}}{CH}-CH_3$

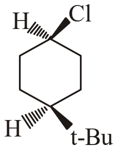
(R) CH_3-CH_2-I

(S)

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

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

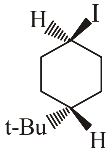
47.



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

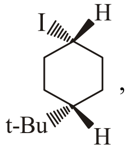
Product and mechanism are respectively

(A)



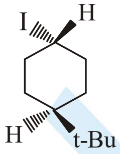
, S_N1

(B)



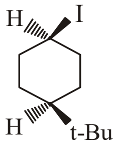
, S_N2

(C)



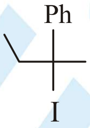
, S_N2

(D)

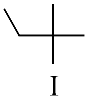


, S_N1

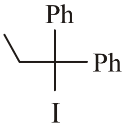
48. Which of the following order of decreasing rate of S_N reaction in CF_3CO_2H is correct



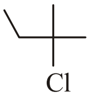
I



II



III



IV

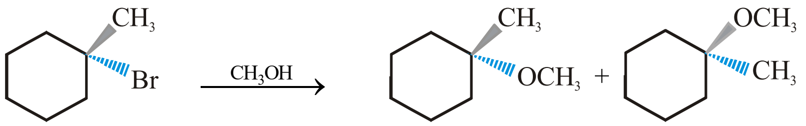
(A) III > I > II > IV

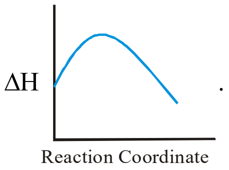
(B) III > I > IV > II

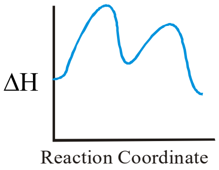
(C) I > III > IV > II

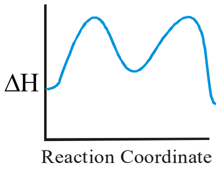
(D) I > III > II > IV

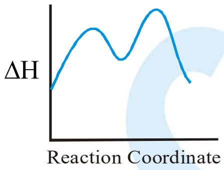
49. Which is the correct reaction coordinate diagram for the following solvolysis reaction ?

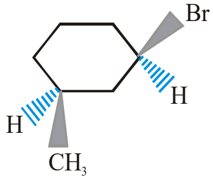


(A)


(B)


(C)


(D)


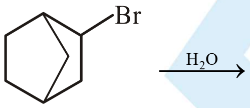
50.


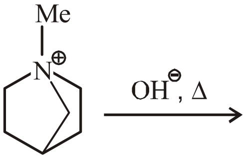
$+ \text{KOH} \xrightarrow{\text{acetone}}$ Product

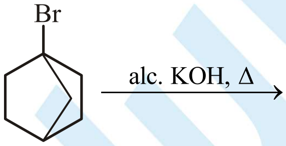
(1R, 3S)–Cis–1–Bromo–3–methylcyclohexane.
The product formed in the reaction is

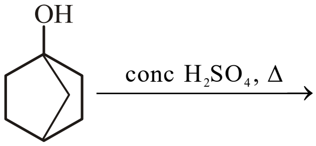
(A) (1R, 3S)–Cis–3–methyl cyclohexanol
(B) (1S, 3S)–Cis–3– methyl cyclohexanol
(C) (1S, 3S)–Trans–3–methyl cyclohexanol
(D) (1R, 3R)–Trans–3–methyl cyclohexanol

51. Which of the following reaction will undergo an elimination reaction and an alkene (major) will be formed in the products.

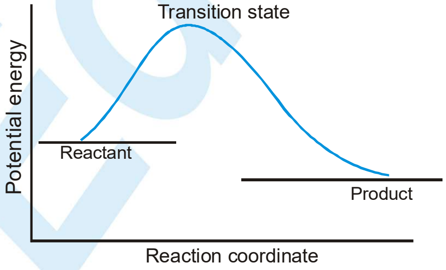
(A)


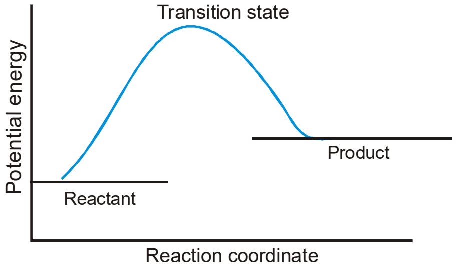
(B)


(C)


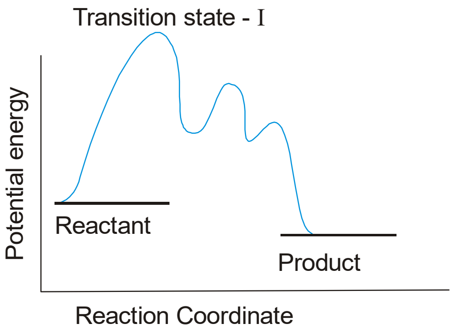
(D)


52. Following are the curves for nucleophilic substitution reaction.

(I)


(II)


(III)



The correct statement (s) is (are)

(A) 'I' is potential energy diagram for S_N2 reaction that takes place with a negative potential energy change.

(B) 'II' is potential energy diagram for S_N2 reaction with a positive potential energy change

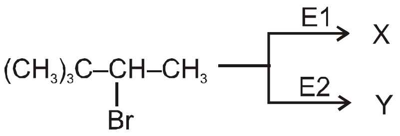
(C) 'III' shows potential energy diagram for S_N1 reaction with large potential energy of activation for first (slowest) step

(D) All of the above

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

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

54.



$(CH_3)_3C-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3 \begin{cases} \xrightarrow{E1} X \\ \xrightarrow{E2} Y \end{cases}$

X and Y are respectively

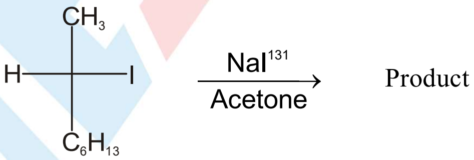
(A) $(CH_3)_2C{=}C(CH_3)_2$ and $(CH_3)_3CCH{=}CH_2$

(B) $(CH_3)_3CCH{=}CH_2$ and $(CH_3)_2C{=}C(CH_3)_2$

(C) $(CH_3)_2CH{-}C(CH_3){=}CH_2$ and $(CH_3)_2C{=}C(CH_3)_2$

(D) $(CH_3)_2C{=}C(CH_3)_2$ and $(CH_3)_2CH{-}C(CH_3){=}CH_2$

55. Which statement is incorrect about the following reaction



2-Iodooctane
(+)

(A) The rate of these reaction depends on both [R–I] and $[{}^{131}I^{\ominus}]$

(B) Loss of optical activity was twice as fast as gain of radioactivity.

(C) Each molecule undergoing substitution, suffers Inversion of configuration

(D) Final solution has radioactive iodine only

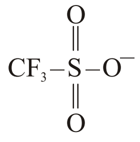
Exercise # 2 Part # I [Multiple Correct Choice Type Questions]

1. The order of decreasing S_N1 reactivities of the halides

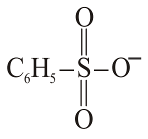
I	II	III
$CH_3CH_2CH_2Cl$	$CH_2=CHCHClCH_3$	$CH_3CH_2CHClCH_3$

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

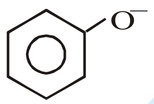
2. Consider the following anions.


$CF_3-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-$

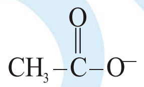
(I)


$C_6H_5-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-$

(II)



(III)


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

(IV)

When attached to sp^3- hybridized carbon, their leaving group ability in nucleophilic substitution reactions decreases in the order

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

3. The basicity of RO^-, HO^-, $RCOO^-$, ROH, and H_2O are of the order -

(A) $HO^- > RO^- > H_2O > ROH > RCOO^-$

(B) $RO^- > HO^- > RCOO^- > ROH > H_2O$

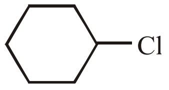
(C) $H_2O > ROH > RCOO^- > HO^- > RO^-$

(D) $ROH > H_2O > HO^- > RCOO^- > RO^-$

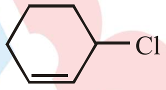
4. Which of the following does/do produce a white precipitate of AgCl on warming with alcoholic silver nitrate?

(A) Allyl chloride **(B)** t-Butyl chloride **(C)** Benzyl chloride **(D)** Vinyl chloride

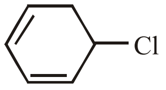
5. What is the order of reactivity of the following compounds towards nucleophilic substitution?



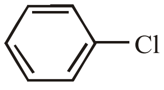
(I)



(II)



(III)



(IV)

(A) I < II < III < IV **(B)** IV < III < II < I

(C) IV < I < II < III **(D)** IV < II < I < III

6. The order of decreasing nucleophilicity of the following is

(A) $H_2O > OH^- > CH_3COO^- > CH_3O^-$ **(B)** $CH_3O^- > OH^- > CH_3COO^- > H_2O$

(C) $CH_3COO^- > CH_3O^- > OH^- > H_2O$ **(D)** $HO^- > CH_3O^- > CH_3COO^- > H_2O$

7. Which of the following are aprotic solvents :

(A) DMSO **(B)** DMF **(C)** H_2O **(D)** CH_3COOH

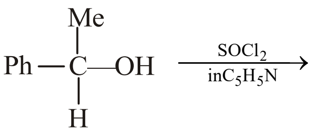
8. Which is/are true statements (s) :

(A) Protonation increases electrophilic nature of carbonyl group

(B) $CF_3SO_3^-$ is better leaving group than $CH_3SO_3^-$

(C) Benzyl carbonium ion is stabilised by resonance

(D) 
$CCl_3CH(OH)_2$ is stable,due to H-Bonding

9. 

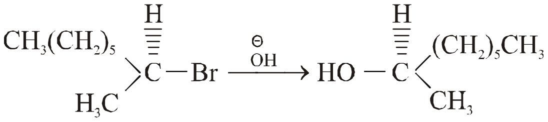
$$\mathrm{Ph-\overset{\displaystyle Me}{\underset{\displaystyle H}{C}}-OH \xrightarrow[\text{in}C_5H_5N]{SOCl_2}}$$

Which statement is true for the above reaction ?

(A) Retention of configuration **(B)** Inversion of configuration

(C) Inversion and Retention both **(D)** None

10. Following reaction is



(A) E_1 **(B)** S_{N^1} **(C)** E_2 **(D)** S_{N^2}

11. On treatment with chlorine in presence of sunlight, toluene gives the product -

(A) o-chloro toluene **(B)** 2, 5-dichloro toluene

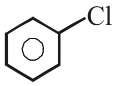
(C) p-chloro toluene **(D)** Benzyl chloride

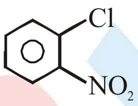
12. In S_{N^1} reaction an optically active substrates mainly gives :

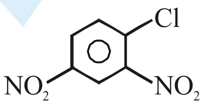
(A) Retention in configuration **(B)** Inversion in configuration

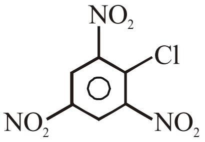
(C) Racemic product **(D)** No product

13. Which of the following undergoes hydrolysis most easily

(A) 

(B) 

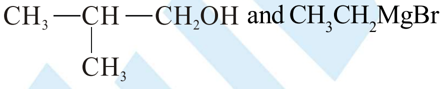
(C) 

(D) 

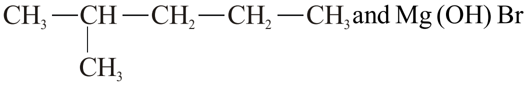
14. A compound 'A' formula of $C_3H_6Cl_2$ on reaction with alkali can give 'B' of formula C_3H_6O or 'C' of formula C_3H_4. 'B' on oxidation gave a compound of the formula $C_3H_6O_2$. 'C' with dilute H_2SO_4 containing Hg^{2+} ion gave 'D' of formula C_3H_6O, which with bromine and alkali gave the sodium salt of $C_2H_4O_2$. Then 'A' is

(A) $CH_3CH_2CHCl_2$ **(B)** $CH_3CCl_2CH_3$ **(C)** $CH_2ClCH_2CH_2Cl$ **(D)** $CH_3CHClCH_2Cl$

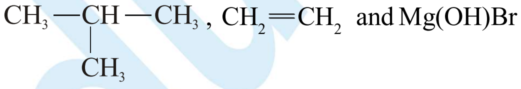
15. Isobutyl magnesium bromide with dry ether and absolute alcohol gives

(A) 

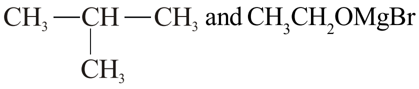
$\mathrm{CH_3-\underset{\displaystyle CH_3}{CH}-CH_2OH}$ and CH_3CH_2MgBr

(B) 

$\mathrm{CH_3-\underset{\displaystyle CH_3}{CH}-CH_2-CH_2-CH_3}$ and Mg (OH) Br

(C) 

$\mathrm{CH_3-\underset{\displaystyle CH_3}{CH}-CH_3}$, $CH_2{=}CH_2$ and Mg(OH)Br

(D) 

$\mathrm{CH_3-\underset{\displaystyle CH_3}{CH}-CH_3}$ and CH_3CH_2OMgBr

16. Alkyl iodides can be prepared by :-

(A) $RCH_2COOAg + I_2 \xrightarrow[\Delta]{CCl_4} RCH_2I$ **(B)** $RCH_2Cl + NaI \xrightarrow[\Delta]{\text{acetone}} RCH_2I + NaCl$

(C) $R{-}OH + HI \longrightarrow RI + H_2O$ **(D)** $CH_4 + I_2 \longrightarrow CH_3I$

17. Which of the following reagents can be used to prepare an alkyl halide :-

(A) NaCl **(B)** $HCl + ZnCl_2$ **(C)** $SOCl_2$ **(D)** PCl_5

18. Which of the following reactions depict the nucleophilic substitution of C_2H_5Br :-

(A) $C_2H_5Br + C_2H_5SNa \longrightarrow C_2H_5SC_2H_5 + NaBr$

(B) $C_2H_5Br \xrightarrow{Na+C_2H_5OH} C_2H_6 + HBr$

(C) $C_2H_5Br + AgCN \longrightarrow C_2H_5NC + AgBr$

(D) $C_2H_5Br + KOH \longrightarrow C_2H_5OH + KBr$

19. For an S_{N^2} reaction, which of the following statements are true :-

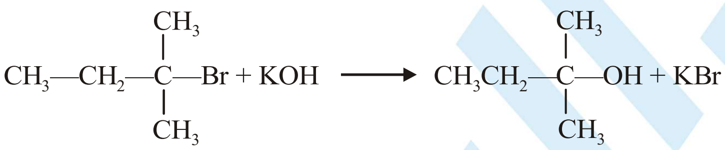
(A) The rate of reaction is independent of the concentration of the nucleophile
(B) The nucleophile attacks the C-atom on the side of the molecule opposite to the group being displaced
(C) The reaction proceeds with simultaneous bond formation and rupture
(D) None of these

20. Which of the following is an S_{N^2} reaction :-

(A) $CH_3CH_2Br + KOH \longrightarrow CH_3CH_2OH + KBr$

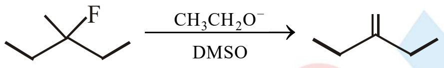
(B) $CH_3CH_2Br + CH_3CH_2ONa \longrightarrow CH_3CH_2OCH_2CH_3 + NaBr$

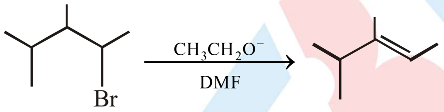
(C) $(CH_3)_3CBr + KOH \longrightarrow (CH_3)_3COH + KBr$

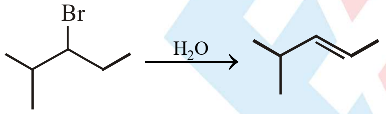
(D) 

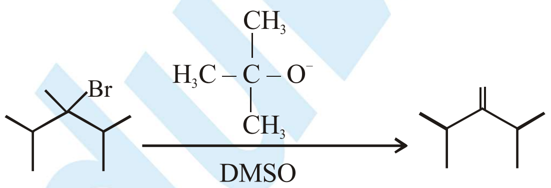
$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + KOH \longrightarrow CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + KBr$$

21. Which of the following reactions represent the major product.

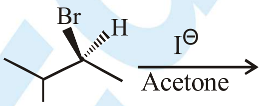
(A) 

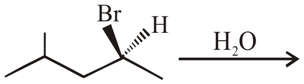
(B) 

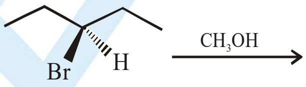
(C) 

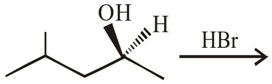
(D) 

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

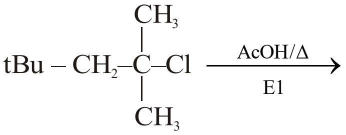
(A) 

(B) 

(C) 

(D) 

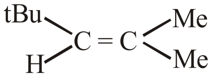
23.



$$tBu-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-Cl \xrightarrow[E1]{AcOH/\Delta}$$

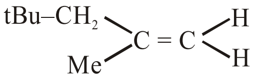
The products of the above reaction ?

(A)



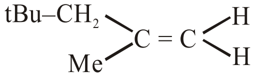
Major

(B)



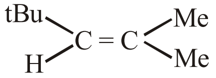
Minor

(C)



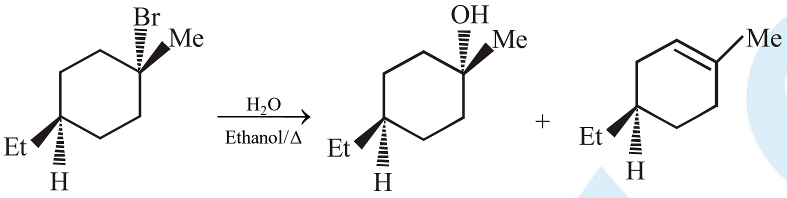
Major

(D)



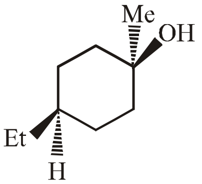
Minor

24. Consider the following E1/S_N1reaction :

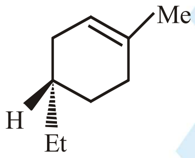


The missing product (s) is (are) :

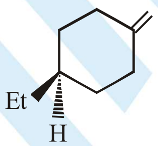
(A)



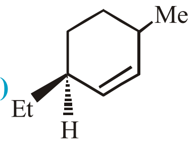
(B)



(C)

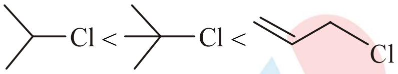


(D)



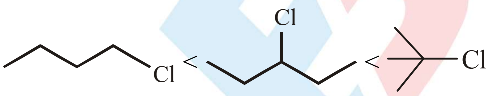
25. Which of the following order is/are correct for the solvolysis in 50% aqueous ethanol at 44.6°C.

(A)

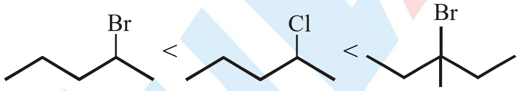


(B)

(C)



(D)



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

Compound	Approx. Relative rate
CH_3CH_2Br	1.0
$CH_3CH_2CH_2Br$	0.28
$(CH_3)_2CHCH_2Br$	0.030
$(CH_3)_3CCH_2Br$	0.00000042

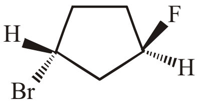
The correct statement (s) is/are :

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

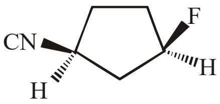
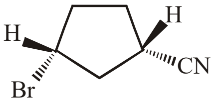
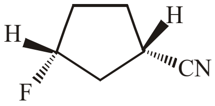
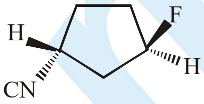
(B) Each of the above reactions is likely to be S_N1

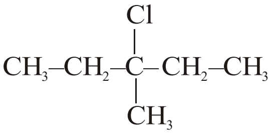
(C) First two reactions follow S_N2 and next two reactions follow S_N1 pathway

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

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

major product of this reaction is.

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

28. 

$$CH_3-CH_2-\underset{CH_3}{\overset{Cl}{C}}-CH_2-CH_3 \xrightarrow{80\%\ EtOH}$$

What is / are true about above reaction ?

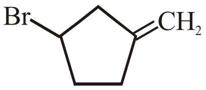
(A) Major product is given by S_N1 reaction.

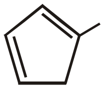
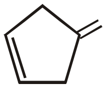
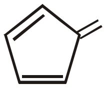
(B) Through E1 mechanism 3 alkenes are formed.

(C) 3-Methylpentan -3-ol is also formed as one of the product.

(D) Fractional distillation of elimination product will give two fractions.

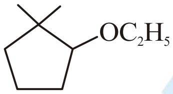
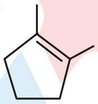
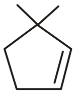
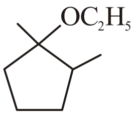
29. Which of the following is/are possible product formed by E1 mechanism for given reaction ?

 $\xrightarrow[\Delta]{CH_3OH}$?

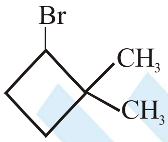
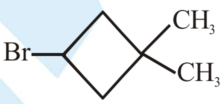
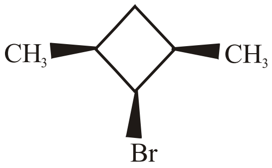
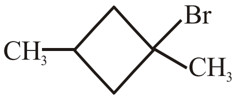
(A)  **(B)**  **(C)**  **(D)** 

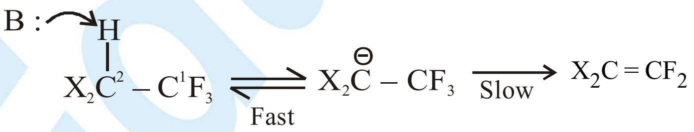
30. Predict the products expected in given reaction

2-Bromo-1, 1-dimethylcycopentane $\xrightarrow[\Delta]{C_2H_5OH}$

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

31. Which of the following compound (s) will yield exclusive (only one) product on dehydrohalogenation by a strong base.

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

32. 

$$X_2\overset{2}{C}H-\overset{1}{C}F_3 \underset{\text{Fast}}{\rightleftharpoons} X_2\overset{\ominus}{C}-CF_3 \xrightarrow[\text{Slow}]{} X_2C=CF_2$$

(X = halogen Cl, Br, I)

Correct statement (s) is (are)

(A) X being electronegative, makes the H (on C-2) more acidic.

(B) Due to electron withdrawal nature of X, it stabilises the carbanion

(C) (X) destabilises the carbanion due to the presence of lone pairs.

(D) The reaction proceeds by an E1 cB pathway.

Part # II [Assertion & Reason Type Questions]

These questions contains, Statement-I (assertion) and Statement-II (reason).

(A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I
(B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I
(C) Statement-I is True, Statement-II is False.
(D) Statement-I is False, Statement-II is True.

1. **Statement-1 :** In the E2 elimination β-H and leaving group must be antiperiplanar.
Statement-2 : In the E2 elimination base abstracts unhindered β-H.

2. **Statement-1 :** Aryl halides undergo nucleophilic substitution with ease.
Statement-2 : The carbon halogen bond in aryl halides has partial double bond character.

3. **Statement-1 :** S_N2 reaction is carried out in the presence of polar aprotic solvents.
Statement-2 : Polar aprotic solvents do not contain acidic hydrogen.

4. **Statement-1 :** Iodide (I^-) is the strongest nucleophile (in protic solvent) among the halide anions
Statement-2 : Iodide is the largest halide anion and is the most weakly solvated in a protic solvent

5. **Statement-I :** Primary benzylic halides are more reactive than primary alkyl halides towards S_{N^1} reaction.
Statement-II : Reactivity depends upon the nature of the nucleophile and the solvent.

6. **Statement-I :** Vinylic halides are reactive towards nucleophilic substitution reaction.
Statement-II : Reactivity is due to the polarity of carbon-halogen bond.

7. **Statement-I :** Aryl halides undergo electrophilic substitution less readily than benzene.
Statement-II : Aryl halide gives only meta product w.r.t. electrophilic substitution.

8. **Statement-I :** Iodination of akanes is carried out by heat in presence of readucing agent.
Statement-II : Iodination of alkanes takepalce explosively.

9. **Statement-I :** Chloropropane has higher boiling point than chloroethane.
Statement-II : Haloalkanes are polar molecules.

10. **Statement-I :** Polar solvent slows down S_{N^2} reaction.
Statement-II : CH_3–Br is less reactive than CH_3Cl.

11. **Statement-I :** Optically active 2-iodibutane on treatment with NaI in acetone undergoes racemisation.
Statement-II : Repeated Walden inversions on the reactant and its product eventually gives a racemic mixture.

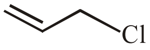
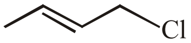
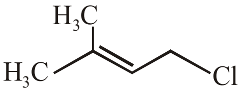
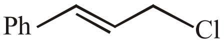
12. **Statement-I :** Free radical chlorination of n-butane gives 72% of 2-chlorobutane and 28% of 1-chlorobutane though it has six primary and four secondary hydrogens.
Statement-II : A secondary hydrogen is abstracted more easily than the primary hydrogen.

13. **Statement-I :** Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.
Statement-II : The reaction occurs by S_{N^1} mechanism.

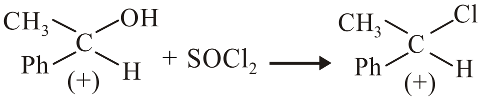
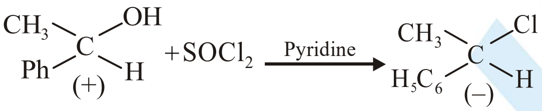
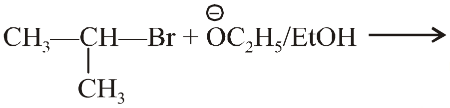
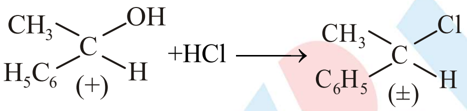
14. **Statement-I :** Boiling point of alkyl halide increases with increasse in molecular weight.
Statement-II : Boiling point of alkylhalides are in the order RI > RBr > RCI > RF.

Exercise # 3 Part # I [Matrix Match Type Questions]

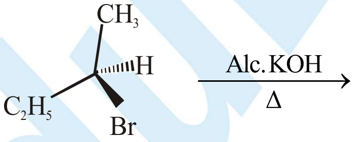
1. Match the column I with column II.

Column-I (Substrate)	**Column-II** (Relative rate of solvolysis in 50% aqueous ethanol at 45°C)
(A) 	**(p)** 7700
(B) 	**(q)** 1
(C) 	**(r)** 91
(D) 	**(s)** 1,30,000

2. Match the column I with column II.

Column-I (reaction)	**Column-II (Mechanism)**
(A) 	**(p)** S_N1
(B) 	**(q)** S_N2
(C)  $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-Br + \overset{\ominus}{O}C_2H_5/EtOH \longrightarrow$	**(r)** S_Ni
(D) 	**(s)** E_2

3. Match the column I and II.

Column I Reaction	**Column II** Type of reaction
(A) 	**(p)** S_N1
(B) 	**(q)** S_N2
(C) 	**(r)** E1
(D) 	**(s)** E2

Part # II [Comprehension Type Questions]

Comprehension # 1

Removal of two atoms or two groups from the substrate is known as elimination reaction. Elimination reaction is always endothermic reaction. The most common elimination reactions are α and β eliminations. The presence of at least one hydrogen on the α-carbon is necessary for α-elimination and on β--carbon is necessary for β-elimination. The driving forces for elimination are **(A)** stability of the olefin formed and **(B)** the relief from steric strain due to crowding in the substrate.

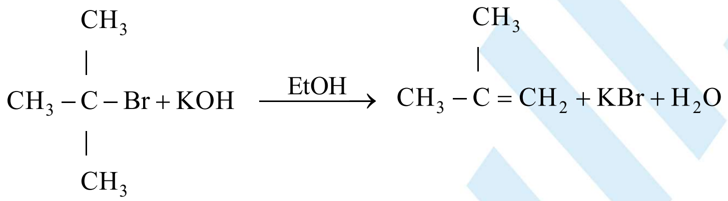
1. Which one of the following compounds can give α-elimination with alc KOH/Δ ?

(A) CCl_4 **(B)** CBr_4 **(C)** CH_2Cl_2 **(D)** CBr_2Cl_2

2. Which of the following alkyl halide is likely to undergo β-elimination most readily

(A) Ethyl bromide **(B)** n-Propyl bromide
(C) iso-Propyl bromide **(D)** tert-Butyl bromide

3. Which of the following is a β-elimination reaction ?

(A) 

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br+KOH\xrightarrow{EtOH}CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2+KBr+H_2O$$

(B) $HOCH_2CH_2Br+NaOH\longrightarrow$  $+NaBr+H_2O$

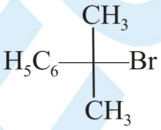
(C) $CHBr_3+(CH_3)_3C-OK\longrightarrow\ :CBr_2+(CH_3)_3COH+KBr$

(D) $BrCH_2CH_2CH_2CH_2OH+NaOH\longrightarrow$  $+\ NaBr+H_2O$

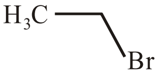
Comprehension # 2

Nucleophilic aliphatic substitution reaction is mainly of two types : S_N1 and S_N2. The S_N1 mechanism is a two step process. Reaction velocity of S_N1 reaction depends only on the concentration of the substrate. Since product formation takes place by the formation of carbocation, optically active substrate gives (+) and (–) forms of the product. In most of the cases the product usually consits of 5-20% inverted product and 80-95% racemised species. The more stable the carbocation, the greater is the proportion of racemisation. In solvolysis reaction, the more nucleophilic the solvent, the greater is the proportion of inversion.

1. Which one of the following compound will give S_N1 reaction predominantly ?

(A) 

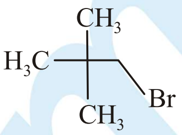
$$H_5C_6-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br$$

(B) 

(C) H_3C-Br **(D)** All of these

2. Which of the following compounds will give S_N1 and S_N2 reactions with considerable rate ?

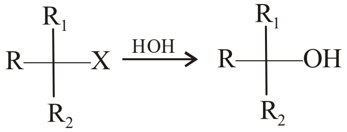
I. $C_6H_5—CH_2—Br$ II. $CH_2=CH—CH_2—Br$ III. $CH_3—CH(Br)CH_3$ IV.



Select the correct answer from the codes given below

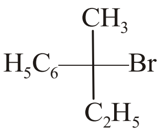
(A) I, II and III **(B)** I, II and IV **(C)** II, III and IV **(D)** I, III and IV

3. For the given reaction

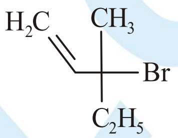


Which substrate will give maximum racemisation ?

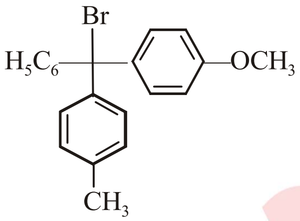
(A)



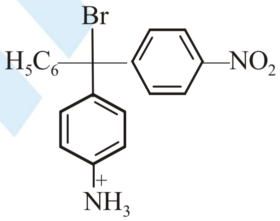
(B)



(C)



(D)



Comprehension # 3

Nucleophilic substitution reactions generally expressed as

$$Nu^- + R — L \longrightarrow R — Nu + L^-$$

Where $Nu^- \longrightarrow$ Nucleophile ; R—L $\longrightarrow$ substrate ; L $\longrightarrow$ leaving group

The best leaving groups are those that become the most stable ions after they depart. Since most leaving groups leave as a negative ion, the best leaving groups are those ions that stabilize a negative charge most effectively.

A good leaving group should be

(A) electron-withdrawing to polarize the carbon

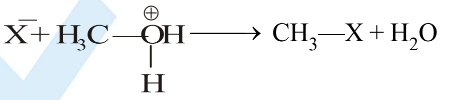
(B) stable once it has left (not a strong base)

(C) polarisable- to maintain partial bonding with the carbon in the transition state (both S_N1 and S_N2). This bonding helps to stabilise the transition state and reduces the activation energy.

1. Among the following which is feasible ?

(A) $X^- + CH_3—CH_2—H \longrightarrow CH_3—CH_2—X + H^-$ **(B)** $X^- + CH_3—OH \longrightarrow CH_3—X + \bar{O}H$

(C)



$X^- + H_3C—\overset{\oplus}{\underset{H}{O}}H \longrightarrow CH_3—X + H_2O$

(D) $X^- + CH_3—CH_3 \longrightarrow CH_3—X + \bar{C}H_3$

2. Among the following which is false statement ?

(A) The weaker the base after the group departs, the better the leaving group

(B) A reactive leaving group would raise the energy of the product, driving the equilibrium towards the reactants

(C) Relative leaving group ability may vary with change of solvent

(D) Better leaving group only increases S_N2 rate, not S_N1.

3. $\underset{(I)}{CH_3Br}$ $\quad \underset{(II)}{CH_3F}$ $\quad \underset{(III)}{CH_3OH}$ $\quad \underset{(IV)}{CH_3OSO_2CF_3}$

The correct order of decreasing reactivity of the above compounds towards CH_3O^- in an S_N2 reaction is :

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

4. $\underset{(I)}{Cl^-}$ $\quad \underset{(II)}{CH_3O^-}$ $\quad \underset{(II)}{CH_3S^-}$ $\quad \underset{(IV)}{I^-}$

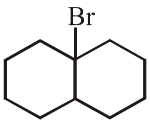
The correct order of increasing leaving group capability of above anoins

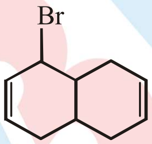
(A) III < IV < II < I **(B)** II < III < I < IV **(C)** II < IV < III < I **(D)** I < III < II < IV

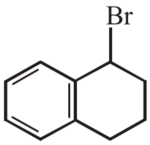
Comprehension # 4

An organic compound A has molecular formula $C_{10}H_{17}Br$ and it is non-resolvable. A does not decolourize brown colour of bromine water solution. A on treatement with $(CH_3)_2COK/(CH_3)_3COH$ yields B as major product. B on treatment with H_2/Pt yields ($C_{10}H_{16}$) which on treatment with Cl_2/hv yields three monochloro derivative. Also B on boiling with acidic permanganate solution yields C($C_{10}H_{16}O_3$). C on heating with sodalime yields D ($C_9H_{16}O$). D on reducing with $LiAlH_4$ followed by heating the product with concentrated H_2SO_4 yields E (C_9H_{16}) as major product. E on treatment with ozone followed by work-up with Zn–H_2O yields 6-Ketononanal.

1. Compound A is :

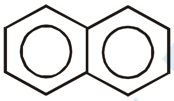
(A) 

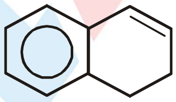
(B) 

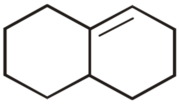
(C) 

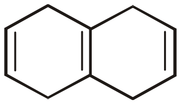
(D) none of these

2. Compound B is :

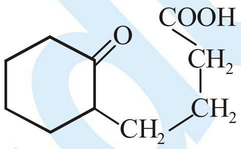
(A) 

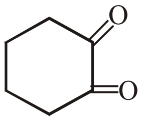
(B) 

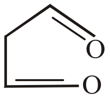
(C) 

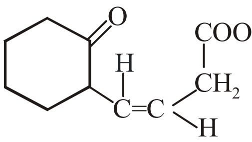
(D) 

3. Compound C is :

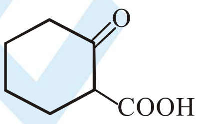
(A) 

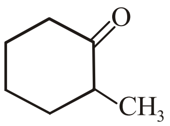
(B) 

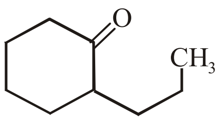
(C) 

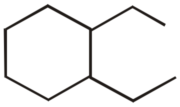
(D) 

4. Compound D is :

(A) 

(B) 

(C) 

(D) 

Exercise # 4

[Subjective Type Questions]

1. Of the following statements, which are true for S_N2 reaction.

(a) Tertiary alkyl halides reacts faster than secondary.

(b) The absolute configuration of product is opposite to that of the reactant when an optically active substrate is used.

(c) The reaction shows first order kinetics.

(d) The rate of the reaction depends markedly on the nucleophilicity of the attacking reagent.

(e) The mechanism is one step.

(f) Carbocations are intermediate.

(g) Rate $\propto$ [Alkyl halides]

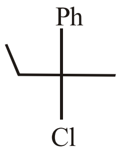
(h) The rate of the raction depends on the nature of the leaving group.

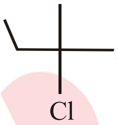
2. Arrange the isomers of molecular formula C_4H_9Cl in order of decreasing rate of reaction with sodium iodide in acetone.

3. There is an overall 29-fold difference in reactivity of 1-chlorohexane, 2-chlorohexane towards potassium iodide in acetone. Which one is the most reactive ? why ?

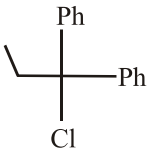
4. Arrange the following compounds in order of :

Decreasing S_N1 reaction rate :


(I)

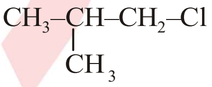

(II)


(III)


(IV)

5. Select the member of each pair that shows faster rate of S_N2 reaction with KI in acetone.

(a) $CH_3–CH_2–CH_2–CH_2–Cl$ and



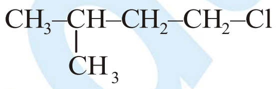
$CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_2–Cl$

(I) (II)

(b) $CH_3–CH_2–CH_2–Cl$ and $CH_3–CH_2–CH_2–Br$

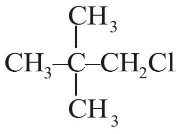
(I) (II)

(c)



$CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_2–CH_2–Cl$

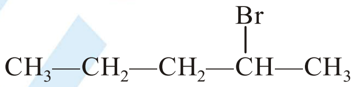
and



$CH_3–\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}–CH_2Cl$

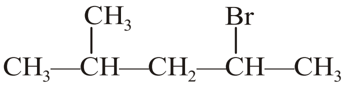
(I) (II)

(d)



$CH_3—CH_2—CH_2—\overset{\displaystyle Br}{\overset{|}{CH}}—CH_3$

and



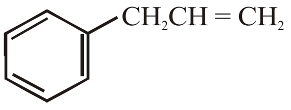
$CH_3—\overset{\displaystyle CH_3}{\overset{|}{CH}}—CH_2—\overset{\displaystyle Br}{\overset{|}{CH}}—CH_3$

(I) (II)

6. Of the following statements which are true for S_N1 reaction.

- **(a)** Tertiary alkyl halides react faster than secondary.
- **(b)** The absolute confuguration of the product is opposite to that of the reactant when an optical active substrate is used.
- **(c)** The reaction shows first order kinetics.
- **(d)** The rate of reaction depends markedly on the nucleophilicity of the nucleophile.
- **(e)** The mechanism is two step.
- **(f)** Carbocations are intermediate.
- **(g)** Rate ∝ [Alkyl halides]
- **(h)** The rate of the raction depends on the nature of the leaving group.

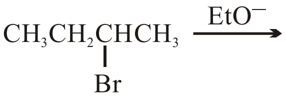
7. Identify the product when A reacts with



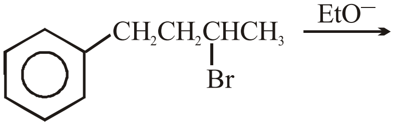
(A)

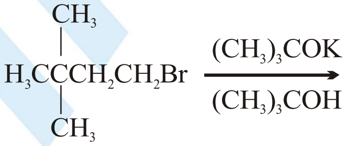
(a) Br_2/Fe **(b)** Br_2/CCl_4 **(c)** NBS **(d)** HBr

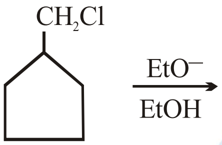
8. Identify major product in the following : $ClCH_2CHCl_2 \xrightarrow{OH^-} CH_2{=}CCl_2$

(a)

$CH_3CH_2\underset{Br}{C}HCH_3 \xrightarrow{EtO^-}$

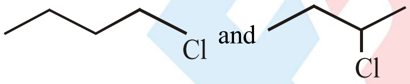
(b) $CH_3CH_2CH_2CH_2Br \xrightarrow{EtO^-}$

(c)


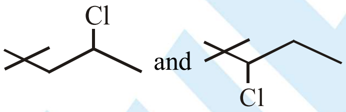
(d)

$H_3C\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK}$

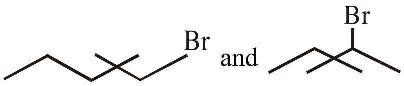
(e)


9. Which is faster in the following pairs of halogen compounds undergoing S_N2 reactions?

(a)


(b)

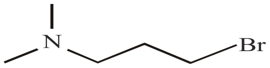

(c)


(d)


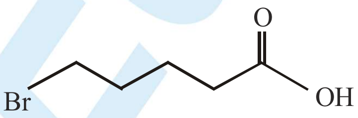
10. R – Mg – Br (A) on reaction with H_2O forms a gas (B), which occupied 1.4 L/g at NTP. What is product when R – Br reacts with benzene in presence of $AlCl_3$?

11. Which of the following alkyl halide could be successfully used to synthesize Grignard reagent and why other fail?

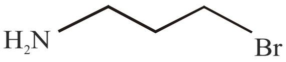
(I)



(II)



(III)



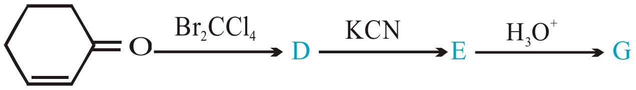
(IV)

12. An alkyl bromide A has molecular formula $C_8H_{17}Br$ and four different structures can be drawn for it, all optically active. A on refluxing with ethanolic KOH solution yields only one elimination product B(C_8H_{16}) which is still enantiomeric. B on treatment with H_2/Pt yields C(C_8H_{18}) which does not rotate the plane polarized light, B on ozonolysis followed by work-up with H_2O_2 yields D($C_7H_{14}O$) as one product which is still resolvable. Deduce structures of A to D.

13. Identify A to G in the following.

(a)

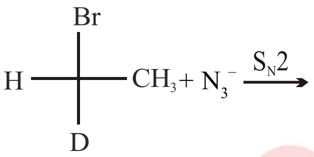
(b)



14. Explain the following observations:

(a) Azide ion (N_3^-) react with 2- bromopentane thousand times faster than with neopentyl bromide in a S_N2 reaction though former is a secondary halide while latter is primary.

(b) What will happen to the stereochemistry of product of the following reaction:\



(c) What will happen to the rate if the concentration of alkyl bromide in (b) is doubled?

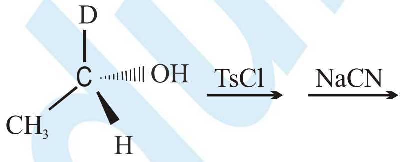
(d) What will happen to the rate if the concentration of azide ion in (b) is doubled?

(e) How the sign of optical rotation of reactant and product are related in (b)

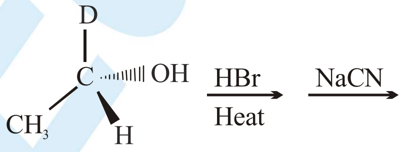
(f) When allowed to stand in dilute H_2SO_4, laevo-rotatory 2-butanol slowly loses optical activity.

15. Provide structure of major product in the following reaction indicating stereochemistry where appropriate:

(a)



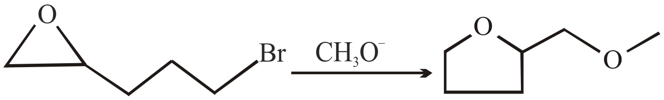
(b)



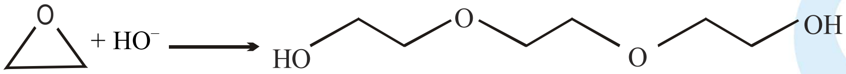
16. Propose mechanism of the following reactions:

(a)

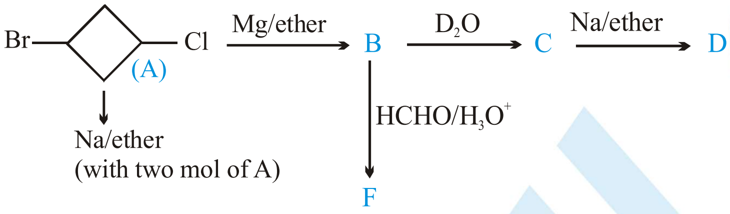
(b)



(c)



17.



Identify B to F

18. Vinyl chloride does not give S_N reaction but allyl chloride gives. Explain.

19. Arrange the following in the increasing order of their ability as a leaving group:

(a) CH_3S^-, CH_3O^-, CF_3^- and F^-

(b) $CF_3SO_3^-$, $CH_3SO_3^-$ and CH_3COO^-

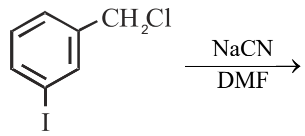
20. RBr when treated with AgCN in a highly polar solvent gives RNC whereas when it is treated with NaCN it gives RCN. Explain.

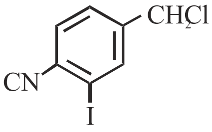
Exercise # 5 Part # I [Previous Year Questions] [AIEEE/JEE-MAIN]

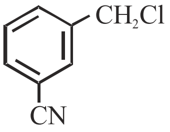
1. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of : **[AIEEE-2005]**
(1) steric hindrance **(2)** inductive effect **(3)** instability **(4)** insolubility

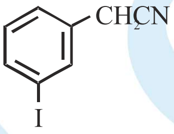
2. Reaction of trans 2–phenyl –1 – bromocyclopentane on reaction with alcoholic KOH produces: **[AIEEE-2006]**
(1) 2–phenylcyclopentene **(2)** 1–phenylcyclopentene
(3) 3-phenylcyclopentene **(4)** 4-phenylcyclopentene

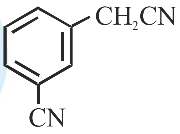
3. The structure of the major product formed in the following reaction is : **[AIEEE-2006]**



(1)


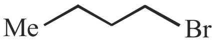
(2)


(3)


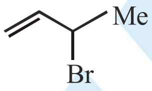
(4)


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

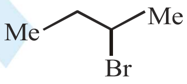
5. Consider the following bromides : **[AIEEE-2010]**



(A)



(B)



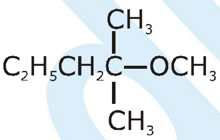
(C)

The correct, order of S_N1 reactivity is
(1) B > C > A **(2)** B > A > C **(3)** C > B > A **(4)** A > B > C

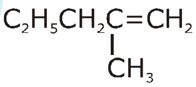
6. What is DDT among the following : **[AIEEE-2012]**
(1) Greenhouse gas **(2)** A fertilizer
(3) Biodegradable pollutant **(4)** Non-biodegradable pollutant

7. 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 MAINS 2013]**
(1) carbanion **(2)** carbene **(3)** carbocation **(4)** free radical

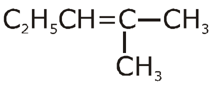
8. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields : **[JEE MAINS 2016]**

(a)


$$C_2H_5CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OCH_3$$

(b)


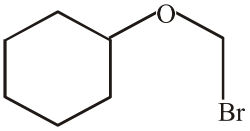
$$C_2H_5CH_2\underset{\displaystyle CH_3}{C}=CH_2$$

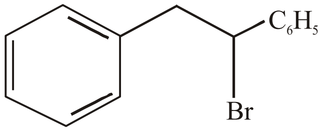
(c)


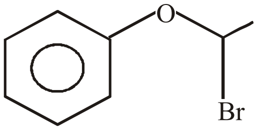
$$C_2H_5CH=\underset{\displaystyle CH_3}{C}-CH_3$$

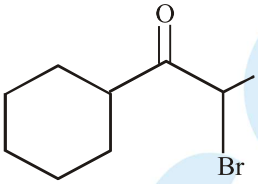
(1) (a) and (c) **(2)** (c) only **(3)** (a) and (b) **(4)** All of these

9. Which of the following, upon treatment with tert-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine ? **[JEE MAINS 2017]**

(1)


(2)


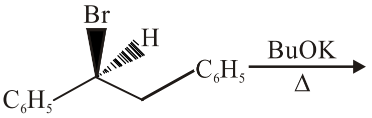
(3)


(4)


10. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is : **[JEE MAINS 2017]**

(1) Six **(2)** Zero **(3)** Two **(4)** Four

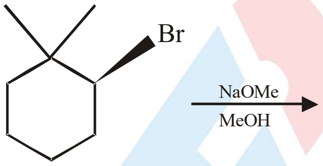
11. The major product obtained in the following reaction is : **[JEE MAINS 2017]**

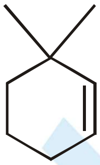


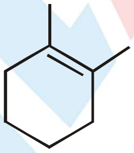
(1) (±) $C_6H_5CH(O^tBu)CH_2C_6H_5$ **(2)** $C_6H_5CH{=}CHC_6H_5$

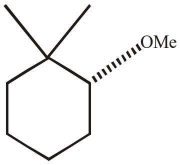
(3) (+) $C_6H_5CH(O^tBu)C_2H_5$ **(4)** (–) $C_6H_5CH(O^tBu)CH_2C_6H_5$

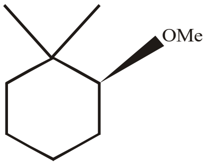
12. The major product of the following reaction is : **[JEE MAINS 2018]**



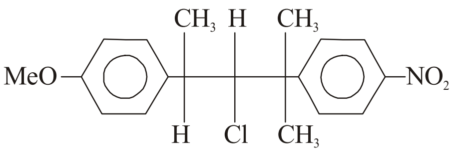
(1)


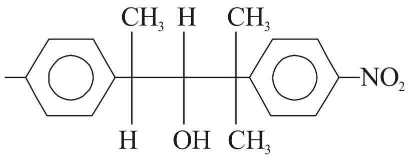
(2)


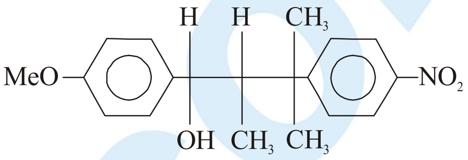
(3)


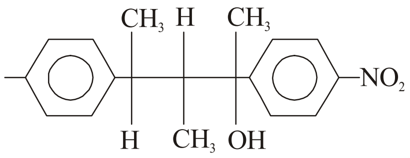
(4)


Part # II [Previous Year Questions][IIT-JEE ADVANCED]

1.  on hydrolysis in presence of acetone : **[IIT-05]**

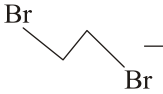
(K) 

(L) 

(M) 

(A) K & L **(B)** only L **(C)** M only **(D)** K & M

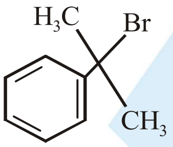
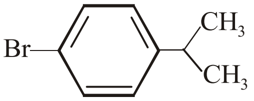
2. The reagent (s) for the following conversion : **[IIT-07]**

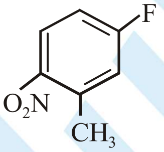
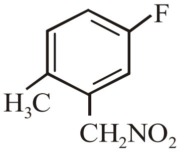
 $\xrightarrow{?}$ $HC\equiv CH$ is /are -

(A) alcoholic KOH **(B)** Alcoholic KOH followed by $NaNH_2$

(C) aquesous KOH followed by $NaNH_2$ **(D)** Zn/CH_3OH

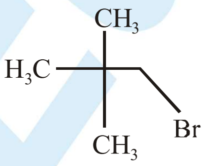
3. Give reasons : **[IIT 2005]**

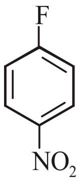
(A) (i)  $\xrightarrow{C_2H_5OH(aq.)}$ acidic solution ; **(ii)**  $\xrightarrow{C_2H_5OH(aq.)}$ neutral

(B) (i)  $\xrightarrow{NaOH(aq)}$ F^- (liberated) ; **(ii)**  $\xrightarrow{NaOH(aq)}$ F^- is not liberated

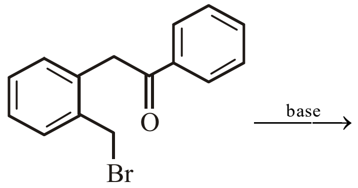
4. An alkyl halide ,**(A)** of formula $C_6H_{11}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes **(B)** and **(C)** C_6H_{10} .Both alkene on hydrogenation give methycyclopentane. Predict the structure of **(A)**, **(B)** and **(C)**.

5. Which would be the major product in each of the following reactions ?

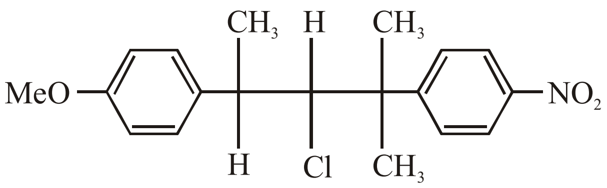
(A)  $\xrightarrow[\Delta]{C_2H_5OH}$

(B)  $\xrightarrow[\Delta]{NaOCH_3}$

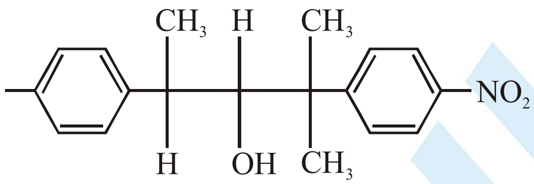
(C)



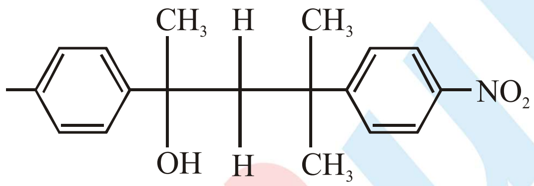
6. The following compound on hydrolysis in aqueous acetone will give: **[IIT 2005]**



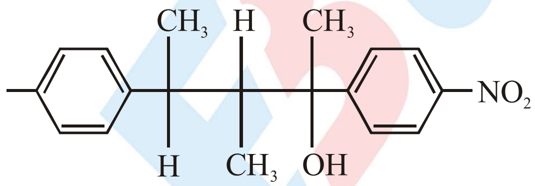
(K)



(L)



(M)



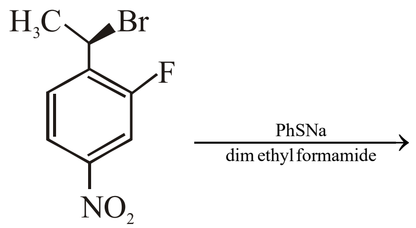
It mainly gives

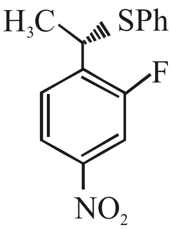
(A) K and L **(B)** Only K **(C)** L and M **(D)** Only M

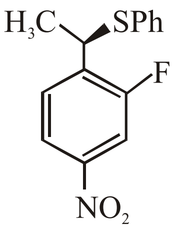
7. Match the following: **[IIT 2006]**

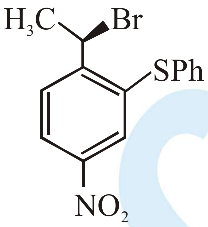
Column I	**Column II**
(A) CH_3–CHBr–CD_3 on treatment with alc. KOH gives CH_2=CH-CD_3 as a major product.	**(P)** E1 reaction
(B) Ph – CHBr - CH_3 reacts faster than Ph-CHBr-CD_3.	**(Q)** E2 reaction
(C) Ph-CD_2-CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph-CD=CH_2 as the major product.	**(R)** E1cb reaction
(D) $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ react with same rate.	**(S)** First order reaction

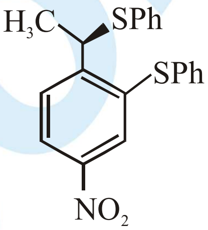
8. The major product of the following reaction is **[IIT 2008]**

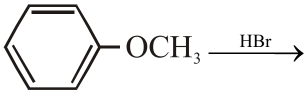


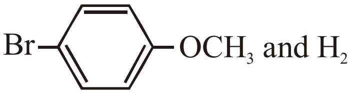
(A) 

(B) 

(C) 

(D) 

9. In the reaction  the products are **[IIT 2010]**

(A) 

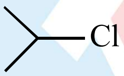
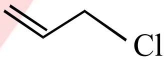
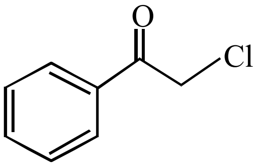
(B) 

(C) 

(D) 

10. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is **[IIT-2011]**

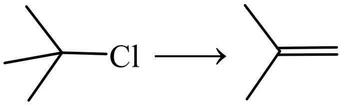
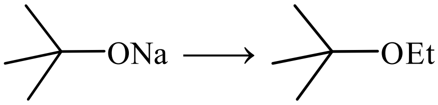
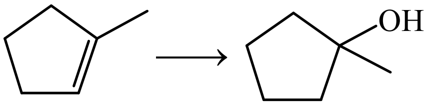
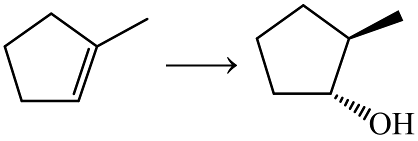
11. KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as - **[IIT 2013]**

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

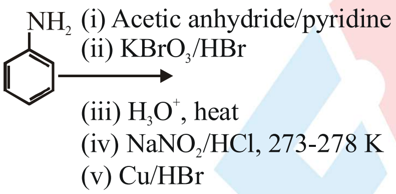
12. Match the chemical conversions in List-I with the appropritate reagents in List-II and select the correct answer using the code given below this lists - **[IIT 2013]**

	List-I		**List-II**
(P)		**(1)**	(i) $Hg(OAc)_2$ (ii) $NaBH_4$
(Q)		**(2)**	NaOEt
(R)		**(3)**	Et-Br
(S)		**(4)**	(i) BH_3 (ii) H_2O_2 /NaOH

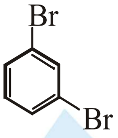
Codes :

	P	Q	R	S
(A)	2	3	1	4
(B)	3	2	1	4
(C)	2	3	4	1
(D)	3	2	4	1

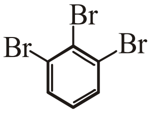
13. The product (s) of the following reaction sequence is (are) : **[JEE (Advanced) 2016)**

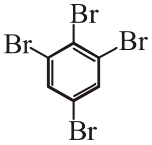


(i) Acetic anhydride/pyridine
(ii) $KBrO_3/HBr$
(iii) H_3O^+, heat
(iv) $NaNO_2/HCl$, 273-278 K
(v) Cu/HBr

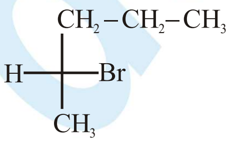
(A) 

(B) 

(C) 

(D) 

14. In the following monobromination reaction, the number of possible chiral products is : **[JEE (Advanced) 2016)**



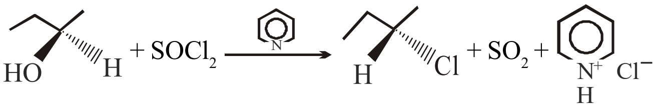
$\xrightarrow[300\ °C]{Br_2\ (1.0\ mole)}$

1.0 mole
(enatiomerically pure)

MOCK TEST

SECTION - I : STRAIGHT OBJECTIVE TYPE

1. The reaction



proceeds by the mechanism

(A) S_{N^1} **(B)** S_{N^2} **(C)** S_Ni **(D)** S_{E^2}

2. The products of reaction of alcoholic silver nitrite with ethyl bromide are

(A) Ethane **(B)** Ethene **(C)** Ethyl alcohol **(D)** Nitro ethane

3. For the reaction

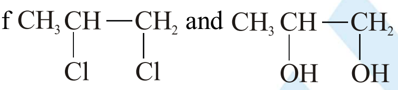
$$CH_3CH(X)CH_2CH_3 \xrightarrow{\text{alc. KOH}} \begin{cases} CH_3-CH=CH-CH_3 \\ CH_2=CH-CH_2-CH_3 \end{cases}$$

(A) $CH_3-CH=CH-CH_3$ predominates **(B)** $CH_2=CH-CH_2-CH_3$ predominates

(C) Both are formed in equal amounts **(D)** The product ratio depends on the halogen

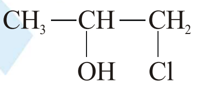
4. Identify 'Z' in the following reaction series, $CH_3.CH_2CH_2Br \xrightarrow{\text{aq.NaOH}} (X) \xrightarrow[\text{Heat}]{Al_2O_3} (Y) \xrightarrow{\text{HOCl}} (Z)$:

(A) Mixture of



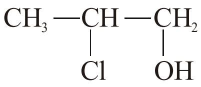
$CH_3\underset{Cl}{CH}-\underset{Cl}{CH_2}$ and $CH_3\underset{OH}{CH}-\underset{OH}{CH_2}$

(B)



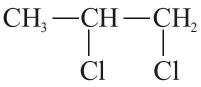
$CH_3-\underset{OH}{CH}-\underset{Cl}{CH_2}$

(C)



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

(D)



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

5. Ethyl alcohol reacts at a faster rate with HI than with HCl in forming the corresponding ethyl halides under identical conditions mainly because -

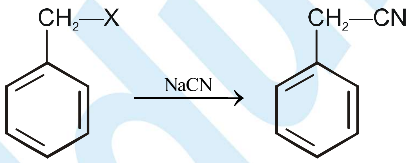
(A) HI, being a stronger acid, protonates ethyl alcohol at oxygen much better and helps substitution

(B) the bond length in HI is much shorter than that in HCl

(C) I^- is a much better leaving group

(D) I^- is a much better nucleophile than Cl^-

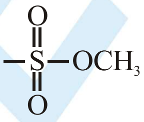
6.



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

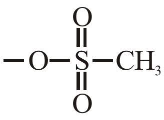
(A) –OH **(B)** $-NH_2$

(C)

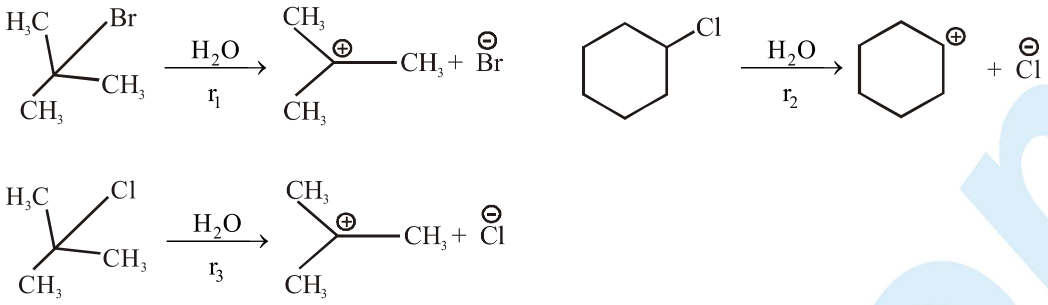


$-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-OCH_3$

(D)



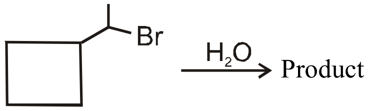
$-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-CH_3$

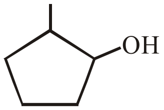
7. 

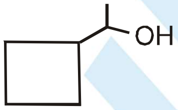
the rates r_1 , r_2 and r_3 are in the order :

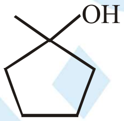
(A) $r_1 > r_2 > r_3$ **(B)** $r_3 > r_1 > r_2$ **(C)** $r_1 > r_3 > r_2$ **(D)** $r_2 > r_1 > r_3$

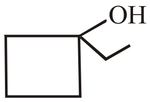
8. What will be the major product of the following reaction



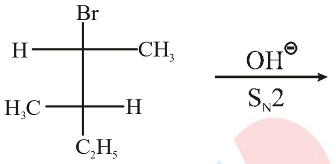
(A) 

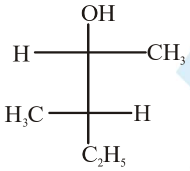
(B) 

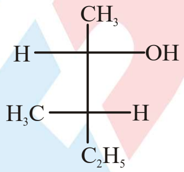
(C) 

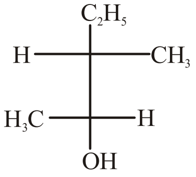
(D) 

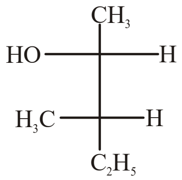
9. In the following reaction the most probable product will be :



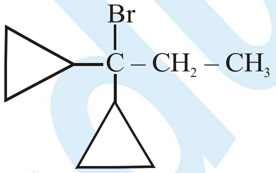
(A) 

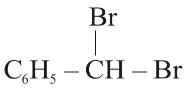
(B) 

(C) 

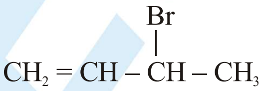
(D) 

10. Which of the following will be most reactive for E1 reaction ?

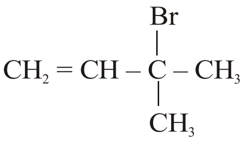
(A) 

(B) 

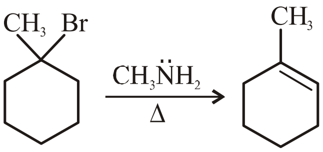
$C_6H_5-\overset{Br}{\overset{|}{C}}H-Br$

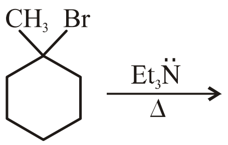
(C) 

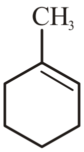
$CH_2=CH-\overset{Br}{\overset{|}{C}}H-CH_3$

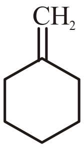
(D) 

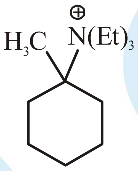
$CH_2=CH-\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3$

11. If  ; Then what will be the major product of the following reaction


major product

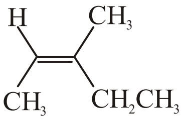
(A) 

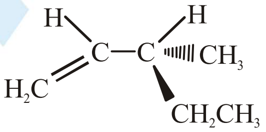
(B) 

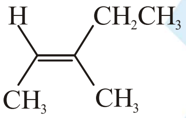
(C) 

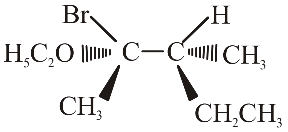
(D) B & C both

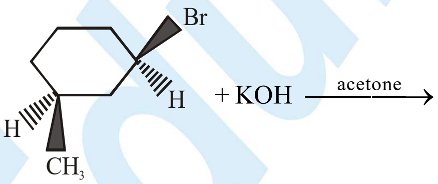
12. Select the formula representing the major product of the following reaction

(A) 

(B) 

(C) 

(D) 

13.  Product

(1R, 3S)–Cis–1–Bromo–3–methylcyclohexane.

The product formed in the reaction is

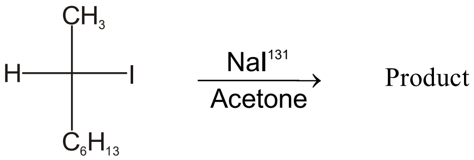
(A) (1R, 3S)–Cis–3–methyl cyclohexanol

(B) (1S, 3S)–Cis–3– methyl cyclohexanol

(C) (1S, 3S)–Trans–3–methyl cyclohexanol

(D) (1R, 3R)–Trans–3–methyl cyclohexanol

14. Which statement is incorrect about the following reaction



2-Iodooctane
(+)

(A) The rate of these reaction depends on both [R–I] and [$^{131}I^{\ominus}$]

(B) Loss of optical activity was twice as fast as gain of radioactivity.

(C) Each molecule undergoing substitution, suffers Inversion of configuration

(D) Final solution has radioactive iodine only

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

15. Which of the following does/do produce a white precipitate of AgCl on warming with alcoholic silver nitrate?

(A) Allyl chloride **(B)** t-Butyl chloride **(C)** Benzyl chloride **(D)** Vinyl chloride

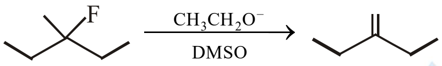
16. Which of the following are aprotic solvents :

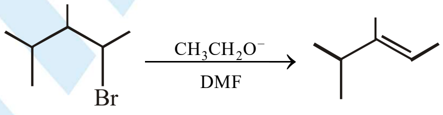
(A) DMSO **(B)** DMF **(C)** H_2O **(D)** CH_3COOH

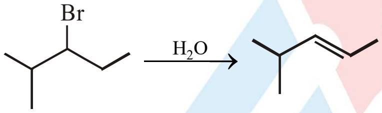
17. Which of the following reagents can be used to prepare an alkyl halide :-

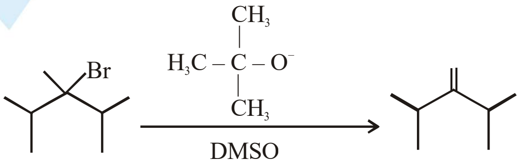
(A) NaCl **(B)** $HCl + ZnCl_2$ **(C)** $SOCl_2$ **(D)** PCl_5

18. Which of the following reactions represent the major product.

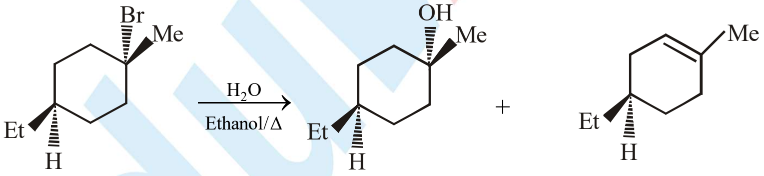
(A)


(B)


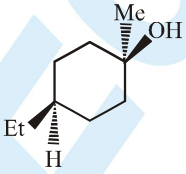
(C)


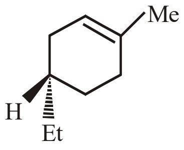
(D)


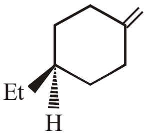
19. Consider the following E1/S_N1 reaction :

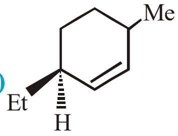


The missing product (s) is (are) :

(A)


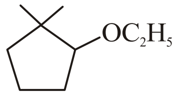
(B)


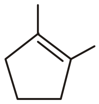
(C)


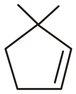
(D)


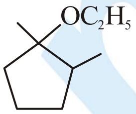
20. Predict the products expected in given reaction

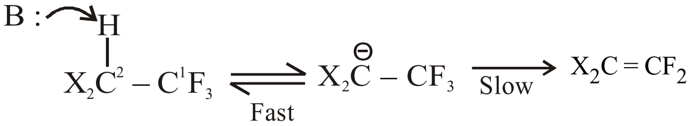
2-Bromo-1, 1-dimethylcycopentane $\xrightarrow[\Delta]{C_2H_5OH}$

(A)


(B)


(C)


(D)


21.


$$X_2\overset{\overset{\curvearrowright H}{|}}{C^2} - C^1F_3 \underset{\text{Fast}}{\rightleftharpoons} X_2\overset{\ominus}{C} - CF_3 \xrightarrow{\text{Slow}} X_2C = CF_2$$

B :

(X = halogen Cl, Br, I)

Correct statement (s) is (are)

(A) X being electronegative, makes the H (on C-2) more acidic.

(B) Due to electron withdrawal nature of X, it stabilises the carbanion

(C) (X) destabilises the carbanion due to the presence of lone pairs.

(D) The reaction proceeds by an E1 cB pathway.

SECTION - III : ASSERTION AND REASON TYPE

These questions contains, Statement-I (assertion) and Statement-II (reason).

(A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I

(B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I

(C) Statement-I is True, Statement-II is False.

(D) Statement-I is False, Statement-II is True.

22. **Statement-1 :** S_N2 reaction is carried out in the presence of polar aprotic solvents.

Statement-2 : Polar aprotic solvents do not contain acidic hydrogen.

23. **Statement-1 :** Iodide (I^-) is the strongest nucleophile (in protic solvent) among the halide anions

Statement-2 : Iodide is the largest halide anion and is the most weakly solvated in a protic solvent

24. **Statement-I :** Primary benzylic halides are more reactive than primary alkyl halides towards S_{N^1} reaction.

Statement-II : Reactivity depends upon the nature of the nucleophile and the solvent.

25. **Statement-I :** Vinylic halides are reactive towards nucleophilic substitution reaction.

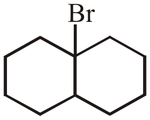
Statement-II : Reactivity is due to the polarity of carbon-halogen bond.

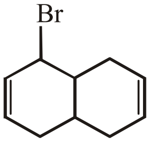
SECTION - IV : COMPREHENSION TYPE

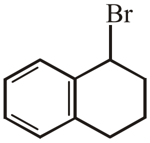
Read the following comprehensions carefully and answer the questions.

An organic compound A has molecular formula $C_{10}H_{17}Br$ and it is non-resolvable. A does not decolourize brown colour of bromine water solution. A on treatement with $(CH_3)_2COK/(CH_3)_3COH$ yields B as major product. B on treatment with H_2/Pt yields ($C_{10}H_{16}$) which on treatment with Cl_2/hv yields three monochloro derivative. Also B on boiling with acidic permanganate solution yields C($C_{10}H_{16}O_3$). C on heating with sodalime yields D ($C_9H_{16}O$). D on reducing with $LiAlH_4$ followed by heating the product with concentrated H_2SO_4 yields E (C_9H_{16}) as major product. E on treatment with ozone followed by work-up with Zn–H_2O yields 6-Ketononanal.

26. Compound A is :

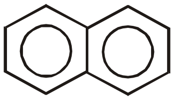
(A) 

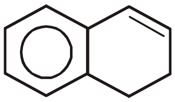
(B) 

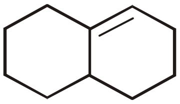
(C) 

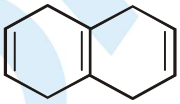
(D) none of these

27. Compound B is :

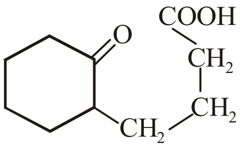
(A) 

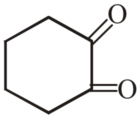
(B) 

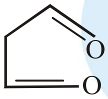
(C) 

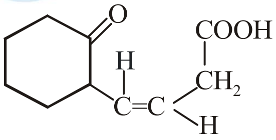
(D) 

28. Compound C is :

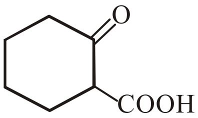
(A) 

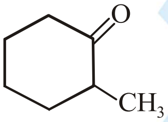
(B) 

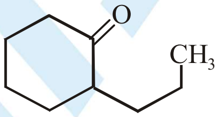
(C) 

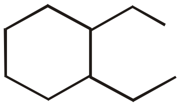
(D) 

29. Compound D is :

(A) 

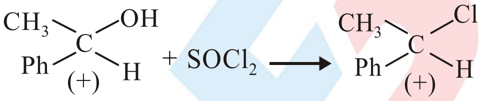
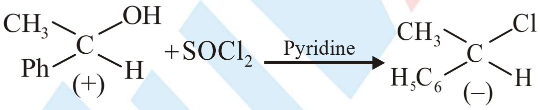
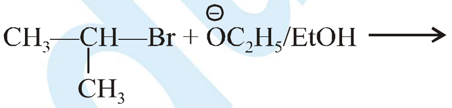
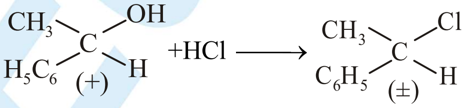
(B) 

(C) 

(D) 

SECTION - V : MATRIX - MATCH TYPE

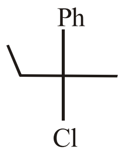
30. Match the column I with column II.

Column-I (reaction)	**Column-II (Mechanism)**
(A) 	**(p)** S_N1
(B) 	**(q)** S_N2
(C)  $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-Br + \overset{\ominus}{O}C_2H_5/EtOH \longrightarrow$	**(r)** S_Ni
(D) 	**(s)** E_2

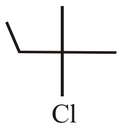
SECTION - VI : SUBJECTIVE TYPE

31. Arrange the following compounds in order of :

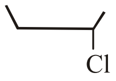
Decreasing S_N1 reaction rate :



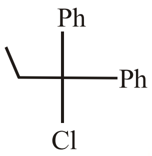
(I)



(II)



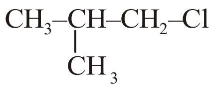
(III)



(IV)

32. Select the member of each pair that shows faster rate of S_N2 reaction with KI in acetone.

(a) $CH_3-CH_2-CH_2-CH_2-Cl$ (I) and

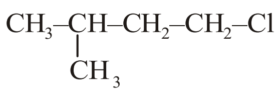


$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-Cl$

(II)

(b) $CH_3-CH_2-CH_2-Cl$ (I) and $CH_3-CH_2-CH_2-Br$ (II)

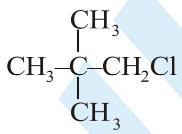
(c)



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

(I)

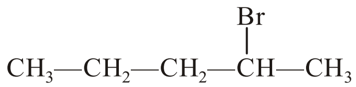
and



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2Cl$

(II)

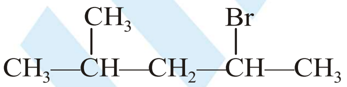
(d)



$CH_3-CH_2-CH_2-\overset{Br}{\overset{|}{CH}}-CH_3$

(I)

and



$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{Br}{\overset{|}{CH}}-CH_3$

(II)

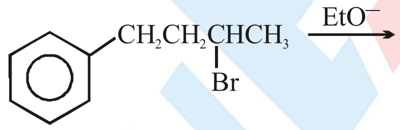
33. Identify major product in the following : $ClCH_2CHCl_2 \xrightarrow{OH^-} CH_2=CCl_2$

(a)

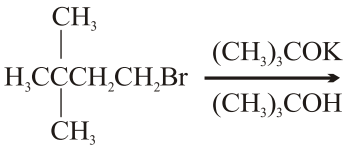
$CH_3CH_2\underset{Br}{\underset{|}{CH}}CH_3 \xrightarrow{EtO^-}$

(b) $CH_3CH_2CH_2CH_2Br \xrightarrow{EtO^-}$

(c)

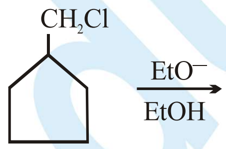


(d)



$H_3C\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK}$

(e)



34. R – Mg – Br (A) on reaction with H_2O forms a gas (B), which occupied 1.4 L/g at NTP. What is product when R – Br reacts with benzene in presence of $AlCl_3$?

ANSWER KEY

EXERCISE - 1

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

EXERCISE - 2 : PART # I

1. C **2.** B **3.** B **4.** A, B, C **5.** C **6.** B **7.** A, B **8.** A, B, C, D **9.** B **10.** D **11.** D
12. C **13.** D **14.** A **15.** D **16.** B, C **17.** B, C, D **18.** A, C, D **19.** B, C **20.** A, B
21. A, B, D **22.** B, D **23.** C, D **24.** A, B, C **25.** B, C **26.** A, D **27.** A, C **28.** A, B, C **29.** B, C
30. A, B, C, D **31.** A, B **32.** A, B, D

PART # II

1. C **2.** D **3.** B **4.** A **5.** B **6.** D **7.** C **8.** D **9.** B **10.** C **11.** A **12.** A **13.** A
14. B

EXERCISE - 3 : PART # I

1. $A \rightarrow q, B \rightarrow r, C \rightarrow s, D \rightarrow p$
2. $A \rightarrow r, B \rightarrow q, C \rightarrow s, D \rightarrow p$
3. $A \rightarrow q, B \rightarrow s, C \rightarrow r, D \rightarrow p$

PART # II

Comprehension # 1 : **1.** In the compound at least one hydrogen on the α - carbon is necessary for α - elimination

2. Tert.butyl bromide is undergo β-elimination most readily due to formation of most stable alkene.

3. A

Comprehension # 2 : **1.** A **2.** A **3.** C

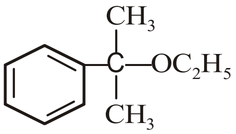
Comprehension # 3 : **1.** C **2.** D **3.** B **4.** B

Comprehension # 4 : **1.** A **2.** C **3.** A **4.** C

EXERCISE - 5 : PART # I

1. 1 **2.** 3 **3.** 3 **4.** 2 **5.** 1 **6.** 4 **7.** 3 **8.** 4 **9.** 1 **10.** 4 **11.** 2 **12.** 1

PART # II

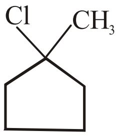
1. A **2.** B **3.** (a) (i) Products are  + HBr (aq.) ; Hence acidic.

(ii) No reaction takes place, as aryl halide is inert to nucleophilic subsititution.

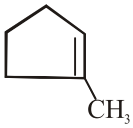
(b) (i) —NO_2 group facilitates the nucleophilic attack because it stabilised the anion formed when attack of $\overline{O}H$ takes place.

(ii) Does not show reaction.

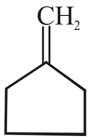
4. (B)



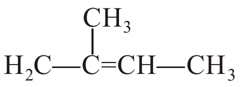
(A)



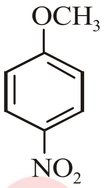
(B)

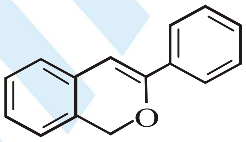


(C)

5. (a) 

$H_2C-\overset{\overset{\large CH_3}{|}}{C}=CH-CH_3$

(b) 

(c) 

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

MOCK-TEST

1. B **2.** D **3.** D **4.** B **5.** D **6.** D **7.** C **8.** C **9.** B **10.** A **11.** B **12.** C **13.** C

14. D **15.** A, B, C **16.** A, B **17.** B, C, D **18.** A, B, D **19.** A, B, C **20.** A, B, C, D **21.** A, B, D **22.** B

23. A **24.** B **25.** D **26.** A **27.** C **28.** A **29.** C **30.** A → (r), B → (q), C → (s), D → (p)