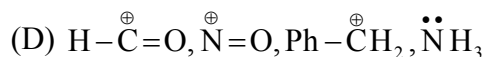
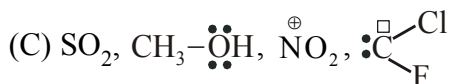
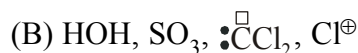
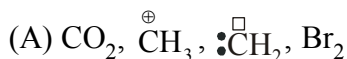


HALOGEN DERIVATIVES

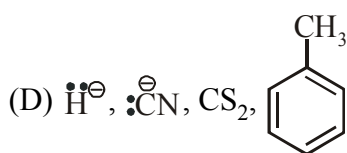
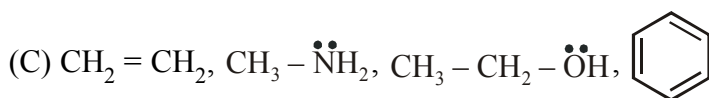
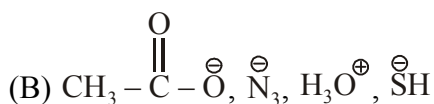
HALOGEN DERIVATIVES

EXERCISE # I (MAINS ORIENTED)

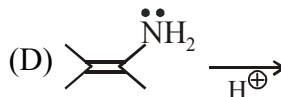
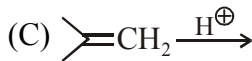
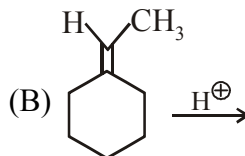
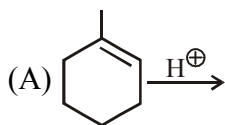
1. Identify set of electrophiles :



2. Identify set of nucleophiles :



3. Which of the following will form 2° carbocation?



4. Incorrect statement about carbocation is :

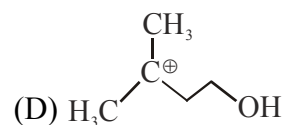
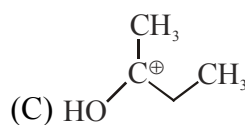
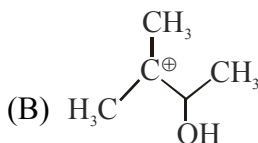
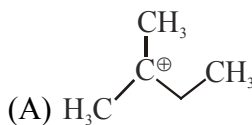
(A) It is lewis acid

(B) It has 6 electrons in valency shell

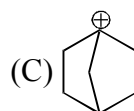
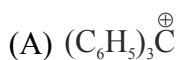
(C) It is electrophile

(D) It is always trigonal planar

5. Which of the following carbocation is most stable ?



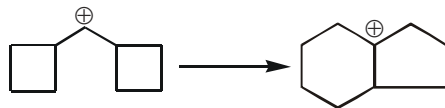
6. Which carbocation is least likely to be formed as an intermediate ?



7. Which one of the following carbocation would you expect to rearrange :

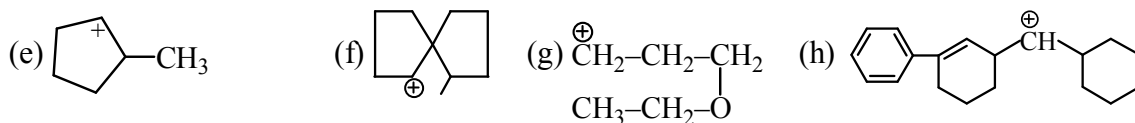


8. How many 1,2-shifts are involved during the course of following reaction :



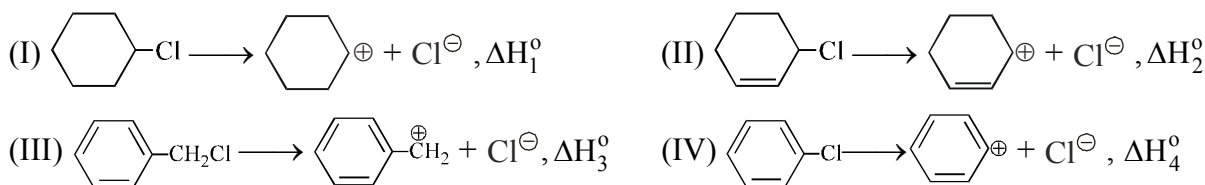
(A) 1 (B) 2 (C) 3 (D) 4

9. How many following carbocation undergo re-arrangement -



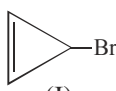
(A) 5 (B) 8 (C) 6 (D) 7

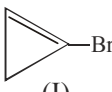
10. For the reactions



The correct decreasing order of enthalpies of reaction for producing carbocation is :

(A) $\Delta H_1^0 > \Delta H_2^0 > \Delta H_3^0 > \Delta H_4^0$ (B) $\Delta H_4^0 > \Delta H_1^0 > \Delta H_2^0 > \Delta H_3^0$
 (C) $\Delta H_3^0 > \Delta H_2^0 > \Delta H_1^0 > \Delta H_4^0$ (D) $\Delta H_2^0 > \Delta H_1^0 > \Delta H_4^0 > \Delta H_3^0$

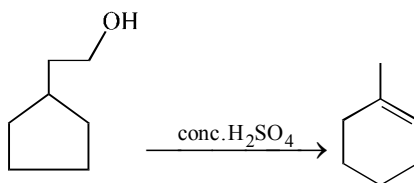
11.  (I), which is not the correct statement :

- (A) I is more soluble in water than bromocyclopropane
 (B) I gives pale yellow ppt. on addition with aq. AgNO_3
 (C) I is having lower dipole moment than bromocyclopropane
 (D) I is more ionic than  (I)

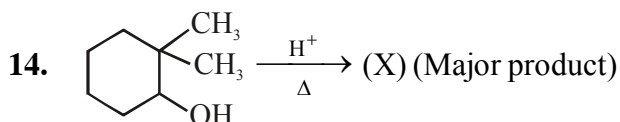
12. A solution of (–) –1-chloro–1-phenylethane in toluene racemises slowly in the presence of a small amount of SbCl_5 , due to the formation of :-

(A) carbanion (B) Carbene (C) carbocation (D) free radical

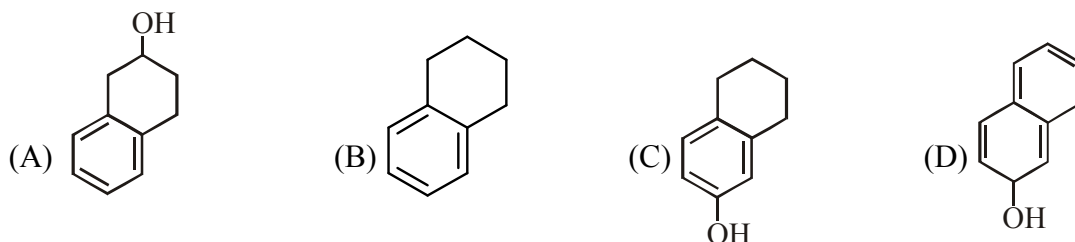
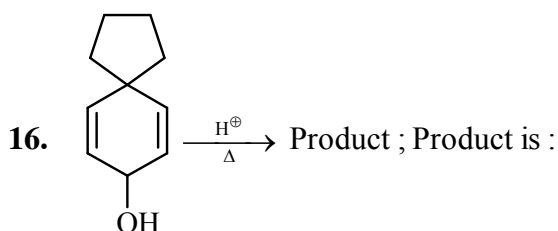
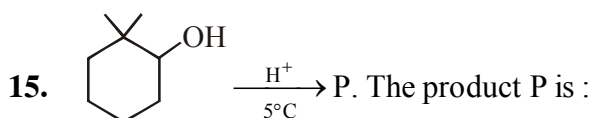
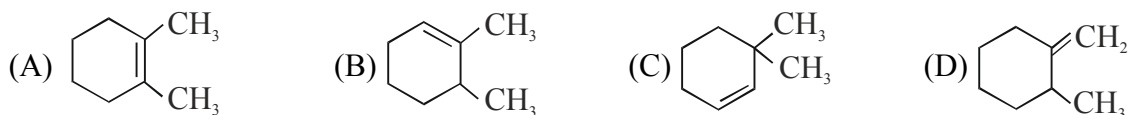
13. How many 1,2-Shifts of carbocation intermediate are involved during the course of following reaction :



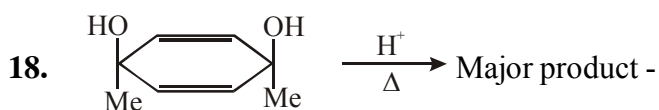
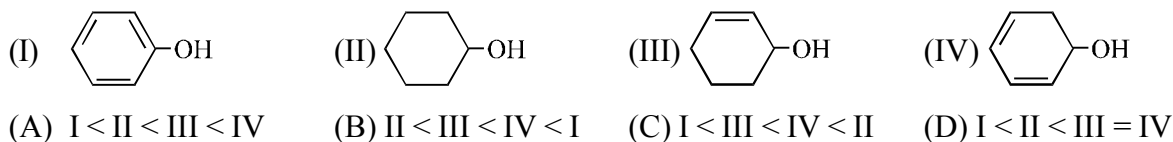
- (A) 1 (B) 2 (C) 3 (D) 4



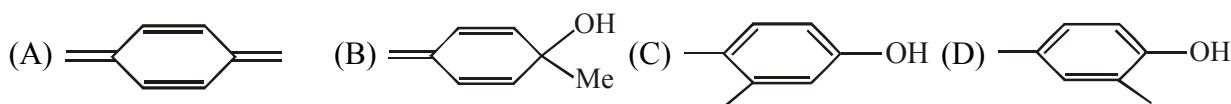
Major product (X) is :



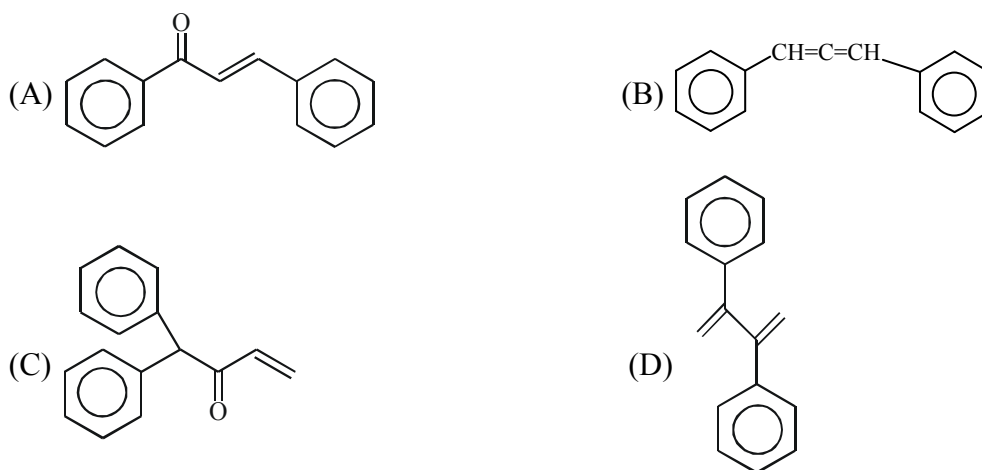
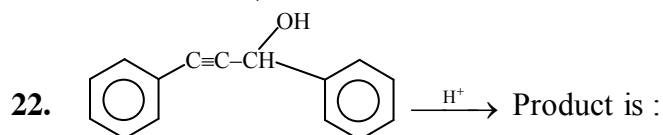
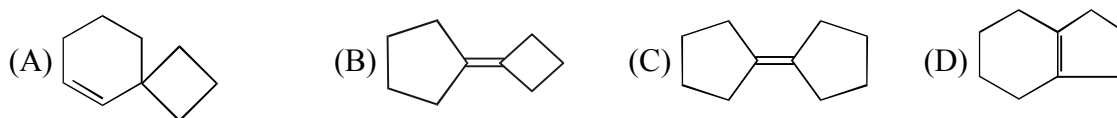
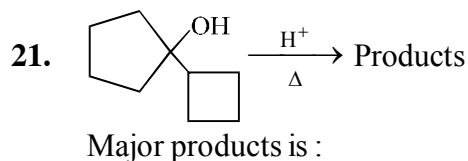
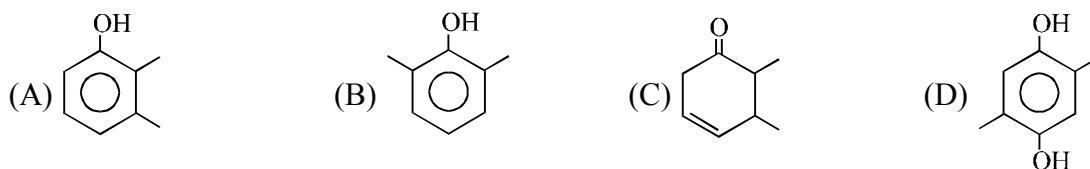
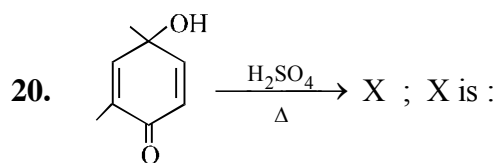
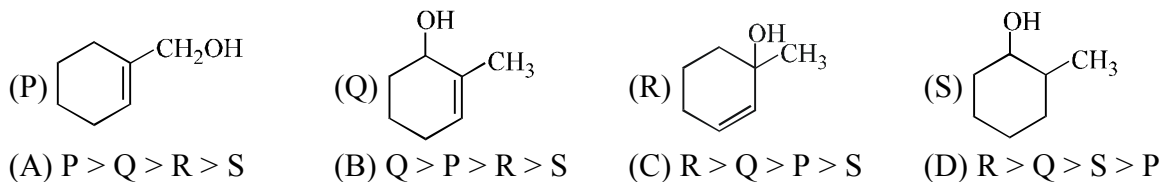
17. Among the given compounds, the correct order of rate of dehydration is :



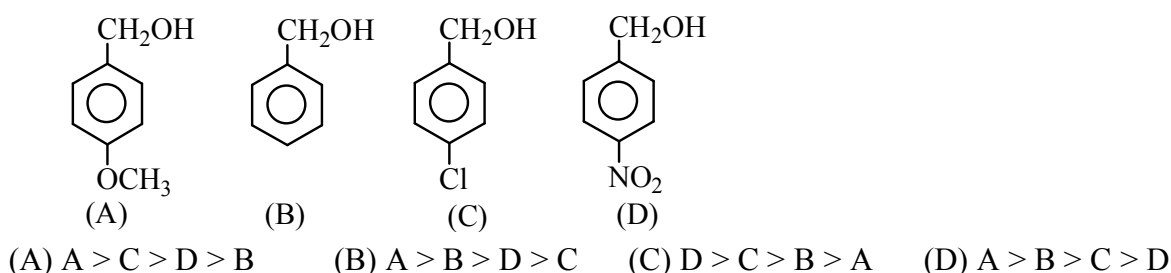
Major product is :



19. Identify the correct order of rate of dehydration when given compounds are treated with conc. H_2SO_4 :

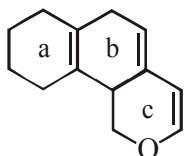


23. What is the decreasing order of rate of reaction with HBr for the following benzyl alcohol and its derivative :



24. Which will dehydrate at fastest rate by H_3PO_4 :

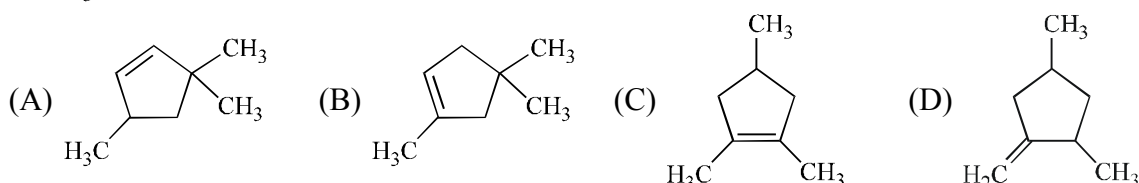
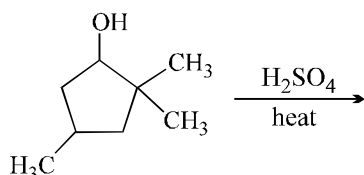
- (A) 2-methyl butan-2-ol (B) 3-methyl butan-2-ol
(C) Butan-1-ol (D) 2-methyl butan-1-ol



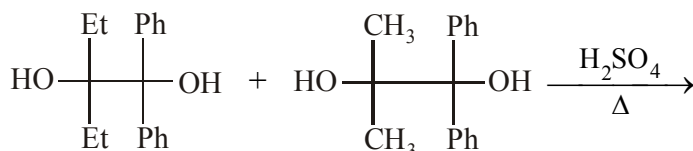
25. **c** The double bond which is most reactive towards attack of electrophile :

- (A) a (B) b (C) c (D) None

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

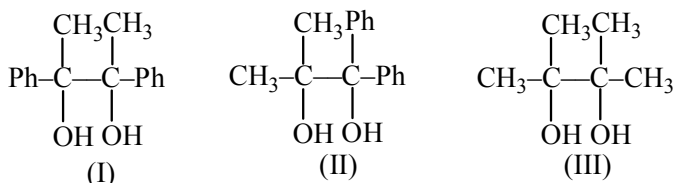


27. How many products are obtained in the given reaction :

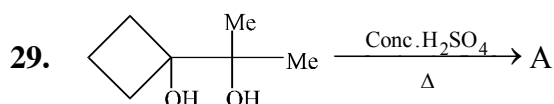


- (A) 1 (B) 2 (C) 3 (D) 4

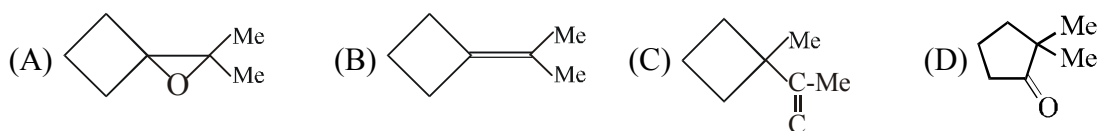
28. Compare rate of reaction towards pinacol pinacolone rearrangement.



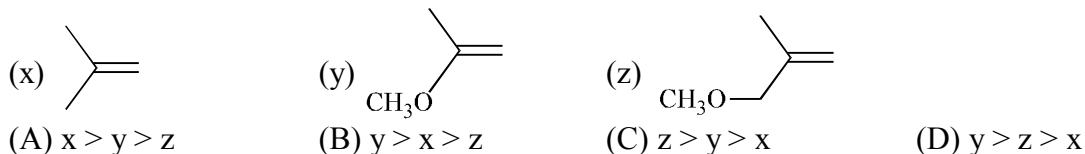
- (A) $\text{II} > \text{III} > \text{I}$ (B) $\text{III} > \text{II} > \text{I}$ (C) $\text{II} > \text{I} > \text{III}$ (D) $\text{I} > \text{II} > \text{III}$



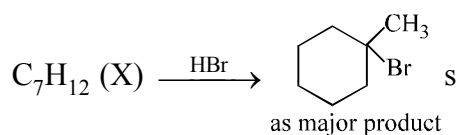
Product A is :



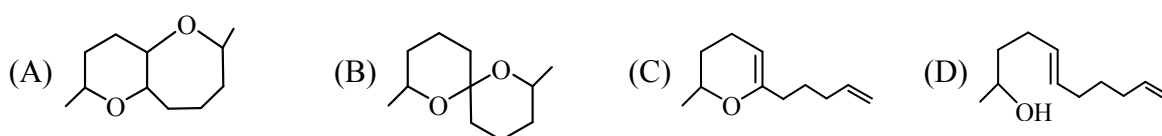
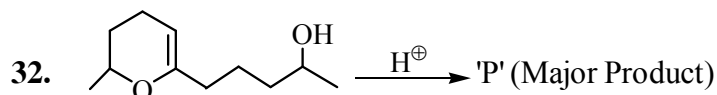
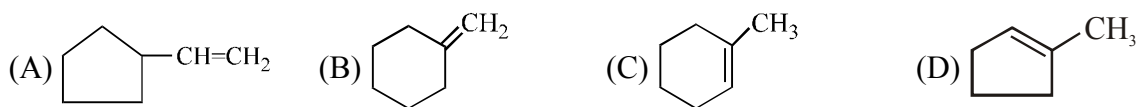
30. What is the order of reactivity with HBr :



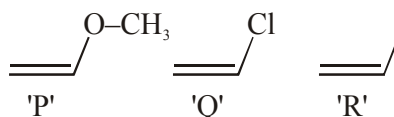
31. In the given reaction



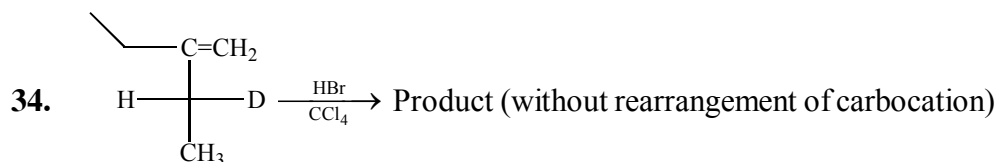
(X) can not be :



33. Arrange the following compounds in decreasing order of electrophilic addition :

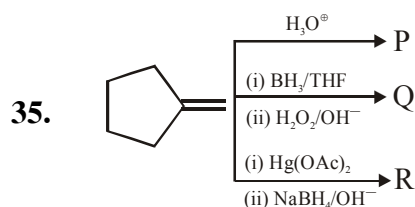


(A) $P > Q > R$ (B) $P > R > Q$ (C) $R > P > Q$ (D) $R > Q > P$



What is stereochemistry of product :

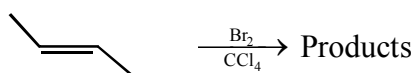
(A) Racemic mixture (B) Optically inactive
(C) Mixture of diastereomers (D) Meso product



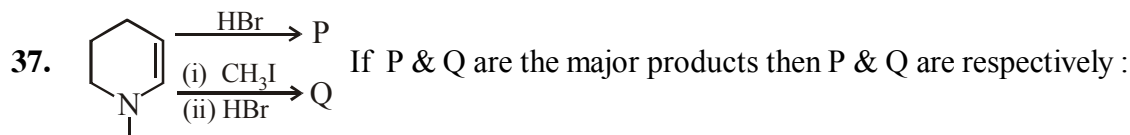
Correct statement regarding products P, Q & R

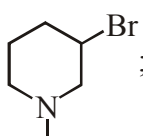
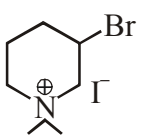
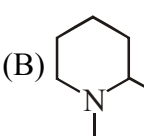
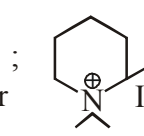
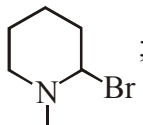
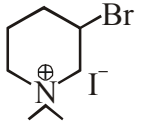
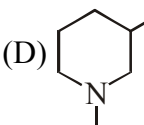
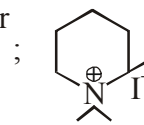
(A) Product P & R are same (B) Product Q & R are same
(C) P & Q are functional isomers (D) Product P, Q & R all are different

36. Select the incorrect statement about the product mixture in the following reaction :

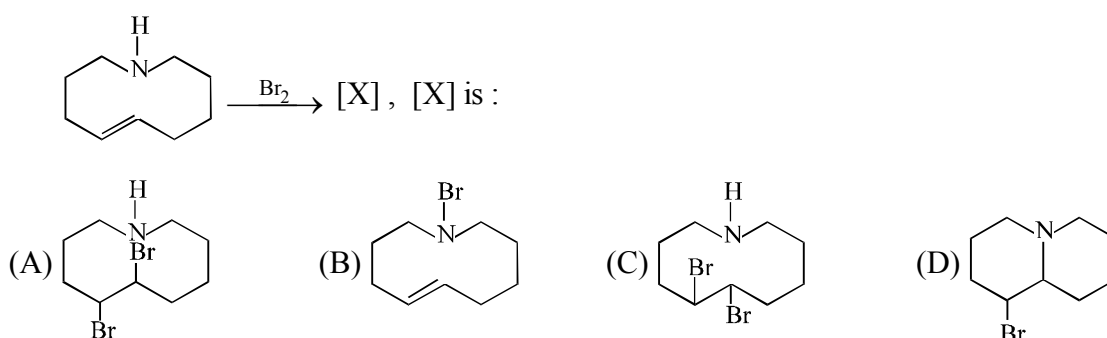


(A) It is optically active (B) It is racemic mixture
(C) It is a resolvable mixture (D) It is a mixture of erythro compounds

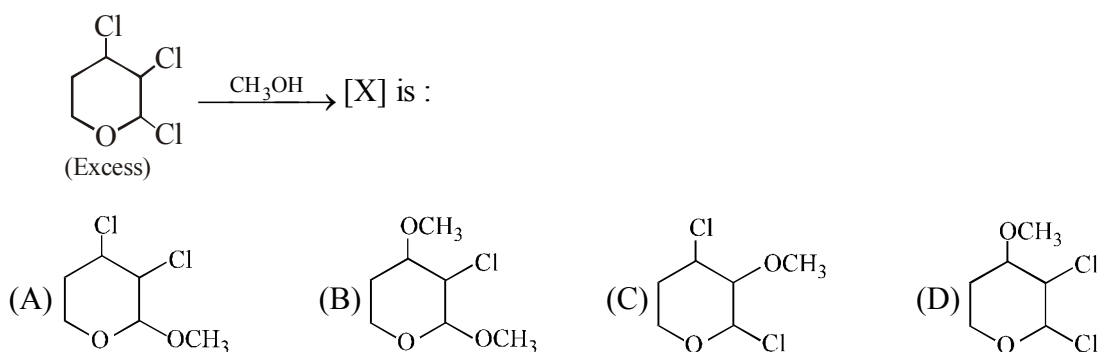


- (A)  ;  (B)  ; 
 (C)  ;  (D)  ; 

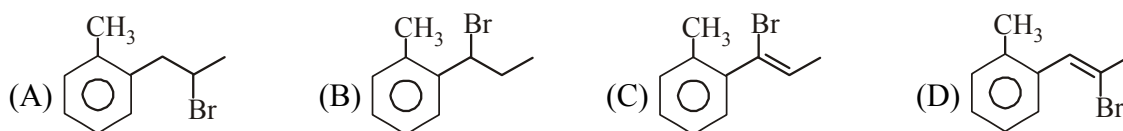
38. In the given reaction :



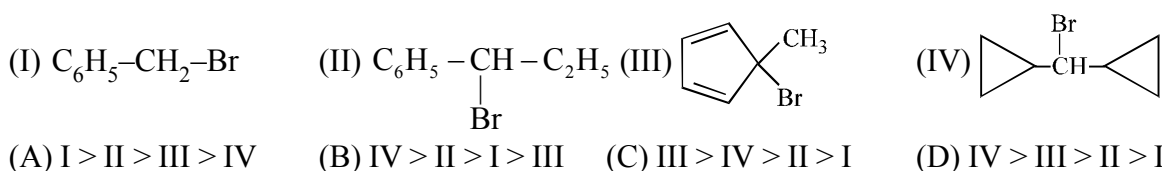
39. In the given reaction:



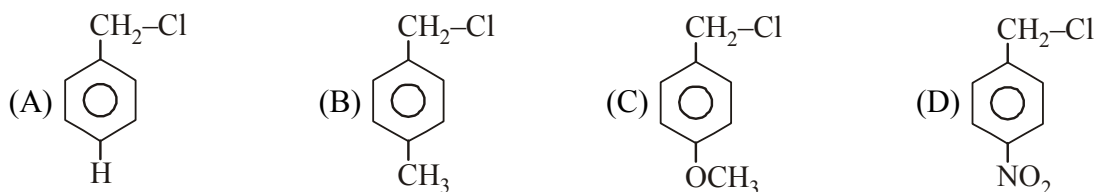
40. Which compound undergoes hydrolysis by the S_N1 mechanism at the fastest rate?



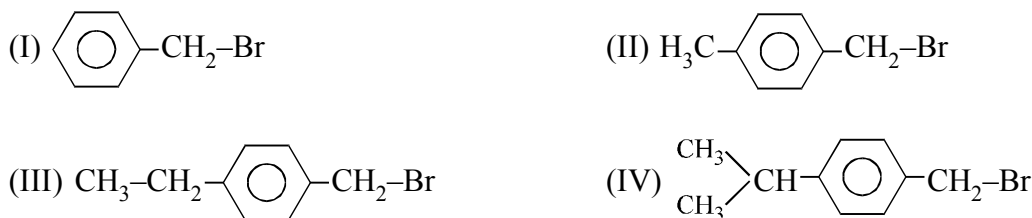
41. Arrange the following compounds in decreasing order of their reactivity for hydrolysis reaction



42. Which of the following is most reactive toward S_N1 reaction.

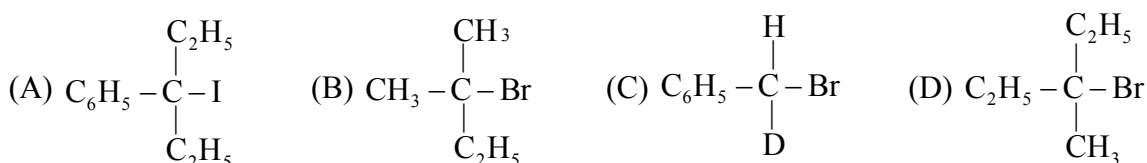


43. Arrange the following compounds in order of decreasing rate of hydrolysis for S_N1 reaction:

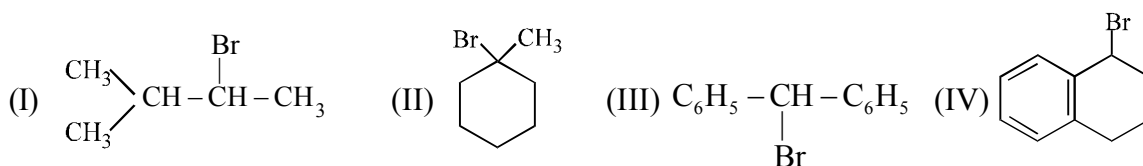


(A) II > III > IV > I (B) IV > III > II > I (C) III > IV > II > I (D) I > II > III > I

44. Which one of the following compounds will give enantiomeric pair on treatment with HOH?



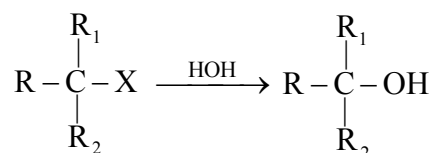
45. Consider the S_N1 solvolysis of the following halides in aqueous formic acid:



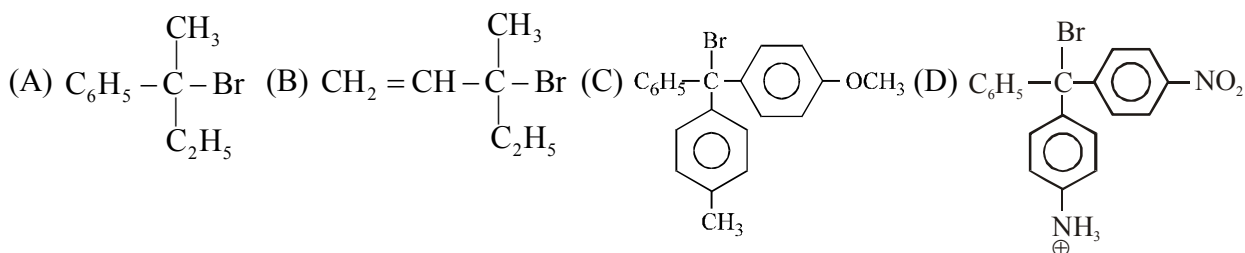
Decide decreasing order of reactivity of above alkyl halide?

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

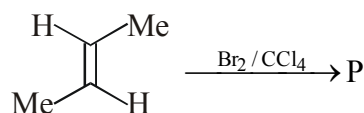
46. For the given reaction



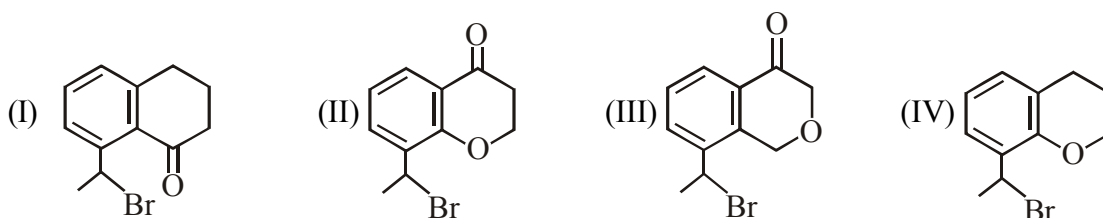
Which substrate will give maximum racemisation?



47. Select incorrect statements about the product (P) of the reaction :

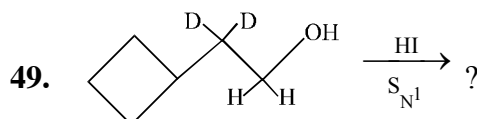


- (A) P is optically inactive due to internal compensation
 (B) P is optically inactive due to the presence of plane of symmetry in the molecule
 (C) The structure of P can have three optical isomers possible.
 (D) P can have four possible optical isomers.
48. Consider the following molecules :

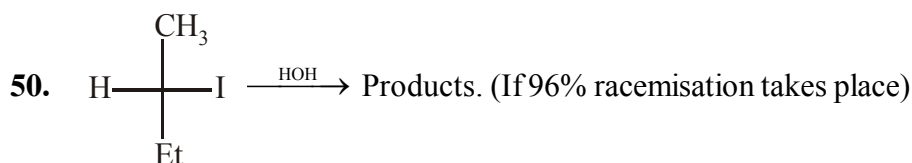
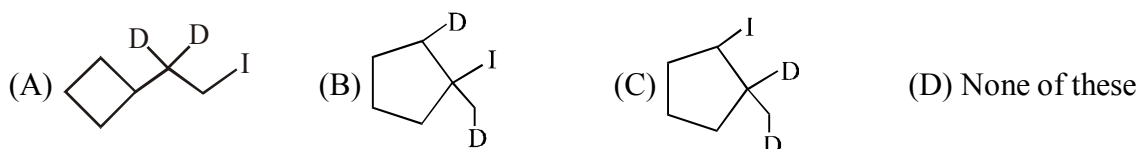


The correct decreasing ease of hydrolysis of alkyl halide is :

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

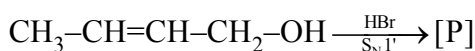


Major product is:



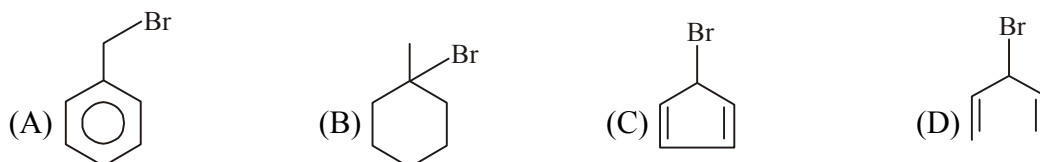
Find out the correct statement about the reaction.

- (A) Among the products 48% S and 48% R configuration containing molecules are present
 (B) Among the products 50% S and 50% R configuration containing molecules are present
 (C) Among the products 48% S and 52% R configuration containing molecules are present
 (D) Among the products 52% S and 48% R configuration containing molecules are present
51. In the given reaction the product [P] can be :



- (A) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{Br}$ (B) $\text{CH}_3 - \overset{\text{Br}}{\underset{|}{\text{CH}}} - \text{CH} = \text{CH}_2$
 (C) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ (D) $\text{CH}_3 - \overset{\text{Br}}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{CH}_2 - \text{OH}$

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



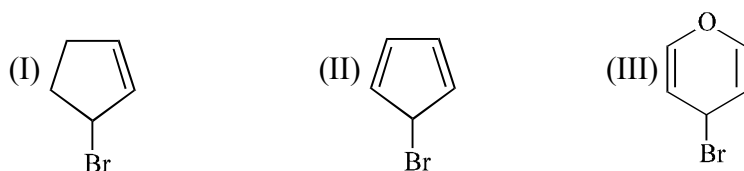
53. Which one of the following compounds will be most reactive for S_N1 reactions ?



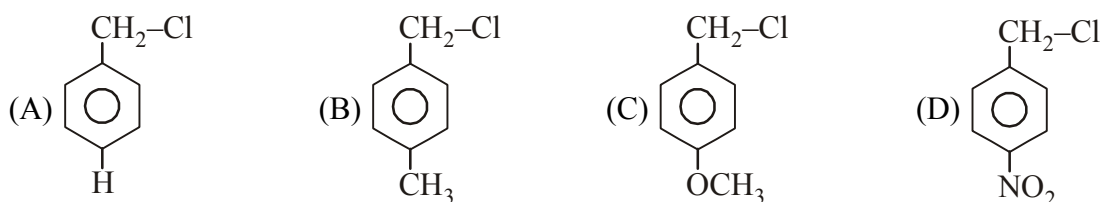
54. Which of the following compounds is most rapidly hydrolysed by S_N1 mechanism ?



55. Among the bromides I–III given below, the order of reactivity in S_N1 reaction is:



56. Which of the following is most reactive toward S_N2 .

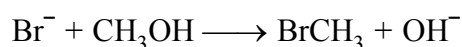


57. For reaction $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

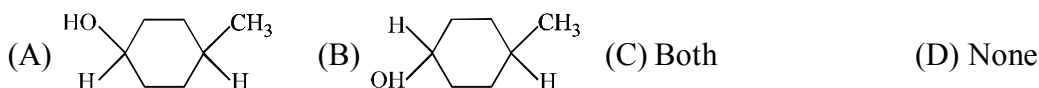
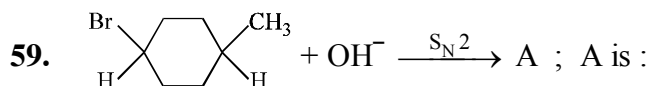
the rate of reaction is given by the expression :



58. Select suitable reason for non-occurrence of the following reaction.

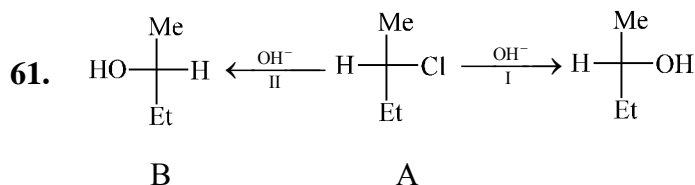


- (A) Attacking nucleophile is stronger one
(B) Leaving group is a stronger base than nucleophile
(C) Alcohols are not good substrate for S_N reaction
(D) Hydroxide ions are weak bases



60. The reactivity of 2-bromo-2-methylbutane (I), 1-bromopentane (II) and 2-bromopentane (III) towards S_N2 displacement is such that :

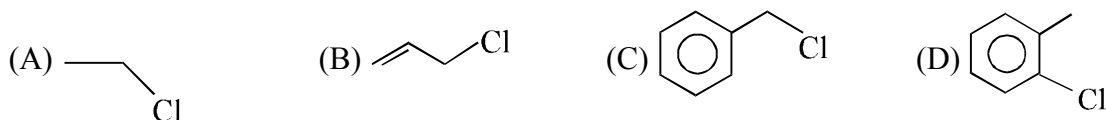
- (A) I > II > III (B) I > III > II (C) II > III > I (D) II > I > III



Mechanism involved :

- (A) I can't be S_N1 (B) II can't be S_N2 (C) I S_N1 & II S_N2 (D) I S_N2 & II S_N1

62. In which of the following replacement of Cl⁻ is most difficult ?

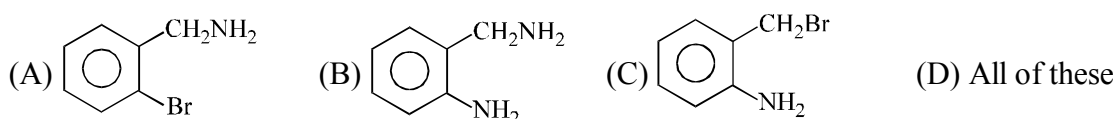
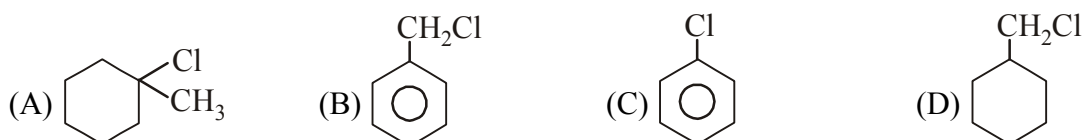


63. Arrange these compounds in order of increasing S_N2 reaction rate :



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

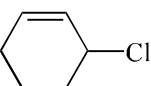
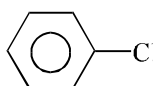
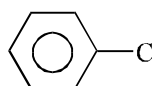
64. Which reaction proceeds faster with NaI in DMSO ?



66. The given compound CH₃-O-CH₂-Br gives which one of the following reactions:

- (A) Only S_N1 (B) Only S_N2
(C) S_N1 as well as S_N2 (D) E₁ only

67. Which will give white ppt. with AgNO_3 ?

- (A)  (B)  (C)  (D) Both A & C

68. Consider the following groups :

- (I) $-\text{OAc}$ (II) $-\text{OMe}$ (III) $-\text{OSO}_2\text{Me}$ (IV) $-\text{OSO}_2\text{CF}_3$

The order of leaving group nature is:

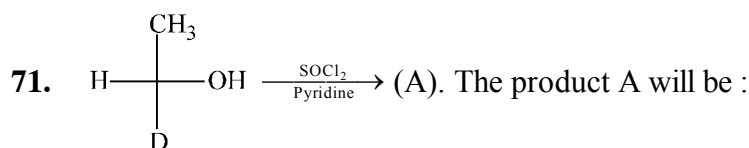
- (A) $\text{I} > \text{II} > \text{III} > \text{IV}$ (B) $\text{IV} > \text{III} > \text{I} > \text{II}$ (C) $\text{III} > \text{II} > \text{I} > \text{IV}$ (D) $\text{II} > \text{III} > \text{IV} > \text{I}$

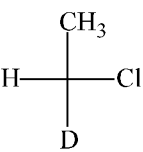
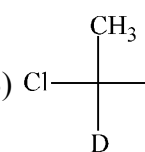
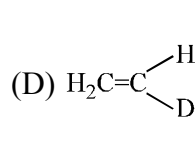
69. When ethyl bromide is treated with moist Ag_2O , the main product is:

- (A) Ethyl ether (B) Ethanol (C) Ethoxy ethane (D) All of these

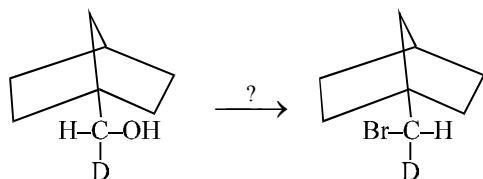
70. When ethyl bromide is treated with dry Ag_2O , the main product is:

- (A) Ethyl ether (B) Ethanol (C) Ethoxy ethane (D) All of these



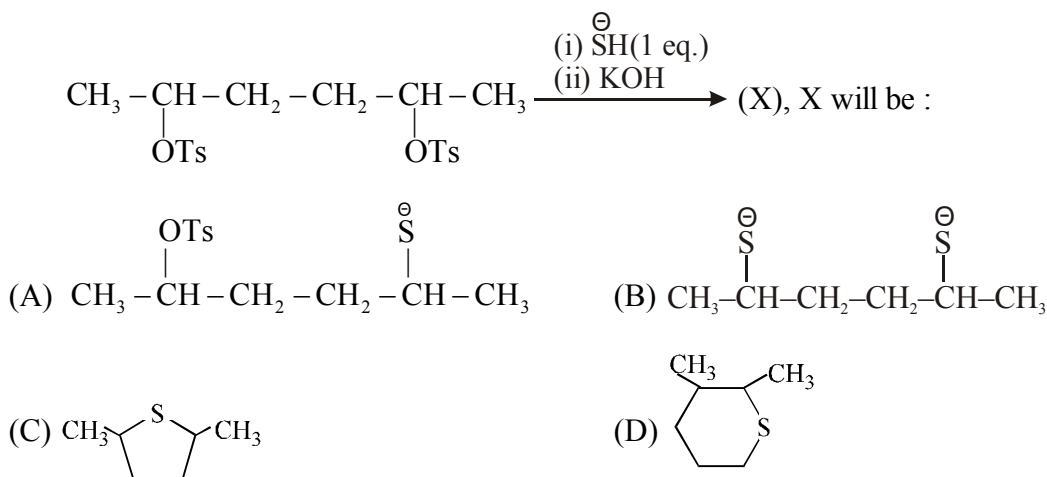
- (A)  (B)  (C) $\text{H}_2\text{C} = \text{CH}_2$ (D) 

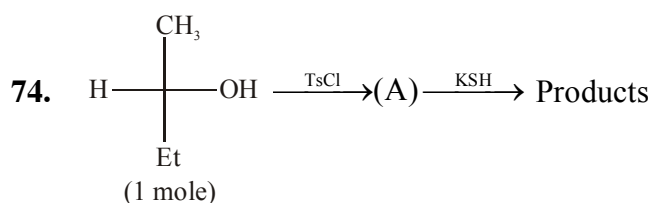
72. Which reaction conditions (reagents) is suitable for the following reaction:



- (A) $\text{Br}_2 / \text{CCl}_4$ (B) SOBr_2 (C) PBr_3 (D) $\text{HBr} / \text{conc H}_2\text{SO}_4$

73. In the given reaction



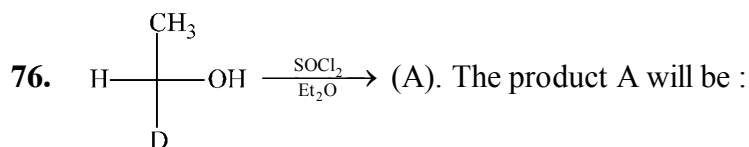


(Assuming all the substrate convert into substitution products containing 0.05 mole of S-configuration) Calculate the percentage of $\text{S}_{\text{N}}2$ mechanism.

- (A) 90% (B) 80% (C) 70% (D) 95%

75. The reaction of SOCl_2 on alkanols to form alkyl chlorides gives good yields because

- (A) Alkyl chlorides are immiscible with SOCl_2
(B) The other products of the reaction are gaseous and escape out
(C) Alcohol and SOCl_2 are soluble in water
(D) The reaction does not occurs via intermediate formation of an alkyl chloro sulphite

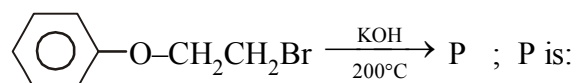


- (A)
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} - \text{C} - \text{Cl} \\ | \\ \text{D} \end{array}$$
 (B)
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{Cl} - \text{C} - \text{H} \\ | \\ \text{D} \end{array}$$
 (C) $\text{H}_2\text{C} = \text{CH}_2$ (D)
$$\begin{array}{c} \text{H} \\ \diagup \\ \text{H}_2\text{C} = \text{C} \\ \diagdown \\ \text{D} \end{array}$$

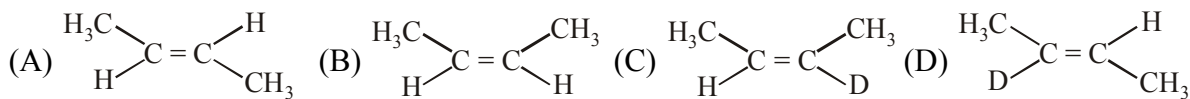
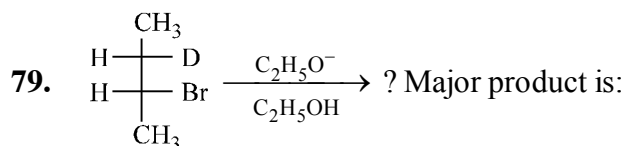
77. In the given pairs, which pair represent correct order of rate dehydrohalogenation reaction.

- (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} < \text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$ (B) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{Cl} < \text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$
(C) $\text{CH}_3\text{CH}_2\text{CH}(\text{I})\text{CH}_3 < \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$ (D) $\text{CH}_3 - \text{CH}_2 - \text{Cl} < \text{CD}_3 - \text{CD}_2 - \text{Cl}$

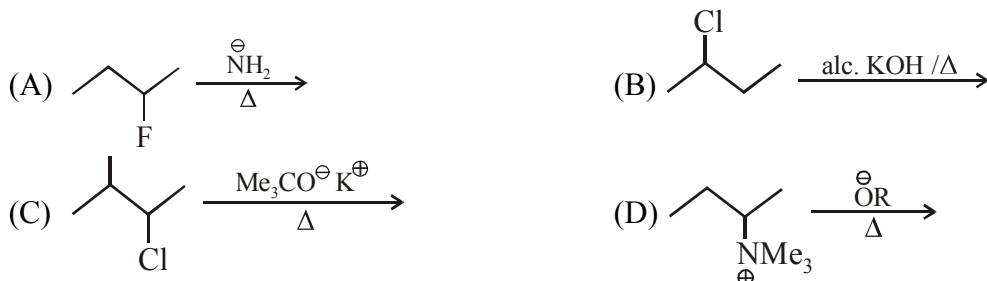
78. The product of the reaction



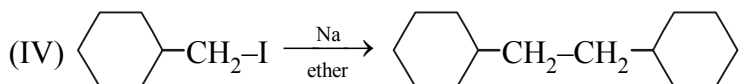
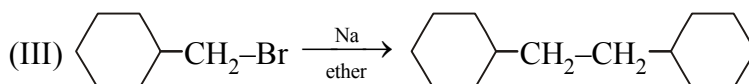
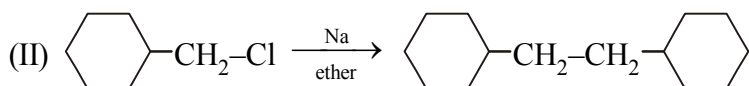
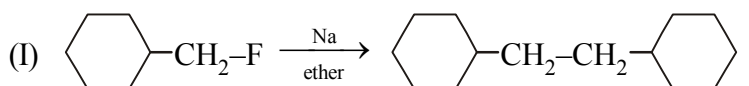
- (A) $\text{C}_6\text{H}_5\text{OH}$ (B) $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$
(C) $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{C}_6\text{H}_5$ (D) $\text{C}_6\text{H}_5\text{OCH}=\text{CH}_2$



80. Which of following reaction(s) produce Saytzeff product as a major product :



81. The correct order of rate of following Wurtz reactions :

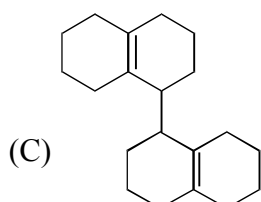
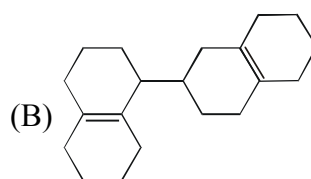
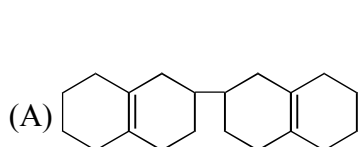
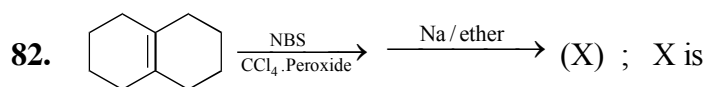


(A) I > II > III > IV

(B) II > I > III > IV

(C) IV > III > II > I

(D) In all rate of Wurtz reaction is same



(D) None of these

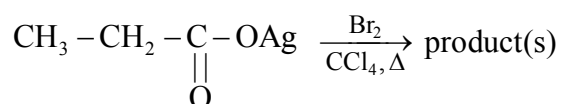
83. Find out the correct order of rate of reaction towards free radical allylic substitution :

- (I) $\text{CH}_3-\text{CH}=\text{CH}_2$ (II) $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$ (III) $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}=\text{CH}_2$
 (A) $\text{I} > \text{II} > \text{III}$ (B) $\text{II} > \text{I} > \text{III}$ (C) $\text{III} > \text{II} > \text{I}$ (D) $\text{III} > \text{I} > \text{II}$

84. What will be the major product, when 2-methyl butane undergoes bromination in presence of light ?



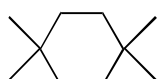
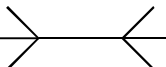
- (A) 1-Bromo-2-methyl butane (B) 2-Bromo-2-methyl butane
 (C) 2-Bromo-3-methyl butane (D) 1-Bromo-3-methyl butane

85. Which can not be the possible product of the given reaction ?



- (A) $\text{CH}_3-\text{CH}_2-\text{Br}$ (B) $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{O}-\text{CH}_2-\text{CH}_3$
 (C) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (D) $\text{CH}_3-\text{CH}_2-\text{CH}_3$

86. Choose that alkane which cannot give only one monochloro derivative upon reaction with chlorine in sun light :

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

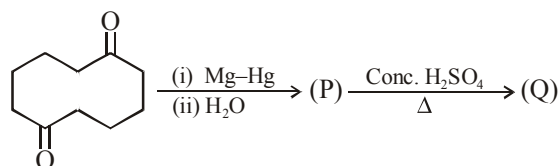
87. 2-chloropentane on halogenation with chlorine gives 2,3, dichloropentane. What will be the structure of free radical species formed in the reaction ?

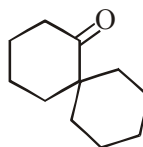
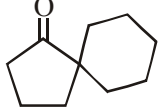
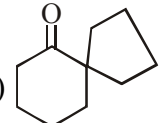
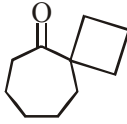
- (A) Tetrahedral (B) Trigonal planar (C) Square planar (D) Pyramidal

88. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be -

- (A) neopentane (B) propane (C) pentane (D) isopentane

89. Major product (Q) of following reaction is :

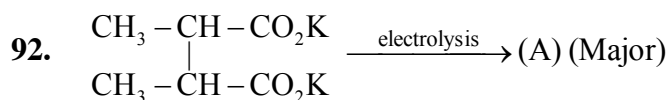
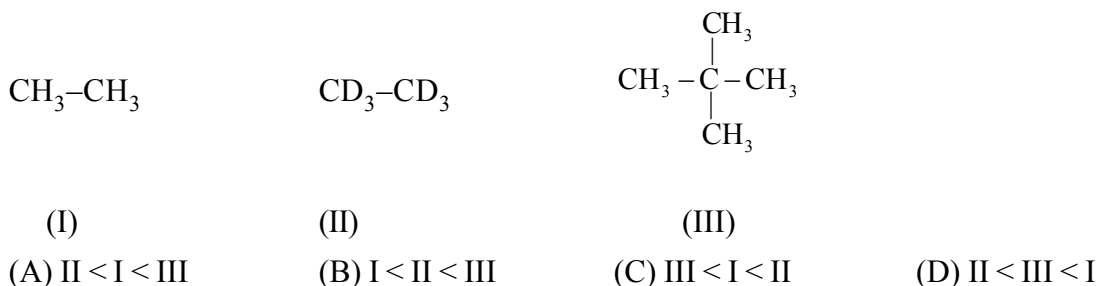


- (A)  (B)  (C)  (D) 

90. 1-Bromo-3-chloro cyclobutane on reaction with 2-equivalent of sodium in ether gives



91. Correct order of rate of photochlorination for following compounds is :



Major product (A) of above reaction :



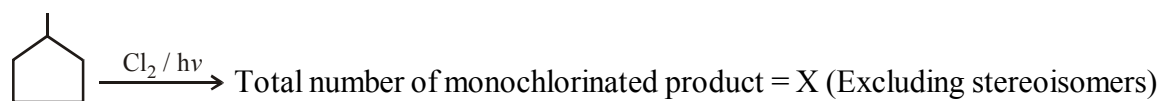
93. During the preparation of ethane by Kolbe's electrolytic method using inert electrode the pH of the electrolyte

- (A) Decreases progressively as the reaction proceeds
 (B) Increases progressively as the reaction proceeds
 (C) Remains constant throughout the reaction
 (D) May decrease if concentration of the electrolytes is not very high

94. When isobutane is chlorinated in the presence of diffused sunlight, then the product formed is :

- (A) Tertiary butyl chloride in major amount
 (B) Isobutyl chloride in major amount
 (C) Both 50 % each
 (D) n-Butyl chloride, isobutyl chloride and sec-butyl chloride are formed

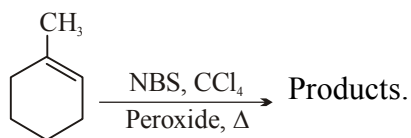
95. Consider the following reactions :



Identify value of X + Y.

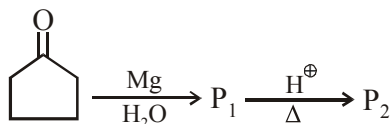
- (A) 8 (B) 9 (C) 11 (D) 10

96. Find out the total no. of products (including stereo) in the given reaction :



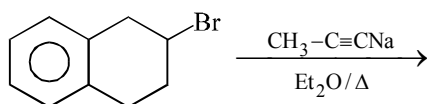
- (A) 8 (B) 9 (C) 10 (D) 11

97. Which of the following is not correct about P_2 :



- (A) It is a spiro compound (B) It is a Ketone
(C) It can show tautomerism (D) Its double bond equivalent is 4
98. On heating glycerol with excess amount of HI, the product formed is—
(A) Allyl iodide (B) Isopropyl iodide
(C) Propylene (D) 1,2,3-tri-iodopropane

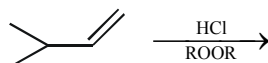
99. In the given reaction:



the products are:

- (A) and (B) +
- (C) (D)

100. Major product of the reaction -

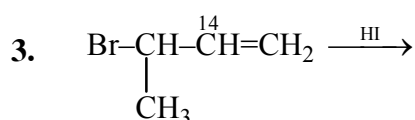
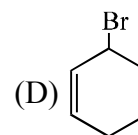
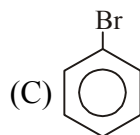
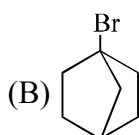
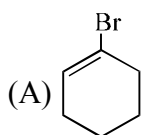


- (A) (B) (C) (D)

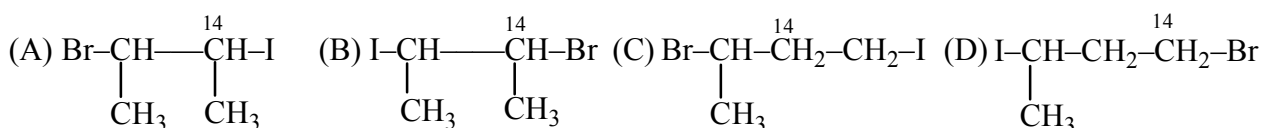
EXERCISE # II (A)

(Choose the correct option. One or more than one are correct)

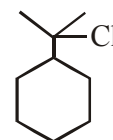
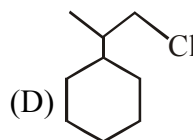
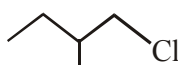
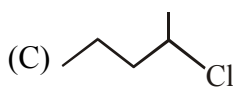
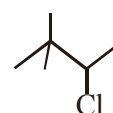
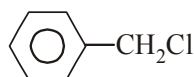
1. Rate of S_N2 depends on :
 (A) Conc of Nucleophile (B) Conc of substrate
 (C) Nature of leaving group (D) Nature of solvent
2. S_N2 reaction will be negligible in



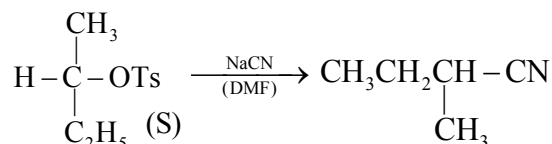
Products which can be obtained during the reaction in good yield :



4. In the given pair in which pair the first compound is more reactive than second towards S_N2 reaction.



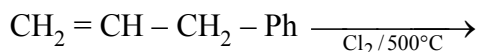
5. Consider the given reaction



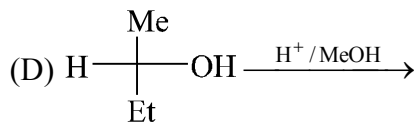
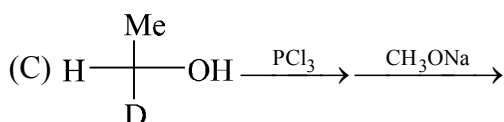
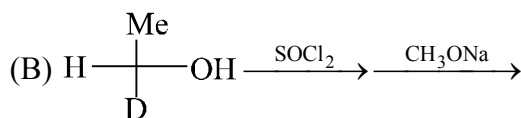
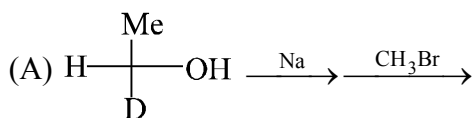
which of following statements is/are correct for the above reaction.

- (A) Product formation takes place due to the breaking of O-Ts
 (B) The reaction is S_N2
 (C) The reaction is S_N1
 (D) Configuration of product is (R)

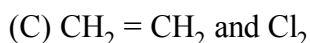
6. Which of the following statements is / are true?
 (A) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-I}$ will react more readily than $(\text{CH}_3)_2\text{CHI}$ for $\text{S}_\text{N}2$ reactions.
 (B) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Cl}$ will react more readily than $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$ for $\text{S}_\text{N}2$ reaction.
 (C) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$ will react more readily than $(\text{CH}_3)_3\text{C-CH}_2\text{-Br}$ for $\text{S}_\text{N}2$ reactions
 (D) $\text{CH}_3\text{-O-C}_6\text{H}_4\text{-CH}_2\text{Br}$ will react more readily than $\text{NO}_2\text{-C}_6\text{H}_5\text{-CH}_2\text{Br}$ for $\text{S}_\text{N}2$ reaction
7. Incorrect statement about alkyl halides is / are:
 (A) Tertiary alkyl halides undergo $\text{S}_\text{N}2$ substitutions
 (B) Alkyl iodides on exposure to sunlight gradually darken
 (C) Photo iodination is irreversible in presence of HIO_3
 (D) A nucleophilic substitution is most difficult in alkyl iodides
8. $\text{S}_\text{N}1$ & $\text{S}_\text{N}2$ is not favourable in
 (A) $\text{H}_2\text{C}=\text{CH-Cl}$ (B) $\text{Ph-CH}_2\text{-Cl}$ (C) Ph-Cl (D) $\text{H}_2\text{C}=\text{CH-CH}_2\text{-Cl}$
9. Correct statement(s) for the product(s) of following reaction.



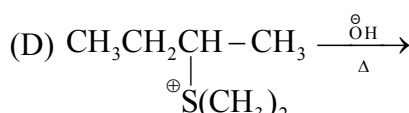
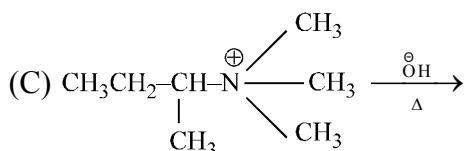
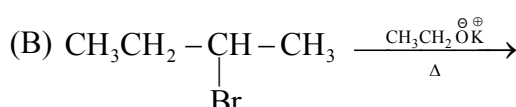
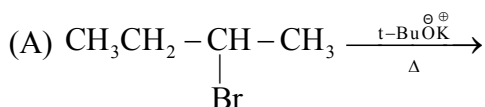
- (A) Four different products are formed
 (B) Two optically active products are formed
 (C) The optically active compound formed here can also be made by the reaction of HCl
 (D) The reaction path is free radical substitution.
10. In which of the following reaction configuration about chiral C is retained in the final product



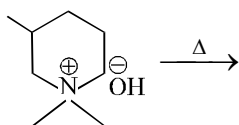
11. A gem dichloride is formed in the reaction :



12. In which product formation takes place according to Hoffmann's rule

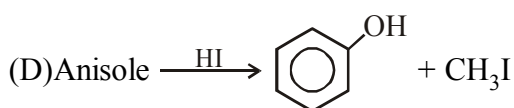
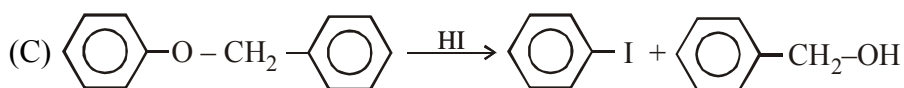


13. Which of following are correct for given reaction

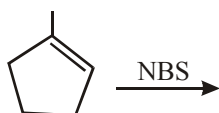


- (A) Major product of reaction is (B) Major product is (C) The reaction is thermal elimination reaction (D) The reaction is E_2 reaction

14. In which case incorrect products are formed :

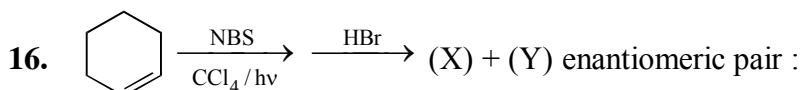


15. In the given reaction :



Find out the correct statement

- (A) It gives total 9 allylic brominated products
(B) 6 fractions are obtained on fractional distillation of product mixture
(C) Substrate has 7 allylic hydrogens
(D) NBS is a brominating agent for allylic positions

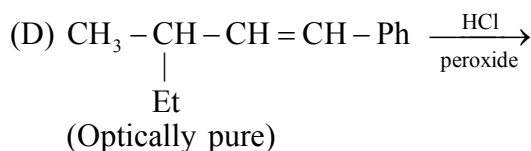
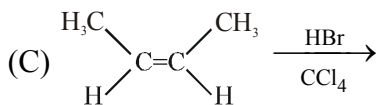
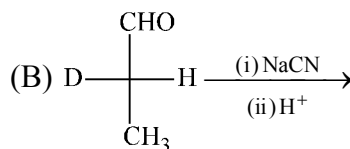
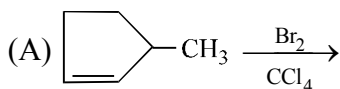


- (A) (B) (C) (D)

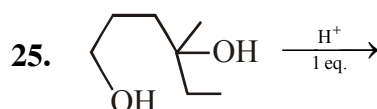
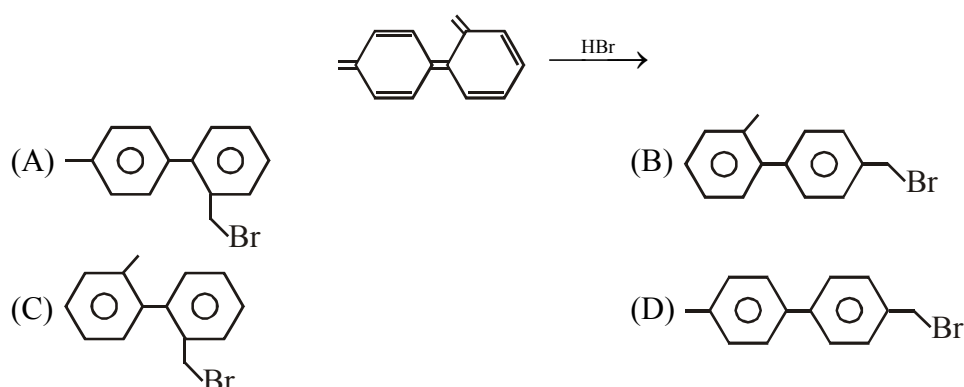
17. Which of the following can be produced by Wurtz reaction in good yield :

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

18. Products formed when HCl adds to 2,4-hexadiene is :
- (A) 4-chloro-2-hexene (B) 2-chloro-3-hexene
(C) 2-chloro-4-hexene (D) 1-chloro-2-hexene
19. Correct statement among the following is/are :
- (A) The rate of hydrolysis of tertiary butyl bromide increases by addition of Ag_2O
(B) Aqueous Ag_2O produces nucleophilic OH^-
(C) The addition of a small amount of oxygen slows down the photochemical chlorination of methane.
(D) $\text{CH}_3\text{CH}_2\text{Cl}$ is more reactive than PhCH_2Cl for bimolecular nucleophilic substitution reaction
20. Incorrect statement among the following is/are :
- (A) $\text{R}-\text{OH}$ with NaI in the presence of phosphoric acid gives $\text{R}-\text{I}$, but not in the absence of phosphoric acid
(B) 2-methyl propane on chlorination ($\text{Cl}_2, h\nu$) gives 1-chloro-2-methyl propane while bromination ($\text{Br}_2, h\nu$) gives 2-bromo-2-methyl propane
(C) Usually higher temperature prefers substitution over elimination
(D) Triphenyl chloromethane cannot be hydrolysed
21. Correct statements among the following is/are :
- (A) Dihaloalkanes having the same type of halogen atoms on same atom are named as alkylidene dihalides
(B) Dihaloalkanes having the same type of halogen atoms on adjacent atoms are named as alkylene dihalides
(C) In common name system gem-dihalides are named as alkylidene halide
(D) In common name system vic-dihalides are named as alkylene halide
22. Which of the following is correct order of nucleophilicity ?
- (A) $(\text{CH}_3\text{CH}_2)_3\text{N} > \text{pyridine}$ (B) $\text{HOO}^- > \text{HO}^-$ in DMSO
(C) $\text{H}_2\text{S} > \text{H}_2\text{O}$ (D) $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{O}^- > \text{CH}_3-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{O}^-$
23. Which of following reaction products are diastereomer of each other :

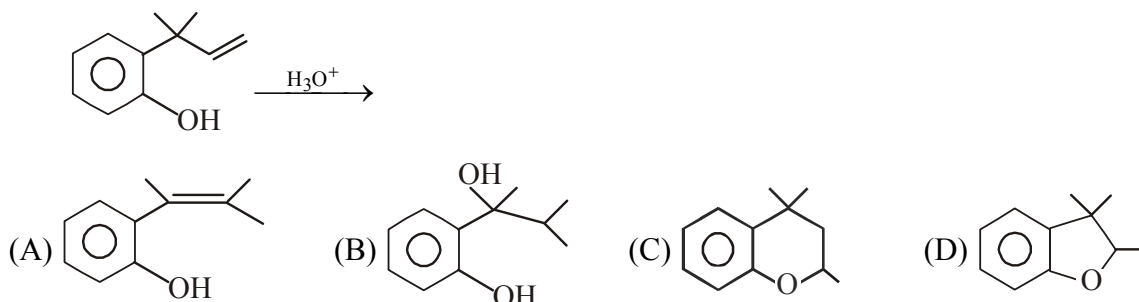


24. Product obtained in given reaction in good yield are :



Correct statements for given reaction :

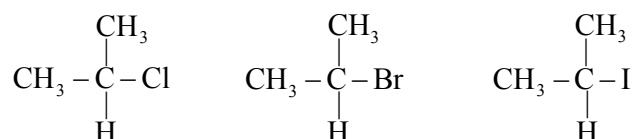
- (A) Product mixture is resolvable
 (B) Product can be separated by fractional distillation of mixture
 (C) Two products possible & both are optically active
 (D) Products are diastereomer
26. Which of the following can be formed during this reaction ?



27. Select **true** statement(s) :

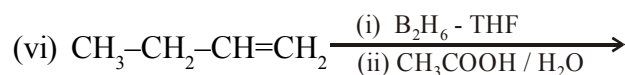
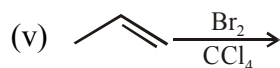
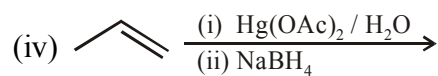
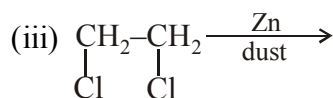
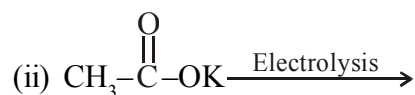
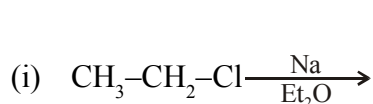
- (A) Cyclopropane decolorizes bromine water
 (B) In general, bromination is more selective than chlorination.
 (C) The 2,4,6-tri-tert, butylphenoxy radical is resistant to dimerization.
 (D) The radical-catalysed chlorination, $\text{ArCH}_3 \rightarrow \text{ArCH}_2\text{Cl}$, occurs faster when $\text{Ar} = \text{phenyl}$ than when $\text{Ar} = \text{p-nitrophenyl}$.

28. From left to right, correct statements are :



- (A) Rate of $\text{S}_{\text{N}}1$ mechanism increases in polar protic solvent
 (B) Rate of $\text{S}_{\text{N}}2$ mechanism increases in DMSO
 (C) Rate of E_2 mechanism increases
 (D) Rate of E_1 mechanism increases

29. Number of following reactions which produces hydrocarbon as major product ?

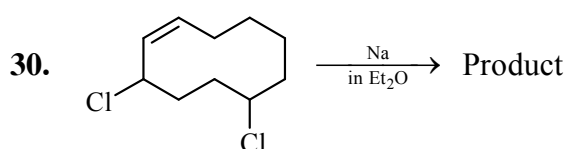


(A) 2

(B) 4

(C) 5

(D) 6



Correct statement is/are :

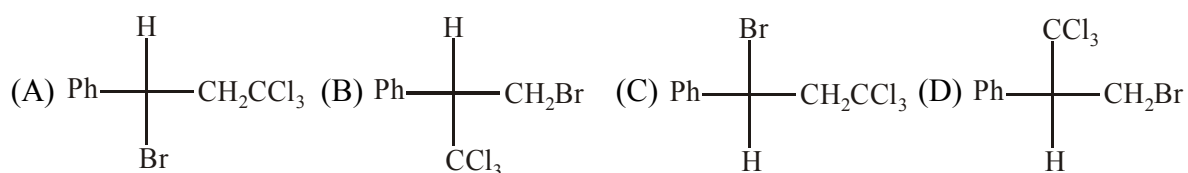
(A) odd no. of double bond equivalent in product

(B) product is bicyclic compound

(C) product can show geometrical isomerism

(D) reaction involve carbocation as intermediate

31. $\text{Ph}-\text{CH}=\text{CH}_2 + \text{BrCCl}_3 \xrightarrow{\text{Peroxide}}$ Product is :



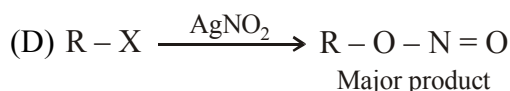
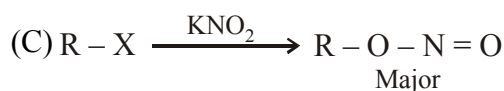
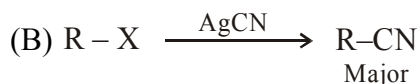
EXERCISE # II (B)

Comprehension Type :

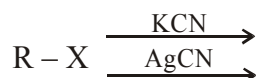
Paragraph for Q.No. 01 to 02

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

1. Correct option among the following :



2. Incorrect statement



(A) KCN is predominately ionic in nature

(B) AgCN is mainly covalent in nature

(C) In AgCN, carbon is the donor atom

(D) In AgCN nitrogen is the donor atom

3. **Statement-1** : HBr shows antimarkownikoff's addition on propene but not HCl.

Statement-2 : H-Br is stronger acid than H-Cl.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

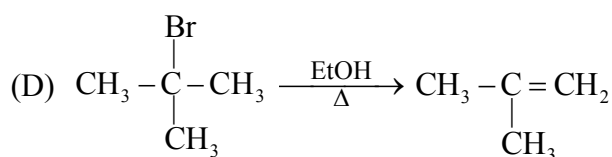
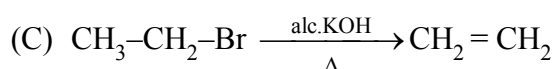
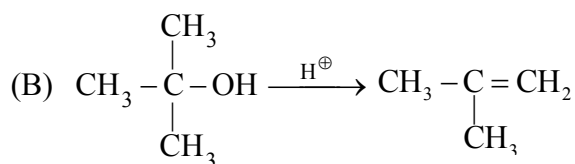
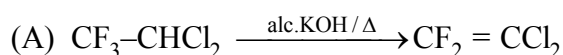
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

4. Match the List I with List II and select the correct answer using the codes given below the Lists.

List I



List II

(P) Elimination Reaction

(Q) Carbocation

(R) Carbanion

(S) Free radical

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

List I

(Reactions)

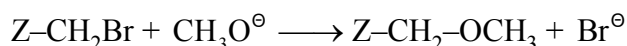
- (A) $\text{CH}_3\text{--O--SO}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{O}^\ominus$
 (B) $\text{CH}_3\text{--CH}_2\text{--I} + \text{PH}_3$
 (C) $\text{HC}\equiv\text{C}^\ominus\text{Na}^\oplus + \text{CH}_3\text{--CH}_2\text{--Br}$
 (D) $\text{CH}_3\text{--Cl} + \text{CH}_3\text{--O}^\ominus$

List II

(Products)

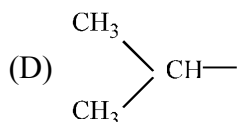
- (P) $\text{CH}_3\text{--CH}_2\text{--PH}_2$
 (Q) $\text{CH}_3\text{--O--C}_2\text{H}_5$
 (R) $\text{CH}_3\text{--O--CH}_3$
 (S) $\text{CH}\equiv\text{C--CH}_2\text{--CH}_3$

6. Match List-I with List-II for given S_N2 reaction & select the correct answer from the codes given below



List-I (Z-)

- (A) $\text{H}-$
(B) CH_3-
(C) C_2H_5-



List-II (relative reactivity)

- (P) 0.1
(Q) 3
(R) 1

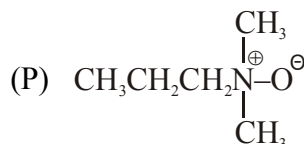
- (S) 100

7. Match the List I with List II and select the correct answer using the codes given below the Lists.

List I

- (A) E_{1CB}
- (B) Saytzeff alkene as major product
- (C) E_2
- (D) E_i

List II



- (Q) $\text{CH}_3\text{CH}_2\text{CH}_2-\text{O}-\underset{\text{S}}{\underset{||}{\text{C}}}-\text{S}-\text{CH}_3$

- (C) E_2
- (D) E_i

- $$\begin{array}{l} \text{(R)} \quad \text{CH}_3 - \text{CH}_2 - \overset{\text{Cl}}{\underset{|}{\text{CH}}} - \text{CH}_3 \\ \text{(S)} \quad \text{C}_6\text{H}_5 - \text{CH}_2 - \underset{\text{F}}{\underset{|}{\text{CH}}} - \text{CH}_3 \end{array}$$

8. Column - I (Reactions)

- (A) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \xrightarrow{\text{HBr}}$
 (B) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \xrightarrow{\text{HBr, Peroxide}}$
 (C) $\text{PhCH}(\text{CH}_3)\text{OH} \xrightarrow{\text{SOCl}_2}$
 (D) $\text{PhCH}(\text{CH}_3)\text{OH} \xrightarrow{\text{HBr}}$

Column - II
(Characteristics)

- (P) Bimolecular
(Q) Carbocation intermediate
(R) Regioselective
(S) Racemic modification
(T) Stereospecific reaction

9. Column - I

(Statements)

- (A) Reactions are concerted
 (B) CH_3X cannot react
 (C) $3^\circ \text{R-X} > 2^\circ \text{R-X} > 1^\circ \text{R-X}$
 (D) R-I reacts faster than R-Cl

Column - II

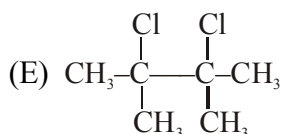
(Consistent path of reaction)

- (P) $\text{S}_{\text{N}}1$
 (Q) $\text{S}_{\text{N}}2$
 (R) $\text{E}1$
 (S) $\text{E}2$

10. Each of the compounds in column A is subjected to further chlorination. Match the following for them :

Column - A

- (A) $\text{CHCl}_2\text{-CH}_2\text{-CH}_3$
 (B) $\text{CH}_2\text{Cl-CHCl-CH}_3$
 (C) $\text{CH}_2\text{Cl-CH}_2\text{-CH}_2\text{-Cl}$
 (D) $\text{CH}_3\text{-CCl}_2\text{-CH}_3$



Column - B

- (P) Optically active original compound
 (Q) Only one trichloro product
 (R) Three trichloro product.
 (S) Four trichloro product
 (T) At least one of the trichloro product is optically active
 (U) Two trichloro products.

11. Column - I

(Intermediate)

- (A) Carbocation
 (B) Carbanion
 (C) Free radical
 (D) Octet complete in one of the intermediate

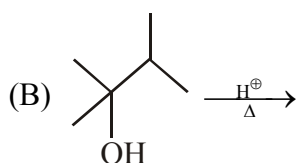
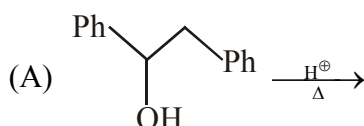
Column - II

- (P) Kolbe Electrolysis
 (Q) Wurtz reaction
 (R) Dehydration of alcohol
 (S) Monocarboxylic acid with sodalime

12. Match the column

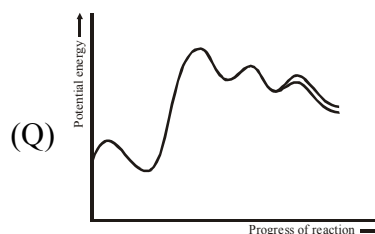
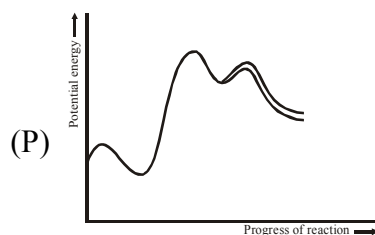
Column-I

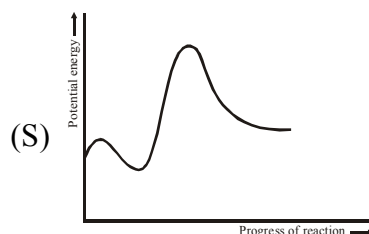
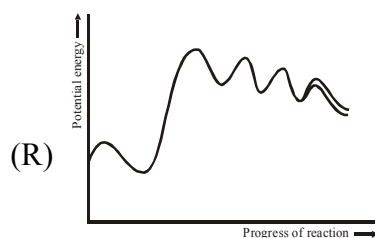
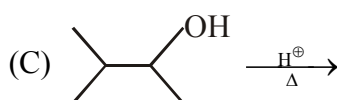
(Reaction)



Column-II

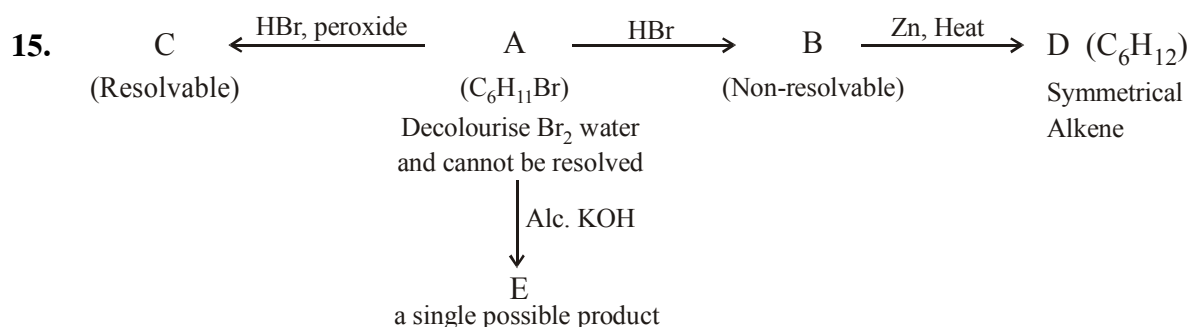
(Potential energy curve)





Subjective Type :

13. RCl is treated with Li in ether to form R – Li, R – Li reacts with water to form isopentane. R – Cl also reacts with sodium to form 2, 7-dimethyloctane. What is the structure of R – Cl.
14. A chloroderivative 'X' on reduction gave a hydrocarbon with five carbon atoms in the molecule. When X is dissolved in ether and treated with sodium, 2, 2, 5, 5-tetramethyl hexane is obtained. What is compound X.



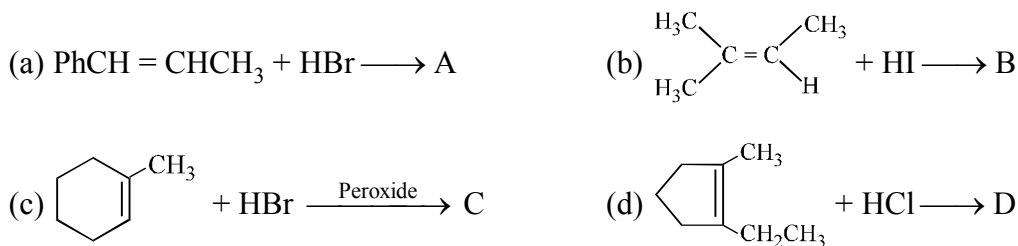
Identify A, C & E in the sequence of reaction.

16. With the help of following data show HBr exhibits the peroxide effect.

	$\Delta H_1^0/\text{kJ mol}^{-1}$	$\Delta H_2^0/\text{kJ mol}^{-1}$
H-X	$\dot{\text{X}} + \text{CH}_2 = \text{CH}_2 \rightarrow \text{XCH}_2 - \dot{\text{C}}\text{H}_2$	$\text{XCH}_2 - \dot{\text{C}}\text{H}_2 + \text{H-X} \rightarrow \text{XCH}_2\text{CH}_3 + \dot{\text{X}}$
	\downarrow	
HCl	-67	+ 12.6
HBr	-25.1	- 50.2
HI	+46	-117.1

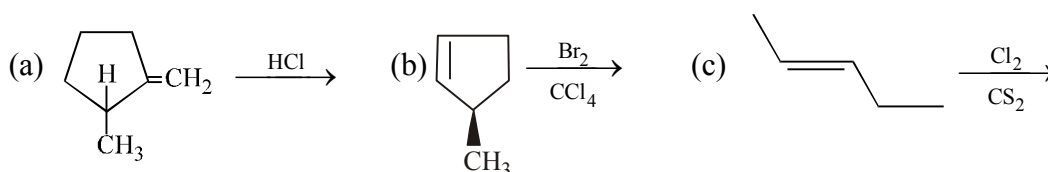
17. Write all the monochlorinated products (including stereo) of isohexane.

18. What are the products of the following reactions ?



19. It required 0.7 g of a hydrocarbon (A) to react completely with Br_2 (2.0 g) and form a non resolvable product. On treatment of (A) with HBr it yielded monobromo alkane (B). The same compound (B) was obtained when (A) was treated with HBr in presence of peroxide. Write down the structure formula of (A) and (B) and explain the reactions involved.

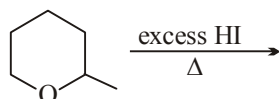
20. Complete following reaction :



21. $\text{CH}_3\text{--CH}_2\text{I}$ reacts more rapidly with strong base in comparison to $\text{CD}_3\text{CH}_2\text{I}$.

22. $\text{CH}\equiv\text{C--CH}_2\text{--CH=CH}_2$, adds up HBr to give $\text{CH}\equiv\text{C--CH}_2\text{--CHBr--CH}_3$ while $\text{CH}\equiv\text{C--CH=CH}_2$ adds up HBr to give $\text{CH}_2=\underset{\text{Br}}{\text{C}}\text{--CH=CH}_2$

23. Predict the product(s) and write the mechanism of the given reaction :



24. What are the products of the following reactions?

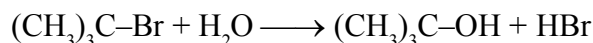


25. A primary alkyl bromide (A), $\text{C}_4\text{H}_9\text{Br}$, reacted with alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give an isomer of (A). When (A) was reacted with sodium metal it gave compound (D), C_8H_{18} , which was different from the compound produced when n-butyl bromide was reacted with sodium. Draw the structure of (A) and write equations for all the reactions.

26. In study of chlorination of propane four products (A,B,C,D) of molecular formula $\text{C}_3\text{H}_7\text{Cl}_2$ were obtained. On further chlorination of the above products A gave one trichloro product, B gave two whereas C and D gave three each. When optically active C was chlorinated one of trichloro propanes was optically active and remaining two were optically inactive. Identify the structures of A, B, C and D, and explain formation of products.

EXERCISE # III (J-MAINS)

1. Following reaction :



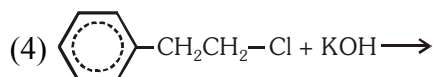
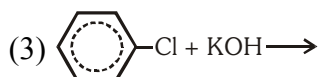
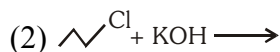
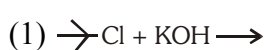
is an example of-

[AIEEE-2002]

- (1) Elimination reaction (2) Free radical substitution
(3) Nucleophilic substitution (4) Electrophilic substitution

2. SN^1 reaction is feasible in-

[AIEEE-2002]



3. Bottles containing $\text{C}_6\text{H}_5\text{I}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in a test tube and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some AgNO_3 solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment.

[AIEEE-2003]

- (1) A was $\text{C}_6\text{H}_5\text{I}$ (2) A was $\text{C}_6\text{H}_5\text{CH}_2\text{I}$
(3) B was $\text{C}_6\text{H}_5\text{I}$ (4) Addition of HNO_3 was unnecessary

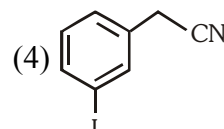
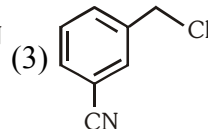
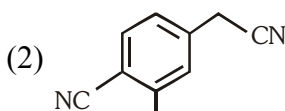
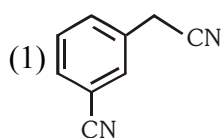
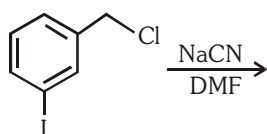
4. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is-

[AIEEE-2004]

- (1) Gammex (2) DDT (3) Freon (4) Hexa chloro ethane

5. The structure of the major product formed in the following reaction is :

[AIEEE-2006]

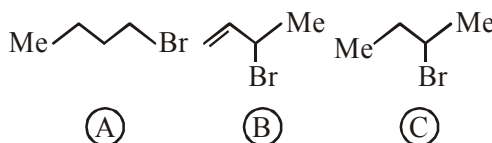


6. Which of the following on heating with aqueous KOH , produces acetaldehyde ? [AIEEE-2009]

- (1) $\text{CH}_2\text{ClCH}_2\text{Cl}$ (2) CH_3CHCl_2 (3) CH_3COCl (4) $\text{CH}_3\text{CH}_2\text{Cl}$

7. Consider the following bromides :-

[AIEEE-2010]



The correct order of S_N^1 reactivity is

- (1) $\text{A} > \text{B} > \text{C}$ (2) $\text{B} > \text{C} > \text{A}$ (3) $\text{B} > \text{A} > \text{C}$ (4) $\text{C} > \text{B} > \text{A}$

8. In S_N^2 reactions, the correct order of reactivity for the following compounds : [JEE(Main)-2014]
 CH_3Cl , $\text{CH}_3\text{CH}_2\text{Cl}$, $(\text{CH}_3)_2\text{CHCl}$ and $(\text{CH}_3)_3\text{CCl}$ is :

- (1) $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$
 (2) $(\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_3\text{CCl}$
 (3) $\text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_3\text{CCl}$
 (4) $\text{CH}_3\text{Cl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$

9. In a nucleophilic substitution reaction : [JEE(Main)-On-Line-2014]



which one of the following undergoes complete inversion of configuration?

- (1) $\text{C}_6\text{H}_5\text{CCH}_3\text{C}_6\text{H}_5\text{Br}$ (2) $\text{C}_6\text{H}_5\text{CHCH}_3\text{Br}$
 (3) $\text{C}_6\text{H}_5\text{CHC}_6\text{H}_5\text{Br}$ (4) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$

10. The major product obtained in the photo catalysed bromination of 2-methylbutane is :-

- (1) 2-bromo-2-methylbutane [JEE(Main)-On-Line-2014]
 (2) 2-bromo-3-methylbutane
 (3) 1-bromo-2-methylbutane
 (4) 1-bromo-3-methylbutane

11. In the presence of peroxide, HCl and HI do not give anti-Markownikoff's addition to alkenes because :- [JEE(Main)-On-Line-2014]

- (1) All the steps are exothermic in HCl and HI
 (2) One of the steps is endothermic in HCl and HI
 (3) HCl is oxidizing and the HI is reducing
 (4) Both HCl and HI are strong acids

12. The major product formed when 1,1,1 - trichloro - propane is treated with aqueous potassium hydroxide is : [JEE(Main)-On-Line-2014]

- (1) 2 - Propanol (2) Propionic acid (3) Propyne (4) 1 - Propanol

13. The synthesis of alkyl fluoride is best accomplished by : [JEE(Main)-2015]

- (1) Finkelstein reaction (2) Swarts reaction
 (3) Free radical fluorination (4) Sandmeyer's reaction

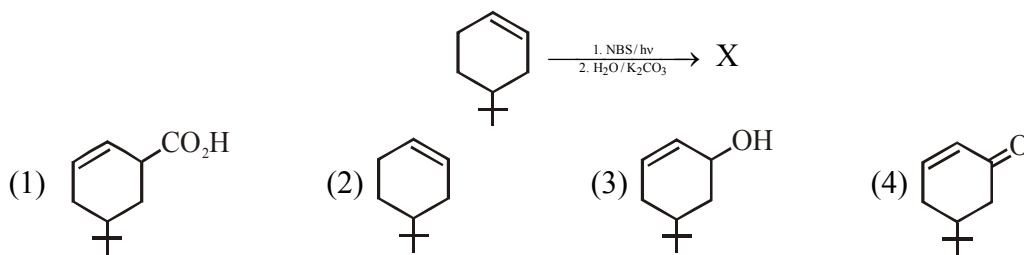
14. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields :

- (1) $\text{C}_2\text{H}_5\text{CH}_2\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{OCH}_3$ (2) $\text{C}_2\text{H}_5\text{CH}_2\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$ (3) $\text{C}_2\text{H}_5\text{CH}=\overset{\text{CH}_3}{\text{C}}-\text{CH}_3$ [JEE-MAIN-2016]

- (1) (1) and (2) (2) All of these (3) (1) and (3) (4) (3) only

15. The product of the reaction given below is :

[JEE-MAIN-2016]



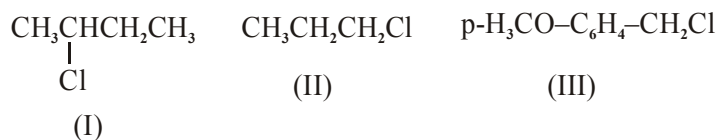
16. The reaction of propene with HOCl ($\text{Cl}_2 + \text{H}_2\text{O}$) proceeds through the intermediate :

[JEE-MAIN-2016]

- (1) $\text{CH}_3\text{-CHCl-CH}_2^+$
- (2) $\text{CH}_3\text{-CH}^+\text{-CH}_2\text{-OH}$
- (3) $\text{CH}_3\text{-CH}^+\text{-CH}_2\text{-Cl}$
- (4) $\text{CH}_3\text{-CH(OH)-CH}_2^+$

17. The increasing order of the reactivity of the following halides for the $\text{S}_{\text{N}}1$ reaction is :

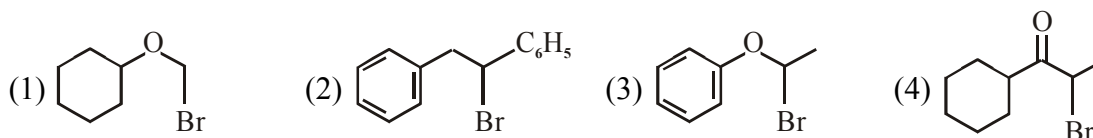
[JEE-MAIN-2017]



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

18. Which of the following, upon treatment with tert-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine ?

[JEE-MAIN-2017]



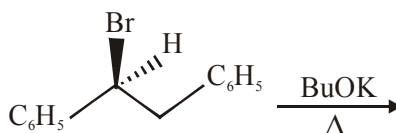
19. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is :

[JEE-MAIN-2017]

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

20. The major product obtained in the following reaction is :

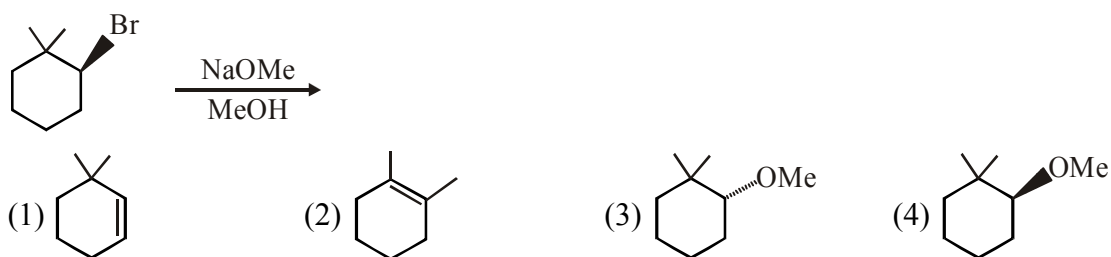
[JEE-MAIN-2017]



- (1) $(\pm)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$
- (2) $\text{C}_6\text{H}_5\text{CH=CHC}_6\text{H}_5$
- (3) $(+)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$
- (4) $(-)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$

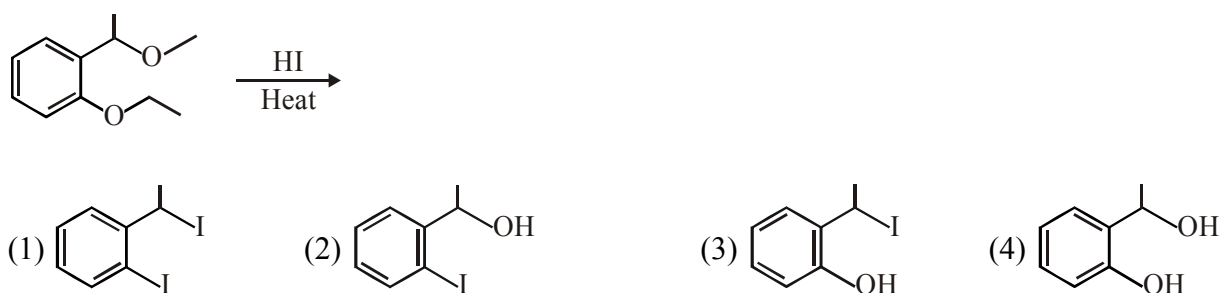
21. The major product of the following reaction is :

[JEE-MAIN-2018]



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

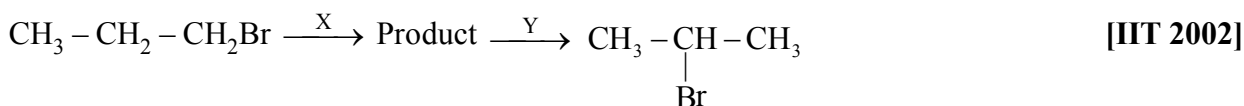
[JEE-MAIN-2018]



EXERCISE # IV (A) (J-ADVANCE OBJECTIVE)

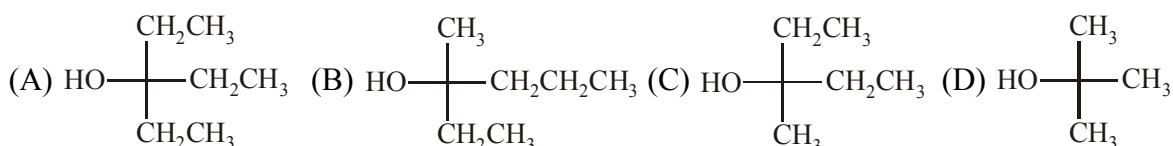
- Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives : [IIT 1990]
 (A) o-cresol (B) p-cresol
 (C) 2,4-dihydroxytoluene (D) Benzoic acid
- Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to [IIT 1990]
 (A) The formation of less stable carbonium ion
 (B) Resonance stabilization
 (C) The inductive effect
 (D) sp^2 hybridised carbon attached to the halogen
- 1-Chlorobutane on reaction with alcoholic potash gives : [IIT 1991]
 (A) 1-butene (B) 1-butanol (C) 2-butene (D) 2-butanol
- The products of reaction of alcoholic $AgNO_2$ with ethyl bromide are [IIT 1991]
 (A) Ethane (B) Ethyl nitrite (C) Nitroethane (D) Ethyl alcohol
- Arrange the following compounds in order of increasing dipole moment [IIT 1996]
 Toluene m-dichlorobenzene o-dichlorobenzene p-dichlorobenzene
 I II III IV
 (A) $I < IV < II < III$ (B) $IV < I < II < III$ (C) $IV < I < III < II$ (D) $IV < II < I < III$
- $(CH_3)_3CMgCl$ reaction with D_2O produces: [IIT 1997]
 (A) $(CH_3)_3CD$ (B) $(CH_3)_3OD$ (C) $(CD_3)_3CD$ (D) $(CH_3)_3OD$
- Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with: [IIT 1998]
 (A) SO_2Cl_2 (B) $SOCl_2$ (C) $Cl_2, (h\nu)$ (D) $NaOCl$
- The order of reactivity of the following alkyl halides for a S_N2 reaction is: [IIT 2000]
 (A) $RF > RC > R-Br > R-I$ (B) $R-F > R-Br > R-Cl > R-I$
 (C) $R-Cl > R-Br > RF > RI$ (D) $R-I > RBr > R-Cl > R-F$
- Which of the following has the highest nucleophilicity? [IIT 2000]
 (A) F^- (B) OH^- (C) CH_3^- (D) NH_2^-
- An S_N2 reaction at an asymmetric carbon of a compound always gives. [IIT 2001]
 (A) an enantiomer of the substance (B) a product with opposite optical rotation
 (C) a mixture of diastereomers (D) a single stereoisomer
- The compound that will react most readily with NaOH to form methanol is [IIT 2001]
 (A) $(CH_3)_4N^+I^-$ (B) CH_3OCH_3 (C) $(CH_3)_3S^+I^-$ (D) $(CH_3)_3CCl$

12. Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformation:

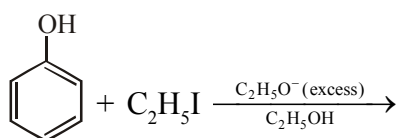


- (A) X = dilute aqueous NaOH, 20°C; Y = HBr / acetic acid, 20°C
 (B) X = concentrated alcoholic NaOH, 80°C; Y = HBr / acetic acid 20°C
 (C) X = dilute aqueous NaOH, 20°C; Y = Br₂ / CHCl₃, 0°C
 (D) X = concentrated alcoholic NaOH, 80°C; Y = Br₂/CHCl₃, 0°C

13. CH₃MgBr + Ethyl ester → which can be formed as product. [IIT 2003]
 (excess)

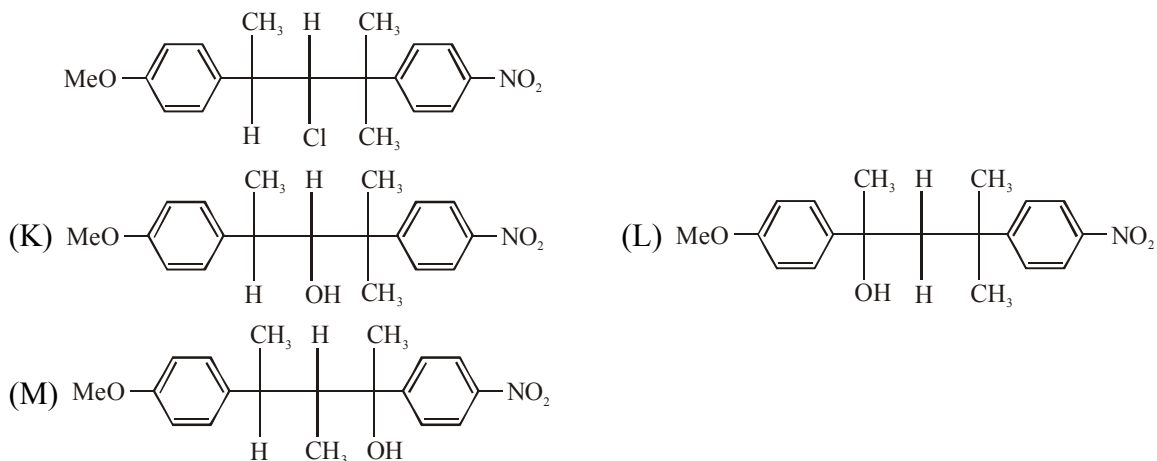


14. The product of following reaction is [IIT 2003]



- (A) C₆H₅OC₂H₅ (B) C₂H₅OC₂H₅ (C) C₆H₅OC₆H₅ (D) C₆H₅I

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



It mainly gives

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

16. Match the following: [IIT 2006]

Column I

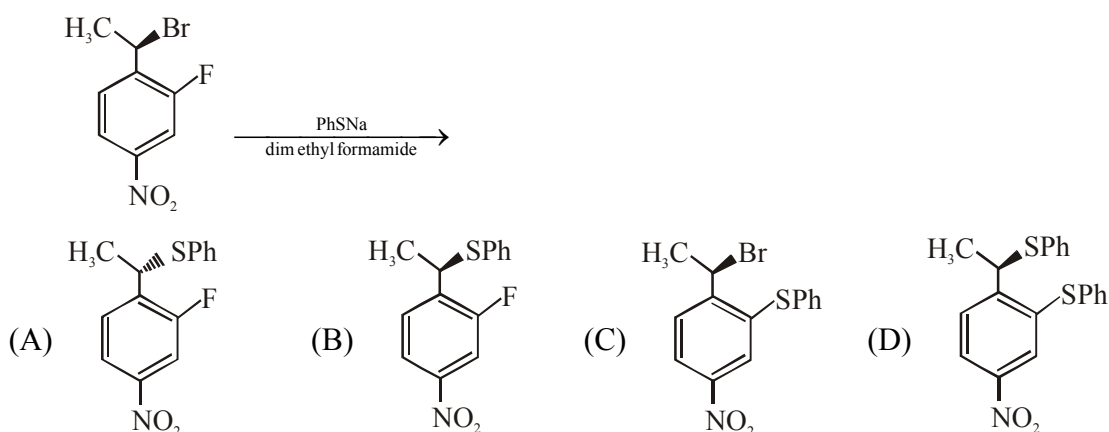
- (A) CH₃-CHBr-CD₃ on treatment with alc. KOH gives CH₂=CH-CD₃ as a major product.
 (B) Ph-CHBr-CH₃ reacts faster than Ph-CHBr-CD₃.
 (C) Ph-CD₂-CH₂Br on treatment with C₂H₅OD/C₂H₅O⁻ gives Ph-CD=CH₂ as the major product.
 (D) PhCH₂CH₂Br and PhCD₂CH₂Br react with same rate.

Column II

- (P) E1 reaction
 (Q) E2 reaction
 (R) E1cb reaction
 (S) First order reaction

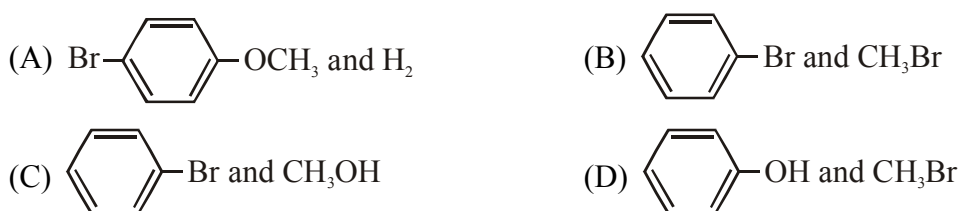
17 The major product of the following reaction is

[IIT 2008]



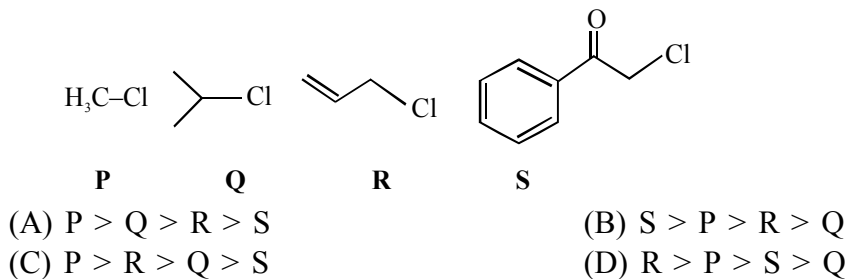
18 In the reaction $\xrightarrow{\text{HBr}}$ the products are

[IIT 2010]



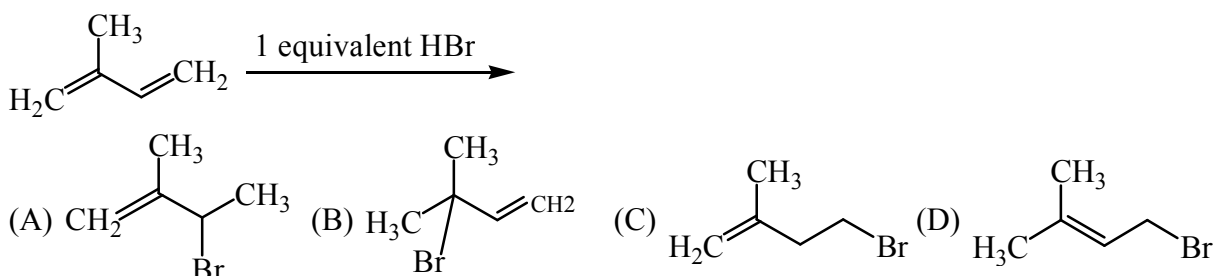
19. KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as -

[IIT 2013]

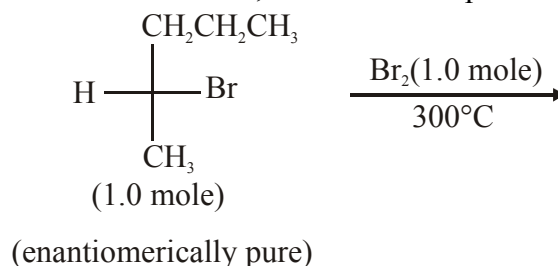


20. In the following reaction, the major product is -

[IIT 2015]

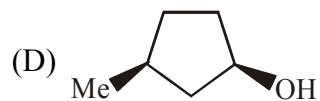
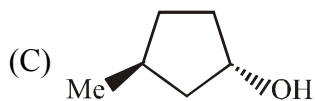
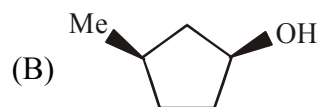
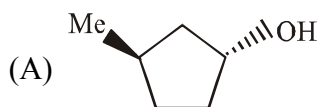
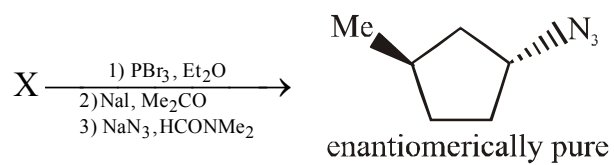


21. In the following monobromination reaction, the number of possible chiral products is [IIT 2016]



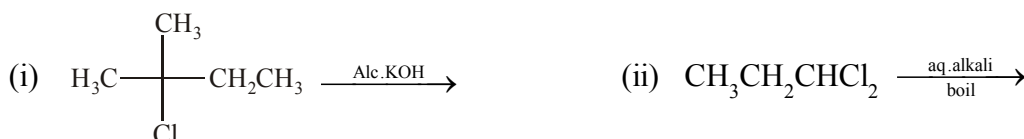
22. In the following reaction sequence, the correct structure(s) of X is (are)

[IIT-2018]

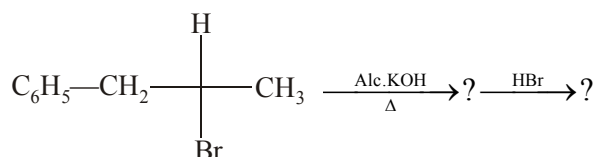


EXERCISE # IV (B) (J-ADVANCE SUBJECTIVE)

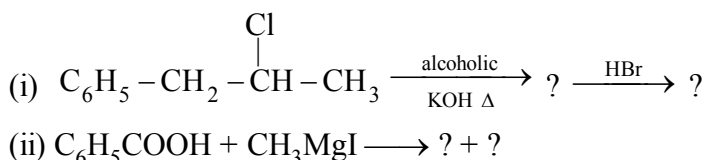
- Fill in the blanks :
 - Butane nitrile can be prepared by heating _____ with alcoholic KCN. [IIT 1992]
 - Amongst three isomers of nitrophenol, the one that is least soluble in water is _____. [IIT 1992]
- Arrange the following in order of their
 - Increasing basicity
 H_2O , OH^- , CH_3OH , CH_3O^-
 - Increasing reactivity in nucleophilic substitution reactions
 CH_3F , CH_3I , CH_3Br , CH_3Cl [IIT 1992]
- Write the structures of the major organic product expected from each of the following reactions: [IIT 1992]



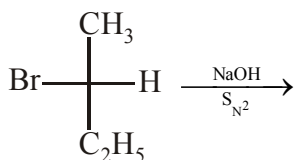
- Identify the major product in the following reaction. [IIT 1993]



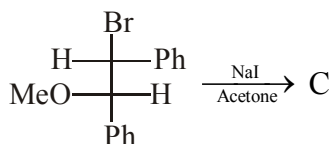
- Identify the major product in the following reactions : [IIT 1993]



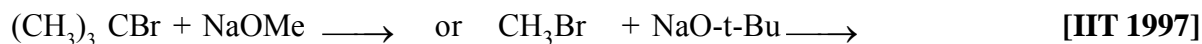
- Aryl halides are less reactive than alkyl halides towards nucleophilic reagents. Give reason. [IIT 1994]
- Draw the stereochemical structure of product in the following reaction. [IIT 1994]



- Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. [IIT 1995]
- An alkyl halide X of formula $\text{C}_6\text{H}_{13}\text{Cl}$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict the structures of X, Y and Z. [IIT 1996]
- Predict the structure of the intermediates/products in the following reaction sequence – [IIT 1996]



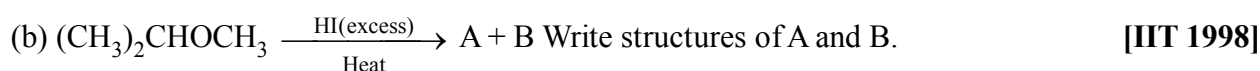
11. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?



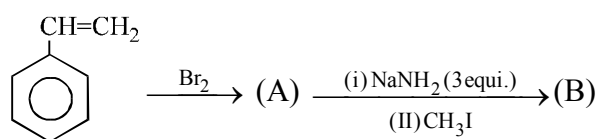
12. Write the structures of the products: [IIT 1998]



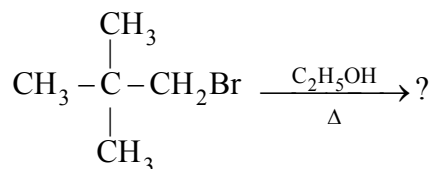
13. (a) $\text{C}_6\text{H}_5\text{CH}_2\overset{\text{C}_6\text{H}_5}{\underset{|}{\text{CH}}}\text{Cl} \xrightarrow[\text{Heat}]{\text{alc. KOH}} \text{A} + \text{B}$ Write structures of (A) and (B).



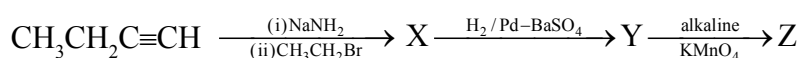
14. Complete the following reaction with appropriate structures of products/reagents. [IIT 1998]



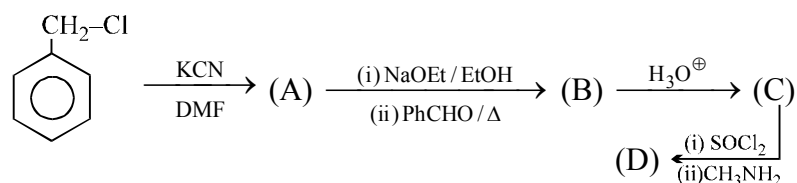
15. What would be major product? [IIT 2000]



16. Identify X, Y and Z in the following synthetic scheme and write their structures [IIT 2002]

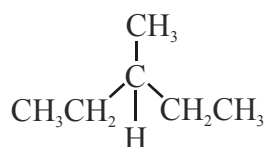


17. Give major products A, B, C and D in following reaction sequence. [IIT 2004]



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

19. The maximum number of isomers (including stereoisomers) that are possible on mono-chlorination of the following compounds, is [IIT 2011]



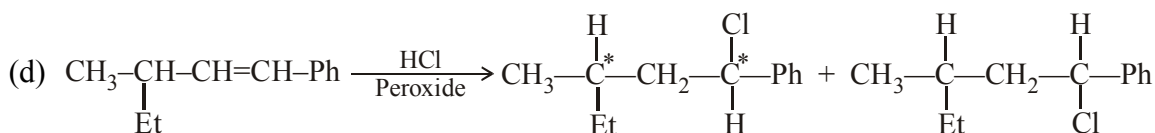
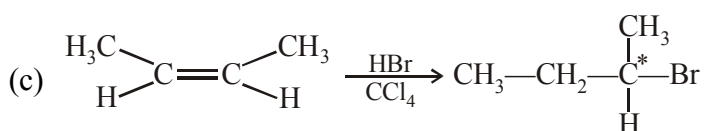
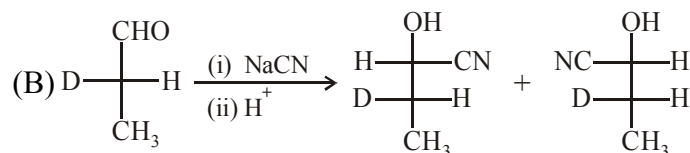
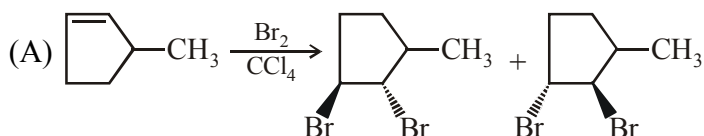
ANSWER-KEY**EXERCISE # I (MAINS ORIENTED)**

1. Ans. (A)	2. Ans. (C)	3. Ans. (D)	4. Ans. (D)	5. Ans. (C)
6. Ans. (C)	7. Ans. (B)	8. Ans. (D)	9. Ans. (B)	10. Ans. (B)
11. Ans. (C)	12. Ans. (C)	13. Ans. (C)	14. Ans. (A)	15. Ans. (D)
16. Ans. (B)	17. Ans. (A)	18. Ans. (D)	19. Ans. (C)	20. Ans. (D)
21. Ans. (D)	22. Ans. (A)	23. Ans. (D)	24. Ans. (A)	25. Ans. (B)
26. Ans. (C)	27. Ans. (B)	28. Ans. (C)	29. Ans. (D)	30. Ans. (B)
31. Ans. (D)	32. Ans. (B)	33. Ans. (B)	34. Ans. (C)	35. Ans. (A)
36. Ans. (A)	37. Ans. (C)	38. Ans. (D)	39. Ans. (A)	40. Ans. (B)
41. Ans. (B)	42. Ans. (C)	43. Ans. (A)	44. Ans. (C)	45. Ans. (A)
46. Ans. (C)	47. Ans. (D)	48. Ans. (D)	49. Ans. (B)	50. Ans. (C)
51. Ans. (B)	52. Ans. (C)	53. Ans. (A)	54. Ans. (C)	55. Ans. (A)
56. Ans. (D)	57. Ans. (C)	58. Ans. (B)	59. Ans. (B)	60. Ans. (C)
61. Ans. (C)	62. Ans. (D)	63. Ans. (A)	64. Ans. (B)	65. Ans. (A)
66. Ans. (C)	67. Ans. (D)	68. Ans. (B)	69. Ans. (B)	70. Ans. (C)
71. Ans. (B)	72. Ans. (C)	73. Ans. (C)	74. Ans. (A)	75. Ans. (B)
76. Ans. (A)	77. Ans. (A)	78. Ans. (D)	79. Ans. (C)	80. Ans. (B)
81. Ans. (C)	82. Ans. (C)	83. Ans. (C)	84. Ans. (B)	85. Ans. (D)
86. Ans. (C)	87. Ans. (B)	88. Ans. (A)	89. Ans. (C)	90. Ans. (C)
91. Ans. (A)	92. Ans. (C)	93. Ans. (B)	94. Ans. (B)	95. Ans. (A)
96. Ans. (B)	97. Ans. (D)	98. Ans. (B)	99. Ans. (B)	100. Ans. (D)

EXERCISE # II (A)

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

23. Ans.



24. Ans. (A,B)

25. Ans. (A,C)

26. Ans. (A,B,D)

27. Ans. (A,B,C,D)

28. Ans. (A,B,C,D)

29. Ans. (B)

30. Ans. (A,B,C)

31. Ans. (A,C)

EXERCISE # II (B)

1. Ans. (C)

2. Ans. (C)

3. Ans. (B)

4. Ans. (A) → P, R ; (B) → P, Q ; (C) → P ; (D) → P, Q

5. Ans. (A)→Q ; (B)→P ; (C)→S ; (D)→R

6. Ans. (A) → S ; (B) → Q ; (C) → R ; (D) → P

7. Ans. (A) → S ; (B) → R, S ; (C) → R ; (D) → P, Q

8. Ans. (A) → P, Q, R, S ; (B) → P, R ; (C) → P, T ; (D) → Q, S

9. Ans. (A) → Q, S ; (B) → P, R, S ; (C) → P, R, S ; (D) → P, Q, R, S

10. Ans. (A) → S, T ; (B) → P, S, T ; (C) → U ; (D) → Q ; (E) → T, U

11. Ans. (A) → R ; (B) → Q, S ; (C) → P, Q ; (D) → Q, S

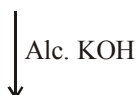
12. Ans. (A) → P ; (B) → P ; (C) → Q ; (D) → R

13. Ans.

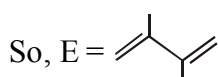
C–I bond being less stable than C–Cl bond and thus on heating heterolytic cleavage of C–I form I^- which gives yellow precipitate with AgNO_3 .



14. Ans. X is $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{Cl} \\ | \\ \text{CH}_3 \end{array}$

15. Ans. Molecule A, $C_6H_{11}Br$ has 1 unsaturation

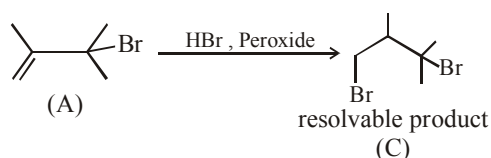


A single possible product, it suggests a symmetrical arrangement



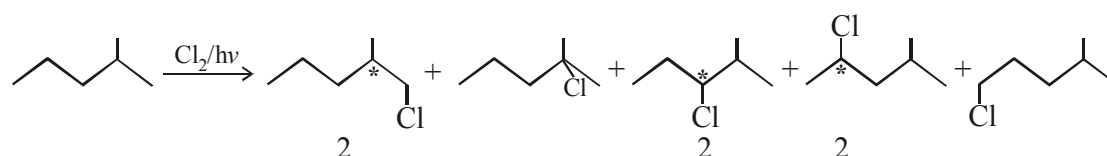
There are only two possibilities of A  or  structure I can be resolved

while structure II cannot be resolved so 'A' :

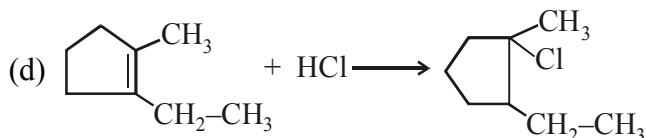
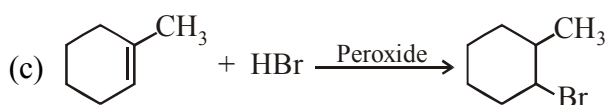
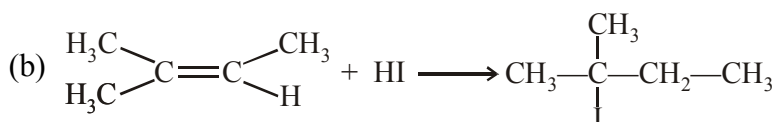
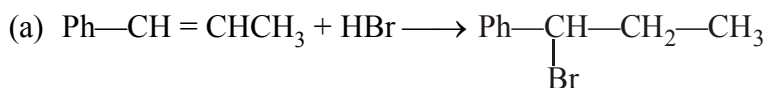


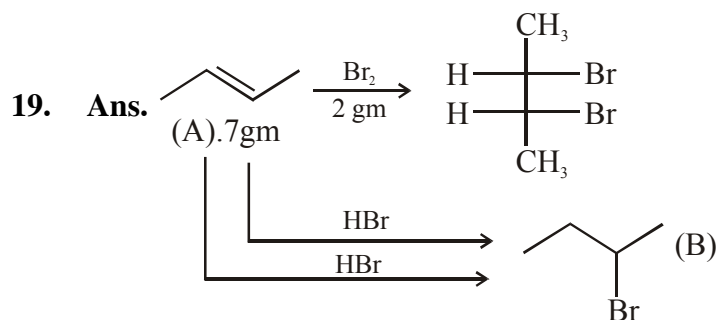
16. Ans. Both step is exothermic with HBr

17. Ans.

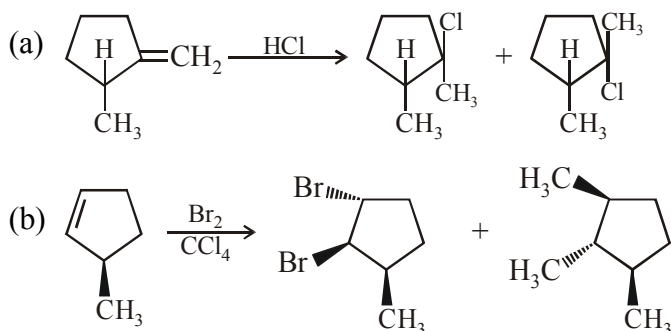


18. Ans.





20. Ans.

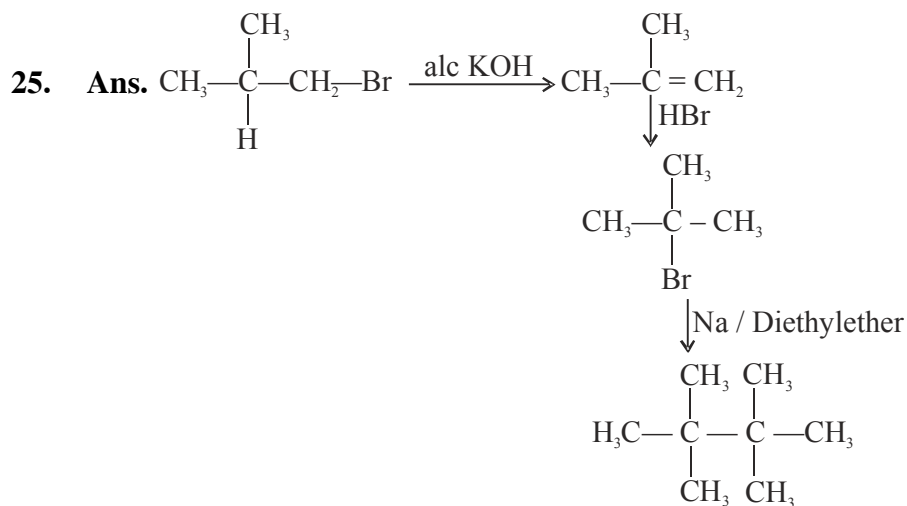
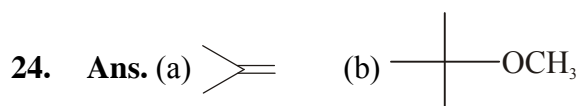
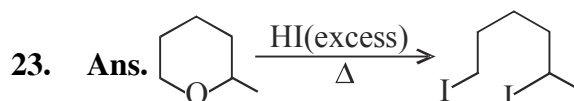


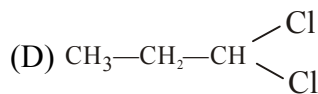
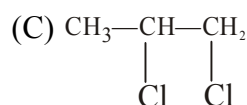
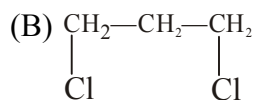
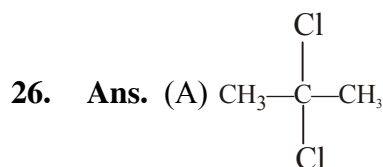
21. Ans.

The elimination of HI (or DI) in presence of strong base shows E2 elimination. The rate determining step involves breaking up of C – H (or C–D) bond. The C–D bond being stronger than C–H and thus elimination is faster in case of $\text{CH}_3 - \text{CH}_2\text{I}$.

22. Ans.

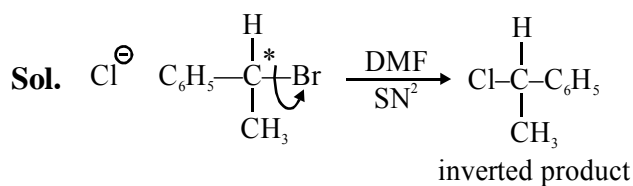
In second compound π bonds are conjugated so due to resonance given product is formed as major product.





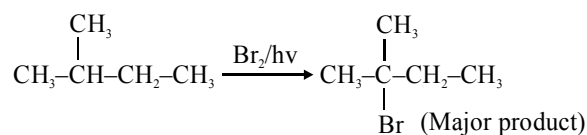
EXERCISE # III (J-MAINS)

- 1.** **Ans. (3)** **2.** **Ans. (1)** **3.** **Ans. (1)** **4.** **Ans. (2)**
- 5.** **Ans. (4)** **6.** **Ans. (2)** **7.** **Ans. (2)** **8.** **Ans. (4)**
- 9.** **Ans. (4)**

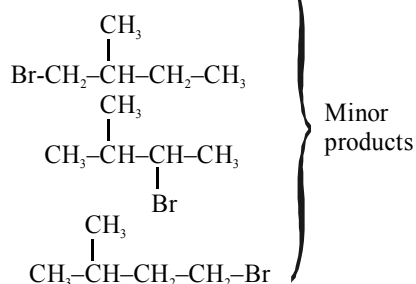


- 10. Ans. (1)**

Sol.



2-Bromo-2-methyl butane



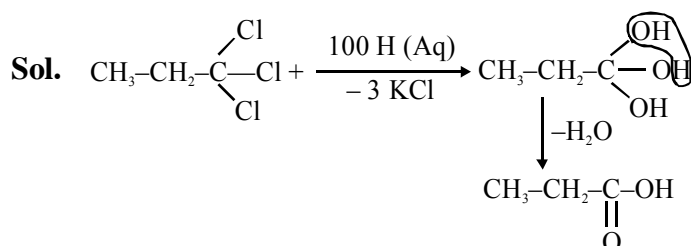
relectivity ratio for bromination is

$$1^\circ : 2^\circ : 3^\circ :: 1 : 82 : 1600$$

Hence 3° product will be major product.

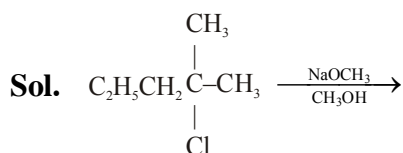
- 11. Ans. (2)**

- 12. Ans. (2)**

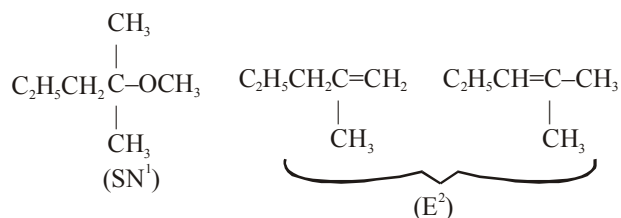


13. Ans. (2)

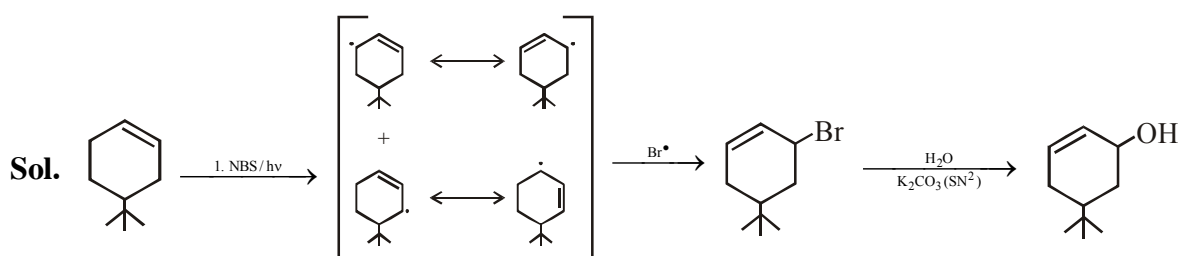
14. Ans. (2)



possible mechanism which takes place is E^2 & SN^1 mechanism. Hence possible products are.

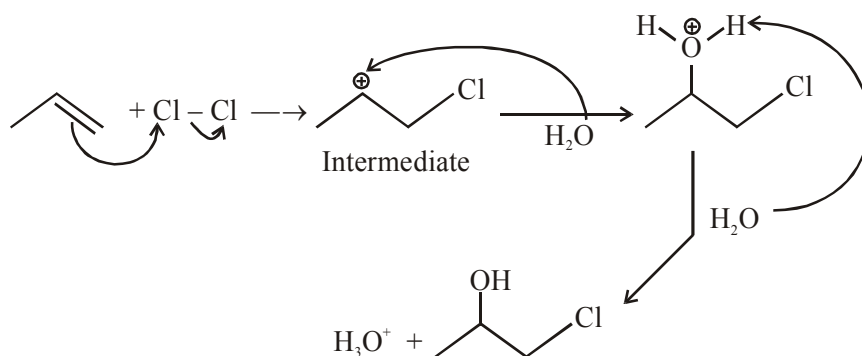


15. Ans. (3)



16. Ans. (3)

Sol.



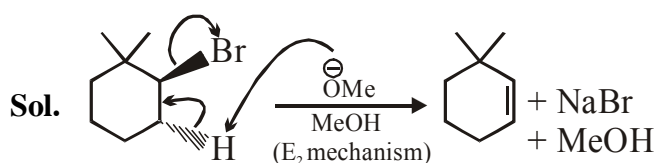
17. Ans. (2)

18. Ans. (1)

19. Ans. (4)

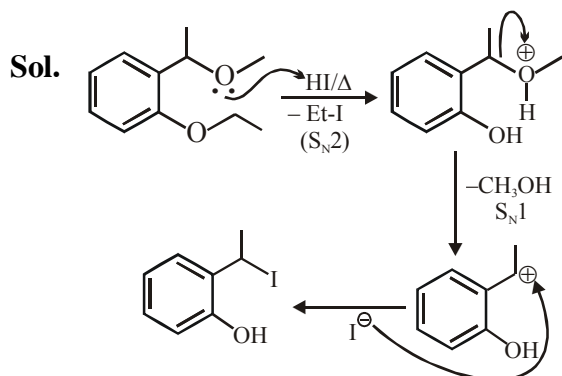
20. Ans. (2)

21. Ans. (1)



Reaction is dehydrohalogenation E^2 -elimination reaction. Elimination takes place in single step and proceed by formation of transition state from anti position.

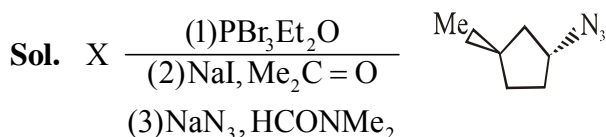
22. Ans. (3)



It is nucleophilic substitution reaction.

EXERCISE # IV (A) (J-ADVANCE OBJECTIVE)

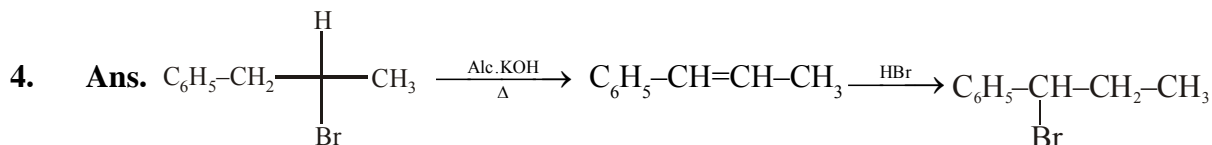
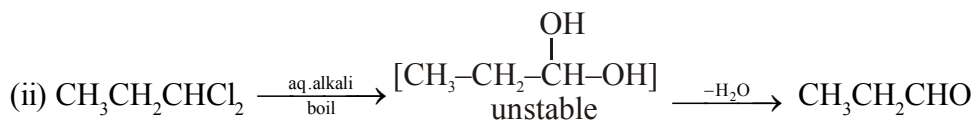
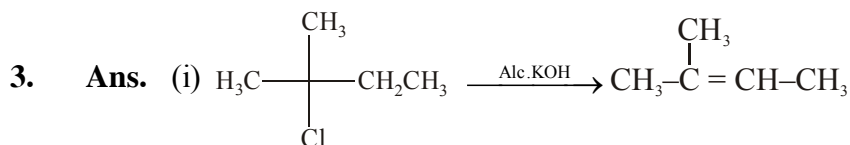
- | | | | | |
|--|---------------|--------------|--------------|--------------|
| 1. Ans. (D) | 2. Ans. (B,D) | 3. Ans. (A) | 4. Ans. (C) | 5. Ans. (B) |
| 6. Ans. (A) | 7. Ans. (A,C) | 8. Ans. (D) | 9. Ans. (C) | 10. Ans. (D) |
| 11. Ans. (A) | 12. Ans. (B) | 13. Ans. (D) | 14. Ans. (B) | 15. Ans. (A) |
| 16. Ans. (A) → Q ; (B) → Q ; (C) → R, S ; (D) → P, S | | | | |
| 17. Ans. (A) | 18. Ans. (D) | 19. Ans. (B) | 20. Ans. (D) | 21. Ans. (5) |
| 22. Ans. (B) | | | | |



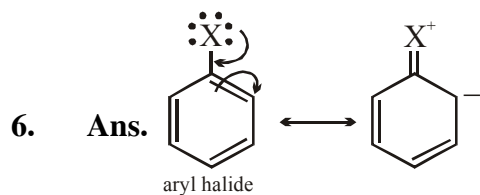
all the three reaction are $\text{S}_{\text{N}}2$ so X is

EXERCISE # IV (B) (J-ADVANCE SUBJECTIVE)

1. Ans. (a) propyl chloride, (b) ortho
2. Ans. (i) $\text{H}_2\text{O} < \text{CH}_3\text{OH} < \text{HO}^- < \text{CH}_3\text{O}^-$
(ii) $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$

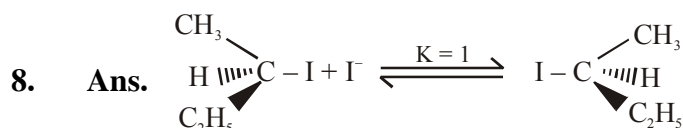
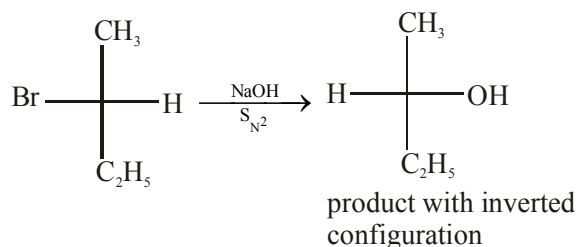


5. Ans. (i) $\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{CH}_3$; $\text{C}_6\text{H}_5 - \overset{\text{Br}}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{CH}_3$ (ii) $\text{C}_6\text{H}_5\text{COOMgI} + \text{CH}_4$



Due to the above resonance phenomena, C-X bond acquire partial double bond character and becomes difficult to break in the rate determining step of $\text{S}_{\text{N}}2$ reaction.

7. Ans. $\text{S}_{\text{N}}2$ reactions leads to inversion of configuration at a-C.



Above equilibrium is established which has equilibrium constant equal to 1. Therefore, equilibrium mixture will have both the enantiomers in equal amount giving racemic mixture.

