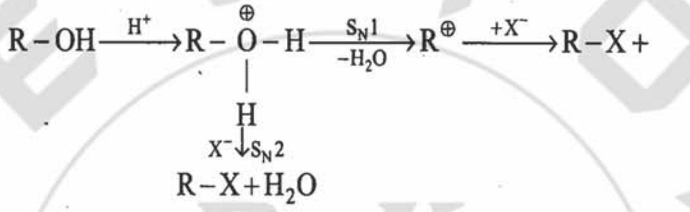
# UNIT-16 : ALKYL AND ARYL HALIDES [JEE – MAIN CRASH COURSE]

## Alkyl Halides

### Preparation of alkyl halides

1. *From alcohols*
   - By using hydrogen halides

     $$R-OH \xrightarrow{HX} R-X+H_2O$$

     $$R-OH \xrightarrow{H^+} R-\overset{\oplus}{O}(H)-H \xrightarrow[-H_2O]{S_N1} R^{\oplus} \xrightarrow{+X^-} R-X+$$

     $$R-\overset{\oplus}{O}(H)-H \xrightarrow{X^-,\ S_N2} R-X+H_2O$$

     (Some rearranged product, if possible)
   - By using phosphorous halides

     $$R-OH+PCl_5 \rightarrow R-Cl+POCl_3+HCl$$

     $$3R-OH+PCl_3 \rightarrow 3R-Cl+H_3PO_3$$

     $$3R-OH+PBr_2 \rightarrow 3R-Br+H_3PO_3$$

     $$3R-OH+PI_3 \rightarrow 3R-I+H_3PO_3$$
   - By using $SOCl_2$ (thionyl chloride)

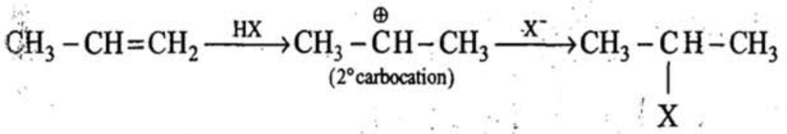
     $$R-OH+SOCl_2 \xrightarrow{\text{pyridine}} R-Cl+SO_2\uparrow+HCl\uparrow$$

     The product alkyl chloride has a configuration inverted with respect to the reactant alcohol (if it is chiral) in the presence of pyridine base. In the absence of a base and polar solvent, the chiral alcohol gives alkyl chloride with retention of configuration.
2. *By halide exchange*

   $$R-Cl \xrightarrow[\text{Acetone}]{\text{NaI}} R-I+NaCl;\ R-Br \xrightarrow[\text{Acetone}]{\text{NaI}} R-I+NaBr$$

   The reaction proceeds by $S_N2$ mechanism and is possible because NaCl and NaBr are precipitated in the reaction, as they are not soluble in weakly polar aprotic solvent.

3. *By addition of H–X to alkenes*



$$CH_3-CH{=}CH_2 \xrightarrow{HX} \underset{(2^\circ\text{carbocation})}{CH_3-\overset{\oplus}{C}H-CH_3} \xrightarrow{X^-} CH_3-\underset{\displaystyle X}{\underset{|}{C}H}-CH_3$$

$$CH_3-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} \underset{(2^\circ\text{radical})}{CH_3-\dot{C}H-CH_2-Br} \xrightarrow{HBr}$$

$$CH_3-CH_2-CH_2Br+\dot{B}r$$

4. From silver salt of carboxylic acid

$$\underset{(X_2=Cl_2\text{ or }Br_2)}{RCOOAg+X_2} \xrightarrow{CCl_4} R-X+AgX\downarrow+CO_2$$

## Chemical properties

1. *Preparation of organometallic compounds*

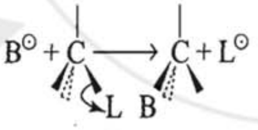
$$R-X \xrightarrow[\text{dry ether}]{Mg} \underset{(\text{Grignard reagent})}{RMgX}$$

$$R-X \xrightarrow[\text{ether}]{2Li} \underset{(\text{Organolithium compound})}{R-Li+LiX}$$

**Mechanism**

$$R-X+Li \rightarrow [R\text{–}X]^- Li^+;\ [R-X]^- \rightarrow R^\bullet + X^-;\ R^\bullet + Li \rightarrow R\text{–}Li$$

2. *Basicity and nucleophilicity*: Nucleophilicity of the species is the ability of the species to attack an electrophilic carbon, while basicity is the ability of the species to remove $H^+$ from an acid. Let us have a species, $B^-$. Its function as a nucleophile is shown as follows:



Its role as a base is indicated as follows:

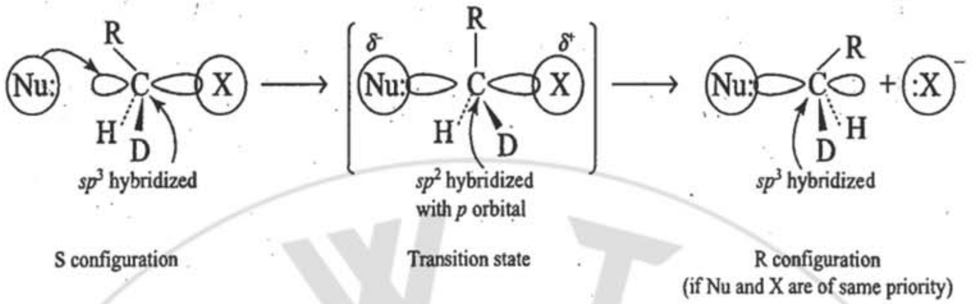
$$B^\odot + H-A \rightleftharpoons B-H+A^\odot$$

The order of nucleophilicity of different species depends on the nature of solvent used. For instance, let us take $F^-$, $Cl^-$, $Br^-$, and $I^-$ with their countercation as $Na^+$ and see their nucleophilicity order in different solvents. There are four categories of solvents, namely non–polar ($CCl_4$), polar protic ($H_2O$), polar aprotic ($CH_3SOCH_3$), and weakly polar aprotic ($CH_3COCH_3$).

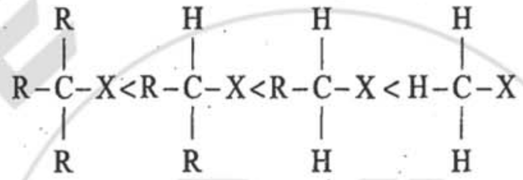
Polar solvents are able to dissociate the salts, i.e., ion-pairs can be separated. On the other hand, non-polar and weakly polar solvents are unable to dissociate salts, so they exist as ion-pairs. The ion-pairing is strong when ions are small and have high charge density.

In non-polar and weakly polar aprotic solvents, all the salts will exist as ion-pairs. The ion-pairing will be strongest with the smallest anion ($F^-$) and weakest with the largest anion ($I^-$). Thus, the nucleophilicity order of $X^-$ in such solvents will be: $F^- > Cl^- > Br^- > I^-$

3. *$S_N2$ reaction*



The reactivity of alkyl halides towards $S_N2$ reaction is as follows:



$$R-\underset{R}{\overset{R}{C}}-X < R-\underset{R}{\overset{H}{C}}-X < R-\underset{H}{\overset{H}{C}}-X < H-\underset{H}{\overset{H}{C}}-X$$

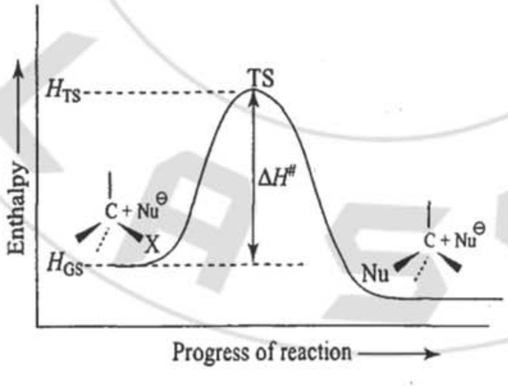
The rate law for the $S_N2$ reaction is given by

$$\text{Rate} = k[R-X]\,[Nu^-]$$

The rate of the $S_N2$ reaction is dependent on the concentration of both RX and $Nu^-$.

$S_N2$ reactions are stereospecific as well as stereoselective.

We know that successful $S_N2$ displacements are exothermic in nature and its energy profile is shown in the adjacent figure.



Thus, in general reactions with charged reactants, the $S_N2$ rate increases with increasing polarity of solvent.

4. *$S_N1$ reaction*

$R-X \xrightarrow{RDS} R^+ + X^-$ Step 1 (slow)

$R^+ + Y^- \longrightarrow R-Y$ Step 2 (fast)

The carbocation generated by the first step has an $sp^2$ hybridized carbon, i.e., the structure is flat (trigonal planar). Thus, a nucleophile will be able to attack the carbocation from the front side as well as from the rear side with equal ease, leading to the formation of two isomers, if the chiral carbon is present in the substrate.

The basic difference between $S_N1$ and $S_N2$ mechanisms is in the timing of the steps. In the $S_N1$ mechanism, first $X^-$ leaves and then $Y^-$ attacks, whereas in an $S_N2$ mechanism, the two things happen simultaneously. The following order of reactivity for $S_N1$ is observed:

$$R-I > R-Br > R-Cl > R-F$$

$$R-\underset{R}{\overset{R}{C}}-X > R-\underset{R}{\overset{H}{C}}-X > R-\underset{H}{\overset{H}{C}}-X > H-\underset{H}{\overset{H}{C}}-X$$

The rate law for the $S_N1$ reaction is given by

$$\text{Rate} = k[R-X]$$

It is generally said that the rate of $S_N1$ reactions is favored in polar solvents than in non-polar solvents.

## Ambident nucleophiles

1. *Attack by $CN^-$ nucleophile ($:^{-}C\equiv N:$)*

$$R-X \xrightarrow{CN^-} \underset{\text{Nitriles}}{R-CN} + \underset{\text{Isonitriles}}{R-NC} + X^-$$

In $CN^-$, carbon (negatively charged) will be a soft base as compared to nitrogen. Hence if the reaction proceeds via $S_N1$ mechanism, which produces a free carbocation (a hard acid), then attack through nitrogen (hard base) will take place. But if the reaction proceeds via $S_N2$ mechanism (small positively charged carbon is soft acid), then attack through carbon (soft base) will take place.

2. *Attack by $NO_2$ nucleophile ($^-O-N=O$)*

$$R-X \xrightarrow{NO_2^-} \underset{\text{Alkane nitrite}}{R-O-N=O} + \underset{\text{Nitroalkane}}{R-NO_2} + X^-$$

In $NO_2^-$, oxygen (negatively charged) will be a hard base as compared to nitrogen. Hence if the reaction proceeds via $S_N1$ mechanism, then attack through oxygen (hard base) will take place to produce alkane nitrite. But if the reaction takes place via $S_N2$ mechanism, then attack through nitrogen (soft base) will take place to give nitroalkane.

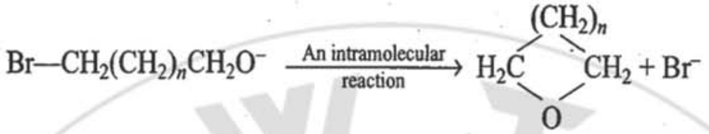
## Intermolecular Versus Intramolecular Displacement Reactions

A molecule with two functional groups is called a bifunctional molecule. If the two functional groups are able to react with each other, two kinds of reactions can take place.

1. *Intermolecular reactions*

$$\mathrm{BrCH_2(CH_2)_nCH_2O^- + Br-CH_2(CH_2)_nCH_2O^-}$$
$$\downarrow \text{An intermolecular reaction}$$
$$\mathrm{BrCH_2(CH_2)_nCH_2OCH_2(CH_2)_nCH_2O^- + Br^-}$$

2. *Intramolecular reactions*



Intramolecular reactions has an advantage in that the reacting groups are tethered close together (entropy factor) and thus do not have to wander through the solvent to find a group with which it reacts. As a result, a low concentration of reactant favors an intramolecular reaction because the two functional groups have a better chance of finding one another if they are in the same molecule. When an intramolecular reaction would form a five- or six-membered ring, it would be highly favored over the intramolecular reaction because of the stability of five- and six-membered rings as they are less strained. Three- and four-membered rings are highly strained, thus they are less stable than five- and six-membered rings. The entropy factor in three-membered ring is so highly favored that three-membered rings are also formed with ease in spite of the fact that they are too strained. The high activation energy for the formation of four-membered rings cancels the advantage gained by tethering, thus they are not easily formed.

## Substitution Versus Elimination Reactions

We know that an alkyl halide can undergo four types of reactions: $S_N1$, $S_N2$, $E_1$, and $E_2$. A given alkyl halide under the given conditions will follow which pathway can be decided in the following manner. The first thing you must look at is the alkyl halide: Is it 1°, 2°, or 3°. If the reactant were a primary alkyl halide, it would undergo $E_2$/$S_N2$ reactions (as their carbocations are favored by a high concentration of a good nucleophile/strong base, whereas a poor nucleophile/weak base favors $E_1$/$S_N1$ reactions. Once you have decided whether the conditions will favor $E_2$/$S_N2$ reactions or $E_1$/$S_N1$ reactions, then you should decide how much of the product will be substitution and how much will be the elimination product. The relative amount of substitution and elimination products can be decided again on the basis of structure of alkyl halide (i.e., 1°, 2°, or 3°) and on the nature of the nucleophile/base. Relative reactivities of alkyl halides in various reactions are as follows:

In an $S_N2$ reaction: $1° > 2° > 3°$
In an $E_2$ reaction: $3° > 2° > 1°$
In an $S_N1$ reaction: $3° > 2° > 1°$
In an $E_1$ reaction: $3° > 2° > 1°$

# Aryl Halides

## Preparation of aryl halides

1. *From diazonium salts*

$$C_6H_6 \xrightarrow[\text{conc. } H_2SO_4]{\text{conc. } HNO_3} C_6H_6NO_2 \xrightarrow[\text{redn.}]{Sn/HCl} C_6H_5NH_2 \xrightarrow[0\text{–}5°C]{HONO}$$

$$\begin{tikzcd} & C_6H_5F \\ & C_6H_5Cl \\ C_6H_5N_2^{+} \arrow[ur, "\text{CuCl}, \Delta"] \arrow[uur, "BF_4^-, \Delta"] \arrow[r, "\text{CuBr}, \Delta"] \arrow[dr, "KI^-, \Delta"'] & C_6H_5Br \\ & C_6H_5I \end{tikzcd}$$

2. *By halogenation of arenes or substituted arenes*

$$ArH + X_2 \xrightarrow{\text{Lewis acid}} ArX + HX$$

where $X_2 = Cl_2$ or $Br_2$; Lewis acid = $FeCl_3$, $AlCl_3$, etc.

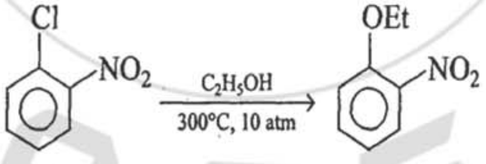
## Chemical properties

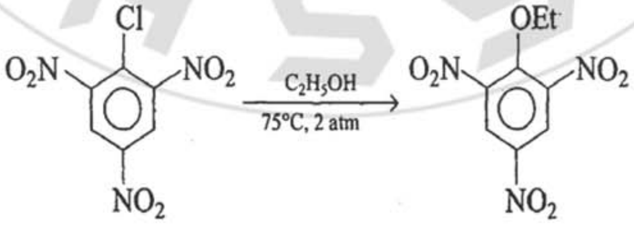
### *Nucleophilic aromatic substitution*

1. *$S_NAr$ mechanism*: Consider the following reaction:

$$Ar - X + Z^- \rightarrow Ar - Z + X^-$$

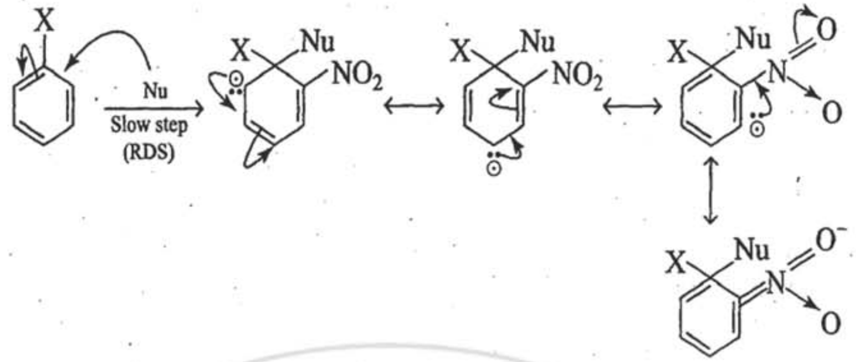
For facile reaction, Ar must contain strongly electron-withdrawing groups at ortho and/or para position to the halogen atom. The reaction involves the formation of carbanion as an intermediate



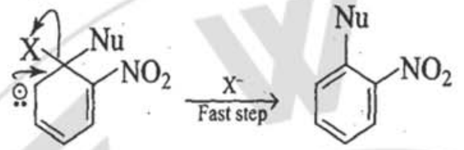


Reaction proceeds through carbanion formation as intermediate. The rate of the reaction increases with the increase in the number of electron-withdrawing groups at ortho and para positions, since the cabanion formed would be readily stabilized.

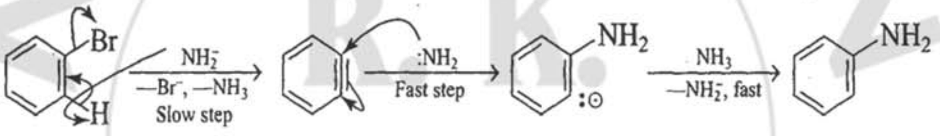
**Step 1:**



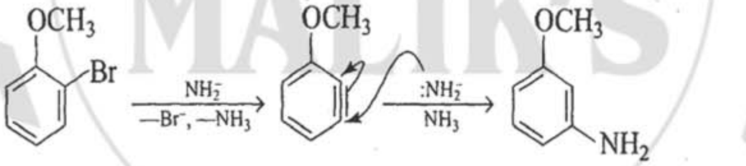
**Step 2:**



2. *Benzyne mechanism*: Unactivated and deactivated aryl halides undergo nucleophilic substitution by benzyne mechanism. In benzyne mechanism, the first step involves elimination, while the second step involves addition of nucleophile.



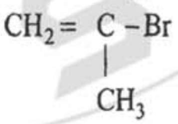
For example,

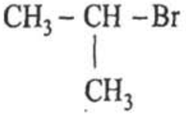


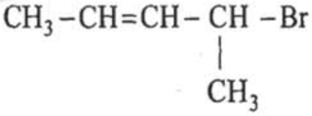
## SOME IMPORTANT EXAMPLES

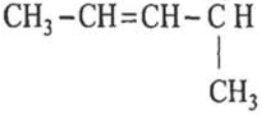
**Example 1** Which one of the following is most reactive of $S_N1$ reaction?

(a) $C_6H_5Cl$

(b) 
$CH_2=\underset{\underset{CH_3}{|}}{C}-Br$

(c) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-Br$

(d) 
$CH_3-CH=CH-\underset{\underset{CH_3}{|}}{CH}-Br$

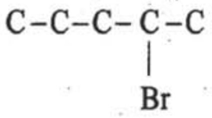
*Solution* The formation of carbocation is the slowest step, so the most stable carbocation will lead to the fastest $S_N1$ reaction.  $CH_3-CH=CH-\underset{\underset{CH_3}{|}}{\overset{(+)}{C}}H$ is allylic, which is stabilized by delocalization.

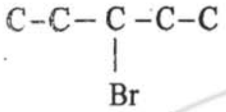
**Example 2** How many structural isomers are possible for compounds having the molecular formula $C_5H_{11}Br$?

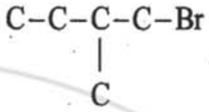
(a) 5 (b) 6 (c) 7 (d) 8

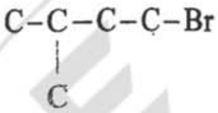
*Solution* (d)

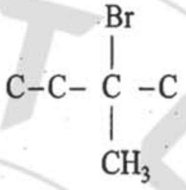
(i) $C-C-C-C-C-Br$

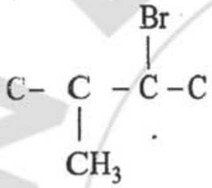
(ii)

$C-C-C-\underset{\underset{Br}{|}}{C}-C$

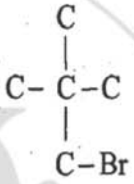
(iii)

$C-C-\underset{\underset{Br}{|}}{C}-C-C$

(iv)

$C-C-\underset{\underset{C}{|}}{C}-C-Br$

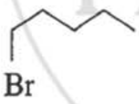
(v)

$C-\underset{\underset{C}{|}}{C}-C-C-Br$

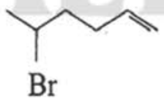
(vi)

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

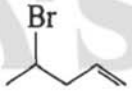
(vii)

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

(viii)

$C-\overset{\overset{C}{|}}{\underset{\underset{C-Br}{|}}{C}}-C$

**Example 3** Rank the following compounds in the order of increasing $E_2$ reaction rate with alcoholic KOH:

(A)


(B)


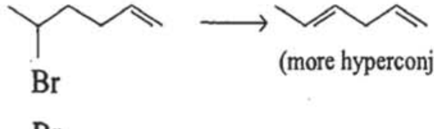
(C)


(a) A < C < B (b) C < B < A (c) A < B < C (d) B < A < C

*Solution* (c)

In $E_2$ mechanism, both the leaving group and H are removed simultaneously, and as $C_2H_5O^{\ominus}$ base is not bulky, therefore is more stable, which means more alkylated alkene will form.

(A)


(B)


(more hyperconjugation)

(C)


(conjugated diene)

**Example 4** Which of the following can be used to prepare 3–bromopropene?

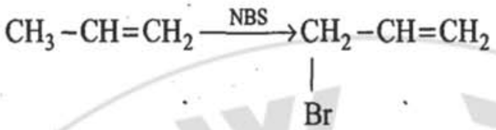
(a) $CH_3CH{=}CH_2 + Br_2 \xrightarrow[30°C]{CCl_4}$

(b) $CH_3CH{=}CH_2 + N$–bromo succinimide$\rightarrow$

(c) $CH_2{=}CH{-}CH_2 + PBr_3 \longrightarrow$

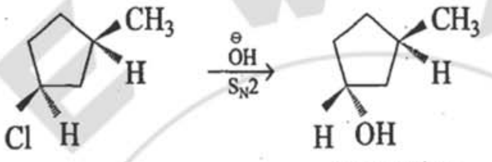
(d) $CH_2{=}CHCH_2Cl + NaBr \xrightarrow{\text{acetone}}$

*Solution* (b) Allylic substitution takes place with NBS.



$$CH_3{-}CH{=}CH_2 \xrightarrow{NBS} \underset{\displaystyle Br}{\underset{|}{CH_2}}{-}CH{=}CH_2$$

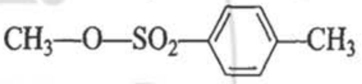
Option (a) will give addition product.



*trans* product

**Example 5** Which of the following substrate is most reactive towards methoxide ion ($Me - \overset{\ominus}{O}$)?

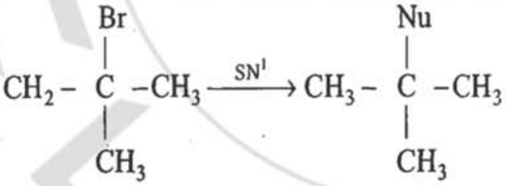
(a) $CH_3 - I$

(b) 

(c) $CH_3 - O - SO_2 - CF_3$

(d) $CH_3 - F$

*Solution* (b)



$$CH_2 - \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}} - CH_3 \xrightarrow{SN^1} CH_3 - \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Nu}{\overset{|}{C}}}} - CH_3$$

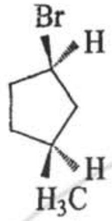
In the presence of weak base, $E_1$ reaction will occur, whereas in the presence of strong base, $E_2$ will occur. But for $S_N2$ mechanism, 1° alkyl halide is required.

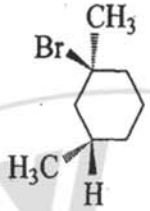
## OBJECTIVE QUESTIONS

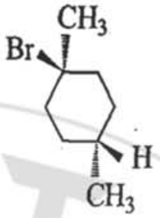
1. Select the regent that will yield the greater amount of substitution on reaction with $CH_3 - CH_2 - Br$:
   (a) $CH_3CH_2OK$ in dimethyl sulfoxide (DMSO)
   (b) $(CH_3)_3COK$ in dimethyl sulfoxide (DMSO)
   (c) Both (a) and (b) will give comparable amount of substitution
   (d) Neither (a) nor (b) will give any amount of substitution

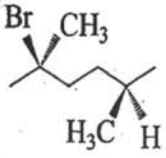
2. Under the specified conditions, substrate X undergoes substitution and elimination reactions to give products A–D. A and B are stereoisomers, but not enantiomers. C and D are enantiomers. A is not an isomer of C. Which of the following could be the starting material X?

$$X \xrightarrow[\Delta]{H_2O} A + B + C + D$$

I. 

II. 

III. 

IV. 

(a) I (b) II (c) III (d) IV

3. Rate limiting $S_N1$ follows the sequence:

$$\overset{\delta\oplus}{R}—\overset{\delta\ominus}{Br} \rightleftharpoons \boxed{R^{\oplus}Br^{\ominus}} \rightleftharpoons \boxed{R^{\oplus}}\boxed{Br^{\ominus}} \rightleftharpoons \boxed{R^{\oplus}} \rightleftharpoons \boxed{Br^{\ominus}}$$

True statement about the sequence on the basis of the assumption that R contains three different groups is:

(a) The more stable carbocation, the greater is the proportion of recemization

(b) The more nucleophilic the solvent, the greater is the proportion of inversion

(c) In above sequence, (b) represents separately solvated pair of ions

(d) All of these

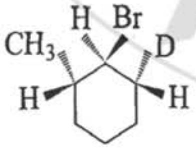
4. Which of the following statements is true?

(a) $CH_3CH_2S^-$ is both a stronger base and more nucleophilic than $CH_3CH_2O^-$

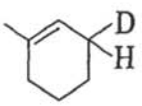
(b) $CH_3CH_2S^-$ is a stronger base but is less nucleophilic than $CH_3CH_2O^-$

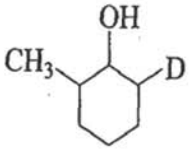
(c) $CH_3CH_2S^-$ is a weaker base but is more nucelophilic than $CH_3CH_2O^-$

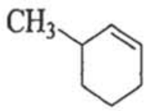
(d) $CH_3CH_2S^-$ is both a weaker base and less nucleophilic than $CH_3CH_2O^-$

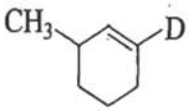
5. 

$\xrightarrow{\text{Alc. KOH}}$ (A). Major product of this reaction is:

(a) 

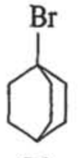
(b) 

(c) 

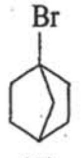
(d) 

6. Rate of $S_N2$ reaction is:

(A)



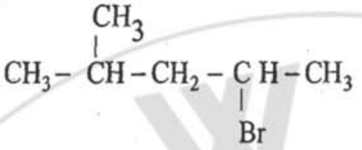
(B)

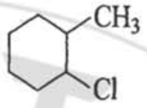


(C)

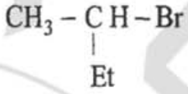
(a) B > A > C (b) C > A > B (c) A > B > C (d) A > C > B

7. Among the given halides, which one will give the same product in both $S_N1$ and $S_N2$ reactions?

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

(II) 

(III) 

(IV) 
$CH_3-\underset{Et}{CH}-Br$

(a) (III) only
(b) (I) and (II)
(c) (III) and (IV)
(d) (I), (III), and (IV)

8. 

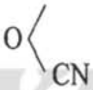
Product of reaction is:

(MOM chloride)

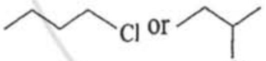
(a) 

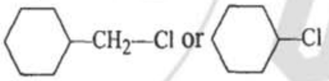
(b) 

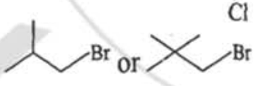
(c) Me–O–CH$_2$ – CH$_2$ –CN

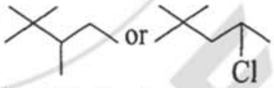
(d) 

9. In the given pair of compounds, in which pair the second compound is more reactive so that first forward $S_N2$ reaction takes place?

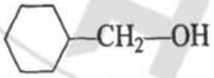
(a) 

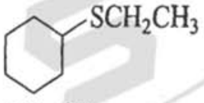
(b) 

(c) 

(d) 

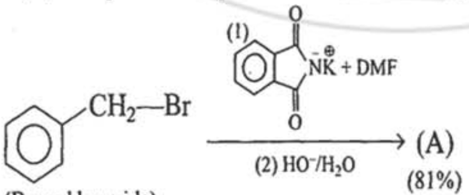
10. Which compound might be synthesized by the $S_N2$ displacement of an alkyl halide?

(a) 

(b) 

(c) Me$_3$C – OCH$_3$

(d) All of these

11. 

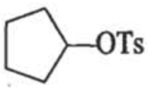
(Benzyl bromide)

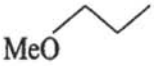
Product (A) of the above reaction is:

(a) Ph – NH$_2$
(b) Ph – CH$_2$ – NH$_2$
(c) Ph – CH – NH – CO H
(d) Ph – CH$_2$ – NH – CHO

12. Which of the following compounds will react faster with NaCN in an $S_N2$ reaction?

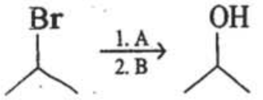
(a) 

(b) 

(c) 

(d) 

13. Which of the given reagents will accomplish the following transformations?



| | A | B |
|---|---|---|
| (a) | $H_3O^+$ | $BH_3$–THF; $H_2O_2$/NaOH |
| (b) | NaOH | $BH_3$–THF; $H_2O_2$/NaOH |
| (c) | HBr in ether | $Hg(Oac)_2/H_2O$; $NaBH_4$ |
| (d) | $NaNH_2$ | $Hg(Oac)_2/H_2O$; $NaBH_4$ |

14. $HC \equiv CNa + Cl-CH_2-CH_2-CH_2-I \rightarrow (A)$. Major product (A) is:

(a) $H-C \equiv C-CH_2-CH_2-CH_2-I$

(b) $CH_2=CH-CH_2-I$

(c) $H-C \equiv C-CH_2-CH_2-CH_2-Cl$

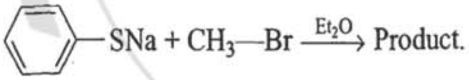
(d) $CH_2=CH-CH_2-Cl$

15. Which of the following molecules would have a carbon–halogen bond most susceptible to nucleolphilic substitution?

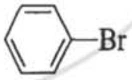
(a) 2-fluorobutane (b) 2-chlorobutane

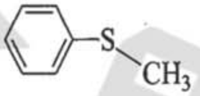
(c) 2-brombutane (d) 2-iodobutane

16. What is the major product obtained in the following reaction?

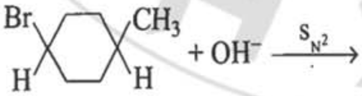


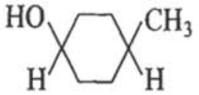
(a) 

(b) 

(c) 

(d) 

17.  A. The product A is:

(a) 

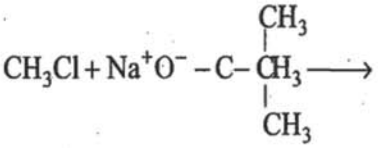
(b) 

(c) Both are correct (d) None is correct

18. Which of the following is most reactive towards nucleophilic substitution reaction?

(a) $CH_2=CH-Cl$ (b) $C_6H_5Cl$

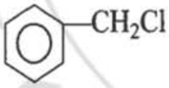
(c) $CH_3CH=CHCl$ (d) $ClCH_2-CH=CH_2$

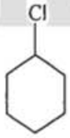
19. Which of the following reaction will not give ether as a major product?
    (a) $CH_3CH_2Cl + Ag_2O(dry) \longrightarrow$
    (b) $(CH_3)_3CCl + CH_3CH_2O^-Na^+ \longrightarrow$
    (c) $CH_3CH_2Cl + Na^+O^-$  $\longrightarrow$
    (d) 
    $CH_3Cl + Na^+O^- - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}H_3 - C - \longrightarrow$

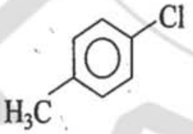
20. In the $S_N2$ reaction of *cis*-3-methylcyclopentyl bromide with alkali, the product formed is:
    (a) a *cis* alcohol
    (b) a *trans* alcohol
    (c) an equimolecular mixture of *cis* and *trans* alcohol
    (d) there is no reaction

21. If a mixture of two alkyl chlorides on treatment with sodium metal in ether solution gives isobutane as one of the products, then the reactants are:
    (a) methyl chloride and propyl chloride
    (b) methyl chloride and ethyl chloride
    (c) isopropyl chloride and ethyl chloride
    (d) isopropyl chloride and methyl chloride

22. Which of the following will be the least reactive towards nucleophilic substitution?

(a) 

(b) 

(c) 

(d) $C_2H_5Cl$

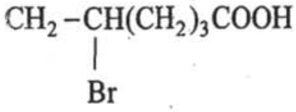
23. Which one of the following compounds will give in the presence of peroxide a product different from that obtained in the absence of peroxide?
    (a) 1-butene, HCl (b) 1-butene, HBr
    (c) 2-butene, HCl (d) 2-butene, HBr

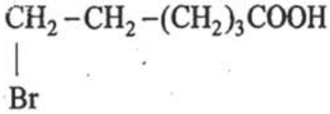
24. Which of the following compounds yields only one product on monochlorination?
    (a) Neopentane (b) Toluene (c) Phenol (d) Aniline

25. The principal organic compound formed in the reaction is:

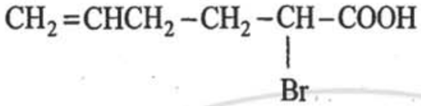
$$CH_2 = CH(CH_2)_3COOH + HBr \xrightarrow{\text{organic peroxide}}$$

Major product

(a) 
$\underset{\mathrm{Br}}{\mathrm{CH_2}}-\mathrm{CH(CH_2)_3COOH}$

(b) 
$\underset{\mathrm{Br}}{\mathrm{CH_2}}-\mathrm{CH_2}-\mathrm{(CH_2)_3COOH}$

(c) $CH_2 = CH(CH_2)_3COBr$

(d) 
$\mathrm{CH_2{=}CHCH_2-CH_2-\underset{Br}{CH}-COOH}$

26. The reactivity order of alkyl halide is 3° > 2° >1° in:

(a) both $S_N1$ and $S_N2$ (b) both $S_N2$ and $E_2$
(c) both $E_1$ and $S_N2$ (d) both $S_N1$ and $E_2$

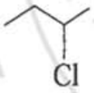
27. Which of the following statements is incorrect?

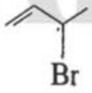
(a) An $S_N1$ reaction proceeds with the inversion of configuration
(b) An $S_N2$ reaction proceeds with stereochemical inversion
(c) An $S_N2$ reaction follows second-order kinetics
(d) The reaction of *tert*-butyl bromide with $OH^-$ follows first–order kinetics

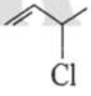
28. 3-Methyl-2-pentene on reaction with HOCl gives:

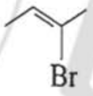
(a) 3-chloro-3-methyl pentanol-2 (b) 2,3-dichloro-3-methyl pentane
(c) 2-chloro-3-methyl pentanol-3 (d) 2,3-dimethyl butanol-2

29. Arrange the following alkyl halides in the increasing reactivity towards nucleophilic substitution reaction:


(A)


(B)


(C)

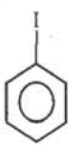

(D)

(a) A > B > D > C (b) A > C > B > D
(c) B > C > A > D (d) D > A > C > B

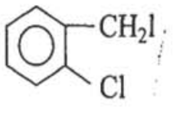
30. Each of the following reaction is given by *tert*-butyl bromide, except:

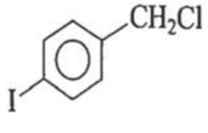
(a) $S_N1$ (b) $S_N2$ (c) $E_1$ (d) $E_2$

31. Which of the following compounds will give yellow precipitate on shaking with aqueous solution of NaOH followed by the addition of $AgNO_3$ solution?

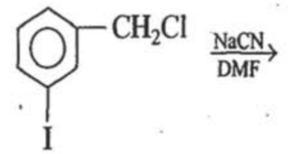
(a) 

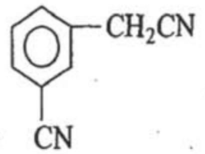
(b) 

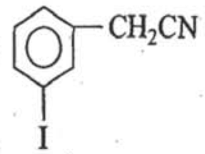
(c) 

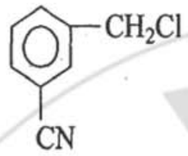
(d) 

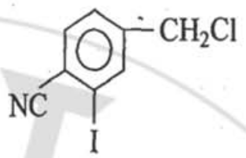
32. The structure of the major product formed in the following reaction is:



(a) 

(b) 

(c) 

(d) 

33. 3-Phenylpropene on reaction with HBr gives (as a major product):

(a) $C_6H_5CH_2CH(Br)CH_3$ (b) $C_6H_5CH(Br)CH_2CH_3$

(c) $C_6H_5CH_2CH_2CH_2Br$ (d) $C_6H_5CH(Br)CH{=}CH_2$

34. Rank the following organometallic compounds in the increasing order of nucleophilicity:

(A) $H_3CMgBr$ (B) $(CH_3)_2Cd$ (C) $CH_3Na$ (D) $CH_3Li$

(a) B < C < D < A (b) B < A < D < C

(c) C < D < A < B (d) D < A < B < C

35. Arrange the following in the increasing order of ease of nucleophilic substitution reaction: chlorobenzene (I); 2,4,6-trinitrochlorobenzene (II); 2,4-dinitrochlorobenzene (III); and 4-nitrochlorobenzene (IV):

(a) I < IV < III < II (b) I < III < IV < II

(c) II < III < IV < I (d) IV < III < II < I

36. $CH_3OH \xrightarrow{PI_3} (A) \xrightarrow{KCN} (B) \xrightarrow{H_2O/H^+} (C)$

The compound (C) is:

(a) $CH_3CN$ (b) $CH_3CH_2NH_2$

(c) $CH_3COOH$ (d) $CH_3CH_2COOH$

37. The following reaction is reversible:

$$\text{Alcohol} + HCl \rightleftharpoons \text{Alkyl halide} + H_2O$$

For the completion of the reaction, we use:

(a) anhydrous $ZnCl_2$ (b) conc. $H_2SO_4$

(c) $CaCl_2$ (d) excess of water

38. Benzyl chloride on hydrolysis gives:

(a) benzyl alcohol (b) benzoic acid

(c) benzaldehyde (d) benzo tri alcohol

39. For the reaction $R-Br \rightarrow R-O-N=O$, the suitable reagent is:

(a) $NaNO_2 + HCl$ (b) $HNO_2$

(c) $AgNO_3$ (d) $KNO_2$

40. Alkyl halide reacts with an alcoholic solution of ammonia to give a mixture of:

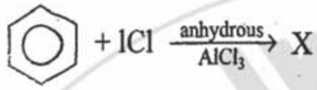
(a) 1° and 2° amines

(b) 1°, 2°, and 3° amines

(c) 1° and 3° amines

(d) 1°, 2°, and 3° amine and quaternary ammonium salt

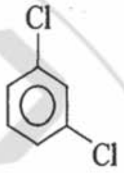
41. What is compound X in the reaction?



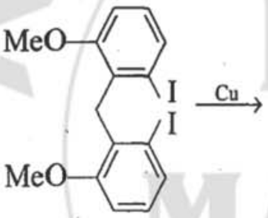
(a) 

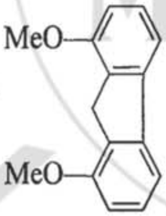
~~(b)~~ 

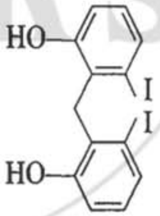
(c) 

(d) 

42. What would be the major product of the given reaction?



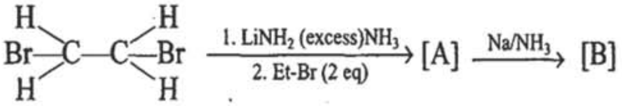
(a) 

(b) 

(c) 

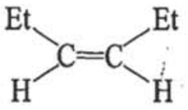
(d) 

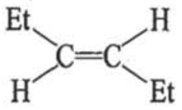
43. On the basis of the given reaction sequence, find out the final product?



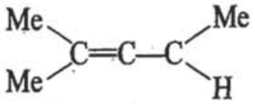
$$BrCH_2-CH_2Br \xrightarrow[\text{2. Et-Br (2 eq)}]{\text{1. LiNH}_2\text{ (excess)NH}_3} [A] \xrightarrow{Na/NH_3} [B]$$

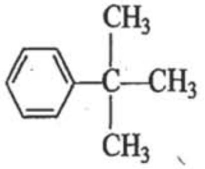
(a) $Et-C\equiv C-Et$ (b) $Et-C\equiv C-H$

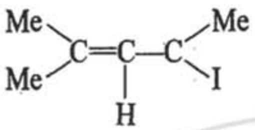
(c) 

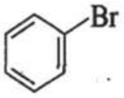
(d) 

44. Which of the following compounds will give yellow precipitate on shaking with aqueous solution of NaOH followed by the addition of $AgNO_3$ solution?

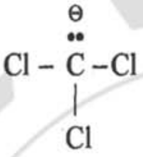
(a) 

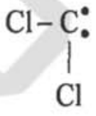
(b) 

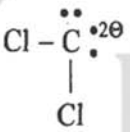
(c) 

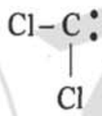
(d) 

45. When chloroform reacts with NaOH an important reactive intermediate is formed. The type of reaction involved and the intermediates formed are respectively:

(a) $E_2$ and 
$\mathrm{Cl}-\underset{\mathrm{Cl}}{\overset{\ominus}{\ddot{\mathrm{C}}}}-\mathrm{Cl}$

(b) $\beta$-elimination and 
$\mathrm{Cl}-\underset{\mathrm{Cl}}{\mathrm{C}}:$

(c) $E_2$ and 
$\mathrm{Cl}-\underset{\mathrm{Cl}}{\ddot{\mathrm{C}}}:^{2\ominus}$

(d) $\alpha$-elimination and 
$\mathrm{Cl}-\underset{\mathrm{Cl}}{\mathrm{C}}:$

## HINTS AND SOLUTIONS

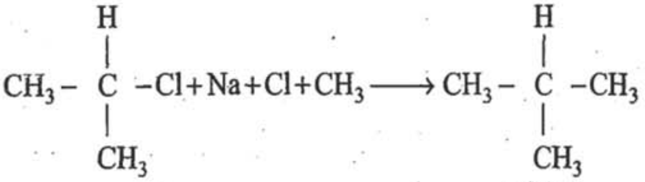
1. (a)
2. (c)
3. (d)
4. (c)
5. (c)
6. (c)
7. (c)
8. (b)
9. (d)
10. (d)
11. (b)
12. (d)
13. (d)
14. (c)
15. (d)
16. (c)
17. (b)

18. (d)

19. (b)

20. (b)

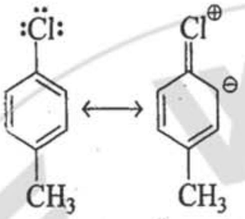
21. (d)



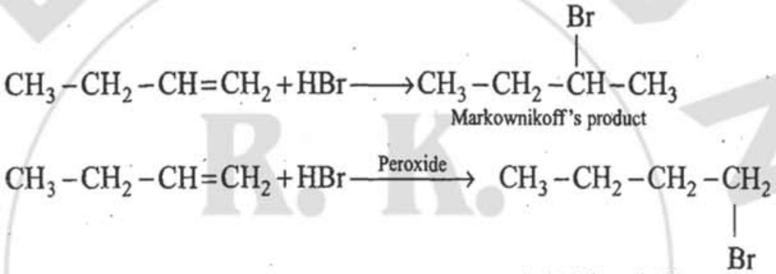
$$CH_3-\overset{H}{\underset{CH_3}{C}}-Cl+Na+Cl+CH_3 \longrightarrow CH_3-\overset{H}{\underset{CH_3}{C}}-CH_3$$

Isobutane

22. (c) Due to partial double bond character, it is difficult to break the double bond.



23. (b) Peroxide effect is observed with HBr only in asymmetric alkene.



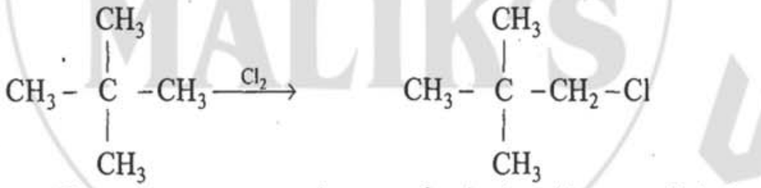
$$CH_3-CH_2-CH=CH_2+HBr \longrightarrow CH_3-CH_2-\overset{Br}{CH}-CH_3$$

Markownikoff's product

$$CH_3-CH_2-CH=CH_2+HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2-\underset{Br}{CH_2}$$

Anti-Markownikoff's product

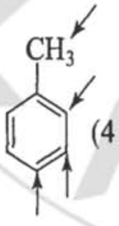
24. (a)



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{Cl_2} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Cl$$

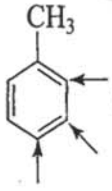
Neopentane only one type of product is possible on monochlorination

(b)



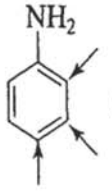
(4 types on monochlorination)

(c)



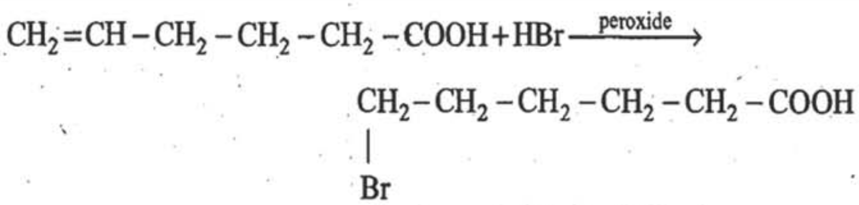
(3 types on monochlorination)

(d)



(3 types on monochlorination)

25. (b)



$$CH_2=CH-CH_2-CH_2-CH_2-COOH+HBr \xrightarrow{peroxide} \underset{\displaystyle Br}{CH_2}-CH_2-CH_2-CH_2-CH_2-COOH$$

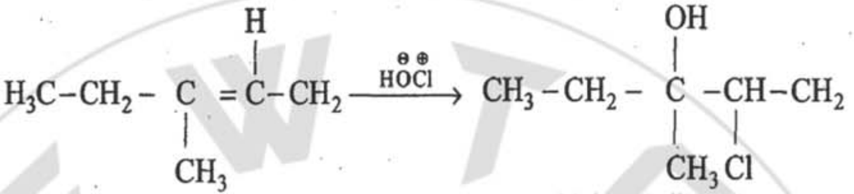
Anti-Markownikoff's rule

–I effect of –COOH group do not operate after second carbon.

26. (d) Conceptual

27. (a) In $S_N1$, racemic mixture is obtained

28. (c)



$$H_3C-CH_2-\underset{\displaystyle CH_3}{C}=\overset{\displaystyle H}{C}-CH_2 \xrightarrow{\overset{\ominus\ \oplus}{HOCl}} CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}-\underset{\displaystyle Cl}{CH}-CH_2$$

Markownikoff's product

29. (c) Stability of formed carbocation and weak bond strength of C – X (X = Br, Cl) favor the SN reaction.

30. (b)
31. (c)
32. (b)
33. (b)
34. (b)
35. (a)
36. (c)
37. (a)
38. (a)
39. (d)
40. (d)
41. (b)
42. (a)
43. (d)
44. (c)
45. (d)