

1. ALKYL AND ARYL HALIDES

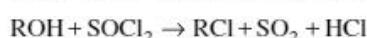
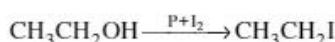
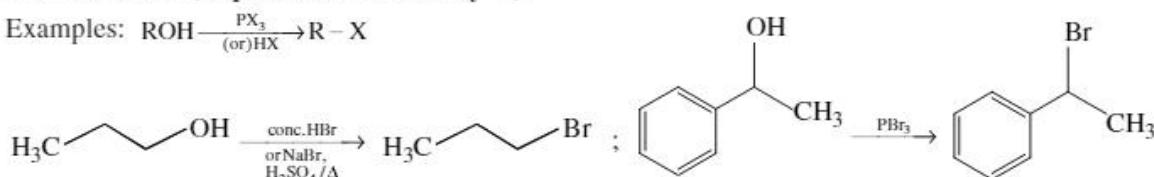
SYNOPSIS

I. CLASSIFICATION, ISOMERISM, PHYSICAL & CHEMICAL PROPERTIES STRUCTURE AND NOMENCLATURE

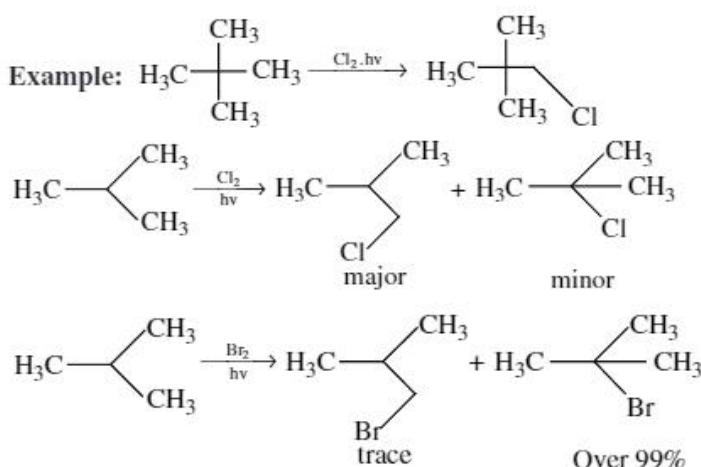
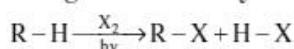
Preparation:

1. From alcohols (Replacement of OH by X)

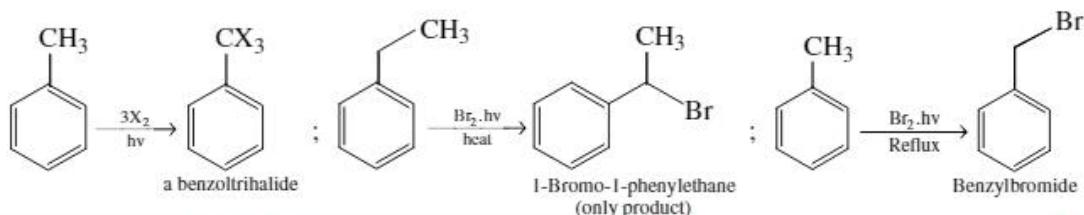
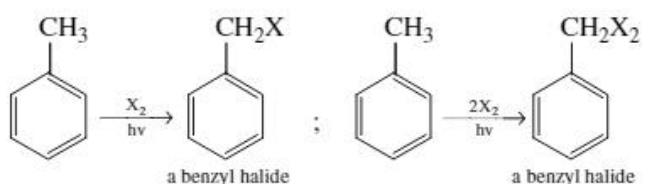
Examples: $\text{ROH} \xrightarrow[\text{(or) HX}]{\text{P}X_3} \text{R-X}$



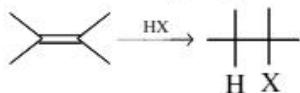
2. Halogenation of Hydrocarbons:



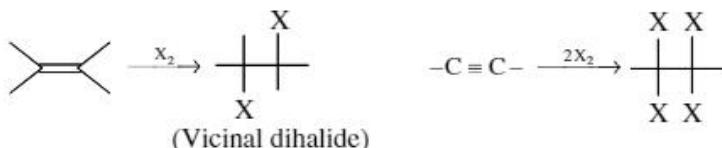
3. Side Chain Halogenation of Alkylbenzenes:



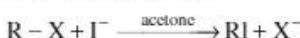
4. Addition of Hydrogen Halides to Alkenes (Discussed under alkenes)



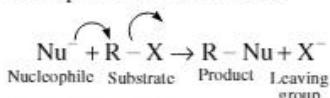
5. Additions of Halogens to Alkenes and Alkynes



6. Halide Exchange



Basic, electron rich reagents are called nucleophilic reagents. The typical reaction of alkyl halides is nucleophilic substitution.

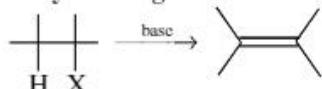


Physical Properties:

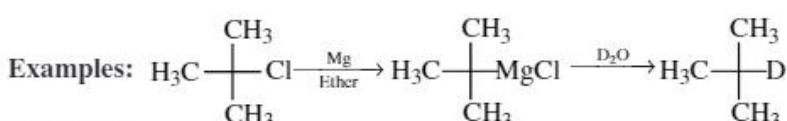
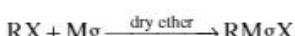
Because of greater molecular weight, haloalkane have considerably higher boiling points than alkanes of the same number of carbons. For a given alkyl group, the boiling point increases with increasing atomic weight of the halogen, So that fluoride has the lowest boiling, and iodide has highest boiling point. In spite of polarity alkyl halides are insoluble in water, probably because of their inability to form hydrogen bonds. They are soluble in typical organic solvents.

Reactions of alkyl Halides

1. Dehydrohalogenation



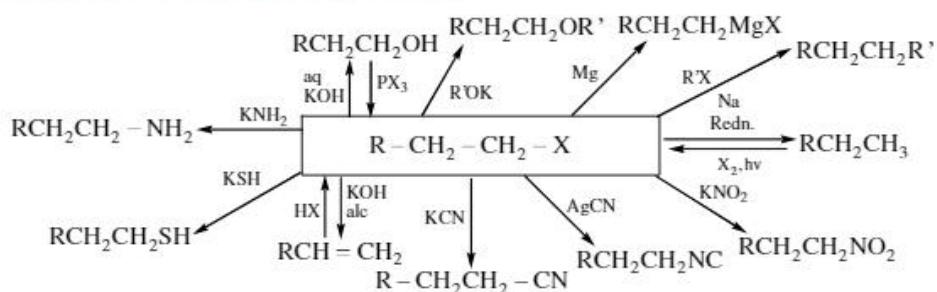
2. Preparation of Grignard reagent



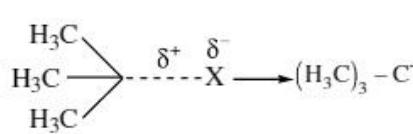
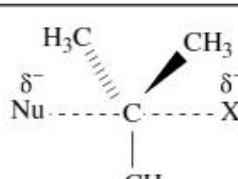
3. Reduction



Characteristic Reaction Chart for Alkyl Halides:

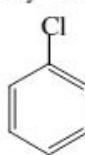


II. S_N1 and S_N2 MECHANISMS & ARYL HALIDES PREPARATION METHODSNucleophilic Displacement By S_N1 and S_N2 Mechanisms

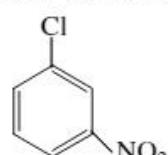
	S_N1	S_N2
Steps	Two i) $R:X \xrightarrow{\text{slow}} R^+ + X^-$ carbonium ion ii) $R^+ + Nu^- \rightarrow RNu$ or $R^+ + Nu \rightarrow RNu^+$	One $R:X + Nu^- \rightarrow RNu + X^-$ or $R:X + Nu \rightarrow RNu^+ + X^-$
Rate	$= K[RX]$ (1st order)	$= K[RX][:NU]$ (2nd order)
TS of slow step		
Stereochemistry Molecularity Reactivity Structure of R Determining factor Nature of X solvent effect on rate	Inversion and reaceimization Unimolecular $3^0 > 2^0 > 1^0 > CH_3$ Stability of R^+ $RI > RBr > RCl > RF$ Rate increases in polar solvent	Inversion (backside attack) Biomolecular $CH_3 > 1^0 > 2^0 > 3^0$ Steric hindrance in R group $RI > RBr > RCl > RF$ With Nu^- there is a large rate increase in polar aprotic solvents rate depends on nucleophilicity $I^- > Br^- > Cl^- ; RS^- > RO^-$
Effect of nucleophile Catalysis	Lewis acid Eg : $Ag^+, AlCl_3, ZnCl_2$	None
Competitive reaction	Elimination rearrangement (E_1)	Elimination (E_2)

ARYL HALIDES

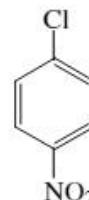
Aryl halides are the compounds that halogen atom already directly attached to the benzene ring. They have general formula ArX .



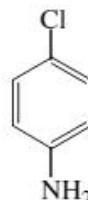
Chlorobenzene



1-Chloro-3-nitrobenzene



1-Chloro-4-nitrobenzene

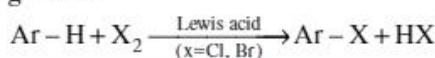


4-chloraniline

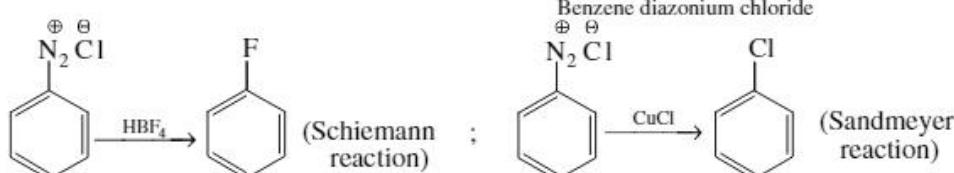
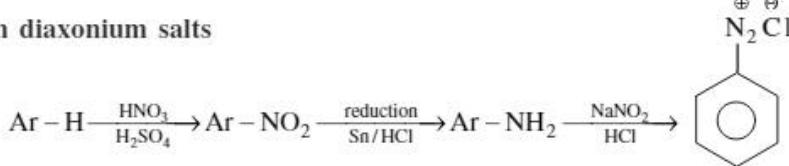
Any halogen compound that contain benzene ring is not classified as aryl halide. Eg. halide. e.g. Benzyl chloride is not an aryl halide, but is a substituted alkly hadie.

Preparation methods of Aryl Halides

Halogenation



From diaxonium salts



III. REACTIONS OF ARYL HALIDES (ADDITION, ELIMINATION & MISLINOS REACTION)

Properties of Aryl halides, Reactivity

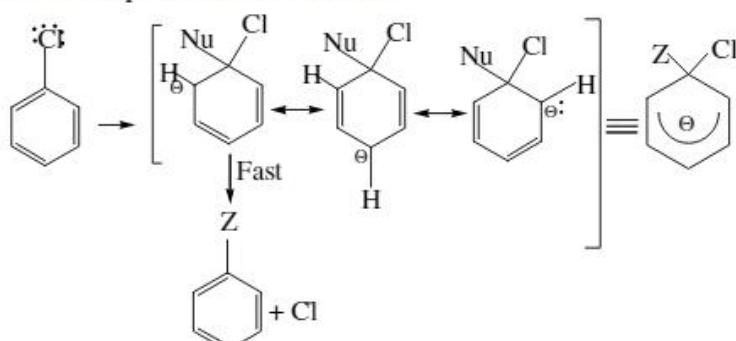
Unlike alkyl halides, aryl halides are less reactive towards Nucleophilic substitution reaction, this can be attributed to their electron release via resonance.

Chlorobenzene molecule give a double character to the carbon-chlorine bond. Now because of this the carbon-chlorine bond has more strength and hence aryl halides are more stable towards Nucleophilic substitution reactions.

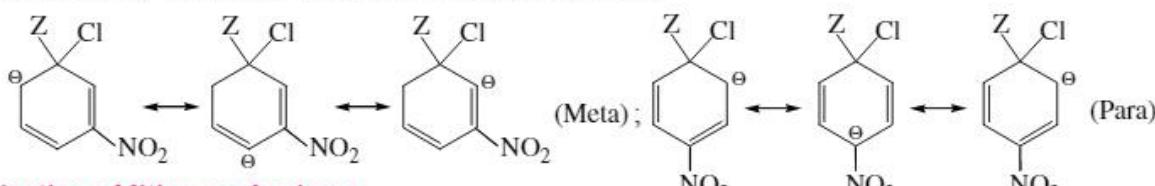
Nucleophilic Substitution reactions:

Aryl halides undergo Nucleophilic substitution reactions when a strong Electron withdrawing group is present on the benzene ring. Electron withdrawing groups activate the benzene ring towards nucleophilic substitution in aryl halides whereas Electron donating groups deactivate the ring.

Mechanism : Bimolecular displacement mechanism

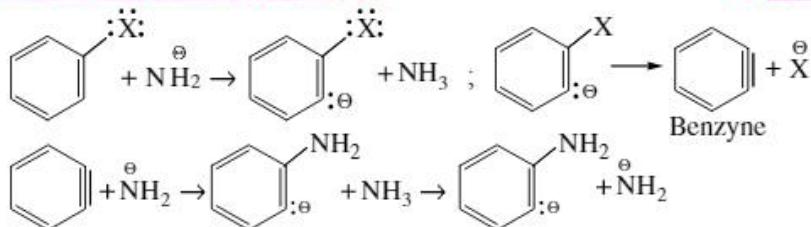


Any factor that stabilizes the carbanion will increase the rate of Nucleophilic substitution reaction by dispersing the charge present on resonating structures. An electron withdrawing group present at meta position does not activate the ring as much as it does from ortho and para position. This can be known by looking at following resonance structures.

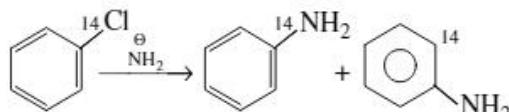


Ellinination-addition mechanism :

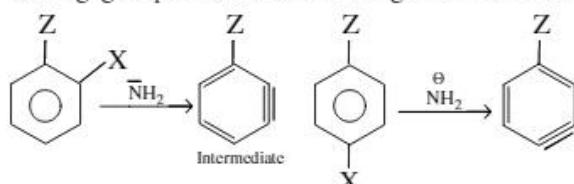
In the absence of an electron withdrawing group, nucleophilic substitution takes place in presence of very strong bases, but the mechanism is entirely different from what we have seen in bimolecular nucleophilic substitution reactions. These reactions proceed by a mechanism called benzyne mechanism.



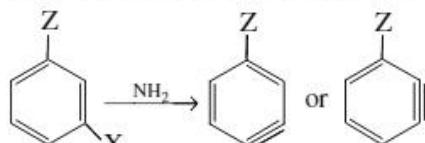
Benzyne is a symmetrical intermediate and can be attacked by nucleophile at both the positions.



Isotopic labeling confirmed that there is an equal chance of abstraction from both carbons. An aryl halide which does not contain alpha hydrogen with respect to halogen does not undergo this reaction. In the reaction involving Benzyne intermediates, two factors affect the position of incoming group, the first one is direction of aryne formation. When there are groups ortho or para to the leaving group, then the following intermediates should be formed.



When a meta group is present, aryne can form in two ways, in such cases



More acidic hydrogen is removed, i.e., an electron attracting 'Z' favours removal of ortho hydrogen while an electron donating 'Z' favours removal of para hydrogen.

LECTURE SHEET

EXERCISE-I

(Classification, Isomerism, Physical & Chemical Properties)

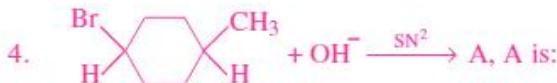
LEVEL-I (MAIN)

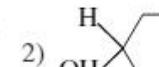
Straight Objective Type Questions

- On heating glycerol with excess amount to HI, the product formed is
 - Allyl iodide
 - Isopropyl iodide
 - Propylene
 - 1,2,3-tri-iodopropane
- The yield of alkyl bromide obtained as a result of heating the dry silver salt of carboxylic acid with bromine in CCl_4 is
 - $1^0 > 3^0 > 2^0$ bromides
 - $1^0 > 2^0 > 3^0$ bromides
 - $3^0 > 2^0 > 1^0$ bromides
 - $3^0 > 1^0 > 2^0$ bromides

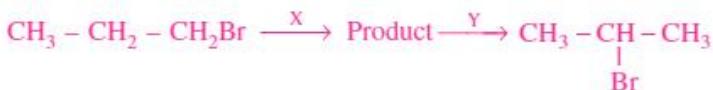
3. The major product formed in the reaction is $\text{Et}-\ddot{\text{S}}-\text{CH}_2-\text{CH}(\text{Cl})\text{CH}_3 \xrightarrow{\text{aq.KOH}}$

- 1) $\text{Et}-\ddot{\text{S}}-\text{CH}_2-\text{CH}(\text{OH})\text{CH}_3$ 2) $\text{Et}-\ddot{\text{S}}-\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$
 3) $\text{Et}-\ddot{\text{S}}-\text{CH}=\text{CH}-\text{CH}_3$ 4) $\text{Et}-\ddot{\text{S}}-\text{CH}_2-\text{CH}=\text{CH}_2$



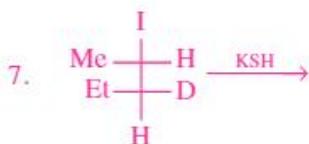
- 1)  2)  3) Both 4) None

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



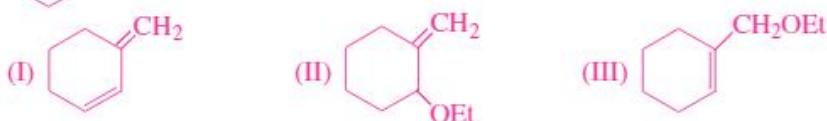
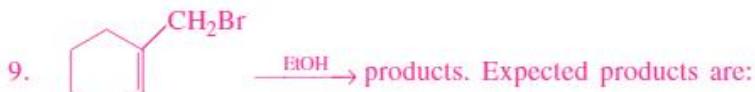
- 1) X = dilute aqueous NaOH, 20°C; Y = HBr/acetic acid, 20°C
 2) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid 20°C
 3) X = dilute aqueous NaOH, 20°C; Y = $\text{Br}_2/\text{CHCl}_3$, 0°C
 4) X = concentrated alcoholic NaOH, 80°C; Y = $\text{Br}_2/\text{CHCl}_3$, 0°C

6. Which of the following will not give ppt with aqueous AgNO_3 :



8. Which of the alkyl halides will undergo $\text{S}_{\text{N}}^{\text{I}}$ reaction at a fastest rate?

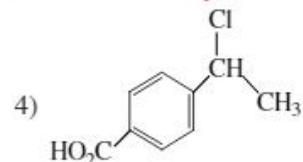
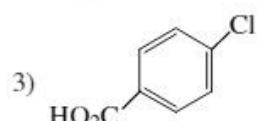
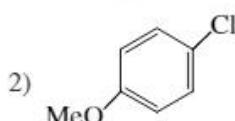
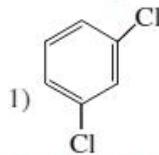
- 1) $\text{Cl}-\text{CH}_2-\text{CN}$ 2) $\text{Cl}-\text{CH}_2-\text{NO}_2$ 3) $\text{Cl}-\text{CH}_2-\text{OMe}$ 4) $\text{Cl}-\text{CH}_2-\text{CH}_3$



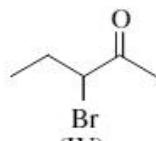
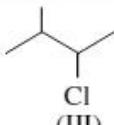
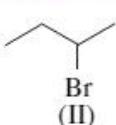
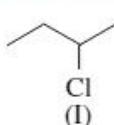
Select correct alternates

- 1) I, II & III 2) I, III 3) II, III 4) I, II

10. The halogen compound most likely to undergo nucleophilic substitution is in which compound



11. Arrange these compounds in order of increasing S_N^2 reaction rate:



1) III < I < II < IV

2) III < II < I < IV

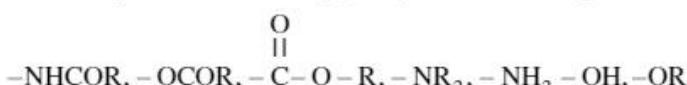
3) IV < III < I < II

4) III < IV < I < II

Numerical Value Type Questions

12. Bromination can take place at $\xrightarrow[NBS/h\nu]{CCl_4}$

13. How many of the following groups are activating towards electrophilic aromatic substitution?



LEVEL-II (ADVANCED)

Straight Objective Type Questions

1. The reaction

Proceeds by the mechanism

a) S_N^1 b) S_N^2 c) S_N^i d) S_E^2

2. To form alkane isonitrile, alkyl halide is reacted with:

a) KCN b) AgCN c) HCN d) NH_4CN

3. Which of the following reagents is the best for preparation of alkyl chloride from an alcohol in pure form

a) PCl_3 b) $SOCl_2$ c) PCl_5 d) Chlorine & Red P

4. In which of the following reactions, the product is 1-chlorobutane?

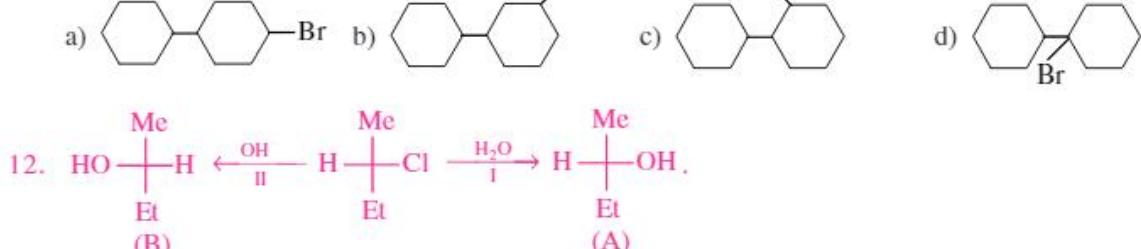
a) 1-Butene + HCl b) 2-Butene + HCl
c) 1-Butene + HCl, ROOR d) None of the above

5. Groove's method is used for preparation of alkyl halides from alcohols using HX and $ZnCl_2$. The order of reactivity is

a) $HCl > HBr > HI$ b) $HI > HBr > HCl$ c) $HCl > HI > HBr$ d) $HI > HCl > HBr$

6. In which of the following reaction, alkyl chloride is not formed
 a) ROH + PCl₃ b) ROH + NaCl c) ROH + SOCl₂ d) Ethane + SO₂Cl₂
7. C₂H₅Cl + X → C₂H₅OH + KCl. 'X' in the above reaction is
 a) Aqueous KOH b) Moist Ag₂O c) Alcoholic KOH d) H₂O
8. Chloroethane on reaction with 'X' to give diethyl ether. 'X' is
 a) NaOH b) H₂SO₄ c) C₂H₅ONa d) CH₃ONa
9. Alkyl halides reacts with alcoholic KCN to give
 a) alkyl cyanides b) Alkyl isocyanides c) Alkane d) Alkene
10. The alkyl halide which possess highest dipole moment is
 a) CH₃F b) CH₃Cl c) CH₃Br d) CH₃I

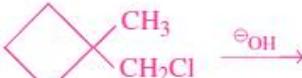
11. Major product for the reaction  is:



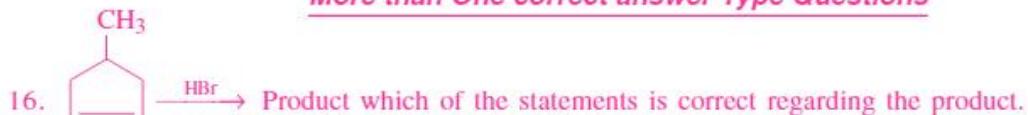
- Steps I and II are
 a) both S_N¹ b) both S_N² c) I S_N¹, II S_N² d) I S_N², II S_N¹

13. The reaction of SOCl₂ on alkanols to form alkyl chlorides gives good yields because
 a) Alkyl chlorides are immiscible with SOCl₂
 b) The other products of the reaction are gaseous and escape out
 c) Alcohol and SOCl₂ are soluble in water
 d) The reaction does not occurs via intermediate formation of an alkyl chloro sulphite

14. The products of reaction of alcoholic AgNO₂ with ethyl bromide are
 a) Ethane b) Ethyl nitrite
 c) Nitroethane d) Ethyl alcohol

15. Which are possible products in following. 



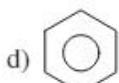
More than One correct answer Type Questions

- a) Product is 1-Bromo-3-methyl cyclopentane
- b) Product contains two chiral centres
- c) Total number of stereoisomers possible is four
- d) The reaction is an electrophilic addition

17. Which of the following statements is right regarding cis and trans-1,4-dibromo cyclohexane

- a) They are diastereoisomers
- b) Both are optically inactive
- c) Trans-compound is more stable than cis compound
- d) Cis-compound is more stable than trans-compound

18. Which of the following is/are polar aprotic solvents

- | | |
|---|--|
| a) CH_3COCH_3 (Acetone) | b) CH_3SOCH_3 (DMSO) |
| c) $\text{HCON}(\text{CH}_3)_2$ (DMF) | d)  |

19. Which of the following reactions depict the nucleophilic substitution of $\text{C}_2\text{H}_5\text{Br}$:

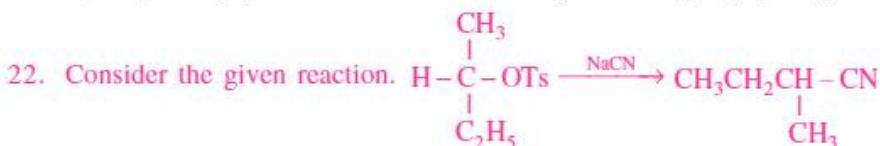
- | | |
|---|--|
| a) $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{SNa} \rightarrow \text{C}_2\text{H}_5\text{SC}_2\text{H}_5 + \text{NaBr}$ | b) $\text{C}_2\text{H}_5\text{Br} \xrightarrow{\text{Na} + \text{C}_2\text{H}_5\text{OH}} \text{C}_2\text{H}_6 + \text{HBr}$ |
| c) $\text{C}_2\text{H}_5\text{Br} + \text{AgCN} \rightarrow \text{C}_2\text{H}_5\text{NC} + \text{AgBr}$ | d) $\text{C}_2\text{H}_5\text{Br} + \text{KOH} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{KBr}$ |

20. For an $\text{S}_{\text{N}}2$ reaction, which of the following statements are true:

- a) The rate of reaction is independent of the concentration of the nucleophile
- b) The nucleophile attacks the C-atom on the side of the molecule opposite to the group being displaced
- c) The reaction proceeds with simultaneous bond formation and rupture
- d) None of these

21. Consider the following statements.

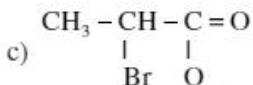
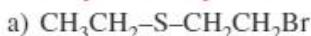
- a) $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--I}$ will react more readily than $(\text{CH}_3)_2\text{CHI}$ for $\text{S}_{\text{N}}2$ reactions.
- b) $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--Cl}$ will react more readily than $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--Br}$ for $\text{S}_{\text{N}}2$ 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) $\text{CH}_3\text{--O--C}_6\text{H}_5\text{--Br}$ 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



Which of following statements are correct for above reaction?

- a) Product formation takes place due to the formation of carbocation
- b) The reaction is $\text{S}_{\text{N}}2$
- c) The reaction is $\text{S}_{\text{N}}1$
- d) Inverted configuration of product is observed

23. Identify the compounds that will undergo NGP reaction



24. In which of following reaction only inverted product will obtained.



25. Rate of S_{N}^2 depends on

a) Conc of Nucleophile

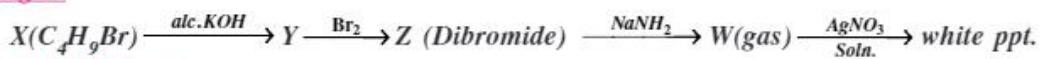
b) Conc of substrate

c) Nature of leaving group

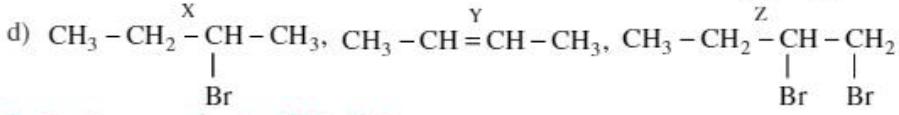
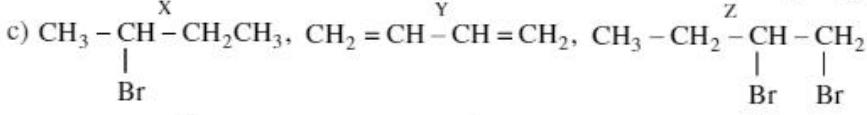
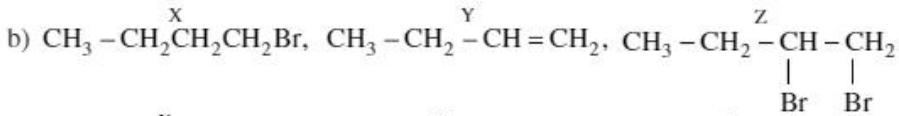
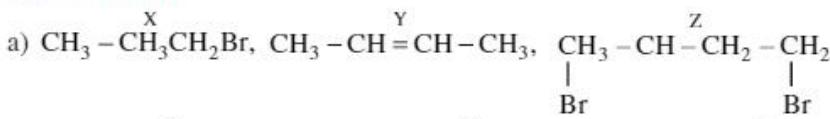
d) Nature of solvent

Linked Comprehension Type Questions

Passage :



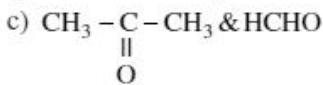
26. X, Y and Z are



27. Reductive ozonolysis of Y yield

a) 2 moles of CH_3CHO

b) $\text{CH}_3\text{CH}_2\text{CHO}$ & HCHO



28. Which of the following statement(s) is/are correct?

a) Y and W are chain isomers

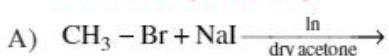
b) Y and W are functional isomers

c) W can be converted into Y with Lindlar catalyst

d) W can be converted into Y with Ni/Pt

Matrix Matching Type Questions

29. Column-I (Reaction)

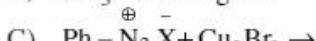


Column-II (Properties)

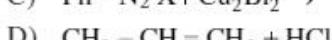
p) Markonikov's addition



q) Sandmayer's reaction



r) Finkelstein reaction



s) Swarts reactions

t) Substitution reaction

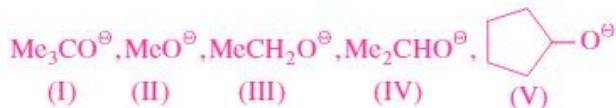
EXERCISE-II

(S_N¹ and S_N² mechanisms & aryl halides preparation methods)

LEVEL-I (MAIN)

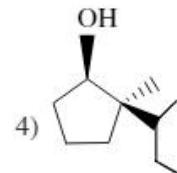
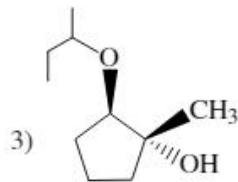
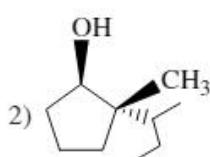
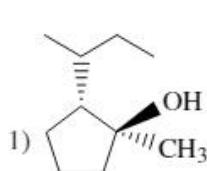
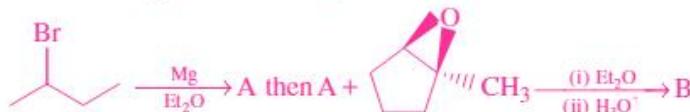
Straight Objective Type Questions

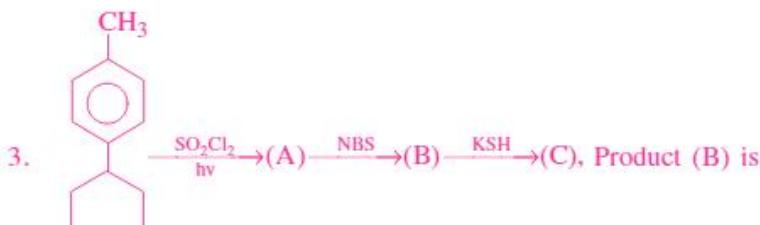
1. The correct order of nucleophile in decreasing order of S_N² reactivity is

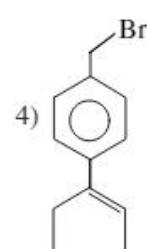
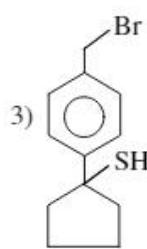
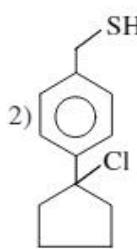
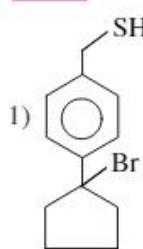


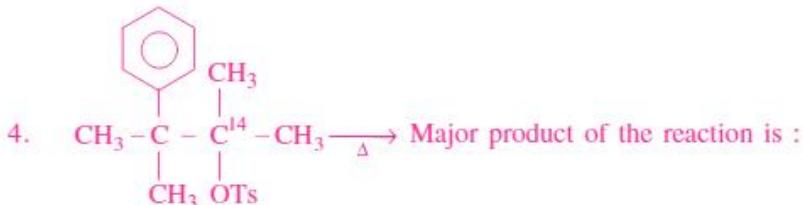
1) I > II > III > IV > V 2) II > III > IV > V > I 3) II > III > V > IV > I 4) I > IV > V > III > II

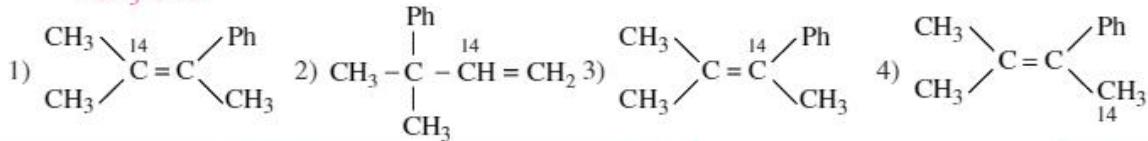
2. What is the product of the given reaction?



3. 



4. 



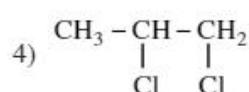
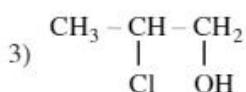
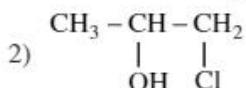
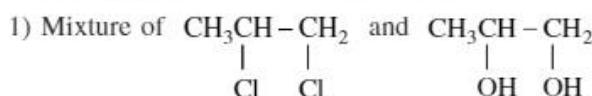
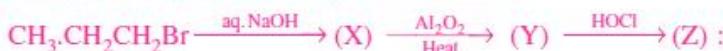
5. In chlorobenzene, the $-Cl$ group:

- 1) Activates the benzene ring more via resonance effect than deactivating it via inductive effect
- 2) Deactivates the benzene ring more via inductive effect than activating it via resonance effect
- 3) Activates the benzene ring via resonance effect and deactivates it via inductive effect. Both these effects are more evenly matched
- 4) None of these

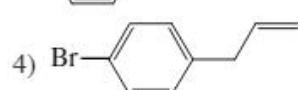
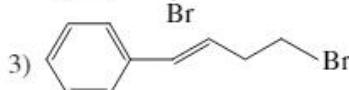
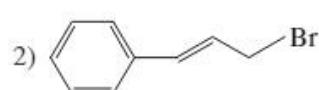
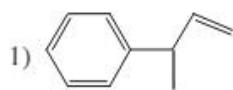
6. Reactivity order of halides for dehydrohalogenation is

- | | |
|--------------------------------------|--------------------------------------|
| 1) $R - F > R - Cl > R - Br > R - I$ | 2) $R - I > R - Br > R - Cl > R - F$ |
| 3) $R - I > R - Cl > R - Br > R - F$ | 4) $R - F > R - I > R - Br > R - Cl$ |

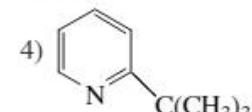
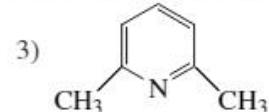
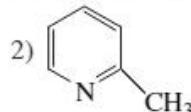
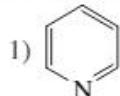
7. Identify 'Z' in the following reaction series,



8. product. Which of the following is the structure of the product?



9. Which of the following react with CH_3I , at a faster rate under S_N2 conditions?

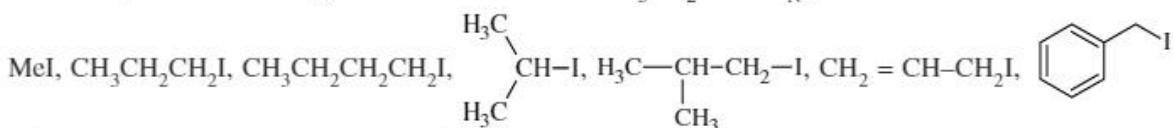


Numerical Value Type Questions

10. $CH_3-C(\text{Br})_2-\text{CH}_3 \xrightarrow{x \text{NaNH}_2} \xrightarrow{y \text{CH}_3I} CH_3-(\text{C}\equiv\text{C})_2-\text{CH}_3 . x$, and y moles consumed value of

$$x + y =$$

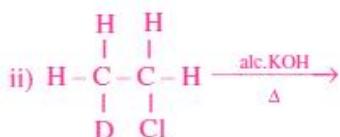
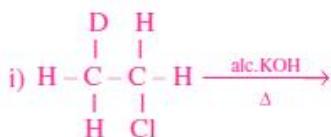
11. How many of the following are less reactive than CH_3CH_2I in a S_N2 reaction?



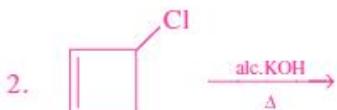
LEVEL-II (ADVANCED)

Straight Objective Type Questions

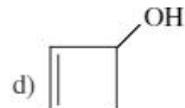
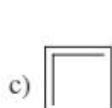
1. Organic product of which of the following reactions will have deuterium in it?



- a) only (i) b) only (ii) c) both (i) & (ii) d) none

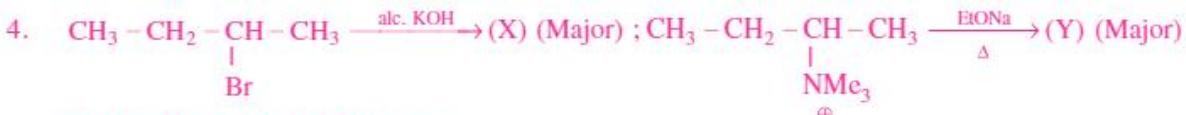


Final product of above reaction is isolated as



3. Correct order of yield of Hofmann alkene in following reaction will be $\text{CH}_3\text{CH}_2\overset{\underset{\text{X}}{|}}{\text{CH}}\text{CH}_3$. X may be F, Cl, Br or I

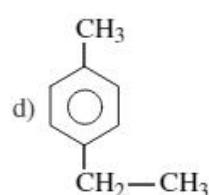
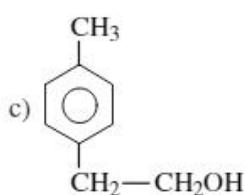
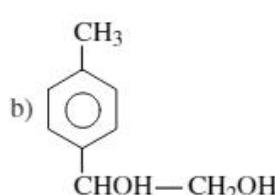
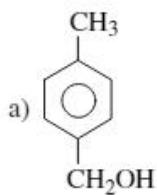
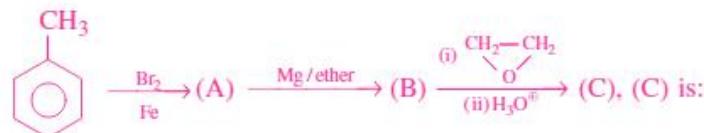
- a) F > Cl > Br > I b) I > Br > Cl > F c) Cl > F > Br > I d) I > Br > F > Cl



Product (X) & (Y) respectively is

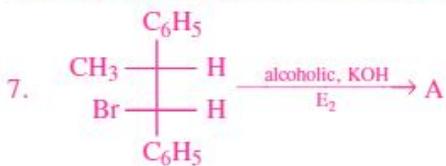
- a) 1-butene, trans-2-butene b) 1-butene, cis-2-butene
c) cis-2-butene, 1-butene d) trans-2-butene, 1-butene

5. Final product of the given reaction:

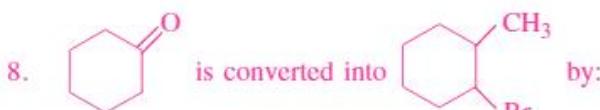


6. For $\text{CH}_3\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^-$, the rate of reaction is given by the expression:

- a) rate = $k[\text{CH}_3\text{Br}]$ b) rate = $k[\text{OH}^-]$
c) rate = $k[\text{CH}_3\text{Br}][\text{OH}^-]$ d) rate = $k[\text{CH}_3\text{Br}]^\circ [\text{OH}^-]^\circ$



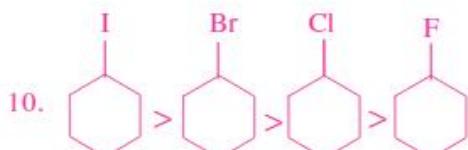
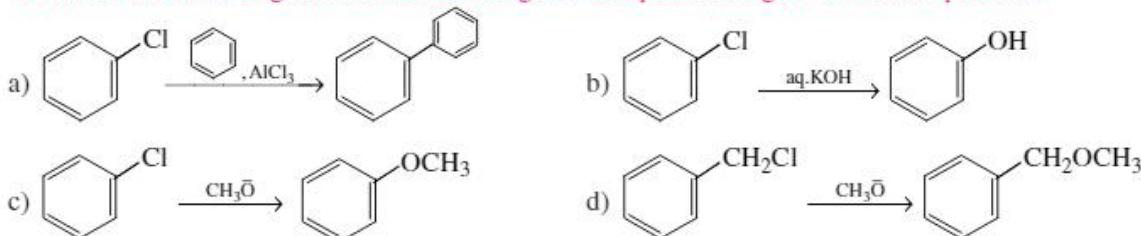
- a)
- b)
- c)
- d) None is correct



- a) (i) CH_3-MgI , H_3O^+ , (ii) H_2SO_4 , Δ , (iii) HBr , R_2O_2
- b) (i) CH_3-MgI , H_3O^+ , (ii) H_2SO_4 , Δ , (iii) HBr
- c) (i) CH_3-MgI , H_3O^+ , (ii) HBr
- d) (i) HBr , R_2O_2 , (ii) CH_3-MgI , H_3O^+

More than One correct answer Type Questions

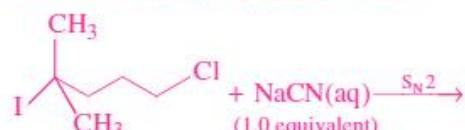
9. Which of the following reactions does not go to completion to give the stated product?



The shown order is a correct order during the rate of:

- a) S_{N}^2 mechanism b) E^2 mechanism c) E^1 mechanism d) S_{N}^1 mechanism

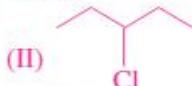
11. Consider the reaction given below.



The correct statement(s) applicable to the above reaction is/are

- a) Cl^- is substituted predominantly b) Cl^- is a better leaving group
 c) substitution of I^- in the above reaction required greater activation energy than for Cl^-
 d) addition of some NaI catalyse the substitution reaction.

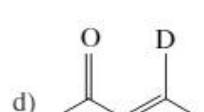
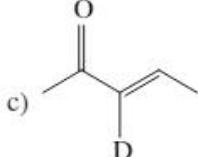
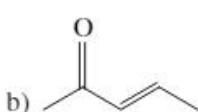
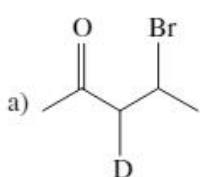
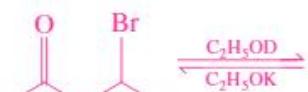
12. Consider the following halides



Which is/are correct statement(s)?

- a) Reactivity for S_N^1 reactions is I > II > III
- b) Reactivity for S_N^2 reactions is I = II = III
- c) Reactivity for S_N^1 reactions I < II < III
- d) Reactivity for S_N^2 reactions I < II < III

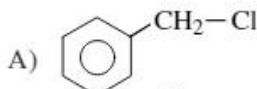
13. The following elimination reaction, if proceeds by $E_1 cb$ mechanism, equilibrium mixture would consist of



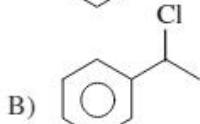
Matrix Matching Type Questions

14. **Column-I**

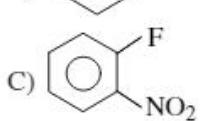
Column-II



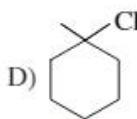
- p) Nucleophilic-aromatic substitution reaction



- q) Elimination reaction



- r) S_N^1 reaction



- s) S_N^2 reaction

15. **Column-I**

Column-II

- A) Dehydrohalogenation
- B) Dehalogenation
- C) Dehydration
- D) Hydrolysis

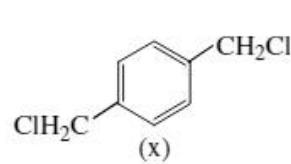
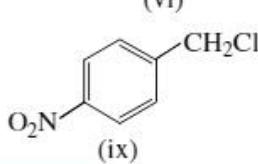
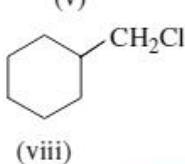
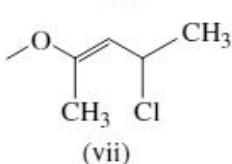
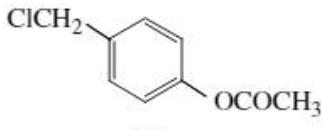
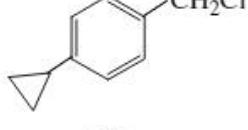
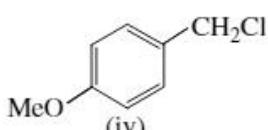
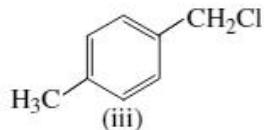
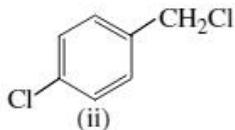
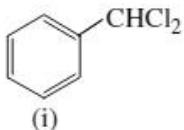
- p) Ethanolic zinc
- q) Conc. H_2SO_4
- r) Aq. KOH
- s) Alc. KOH

Integer Type Questions

16. No of chlorine atoms present in DDT (insecticide) are ____

17. $\xrightarrow{\text{NBS/CCl}_4}$. Total no. of isomers (including stereoisomers) obtained in the above reaction are _____

18. How many of the following undergo solvolysis reaction faster than benzyl chloride?



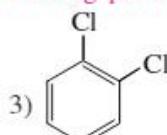
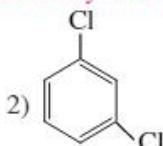
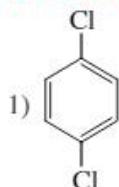
EXERCISE-III

(Reactions of Arylhalides (Addition, Elimination & Miscellaneous reaction))

LEVEL-I (MAIN)

Straight Objective Type Questions

1. Which of the following is likely to have highest melting point



4) All posses same m.p. as they are isomers

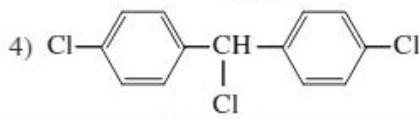
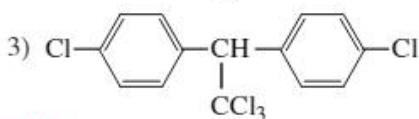
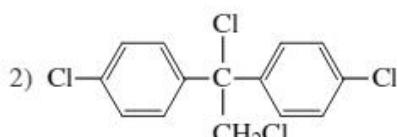
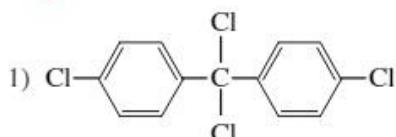
2. Reactivity order with respect to alkyl group of Hunsicker reaction is

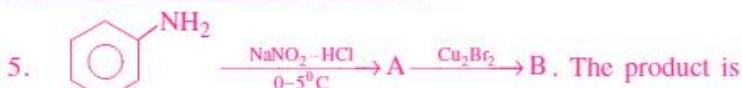
- 1) $1^0 > 2^0 > 3^0$ 2) $3^0 > 2^0 > 1^0$ 3) $3^0 = 2^0 > 1^0$ 4) $1^0 = 2^0 > 3^0$

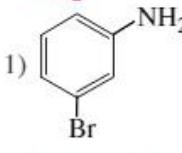
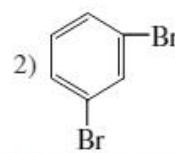
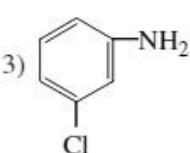
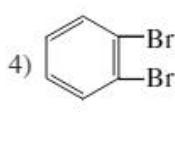
3. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{Mg/ether}} \text{A} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{B}, \text{A} \xrightarrow{\text{D}_2\text{O}} \text{C}$; B & C are

- 1) $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3, \text{CH}_3\text{CH}_2\text{CH}_3$ 2) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3, \text{CH}_3\text{CH}_2\text{CH}_2\text{D}$
 3) $\text{CH}_3\text{CH}_2\text{CH}_3, \text{CH}_3\text{CH}_2\text{CH}_2\text{D}$ 4) $\text{CH}_3\text{CH}_2\text{CH}_3, \text{CH}_3\text{CH}_2\text{CH}_2\text{OD}$

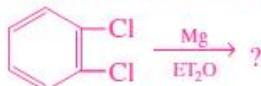
4.

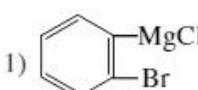
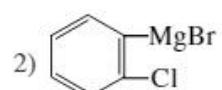
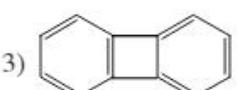


5. 

- The product is
- 1) 
 - 2) 
 - 3) 
 - 4) 

6. What is the product of the following reaction?



- 1) 
- 2) 
- 3) 
- 4) None of these

7. 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) Benzoic acid

8. Arrange the following compounds in order of increasing dipole moment

- | | | | |
|----------------------|-----------------------|------------------------|-----------------------|
| I) Toluene | II) m-dichlorobenzene | III) o-dichlorobenzene | IV) p-dichlorobenzene |
| 1) I < IV < II < III | 2) IV < I < II < III | 3) IV < I < III < II | 4) IV < II < I < III |

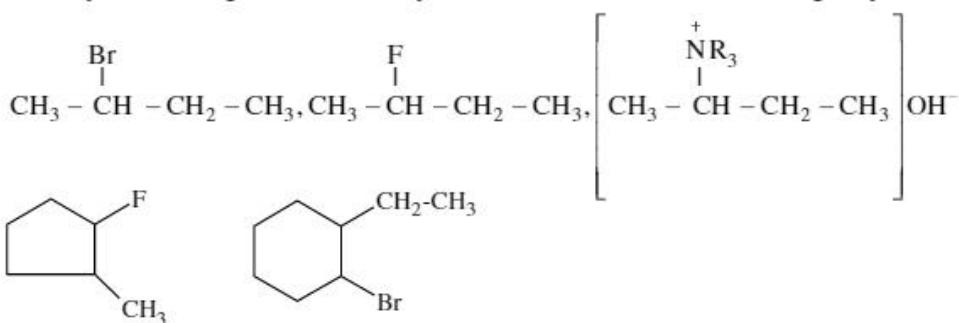
9. In the reaction of p-chloro toluene with KNH_2 in liq. NH_3 , the major product is:

- 1) o-toluidine
- 2) m-toluidine
- 3) p-toluidine
- 4) p-chloraniline

Numerical Value Type Questions

10. Number of different products formed in mononitration of 1, 3 – dibromo benzene including minor products is

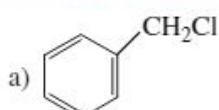
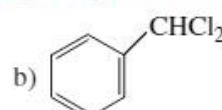
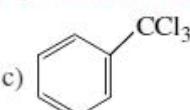
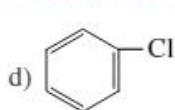
11. How many can undergo elimination by Hoffman's orientation on heating in presence of alc. KOH?

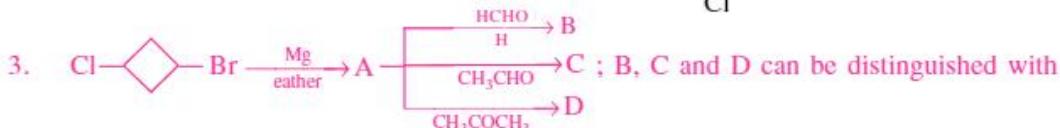
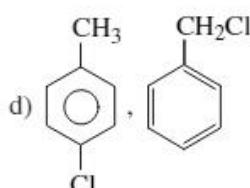
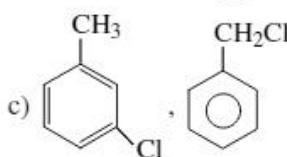
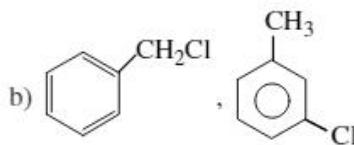
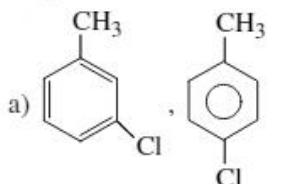
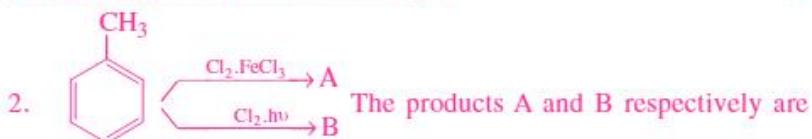


LEVEL-II (ADVANCED)

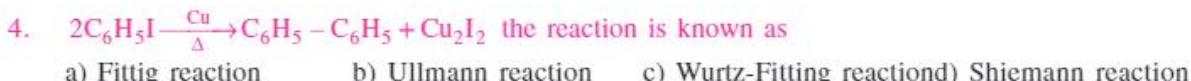
Straight Objective Type Questions

1. In which of the following compounds more meta product is obtained on electrophilic substitution

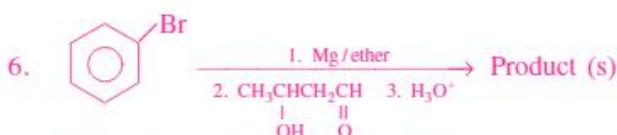
- a) 
- b) 
- c) 
- d) 



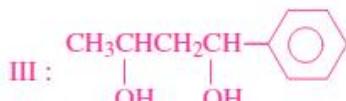
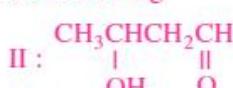
- a) Baeyer's reagent b) Lucas reagent c) Tollen's reagent d) Schiff's reagent



- a) it forms a complex with $AgNO_3$ b) it does not ionise to give Cl^- ions
 c) precipitate is soluble in CCl_4 d) $AgNO_3$ does not give Ag^+ ions.



Select the product from the following

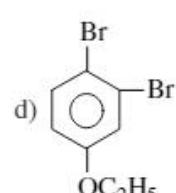
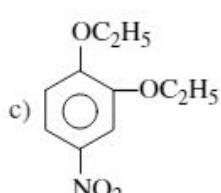
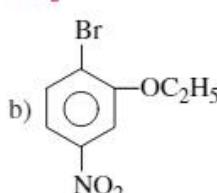
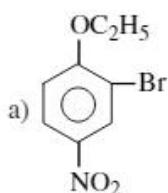
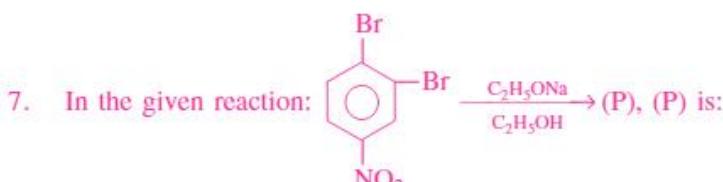


a) III

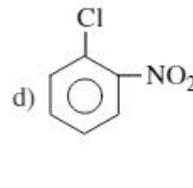
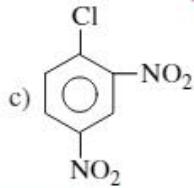
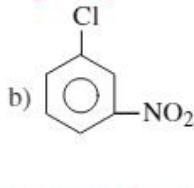
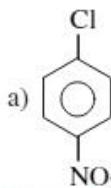
b) I, III

c) I, II

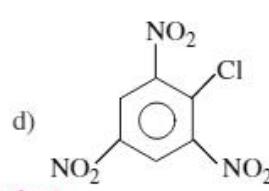
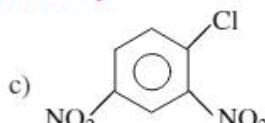
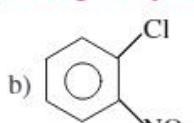
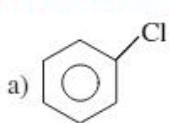
d) II, III



8. Which one of the following compounds is most reactive for ArS_{N}^2 reaction?



9. Which of the following undergoes hydrolysis most easily?



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

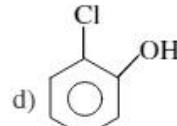
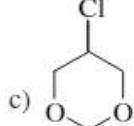
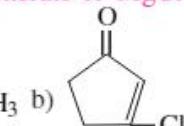
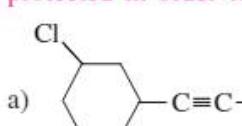
- a) o-chloro toluene b) 2,5-dichloro toluene c) p-chloro toluene d) Benzyl chloride

More than One correct answer Type Questions

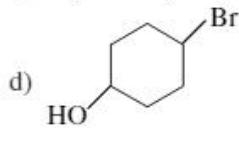
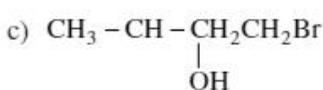
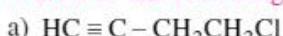
11. Benzyl chloride ($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$) can be prepared from toluene by chlorination with:

- a) SO_2Cl_2 b) SOCl_2 c) Cl_2/hv d) NaOCl

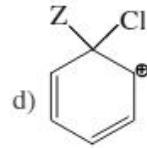
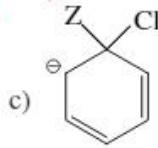
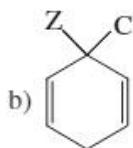
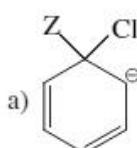
12. Organic halide that posses a functional group that react with $\text{R}-\text{MgX}$ cannot themselves form a grignard reagent. Indicate which of the following chlorides need to have its other functional group protected in order to generate $\text{R}-\text{MgCl}$



13. Which of the following does not form Grignard reagent?



14. Which of the following is the correct resonance structure, of the species formed in the nucleophilic substitution of chlorobenzene with Z (a nucleophile)



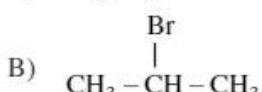
Matrix Matching Type Questions

15. **Column-I**

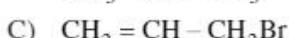


Column-II

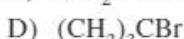
- p) Undergoes E_2 reaction



- q) Undergoes S_{N}^2 reaction

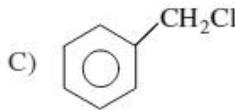
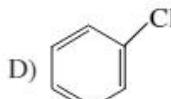


- r) Carbocation is formed



- s) Undergoes S_{N}^1 reaction

16. Column-I

- A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
- B) $\text{CH}_2 = \text{CH} - \text{CH}_2\text{Cl}$
- C) 
- D) 

Column-II

- p) Undergoes free radical substitution with $\text{Cl}_2 - h\nu$
- q) Nucleophilic substitution under normal conditions
- r) Nucleophilic substitution under drastic condition
- s) Undergoes electrophilic substitutions

KEY SHEET (LECTURE SHEET)

EXERCISE-I

LEVEL-I

- 1) 2 2) 2 3) 2 4) 2 5) 2 6) 2 7) 4 8) 3
 9) 3 10) 4 11) 1 12) 1,3,4 13) 4

LEVEL-II

- 1) b 2) b 3) b 4) d 5) b 6) b 7) a 8) c
 9) a 10) b 11) d 12) c 13) b 14) c 15) a 16) abcd
 17) abc 18) abc 19) bc 20) acd 21) ac 22) bd 23) abcd
 24) b 25) abcd 26) b 27) b 28) c 29) A-rt; B-st; C-qt; D-p

EXERCISE-II

LEVEL-I

- 1) 3 2) 1 3) 2 4) 3 5) 3 6) 2 7) 2 8) 1
 9) 1 10) 8 11) 4

LEVEL-II

- 1) c 2) a 3) a 4) d 5) c 6) c 7) a 8) a
 9) abc 10) abcd 11) acd 12) b 13) abc
 14) A-rs; B-qr; C-p; D-qr 15) A-s; B-p; C-q; D-r 16) 5 17) 9
 18) 5

EXERCISE-III

LEVEL-I

- 1) 1 2) 1 3) 3 4) 3 5) 2 6) 3 7) 4 8) 2
 9) 2 10) 3 11) 3

LEVEL-II

- 1) c 2) d 3) b 4) b 5) b 6) c 7) a 8) c
 9) d 10) d 11) ac 12) bd 13) abcd 14) abc
 15) A-pq; B-pqr; C-qr; D-prs 16) A-pq; B-pq; C-pqs; D-rs

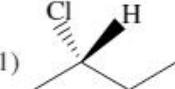
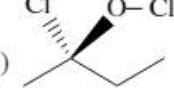
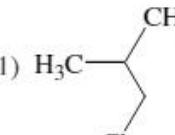
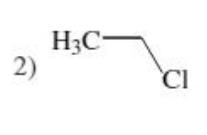
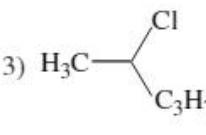
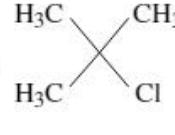
 PRACTICE SHEET

EXERCISE-I

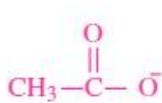
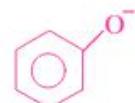
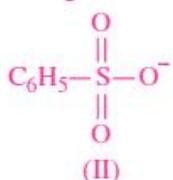
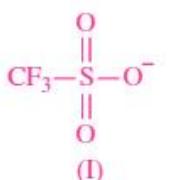
(Classification, Isomerism, Physical & Chemical Properties)

LEVEL-I (MAIN)

Straight Objective Type Questions

1. The product formed in the reaction  + $\text{SOCl}_2 \rightarrow$ is
- 1)  2)  3)  4) 
2. 1,3-Dibromopropane reacts with metallic zinc to form
 1) propene 2) cyclopropane 3) propane 4) hexane
3. Consider the following reaction sequence, $\text{CH}_3\text{C}\equiv\text{CH} \xrightarrow[\text{HgSO}_4]{\text{aq. H}_2\text{SO}_4} \text{A} \xrightarrow[\text{Heat}]{\text{PCl}_5} \text{B}$. The products (A) and (B) are, respectively,
 1) CH_3COCH_3 and $\text{CH}_3\text{CCl}_2\text{CH}_3$ 2) $\text{CH}_3\text{CH}_2\text{CHO}$ and $\text{CH}_3\text{CH}_2\text{CHCl}_2$
 3) $\text{CH}_3\text{CHOHCH}_3$ and $\text{CH}_3\text{CHClCH}_3$ 4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
4. Which of the following has highest dipole moment?
 1) CH_3Cl 2) CH_3F 3) CH_3Br 4) CH_3I
5. Which one of the following compounds most readily undergoes substitution by $\text{S}_{\text{N}}2$ mechanism?
 1)  2)  3)  4) 
6. Most stable carbocation formed from $(\text{CH}_3)_3\text{C}-\text{Br}$, $(\text{C}_6\text{H}_5)_3\text{CBr}$, $(\text{C}_6\text{H}_5)_2\text{CHBr}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ would be
 1) $\text{C}_6\text{H}_5\text{CH}_2^+$ 2) $(\text{CH}_3)_3\text{C}^+$ 3) $(\text{C}_6\text{H}_5)_3\text{C}^+$ 4) $(\text{C}_6\text{H}_5)_2\text{CH}^+$
7. Ethyldiene chloride can be prepared by the reaction of HCl and
 1) Ethane 2) Ethylene 3) Acetylene 4) Ethylene glycol
8. The reaction of $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_5-\text{OH}$ with HBr gives
 1) $\text{CH}_3\text{CH}_2(\text{Br})\text{CH}-\text{C}_6\text{H}_5-\text{OH}$ 2) $\text{CH}_3\text{CH}_2(\text{Br})\text{CH}-\text{C}_6\text{H}_5-\text{Br}$
 3) $\text{CH}_3-\text{CH}(\text{Br})-\text{CH}_2-\text{C}_6\text{H}_5-\text{OH}$ 4) $\text{CH}_2(\text{Br})-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_5-\text{OH}$
9. The order of decreasing nucleophilicity of the following is
 1) $\text{H}_2\text{O} > \text{OH}^- > \text{CH}_3\text{COO}^- > \text{CH}_3\text{O}^-$ 2) $\text{CH}_3\text{O}^- > \text{OH}^- > \text{CH}_3\text{COO}^- > \text{H}_2\text{O}$
 3) $\text{CH}_3\text{COO}^- > \text{CH}_3\text{O}^- > \text{OH}^- > \text{H}_2\text{O}$ 4) $\text{HO}^- > \text{CH}_3\text{O}^- > \text{CH}_3\text{COO}^- > \text{H}_2\text{O}$

10. Consider the following anions.



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

- 1) I > II > III > IV 2) I > II > IV > III 3) IV > I > II > III 4) IV > III > II > I
11. The basicity of RO^- , HO^- , RCOO^- , ROH and H_2O are of the order
- 1) $\text{HO}^- > \text{RO}^- > \text{H}_2\text{O} > \text{ROH} > \text{RCOO}^-$ 2) $\text{RO}^- > \text{HO}^- > \text{RCOO}^- > \text{ROH} > \text{H}_2\text{O}$
 3) $\text{H}_2\text{O} > \text{ROH} > \text{RCOO}^- > \text{HO}^- > \text{RO}^-$ 4) $\text{ROH} > \text{H}_2\text{O} > \text{HO}^- > \text{RCOO}^- > \text{RO}^-$

Numerical Value Type Questions

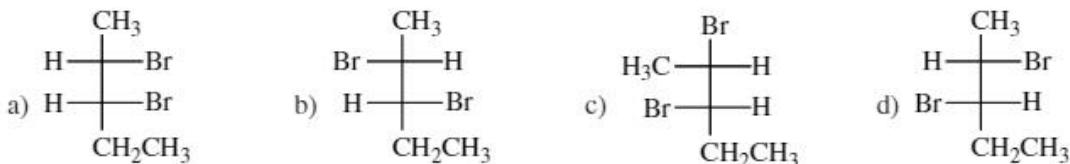
12. The number of structural isomers possible for $\text{C}_5\text{H}_{11}\text{Br}$ is
13. Minimum number of carbon atom in an alkyl chloride to exhibit optical activity is

LEVEL-II (ADVANCED)

Straight Objective Type Questions

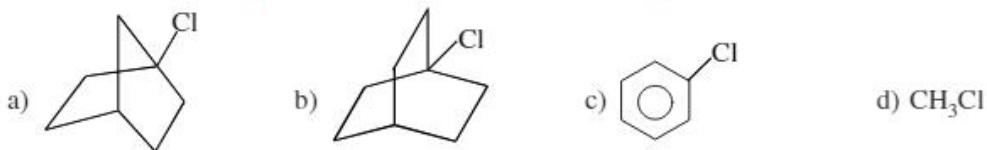
1. $\text{C}_2\text{H}_4 \xrightarrow{\text{Br}_2} \text{X} \xrightarrow{\text{KCN}} \text{Y}$; Y is
- a) $\text{CH}_3\text{CH}_2\text{CN}$ b) $\text{NC}-\text{CH}_2-\text{CH}_2-\text{CN}$
 c) $\text{Br}-\text{CH}_2-\text{CH}_2\text{CN}$ d) $\text{Br}-\text{CH}=\text{CHCN}$
2. Which of the following is least reactive in a nucleophilic substitution reaction?
- a) $\text{CH}_2=\text{CHCl}$ b) $\text{CH}_3\text{CH}_2\text{Cl}$ c) $\text{CH}_2=\text{CHCH}_2\text{Cl}$ d) $(\text{CH}_3)_3\text{C}-\text{Cl}$
3. Ethyl alcohol reacts at a faster rate with HI than with HCl in forming the corresponding ethyl halides under identical conditions mainly because
- a) HI, being a stronger acid, protonates ethyl alcohol at oxygen much better and helps substitution
 b) the bond length in HI is much shorter than that in HCl
 c) I^- is a much better leaving group
 d) I^- is a much better nucleophile than Cl^-
4. Name of $\text{H}_3\text{C}-\text{HC}(\text{Br})_2$ is
- a) Ethyldene bromide b) Gem-dibromide
 c) In IUPAC name it is known as 1,1-dibromo ethane d) Any of the above
5. For the compounds CH_3Cl , CH_3Br , CH_3I and CH_3F , the correct order of increasing C-halogen bond length is:
- a) $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$ b) $\text{CH}_3\text{F} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl} < \text{CH}_3\text{I}$
 c) $\text{CH}_3\text{F} < \text{CH}_3\text{I} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl}$ d) $\text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{F} < \text{CH}_3\text{I}$
6. Which of the following vicinal halide is unstable?
- a) $\text{CH}_3-\underset{\text{Cl}}{\underset{|}{\text{CH}}}-\text{CH}_2\text{Cl}$ b) $\text{CH}_3-\underset{\text{Br}}{\underset{|}{\text{CH}}}-\text{CH}_2\text{Br}$ c) $\text{CH}_3-\underset{\text{I}}{\underset{|}{\text{CH}}}-\text{CH}_2\text{I}$ d) All are unstable

7. A primary alkyl iodide on treatment with dry silver oxide gives
 a) Diethyl ether b) Ethyl methyl ether c) An alcohol d) An ether
8. Which of the following alkoxide nucleophiles is more reactive towards S_N^2 reaction
 a) CH_3O^- b) $\text{CH}_3\text{CH}_2\text{O}^-$ c) $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{O}^- \\ | \\ \text{CH}_3 \end{array}$ d) $(\text{CH}_3)_3\text{CO}^-$
9. Which of the following primary halides is most reactive towards S_N^1 reaction
 a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ b) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$
 c) $\text{CH}_3\text{CH}_2\text{O} - \text{CH}_2\text{CH}_2\text{Cl}$ d) 
10. Which (S)-2-bromopentane is brominated, several 2,3-dibromopentanes are formed, which of the following is not formed?



More than One correct answer Type Questions

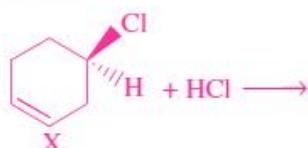
11. The less reactive alkyl halide towards reaction than ethyl chloride



12. Which of the following reagents can bring about free radical chlorination of propane?

- a) SOCl_2 b) SO_2Cl_2 c) Cl_2/hv d) PCl_3

13. Consider the following reaction:



When a pure enantiomer of X is taken in the above reaction, correct completion regarding the reaction is/are

- a) Four (stereo) different dichlorocyclohexane are formed as significant products
 b) a pair of enantiomers is formed
 c) two pairs of diastereomers are formed
 d) product mixture has zero specific rotation
14. Which of the following does/do produces a white precipitate of AgCl on warming with alcoholic silver nitrate?
 a) Allyl chloride b) t-Butyl chloride
 c) benzyl chloride d) Vinyl chloride

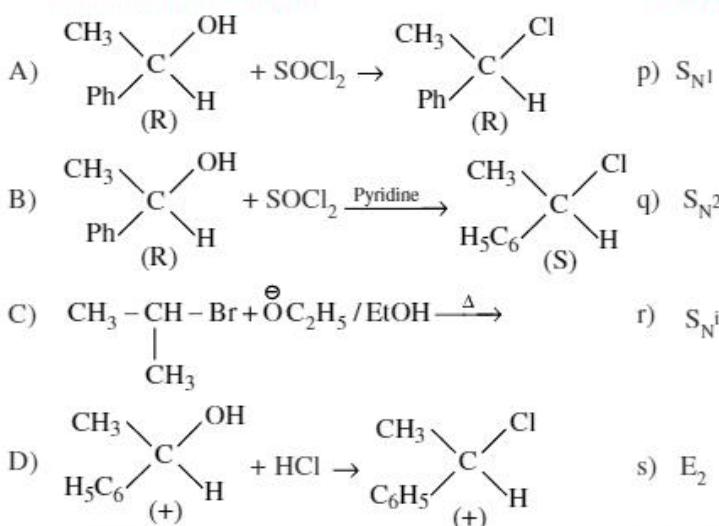
15. Which is/are true statement(s):

- Protonation increases electrophilic nature of carbonyl group
- CF_3SO_3^- is better leaving group than CH_3SO_3^-
- Benzyl carbonium ion is stabilized by resonance
- $\text{CCl}_3\text{CH}(\text{OH})_2$ is stable, due to H-Bonding

Matrix Matching Type Questions

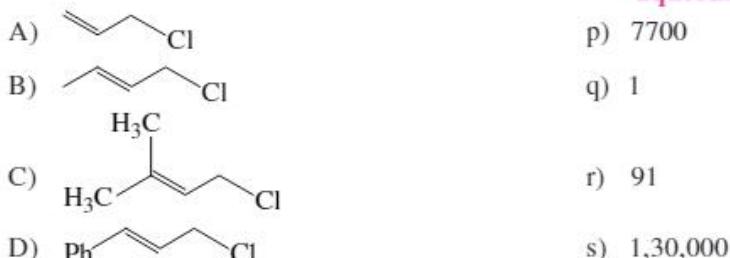
16. Column-I (Reaction)

Column-II (Mechanism)



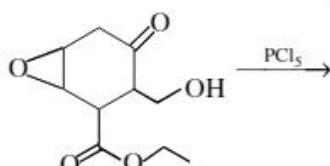
17. Column-I
(Substrate)

Column-II
(Relative rate of solvolysis in 50% in aqueous ethanol at 45°C)

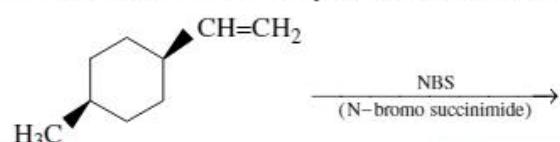


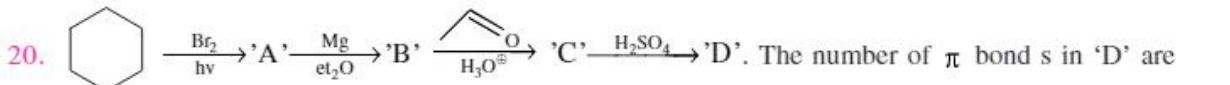
Integer Type Questions

18. Find the maximum number of chlorine atom which is present in major products of following reaction.



19. Find the total number of possible monobrominate product obtained during the reaction.



20. 
21. $\text{CHCl}_3 \xrightarrow[\text{HgSO}_4/\text{H}_2\text{SO}_4]{\text{Ag Powder}} \text{'A}' \xrightarrow[500^\circ\text{C}]{\text{Cu red hot}} \text{'B}' \xrightarrow{\text{CH}_3\text{COCl}} \text{'C}' \xrightarrow{\text{AlCl}_3} \text{'D'} \xrightarrow{\text{PCl}_5} \text{'E'} \xrightarrow{3\text{NaNH}_2} \text{'F'} \xrightarrow{\text{CH}_3\text{I}} \text{'G'}$. The no. of oxygen atoms in 'G' are _____.
22. How many primary halides (excluding stereo isomers) are possible for the molecular formula $\text{C}_5\text{H}_{11}\text{Br}$?

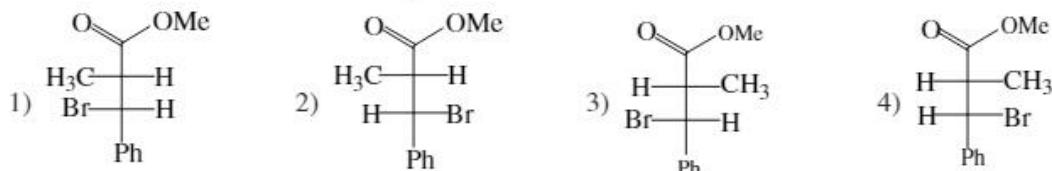
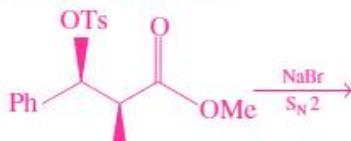
EXERCISE-II

(S_N^1 and S_N^2 mechanisms & aryl halides preparation methods)

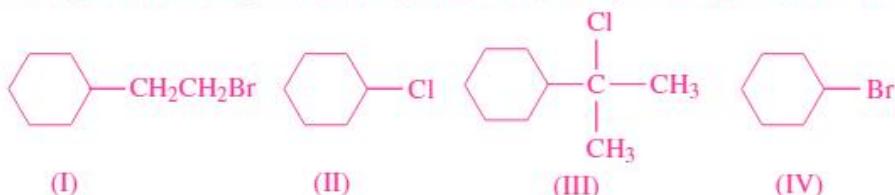
LEVEL-I (MAIN)

Straight Objective Type Questions

1. Which statement is true about S_N^2 mechanism?
- The rate of reaction increases on increasing strength of the nucleophile
 - The reaction is faster in polar aprotic solvents
 - The rate of reaction increases as the leaving group ability increases
 - All of the above
2. Which is the product of the given reaction?



3. Arrange the following in increasing order of reactivity in an S_N^2 reaction with KI in acetone solvent.

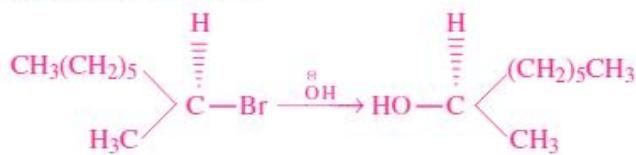


- 1) I < IV < III < II 2) IV < I < III < II 3) II < III < I < IV 4) III < II < I < IV

4. Which of the following species is involved in the mechanism of $\bar{\text{O}}\text{H}$ substitution of chlorobenzene



5. Following reaction is



- 1) E₁ 2) S_N¹ 3) E₂ 4) S_N²

Numerical Value Type Questions

6. How many of the following nucleophiles are better than NH₃ for nucleophilic substitution reaction?



LEVEL-II (ADVANCED)

Straight Objective Type Questions

1. The characteristic reaction of alkyl halides are
 - a) Electrophilic substitution reactions
 - b) Electrophilic addition reactions
 - c) nucleophilic addition reactions
 - d) Nucleophilic substitution reaction
2. Most reactive halide towards S_N¹ reaction is
 - a) n-Butyl chloride
 - b) Sec-Butyl chloride
 - c) Tert-Butyl chloride
 - d) Allyl chloride
3. Which of the following alkyl halides is hydrolysed by S_N¹ mechanism?
 - a) CH₃ – Br
 - b) CH₃CH₂ – Br
 - c) CH₃CH₂CH₂ – Br
 - d) (CH₃)₃C – Br
4. In S_N¹ reactions rate of reaction depends on
 - 1) concentration of alkyl halide
 - 2) concentration of nucleophile
 - 3) nature of alkyl halide
 - a) All
 - b) '1' and '3' only
 - c) '1', '2' only
 - d) '3' only
5. Which of the following is more nucleophilic in protic solvent?
 - a) SH⁻
 - b) I⁻
 - c) OH⁻
 - d) H₂O
6. Order of nucleophilicity of oxygen containing nucleophiles
 - a) RO⁻ > OH⁻ > ROH > H₂O
 - b) H₂O > ROH > OH⁻ > RO⁻
 - c) RO⁻ > ROH > OH⁻ > H₂O
 - d) H₂O > OH⁻ > RO⁻ > ROH
7. Order of nucleophilicity of halide ions in aprotic solvent
 - a) I⁻ > Br⁻ > Cl⁻ > F⁻
 - b) F⁻ > Br⁻ > Cl⁻ > I⁻
 - c) F⁻ > Cl⁻ > Br⁻ > I⁻
 - d) I⁻ > Cl⁻ > Br⁻ > F⁻
8. Which of the following is/are protic solvents?
 - a) HCOOH
 - b) $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$
 - c) CH₃OH
 - d) All the above

9. Which of the following is/are aprotic solvents?
- CH_3COCH_3
 - $\text{HCON}(\text{CH}_3)_2$
 - CH_3SOCH_3
 - All the above
10. Which of the following is the best leaving group in a nucleophilic substitution reaction?
- F_3CSO_3^- (Triflate)
 - H_3CSO_3^- (Mesylate)
 - $\text{Br}-\text{C}_6\text{H}_4-\text{SO}_3^-$ (Brosylate)
 - $\text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_3^-$ (Tosylate)

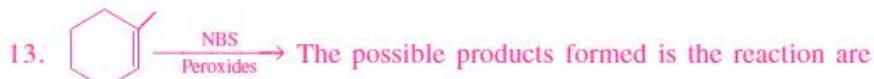
More than One correct answer Type Questions

11. Which statements is/are right regarding S_{N}^1 reactions is false?

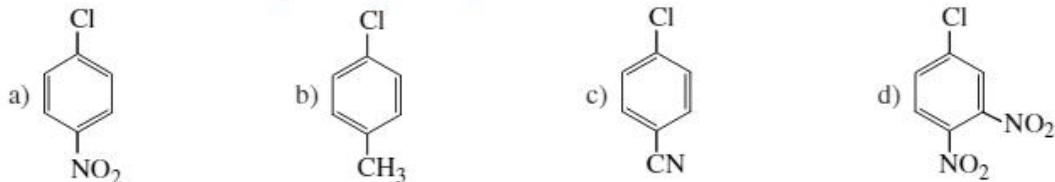
- The rate of reaction is influenced by Conc of nucleophile
- The reaction takes places in two steps
- Racemization takes place
- Molecularity of the reaction is two



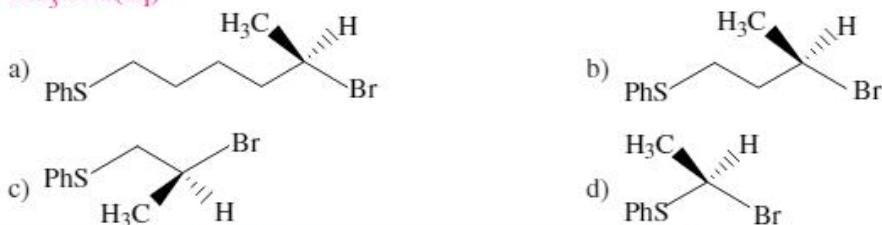
- A pale yellow precipitate of AgBr is formed
- A white precipitate of AgCl is formed
- No precipitate is formed
- It is a nucleophilic substitution reaction



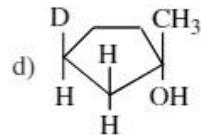
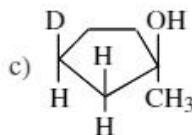
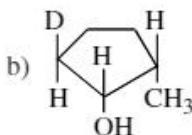
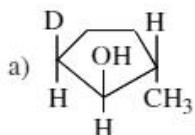
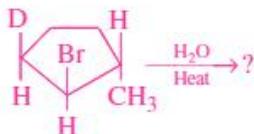
14. Which of the following undergo nucleophilic substitution faster than that of chlorobenzene?



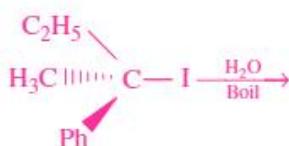
15. Pick out the alkyl bromides which proceeds with retention of configuration in an S_{N}^2 reaction with $\text{CH}_3\text{ONa(aq)}$



16. When the reactants shown below undergo substitution, which of the products will form?

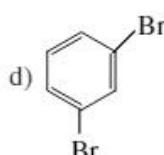
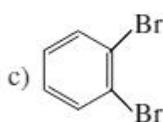
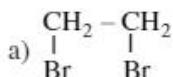


17. If a pure dextrorotatory enantiomer of the substrate of the following reaction is boiled with water, the correct statement(s) regarding S_N1 products(s) is/are

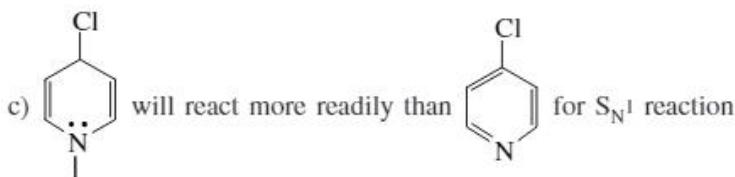
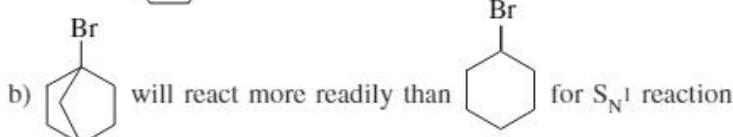
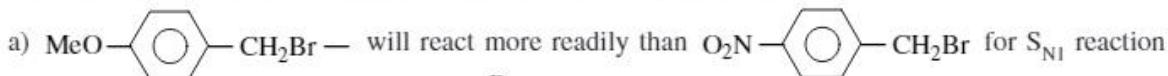


- a) product would be pure laevorotatory
- b) product would consist of both laevo and dextrorotatory enantiomers
- c) product would be racemic mixture
- d) product would be optically active with enantiomer of retention configuration predominating

18. Which of the following will not form Grignard reagent with Mg/dry ether?

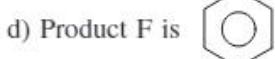
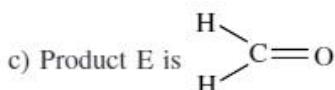
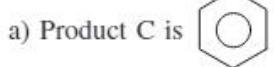
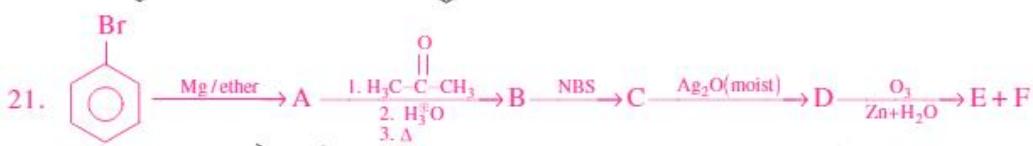
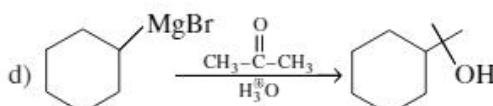
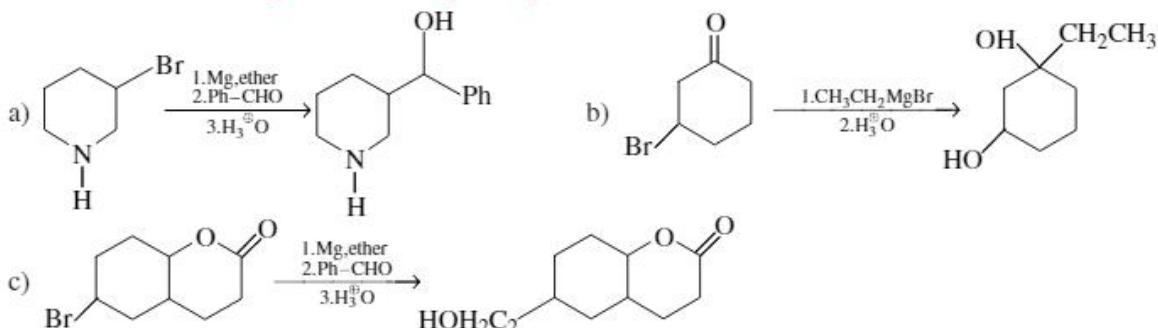


19. Consider the following statements and pick up the correct statements:



d) S_N1 reaction occurs in polar protic solvent

20. Point out the following incorrect Grignard synthesis:

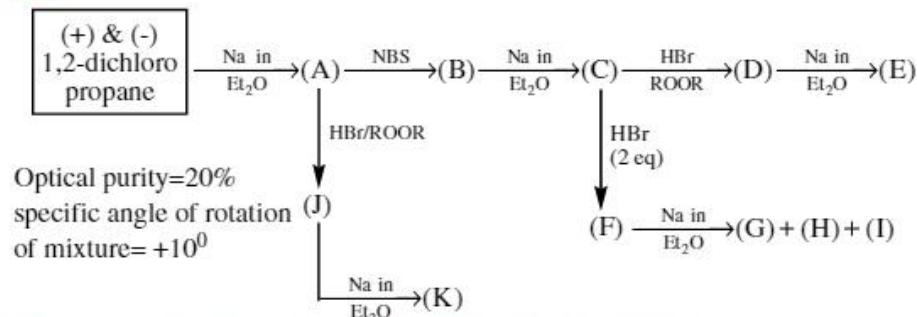


22. Aryl halide undergo:

- a) Fittig reaction
b) Ullmann reaction
c) Wurtz reaction
d) Grignard reagent synthesis

Linked Comprehension Type Questions

Passage :



23. The compound with maximum double bond equivalent is

- a) B b) C c) A d) E

24. Which statement is incorrect?

- a) K and C both are hydrocarbons
b) A and C both are unsaturated hydrocarbons
c) E and G are cyclic hydrocarbons
d) D and F are functional isomers

25. The reaction which involve electrophilic addition reaction is

a) A → B

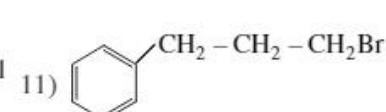
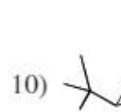
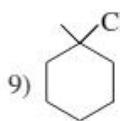
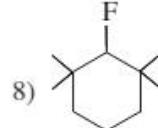
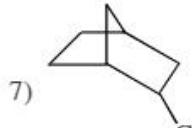
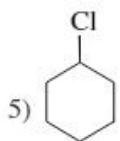
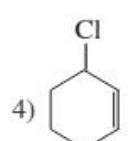
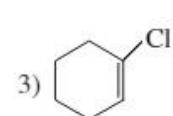
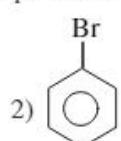
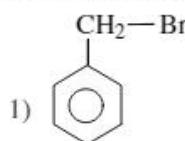
b) B → C

c) C → F

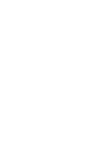
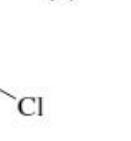
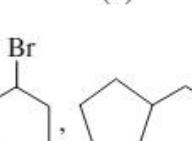
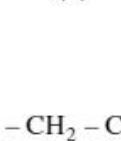
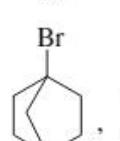
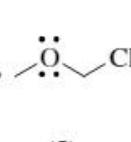
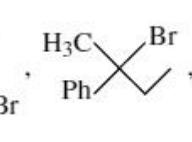
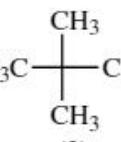
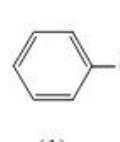
d) C → D

Integer Type Questions

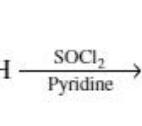
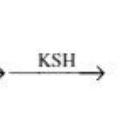
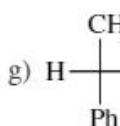
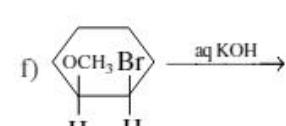
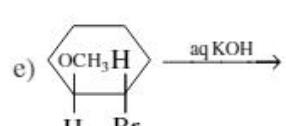
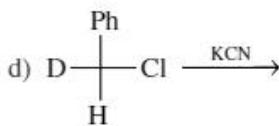
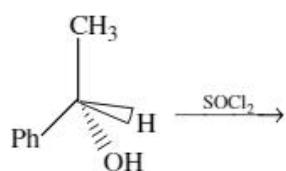
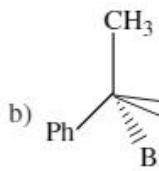
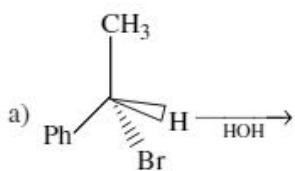
26. X = The number of compounds do not show S_N^2 .

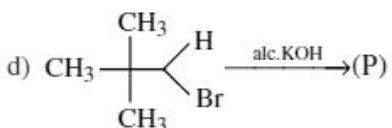
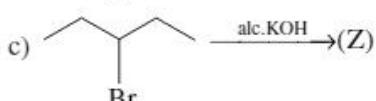
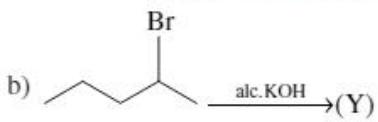
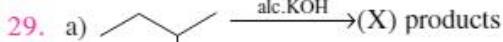


27. Identify number of substrate those can give S_N^1 and S_N^2 reaction both



28. Find out number of reactions those proceed with only retention of configuration.





Sum of X + Y + Z + P =

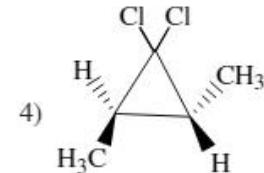
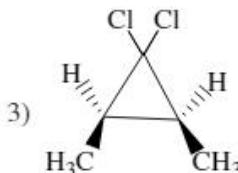
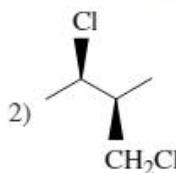
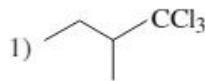
EXERCISE-III

(Reactions of Arylhalides (Addition, Elimination & Miscellaneous reaction))

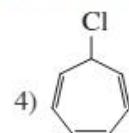
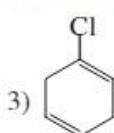
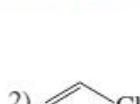
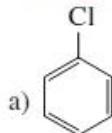
LEVEL-I (MAIN)

Straight Objective Type Questions

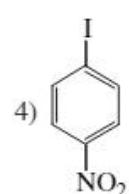
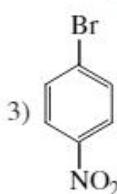
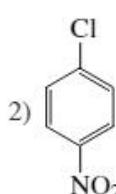
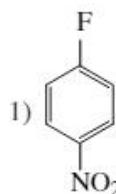
- Consider the following reaction, $\text{CCl}_4 + \text{aq. KOH} \rightarrow$ the major product in the above reaction is
 1) K_2CO_3 2) CO_2 3) $\text{C}(\text{OH})_4$ 4) HCOOK
- Nitro chloropicrin is prepared by the action of chloroform and
 1) hot KNO_3 (aq) 2) hot NaNO_2 (aq)
 3) hot conc. HNO_3 4) hot dil. NaNO_2 (aq) + NaNO_2 (aq)
- The end product in the following reaction is



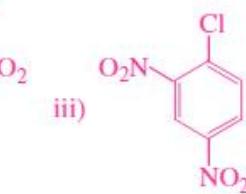
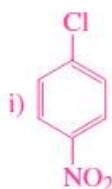
- Which of the following compound will give curdy precipitate with AgNO_3 solution?



- Which of the following compounds will show faster Ar $\text{S}_{\text{N}}2$ reaction?

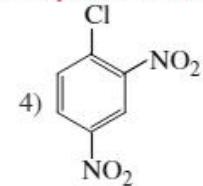
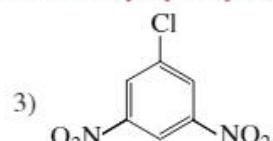
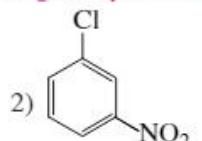
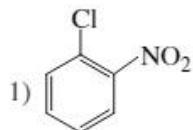


6. Correct reactivity order for Aromatic nucleophilic substitution (ArS_N) reaction for the following is:



- 1) i > ii > iii > iv 2) ii > i > iv > iii 3) ii > iv > iii > i 4) iii > ii > iv > i

7. Which one of the following compound will be most readily hydrolyzed in aqueous alkali?



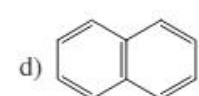
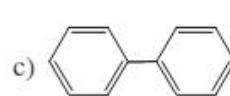
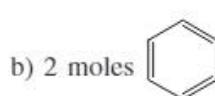
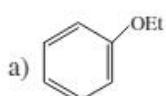
Numerical Value Type Questions

8. The minimum number of carbon atoms to be present in monohalogen derivative of alkane to be optically active is

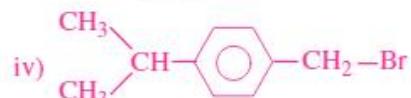
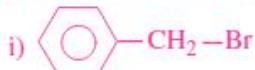
LEVEL-II (ADVANCED)

Straight Objective Type Questions

1. The product Z in the given reaction is : $2 \text{C}_6\text{H}_5\text{Br} + 2\text{Na} \xrightarrow{\text{dry ether (Et}_2\text{O)}} \text{Z} + 2\text{NaBr}$



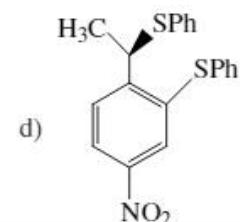
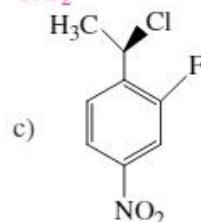
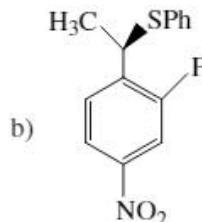
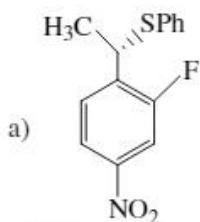
2. Arrange the following compounds in decreasing order of rate of solvolysis reaction.

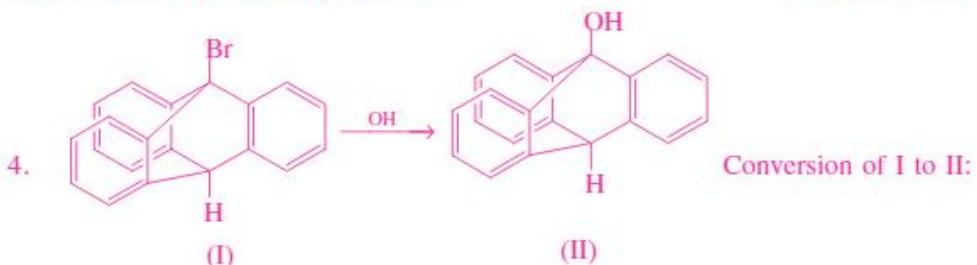


- a) iii > iv > ii > i b) iv > iii > ii > i

- c) ii > iii > iv > i d) i > ii > iii > iv

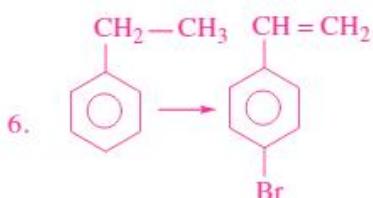
3. The major product of the following reaction is





5. $\text{CHCl}_2 - \text{CF}_3 \xrightarrow[\Delta]{\text{alc. KOH}} \text{CCl}_2 = \text{CF}_2$. Which of the following statements is not true about the above reaction?

 - a) It is unimolecular reaction
 - b) It is second order reaction
 - c) Reaction proceeds through formation of carbonium ion
 - d) Mechanism of the reaction is the E₁ cB.

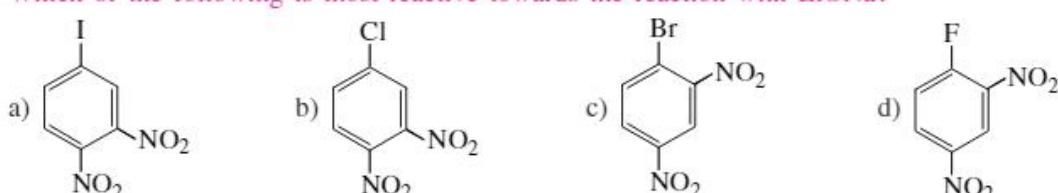


Select the best series of reagents to bring about the above conversion :

- a) i) NBS/CCl₄ ii) CH₃ONa/CH₃OH iii) Fe/Br₂
b) i) Fe/Br₂ ii) NBS/CCl₄ iii) CH₃ONa/CH₃OH
c) i) Br₂/hv ii) CH₃ONa/CH₃OH iii) HBr
d) i) Br₂/hv ii) NBS/CCl₄ iii) CH₃ONa/CH₃OH

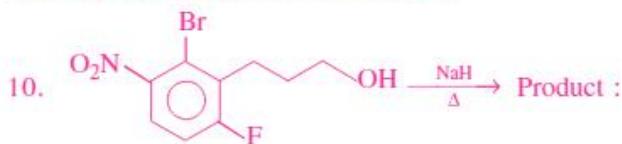
7. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides which is not true

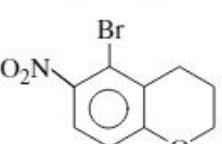
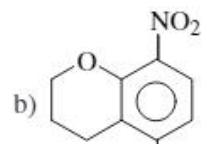
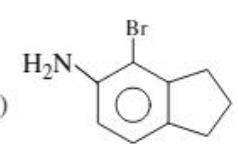
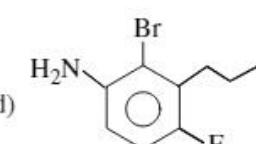
a) the formation of less stable carbocation ion in aryl halides
b) double bond character in C–X bond of aryl halides
c) longer carbon halogen bond in aryl halides
d) sp²-hybridized carbon bonded to halogen in aryl halides.



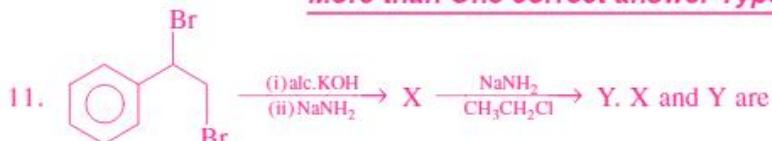
9. The sequence of steps involved in aromatic nucleophilic substitution involving a benzyne intermediate is :

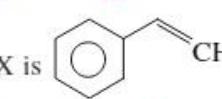
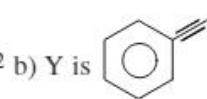
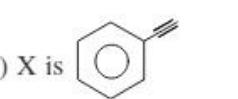
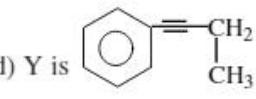
 - a) Addition-elimination
 - b) Elimination-addition
 - c) Addition-rearrangement
 - d) Elimination-rearrangement

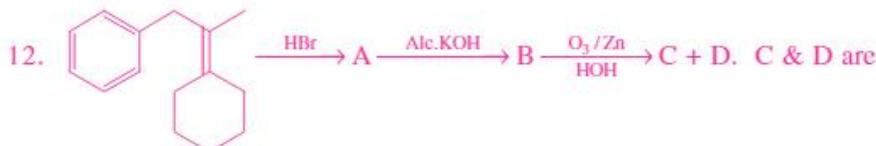


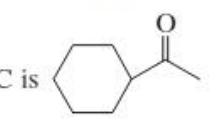
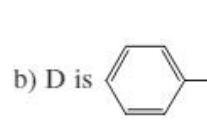
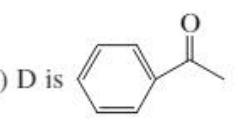
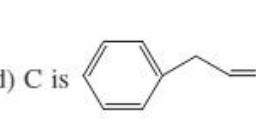
- a)  b)  c)  d) 

More than One correct answer Type Questions

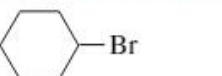
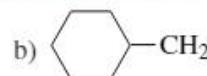
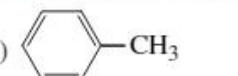
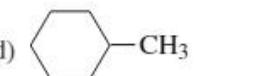


- a) X is  b) Y is  c) X is  d) Y is 

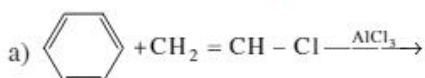
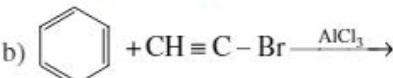
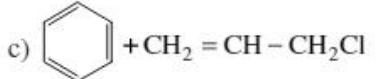
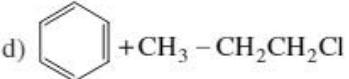


- a) C is  b) D is  c) D is  d) C is 

13. The product obtained by reduction of Benzyl bromide with, LiAlH_4 is

- a)  b)  c)  d) 

14. Which of the following reaction does not takes place to give the product?

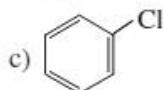
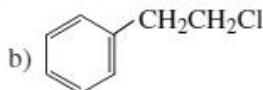
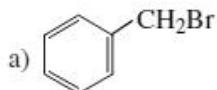
- a)  b) 
 c)  d) 

Linked Comprehension Type Questions

Passage-I :

Aliphatic nucleophilic substitution mainly place by two mechanisms (i.e.,) S_{N1} & S_{N2} . Primary halides mainly undergo by S_{N2} mechanism and are favourable in polar aprotic solvents. S_{N1} reactions takes place mainly by tertiary halide and are more favourable in polar protic solvents. In case of tertiary halides, E_1 comes competition to S_{N1} reaction. Keeping in view of these general points, answer the following questions.

15. Which of the following reactions, the reaction takes place by S_N1 mechanism mainly.



16. $(+)\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Cl} \rightarrow (\pm)\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$ in which of the following solvents, the above reaction is most favourable

- a) 75% water + 25% CH_3OH
c) 100% methanol

- b) 25% water + 75% methanol
d) 10% water + 90% methanol

Passage-II :

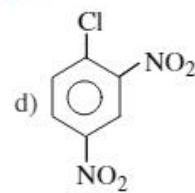
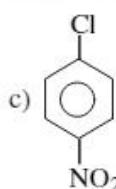
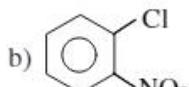
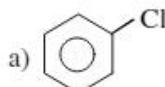
Aryl halides are less reactive than alkyl halides due to the presence partial double character of C-X bond in aryl halides. Arly halides undergo nucleophilic substitution reactions, if electron withdrawing groups are introduced in ortho & para-positions in aryl halides. The reaction mechanism involves two steps. Keeping these points in view answer the following questions.

17. Which of the following is the correct order of reactivity of the aryl halides with a given nucleophile?



- a) I > II > III > IV b) IV > III > II > I c) I ≈ II ≈ III ≈ IV d) I >> II ≈ III ≈ IV

18. Which compound undergo nucleophilic substitution under mild conditions?



19. The number of resonance structure possible for chlorobenzene is

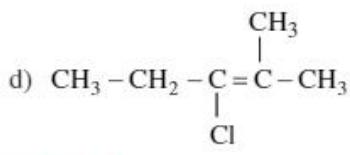
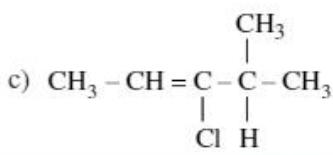
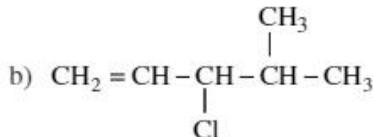
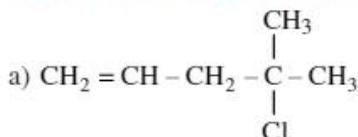
- a) Three b) Four c) Five d) Two

Passage-III :

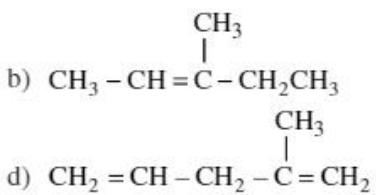
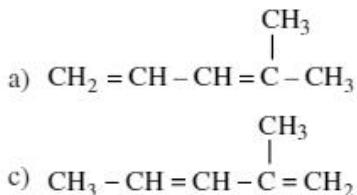
Compound A($\text{C}_6\text{H}_{11}\text{Cl}$), decolorise bromine in CCl_4 . Catalytic reduction of A gave 2-methyl, 3-Chloro pentane. A on reaction with alc. KOH gave B as only product. B on ozonolysis gave

HCHO , $\begin{matrix} \text{CHO} \\ | \\ \text{CHO} \end{matrix}$ & CH_3COCH_3 . Follow the sequence of reactions and answer the following questions.

20. Which of the following is the structure of 'A'?



21. The structure of 'B' is

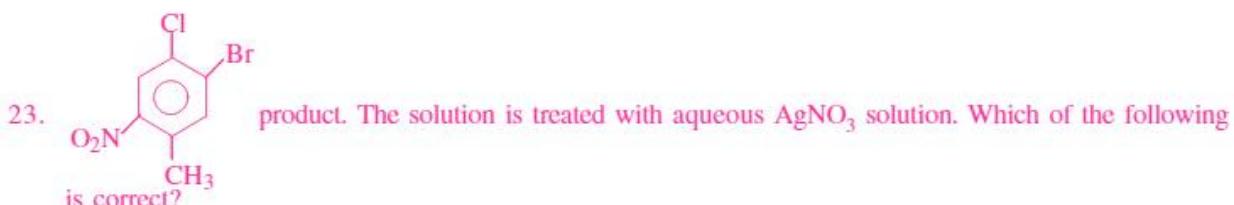


22. Number of stereoisomers of compound A is

- a) Three b) Four c) Two d) Zero

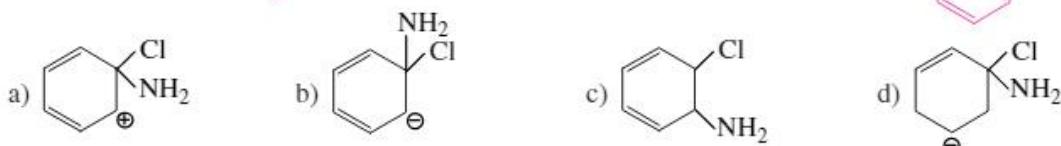
Passage-IV:

The nucleophilic substitution reaction taking place in aromatic system are designated as S_NAr . In fact aryl halides do not easily undergo nucleophilic substitution under ordinary conditions. However, introduction of electron-withdrawing groups in *o*, *p*-positions makes the reaction to go faster. Keeping these general points in view answer the following questions.



- a) A white precipitate of AgCl is formed
 - b) A pale yellow precipitate of AgBr is formed
 - c) No precipitate of any kind is observed
 - d) A mixture of AgCl + AgBr formed

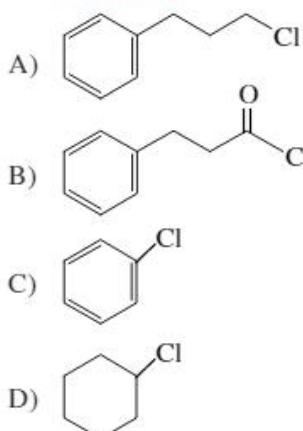
24. Which of the following structures is correct in the mechanism of the reaction



Matrix Matching Type Questions

25. **Column-I**

Column-II



- p) Friedel-Crafts reaction
 - q) Electrophilic substitution
 - r) Nucleophilic substitution (under suitable conditions)
 - s) Dehydrohalogenation

26. Column-I (Reaction)

- A) S_N1
B) S_N2
C) E₁
D) E₂

Column-II (Type of reaction)

- p) 3°alkylhalide >2°alkylhalides>1°alkylhalide
q) 1°alkylhalide >2°alkylhalides>3°alkylhalide
r) High concentration of strong base
s) Polar protic solvent

Integer Type Questions

27. Number of chlorine atoms present in gammoxene.
 28. When 1,3-butadiene reacts with HBr, how many products are formed (including stereo isomers)?
 29. Number of isomers for the compound with the molecular formula C₂BrClFI is _____.
 30. Number of stereoisomers for 2-chloro-3-pentene
 31. The number of stereoisomers possible for 2,3,4-trichloropentane

KEY SHEET (PRACTICE SHEET)

EXERCISE-I

- | | | | | | | | | |
|-----------------|------------------------|------------------------|---------|--------|--------|---------|----------|------|
| LEVEL-I | 1) 2 | 2) 2 | 3) 1 | 4) 1 | 5) 2 | 6) 3 | 7) 3 | 8) 1 |
| | 9) 2 | 10) 2 | 11) 2 | 12) 8 | 13) 4 | | | |
| LEVEL-II | 1) b | 2) a | 3) d | 4) d | 5) a | 6) c | 7) d | 8) a |
| | 9) d | 10) b | 11) abc | 12) bc | 13) ac | 14) abc | 15) abcd | |
| | 16) A-r; B-q; C-s; D-p | 17) A-q; B-r; C-p; D-s | | | 18) 5 | 19) 3 | | |
| | 20) 1 | 21) 1 | 22) 4 | | | | | |

EXERCISE-II

- | | | | | | | | | |
|-----------------|--------|---------|---------|---------|----------|----------|---------|---------|
| LEVEL-I | 1) 4 | 2) 4 | 3) 2 | 4) 1, 2 | 5) 4 | 6) 5 | | |
| LEVEL-II | 1) d | 2) c | 3) d | 4) b | 5) a | 6) a | 7) c | 8) d |
| | 9) d | 10) a | 11) ad | 12) bd | 13) abc | 14) accd | 15) abc | 16) abd |
| | 17) bd | 18) abc | 19) acd | 20) ac | 21) abcd | 22) abd | 23) b | 24) d |
| | 25) c | 26) 5 | 27) 6 | 28) 3 | 29) 8 | | | |

EXERCISE-III

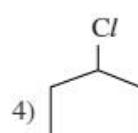
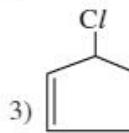
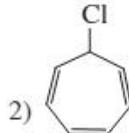
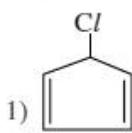
- | | | | | | | | | |
|-----------------|-------------------------------|----------------------------|--------|--------|-------|--------|-------|-------|
| LEVEL-I | 1) 1 | 2) 3 | 3) 4 | 4) 4 | 5) 1 | 6) 3 | 7) 4 | 8) 4 |
| LEVEL-II | 1) c | 2) c | 3) a | 4) d | 5) d | 6) b | 7) c | 8) d |
| | 9) b | 10) a | 11) cd | 12) ab | 13) c | 14) ab | 15) a | 16) a |
| | 17) a | 18) d | 19) c | 20) b | 21) a | 22) c | 23) b | 24) b |
| | 25) A-pqrs; B-pq; C-qr; D-prs | 26) A-ps; B-qr; C-ps; D-pr | | | | | | |
| | 27) 6 | 28) 2 | 29) 6 | 30) 4 | 31) 4 | | | |

ADDITIONAL PRACTICE EXERCISE

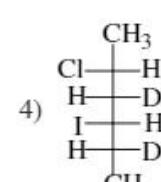
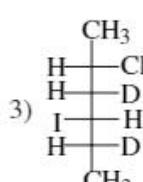
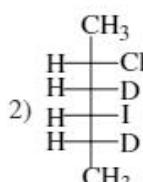
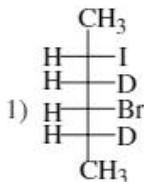
LEVEL-I (MAIN)

Straight Objective Type Questions

1. Which of the following is least reactive toward S_N^1 ?



- 2.



3. Order of nucleophilicity in polar protic solvent?

- 1) $I^- > Br^- > Cl^- > F^-$
3) $F^- > I^- > Br^- > Cl^-$

- 2) $F^- > Cl^- > Br^- > I^-$
4) $I^- > Cl^- > Br^- > F^-$

Numerical Value Type Questions

4. How many alkenes are formed by E_2 elimination of HBr from 2-bromo-2,3-dimethylhexane using a strong base such as sodium methoxide?
5. How many alkenes are formed by E_1 elimination of HCl from 3-chloro-3,4-dimethylheptane in methanol?

LEVEL-II

LECTURE SHEET (ADVANCED)

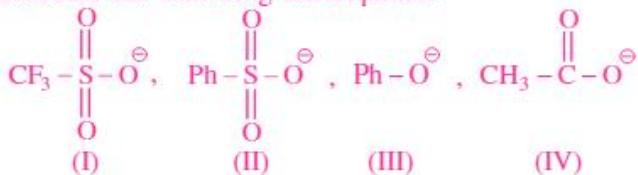
Straight Objective Type Questions

1. In the following compound, arrange the reactivity of different bromine atoms toward NaSH in decreasing order:



- a) P > Q > R > S b) S > Q > P > R c) Q > S > P > R d) P > S > Q > R

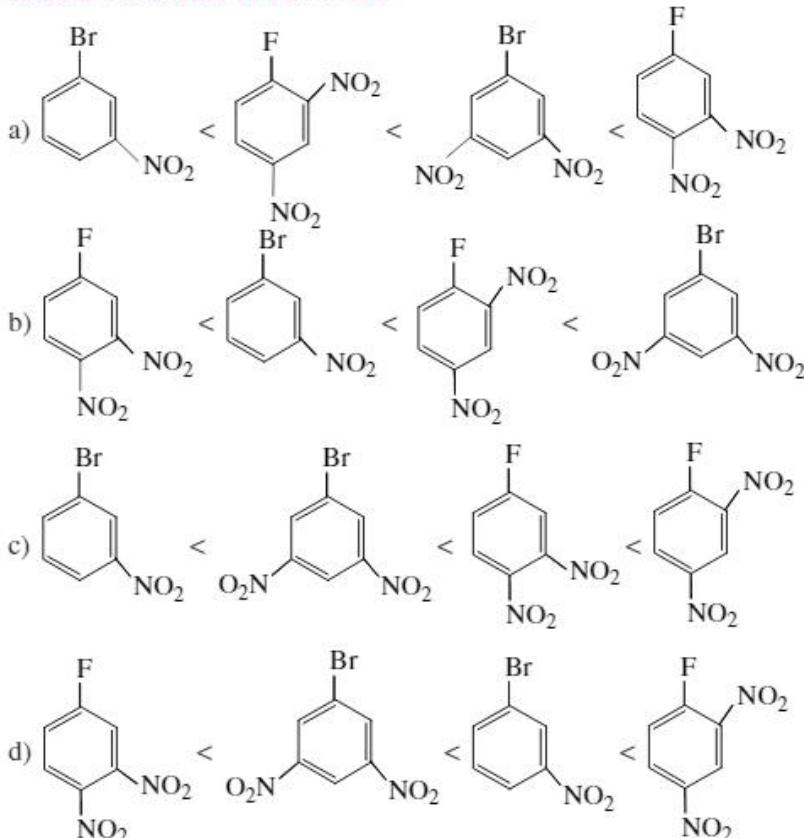
2. Consider the following nucleophiles.



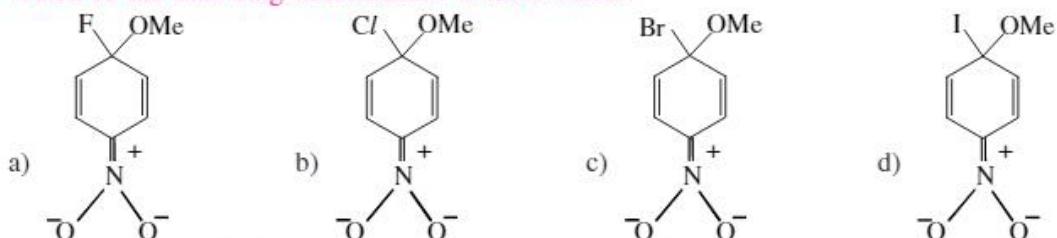
when attached to sp^3 -hybridized carbon, their leaving group ability in nucleophilic substitution reaction decreases in the order:

- a) I > II > III > IV b) I > II > IV > III c) IV > I > II > III d) IV > III > II > I

3. Which of the following correctly ranks the aryl halides in decreasing order of reactivity toward sodium methoxide in methanol?



4. Which of the following intermediates is more stable?



5. reaction-1: $\text{C}_2\text{H}_5\text{I} + \text{CN}^- \xrightarrow{\text{H}_2\text{O}}$; reaction-2: $\text{C}_2\text{H}_5\text{I} + \text{CN}^- \xrightarrow{\text{DMF}}$

- a) Reaction 1 is faster b) Reaction 2 is faster
 c) Both the reactions go at same rate d) Rates can't be compared

More than One correct answer Type Questions

6. Choose the correct among the following statements:

- a) will react more readily than for S_N^2 reaction
- b) will react more readily than for S_N^2 reaction
- c) will react more readily than for S_N^2 reaction
- d) will react more readily than for S_N^2

7. Consider the following statements and pick up the correct statmenets:

- a) will react more readily than for S_N^1 reaction
- b) will react more readily than for S_N^1 reaction
- c) will react more readily than for S_N^1 reaction.
- d) S_N^1 reaction occurs in polar solvent

8. Identify the compounds which may give NGP reaction:

- a)
- b)
- c)
- d)

9. In which of the following reaction neither S_N^1 nor S_N^2 take place?

- a)
- b) $H_2C = CH - Cl$
- c)
- d) $CH_3 - Cl$

10. \xrightarrow{KSH} Correct statement regarding given reaction will be:

- a) Above reaction is S_N^2
- b) Inversion of configuration takes place during given reaction
- c) Biomolecular reaction
- d) Second order reaction

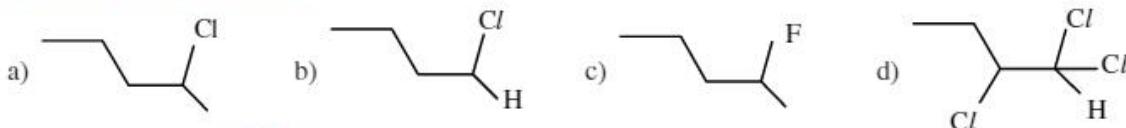
PRACTICE SHEET (ADVANCED)

More than One correct answer Type Questions

1. The negative charge on the carbon atom in the ion shown below can be stabilized by



- a) resonance of the $-\text{CH} = \text{CH}_2$ group b) hyperconjugation of the $-\text{CH}_3$ group
 c) inductive effect of the $-\text{F}_3\text{C}$ group d) inductive effect of the $-\text{CH}=\text{CH}_2$ group
 2. Identify the alkyl halide(s) that produce a terminal alkene as major product on treatment with alcoholic NaOH or KOH

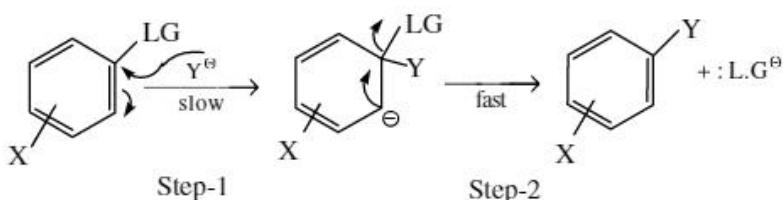


3. Phenol + $\text{C}_2\text{H}_5\text{I} \xrightarrow[\text{Ethylalcohol}]{\text{C}_2\text{H}_5\text{ONa}}$ The possible products are

- a) $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ b) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ c) $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$ d) $\text{C}_6\text{H}_5\text{I}$

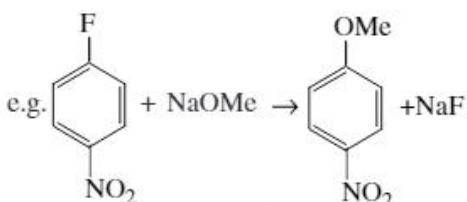
Linked Comprehension Type QuestionsPassage-I :

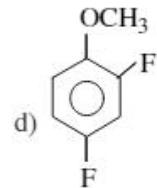
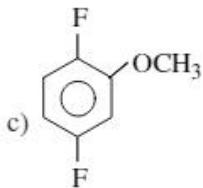
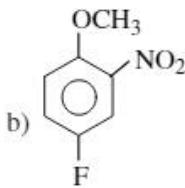
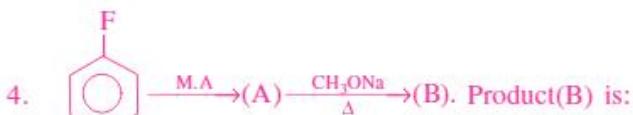
Nucleophilic aromatic substitution:



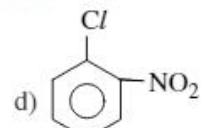
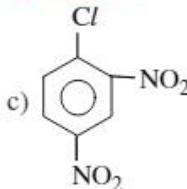
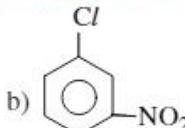
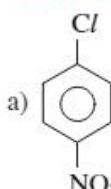
The species that adds to the aromatic ring in step-1 needs to be a nucleophile such as methoxide (CH_3O^-) instead of an electrophile such as nitronium ion (NO_2^+).

Step-1 will be facilitated by electron withdrawing rather than electron donating substituents. Substituents that are deactivating in electrophilic aromatic substitution are activating in nucleophilic aromatic substitution the effect is most pronounced for strongly electron withdrawing group *ortho* and/or *para* to the leaving group. In order of step-2 to occur, the pair of electrons bonding the leaving group to the ring are lost with the leaving group, rather than becoming part of the ring's π system. MA = mixed acid ($\text{HNO}_3 + \text{H}_2\text{SO}_4$)





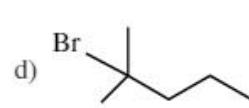
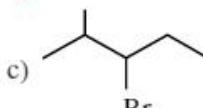
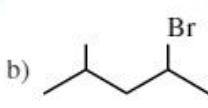
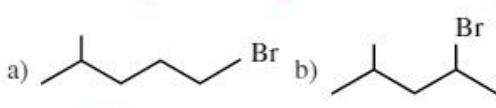
5. Which of the following compounds is most reactive towards $\text{ArS}_{\text{N}2}$ reaction?

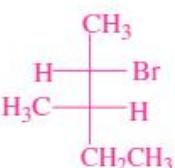


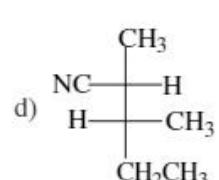
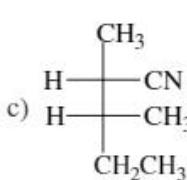
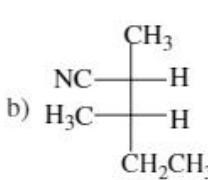
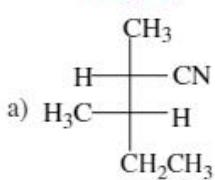
Passage-II :

These problems differ from those in earlier chapters in that they directly test your knowledge of core material rather than using a descriptive passage to extend the material or introduce new ideas. The number of factors that contribute to nucleophilic substitution can be daunting. The really major ones, though, are few and readily applied to specific by using the S_{N}^1 and S_{N}^2 mechanism to guide your analysis.

6. Which compound undergoes substitution by the S_{N}^1 mechanism at the fastest rate?



7.  $\xrightarrow[\text{DMSO}, 25^\circ\text{C}]{\text{NaCN}}$ What is the major product of the reaction shown?



Matrix Matching Type Questions

8. Column-I

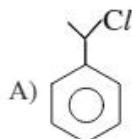
- A) $E_1\text{cb}$
- B) S_{N}^2
- C) E_1
- D) S_{N}^1

Column-II

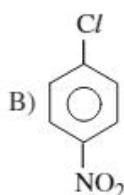
- p) First order
- q) No rearrangement
- r) Rearrangement
- s) Strong nucleophile
- t) Inversion of configuration

9. Column-I

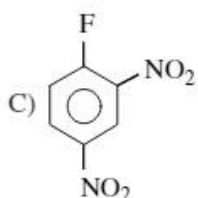
Column-II



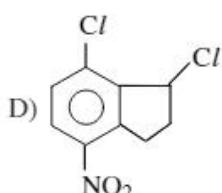
p) Undergo S_NAr (Nucleophilic aromatic substitution) with CH_3O^-



q) Undergo S_N^1 reaction with H_2O



r) Undergo S_N^2 reaction with aq. KOH.

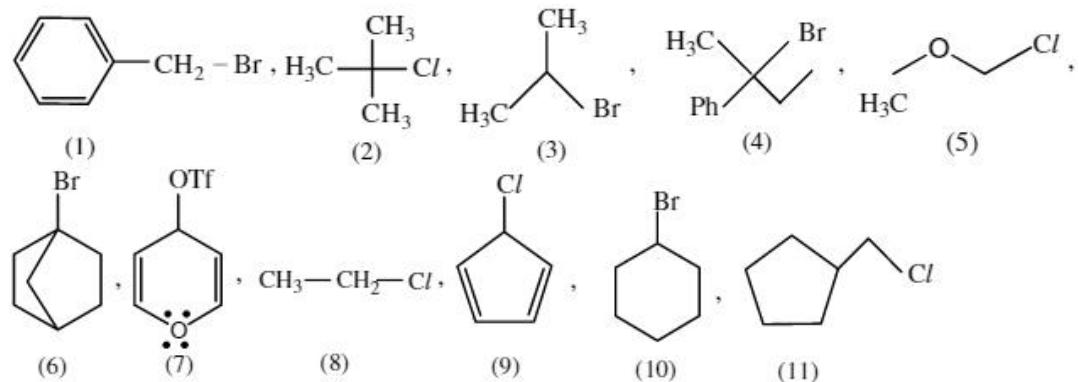


s) Undergo E_2 reaction with alc. KOH

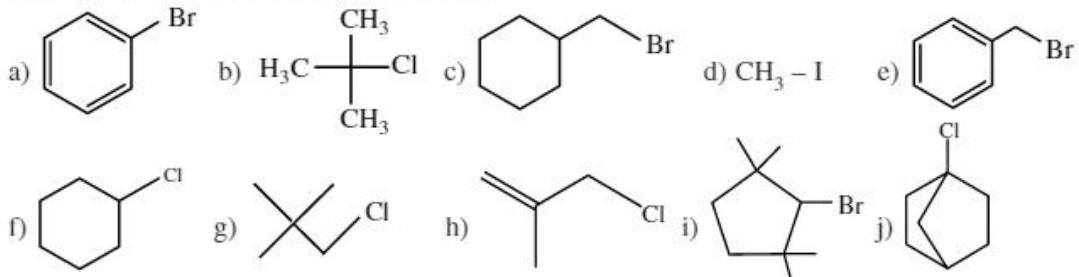
t) Undergo E_1 reaction with EtOH on strong heating.

Integer Type Questions

10. Identify the substrate those can give S_N^1 and S_N^2 reaction both.

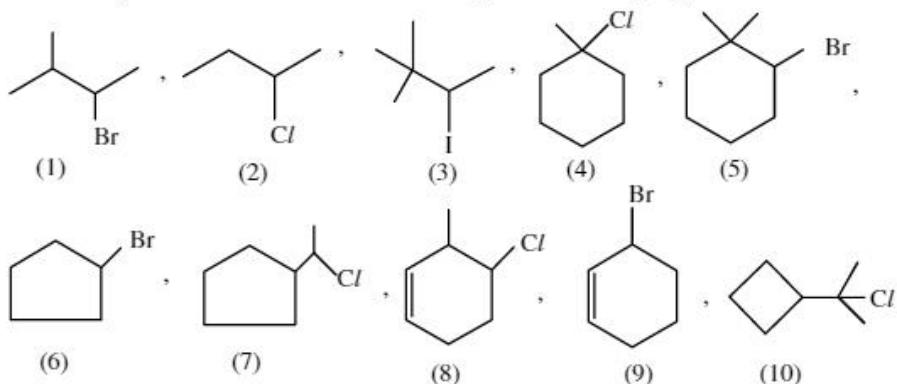


11. Examine the ten structures shown below.

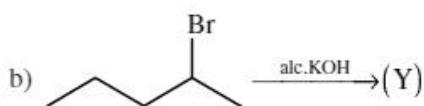


How many compounds give S_N^2 reaction on treatment with NaSH?

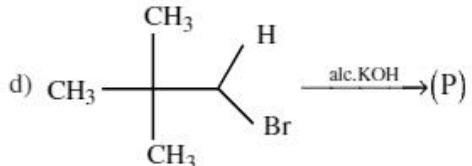
12. How many substrates will show rearrangement during S_N^1 reaction?



13. a) $\xrightarrow{\text{alc.KOH}}$ (X) products



c) $\xrightarrow{\text{alc.KOH}}$ (Z)



Sum of X + Y + Z + P =

14. $\xrightarrow{\text{XHI}}$ how many (X) moles of HI consumed?

KEY SHEET (ADDITIONAL PRACTICE EXERCISE)

LEVEL-I (MAIN)

- 1) 1 2) 3 3) 1 4) 2 5) 5

LEVEL-II

LECTURE SHEET (ADVANCED)

- 1) c 2) b 3) c 4) a 5) b 6) acd 7) acd 8) abc 9) abc 10) abcd

PRACTICE SHEET (ADVANCED)

- 1) acd 2) bcd 3) ab 4) b 5) c 6) d 7) b
 8) A-pq; B-qst; C-pr; D-pr 9) A-qrst; B-p; C-p; D-qrst 10) 6 11) 5 12) 6
 13) 8 14) 2

