

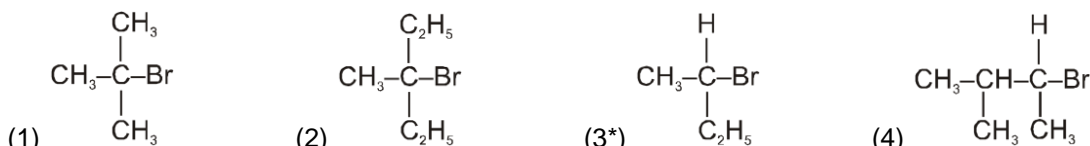
## Exercise-1

Marked Questions may have for Revision Questions.

### PART - I : OBJECTIVE QUESTIONS

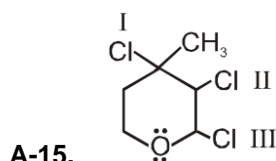
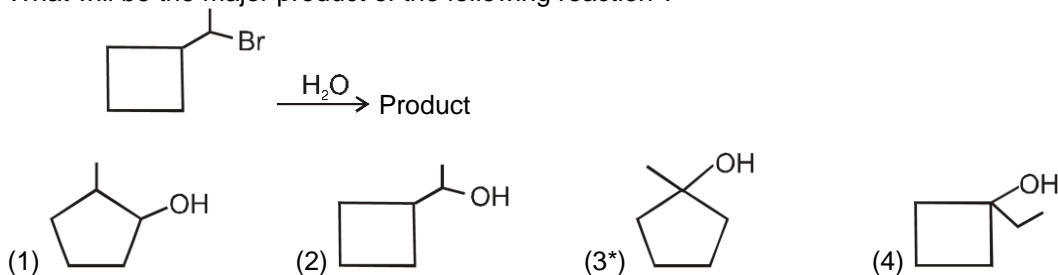
#### Section (A) : Unimolecular Nucleophilic substitution reactions of alkyl halides ( $S_N1$ )

- A-1.** Substitution reactions involve :  
 (1\*) Cleavage of a  $\sigma$ -bond and formation of a new  $\sigma$ -bond  
 (2) Cleavage of two  $\sigma$ -bond and formation of a new  $\pi$ -bond  
 (3) Cleavage of a  $\pi$ -bond and formation of two new  $\sigma$ -bond  
 (4) None of these
- A-2.** Following reaction  $(CH_3)_3CBr + C_2H_5OH \longrightarrow (CH_3)_3COC_2H_5 + HBr$  is an example of :  
 (1) Elimination reaction (2) Free radical substitution  
 (3\*) Nucleophilic substitution (4) Electrophilic substitution
- A-3.** Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to  
 (1) The formation of less stable carbanion (2) Longer carbon halogen bond  
 (2) The inductive effect (4\*)  $sp^2$ -hybridized carbon attached to the halogen.
- A-5.**  $S_N1$  reactions occur through the intermediate formation of-  
 (1\*) Carbocations (2) Carbanions (3) Free radicals (4) None of these
- A-6.**  $S_N1$  reactions are favoured by -  
 (1) Non-polar solvents.  
 (2\*) Bulky groups on the carbon atom attached to the halogen atom.  
 (3) Small groups on carbon atom attached to the halogen atom.  
 (4) None of these.
- A-7.** Which of the following undergoes nucleophilic substitution by  $S_N1$  mechanism :  
 (1) Ethyl chloride (2) Vinyl chloride (3\*) Benzyl chloride (4) Chloro benzene
- A-8.** The rate of reaction of alkyl halides depends upon.  
 (1) Nature of alkyl group  
 (2) Nature of halogen atom  
 (3\*) Nature of both alkyl group and halogen atoms  
 (4) None of the above
- A-9.**  $S_N1$  reactivity of the following halides, [NSEC-2009]  
 (i)  $(CH_3)_3CBr$  (ii)  $(C_6H_5)_2CHBr$  (iii)  $(C_6H_5)_2C(CH_3)Br$  (iv)  $(CH_3)_2CHBr$   
 (1)  $iv > i > ii > iii$  (2)  $ii > i > iii > iv$  (3)  $i > iii > ii > iv$  (4\*)  $iii > ii > i > iv$
- A-10.** The number of transition state/s and intermediate/s in a unimolecular nucleophilic substitution reaction are respectively- [NSEC-2010]  
 (1) 3, 1 (2) 2, 2 (3\*) 2, 1 (4) 1, 1
- A-11.** When the concentration of alkyl halide is doubled and the amount of  $H_2O$  taken as solvent is reduced to half, the rate of  $S_N1$  reaction increases by:  
 (1) 3 times (2\*) 2 times (3) 1.5 times (4) No change
- A-12.** Which one of the following compounds will give (d) and (l) form in  $S_N1$  reaction (as major product) ?



- A-13.** In an  $\text{S}_{\text{N}}1$  reaction, the configuration of the product undergoes :  
 (1) inversion (2\*) racemization (3) retention (4) difficult to predict

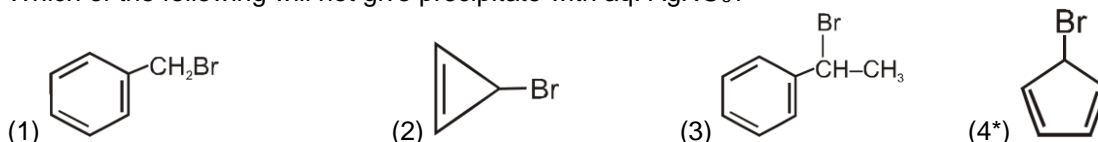
- A-14.** What will be the major product of the following reaction ?



The rate of reaction with  $\text{AgNO}_3$  will be :

- (1)  $\text{I} > \text{II} > \text{III}$  (2\*)  $\text{III} > \text{I} > \text{II}$  (3)  $\text{III} > \text{II} > \text{I}$  (4)  $\text{I} > \text{III} > \text{II}$

- A-16.** Which of the following will not give precipitate with aq.  $\text{AgNO}_3$ ?

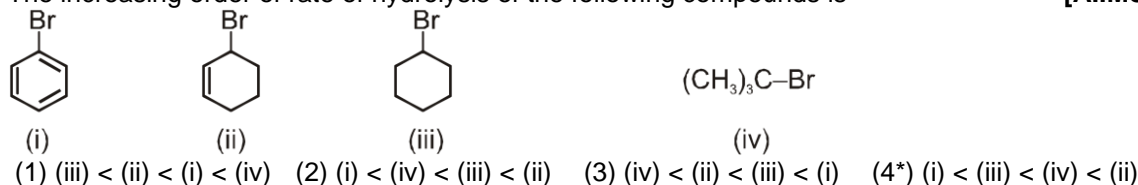


- A-17.** Which of the following alkyl halide is most readily hydrolysed?

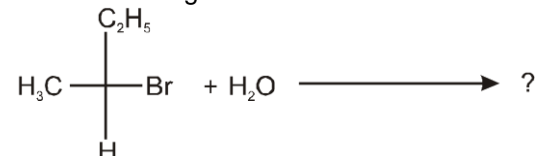
- (1)  $\text{C}_6\text{H}_5\text{Cl}$  (2)  $(\text{C}_6\text{H}_5)_2\text{CHCl}$  (3)  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  (4\*)  $(\text{C}_6\text{H}_5)_3\text{CCl}$

- A-18.** The increasing order of rate of hydrolysis of the following compounds is

[AIIMS 2009]

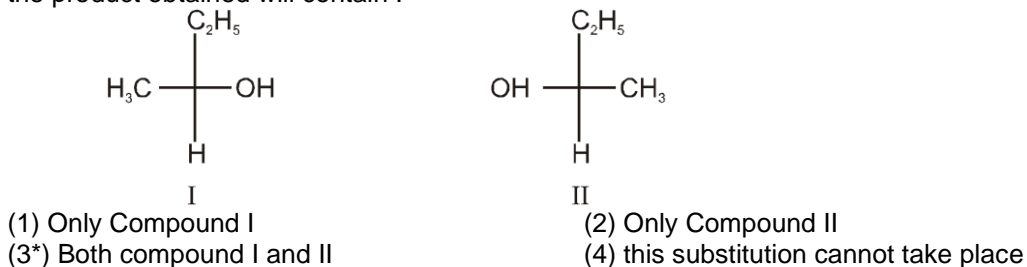


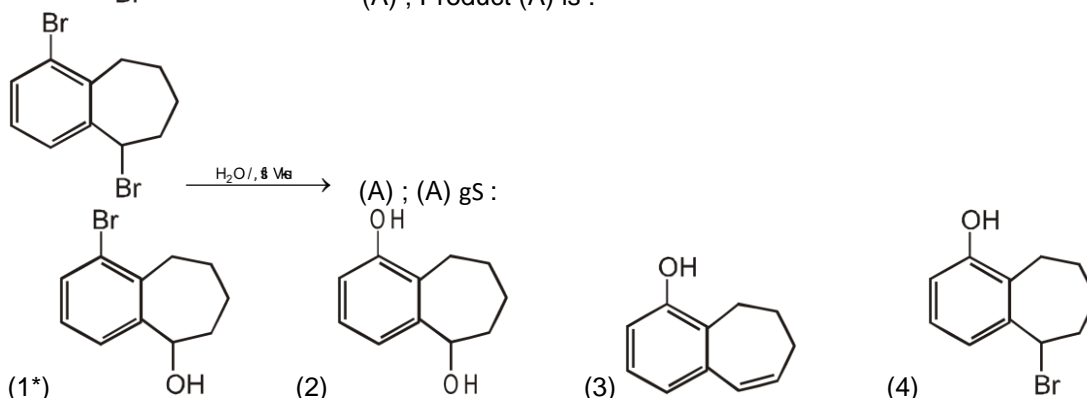
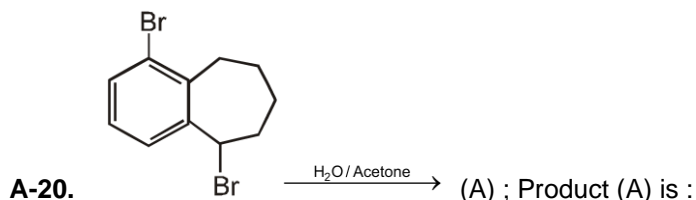
- A-19.** In the reaction given below :



the product obtained will contain :

[NSEC-2013]





**Section (B) : Biomolecular Nucleophilic substitution reactions of alkyl halides ( $\text{S}_{\text{N}}2$ )**

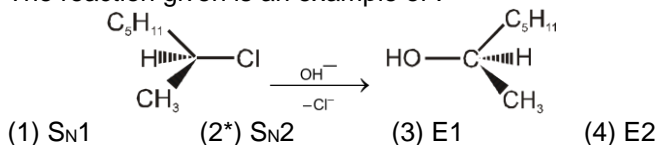
B-1. Which one of the following statement is wrong about  $\text{S}_{\text{N}}2$  reaction ?

- (1\*) The rate of reaction is independent of the concentration of nucleophile.  
 (2) Nucleophile attacks the carbon from the side opposite to where the leaving group is attached.  
 (3) Only in one step the bond formation and bond breaking takes place.  
 (4) The rate of reaction  $\propto [\text{substrate}] [\text{nucleophile}]$

B-2. When the concentration of alkyl halide is tripled and the concentration of  $\text{OH}^-$  ion is reduced to half, the rate of  $\text{S}_{\text{N}}2$  reaction increases by:

- (1) 3 times (2) 2 times (3\*) 1.5 times (4) 6 times

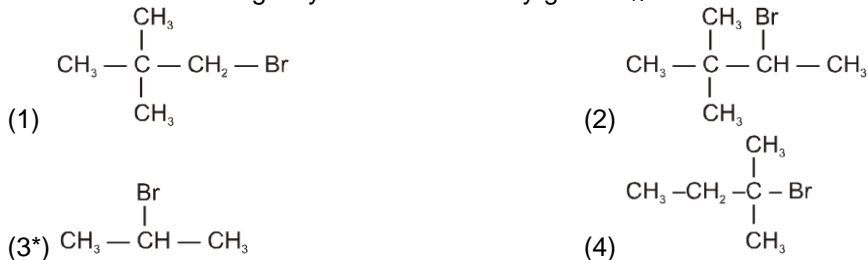
B-3. The reaction given is an example of :



B-4.  $\text{S}_{\text{N}}2$  mechanism proceeds through intervention of

- (1) Carbonium ion (2\*) Transition state (3) Free radical (4) Carbanion

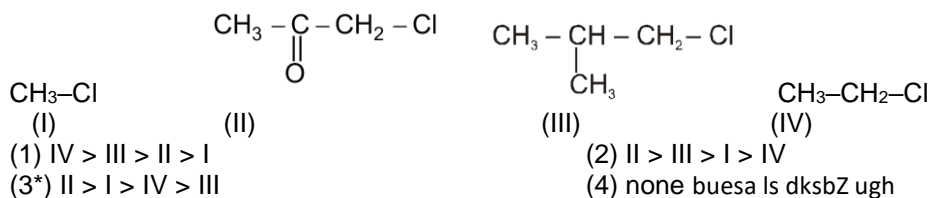
B-5. Which of the following alkyl halide will readily gives  $\text{S}_{\text{N}}2$  reaction ?



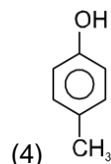
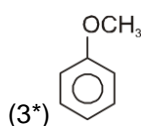
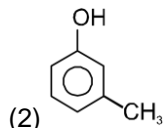
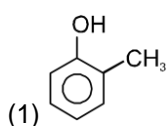
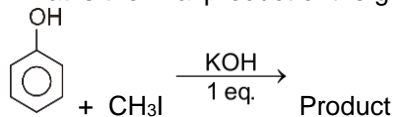
B-6. Select the **incorrect** statement among the following :

- (1)  $\text{S}_{\text{N}}1$  reaction involve two steps (2)  $\text{S}_{\text{N}}2$  reactions involve single step  
 (3)  $\text{S}_{\text{N}}2$  reaction involves transition state (4\*)  $\text{S}_{\text{N}}2$  reaction involve carbonium ion intermediate

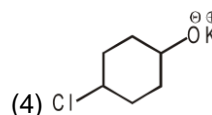
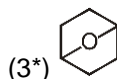
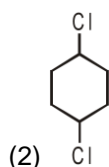
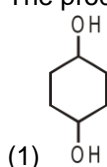
B-7. The decreasing order of rate of  $\text{S}_{\text{N}}2$  reaction is :



B-8. What is the final product of the given reaction ?

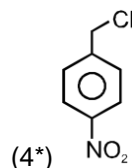
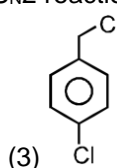
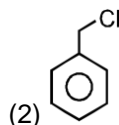
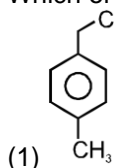


B-9. The product is :

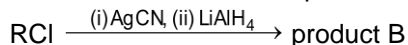
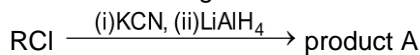


B-10. Reaction of alkyl halides with ethanolic KCN predominantly gives :  
 (1) Alkyl carbylamines (2\*) Alkyl cyanides (3) Nitroalkanes (4) Alkyl nitrites

B-11. Which of the following is most reactive towards  $\text{S}_{\text{N}}2$  reaction ?



B-12. In the reactions given below:

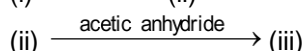
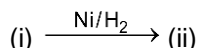
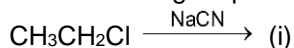


the compounds A and B are :

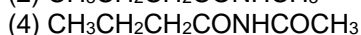
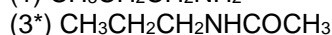
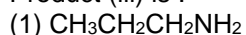
- (1) chain isomers (2) position isomers (3\*) functional isomers (4) metamers.

[NSEC-2006]

B-13. In the following sequence:



Product (iii) is :



[NSEC-2006]

B-14. In Williamson's synthesis, ethoxyethane is prepared by :

(1) Passing ethanol over heated alumina

(2\*) Heating sodium ethoxide with ethyl bromide

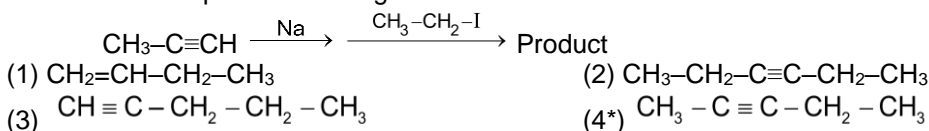
- (3) Treating ethyl alcohol with excess of  $\text{H}_2\text{SO}_4$  at 430 – 440 K  
 (4) Heating ethanol with dry  $\text{Ag}_2\text{O}$

**B-15.**  $\text{C}_2\text{H}_5\text{Cl} \xrightarrow{\text{NH}_3} \text{'A'} \xrightarrow{\text{C}_2\text{H}_5\text{Cl}} \text{'B'} \xrightarrow{\text{C}_2\text{H}_5\text{Cl}} \text{'C'}$   
 A, B and C respectively are : [RPMT 2011]  
 (1\*)  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $(\text{C}_2\text{H}_5)_3\text{N}$  (2)  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{C}_2\text{H}_5\text{NH}-\text{Cl}$ ,  $\text{C}_2\text{H}_5-\text{NCl}_2$   
 (3)  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{CH}_2=\text{CH}_2$ ,  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{C}_2\text{H}_5$  (4)  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_3\text{N}$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$

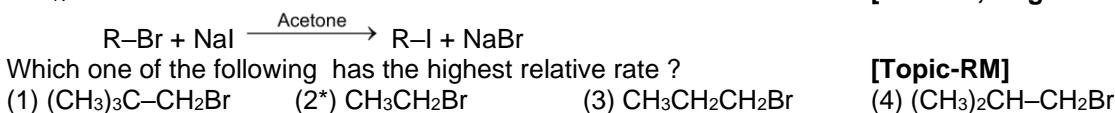
**B-16.** The order of reactivity of ammonia with the following compound is : [NSEC-2011]  
 (I)  $\text{CH}_2=\text{CHBr}$  (II)  $\text{CH}_3-\text{CH}_2-\text{COCl}$  (III)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Cl}$  (IV)  $(\text{CH}_3)_3\text{C}-\text{Br}$   
 (1)  $\text{IV} > \text{II} > \text{I} > \text{III}$  (2\*)  $\text{II} > \text{IV} > \text{III} > \text{I}$  (3)  $\text{III} > \text{IV} > \text{II} > \text{I}$  (4)  $\text{I} > \text{IV} > \text{II} > \text{III}$

**B-17.** The product obtained on reaction of alkyl halide with  $\text{AgNO}_2$  is [NSEC-2006]  
 (1) alkyl nitrate (2\*) nitroalkane (3) alkyl nitrite (4) nitrosoalkane.

**B-18.** What is the final product of the given reaction :



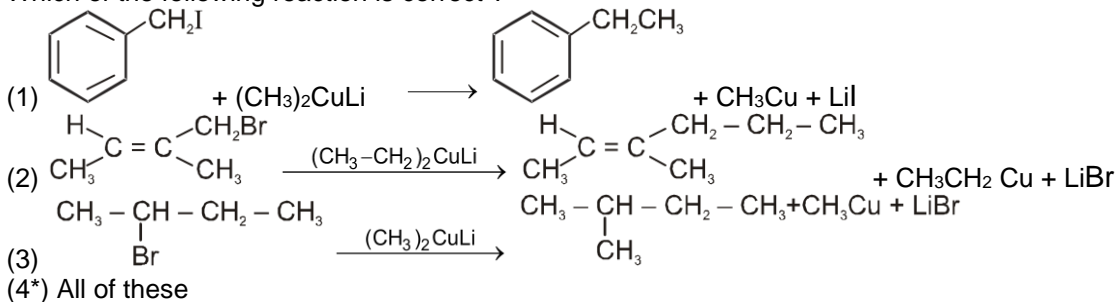
**B-19.** In  $\text{S}_{\text{N}}2$  substitution reaction : [RVP Sir, Aug. 2014]



**B-20.** Which of the following alkanes can be synthesized by the Wurtz reaction in good yield ?

- (1)  $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}(\text{CH}_3)_2$  (2\*)  $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)_2$   
 (3)  $\text{CH}_3-\text{CH}_2-\text{C}(\text{CH}_3)_2\text{CH}_2-\text{CH}_3$  (4)  $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$

**B-21.** Which of the following reaction is correct ?



**B-23.** Among the following isomeric chloro compounds, the compound which will undergo  $\text{S}_{\text{N}}2$  reaction readily is: [NSEC-2009]  
 (1) 4-chloro-1-butene (2) 1-chloro-1-butene (3\*) 1-chloro-2-butene (4) 2-chloro-1-butene

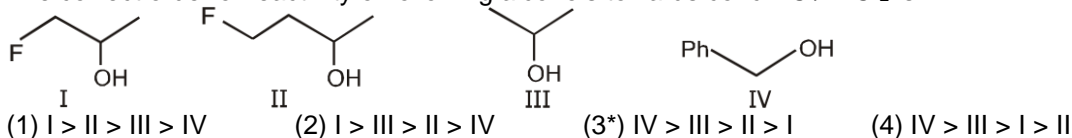
### Section (C) : Nucleophilic substitution ( $\text{S}_{\text{N}}$ ) reaction of alcohols

**C-1.** Primary, secondary and tertiary alcohols are distinguished by  
 (1) Oxidation method (2) Lucas test (3) Victor mayer's test (4\*) All of the above

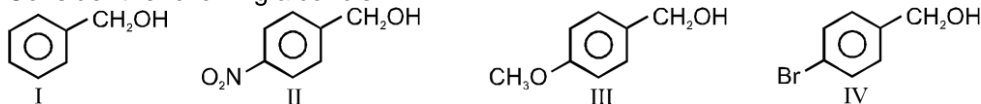
**C-2.** Lucas reagent is : [AFMC-2006]  
 (1) anhy.  $\text{ZnCl}_2$  and  $\text{NH}_3$  (2) anhy.  $\text{ZnCl}_2$  and  $\text{CaCl}_2$   
 (3\*) anhy.  $\text{ZnCl}_2$  and conc.  $\text{HCl}$  (4) anhy.  $\text{ZnCl}_2$  and  $\text{HCl}$  gas

**C-3.** Which of the following major product will be obtained when neopentyl alcohol is treated with conc.  $\text{HCl}$  in presence of  $\text{ZnCl}_2$   
 (1) t-butyl chloride (2) isobutylene (3\*) t-pentyl chloride (4) Neo pentyl chloride

C-4. The correct order of reactivity of following alcohols towards conc. HCl/ZnCl<sub>2</sub> is :

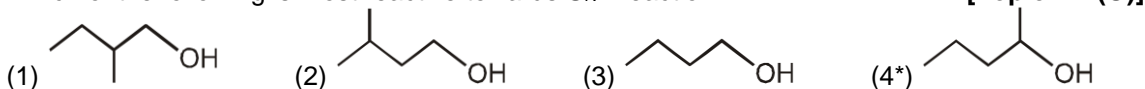


C-5. Consider the following alcohols :

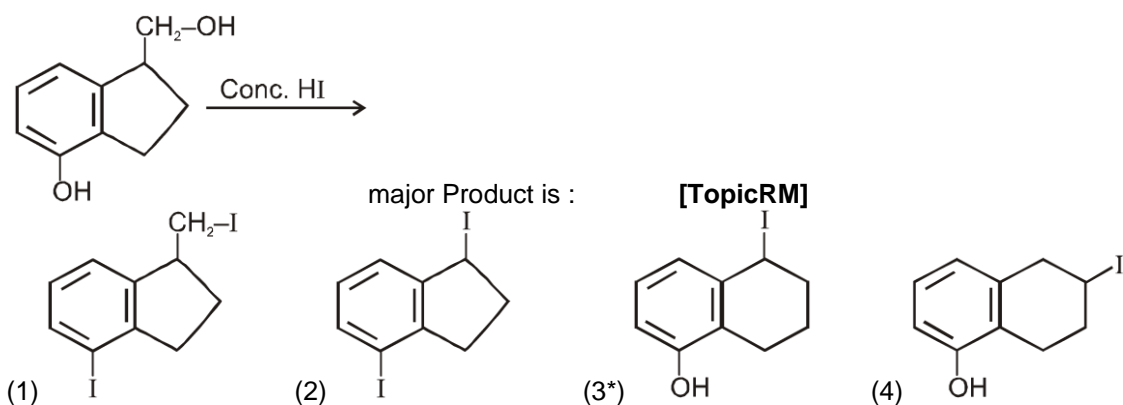


The order of decreasing reactivities of these alcohols towards nucleophilic substitution with HBr is  
 (1\*) III > I > IV > II      (2) III > I > II > IV      (3) I > III > IV > II      (4) I > III > II > IV

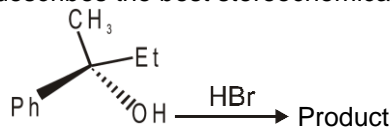
C-6. Which of the following is most reactive towards S<sub>N</sub>1 reaction :



C-7.



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



- (1) Inversion of configuration occurs at the carbon undergoing substitution.  
 (2) Retention of configuration occurs at the carbon undergoing substitution.  
 (3\*) Racemization occurs at the carbon undergoing substitution.  
 (4) The carbon undergoing substitution is not stereogenic.

C-9. What is the correct order of reactivity of alcohols in the following reaction?



[Topic-RM] [By MG Sir Dec. 2013]

- (1) Ethanol > Propan-1-ol > Butan-1-ol      (2) Butan-1-ol > Propan-1-ol > Butan-2-ol  
 (3) Neopentyl alcohol > t-Butyl alcohol > Methanol      (4\*) t-Butyl alcohol > Butan-2-ol > Propan-1-ol

C-10. Ethanol when reacted with PCl<sub>5</sub> gives A, POCl<sub>3</sub> and HCl. A reacts with silver nitrite to form B (major product) and AgCl. A and B respectively are :

[AIIMS 2013]

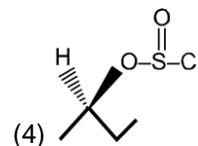
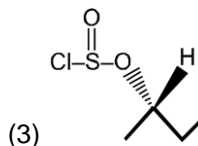
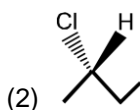
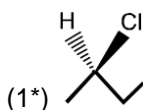
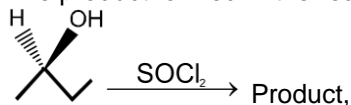
- (1) C<sub>2</sub>H<sub>5</sub>Cl and C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>      (2) C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>  
 (3\*) C<sub>2</sub>H<sub>5</sub>Cl and C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>      (4) C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>

C-11. Thionyl chloride method is preferred over phosphorus pentachloride method for the preparation of alkyl chloride because-

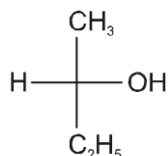
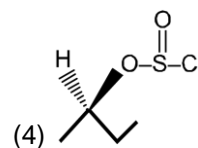
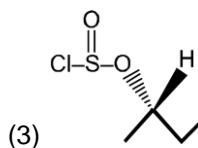
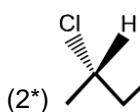
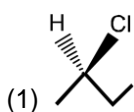
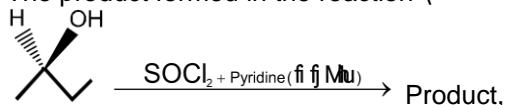
- (1) The reaction goes to completion.

- (2\*) The by-products being gases escape into the atmosphere leaving behind almost pure alkyl chloride.  
 (3) Thionyl chloride is cheap while phosphorus pentachloride is costly.  
 (4) None of the above.

C-12. The product formed in the reaction \



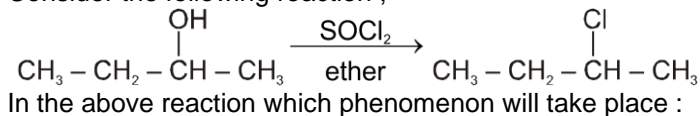
C-13. The product formed in the reaction \



C-14. (D-2-Butanol)  $\xrightarrow{\text{PCl}_5}$  X ; (X) is :

- (1) S-2-Chlorobutane (2\*) R - 2-Chlorobutane  
 (3) mixture of R and S 2-Chlorobutane (4) 1-Chlorobutane

C-15. Consider the following reaction ;

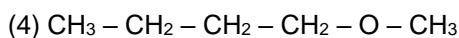
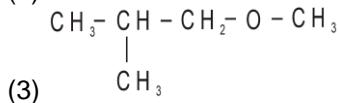
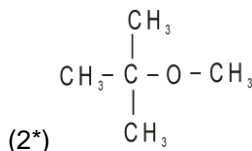
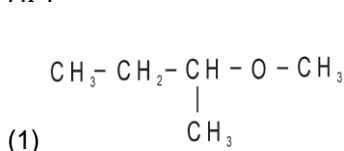


In the above reaction which phenomenon will take place :

- (1) Inversion (2\*) Retention (3) Racemisation (4) Isomerisation

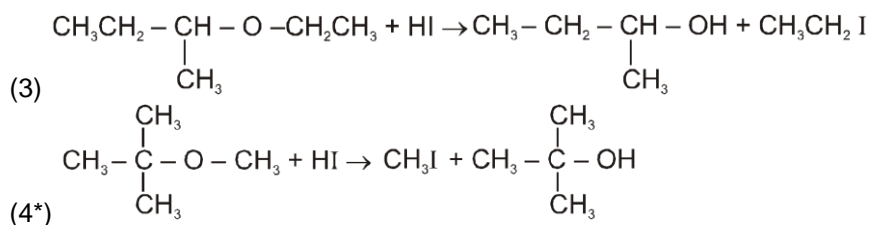
#### Section (D): Preparation and chemical reactions of ethers

D-1. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI ? [NEET 2013]



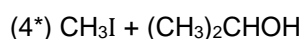
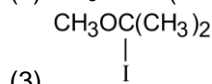
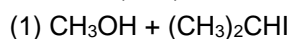
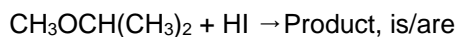
D-2. Some reactions of ethers are given. Which one is not true ? [RPMT 2014]

- (1)  $\text{C}_6\text{H}_5\text{CH}_2 - \text{O} - \text{C}_6\text{H}_5 + \text{HI} \rightarrow \text{C}_6\text{H}_5\text{CH}_2 - \text{I} + \text{C}_6\text{H}_5 - \text{OH}$   
 (2)  $\text{CH}_3 - \text{O} - \text{CH}_2\text{CH}_3 + \text{HI} \longrightarrow \text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{OH}$



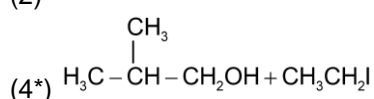
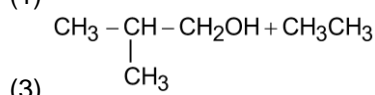
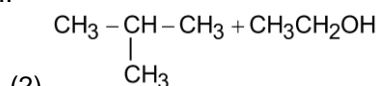
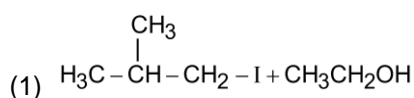
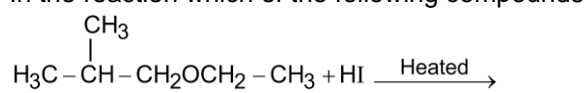
D-3. The major organic product in the reaction,

[AIPMT 2006]



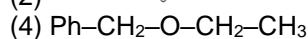
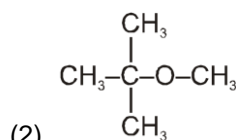
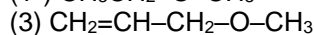
D-4. In the reaction which of the following compounds will be formed?

[AIPMT 2007]



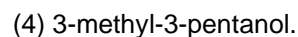
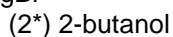
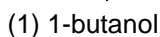
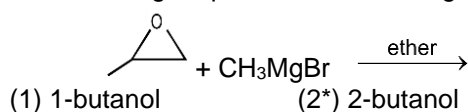
D-5.  $\text{S}_{\text{N}}2$  reaction readily occurs in :

[AIIMS 2011]



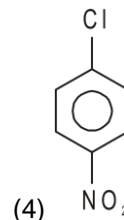
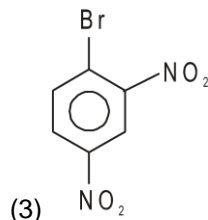
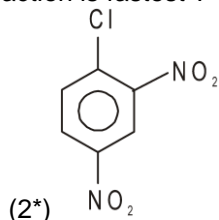
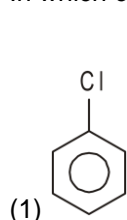
D-6. The following sequence of reactions give

[NSEC-2004]

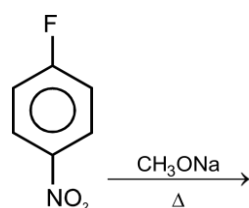


### Section (E) : Preparation and nucleophilic substitution of aryl halides

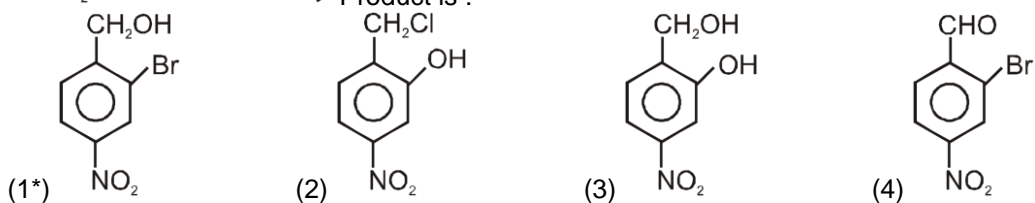
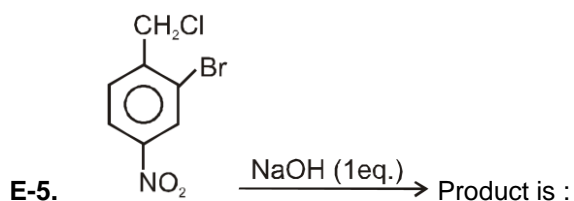
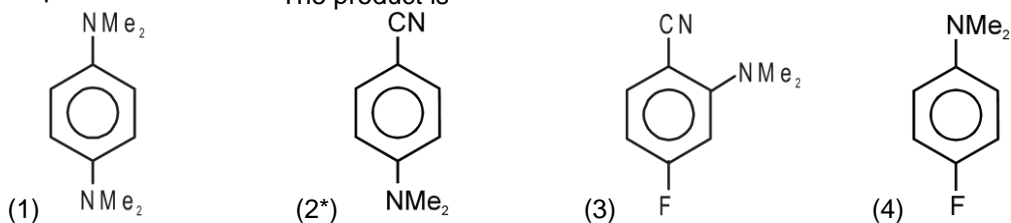
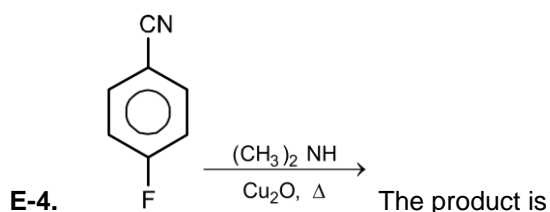
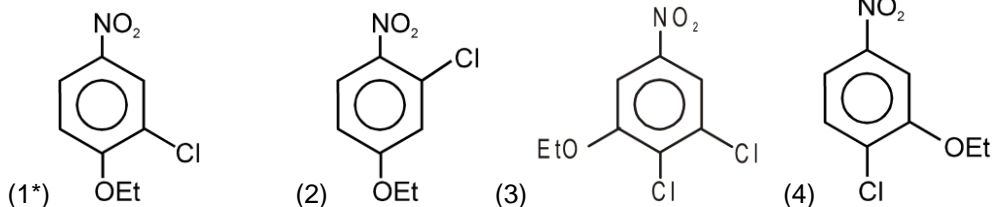
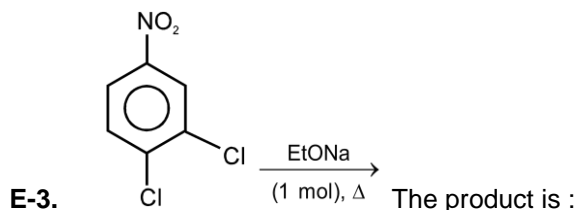
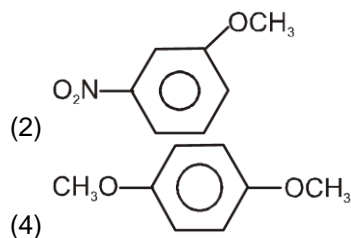
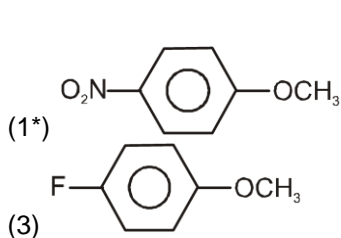
E-1. In which case  $\text{S}_{\text{N}}2$  Ar reaction is fastest ?



E-2.







**E-6.** Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to : [JEE 1990]

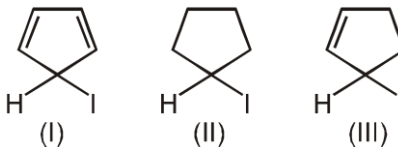
- (1) The formation of less stable carbonium ion
- (2\*) C-X bond has partial double character in aryl halides
- (3) Longer carbon-halogen bond
- (4) The inductive effect

- E-7. The compound which undergoes hydrolysis on just warming with water and forms the corresponding hydroxyl derivative is [NSEC-2014]  
 (1\*) 2,4,6-trinitrochlorobenzene (2) 2-chloro-1-butene  
 (3) 2-chloro-2-methylbutane (4) 2, 4-dimethoxychlorobenzene

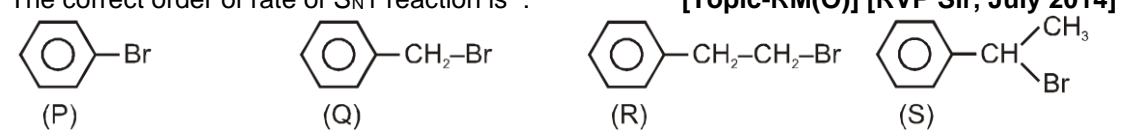
## Exercise-2

### PART - I : OBJECTIVE QUESTIONS

Marked Questions may have for Revision Questions.

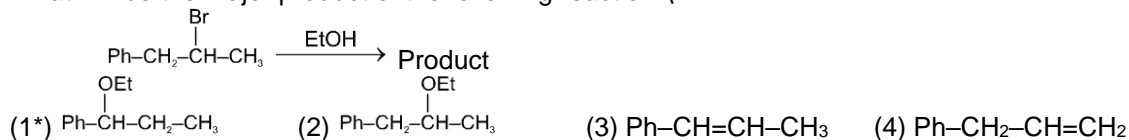
- The least reactive alkyl chloride towards substitution reaction is :  
 (1) Methyl chloride (2) Allyl chloride (3) Ethyl chloride (4\*) Vinyl chloride
- The order of the rate of formation of carbocations from the following iodo compounds is : [NSEC-2007]  
  
 (1) I > II > III (2) I > III > II (3\*) III > II > I (4) III > I > II
- What is the effect of doubling the concentration of HCl on the rate of reaction between t-butyl alcohol and HCl ? [NSEC-2000]  
 (1\*) It has no effect on the rate of reaction  
 (2) It halves the rate of reaction  
 (3) It doubles the rate of reaction  
 (4) It is not possible to predict its effect on the reaction.
- Select the most correct statement among the following : [NSEC-2013]  
 (1) S<sub>N</sub>1 mechanism takes place in non-polar solvents  
 (2) S<sub>N</sub>2 mechanism in chiral substrates gives racemic mixtures as products  
 (3\*) S<sub>N</sub>1 mechanism is encouraged by polar solvents  
 (4) The solvent never influences the mechanism
- Which of the following statement is correct for S<sub>N</sub>1 reaction :  
 (1) Intermediate of S<sub>N</sub>1 reaction is carbocation. (2) It is two step process.  
 (3) Its rate depends only on concentration of reactant. (4\*) All of these
- Which of them is correct order for solvolysis rate in aqueous acetone ?  

CH <sub>3</sub> O-CH=CH-CH <sub>2</sub> -Cl	P
CH <sub>3</sub> -O-C(CH <sub>2</sub> )=CH <sub>2</sub> -Cl	Q
CH <sub>3</sub> O-CH <sub>2</sub> -CH=CH-Cl	R
CH <sub>3</sub> O-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -Cl	S

 (1) R > P > Q > S (2) P > Q > R > S (3) Q > P > S > R (4\*) P > Q > S > R
- The correct order of rate of S<sub>N</sub>1 reaction is : [Topic-RM(O)] [RVP Sir, July 2014]  
  
 (P) (Q) (R) (S)

- (1\*)  $S > Q > R > P$       (2)  $S > R > P > Q$       (3)  $P > Q > R > S$       (4)  $S > R > Q > P$

10. What will be the major product of the following reaction \

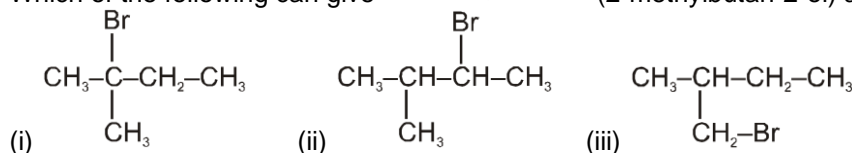


12. The correct increasing order of the reactivity of halides for  $S_N1$  reaction is :

[AIIMS 2006]

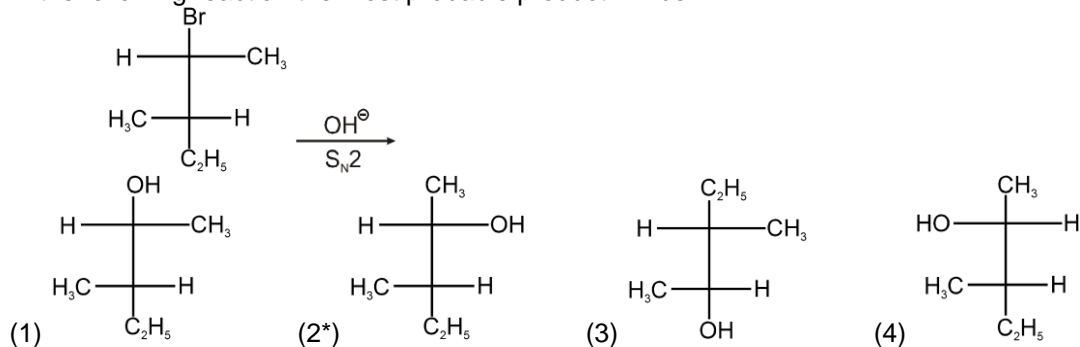
- (1\*)  $\text{CH}_3-\text{CH}_2-\text{X} < (\text{CH}_3)_2\text{CH}-\text{X} < \text{CH}_2=\text{CH}-\text{CH}_2-\text{X} < \text{PhCH}_2-\text{X}$
- (2)  $(\text{CH}_3)_2\text{CH}-\text{X} < \text{CH}_3-\text{CH}_2-\text{X} < \text{CH}_2=\text{CH}-\text{CH}_2\text{X} < \text{PhCH}_2-\text{X}$
- (3)  $\text{PhCH}_2-\text{X} < (\text{CH}_3)_2\text{CH}-\text{X} < \text{CH}_3-\text{CH}_2-\text{X} < \text{CH}_2=\text{CH}-\text{CH}_2-\text{X}$
- (4)  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{X} < \text{Ph}-\text{CH}_2-\text{X} < (\text{CH}_3)_2\text{CH}-\text{X} < \text{CH}_3-\text{CH}_2-\text{X}$

17. Which of the following can give  $\begin{array}{c} \text{OH} \\ | \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$  (2-methylbutan-2-ol) as major product :

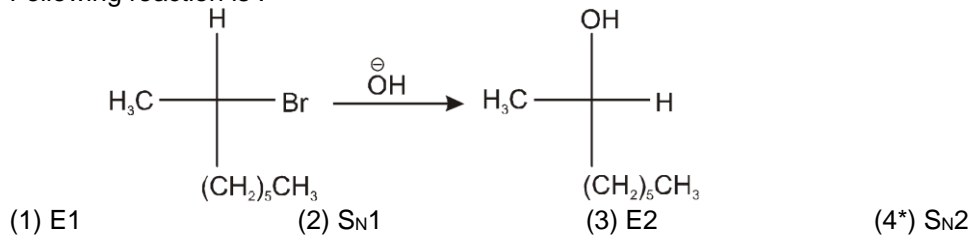


- (1\*) i, ii & iii      (2) ii & iii only      (3) i & iii only      (4) i & ii only

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



19. Following reaction is :



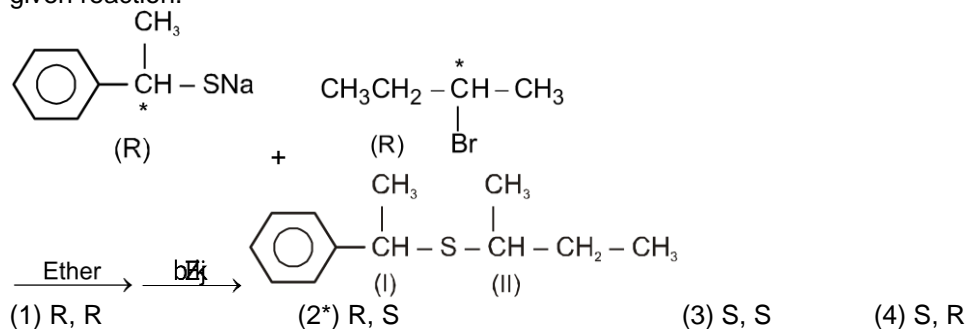
20.  $\text{C}_4\text{H}_8\text{Cl}_2 \xrightarrow{\text{aq. NaOH}}$  Compound (Y)

(X)

If compound (Y) can give yellow precipitate with both 2, 4-DNP and  $\text{I}_2 / \text{NaOH}$  then (X) can be :

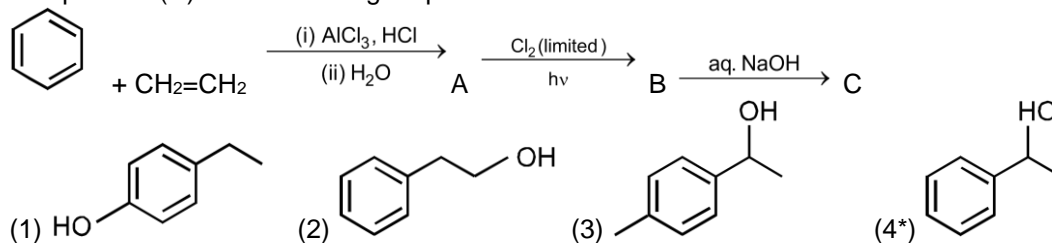


21. An  $\text{S}_{\text{N}}2$  reaction at an asymmetric carbon of a compound always gives :  
 (1) an enantiomer of the substrate (2) a product with opposite optical rotation  
 (3) a mixture of diastereomers (4\*) a single stereoisomer
22. Which configuration will be adopted by the product at carbon atoms marked (I) and (II) respectively in the given reaction.

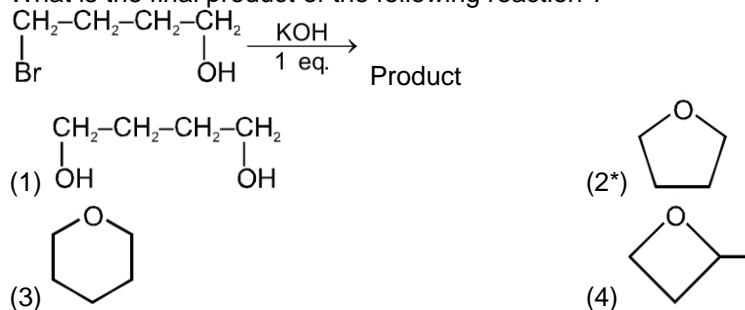


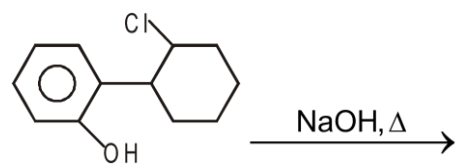
23. The product (C) of the following sequence of reactions is :

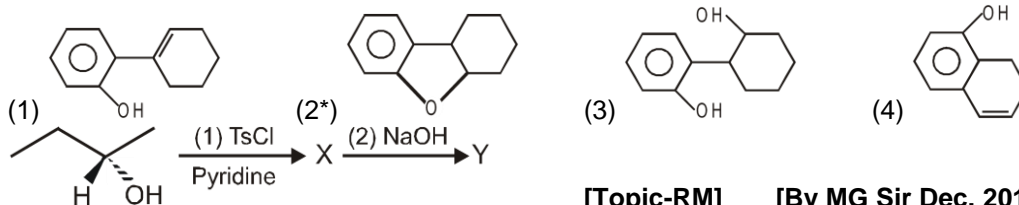
[NSEC-2011]



24. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives:  
 (1) o-Cresol (2) p-Cresol  
 (3) 2,4-Dihydroxytoluene (4\*) Benzyl alcohol
25. What is the final product of the following reaction ?



26.  Major product is :  
 (MG sir Dec.2013) [Topic-RM(O)]



[Topic-RM] [By MG Sir Dec. 2013]

Which is correct option for the above reaction.

- (1) Reaction 2<sup>nd</sup> follows unimolecular mechanism mainly.  
 (2) Reactant & product Y have same configuration  
 (3\*) In the reaction 2<sup>nd</sup> Walden inversion takes place at  $\alpha$  carbon.  
 (4) All are correct.

28. By heating which mixture propane nitrile will be obtained ? [RPMT 2011]

- (1) Ethyl alcohol + KCN (2) Propyl alcohol + KCN  
 (3\*) Ethyl chloride + KCN (4) Propyl chloride + KCN

29. The appropriate sequence of reactions for obtaining 2-phenylbutanoic acid from benzene is [NSEC-2015]

- (1) (i) 1-chlorobutane/ $\text{AlCl}_3$  (ii) limited  $\text{Cl}_2$ , light (iii) aq.  $\text{NaCN}$  (iv)  $\text{H}^+$ ,  $\text{H}_2\text{O}$ , heat  
 (2) (i) 2-chlorobutane/ $\text{AlCl}_3$  (ii)  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$   
 (3\*) (i) propanoyl chloride/ $\text{AlCl}_3$  (ii)  $\text{Zn-Hg}/\text{HCl}$  (iii) limited  $\text{Cl}_2(\text{g})$ , light (iv) aq.  $\text{NaCN}$  (v)  $\text{H}^+$ ,  $\text{H}_2\text{O}$ , heat  
 (4) (i) butanoyl chloride/ $\text{AlCl}_3$  (ii)  $\text{NaBH}_4$  (iii)  $\text{CuCN}$  (iv)  $\text{H}^+$ ,  $\text{H}_2\text{O}$ , heat

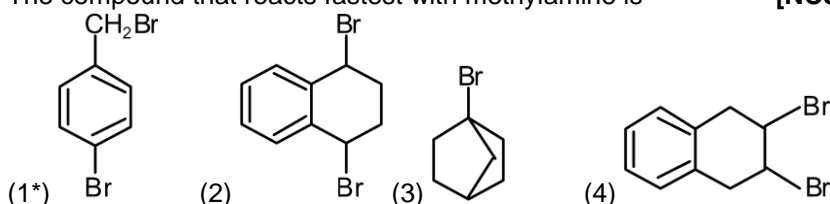
30. The substances used for the preparation of ether by Williamson's synthesis are : [NSEC-2009]

- (1)  $(\text{CH}_3)_3\text{CBr}$  and  $\text{CH}_3\text{ONa}$  (2)  $(\text{CH}_3)_3\text{CBr}$  and  $\text{CH}_3\text{OH}$   
 (3\*)  $\text{CH}_3\text{Br}$  and  $(\text{CH}_3)_3\text{CONa}$  (4)  $\text{CH}_3\text{Br}$  and  $(\text{CH}_3)_3\text{COH}$

31. From Williamson's synthesis preparation of which of the following is possible? [AFMC 2007]

- (1) Only symmetrical ethers (2) Only asymmetrical ethers  
 (3\*) Both (1) and (2) (4) None of the above

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



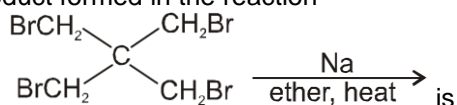
33. Find the identity of compound B in the following reaction sequence [NSEC-2000]



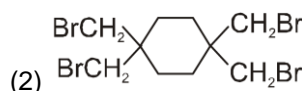
1 mol 1 mol

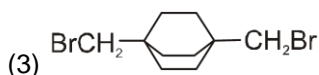
- (1\*) trans-1,2-dichloro-1-hexene (2) cis-1,2-dichloro-1-hexene  
 (3) cis-1,2-dichlorobutane (4) trans-2,3-dichloro-2-hexene

34. The product formed in the reaction



- (1)  $(\text{BrCH}_2)_3\text{CCH}_2\text{CH}_2\text{C}(\text{CH}_2\text{Br})_3$





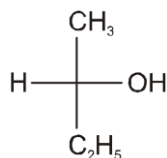
35. The best reaction sequence to convert 2-methyl-1-bromopropane into 4-methyl-2-bromopentane is  
 (1) (i) Mg in ether (ii) acetaldehyde (iii)  $H^+$ ,  $H_2O$  (iv)  $\Delta$  (v) HBr,  $H_2O_2$  [NSEC-2015]  
 (2\*) (i)  $NaC\equiv CH$  in ether (ii)  $H_2$ , Lindlar catalyst (iii) HBr, no peroxide  
 (3) (i) alcoholic KOH (ii)  $CH_3COOOH$  (iii)  $H_2/Pt$  (iv) HBr, heat  
 (4) (i)  $NaC\equiv CH$  in ether (ii)  $H_3O^+$  +  $HgSO_4$  (iii) HBr, heat

36. For the reaction,  $C_2H_5OH + HX \xrightarrow{ZnX_2} C_2H_5X$ , the order of reactivity is :  
 (1)  $HI > HCl > HBr$  (2\*)  $HI > HBr > HCl$  (3)  $HCl > HBr > HI$  (4)  $HBr > HI > HCl$

37. The reaction,  $Alcohol + HCl \rightleftharpoons Alkyl\ halide + H_2O$  is reversible. For the completion of the reaction..... is used  
 (1\*) Anhydrous  $ZnCl_2$  (2) Concentrated  $H_2SO_4$  (3) Excess of water (4) Calcium chloride

38. In Lucas test of alcohols, the appearance of cloudiness is due to the formation of-  
 (1) Aldehydes (2) Ketones (3) Acid chlorides (4\*) Alkyl chlorides

39. The  $-OH$  group of an alcohol or carboxylic acid can be replaced by  $-Cl$  using [AIPMT 2004]  
 (1\*) Phosphorus pentachloride (2) hypochlorous acid  
 (3) chlorine (4) hydrochloric acid



40. (D-2-Butanol)  $\xrightarrow{SOCl_2}$  X ; (X) is :  
 (1\*) S-2-Chlorobutane (2) R - 2-Chlorobutane  
 (3) mixture of R and S 2-Chlorobutane (4) 1-Chlorobutane

41. C-O bond in ether can be easily broken by : [RPMT 2004]  
 (1\*) HI (2) HCl (3) HBr (4) HF

42. Ethyl phenyl ether is treated with conc. HI at  $0^\circ C$  and the mixture of products is treated with thionyl chloride. The products formed are- [NSEC-2010]  
 (1) Ethanol + Chlorobenzene (2) Phenol + Iodoethane  
 (3) Iodoethane + Chlorobenzene (4\*) Chloroethane + Phenol

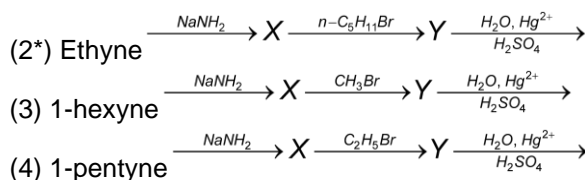
43. 1-Phenoxypropane is treated with excess of conc. HI at  $0^\circ C$  and the mixture of products is treated with thionyl chloride. The products formed are [NSEC-2014]  
 (1) n-propanol + Chlorobenzene (2\*) Phenol + n-propyl chloride  
 (3) n-propyl chloride + Chlorobenzene (4) n-propyl chloride + Phenol

44. Consider the reactions :  
 (i)  $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH-CH_2OC_2H_5 + HBr$   
 (ii)  $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH-CH_2OC_2H_5 + Br^-$

The mechanisms of reactions (i) and (ii) are respectively : [AIPMT 2011]  
 (1\*)  $S_N1$  and  $S_N2$  (2)  $S_N1$  and  $S_N1$  (3)  $S_N2$  and  $S_N2$  (4)  $S_N2$  and  $S_N1$

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

$$(1) \text{ Propyne } \xrightarrow{NaNH_2} X \xrightarrow{n-C_4H_9Br} Y \xrightarrow[H_2SO_4]{H_2O, Hg^{2+}}$$




## PART - II : MISCELLANEOUS QUESTIONS

### Section (A) : ASSERTION/REASONING

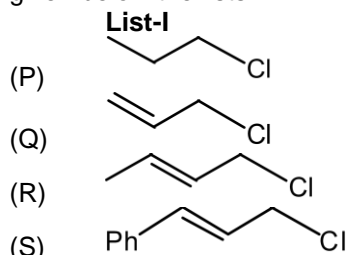
**DIRECTIONS :** Each question has 4 choices (1), (2), (3) and (4) out of which ONLY ONE is correct.

- (1) Both assertion and reason are correct, and the reason is the correct explanation for the assertion
- (2) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion
- (3) The assertion is incorrect, but the reason is correct
- (4) Both are assertion and reason are incorrect

- A-1. Assertion :** The major products formed by heating  $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_3$  with HI are  $\text{C}_6\text{H}_5\text{CH}_2\text{I}$  and  $\text{CH}_3\text{OH}$ .  
**Reason :** Benzyl cation is more stable than methyl cation. [AIIMS 2004]
- A-2. Assertion :** Ethyl chloride is more reactive than vinyl chloride towards nucleophilic substitution reaction.  
**Reason :** In vinyl chloride, the  $-\text{Cl}$  is bonded to  $\text{sp}^2$ -hybridized carbon of an alkene.
- A-3. Assertion :** Di-tert. butyl ether cannot be prepared by williamson's ether synthesis.  
**Reason :** Tert. butyl bromide on treatment with sodium tert. butoxide preferentially undergoes elimination to form isobutylene and tert. butyl alcohol.
- A-5. Assertion:** By-products are most frequently observed in  $\text{S}_{\text{N}}1$  reactions.  
**Reason:** Carbocation intermediates undergoes rearrangements.
- A-6. Assertion:** Ammonolysis of alkyl halides is not a suitable method for the preparation of pure primary amines.  
**Reason:** Ammonolysis of alkyl halides yield mixture of amines.
- A-7. Assertion:** A bridge head halide like norboryl bromide  is inert for  $\text{S}_{\text{N}}1$  reaction.  
**Reason :** Carbonium ion at bridgehead positions cannot be formed because planarity is prohibited
- A-8. Assertion :**  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$  reacts faster with Ethyl alcohol than  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$  by  $\text{S}_{\text{N}}1$  mechanism. [MG sir, Aug. 2014] Topic-RM(O)  
**Reason :** Carbocation of  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$  is less stable than  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$
- A-9. Assertion :** Presence of carbonyl group in an primary alkyl halide facilitates for  $\text{S}_{\text{N}}2$  reaction.  
**Reason :** Carbonyl group creates the electron deficiency at  $\alpha$ -carbon so that nucleophilic attack becomes easier. [MG sir, Aug. 2014] Topic-RM(O)
- A-0. Assertion :**  $\text{S}_{\text{N}}1$  reaction is basically a solvolysis reaction. [AIIMS 2010]  
**Reason :** Polar protic solvents help the substrate to ionise and by the way get involved in  $\text{S}_{\text{N}}1$  reaction.
- A-2. Assertion :**  $\text{S}_{\text{N}}2$  reaction of an optically active alkyl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation. [AIIMS 2013]  
**Reason:**  $\text{S}_{\text{N}}2$  reaction always proceed with inversion of configuration in alkyl halide.

### Section (B) : MATCH THE COLUMN

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



- List-II**
- (1) 1
- (2) 0.07
- (3) 7700
- (4) 91

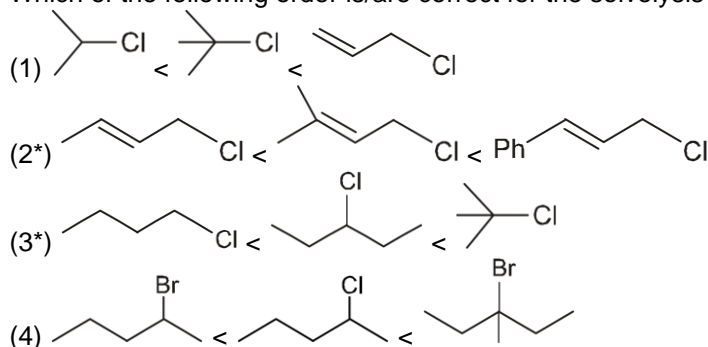
**Codes**

- (1\*) P-2 ; Q-1 ; R-4 ; S-3
- (3) P-1 ; Q-2 ; R-3 ; S-4

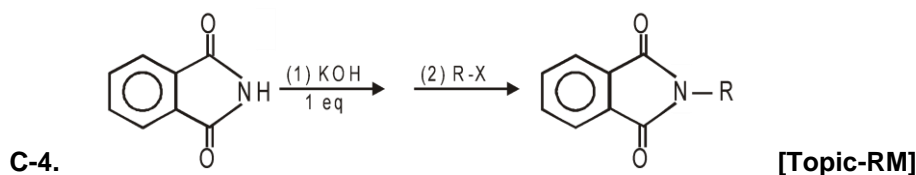
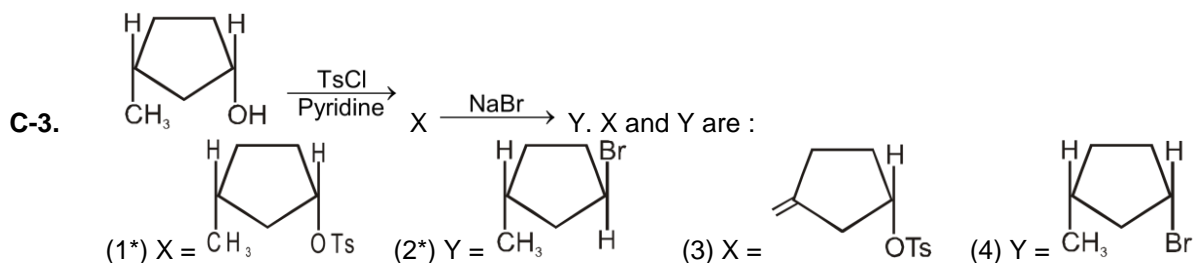
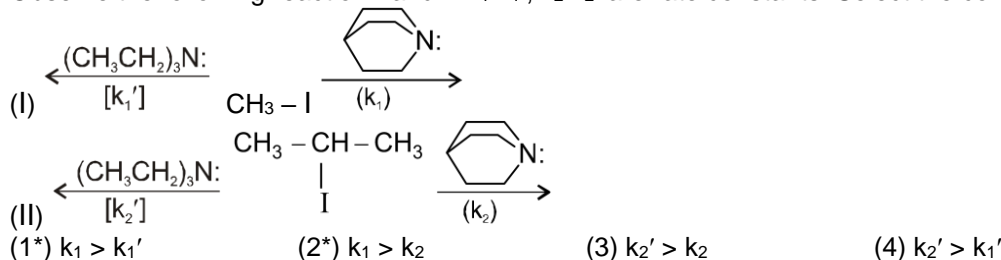
- (2) P-2 ; Q-1 ; R-3 ; S-4
- (4) P-1 ; Q-2 ; R-4 ; S-3

**Section (C) : ONE OR MORE THAN ONE OPTIONS CORRECT**

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



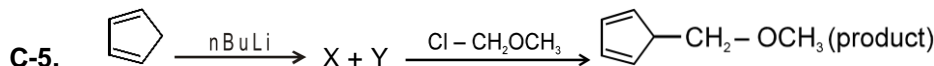
**C-2.** Observe the following reaction I and II  $k_1$   $k_1'$ ,  $k_2$   $k_2'$  are rate constants. Select the correct option(s).



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

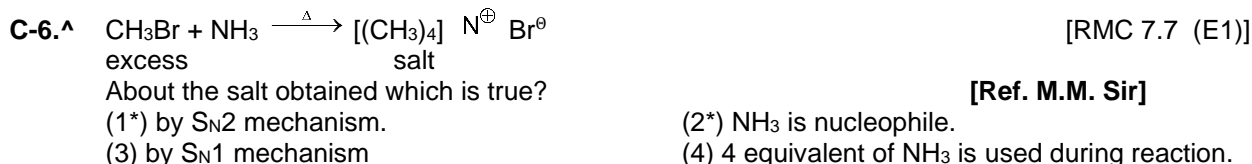


- (1)  $\text{CH}_3\text{—CH}_2\text{—Br} < \begin{array}{c} \text{CH}_3\text{—CH—CH}_3 \\ | \\ \text{Br} \\ | \\ \text{Ph—CH—CH}_3 \\ | \\ \text{Br} \end{array}$  (2)  $\text{Ph—Cl} > \text{CH}_3\text{—Cl}$
- (3\*)  $\text{Ph—CH}_2\text{—Br} > \begin{array}{c} \text{CH}_3\text{—CH—CH}_3 \\ | \\ \text{Br} \\ | \\ \text{Ph—CH—CH}_3 \\ | \\ \text{Br} \end{array}$  (4\*)  $\text{CH}_2=\text{CH—CH}_2\text{—Cl} > \text{CH}_3\text{—CH}_2\text{—CH}_2\text{—Cl}$



In the above reaction which of the following are correct.

- (1\*) step-1 is an acid-base reaction (2\*) step-2 is an  $\text{S}_{\text{N}}2$  reaction  
(3\*) X = n-Butane ; Y = aromatic compound (4) the nucleophile in 2<sup>nd</sup> reaction is  $:\text{Bu}^\ominus$

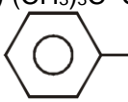
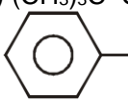
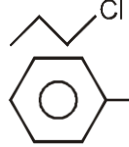
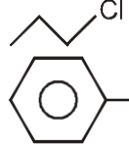


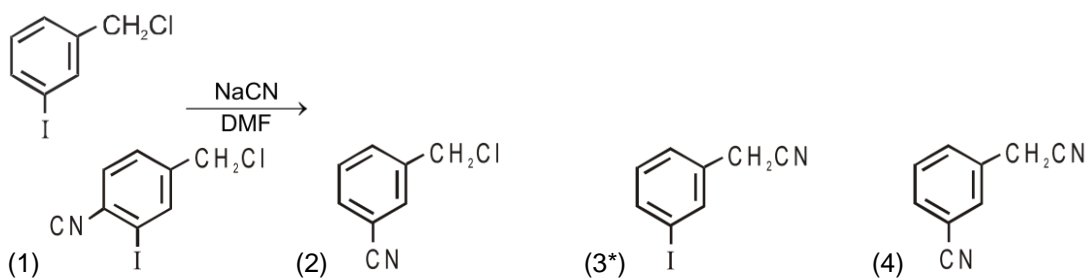
## Exercise-3

Marked Questions may have for Revision Questions.

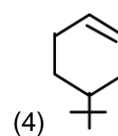
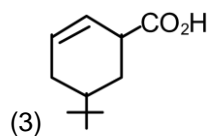
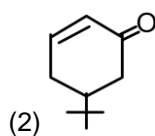
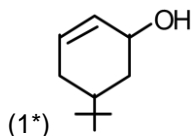
### PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

#### OFFLINE JEE-MAIN

- $\text{S}_{\text{N}}1$  reaction is feasible in : [AIEEE-2002, 3/225]  
 (1\*)  $(\text{CH}_3)_3\text{C—Cl} + \text{KOH} \longrightarrow$   
 +  $\text{KOH} \longrightarrow$   
 (3)  +  $\text{KOH} \longrightarrow$   
 (2)  +  $\text{KOH} \longrightarrow$   
 (4)  +  $\text{KOH} \longrightarrow$
- The reaction :  $(\text{CH}_3)_3\text{C—Br} \xrightarrow{\text{H}_2\text{O}} (\text{CH}_3)_3\text{C—OH}$  is an example of - [AIEEE-2002, 3/225]  
 (1) elimination reaction. (2\*) substitution reaction.  
 (3) free radical reaction. (4) rearrangement reaction.
- 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  $\text{NaOH}$  solution. The end solution in each tube was made acidic with dilute  $\text{HNO}_3$  and then some  $\text{AgNO}_3$  solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment ? [AIEEE-2003, 3/225]  
 (1\*) A was  $\text{C}_6\text{H}_5\text{I}$  (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  $\text{HNO}_3$  was unnecessary
- Tertiary alkyl halides are practically inert to substitution by  $\text{S}_{\text{N}}2$  mechanism because of : [AIEEE-2005, 3/225]  
 (1\*) steric hinderance (2) inductive effect (3) instability (4) insolubility
- Alkyl halides react with dialkyl copper reagents to give [AIEEE-2005, 3/225]  
 (1) alkenes (2) alkyl copper halides (3\*) alkanes (4) alkenyl halides
- The structure of the major product formed in the following reaction is : [AIEEE-2006, 3/165]



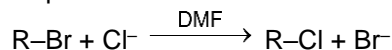
7. Which of the following is the correct order of decreasing  $S_N2$  reactivity ? [AIEEE-2007, 3/120]  
 (1)  $RCH_2X > R_3CX > R_2CHX$  (2\*)  $RCH_2X > R_2CHX > R_3CX$   
 (3)  $R_3CX > R_2CHX > RCH_2X$  (4)  $R_2CHX > R_3CX > RCH_2X$
8. The organic chloro compound, which shows complete stereochemical inversion during an  $S_N2$  reaction, is:  
 (1)  $(CH_3)_3CCl$  (2)  $(CH_3)_2CHCl$  (3\*)  $CH_3Cl$  (4)  $(C_2H_5)_2CHCl$
9. Which of the following on heating with aqueous KOH, produces acetaldehyde ? [AIEEE-2009, 4/144]  
 (1)  $CH_3CH_2Cl$  (2)  $CH_2ClCH_2Cl$  (3\*)  $CH_3CHCl_2$  (4)  $CH_3COCl$
10. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous  $ZnCl_2$ , is [AIEEE-2010, 4/144]  
 (1) 2-Butanol (2\*) 2-Methylpropan-2-ol (3) 2-Methylpropanol (4) 1-Butanol
11. Consider the following bromides : [AIEEE-2010, 4/144]  
  
 (A) (B) (C)  
 The correct order of  $S_N1$  reactivity is :  
 (1\*)  $B > C > A$  (2)  $B > A > C$  (3)  $C > B > A$  (4)  $A > B > C$
12. A solution of (–)-1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of  $SbCl_5$ , due to the formation of : [JEE(Main) 2013, 4/120]  
 (1) carbanion (2) carbene (3\*) carbocation (4) free radical
13. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism : [JEE(Main) 2013, 4/120]  
 (1) secondary alcohol by  $S_N1$  (2\*) tertiary alcohol by  $S_N1$   
 (3) secondary alcohol by  $S_N2$  (4) tertiary alcohol by  $S_N2$
14. In  $S_N2$  reactions, the correct order of reactivity for the following compounds :  $CH_3Cl$ ,  $CH_3CH_2Cl$ ,  $(CH_3)_2CHCl$  and  $(CH_3)_3CCl$  is : [JEE(Main) 2014, 4/120]  
 (1)  $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$   
 (2\*)  $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$   
 (3)  $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$   
 (4)  $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$
15. The synthesis of alkyl fluorides is best accomplished by : [JEE(Main) 2015, 4/120]  
 (1) Free radical fluorination (2) Sandmeyer's reaction  
 (3) Finkelstein reaction (4\*) Swarts reaction
16. The product of the reaction give below is : [JEE(Main) 2016, 4/120]



ONLINE JEE-MAIN

1. Allyl phenyl ether can be prepared by heating : [JEE(Main) 2014 Online (09-04-14), 4/120]  
 (1)  $\text{C}_6\text{H}_5\text{Br} + \text{CH}_2=\text{CH}-\text{CH}_2-\text{ONa}$  (2\*)  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Br} + \text{C}_6\text{H}_5\text{ONa}$   
 (3)  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{Br} + \text{CH}_3-\text{ONa}$  (4)  $\text{CH}_2=\text{CH}-\text{Br} + \text{C}_6\text{H}_5-\text{CH}_2-\text{ONa}$

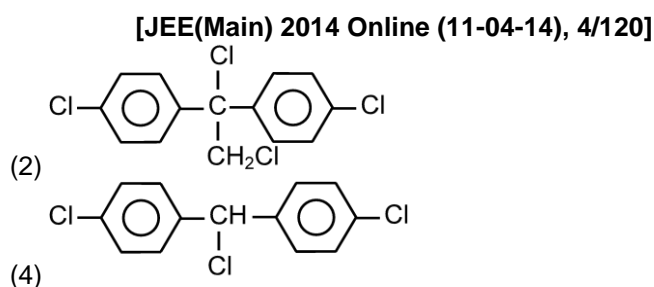
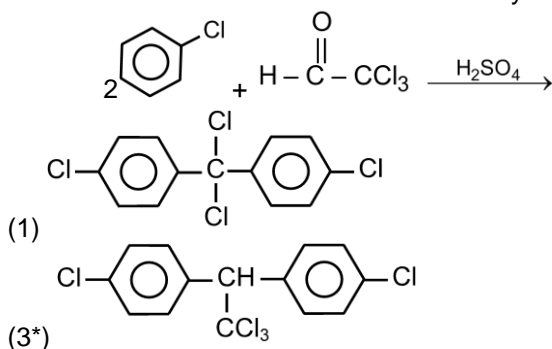
2. In a nucleophilic substitution reaction :



Which one of the following undergoes complete inversion of configuration ?

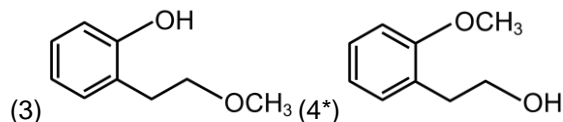
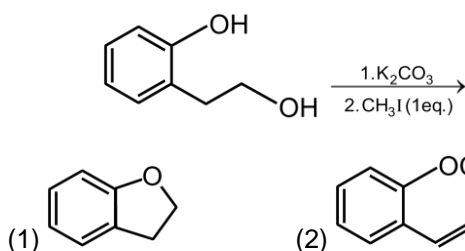
[JEE(Main) 2014 Online (09-04-14), 4/120]

3. Chlorobenzene reacts with trichloroacetaldehyde in the presence of  $\text{H}_2\text{SO}_4$ , the major product formed is :



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

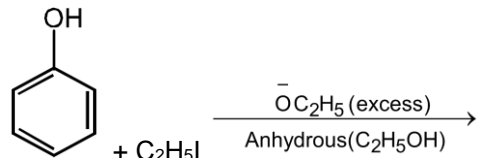
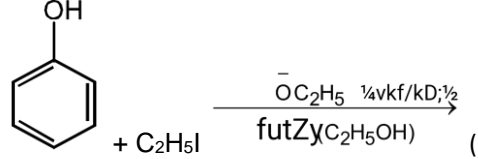
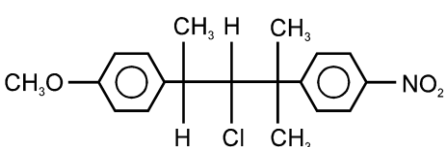

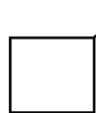
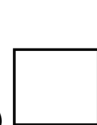

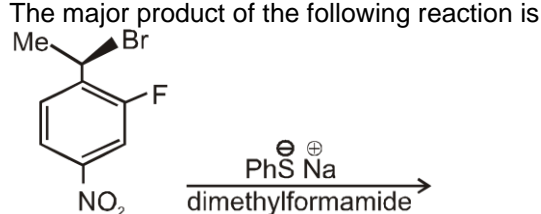
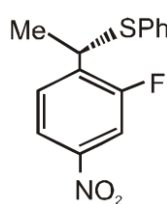
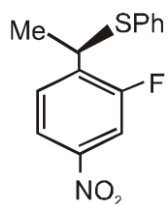
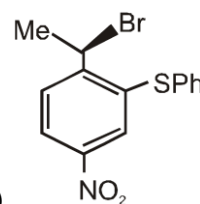
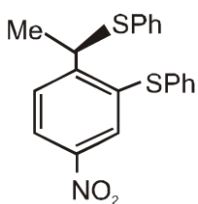
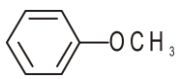
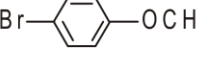
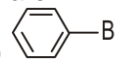
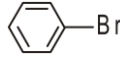
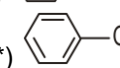
5. The major product of the following reaction is : [JEE(Main) 2017 Online (08-04-17), 4/120]

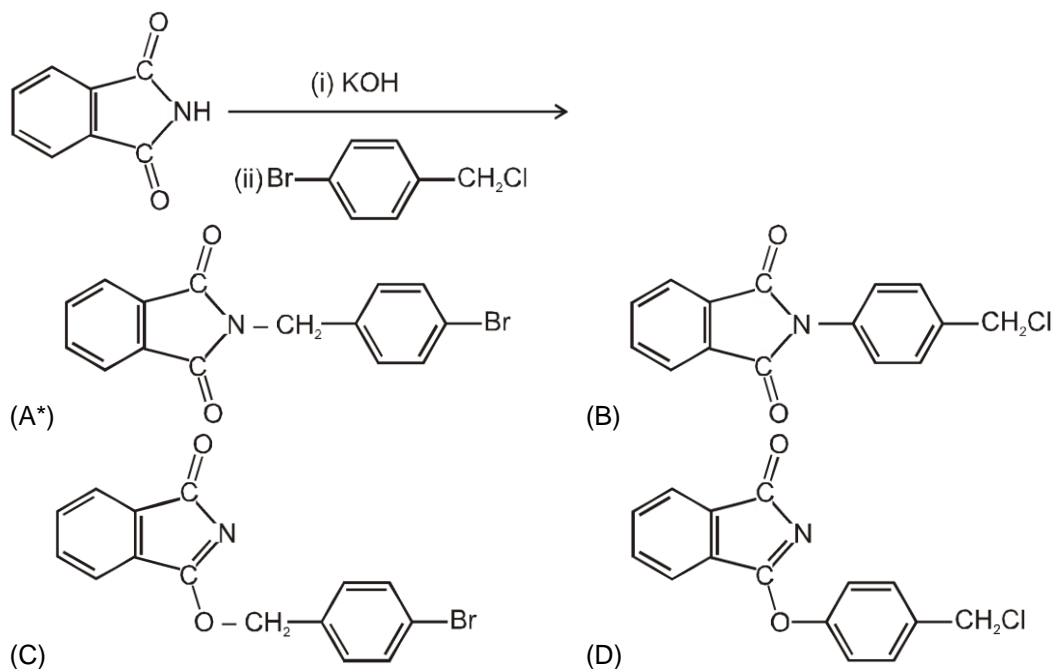


PART - II : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

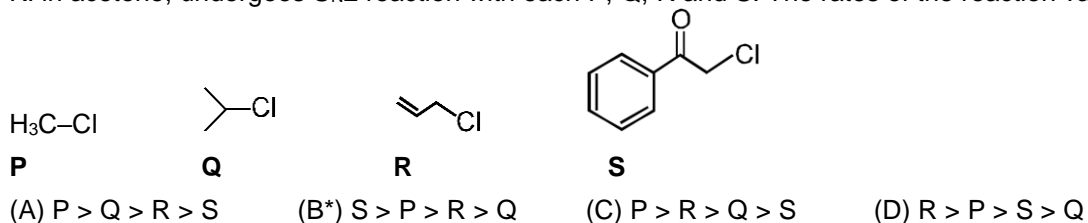
\* Marked questions may have more than one correct option.

1. An  $\text{S}_{\text{N}}2$  reaction at an asymmetric carbon of a compound always gives : [IIT-JEE-2001(S), 1/35]  
 (A) an enantiomer of the substrate (B) a product with opposite optical rotation  
 (C) a mixture of diastereomers (D\*) a single stereoisomer
2. The compound that will react most readily with  $\text{NaOH}$  to form methanol is : [IIT-JEE-2001(S), 1/35]  
 (A)  $(\text{CH}_3)_4\text{N}^+\text{I}^-$  (B)  $\text{CH}_3\text{OCH}_3$  (C\*)  $(\text{CH}_3)_3\text{S}^+\text{I}^-$  (D)  $(\text{CH}_3)_3\text{C}-\text{Cl}$

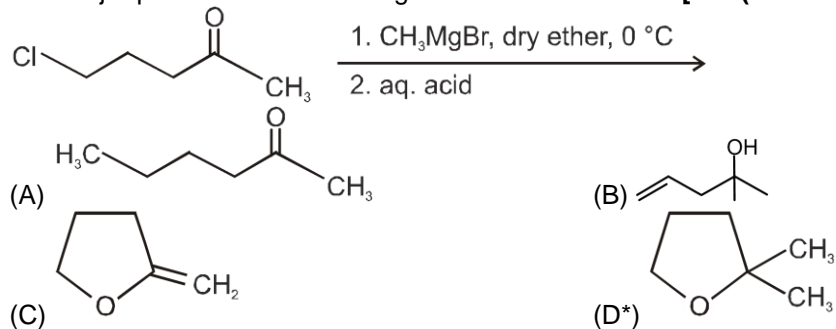
3.  product, major product is [JEE-2003(S), 3/84]
3.  (A) C<sub>6</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> (B\*) C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> (C) C<sub>6</sub>H<sub>5</sub>OC<sub>6</sub>H<sub>5</sub> (D) C<sub>6</sub>H<sub>5</sub>I [JEE-2003(S), 3/84]
4.  is reacted with aqueous acetone it gives following products. [JEE(S)2005, 3/84]  
 (A\*) K, L (B) K, M (C) L only (dsoy L) (D) M only (dsoy M)
5. 1-Bromo-3-chlorocyclobutane will react with two moles of Na in ether producing [JEE-2005(S), 3/84]  
 (A\*)  (B)  (C)  (D) 
6. The major product of the following reaction is [JEE-2008, 3/162]  
  
 (A\*)  (B)  (C)  (D) 
7. In the reaction  the products are : [JEE-2010, 3/163]  
 (A)  and H<sub>2</sub> (B)  and CH<sub>3</sub>Br  
 (C)  and CH<sub>3</sub>OH (D\*)  and CH<sub>3</sub>Br
8. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are : [JEE-2010, 3/163]  
 (A) BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>C≡CH (B) BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C≡CH  
 (C) BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>C≡CH (D\*) BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>C≡CH
9. The major product of the following reaction is : [JEE-2011, 3/160]



10. KI in acetone, undergoes S<sub>N</sub>2 reaction with each P, Q, R and S. The rates of the reaction vary as



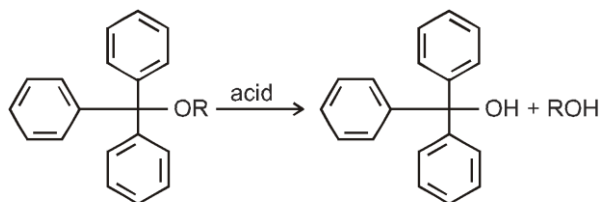
11. The major product in the following reaction is : [JEE(Advanced)-2014, 3/120]



12. The acidic hydrolysis of ether (X) shown below is fastest when:

[JEE(Advanced)-2014, 3/120]

[Figure]

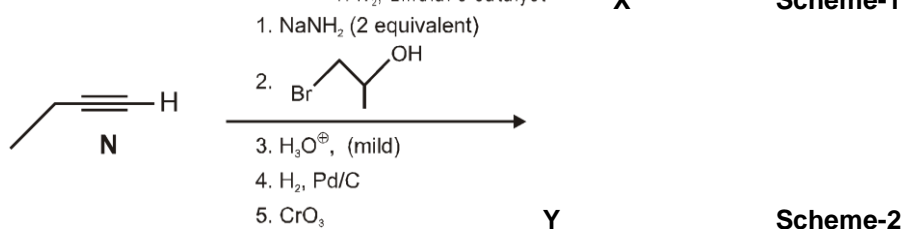
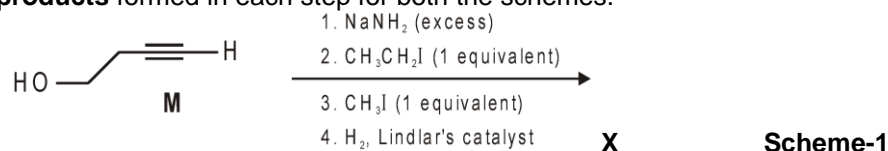


[X]

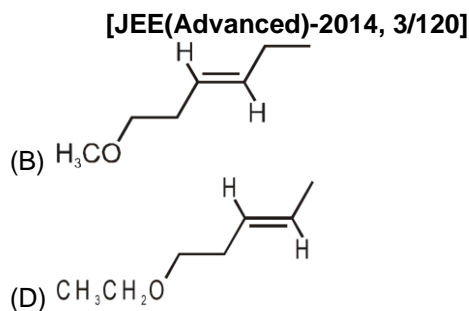
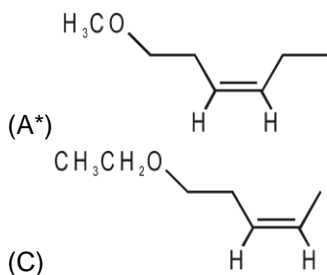
- (A) one phenyl group is replaced by a methyl group.  
 (B) one phenyl group is replaced by a para-methoxyphenyl group.  
 (C\*) two phenyl groups are replaced by two para-methoxyphenyl groups.  
 (D) no structural change is made to X.

Paragraph for questions 13 and 14

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

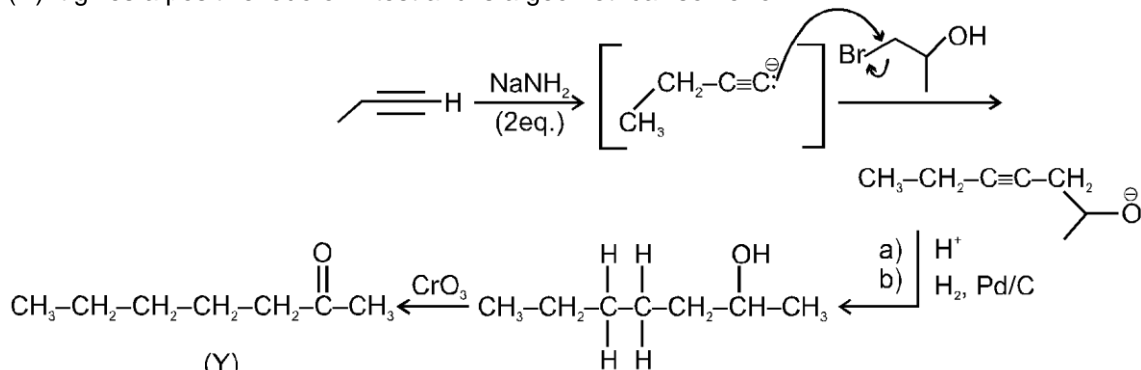


13. The product **X** is :



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

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



Sol.

(Y) can give iodoform test (but not Tollen's test and it is a functional isomer of (X))

## Additional Problems for Self Practice (APSP)

### PART - I : PRACTICE TEST PAPER

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

Max. Marks : 120

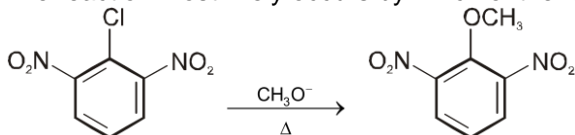
Max. Time : 1 Hr.

#### Important Instructions

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

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

[Aro 4.1, (M2)]

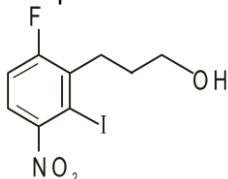


- (1\*) Addition-elimination  
(3) Elimination-addition

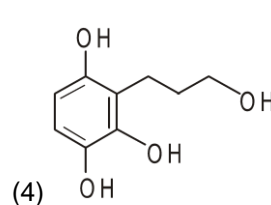
- (2) addition only  
(4) Neither of these

2. The product 'P' is

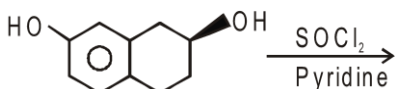
[Ref. VPM madam] [Aro 4.1 (T1)]



- (1)
- (2)
- (3\*)



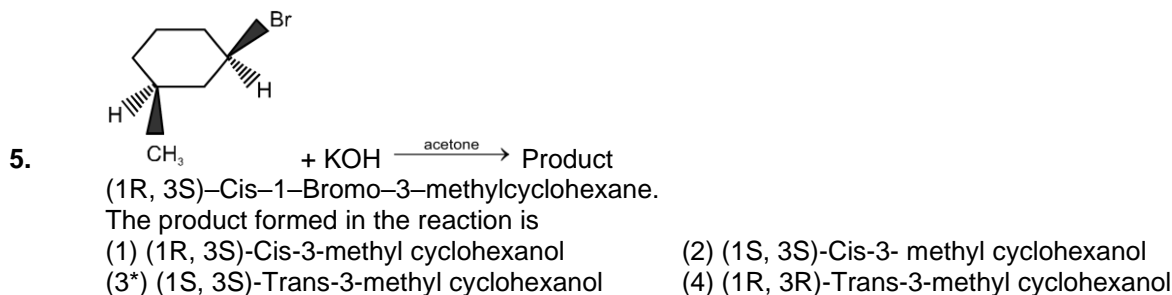
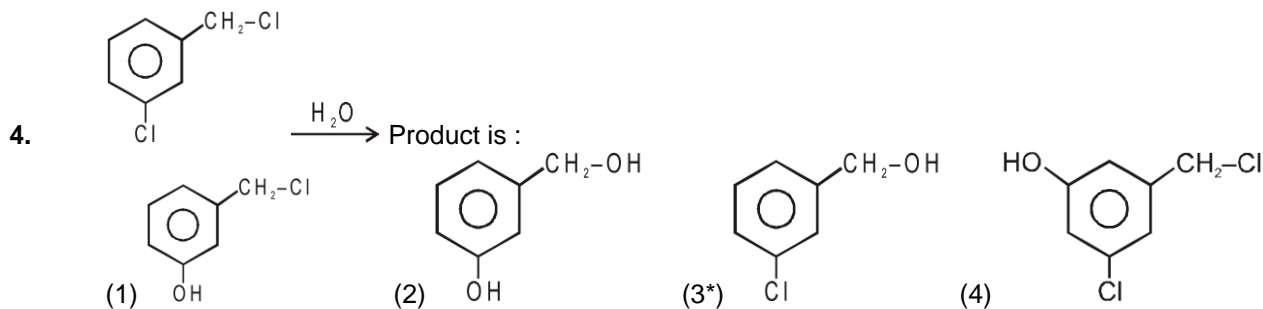
- 3.



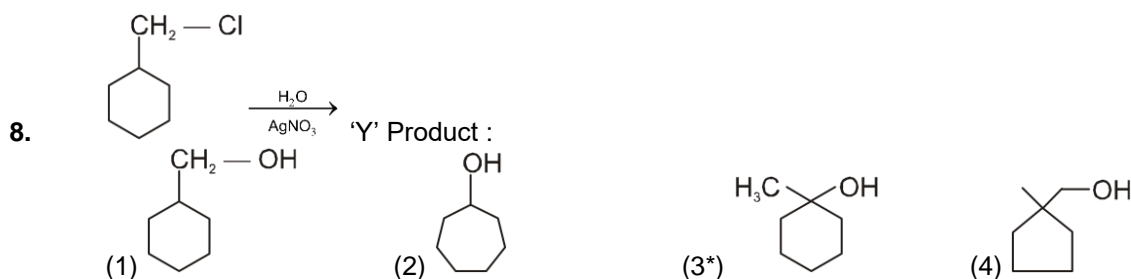
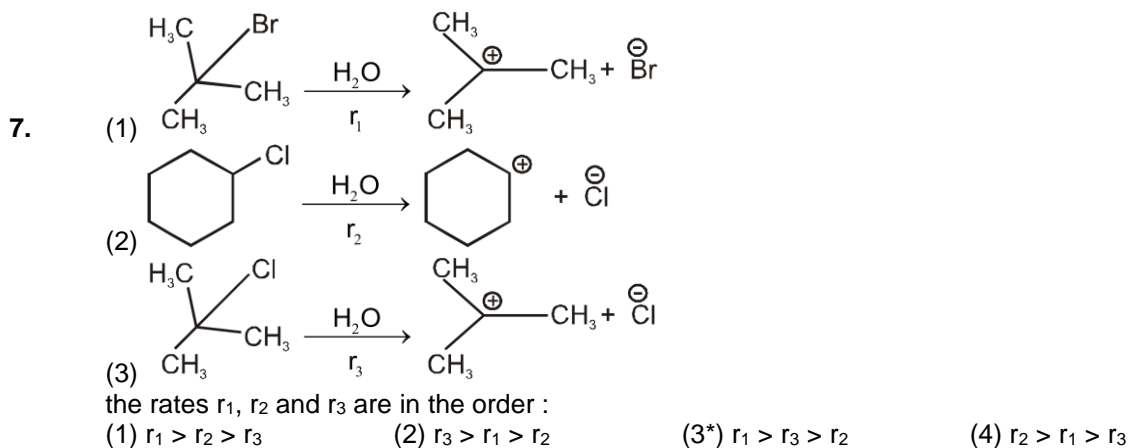
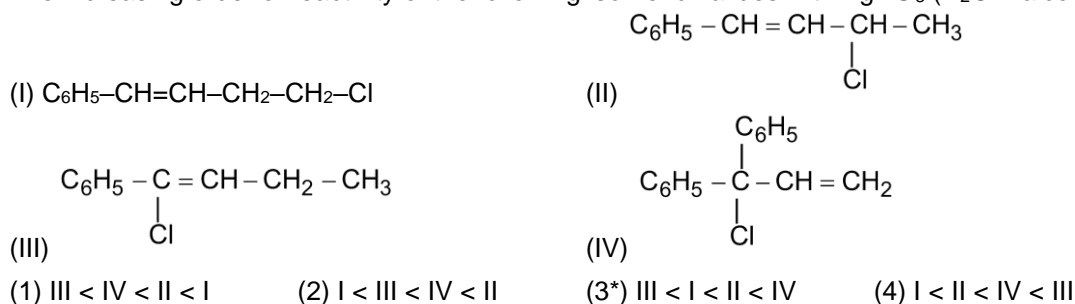
Product is :

- (1)
- (3)

- (2\*)
- (4)



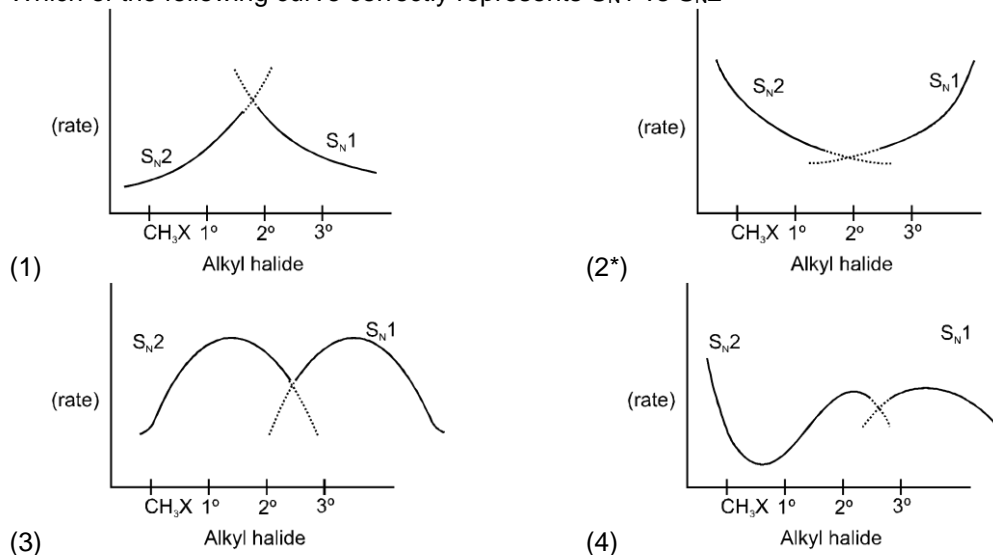
6. The increasing order of reactivity of the following isomeric halides with  $\text{AgNO}_3$  ( $\text{H}_2\text{O}$  + alcohol) is :



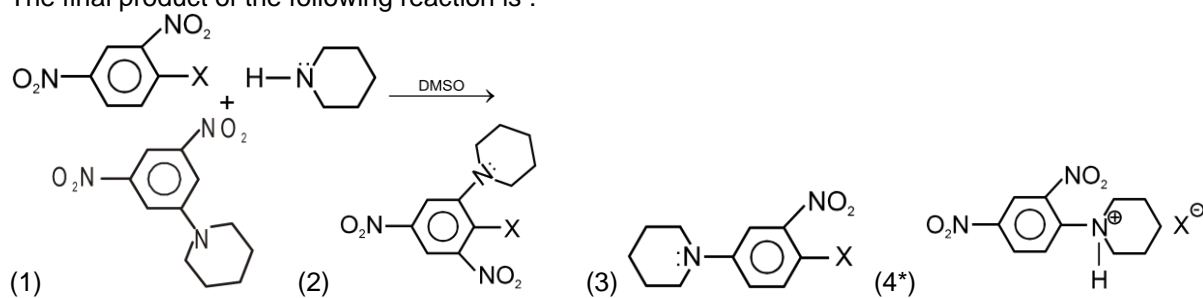


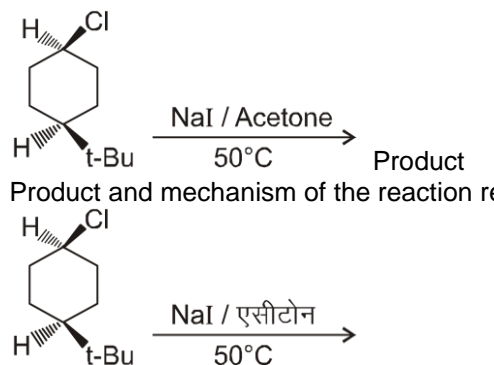

9.  $\text{CH}_3\text{--CH}_2\text{--CH--CH}_3$   
 $\text{OH}$   
 $\xrightarrow{\text{HCl/ZnCl}_2} [\text{X}]$   
 Identify product X and the mechanism of the reaction.  
 (1)  $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--Cl}$  &  $\text{S}_{\text{N}}1$   
 $\text{CH}_3\text{--CH--CH}_2\text{--CH}_3$   
 $\text{Cl}$   
 (3\*) &  $\text{S}_{\text{N}}1$   
 (2)  $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--Cl}$  &  $\text{S}_{\text{N}}2$   
 $\text{CH}_3\text{--CH--CH}_2\text{--CH}_3$   
 $\text{Cl}$   
 (4) &  $\text{S}_{\text{N}}2$

10. Which of the following curve correctly represents  $\text{S}_{\text{N}}1$  vs  $\text{S}_{\text{N}}2$

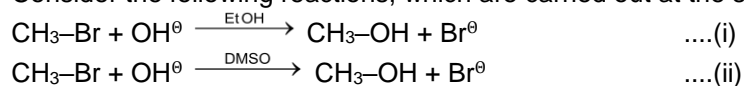


11. The final product of the following reaction is :



12.   
 Product and mechanism of the reaction respectively is :
- 

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

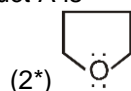


Which of the following statement is correct about these reactions.

- (1) Both the reactions take place at the same rate
- (2) The first reaction takes place faster than second reaction.
- (3\*) The second reaction takes place faster than first reaction.
- (4) Both the reactions take place by  $S_N1$  mechanism

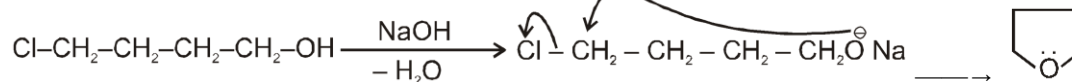
14.  $\text{Cl}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{NaOH(aq.)}} \text{A}$ , the product A is

- (1)  $\text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$   
 $\text{Cl}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_2\text{OH}$
- (3)



- (4)  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{ONa}$

Sol.

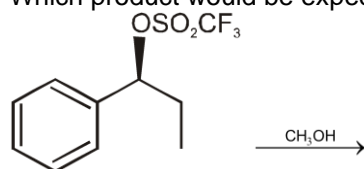


15. Which of the following reactions is the best choice for preparing methyl cyclohexyl ether ?

- (1\*) +  $\text{CH}_3\text{I} \longrightarrow$
- (3) +  $\text{CH}_3\text{I} \longrightarrow$

- (2) +  $\text{CH}_3\text{ONa} \longrightarrow$
- (4) +  $\text{CH}_3\text{OH} \longrightarrow$

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



- (1\*)
- (3)

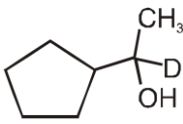
- (2)
- (4)

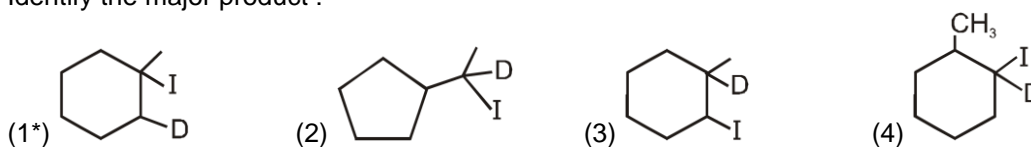
17. Select correct statement

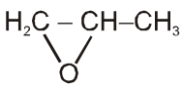
- (1) Solvolysis of  $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2-\text{Cl}$  in ethanol is faster than primary alkyl chloride ( $25^\circ\text{C}$ )
- (2)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{OH}$  when reacts with  $\text{HBr}$  give a mixture of 1-bromo-2-butene and 3-bromo 1-butene.
- (3) When solution of 3-buten-2-ol in aqueous sulphuric acid is allowed to stand for one week, it was found to contain both 3-buten-2-ol and 2-buten-1-ol
- (4\*) All of these

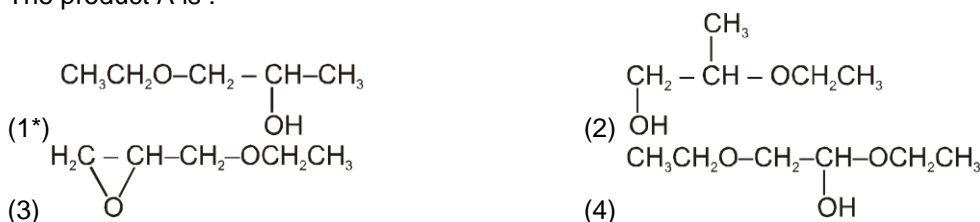
18.  $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_2-\text{C}_6\text{H}_5$  can be prepared from Williamson's synthesis, using :

- (1)  $(\text{CH}_3)_3\text{C}-\text{Cl}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{ONa}$
- (2\*)  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  and  $(\text{CH}_3)_3\text{C}-\text{ONa}$
- (3)  $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_2-\text{Cl}$  and  $\text{C}_6\text{H}_5\text{ONa}$
- (4) All of these

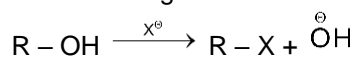
19.   $\xrightarrow{\text{HI}}$  Product,  
Identify the major product :



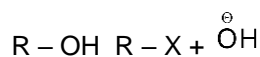
20.   $\xrightarrow[\text{EtOH}]{\text{EtO}^-\text{K}^+}$  A  
The product A is :



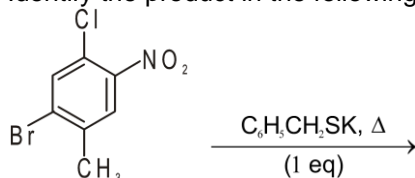
21. Which of the following statement is not true ?  
(1) Nucleophiles possess unshared pairs of electron which are utilized in forming bonds with electrophilic substrate.  
(2) The cyanide ion is an ambident nucleophile and causes nucleophilic substitution of alkyl halide by either of its carbon atom or nitrogen atom.  
(3) The nitrite ion is an ambident nucleophile and causes nucleophilic substitution of alkyl halide by either of its oxygen atom or nitrogen atom.  
(4\*) Strength of nucleophile generally decreases on going down a group in the periodic table.
22. Which of the following statements are correct for the given alcohol ?

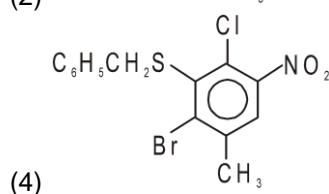
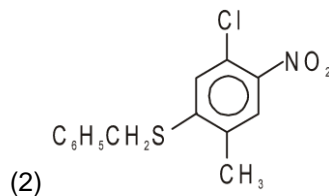
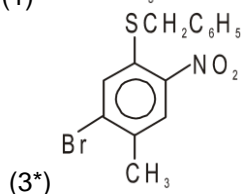
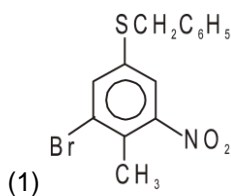


- (1\*) Reaction will not take place because  $\text{OH}^\ominus$  is poor leaving group ;  $\text{X}^\ominus$  is weak base and  $\text{OH}^\ominus$  is strong base  
(2) Reaction will not take place because  $\text{OH}^\ominus$  is poor leaving group ;  $\text{X}^\ominus$  is strong base and  $\text{OH}^\ominus$  is weak base.  
(3) Reaction will not take place because  $\text{OH}^\ominus$  is strong leaving group ;  $\text{X}^\ominus$  is strong base and  $\text{OH}^\ominus$  is weak base.  
(4) Reaction will not take place because  $\text{OH}^\ominus$  is good leaving group ;  $\text{X}^\ominus$  is weak base and  $\text{OH}^\ominus$  is strong base.

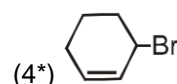
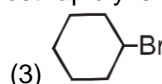
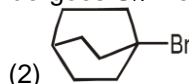
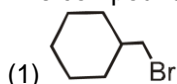


23. Identify the product in the following reaction ?





24. The compound which undergoes  $S_N1$  reaction most rapidly is [NSEC-2003]



25. Which of the following compound is least reactive in the nucleophilic aromatic substitution reaction with NaOH ?

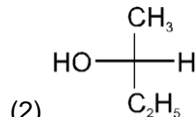
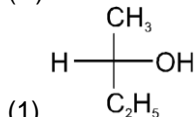
(1) p-nitrofluorobenzene

(2) p-nitrochlorobenzene

(3) p-nitrobromobenzene

(4\*) p-nitroiodobenzene

26. (R)-2-Bromobutane is allowed to react with aqueous KOH. Identify the product formed in the reaction ?



(3\*) Equimolar amount of (1) & (2)

(4) None of these

27. The reagent which can react with 1-chlorobutane to give substitution reaction is [NSEC-2003]

(1)  $AlCl_3$

(2) KOH-MeOH

(3\*) NaCN

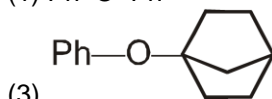
(4) Mg-ether

28. Which of the following ether can be prepared by williamson's synthesis method. ?

(1) Ph-O-Ph

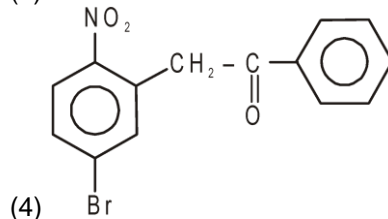
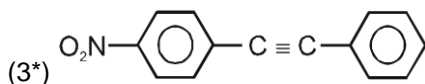
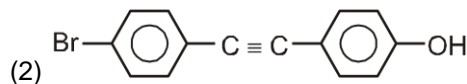
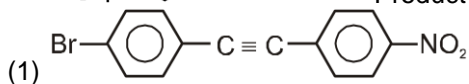
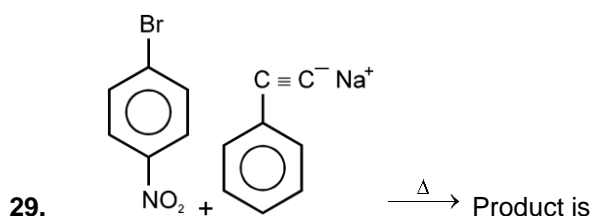
(2)  $(CH_3)_3C-O-C(CH_3)_3$

[By MG Sir Dec. 2013]



(4\*) Ph-O-CH<sub>2</sub>-Ph

[Topic-RM]



30. Which of the following alkyl chlorides will undergo  $S_N2$  reaction most readily ?

(1\*) 1-chloro-4-methylpentane

(2) 2-chloro-4-methylpentane

(3) 2-chloro-2-methylpentane

(4) 3-chloro-2-methylpentane

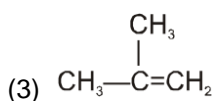
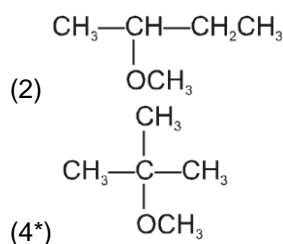
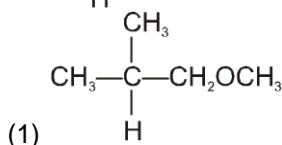
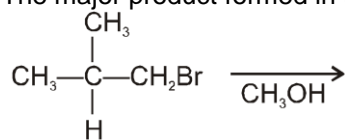
**Practice Test (IIT-JEE (Main Pattern))**  
**OBJECTIVE RESPONSE SHEET (ORS)**

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

**PART - II : PRACTICE QUESTIONS**

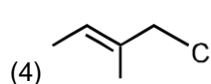
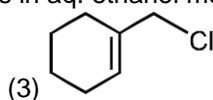
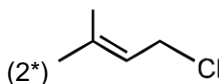
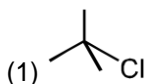
1. The major product formed in the following reaction is :

[AIIMS 2005]

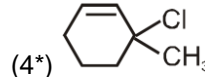
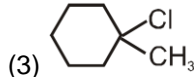
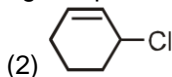
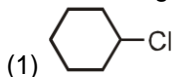


2. The compound that undergoes solvolysis in aq. ethanol most easily is

[NSEC-2015]



3. Which among the following compounds will be most reactive for  $\text{S}_{\text{N}}1$  reaction ?



4. Among the following, the one which reacts most readily with ethanol is

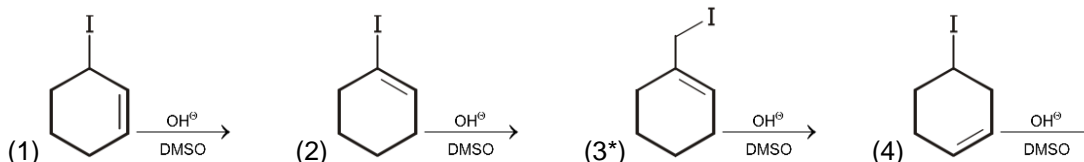
(1) p-nitro benzyl bromide

(2) p-chloro benzyl bromide

(3\*) p-methoxy benzyl bromide

(4) p-methyl benzyl bromide

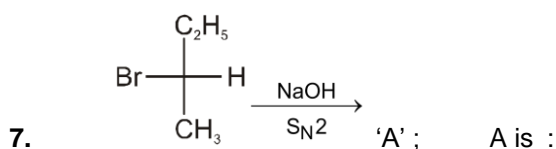
5. Which of the following reaction is most readily completed ?



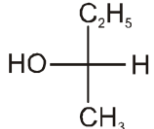
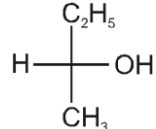
6. Which of the following is most reactive towards nucleophilic substitution reaction by both  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanism ?

[Aug. 2014]

- (1)  $\text{H}_2\text{C}=\text{CH}-\text{Cl}$  (2)  $\text{C}_6\text{H}_5\text{Cl}$  (3)  $\text{CH}_3\text{CH}=\text{CHCl}$  (4\*)  $\text{ClCH}_2-\text{CH}=\text{CH}_2$



[RPMT 2011]

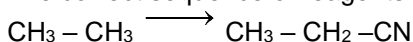
- (1)  (2\*)   
(3) 1 : 1 mixture of both (1) and (2) (4)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$

8. Arrange in order of decrease in rates of  $\text{S}_{\text{N}}2$  reaction.

[NSEC-2005]

- I.  II.  $\text{CH}_3\text{Cl}$  III.  IV.   
(1)  $\text{I} > \text{II} > \text{III} > \text{IV}$  (2)  $\text{VI} > \text{II} > \text{I} > \text{III}$  (3\*)  $\text{II} > \text{I} > \text{III} > \text{IV}$  (4)  $\text{III} > \text{II} > \text{IV} > \text{I}$ .

9. The correct sequence of reagents for following reaction is :

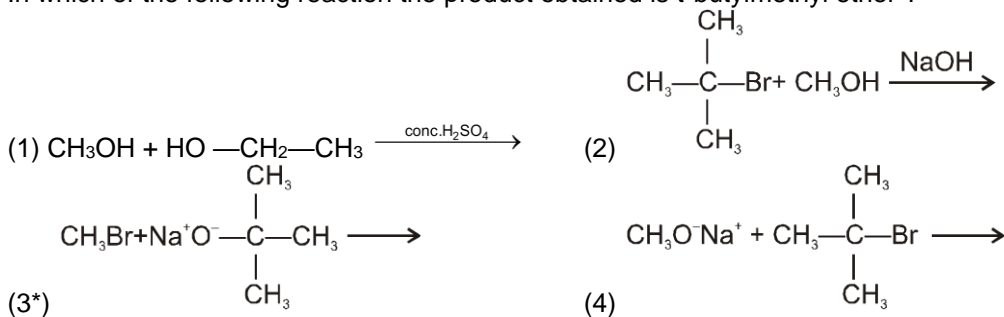


- (1) (i)  $\text{HCl}$  (ii)  $\text{KCN}$  (2)  $\text{KCN}$   
(3\*) (i)  $\text{Cl}_2/h\nu$  (monochlorination) (ii)  $\text{KCN}$  (4) (i)  $\text{NaCl}$  (ii)  $\text{KCN}$

10. Isopropyl cyanide can be obtained by the reaction between :

- (1)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$  and  $\text{AgCN}$  (2\*)  $\text{CH}_3\text{CHBrCH}_3$  and  $\text{KCN}$   
(3)  $(\text{CH}_3)_2\text{CHI}$  and  $\text{AgCN}$  (4)  $(\text{CH}_3)_2\text{CHCl}$  and  $\text{HCN}$

11. In which of the following reaction the product obtained is t-butylmethyl ether ?



12. The major product in the following reaction is :

[NSEC-2008]



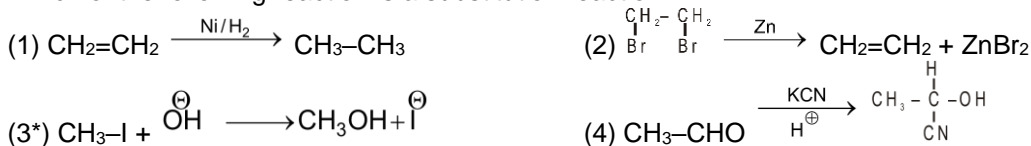


13. Power alcohol is the mixture of :  
 (1) Absolute alcohol + Methyl alcohol (2\*) Absolute alcohol + Petrol  
 (3) Rectified alcohol + Petrol (4) Denatured alcohol + Petrol

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



15. Which of the following reaction is a substitution reaction ?



16. In  $\text{S}_\text{N}2$  reaction if we doubled the concentration of reactant and nucleophile the rate of  $\text{S}_\text{N}2$  reaction increases by :  
 (1) 2 times (2\*) 4 times (3) 8 times (4) No change

17. Reaction of methyl bromide with an alcoholic solution of silver cyanide predominantly gives :  
 (1) Acetonitrile (2\*) Methyl isocyanide (3) Methyl isocyanate (4) Methyl isothiocyanate

18. Which of the following give fastest reaction with Lucas reagent ? **[Topic-RM (O)]**



19. Lucas reagent reacts fastest with : **[RPMT 2007]**  
 (1) butanol-1 (2) butanol-2  
 (3\*) 2-methyl-propanol-2 (4) 2-methyl-propanol-1

20. Find the product for :  $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}_6\text{H}_5 + \text{HI}$  (excess) **[AIIMS 2011]**  
 (1\*)  $\text{HO}-\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_6\text{H}_5\text{CH}_2-\text{I}$ ,  $\text{CH}_3\text{CH}_2-\text{I}$  (2)  $\text{C}_6\text{H}_5\text{CH}_2-\text{OH}$ ,  $\text{CH}_3\text{CH}_2-\text{I}$ ,  $\text{I}-\text{CH}_2\text{CH}_2-\text{OH}$   
 (3)  $\text{I}-\text{CH}_2\text{CH}_2-\text{I}$ ,  $\text{C}_6\text{H}_5\text{CH}_2-\text{I}$ ,  $\text{CH}_3\text{CH}_2-\text{OH}$  (4)  $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$ ,  $\text{C}_6\text{H}_5\text{CH}_2-\text{I}$ ,  $\text{CH}_3\text{CH}_2-\text{OH}$