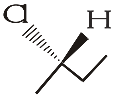
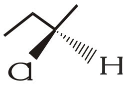
EXERCISE-01 CHECK YOUR GRASP

SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

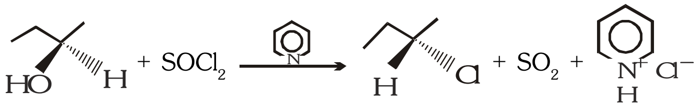
1. The product formed in the reaction  + $SOCl_2 \rightarrow$ is-

(A) 

(B) 

(C) 

(D) 

2. The reaction 

proceeds by the mechanism

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

3. 1, 3- Dibromopropane reacts with metallic zinc to form

(A) propene (B) cyclopropane (C) propane (D) hexane

4. Consider the following reaction sequence,

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

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

(A) CH_3COCH_3 and $CH_3CCl_2CH_3$ (B) CH_3CH_2CHO and $CH_3CH_2CHCl_2$

(C) $CH_3CHOHCH_3$ and $CH_3CHClCH_3$ (D) $CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2Cl$

5. Which of the following has highest dipole moment:

(A) CH_3Cl (B) CH_3F (C) CH_3Br (D) CH_3I

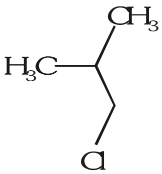
6. In S_{N^1} the first step involves the formation of

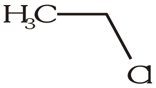
(A) free radical (B) carbanion (C) cabocation (D) final product

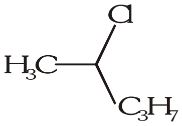
7. To form alkane isonitrile, alkyl halide is reacted with:

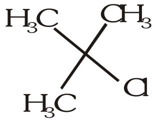
(A) KCN (B) AgCN (C) HCN (D) NH_4CN

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

(A) 

(B) 

(C) 

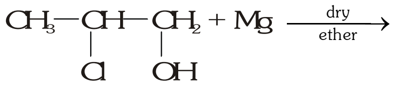
(D) 

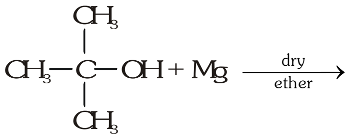
9. Sec. Butyl chloride undergo alkaline hydrolysis in the polar solvent by

(A) S_{N^2} (B) S_{N^1} (C) S_{N^1} and S_{N^2} (D) none of these

10. Grignard reagent can be prepared by

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

(B)

$CH_3-\underset{\substack{|\\ Cl}}{CH}-\underset{\substack{|\\ OH}}{CH_2} + Mg \xrightarrow[\text{ether}]{\text{dry}}$

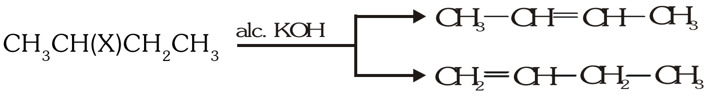
(C)

$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-OH + Mg \xrightarrow[\text{ether}]{\text{dry}}$

(D) All of them

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

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

12. For the reaction



(A) $CH_3-CH=CH-CH_3$ predominates

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

(C) Both are formed in equal amounts

(D) The product ratio depends on the halogen

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

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

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

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

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

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

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

(A) 1–phenylpropene

(B) 2–phenylpropene

(C) 1–phenylpropane–2–ol

(D) 1–phenylpropan–1–ol

17. Grignard reagent is obtained when magnesium is treated with

(A) Alkyl halide in presence of alcohol

(B) Alkyl halide in presence of phenol

(C) Alkyl halide in presence of dry ether

(D) Alkyl halide in presence of alcoholated ether

18. Ethylene reacts with bromine to form -

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

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

(A) CH_3CH_2CN

(B) $NC-CH_2-CH_2-CN$

(C) $Br-CH_2-CH_2CN$

(D) $Br-CH=CHCN$

20. Reactivity order of halides for dehydrohalogenation is

(A) R – F > R – Cl > R – Br > R – I

(B) R – I > R – Br > R – Cl > R – F

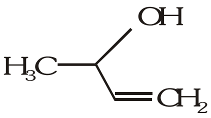
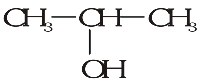
(C) R – I > R – Cl > R – Br > R – F

(D) R – F > R – I > R – Br > R – Cl

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

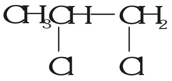
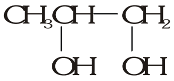
(A) $CH_2=CHCl$ (B) CH_3CH_2Cl (C) $CH_2=CHCH_2Cl$ (D) $(CH_3)_3C-Cl$

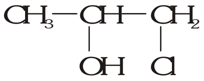
22. The correct reactivity order of alcohols towards H–X will be

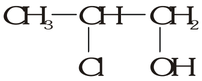
(I) $CH_2{=}CH{-}OH$ (II)  (III) $CH_3{-}CH_2{-}OH$ (IV)  $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

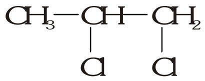
(A) II > I > III > IV (B) IV > III > II > I (C) II > IV > I > III (D) II > IV > III > I

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

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

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

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

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

24. For the reaction,

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

(A) HI > HCl > HBr (B) HI > HBr > HCl (C) HCl > HBr > HI (D) HBr > HI > HCl

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

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

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

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

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

CHECK YOUR GRASP **ANSWER KEY** EXERCISE -1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	B	B	A	A	C	B	B	C	A	C	D	D	B	C
Que.	16	17	18	19	20	21	22	23	24	25					
Ans.	A	C	B	B	B	A	D	B	B	D					

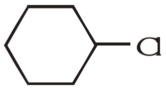
EXERCISE–02 BRAIN TEASERS

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

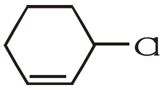
1. Which of the following does/do produce a white precipitate of AgCl on warming with alcoholic silver nitrate?

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

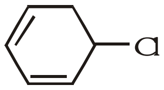
2. What is the order of reactivity of the following compounds towards nucleophilic substitution?



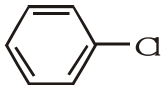
(I)



(II)



(III)



(IV)

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

3. The order of decreasing nucleophilicity of the following is

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

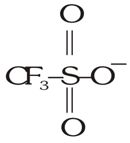
(C) $CH_3COO^- > CH_3O^- > OH^- > H_2O$ (D) $HO^- > CH_3O^- > CH_3COO^- > H_2O$

4. The order of decreasing S_N1 reactivities of the halides

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

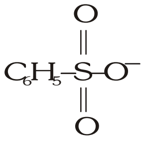
(A) I > II > III (B) II > I > III (C) II > III > I (D) III > II > I

5. Consider the following anions.



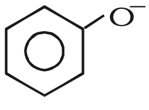
$CF_3-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-$

(I)

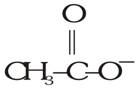


$C_6H_5-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-$

(II)



(III)



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

(IV)

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

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

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

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

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

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

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

7. Which of the following are aprotic solvents :

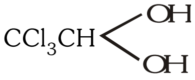
(A) DMSO (B) DMF (C) H_2O (D) CH_3COOH

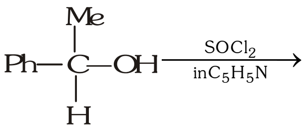
8. Which is/are true statements (s) :

(A) Protonation increases electrophilic nature of carbonyl group

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

(C) Benzyl carbonium ion is stabilised by resonance

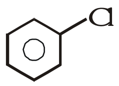
(D)  $CCl_3CH(OH)_2$ is stable,due to H-Bonding

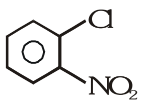
9. 
$Ph-\underset{H}{\overset{Me}{C}}-OH \xrightarrow[inC_5H_5N]{SOCl_2}$

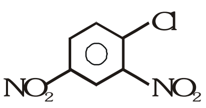
Which statement is true for the above reaction ?

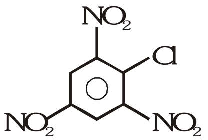
(A) Retention of configuration
(B) Inversion of configuration
(C) Inversion and Retention both
(D) None

10. Which of the following undergoes hydrolysis most easily

(A) 

(C) 

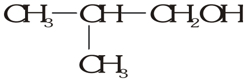
(C) 

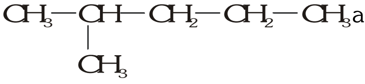
(D) 

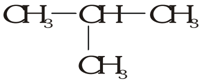
11. A compound 'A' formula of $C_3H_6Cl_2$ on reaction with alkali can give 'B' of formula C_3H_6O or 'C' of formula C_3H_4. 'B' on oxidation gave a compound of the formula $C_3H_6O_2$. 'C' with dilute H_2SO_4 containing Hg^{2+} ion gave 'D' of formula C_3H_6O, which with bromine and alkali gave the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

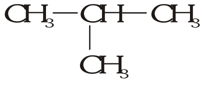
(A) $CH_3CH_2CHCl_2$
(B) $CH_3CCl_2CH_3$
(C) $CH_2ClCH_2CH_2Cl$
(D) $CH_3CHClCH_2Cl$

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

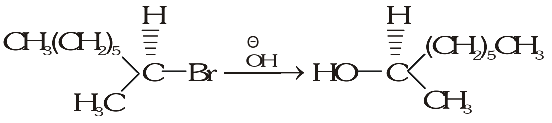
(A) 
$CH_3-\underset{CH_3}{CH}-CH_2OH$ and CH_3CH_2MgBr

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

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

(D) 
$CH_3-\underset{CH_3}{CH}-CH_3$ and CH_3CH_2OMgBr

13. Following reaction is



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

14. 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

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

(A) Retention in configuration
(B) Inversion in configuration
(C) Racemic product
(D) No product

16. Alkyl iodides can be prepared by :-

(A) $RCH_2COOAg + I_2 \xrightarrow[\Delta]{CCl_4} RCH_2I$

(B) $RCH_2Cl + NaI \xrightarrow[\Delta]{acetone} RCH_2I + NaCl$

(C) $R-OH + HI \longrightarrow RI + H_2O$

(D) $CH_4 + I_2 \longrightarrow CH_3I$

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

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

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

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

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

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

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

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

(A) The rate of reaction is independent of the concentration of the nucleophile

(B) The nucleophile attacks the C-atom on the side of the molecule opposite to the group being displaced

(C) The reaction proceeds with simultaneous bond formation and rupture

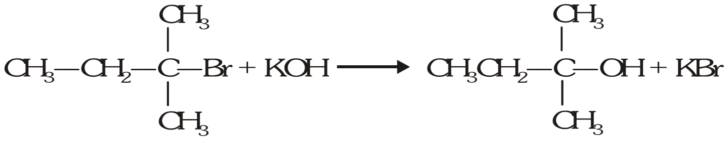
(D) None of these

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

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

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

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

(D) 

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

BRAIN TEASERS **ANSWER KEY** EXERCISE -2

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

EXERCISE–03 MISCELLANEOUS TYPE QUESTIONS

TRUE OR FALSE :

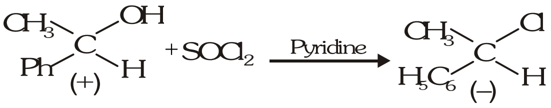
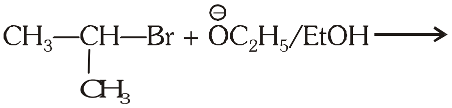
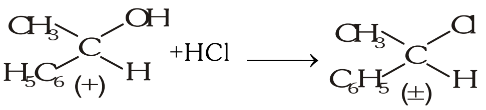
1. Alkyl halides follow the reactivity sequence,
   R—I > R—Br > R—Cl > R—F
2. Vinyl chloride reacts with dilute NaOH to form vinyl alcohol.
3. Allyl chloride is more reactive than vinyl chloride.
4. Tertiary butyl bromide undergoes S_N1 reactions.
5. Both vic- and gem-dihalides on heating with zinc dust in presence of alcohol form same alkene.

FILL IN THE BLANKS :

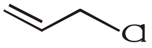
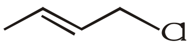
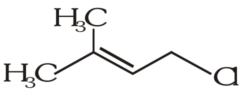
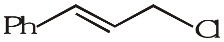
1. The interaction of elemental sulphur with Grignard reagent gives ....
2. An alkyl halide may be converted into alcohol by ....reaction
3. Diethyl ether is obtained from ethyl bromide by treating it with .... and the name of the reaction is ....
4. Allyl chloride is a .... compound while vinyl chloride is inert towards nucleophilic substitution.
5. The dihalides in which halogen atoms are attached to adjacent carbon atoms are termed as.............. .
6. Alkyl halides are formed when thionyl chloride and .... are refluxed in presence of pyridine.
7. Ethylene chloride on hydrolysis with aq. KOH forms.............. .

MATCH THE COLUMN

1. Match the column I with column II.

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

2. Match the column I with column II.

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

ASSERTION & REASON QUESTION :

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

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

1. **Statement-I** : Iodination of akanes is carried out by heat in presence of readucing agent.

   Because

   Statement-II : Iodination of alkanes takepalce explosively.

2. **Statement-I** : Chloropropane has higher boiling point than chloroethane.

   Because

   Statement-II : Haloalkanes are polar molecules.

3. **Statement-I** : Polar solvent slows down S_{N^2} reaction.

   Because

   Statement-II : CH_3–Br is less reactive than CH_3Cl.

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

   Because

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

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

   Because

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

6. **Statement-I** : Aryl halides undergo electrophilic substitution less readily than benzene.

   Because

   Statement-II : Aryl halide gives only meta product w.r.t. electrophilic substitution.

7. **Statement-I** : Optically active 2-iodibutane on treatment with NaI in acetone undergoes racemisation.

   Because

   Statement-II : Repeated Walden inversions on the reactant and its product eventually gives a racemic mixture.

8. **Statement-I** : Free radical chlorination of n-butane gives 72% of 2-chlorobutane and 28% of 1-chlorobutane though it has six primary and four secondary hydrogens.

   Because

   Statement-II : A secondary hydrogen is abstracted more easily than the primary hydrogen.

9. **Statement-I** : Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.

   Because

   Statement-II : The reaction occurs by S_{N^1} mechanism.

10. **Statement-I** : Boiling point of alkyl halide increases with increasse in molecular weight.

    Because

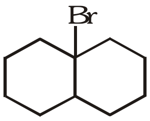
    Statement-II : Boiling point of alkylhalides are in the order RI > RBr > RCI > RF.

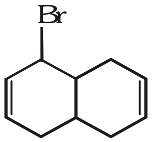
COMPREHENSION BASED QUESTIONS :

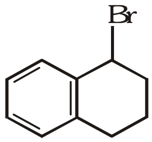
Comprehension # 1

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

1. Compound A is :

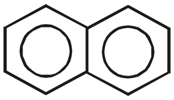
(A) 

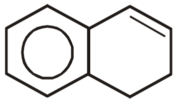
(B) 

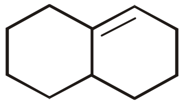
(C) 

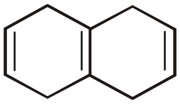
(D) none of these

2. Compound B is :

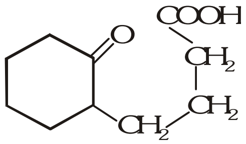
(A) 

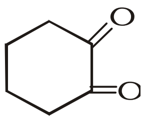
(B) 

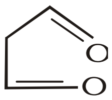
(C) 

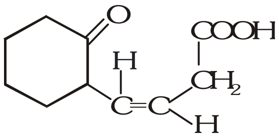
(D) 

3. Compound C is :

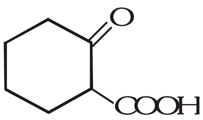
(A) 

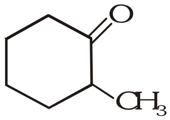
(B) 

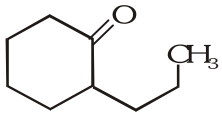
(C) 

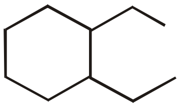
(D) 

4. Compound D is :

(A) 

(B) 

(C) 

(D) 

Comprehension # 2

Nucleophilic substitution reactions generally expressed as

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

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

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

(a) electron-withdrawing to polarize the carbon

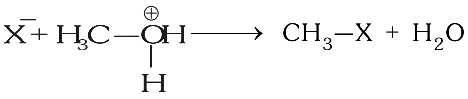
(b) stable once it has left (not a strong base)

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

1. Among the following which is feasible ?

(A) $X^- + CH_3-CH_2-H \longrightarrow CH_3-CH_2-X + H^-$

(B) $X^- + CH_3-OH \longrightarrow CH_3-X + \overset{-}{O}H$

(C) 

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

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

2. Among the following which is false statement ?

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

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

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

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

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

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

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

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

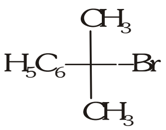
The correct order of increasing leaving group capability of above anoins

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

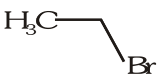
Comprehension # 3

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

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

(A) 

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

(B) 

(C) H_3C-Br

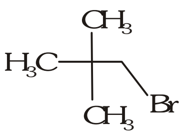
(D) All of these

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

I. $C_6H_5-CH_2-Br$

II. $CH_2=CH-CH_2-Br$

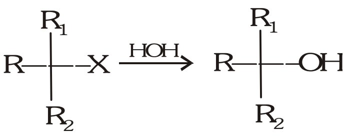
III. $CH_3-CH(Br)CH_3$

IV. 

Select the correct answer from the codes given below

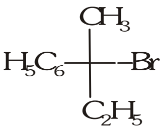
(A) I, II and III (B) I, II and IV (C) II, III and IV (D) I, III and IV

3. For the given reaction

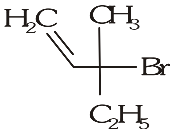


Which substrate will give maximum racemisation ?

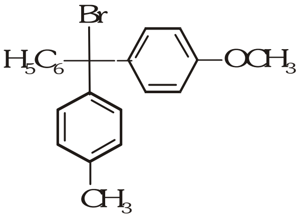
(A)



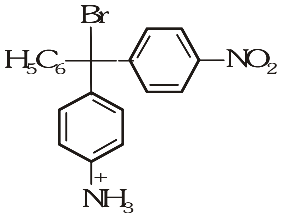
(B)



(C)



(D)



MISCELLANEOUS TYPE QUESTION **ANSWER KEY** EXERCISE -3

- *True / False*

1. T 2. F 3. T 4. T 5. F

- *Fill in the Blanks*

1. thioalcohol 2. nucleophilic substitution 3. sodium ethoxide, williamson's synthesis
4. reactive 5. vic-dihalides or alkylene halides 6. alcohols
7. glycol

- *Match the Column*

1. (A) → r ; B → q ; (C) → s ; (D) → p 2. (A) → q ; (B) → r ; (C) → s ; (D) → p

- *Assertion - Reason Questions*

1. D 2. B 3. C 4. B 5. D 6. C 7. A
8. A 9. A 10. B

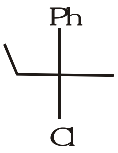
- *Comprehension Based Questions*

Comprehension #1 : 1. (A) 2. (C) 3. (A) 4. (C)
Comprehension #2 : 1. (C) 2. (D) 3. (B) 4. (B)
Comprehension #3 : 1. (A) 2. (A) 3. (C)

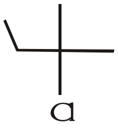
EXERCISE–04 [A] CONCEPTUAL SUBJECTIVE EXERCISE

1. Arrange the following compounds in order of :

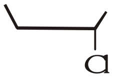
Decreasing S_N1 reaction rate :



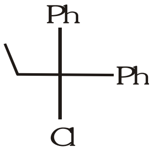
(I)



(II)



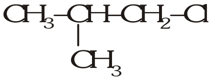
(III)



(IV)

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

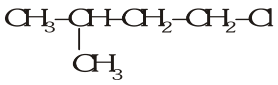
(a) $CH_3-CH_2-CH_2-CH_2-Cl$ (I) and



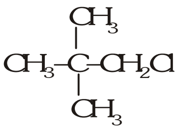
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-Cl$ (II)

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

(c)

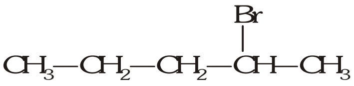


$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-Cl$ (I) and

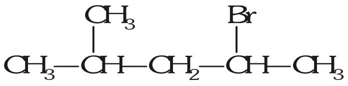


$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2Cl$ (II)

(d)



$CH_3-CH_2-CH_2-\overset{Br}{\overset{|}{CH}}-CH_3$ (I) and



$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{Br}{\overset{|}{CH}}-CH_3$ (II)

3. Of the following statements which are true for S_N1 reaction.
(a) Tertiary alkyl halides react faster than secondary.
(b) The absolute confuguration of the product is opposite to that of the reactant when an optical active substrate is used.
(c) The reaction shows first order kinetics.
(d) The rate of reaction depends markedly on the nucleophilicity of the nucleophile.
(e) The mechanism is two step.
(f) Carbocations are intermediate.
(g) Rate ∝ [Alkyl halides]
(h) The rate of the raction depends on the nature of the leaving group.

4. Of the following statements, which are true for S_N2 reaction.
(a) Tertiary alkyl halides reacts faster than secondary.
(b) The absolute configuration of product is opposite to that of the reactant when an optically active substrate is used.
(c) The reaction shows first order kinetics.
(d) The rate of the reaction depends markedly on the nucleophilicity of the attacking reagent.
(e) The mechanism is one step.

(f) Carbocations are intermediate.

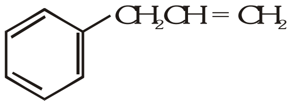
(g) Rate ∝ [Alkyl halides]

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

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

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

7. Identify the product when A reacts with



(A)

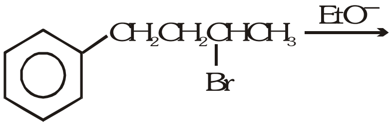
(a) Br_2/Fe (b) Br_2/CCl_4 (c) NBS (d) HBr

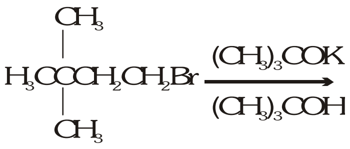
8. Identify major product in the following : $ClCH_2CHCl_2 \xrightarrow{OH^-} CH_2{=}CCl_2$

(a) 

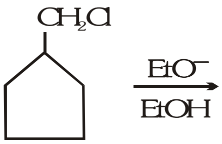
$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow{EtO^-}$

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

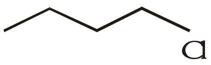
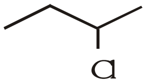
(c) 

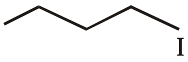
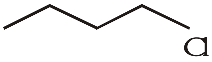
(d) 

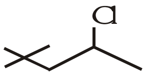
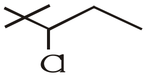
$H_3C\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK}$

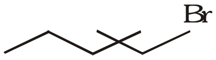
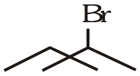
(e) 

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

(a)  and 

(b)  and 

(c)  and 

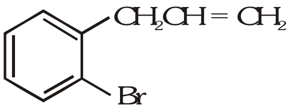
(d)  and 

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

ANSWER KEY

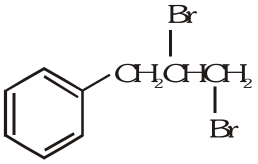
1. IV > I > II > III
2. (a) I (b) II (c) I (d) I
3. (a) T (b) F (c) T (d) F (e) T (f) T (g) T (h) T
4. (a) F (b) T (c) F (d) T (e) T (f) F (g) F (h) T
5. 1 > 2 > 3 Anion of acetic acid is more stabilised by resonance than phenoxide ion.
6. 1-chlorohexane

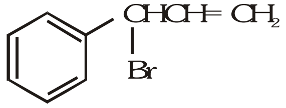
   Because it follows Sn2 path.

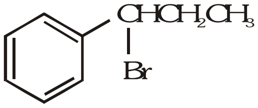
7. (a) 

and para

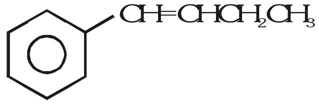
Ortho

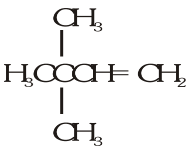
(b) 

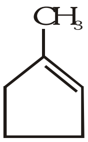
(c) 

(d) 

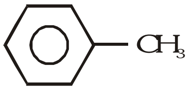
(1, 2-H$^-$ shift gives more stable benzylic carbocation)

8. (a) $CH_3CH = CHCH_3$ (b) $CH_3CH = CHCH_3$ (c) 

(d) 
$H_3C\overset{CH_3}{\underset{CH_3}{C}}CH=CH_2$

(e) 

9. Ease of backside attack (less steric hindrance) decides which undergoes S_N2 faster (except in (b) in which iodide is better leaving group). In all cases first one is fater than the other for S_N2 reaction.

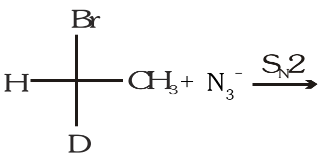
10. Gas B is CH_4, hence A is CH_3MgBr. CH_3Br forms  on reaction with benzene.

EXERCISE–04 [B] BRAIN STORMING SUBJECTIVE EXERCISE

1. Explain the following observations:

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

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



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

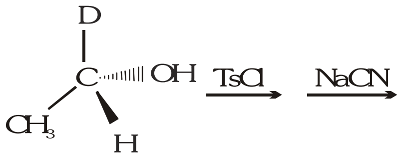
(d) What will happen to the rate if the concentration of azide ion in (b) is doubled?

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

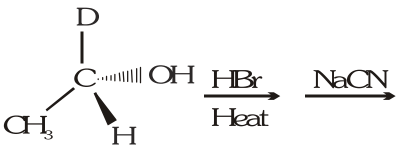
(f) When allowed to stand in dilute H_2SO_4, laevo-rotatory 2-butanol slowly loses optical activity.

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

(a)



(b)

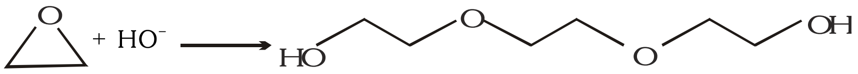


3. Propose mechanism of the following reactions:

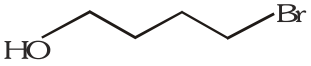
(a)

(b)

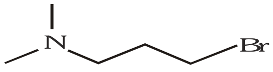
(c)



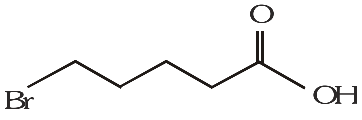
4. Which of the following alkyl halide could be successfully used to synthesize Grignard reagent and why other fail?



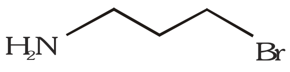
(I)



(II)



(III)



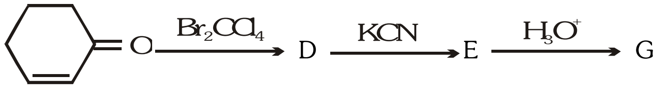
(IV)

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

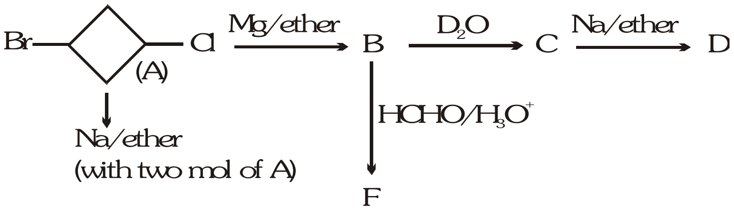
6. Identify A to G in the following.

(a)

(b)



7.



Identify B to F

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

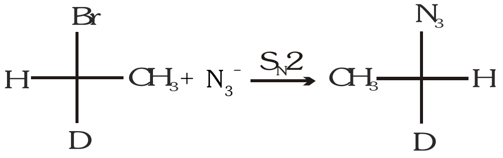
9. Arrange the following in the increasing order of their ability as a leaving group:

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

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

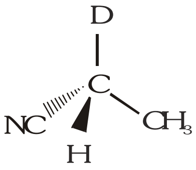
10. RBr when treated with AgCN in a highly polar solvent gives RNC whereas when it is treated with NaCN it gives RCN. Explain.

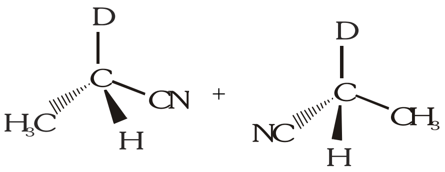
1. (a) Though neopentylbromide is primary, bulky tertiary butyl group possess very large steric hindrance to the attack of bulky nucleophile N_3^-.

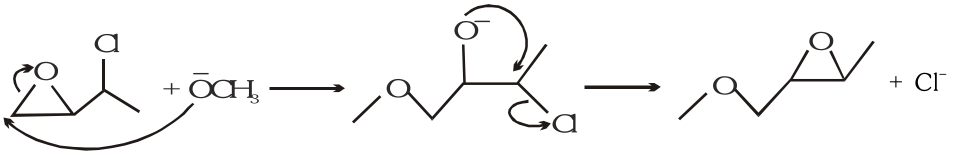
(b) 

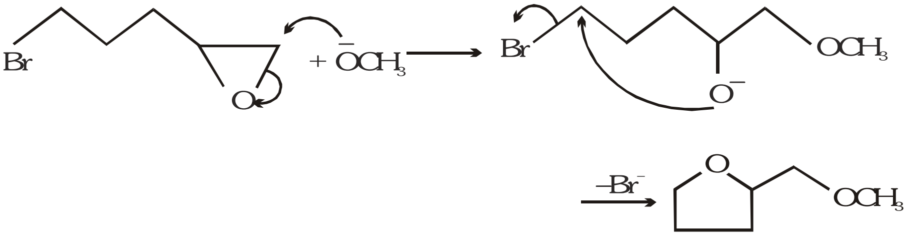
(c) Rate will double (d) Rate will double

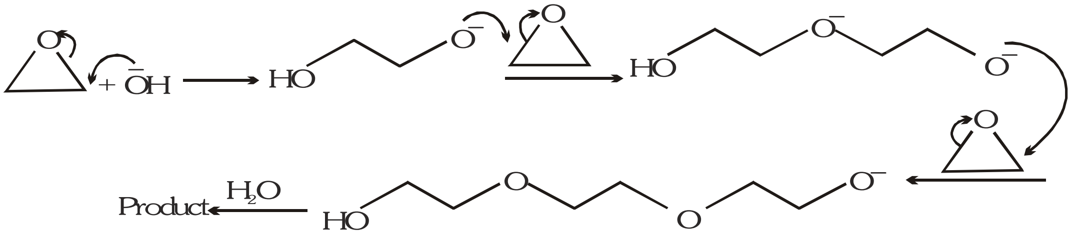
(e) not related (f) Recemization occur through carbocation intermediate

2. (a) 

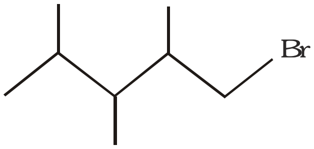
(b) 

3. (a) 

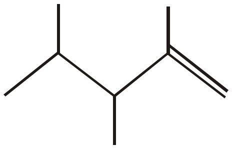
(b) 

(c) 

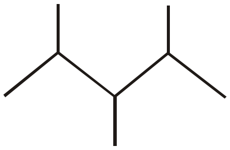
4. Only II can be used for successful synthesis of Grignard reagent, rest all contain acidic proton and will react with R^- (from Grignard reagent) forming alkane.

5. 

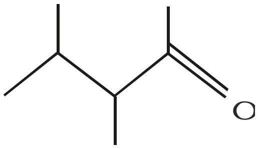
A



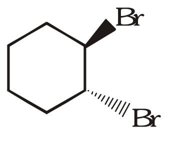
B

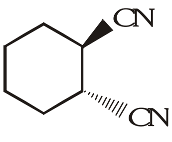


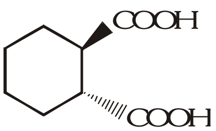
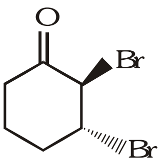
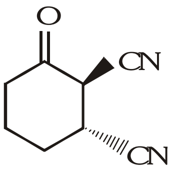
C

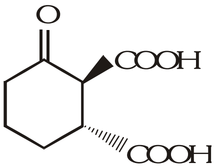
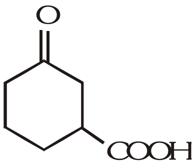


D

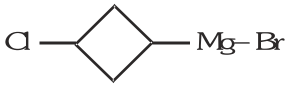
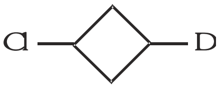
6. (A) 

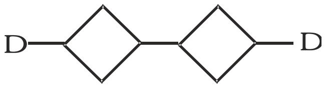
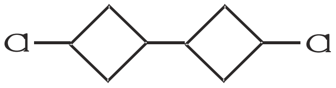
(B) 

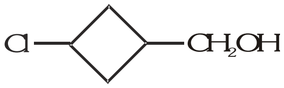
(C) 
(D) 
(E) 

(F) 
(G) 

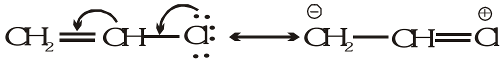
(decarboxylation takes place on heating when there is a keto group at β- position)

7. (B) 
(C) 

(D) 
(E) 

(F) 

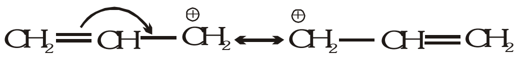
8. In Vinyl chloride, C – Cl bond is stable due to resonance (as in chlorobenzene)



$CH_2=CH-\ddot{\underset{\cdot\cdot}{Cl}}: \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{Cl}$

Hence S_N reaction in which Cl is replaced by nucleophile is not possible. In addition to this, sp^2- hybridised carbon is more acidic than sp^3- carbon, hence removal of proton (H^+) is easier than removal of halide (Cl^-) In allyl chloride, S_N reaction is easier since allyl carbocation formed after removal of Cl^- is stabilised by resonance.

$$CH_2=CHCH_2Cl \longrightarrow \underbrace{CH_2=CH\overset{\oplus}{C}H_2}_{\text{Allyl carbocation}}+Cl^-$$



$CH_2=CH-\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH_2$

9. (a) $CF_3^- < CH_3O^- < CH_3S^-$; (b) $CH_3COO^- < CH_3SO_3^- < CF_3SO_3^-$

10. As $[CN]^-$ is an ambident nuicleophile which ahve two nucleophile which have two nucleophilic sites and can attack from either side. In a highly polar solvent, AgCN promotes the formation of carbocation R^+, precipitation of AgBr.

$$R-BR + Ag^+\ [CN^-] \xrightarrow[\text{slow}]{\overset{\ominus}{\underset{\cdot\cdot}{C}}\equiv\ddot{N} \rightarrow C=\overset{\ominus}{\ddot{\underset{\cdot\cdot}{N}}}} R+ + CN- + \ddot{Ag}Br\downarrow \xrightarrow{\text{fast}} R-N+ \equiv C^-$$

In the absence of such promotion by Ag^+, with $Na+[CN]^-$, the resulting S_N2 reaction is found to proceed with preferential attack on the atom in the nucleophile which is more polarisable i.e. C.

$$NC^- + R - Br \longrightarrow \underset{\text{Transition State}}{[NC^{\delta-}....R....Br^{\delta-}]} \longrightarrow N \equiv C - R + Br^-$$

EXERCISE–05 PREVIOUS YEARS QUESTIONS

1. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives-
(A) o-cresol (B) p-cresol [IIT-90]
(C) 2, 4 dihydroxytoluene (D) Benzoic acid

2. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to-
(A) The formation of less stable carbonium ion (B) Resonance stabilization [IIT-90]
(C) The inductive effect (D) sp^2 hybridised carbon attached to the halogen

3. 1-Chlorobutane on reaction with alcoholic potash gives - [IIT-91]
(A) 1–butene (B) 1–butanol (C) 2–butene (D) 2–butanol

4. In the addition of HBr to propene in the absence of peroxides, the first step involves the addition of -
(A) H^+ (B) Br^- (C) $H^\bullet$ (D) $Br^\bullet$ [IIT-93]

5. Arrange the following compounds in order of increasing dipole moment : [IIT-96]
(I) Toluene ; (II) m-dichlorobenzene ; (III) o-dichlorobenzene ; (IV) p-dichlorobenzene
(A) I < IV < II < III (B) IV < I < II < III (C) I < IV < II < III (D) IV < II < I < III

6. In the reaction of p-chloro toluene with KNH_2 in liq. NH_3, the major product is - [IIT-97]
(A) o-toluidine (B) m-toluidine (C) m-chloroaniline (D) p-chloroaniline

7. $(CH_3)_3CMgCl$ reaction with D_2O produces : IIT-97]
(A) $(CH_3)_3CD$ (B) $(CH_3)_3OD$ (C) $(CD_3)_3CD$ (D) $(CH_3)_3OD$

8. The intermediate during the addition of HCl to propene in presence of peroxide is - [IIT-97]
(A) $CH_3\dot{C}HCH_2Cl$ (B) $CH_3\overset{+}{C}HCH_3$ (C) $CH_3\dot{C}HCH_2$ (D) $CH_3CH_2\dot{C}H_2$

9. The number of possible enantiomeric pairs that can be produced during monochlorination of isopentane-
(A) 2 (B) 3 (C) 4 (D) 1 [IIT-97]

10. During debromination of meso-2,3-dibromobutane, with Zn dust/CH_3COOH the major compound formed is - [IIT-97]
(A) n-butane (B) 1-butene (C) cis-2-butene (D) trans-2-butene

11. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with [IIT-98]
(A) SO_2Cl_2 (B) $SOCl_2$ (C) PCl_5 (D) NaOCl

12. Toluene, when treated with Br_2/Fe, gives o and p-bromotoluene, because the CH_3 group -
(A) is ortho and para directing (B) is meta directing [IIT-99]
(C) deactivates the ring by hyperconjugation (D) deactivates the ring

13. A solution of (+) 2–chloro–2phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$ due to the formation of - [IIT-99]
(A) Carbanion (B) Carbene (C) Free-radical (D) Carbocation

14. The order of reactivity of the following alkyl halides for a S_{N^2} reaction is - [IIT-2000]
(A) RF > RCl > R –Br > R–I (B) R–F > R –Br > R–Cl > R–I
(C) R–Cl > R –Br > R–F > R–I (D) R–I > R –Br > R–Cl > R–F

15. Which of the following has the highest nucleophilicity : [IIT-2000]
(A) F^- (B) OH^- (C) CH_3^- (D) NH_2^-

16. An S_{N^2} reaction at an asymmetric carbon of a compound always gives : [IIT-2001]
(A) an enantiomer of the substrate (B) a product with opposite optical rotation
(C) a mixture of diastereomers (D) a single stereoisomer

17. The number of isomer for the compound with molecular formula $C_2BrCl\ FI$ is - **[IIT-01]**

(A) 3 (B) 4 (C) 5 (D) 6

18. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov's addition to alkenes because : **[IIT-01]**

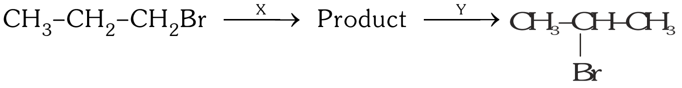
(A) both are highly ionic

(B) one is oxidising and the other is reducing

(C) one of the steps in endothermic in both the cases

(D) all the steps are exothermic in both the reactions

19. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations -**[IIT-02]**



$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

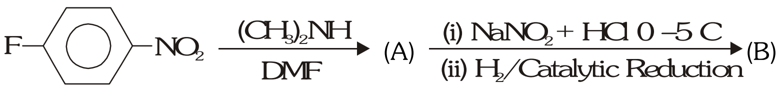
(A) X = dilute aqueous NaOH, 20 C, Y= HBr/acetic acid, 20 C

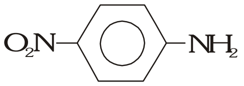
(B) X = concentrated alcoholic NaOH, 80 C; Y = HBr/acetic acid, 20

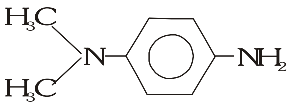
(C) X = dilute aqueous NaOH 20 , Y = $Br_2/CHCl_3$, 0 C

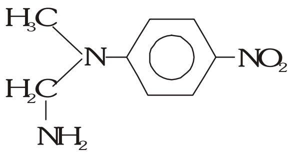
(D) X = concentrated alcoholic NaOH, 80 C; Y = $Br_2/CHCl_3$, 0 C

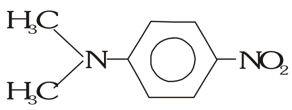
20. **[IIT-03]**

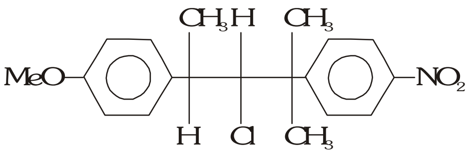


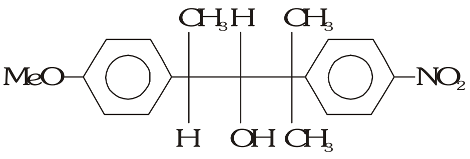
(A)


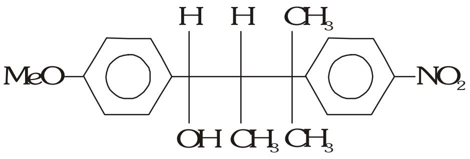
(B)


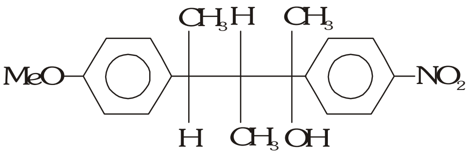
(C)


(D)


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

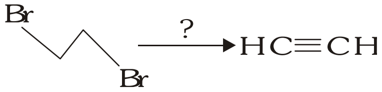
(K)


(L)


(M)


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

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



$HC\equiv CH$ is /are -

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

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

23. In the following groups : [IIT-97]

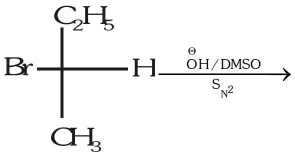
(I) $-OAc$; (II) $-OMe$; (III) $-OSO_2Me$; (IV) OSO_2CF_3

the order of leaving group ability is -

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

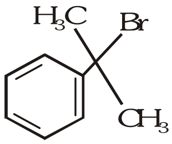
24. $CH_3CH_2CHCl_2 \xrightarrow{Aq.\ KOH} ?$ [IIT 1991]

25. Draw the stereochemical structure of the products in the following reaction. [IIT 1994]

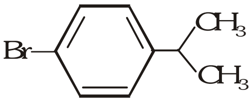


26. Give reasons : [IIT 2005]

(a) (i)

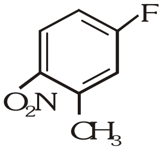


$\xrightarrow{C_2H_5OH(aq.)}$ acidic solution ; (ii)

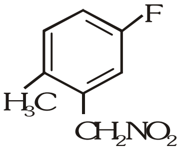


$\xrightarrow{C_2H_5OH(aq.)}$ neutral

(b) (i)



$\xrightarrow{NaOH(aq)} F^-$ (liberated) ; (ii)

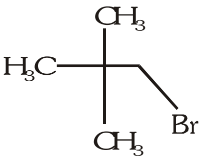


$\xrightarrow{NaOH(aq)} F^-$ is not liberated

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

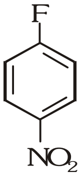
28. Which would be the major product in each of the following reactions ?

(a)



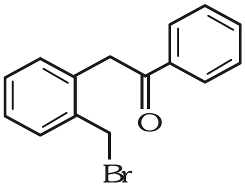
$\xrightarrow[\Delta]{C_2H_5OH}$

(b)



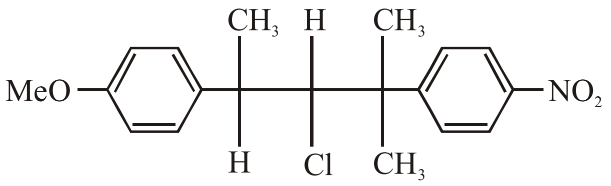
$\xrightarrow[\Delta]{NaOCH_3}$

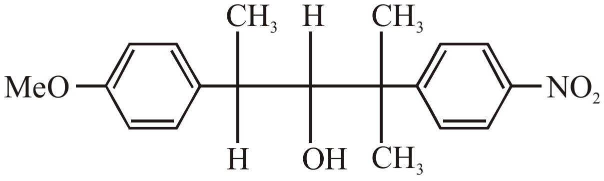
(c)

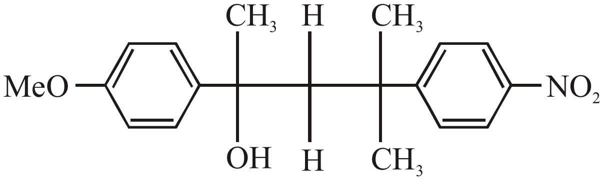


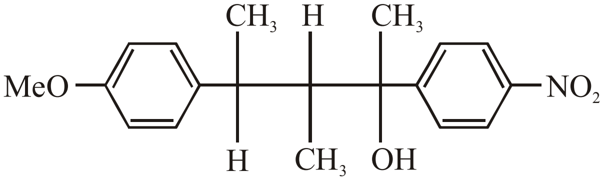
$\xrightarrow{base}$

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



(K) 

(L) 

(M) 

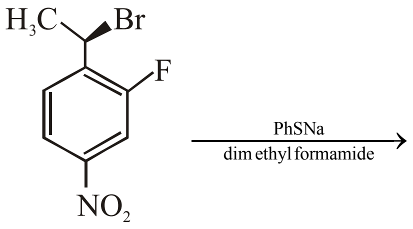
It mainly gives

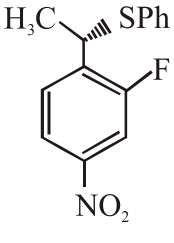
(A) K and L (B) Only K (C)L and M (D) Only M

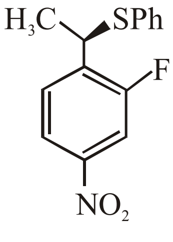
30. Match the following: [IIT 2006]

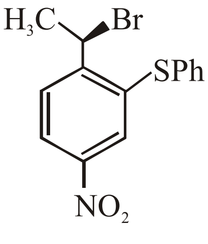
Column I	**Column II**
(A) CH_3–CHBr–CD_3 on treatment with alc. KOH gives CH_2=CH-CD_3 as a major product.	(P) E1 reaction
(B) Ph – CHBr - CH_3 reacts faster than Ph-CHBr-CD_3.	(Q) E2 reaction
(C) Ph-CD_2-CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph-CD=CH_2 as the major product.	(R) E1cb reaction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

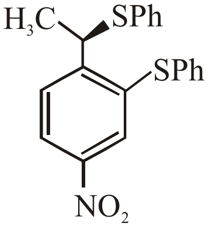
31. The major product of the following reaction is [IIT 2008]

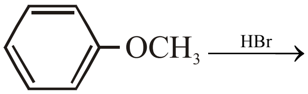


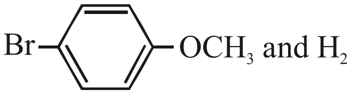
(A) 

(B) 

(C) 

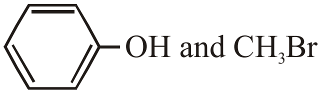
(D) 

32. In the reaction  the products are [IIT 2010]

(A) 

(B) 

(C) 

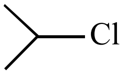
(D) 

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

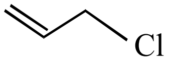
34. KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as - [IIT 2013]

$H_3C{-}Cl$

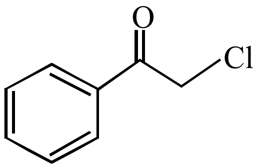
P



Q



R

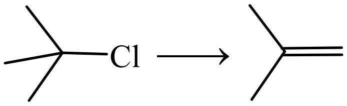


S

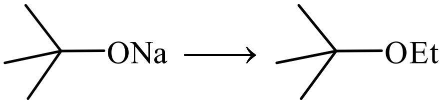
(A) P > Q > R > S
(B) S > P > R > Q
(C) P > R > Q > S
(D) R > P > S > Q

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

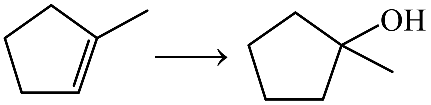
List-I **List-II**

(P) 

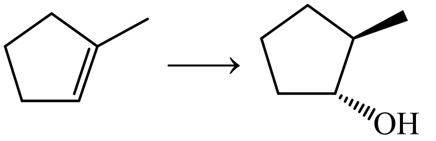
(1) (i) $Hg(OAc)_2$ (ii) $NaBH_4$

(Q) 

(2) NaOEt

(R) 

(3) Et-Br

(S) 

(4) (i) BH_3 (ii) H_2O_2 /NaOH

Codes :

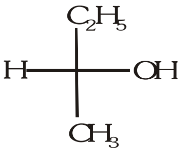
	P	Q	R	S
(A)	2	3	1	4
(B)	3	2	1	4
(C)	2	3	4	1
(D)	3	2	4	1

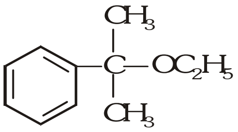
PREVIOUS YEARS QUESTIONS

ANSWER KEY

EXERCISE -5

1. (D) 2. (B) 3. (A) 4.(A) 5. (B) 6. (D) 7.(A) 8. (B)
9. (A) 10. (C) 11. (A) 12. (A) 13. (D) 14. (D) 15. (C) 16. (D)
17. (D) 18. (C) 19. (B) 20. (B) 21. (A) 22. (B) 23. (B)
24. CH_3-CH_2-CHO

25. 

26. (a) (i) Products are 

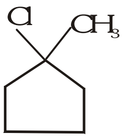
+ HBr (aq.) ; Hence acidic.

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

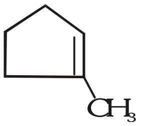
(b) (i) $-NO_2$ group facilitates the nucleophilic attack because it stabilised the anion formed when attack of $\overline{O}H$ takes place.

(ii) Does not show reaction.

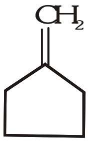
27. (B)



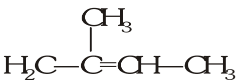
(A)

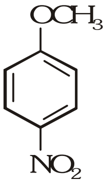


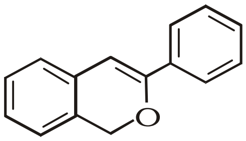
(B)



(C)

28. (a) 
$H_2C-\overset{CH_3}{\underset{}{C}}=CH-CH_3$

(b) 

(c) 

29. A,C 30. D 31. C 32. D 33. A
34. B 35. A