Level-II

Chapter 11

Haloalkanes and Haloarenes

Solutions

SECTION - A

Objective Type Questions (One option is correct)

1. Consider the following reaction :

Reaction : (I)

$Et - S - CH_2 - CH_2Cl \xrightarrow{H_2\underset{\cdot\cdot}{\ddot{O}}} Et - S - CH_2 - CH_2OH$

Reaction : (II)

$EtO - CH_2CH_2Cl \xrightarrow{H_2\underset{\cdot\cdot}{\ddot{O}}} EtO\text{-}CH_2CH_2OH$

Select the correct statement.

(1) Rate of reaction (I) is more than reaction (II) because S act as neighbouring group

(2) Rate of reaction (II) is more than reaction (I) because O act as neighbouring group

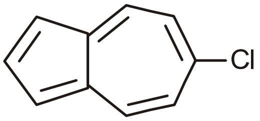
(3) Rate of reaction (I) is more than reaction (II) because S can not act as neighbouring group

(4) Rate of reaction (II) is more than reaction (I) because O can not act as neighbouring group

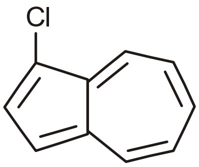
Sol. Answer (1)

Electronegativity of 'S' is less than 'O'. It shows more neighbouring group.

2. Consider the below halogen substituted azulenes



(A)



(B)

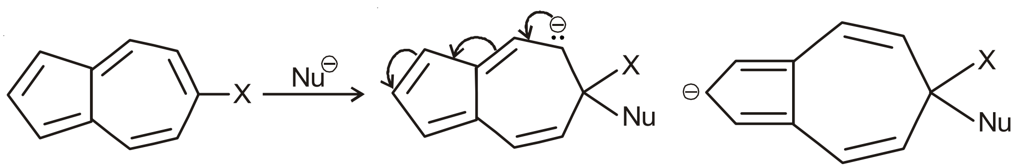
(1) A is more reactive than B towards nucleophilic aromatic substitution reaction with NaOH

(2) A is less reactive than B towards nucleophilic aromatic substitution reaction with NaOH

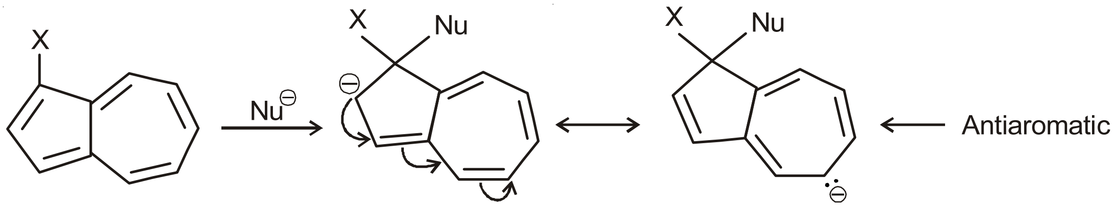
(3) Both A and B are equally reactive towards nucleophilic aromatic substitution with NaOH

(4) Rate of A and B towards nucleophillic aromatic sustitution with NaOH cannot be compared

Sol. Answer (1)



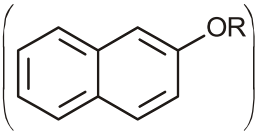
The intermediate have aromatic ring of five carbon so highly stable



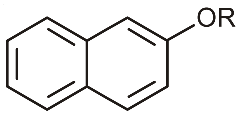
3. Consider the below given statements.

S_1 : In protic solvent the β- naphthoxide ion is alkylated at position I when R–Br is added

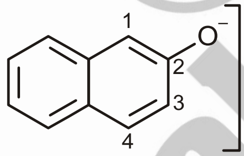
S_2 : In protic solvent the β- naphthoxide ion on reaction with R-Br almost exclusively forms the ether



S_3 : In D.M.F solvent β- naphoxide ion on reaction with R–Br froms exclusively the ether



[Given β-naphthoxide ion is



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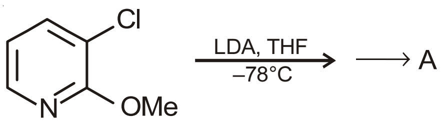
The incorrect statement among the following is/are

(1) Only S_1 (2) Only S_2 (3) Only S_3 (4) Only S_2 and S_3

Sol. Answer (2)

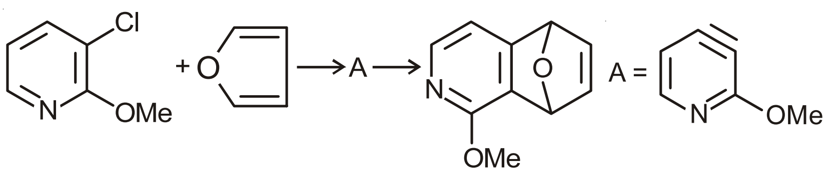
The naphthoxide ion acts as ambident nucleophile (C as well as oxygen act as nucleophilic centre. When polar protic solvent is added, that forms bond with H^+ so nueclophilicity of oxygen atom decreases and C-alkylation takes place but in polar aprotic solvent 'O' alkylation takes place.

4. A on reaction with furan form B as major product. The number of H-atom in one molecule of B are

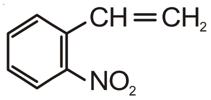


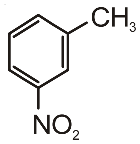
(1) 6 (2) 9 (3) 10 (4) 12

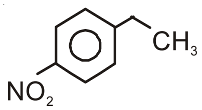
Sol. Answer (2)

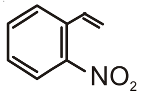


5. Hydrocarbon Y give racemic mixture on reaction with Cl_2 in the presence of sunlight to form monochlorinated product. The hydrocarbon does not discharge colour of Br_2 water in the presence of CCl_4. This hydrocarbon reacts with C_2H_5Cl in the presence of $AlCl_3$. This hydrocarbon on nitration mainly produces

(1) 

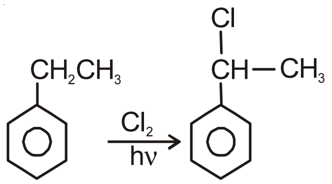
(2) 

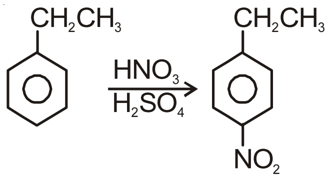
(3) 

(4) 

Sol. Answer (3)

Since it doesnot discharge Br_2/CCl_4 it means it cannot be (1) and (4)





6. Choose correct order of reactivity towards S_N1 reaction.

(1) n-butyl bromide > sec butyl bromide (2) 2-bromo-2-methyl butane < 2-Bromobutane

(3) Vinyl iodide < Allyl bromide (4) 2-chloro butane > 2-iodobutane

Sol. Answer (3)

Allyl carbocation is resonance stablised.

7. Following set of reactions takes place

Reaction I : $C_2H_5Br \xrightarrow{\text{moist } Ag_2O} \underset{\text{major product}}{X} + AgBr$

Reaction II : $C_2H_5Br \xrightarrow{\text{dry silver oxide}} \underset{\text{major product}}{Y} + AgBr$

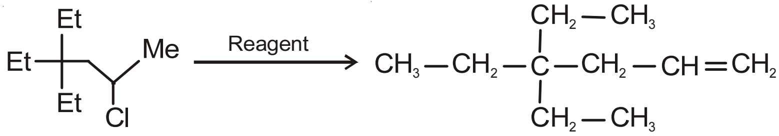
Select correct statement.

(1) Both X and Y are same compounds (2) X and Y are functional isomers of each other

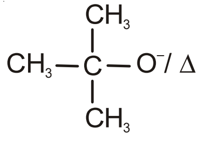
(3) Y on dry heating changes to X (4) Y is ether and X is alcohol

Sol. Answer (4)

X : $C_2H_5 – OH$; Y : $C_2H_5 – O – C_2H_5$

8. 

Among following best reagent for following conversion is

(1) $NaNH_2$ (2) alc. KOH/Δ (3)  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^-/\Delta$ (4) aq. KOH/Δ

Sol. Answer (3)

Bulky base prefers least hindred H.

9. Which of the following is not correct ?

(1) Sandmeyers reaction is used to prepare arylchloride and aryl bromide

(2) Gattermann's reaction is modification of sandmeyer's reaction

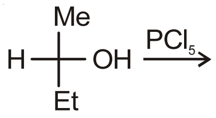
(3) Chlorobenzene can be prepared by chlorination of benzene in the presence of $FeCl_3$

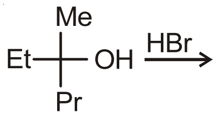
(4) We can get good yeild of Iodobenzene just by heating benzene with Iodine in the presence of Iodide

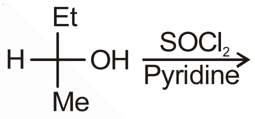
Sol. Answer (4)

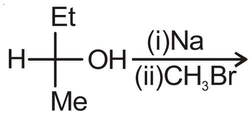
Iodination is reversible.

10. In which of following reactions configuration about chiral carbon is retained?

(1) 
$\mathrm{H}-\overset{\mathrm{Me}}{\underset{\mathrm{Et}}{\mathrm{C}}}-\mathrm{OH} \xrightarrow{PCl_5}$

(2) 
$\mathrm{Et}-\overset{\mathrm{Me}}{\underset{\mathrm{Pr}}{\mathrm{C}}}-\mathrm{OH} \xrightarrow{HBr}$

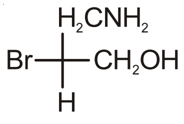
(3) 
$\mathrm{H}-\overset{\mathrm{Et}}{\underset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{OH} \xrightarrow[\text{Pyridine}]{SOCl_2}$

(4) 
$\mathrm{H}-\overset{\mathrm{Et}}{\underset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{OH} \xrightarrow[\text{(ii)}CH_3Br]{\text{(i)Na}}$

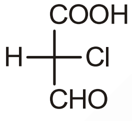
Sol. Answer (4)

No bond of chiral C broken.

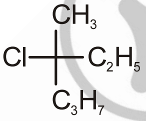
11. Following are compounds I, II, III


$\mathrm{Br}-\overset{H_2CNH_2}{\underset{\mathrm{H}}{\mathrm{C}}}-CH_2OH$

I


$\mathrm{H}-\overset{\mathrm{COOH}}{\underset{\mathrm{CHO}}{\mathrm{C}}}-\mathrm{Cl}$

II


$\mathrm{Cl}-\overset{CH_3}{\underset{C_3H_7}{\mathrm{C}}}-C_2H_5$

III

Select correct statement.

(1) All compounds I, II and III have S configuration

(2) Compound II and III are equally reactive towards Nucleophilic substitution (S_N1)

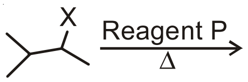
(3) Compound II has different configuration from I and III

(4) Compound I has different configuration from II and III

Sol. Answer (3)

Compound I and III have S-configuration.

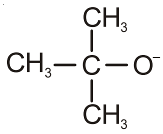
12. Consider following reaction



Compound A (major)

Where X is halogen and P is reagent used for reaction then correct statement is

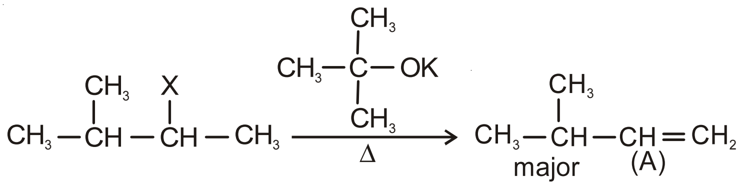
(1) If reagent P is potassium hydroxide in alcohol then compound A is alcohol

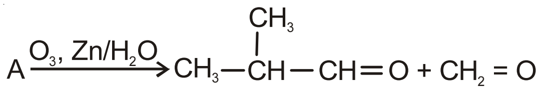
(2) If reagent P is 
$CH_3-\overset{CH_3}{\underset{CH_3}{\mathrm{C}}}-O^-$
the product B on reductive ozonolysis give aldehyde containing one carbon atom as one of products

(3) If P is potassium hydroxide is used when water is medium then main product is alkene

(4) If reagent P is C_2H_5ONa then rearranged product is formed and mechanism is S_N2

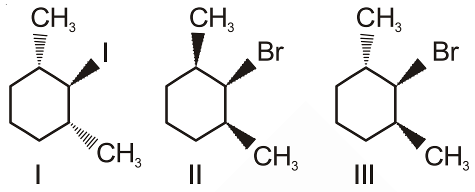
Sol. Answer (2)





$$A \xrightarrow{O_3,\ Zn/H_2O} CH_3-\overset{CH_3}{\overset{|}{C}H}-CH=O + CH_2=O$$

13. Assume following set of compounds which undergo elimination (E_2)



Correct statement among following is

(1) Compound I is more reactive than compound II

(2) Compound I and III are equally reactive

(3) Compound II is more reactive than I as well as III

(4) Compound I is more reactive than compound III

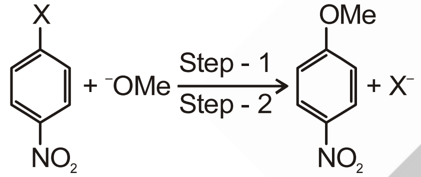
Sol. Answer (3)

Order of reactivity

II > III > I

More number of anti hydrogen

14. Consider following reaction



X = F, Cl, Br, I

The incorrect statement among following is

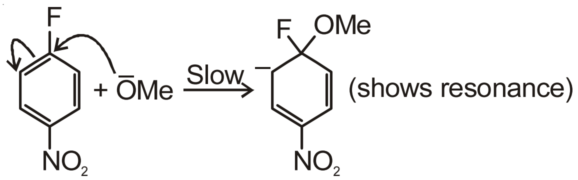
(1) Reaction occurs in two steps and second step involving loss of leaving group is RDS

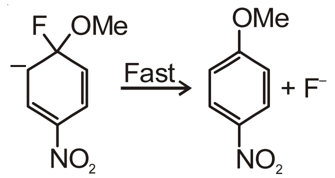
(2) Reactivity is maximum if X = F

(3) The first step involving attack of $^{-}$OMe is RDS

(4) Fluoride is poor leaving group

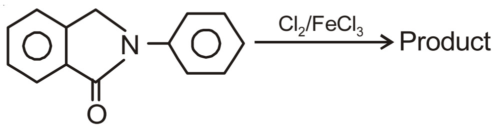
Sol. Answer (1)

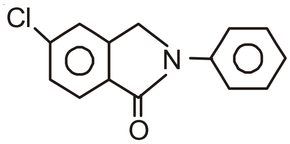


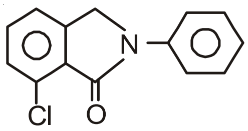


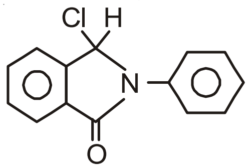
EN of F is maximum so it stabilises negative charge more.

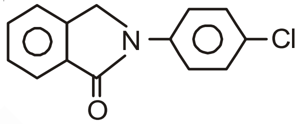
15. Product formed in following reaction is



(1) 

(2) 

(3) 

(4) 

Sol. Answer (4)

Substitution occurs at activated ring.

16. Which combination among following give compound which on reaction with conc. HNO_3 give a gas which bring tear in eyes?

(1) Iodine + Ethyl alcohol $\xrightarrow{\Delta}$

(2) Benzene + Acetyl chloride $\xrightarrow{AlCl_3}$

(3) Ethyl alcohol + Bleaching powder suspended in water $\xrightarrow{\Delta}$

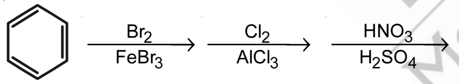
(4) Propyl chloride $\xrightarrow{NaBH_4}$

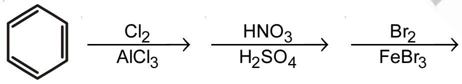
Sol. Answer (3)

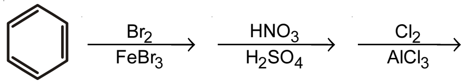
$$C_2H_5OH \xrightarrow[\text{Powder}]{\text{Bleaching}} CHCl_3$$

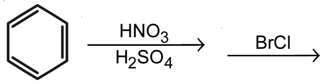
$$CHCl_3 \xrightarrow{HNO_3} \underset{\text{chloropicrin tear gas}}{CCl_3NO_2}$$

17. Which of following scheme would be best for synthesis of 1-Bromo - 2-chloro - 4-nitrobenzene?

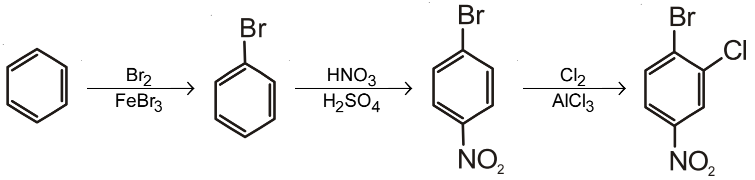
(1) 

(2) 

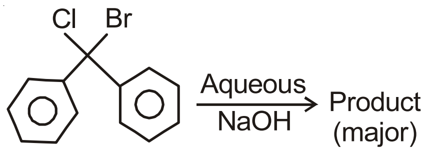
(3) 

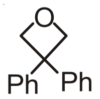
(4) 

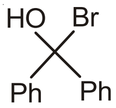
Sol. Answer (3)

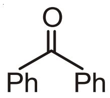


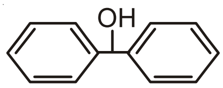
18. The major product of reaction is



(1) 

(2) 

(3) 

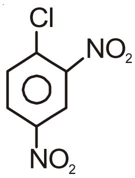
(4) 

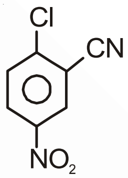
Sol. Answer (3)

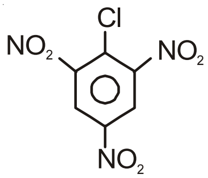
Hydrolysis of Geminal dihalides produces carbonyl compound.

19. Among the following, select the compound which undergoes hydrolysis at maximum rate.

(1) 

(2) 

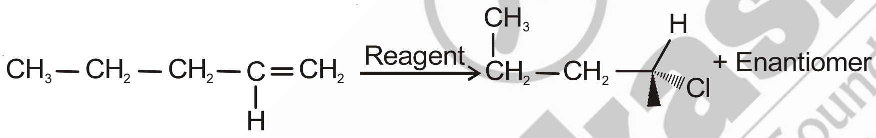
(3) 

(4) 

Sol. Answer (4)

More is number of EWG more is rate of reaction.

20. The reagent used for following reaction is



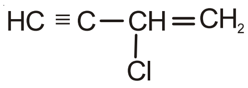
(1) NaCl (2) KCl (3) Cl_2 (4) HCl

Sol. Answer (4)

Carbocation is formed with HCl.

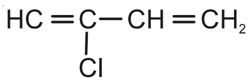
21. The major product of reaction is

$HC\equiv C-CH=CH_2 \xrightarrow[CCl_4]{1\text{ eq. HCl}}$ Product

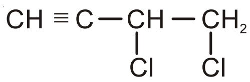
(1) 

$HC\equiv C-CH(Cl)-CH=CH_2$

(2) $HC\equiv C-CH=CH-Cl$

(3) 

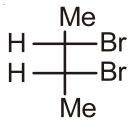
$HC=C(Cl)-CH=CH_2$

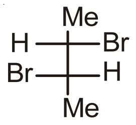
(4) 

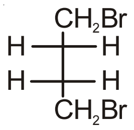
$CH\equiv C-CH(Cl)-CH_2(Cl)$

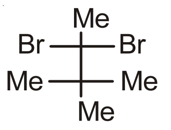
Sol. Answer (3)

22. Compound X is treated with $H_2/Pd/BaSO_4$ to give Y which was further treated with Bromine in the presence of CCl_4 to give Z. If X has formula C_4H_6 and it decolourises Br_2 water. X on reductive ozonolysis give Butane - 2, 3–dione. Then compound Z can be

(1) 

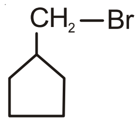
(2) 

(3) 

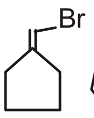
(4) 

Sol. Answer (2)

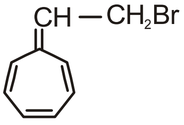
23. Among following compounds, select the correct order of reactivity towards S_N1.



I



II



III

(1) III is more reactive than I

(2) II is more reactive than III

(3) I is less reactive than II

(4) Both I and III are equally reactive

Sol. Answer (1)

Stable intermediate.

SECTION - B

Objective Type Questions (More than one options are correct)

1. There are two different ways of making 2-ethoxyoctane from 2-octanol using the Williamson ether synthesis

Method-I: When pure (–) octan-2-ol of specific rotation –8.24° is treated with sodium metal and then ethyl iodides the product is 2-ethoxyoctane with a specific rotation of –15.6°.

Method-II: When pure (–) 2-octan-2-ol is treated with tosyl chloride and pyridine and then with sodium ethoxide, the product is 2-ethoxy octane with specific rotation x°.

On the basis of this information, select the correct statement(s).

(1) Value of x is + 8.24°

(2) Value of x is + 15.6°

(3) In 2-Ethoxyoctane formed by method-I, the configuration of chiral carbon is same as of reactant

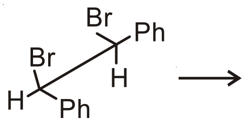
(4) In 2-ethoxyoctane produced method-II, the configuration of chiral carbon is different than reactant

Sol. Answer (2, 3, 4)

In method I, bond between chiral centre and oxygen is not broken so retention of configuration occur while in method II, inversion of configuration takes place so 2-ethoxy octane obtained method I and method II are enantiomers.

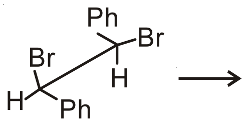
2. Consider the given E_2 reaction in which HBr is eliminated.

Reaction-I :



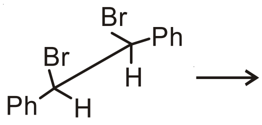
Major organic product (M)

Reaction-II :



Major organic product (N)

Reaction-III :



Major organic product (O)

Select the correct statement(s).

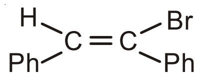
(1) M and N are diastereomers

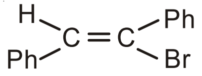
(2) M and O are identical compound

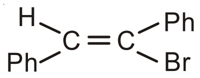
(3) N and O are identical compound

(4) M is an (E) alkene while O is (Z) alkene

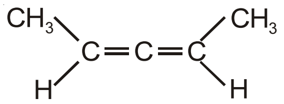
Sol. Answer (1, 3, 4)

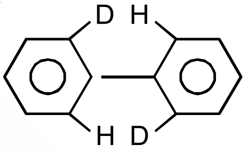
M →


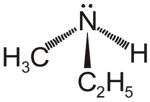
N →


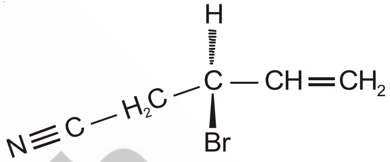
O →


3. Which of the following cannot be resolved into enantiomers?

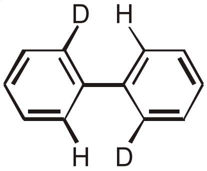
(1)


(2)


(3)


(4)


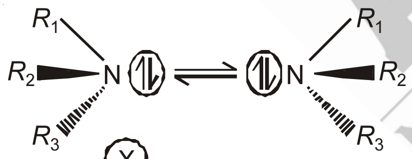
Sol. Answer (2, 3)



Ⓦ

It has free rotation along C – C bond. Connecting two rings and hence the molecule will have plane of symmetry. Therefore it is achiral.

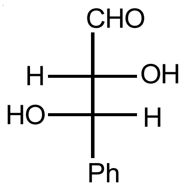
Moreover, trisubstituted amines ($NR_1R_2R_3$) always exist in dynamic equilibrium with its enantiomer.

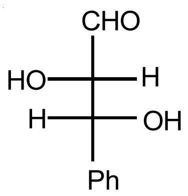
i.e.,


Ⓧ

Ⓦ and Ⓧ cannot be resolved.

4. Consider the following pair of compounds





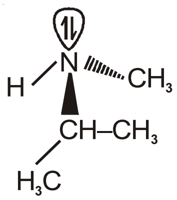
Which of the following statement is correct?

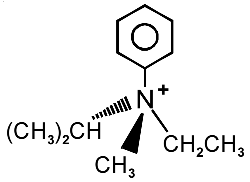
(1) Both are enantiomers
(2) Both are in threo form
(3) Both are diastereomers
(4) Both are in erythro form

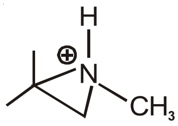
Sol. Answer (1, 2)

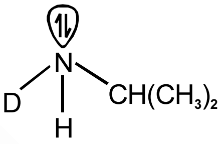
Both are non super impossible mirror image of each other and OH are in different side.

5. Which of the following compounds can be resolved into enantiomers?

(1) 

(2) 

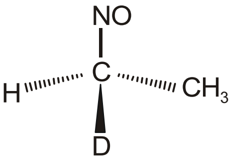
(3) 

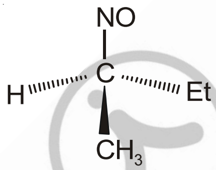
(4) 

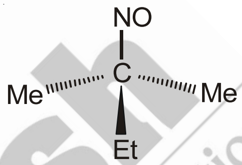
Sol. Answer (2, 3)

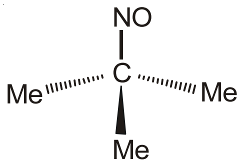
In (1) and (4) enantiomers are in dynamic equilibrium due to low barrier of interconversion.

6. Which of the following nitroso compounds are in dynamic equilibrium with their tautomers?

(1) 

(2) 

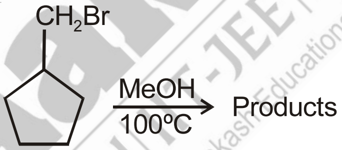
(3) 

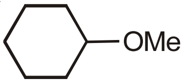
(4) 

Sol. Answer (1, 2)

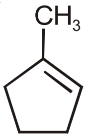
Both have α-hydrogen.

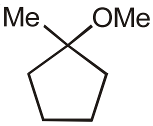
7. Which of the following products are expected from the solvolysis of bromomethyl cyclopentane?



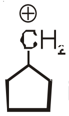
(1) 

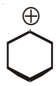
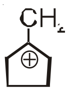
(2) 

(3) 

(4) 

Sol. Answer (1, 2, 3, 4)

In this reaction,  is formed, which can show ring expansion and as well as rearrangement converted into

 and  . After this both carbocation can show elimination as well as substitution reaction. So, all products are formed.

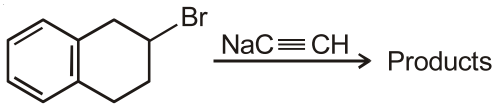
8. Which of the following reactions follows concerted mechanism?

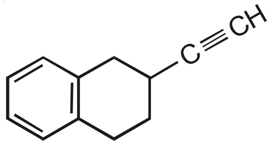
(1) S_N1 (2) S_N2 (3) E_1 (4) E_2

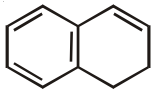
Sol. Answer (2, 4)

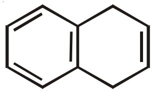
S_N2 and E_2 are the concerted mechanism, in which no intermediate is formed.

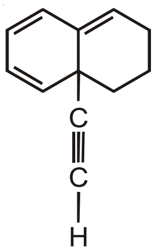
9. What would be the probable products of the given reaction?



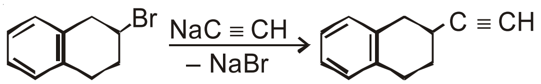
(1) 

(2) 

(3) 

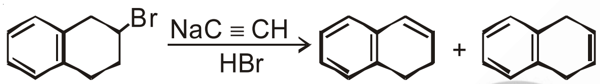
(4) 

Sol. Answer (1, 2, 3)

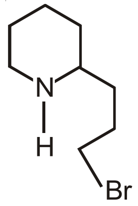


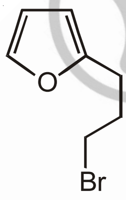
(Substitution Reaction)

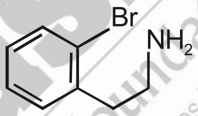
$CH\equiv\overset{\ominus}{C}$ acts as strong base and it shows dehydrohalogenation

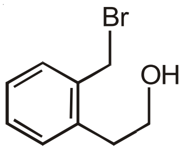


10. Under the presence of alkali which of the following substrate will give intramolecular S_N2 reaction?

(1) 

(2) 

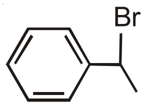
(3) 

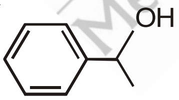
(4) 

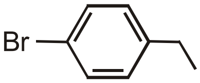
Sol. Answer (1, 4)

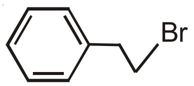
In 2nd option, O atom has no hydrogen atom and in 3rd option, Br atom is attached with benzene ring so, only the substrate of (1) and (4) will give intramolecular S_N2 reaction.

11. Dehydrohalogenation and acidcatalyzed dehydration reactions are frequently used to prepare alkenes from corresponding alkylhalides and alcohols. Out of the given substrates which can be used to prepare styrene?

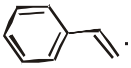
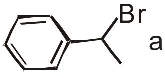
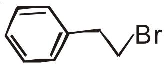
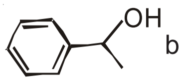
(1) 

(2) 

(3) 

(4) 

Sol. Answer (1, 2, 4)

Styrene is  .It can be prepared from  and  by dehydrohalogenation and from  by acid catalyzed dehydration.

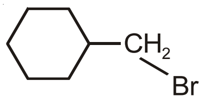
12. When ethyl chloride reacts with ethanolic sodium nitrite, products formed are

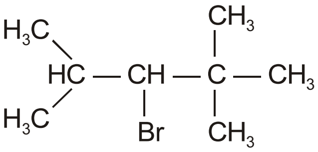
(1) Ethylnitrite (2) Nitroethane (3) Ethanol (4) Diethylether

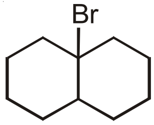
Sol. Answer (1, 2)

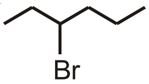
$$C_2H_5Cl\xrightarrow[\text{(Alcoholic)}]{NaNO_2}\underset{\text{Ethyl nitrite (Major)}}{[C_2H_5-O-NO]}+\underset{\text{Nitroethane (Minor)}}{[C_2H_5-NO_2]}$$

13. Which of the following alkylhalides will give one alkene (more than 90%) on dehydrohalogenation under the presence of sodium alkoxide and Ethanol?

(1) 

(2) 

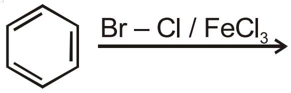
(3) 

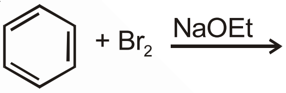
(4) 

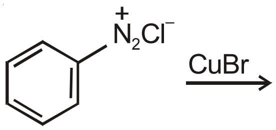
Sol. Answer (1, 2, 3)

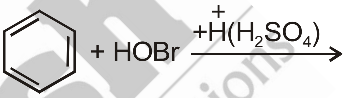
Tertiary alkyl halides mostly give elimination reaction rather than substitution reaction. Because it can produce most stable alkene.

14. Which of the following reactions can be used to introduce bromine atom in benzene ring?

(1) 

(2) 

(3) 

(4) 

Sol. Answer (1, 3, 4)

In option (1) and (4) Br can be introduced in aromatic ring through electrophilic substitution reaction. While in option (3) Br can be introduced through diazotization.

15. Aryl halides are practically inert towards nucleophilic substitution reactions. The reasons for this fact are

(1) Because C — X bond has partial double bond character due to conjugation between lone pair of X and π electrons of aromatic ring

(2) No S_N1 reaction because aryl carbocations are unstable

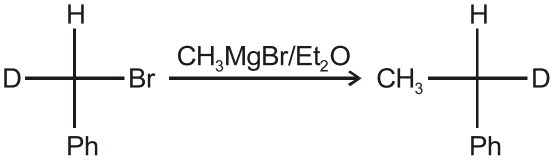
(3) No S_N2 reaction because aromatic π electron cloud do not allow backside attack of Nu^-

(4) Product obtained through nucleophilic substitution reactions are non aromatic

Sol. Answer (1, 2, 3)

Aryl halides are inert towards nucleophilic substitution reaction because C – X bond has partial double character and $Nu^{\ominus}$ can't attack on back side due to π electron cloud and aryl carbocations are unstable.

16. Consider the following reaction



Correct statement regarding the given product is

(1) Inversion of configuration occurs at chiral centre

(2) The reaction follows S_N2 mechanism

(3) Rate of reaction increases with increasing the concentration of CH_3MgBr

(4) The reaction follows S_N1 mechanism and hence racemization occurs

Sol. Answer (2, 3)

The reaction is S_N2 because inversion of configuration takes place but it is not necessary that the optical rotation is inverted. It may or may not be. In this reaction, reactant and product are present in R configuration. So, inversion of configuration at chiral centres does not take place.

17. Which of the following statements are true about aryl halides?

(1) Formation of phenol from chlorobenzene through Dow's process involves S_N2 mechanism

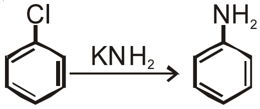
(2) Presence of electron withdrawing groups at o- and p-positions in aryl halide leads to the greater reactivity towards a nucleophile

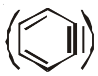
(3) When chlorobenzene is treated with KNH_2 benzyne intermediate is formed

(4) At NTP chlorobenzene reacts with NaOMe to give phenylmethyl ether

Sol. Answer (2, 3)

Presence of electron withdrawing groups at ortho and para positions in aryl halide leads to the greater reactivity towards a nucleophile.



In this reaction, benzyne  intermediate is formed.

Benzene ring should be framed as hexagon.

18. Which of the following reagents can be used to convert alkyl halide into alkane?

(1) Action of Grignard reagent

(2) Action of Bu_3SnH

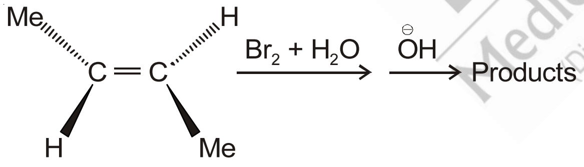
(3) Action of superacid

(4) Action of $K^+O^-C(CH_3)_3$

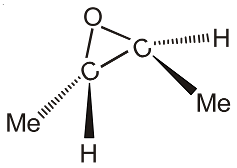
Sol. Answer (1, 2)

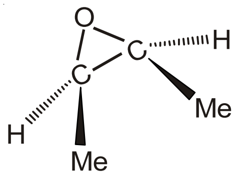
Action of Grignard reagent and Bu_3SnH can be used to convert alkyl halide into alkane. Super acid is used for oxidation and $K^+O^-C(CH_3)_3$ is used as dehydrohalogenating agent.

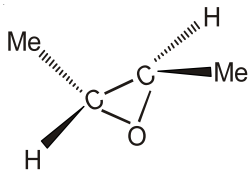
19. Consider the following sequence of reaction.

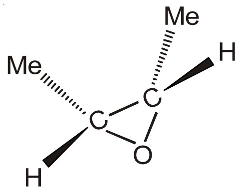


Identify the structures of products.

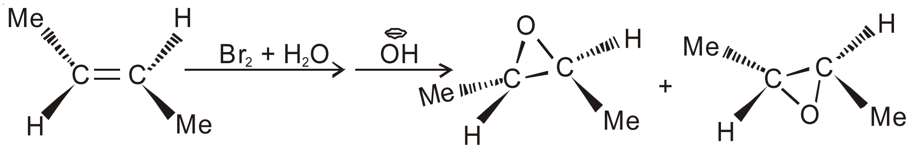
(1) 

(2) 

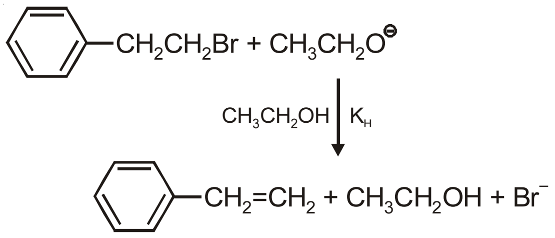
(3) 

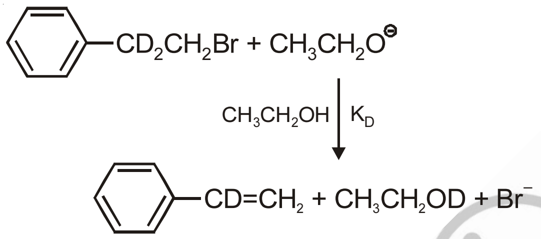
(4) 

Sol. Answer (1, 3)



20.





If K_H and K_D are the rate constant of their respective reactions then which of the following is/are true for reactions?

(1) At same temperature K_H is found to be 7.1 times K_D

(2) At same temperature K_D is found to be 7.1 times K_H

(3) Less energy required to break a C—H bond compared to C—D bond

(4) Less energy required to break a C—D bond compared to C—H bond

Sol. Answer (1, 3)

A carbon-deuterium bond stronger than carbon-hydrogen bond.

SECTION - C

Linked Comprehension Type Questions

Comprehension-I

Compound which rotates the plane polarised light is known as optically active compound. On the basis of direction of rotation, two forms of an optically active compounds are termed as dextro and laevo rotatory. The two are termed as enantiomers. If we have a 1 : 1 mixture of *d* and *l* isomers of a given chiral compound, optical rotation of such mixture is zero. Such a mixture is optically inactive and is called a racemic modification.

The net specific rotation of any mixture of the *d* and *l* isomers of a given chiral compound is equal to the weighted average of the rotations due to both the isomers. Mathematically, it can be expressed as:

$$[\alpha]_{net} = f_d[\alpha_d] + f_l[\alpha_l]$$

where f_d and f_l are fractions of *d* and *l* isomers respectively and $[\alpha_d], [\alpha_l]$ are their specific rotations.

1. The pure *d* isomer of certain chiral compound has $[\alpha]_d^{25} = +55^\circ$. A non racemic mixture of this compound has a net $[\alpha]_d^{25} = -11^\circ$. What is the fraction of this isomer in mixture?

(1) 0.40 (2) 0.60 (3) 0.30 (4) 0.70

Sol. Answer (1)

Rotation is –11º, it means 80% Racemisation and 20% inversion takes place. Or 60% inversion and 40% retention takes place.

2. What is the enantiomeric excess in any pure sample of an optically active substance?

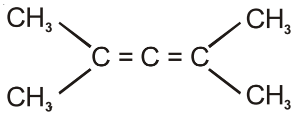
(1) 50% (2) 100%

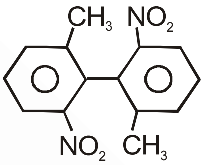
(3) 0% (4) Depends upon the specific rotation

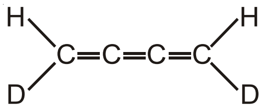
Sol. Answer (2)

It is 100%.

3. Which of the following molecule can resolved into enantiomers?

(1)


(2)


(3)


(4) All of these

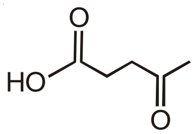
Sol. Answer (2)

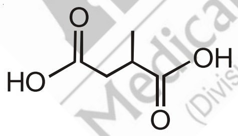
Only (2) is chiral and hence resolvable.

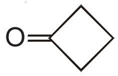
Comprehension-II

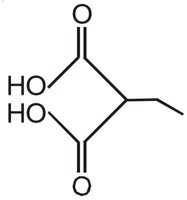
A compound Ⓐ has molecular formula C_5H_9Cl. It does not react with bromine in CCl_4. On treatment with a strong base it produces a single compound Ⓑ. Ⓑ has a molecular formula C_5H_8 and reacts with Baeyer's reagent. Reductive ozonolysis of Ⓑ produces a compound Ⓒ which has a molecular formula $C_5H_8O_2$.

1. What would be the oxidative ozonolysis product of B?

(1)


(2)


(3) HCOOH +


(4)


Sol. Answer (2)

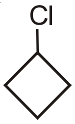
2. Formation of Ⓑ from Ⓐ involves

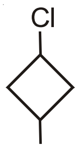
(1) S_N2 mechanism (2) E_1 mechanism

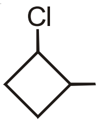
(3) E_2 mechanism (4) 50% E_1 and 50% E_2 mechanism

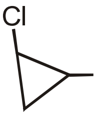
Sol. Answer (3)

3. On the basis of the given data what would be the structure of A?

(1)


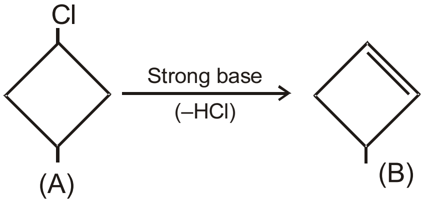
(2)


(3)


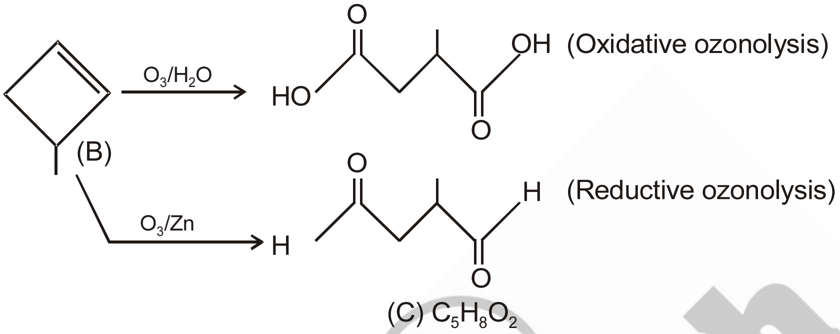
(4)


Sol. Answer (2)

Compound (A) doesn't react with Br_2 in CCl_4. It shows that it has no double bond and compound is cyclic and it gives a single compound, So, — CH_3 and —Cl is attached symmetrically.

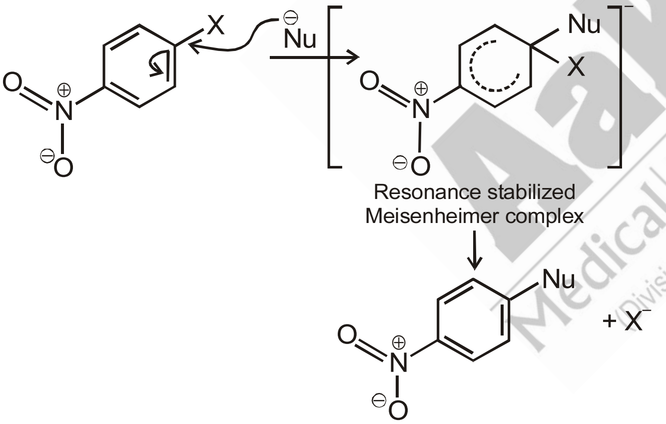


Formation of (B) from (A) follows E_2 mechanism.

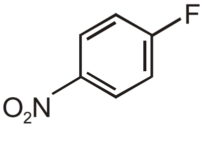


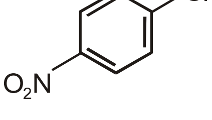
Comprehension-III

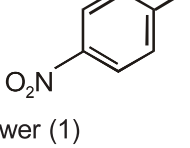
Because of the resonance stabilization of Arylhalides they are unreactive towards normal nucleophilic substitution reactions. However arylhalides having strong electron withdrawing groups at ortho and para positions give aromatic nucleophilic substitution reactions (S_NAr mechanism), which involves a resonance stabilized carbanion called Meisenheimer complex.

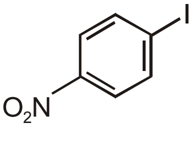


1. Which arylhalide is most reactive towards S_NAr mechanism?

(1)


(2)


(3)


(4)


Sol. Answer (1)

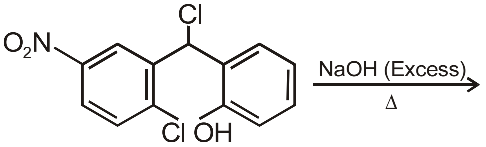
Aryl-fluoride is most reactive towards Nucleophilic aromatic substitution because it provides more stable Meisenheimer complex.

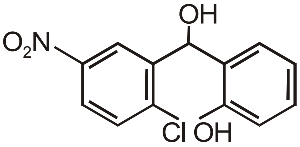
2. Which of the following statement is/are true?
   (1) S_NAr proceeds through elimination / addition mechanism
   (2) Formation of elimination product is the rate determining step
   (3) Formation of Meisenheimer complex is the rate determining step
   (4) S_NAr mechanism involves inversion of configuration

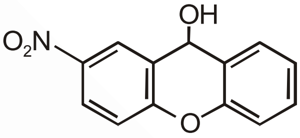
Sol. Answer (3)

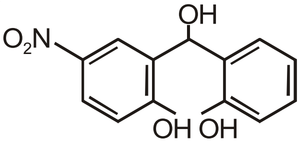
Formation of Meisenheimer complex is the rate determining step.

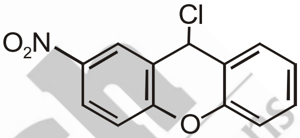
3. What would be the product of the given reaction?



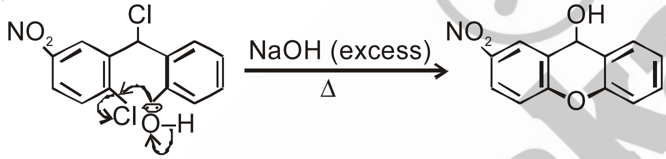
(1)


(2)


(3)


(4)


Sol. Answer (2)

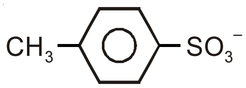


The Cl atom which is attached with benzene ring replaces easily due to presence of —NO_2 group at p-position w.r.t. Cl.

SECTION - D

Matrix-Match Type Questions

1. Match the following.

	Column-I		**Column-II**
(A)	I^-	(p)	A good leaving group
(B)	F^-	(q)	Very weak base
(C)	 $CH_3-C_6H_4-SO_3^-$	(r)	A good nucleophile in polar protic solvent
(D)	OH^-	(s)	A poor leaving group

Sol. Answer A(p, q, r), B(s), C(p, q), D(s)

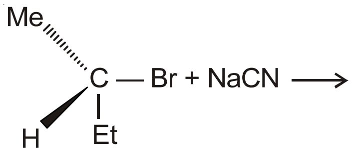
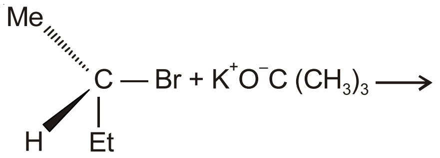
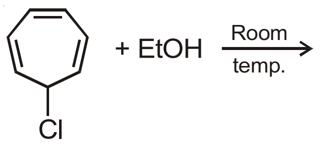
(A) I^- is weak base, good leaving group and good nucleophile in polar protic solvent.

(B) F^- is poor leaving group due to strong base.

(C)  $CH_3-C_6H_4-SO_3^-$ is good leaving group due to weak base.

(D) $\bar{O}H$ is poor leaving group due to strong base.

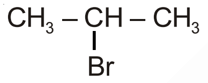
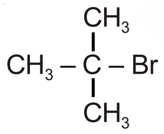
2. Match Column-I reaction condition with Column-II mechanistic path for the formation of major product.

Column-I (Reaction condition)	**Column-II (Mechanistic path)**
(A) 	(p) E_2
(B) 	(q) S_N2
(C) 	(r) S_N1
(D) $(CH_3)_3C-OH \xrightarrow{+H^{\oplus},\Delta}$	(s) E_1

Sol. Answer A(q), B(p), C(r), D(s)

See reaction conditions and mechanism of classical reaction.

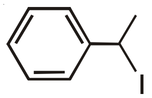
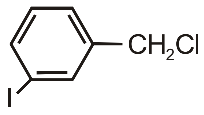
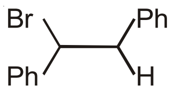
3. Match the following reactant in Column-I with reducing agent in Column-II to produce alkane.

Column-I (Reactant)	**Column-II (Reducing agent)**
(A) $CH_3-CH_2-CH_2Cl$	(p) $LiAlH_4$
(B)  $CH_3-\underset{\displaystyle Br}{\underset{\vert}{CH}}-CH_3$	(q) $NaBH_4$
(C)  $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-Br$	(r) Bu_3SnH
(D) CH_3CH_2Br	(s) Red P + HI

Sol. Answer A(p, r, s), B(p, q, r, s), C(q, r, s), D(p, q, r, s)

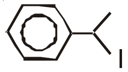
See reagents and conditions.

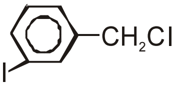
4. Match the **Column-I** with **Column-II.**

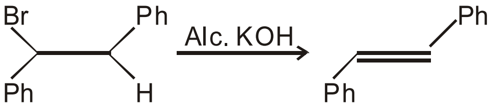
Column-I (Compounds)	**Column-II (Properties indicated)**
(A) $CH_2=CH-CH_2Cl$	(p) White precipitate with Aqueous $AgNO_3$
(B) 	(q) Yellow precipitate with $AgNO_3$
(C) 	(r) Fairly reactive towards E_2
(D) 	(s) Fairly reactive towards S_N reaction

Sol. Answer A(p, s), B(q, r, s), C(p, s), D(r)

(A) $CH_2 = CH - CH_2 - Cl \xrightarrow[H_2O]{AgNO_3} \underset{\text{White ppt.}}{AgCl\downarrow} + CH_2 = CH - CH_2 - OH.$

(B)  gives E_2 as well as S_N reaction and also gives yellow ppt. of AgI with $AgNO_3$

(C)  gives white ppt. of AgCl with $AgNO_3$

(D) 

SECTION - E

Assertion-Reason Type Questions

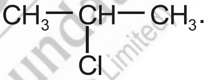
1. STATEMENT-1 : Aryl halides are more reactive than alkyl halides towards nucleophilic substitution reaction.

and

STATEMENT-2 : Aryl halides have stronger C — X bond as compared to alkyl halides.

Sol. Answer (4)

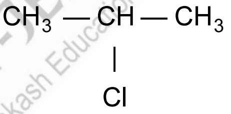
Aryl halides are less reactive than alkyl halides towards nucleophilic substitution reaction because in aryl halide C —X bond has partial double bond character.

2. STATEMENT-1 : $CH_3—O—CH_2—Br$ is hydrolyzed more readily than  $\underset{\displaystyle Cl}{CH_3-CH-CH_3}$.

and

STATEMENT-2 : Secondary halides are more reactive than primary alkyl halides towards hydrolysis.

Sol. Answer (2)

$CH_3 — O — CH_2 — Br$ is hydrolyzed more readily than  $\underset{\displaystyle Cl}{CH_3 - CH - CH_3}$ because C — O bond is more polar than C — Cl bond.

3. STATEMENT-1 : $CHCl_3$ is more acidic than CHF_3.

and

STATEMENT-2 : $\overset{\ominus}{C}Cl_3$ is stabilized through pπ - dπ back bonding.

Sol. Answer (1)

$CHCl_3$ is more acidic than CHF_3 because $\overset{\ominus}{C}Cl_3$ is stabilized through pπ — dπ back bonding while $\overset{\ominus}{C}F_3$ is stabilized by –I effect of F atom.

4. STATEMENT-1 : S_N2 reaction of $CH_3–Br$ is faster in DMSO than in H_2O.

and

STATEMENT-2 : DMSO has greater capability to solvate nucleophile.

Sol. Answer (3)

In polar aprotic solvent like DMSO, S_N2 reaction is faster than in polar protic solvent like H_2O. Polar protic solvent has greater capability to solvate nucleophile than polar aprotic solvent.

5. STATEMENT-1 : When treated with $AgNO_2$ ethyl bromide gives. $CH_3CH_2 – NO_2$ as the major product.

and

STATEMENT-2 : $\overset{\ominus}{N}O_2$ is an ambident nucleophile.

Sol. Answer (2)

When ethyl bromide is treated with $AgNO_2$ then $CH_3CH_2 — NO_2$ is the major product because $AgNO_2$ is covalent compound. However, $\overset{\ominus}{N}O_2$ is an ambident nucleophile.

6. STATEMENT-1 : Tertiary alkyl halides are more reactive than 1° alkyl halide towards elimination.

and

STATEMENT-2 : Tertiary alkyl halides give more stable carbanion.

Sol. Answer (3)

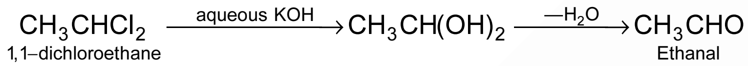
Tertiary alkyl halides are more reactive than 1° alkyl halide towards elimination because it gives most stable alkene.

7. STATEMENT-1 : 1, 1-dichloroethane on treatment with aq. KOH yield ethanal.

and

STATEMENT-2 : Ethylene dichloride is a unsaturated compound.

Sol. Answer (3)



$$\underset{\text{1,1–dichloroethane}}{CH_3CHCl_2} \xrightarrow{\text{aqueous KOH}} CH_3CH(OH)_2 \xrightarrow{—H_2O} \underset{\text{Ethanal}}{CH_3CHO}$$

Ethylene dichloride ($Cl — CH_2 — CH_2 — Cl$) is not an unsaturated compound.

SECTION - F

Integer Answer Type Questions

1. Total type of reactions of an alkyl halide can give out of the given reaction type:

S_N1,	S_N2,	E_1,	E_2,	E_{ICB},	S_Ni
I	II	III	IV	V	VI

Sol. Answer (5)

S_Ni reaction is given by alcohol, not by alkyl halide.

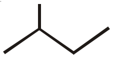
2. How many of the given reagents can be used to convert alcohol into alkyl halide?

NaBr	NaCl	HBr	PCl_3	$SOCl_2$
I	II	III	IV	V
HCl (conc.)/$ZnCl_2$ (anhy),		NaI	HI	PCl_5
VI		VII	VIII	IX

Sol. Answer (6)

Only NaCl, NaBr and NaI can't be used to convert alcohol into alkyl halide.

3. Total number of monochloroderivatives (including stereoisomers) possible for the given compound would be



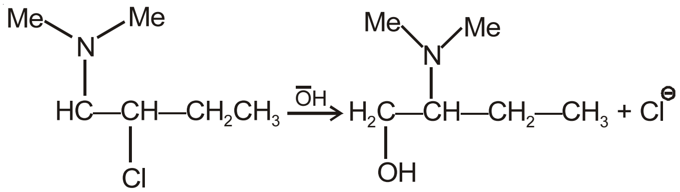
Sol. Answer (6)

4. How many of the given nucleophiles will predominantly give substitution reaction with 3-bromo-cyclohexene?

$\overset{\ominus}{N}H_2, CH_3CO\overline{O}, \overset{\ominus}{N}_3, (CH_3)_3C\overline{O}, \overline{S}H, I^-, Br^-, CH_3\overline{S}$, alc. KOH

Sol. Answer (6)

5. What would be order of the given reaction?

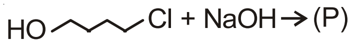


$$\mathrm{HC(NMe_2)-CH(Cl)-CH_2CH_3} \xrightarrow{\overline{O}H} \mathrm{H_2C(OH)-CH(NMe_2)-CH_2-CH_3} + \mathrm{Cl^{\ominus}}$$

Sol. Answer (2)

Due to neighbouring group participate of nitrogen lone pair.

6. Consider the following reaction



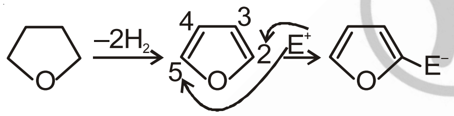
P is the major organic product. Due to dehydrogenation of P, two mol of H_2 is removed and P convert into an aromatic compound A. In A, oxygen is first numbered atom according to IUPAC nomenclature. The E^+ attack on A to form a major product in electrophilic aromatic substitution reaction. The number of carbon at which electrophile attack is x, then $(x + 6)^2$ is [x is the minimum number possible]

Sol. Answer (64)

x = 2

$(x + 6)^2 = 64$

P →



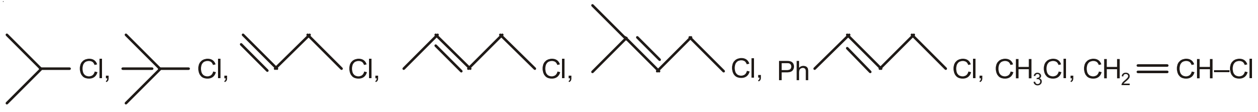
7. Halogen are ortho/para director but they are deactivating. The molar mass of halobenzene is M that have maximum ratio of para to ortho product during the nitration. The value of $\frac{M}{4}$ is (molar mass of C, H, F, Cl, Br and I is 12, 1, 19, 35, 79 and 127 respectively)

Sol. Answer (24)

has highest ratio of para to ortho product

M = 96, $\frac{M}{4} = 24$

8. Some of the alkyl halide are given in which x alkyl halides have more rate of reaction than n-propylchloride in S_N1 reaction with 50% aqueous ethanol



Value of 2x is

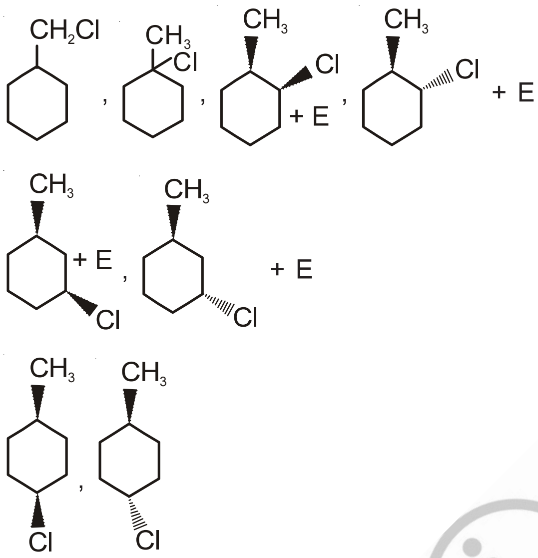
Sol. Answer (12)

x = 6

The alkyl halide which form stable carbocation than $CH_3CH_2CH_2^+$ show higher rate than $CH_3CH_2CH_2Cl$.

9. If methyl cyclohexane is treated with Cl_2 in the presence of UV light certain isomers will form. If n number of isomers (including stereoisomes) having molecular formula $C_7H_{13}Cl$ will be formed, then the value of $\left(\frac{10.n}{3}\right)$ will be equal to

Sol. Answer (40)



(E is the enantiomer of the corresponding isomer)

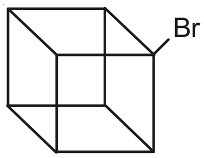
n = 12

10. Consider the following statements :

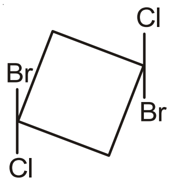
a. Substitution reaction in alkyl halides is possible in both aqueous and polar aprotic medium.

b. The nucleophilic strength and basic strength for $\overset{-}{C}H_3$, $\overset{-}{N}H_2$, $\overset{-}{O}H$ and F^- have same order.

c. SCN^- is an ambident nucleophile.

d. 

the double bond equivalence of this molecule is 6.

e. 

has centre of symmetry.

f. Butane – 2 – ol is optically active.

The sum of correct statements number is

[Suppose statements 1 and 4 is only correct, then your answer would be 5 (*i.e.*, 1 + 4 = 5)]

Sol. Answer (17)

Except statement 4 all are correct, its double bond equivalence is 5.

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