# **ALKYL HALIDES**

Substitution Reactions  $(S_{N^1}, S_{N^2}, S_{N^i})$ 



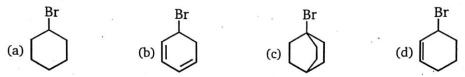
# LEVEL- ]

1. Which of the following is not expected to be intermediate of the following reaction?

$$\stackrel{\text{I}}{\longrightarrow} \stackrel{\text{H}_2\text{O}}{\longrightarrow} \stackrel{\text{OH}}{\longrightarrow}$$

2. Br 
$$\xrightarrow{CH_3}$$
  $+ \text{NaI} \xrightarrow{\text{Acetone}}$  product;  $S_{N^2}$  product of the reaction is :  $CH_2 - CH_3$ 

**3.** Rate of  $S_{N^2}$  will be negligible in :



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

$$(a) \xrightarrow{CH_2-Br} \xrightarrow{NH_3} product$$

$$CH_2-NH_2 \longrightarrow CH_2-Br$$

$$NH_2 \longrightarrow CH_2-NH_2 \longrightarrow CH_2-NH_2$$

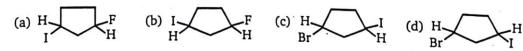
$$NH_2 \longrightarrow NH_2 \longrightarrow CH_2-NH_2$$

5.  $Cl - CH_2 - CH_2 - CH_2 - Cl + I^- \xrightarrow{DMF}$  product; Major product of this reaction is:  $CH_3$ 

$$\begin{array}{c} \text{CH}_{3} & \text{CH}_{3} \\ \text{(a) } \text{I}-\text{CH}_{2}-\text{C}-\text{CH}_{2}-\text{CH}_{2}-\text{Cl} \\ \text{CH}_{3} & \text{CH}_{2}-\text{C}-\text{CH}_{2}-\text{CH}_{2}-\text{I} \\ \text{CH}_{3} & \text{CH}_{3} \\ \text{CC) } \text{H}_{2}\text{C}=\text{C}-\text{CH}_{2}-\text{CH}_{2}=\text{Cl} \\ \end{array}$$

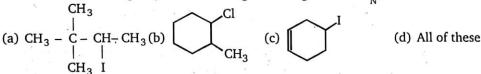
- **6.** Which of the following expressions is representative of the rate law for a  $S_{N^2}$  reaction?
  - (a) Rate = k [electrophile]
- (b) Rate = k [electrophile] [nucleophile]
- (c) Rate = k [nucleophile]<sup>2</sup>
- (d) Rate =  $k[electrophile]^2$

7.  $H \xrightarrow{F+} NaI (1 \text{ mole}) \xrightarrow{Acetone} (A)$ ; Major product of this reaction is:

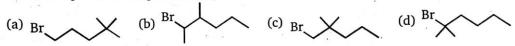


#### **ALKYL HALIDES (SUBSTITUTION)**

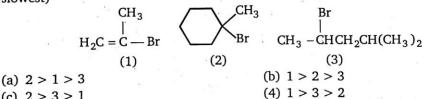
**8.** Which of the following alkyl halide undergo rearrangement in  $S_{N^1}$  reaction?



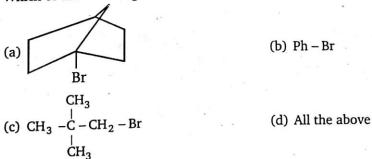
- 9. Arrange the following three chlorides in decreasing order towards S<sub>N1</sub> reactivity.
  - (1) Cl (2) Cl (3) Cl (b) 2 > 3 > 1 (c) 2 > 1 > 3 (d) 3 > 2 > 1
- 10. Which compound undergoes nucleophilic substitution with NaCN at the fastest rate?

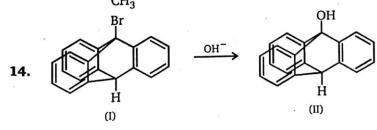


11. Rank the following in order of decreasing rate of solvolysis with aqueous ethanol (fastest  $\rightarrow$  slowest)



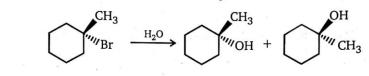
- (c) 2 > 3 > 1
   (4) 1 > 3 > 2
   The reaction of 4-bromobenzyl chloride with sodium cyanide in ethanol leads to the formation of:
  - (a) 4-bromobenzyl cyanide
- (b) 4-cyanobenzyl chloride
- (c) 4-cyanobenzyl cyanide
- (d) 4-bromo-2-cyanobenzyl chloride
- 13. Which of the following reactant will not favour nucleophilic substitution reaction?

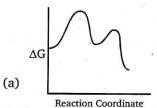


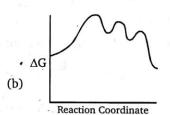


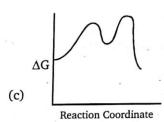
Conversion of I to II:

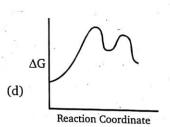
- (b) takes place by S<sub>N²</sub>(d) does not take place
- (a) takes place by  $S_{N^1}$ (c) takes place both by  $S_{N^1}$  and  $S_{N^2}$
- 15. Which is the correct reaction coordinate diagram for the following solvolysis reaction?



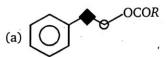


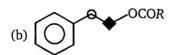






product; Product of this reaction is:





(c) both (a) and (b)

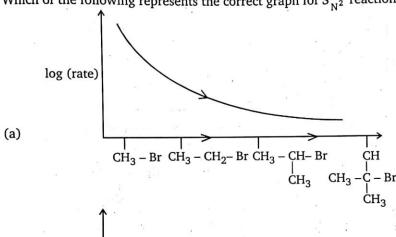
(d) None of these

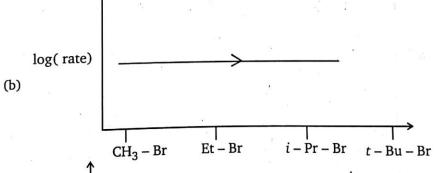
17. 
$$CH_3$$
 $\longrightarrow$   $(A)$   $\xrightarrow{CH_3SNa}$   $(B)$ , Product  $(B)$  is:

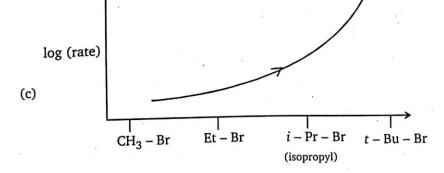
(a) 
$$CH_2$$
-S- $CH_3$  (b)  $S$ - $CH_3$ 

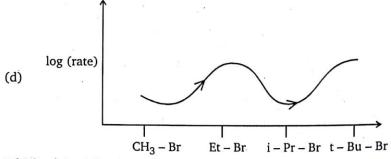
(d) None of these

Which of the following represents the correct graph for S  $_{\mathrm{N}^2}$  reaction ? 18.

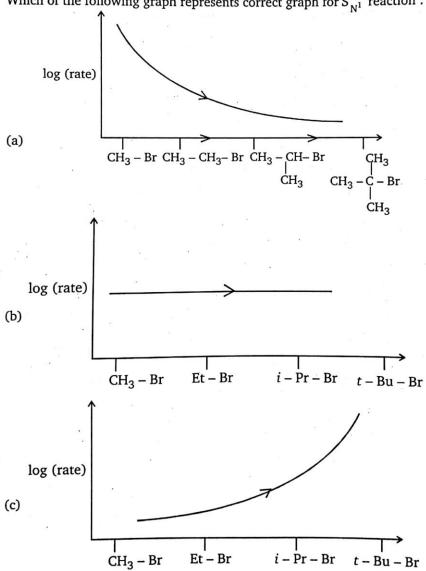


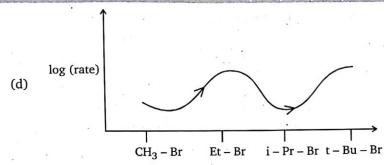




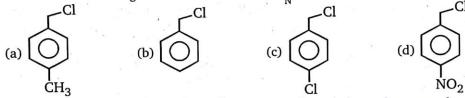


**19.** Which of the following graph represents correct graph for  $S_{N^1}$  reaction :





**20.** Which of the following is most reactive toward  $S_{N^2}$  reaction?



21. Among the given pairs, in which pair first compound reacts faster than second compound in  $S_{N^1}$  reaction?

(a) 
$$CH_3 - CH_2 - CH_2 - CH_2 - Br \text{ or } CH_3 - CH_2 - CH - CH_3$$

$$CH_3 \qquad CH_3$$
(b)  $CH_3 - C - CH_2 - CH_2 \text{ or } CH_3 - CH - CH - CH_3$ 

$$Br \qquad Br$$

(c) 
$$CH_3$$
  $CH_3$   $CH_3$  (d)  $CH_3 - C - CH_3$  or  $CH_3 - C - CH_3$ 

22. What is the major product of the following reaction?

$$H_2C = CH - CH_2 - OH \xrightarrow{BBr} Product$$

Br
(a) 
$$CH_3 - CH - CH_2 - Br$$
(b)  $H_2C = CH - CH_2 - Br$ 
OH
(c)  $CH_3 - CH - CH_2 - OH$ 
(d)  $CH_3 - CH - CH_2 - OH$ 

**23.**  $S_{N^1}$  and  $S_{N^2}$  products are same with (excluding stereoisomer):

**24.** Consider the nucleophilic attacks given below. Select in each pair that shows the greater  $S_{N^2}$  reaction rate.

or

or

$$A$$
)  $Br + CN$  or

(B) 
$$H_3C - Br + -SH$$

 $H_3C - Br + CH_3SH$ 

$$(C)$$
  $\longrightarrow$   $Br + Cl^-$  or

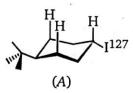
$$\begin{array}{c}
 & \text{Br} + I^{-} \text{ in DMSO} \\
\end{array}$$

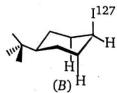
(D) 
$$\bigcirc$$
 Br + Cl

(b) (II); (III); (V); (VIII)

(d) (I); (III); (V); (VII)

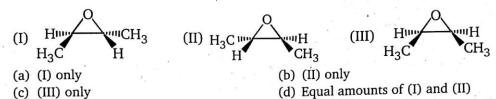
**25.** Which of the two stereoisomers of 4*t*-butylcyclohexyl iodide ( $^{127}$  I<sup>-</sup>) will undergo S<sub>N<sup>2</sup></sub> substitution with  $^{128}$  I<sup>-</sup> faster, and why?





- (a) A will react faster because it is the more stable of the two isomers
- (b) A will react faster because it will yield a more stable product, and the transition state for both reactions is of the same energy
- (c) A will react faster because the approach of <sup>128</sup> I<sup>-</sup> can depart unhindered.
- (d) B will react faster because it is less stable than A, and the transition state for both reactions is of the same energy

**26.** (*Z*)-2-Butene reacts with  $Br_2/H_2O$ . The resulting bromohydrin when treated with methoxide in methanol undergoes an intramolecular  $S_{N^2}$  reaction. Taking into consideration the stereochemical consequences of the reaction mechanism involved, choose the final product(s) of these transformations.



27. Rank the following species in order of decreasing nucleophilicity in a polar protic solvent (most → least nucleophilic):

28. Identify products of the given reactions:

Reaction-1

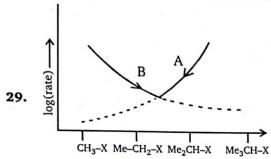
NMe<sub>2</sub>

$$CH_3CO_2Na \atop CH_3CO_2Na \atop CH_3CO_2Na \atop CH_3CO_2H} Product$$

Reaction-2

$$CH_3CO_2Na \atop CH_3CO_2H} Product$$

$$CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop CH_3 \atop CH_3 CO_2H \atop CH_3 \atop C$$



Which of the following is true about given graphs A and B?

(a) 
$$A \rightarrow S_{N^1} \quad B \rightarrow S_{N^2}$$
  
(c)  $A \& B \rightarrow E_1$ 

(b) 
$$A \rightarrow S_{N^2}$$
,  $B \rightarrow S_{N^1}$ 

(c) 
$$A \& B \rightarrow E$$

(d) 
$$A \& B \xrightarrow{N} E_2$$

30. In each of the following groups, which is the strongest (best) nucleophile?

(I) (1) 
$$H_3C - O^-$$

(3) 
$$H_3 C - S^-$$
 in  $CH_3OH$ 

31. 
$$\bigcirc \bigcup_{\substack{\parallel \\ 0}} - (CH_2)_4 - CH_2 - Cl \xrightarrow{\text{NaNH}_2 \atop \text{dimethoxy ethane}} (A); \text{ Product } (A) \text{ is } :$$

(c) 
$$CH_2$$
  $CH_2 - NH_2$ 

Which of the following reaction is an elimination reaction? 32.

(a) 
$$H$$
  $H_2SO_4$   $+ H$ 

(c) 
$$\xrightarrow{H}$$
  $\xrightarrow{\text{NaOCH}_3}$   $\xrightarrow{\text{OCH}_4}$ 

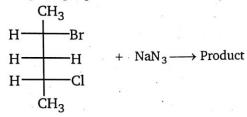
(d) both (a) and (b)

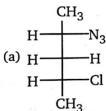
33. 
$$CH_2 - Cl \xrightarrow{CH_3OH(S_{N^1})} Product$$

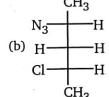
Which of the following products can be obtained from above reaction?

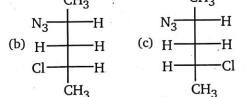
(a) 
$$CH_2 - OCH_3$$
 (b)  $CH_3O O$  (c)  $CH_3$  (d) All of these

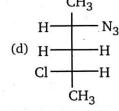
What is the principal product of the following reaction? 34.











What would be the effect of increasing solvent polarity on the rate of each of the following 35. reactions ? (Nu = neutral nucleophile)

(A) Nu + 
$$R - L \longrightarrow \overset{\oplus}{\text{Nu}} - R + L^{-}$$

- (b) decreases (a) increases
- (c) constant
- (d) can not be predicted

**(B)** 
$$R - L^{\oplus} \longrightarrow R^{\oplus} + : L$$

- (a) increases
- (b) decreases
- (c) constant
- (d) cannot predict

Which of the following is most reactive toward S  $_{\mathrm{N}^2}$  reaction ? 36.

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

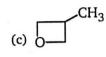
(b) 
$$Ph - CH_2 - Cl$$

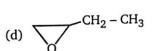
(d) 
$$Ph - C - CH_2 - Cl$$
 $\parallel$ 
O

4-chloro-1-butanol + NaOH  $\longrightarrow$  (B) 37. Product (B) of the above reaction is:









- **38.** In the given pairs of alkyl-halide, in which pair the first compound is more reactive than second compound toward  $S_{M^2}$  reaction?
  - (a)  $(CH_3)_2CHBr$  or  $CH_3 CH_2 CH_2 Br$
  - (b)  $CH_3 CH_2 CH_2 Br$  or  $CH_3 CH_2 CH_2 I$
  - (c) Ph Br or  $CH_3 CH_2 CH_2 Br$
  - (d)  $CH_2 = CH CH_2 Cl$  or  $H_2C = CH Cl$
- **39.** In the given pair of reaction in which pair the second reaction is more reactive than first toward  $S_{N^2}$  reaction?
  - (a)  $CH_3 CH_2 Cl + CH_3 CH_2 O^- \longrightarrow Et O Et$  (or)

$$CH_2 - CH_2 - Cl + CH_3 - CH_2 - OH \longrightarrow Et - O - Et$$

(b)  $CH_3 - CH_2 - Cl + EtO^- \longrightarrow Et - O - Et$  (or)

$$CH_3 - CH_2 - Cl + EtS^- \longrightarrow CH_3 - CH_2 - S - Et$$

(c)  $\operatorname{Et} - \operatorname{Cl} + \operatorname{CH}_3 \operatorname{O}^- \longrightarrow \operatorname{Et} - \operatorname{O} - \operatorname{CH}_3$  (or)

$$\underbrace{\text{Et} - \text{Cl} + \text{CH}_3\text{O}^-}_{(2\text{m})} \longrightarrow \text{Et} - \text{O} - \text{CH}_3$$

(d)  $Et - Br + Ph_3P \longrightarrow Et - PPh_3$  (or)

$$Et - Br + Ph_3N \longrightarrow E + -NPh_3$$

- **40.** Among the following pair of reactions in which pair the second reaction is more reactive than first in  $S_{N^1}$  reaction?
  - (a)  $Me_3CCl + H_2O \longrightarrow Me_3COH$
- (or)  $Me_3CBr + H_2O \longrightarrow Me_3COH$
- (b)  $Me_3CCl + CH_3OH \longrightarrow Me_3C \longrightarrow OCH_3$  (or)  $Me_3C \longrightarrow Cl + H_2O$



- (c)  $Me_3CCl+ H_2O \longrightarrow$  (or)  $Me_3CCl+ H_2O$ (2M)
- (d) All of these
- **41.** Which is a true statement concerning the transition state of an  $S_{N^2}$  reaction?
  - (a) Closely resembles a carbocation intermediate
  - (b) The electrophile is responsible for the reaction
  - (c) Lower is energy than the starting materials
  - (d) Involves both the nucleophile and electrophile
- **42.** Increasing the concentration of a nucleophile in a typical  $S_{N^2}$  reaction by a factor of 10 will cause the reaction rate to :
  - (a) increase by a factor of 10
- (b) increase by a factor of 102
- (c) decrease by a factor of 10
- (d) remain about the same
- **43.** Decreasing the concentration of an electrophile in a typical  $S_{N^2}$  reaction by a factor of 3 will cause the reaction ratio to :
  - (a) increase by a factor of 3
- (b) increase by a factor of 32
- (c) decrease by a factor of 3
- (d) remain about the same

44. Increasing the concentration of an electrophile in a typical  $S_{N^2}$  reaction by a factor of 3 and the concentration of the nucleophile by a factor of 3 will change the reaction rate to:

con act act act ac

- (a) increase by a factor of 6
- (b) increase by a factor of 9
- (c) decrease by a factor of 3
- (d) remain about the same
- **45.** Consider the following reaction and select the best choice that represents the reaction.

$$CH_3$$

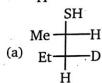
$$Na^{\oplus -SCH_2CH_3} \rightarrow Product$$

$$\text{(a)} \qquad \qquad \begin{array}{c} \text{CH}_3 \\ \text{SCH}_2\text{CH}_3 \end{array}$$

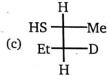
(c) 
$$CH_3$$
  
 $SCH_2CH_3$ 

$$(d) \begin{array}{c} CH_3 & CH_3 \\ & & \\ & & \\ H & \\ \end{array} S - CH_2CH_3$$

46.  $Et \xrightarrow{H} D \xrightarrow{KSH} Product; Identify the product.$ 



$$\begin{array}{ccc}
 & H \\
 & Me & H \\
 & Et & D
\end{array}$$



$$\begin{array}{c}
\text{SH} \\
\text{H} \longrightarrow \text{Me} \\
\text{(d)} \\
\text{Et} \longrightarrow \text{D}
\end{array}$$

47. The reaction,

$$H_{III}OH + SOCl_2 \longrightarrow H_{III}Cl + SO_2 + HCl$$

proceeds by the..... mechanism.

- (a) S<sub>Ni</sub>
- (b) S<sub>N<sup>2</sup></sub>
- (c) S<sub>E2</sub>
- (d) S<sub>N1</sub>

48. Consider the following anions.

$$CF_3 - S - O^ C_6H_5 - S - O^ C_6H_5 - S - O^ CH_3 - C - O^ CH_3 - C - O^ CH_3 - C - O^-$$

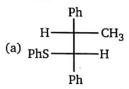
When attached to  $sp^3$ -hybridized carbon, their leaving group ability in nucleophilic substitution reaction decreases in the order :

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

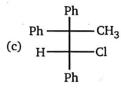
49.  $Cl \xrightarrow{Ph} H \xrightarrow{Ph SNa} Principal organic product of the reaction will be :

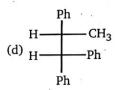
Ph

<math>S_{N^2}$ 



$$\begin{array}{c|c}
 & Ph \\
 & H \longrightarrow CH_3 \\
 & H \longrightarrow SPh \\
\end{array}$$





- **50.** Reaction of *R*-2-butanol with *p*-toluenesulphonyl chloride in pyridine followed by reaction with LiBr gives:
  - (a) R-2-butyl bromide

(b) S-2-butyl tosylate

(c) R-2-butyl tosylate

- (d) S-2-butyl bromide
- **51.** The compound which undergoes  $S_{N^1}$  reaction most rapidly is:
  - (a) Br

(b) Br

(c)  $\sim$  CH<sub>2</sub>Br

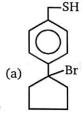
- (d) Br
- 52. Addition of KI accelerates the hydrolysis of primary alkyl halides because:
  - (a) KI is soluble in organic solvents
  - (b) the iodide ion is a weak base and a poor leaving group
  - (c) the iodide ion is a strong base
  - (d) the iodide ion is a powerful nucleophile as well as a good leaving group
- **53.** Which of the following phrases are not correctly associated with  $S_{N^1}$  reaction?
  - (1) Rearrangement is possible
  - (2) Rate is affected by polarity of solvent
  - (3) The strength of the nucleophile is important in determining rate
  - (4) The reactivity series is tertiary > secondary > primary
  - (5) Proceeds with complete inversion of configuration
  - (a) 3, 5

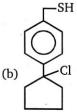
(b) 5 only

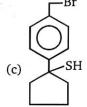
(c) 2, 3, 5

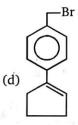
(d) 3 only

54. 
$$\underbrace{ \begin{array}{c} \text{CH}_3 \\ \text{SO}_2\text{Cl}_2 \\ h\nu \end{array}} (A) \xrightarrow{\text{NBS}} (B) \xrightarrow{\text{KSH}} (C) \text{, Product } (C) \text{ is :}$$

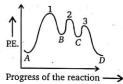








**55.** Energy profile diagram for an exothermic reaction,  $A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D$ , is given below.



The rate determining step of the reaction is :

(a) 
$$A \longrightarrow B$$

(b) 
$$B \longrightarrow C$$

(c) 
$$C \longrightarrow L$$

(d) can not predict

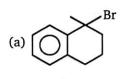
56. 
$$(A)$$

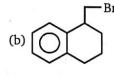
NBS

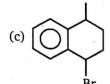
(A)

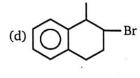
Major

Major product is (A) is:







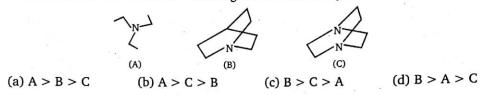


 $\underset{S_{N^2} \text{ conditions}}{\text{LiBr/DMSO}} \text{Major product } (X)$ 

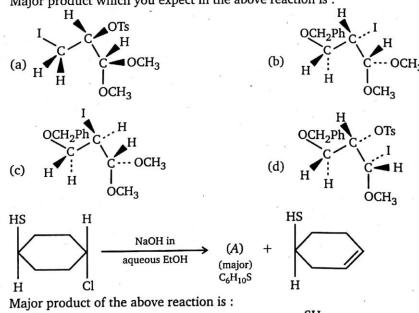
The product X is:

60.

Relative rate of reaction of the following amine with methyl iodide is: 58.



Major product which you expect in the above reaction is:



61. 
$$CH_3 - C - C^{14} - CH_3 \xrightarrow{\Delta} Major product of the reaction is: CH3 OTs$$

(a) 
$$CH_3 \sim C = C < CH_3$$

(b) 
$$CH_3 - CH_2 = CH_2$$
  
 $CH_2 = CH_2$ 

(c) 
$$CH_3$$
  $C = C$   $CH_3$ 

(d) 
$$CH_3$$
  $C = C$   $CH_3$   $C = C$ 

62. The decreasing order of reactivity of the compounds given below towards solvolysis under identical conditions is:

$$CH_{3} - C - CH_{3} \qquad CH_{3} - C - CH_{3}$$

$$(I) \qquad (II) \qquad (III)$$

$$CH_{3} - C - CH_{3}$$

(a) 
$$II > III > I$$

(b) 
$$I > II > III$$

(c) 
$$III > II > I$$

$$II < I < II$$
 (b)

63. OH 
$$\frac{1. \text{One Eq. NaOH}}{2 \text{ MeBr}} (A); \text{ Product } (A) \text{ is :}$$

- (d) None of these
- (R)-2-octyl tosylate is solvolyzed in water under ideal  $S_{N^1}$  conditions. The product(s) will 64.
  - (a) R-2-octanol and S-2-octanol in a 1:1 ratio
  - (b) R-2-octanol and S-2-octanol in a 1.5:1 ratio
  - (c) R-2-octanol only
  - (d) S-2-octanol only

- **65.** From each of the following pairs select the compound that will react faster with sodium iodide in acetone:
  - Pair-A: (1) 2 Chloropropane
- (2) 2- Bromopropane
- Pair-B: (3) 1 Bromobutane
- (4) 2- Bromobutane

- (a) 1,3
- (b) 1,4
- (c) 2,3
- (d) 2,4
- **66.** Among the given halides, which one will give same product in both  $S_{N^1}$  and  $S_{N^2}$  reactions.
  - (I) CH<sub>3</sub> CH CH<sub>2</sub> CH CH<sub>3</sub>

    Br
- (II) Cl CH<sub>3</sub>

(III) Cl

(IV) CH<sub>3</sub> -CH - Br

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

- **67.** Product(s) formed during this reaction is/are:
  - $CH_2 \overline{C}H_2 OTs$   $\overline{C}H_2 CH_2 OAc$
- $\xrightarrow{\text{AcONa}} \text{Product ? [ C}^* = \text{isotopic carbon]}$
- $CH_2 \overset{*}{C}H_2 OTs$
- (b)  $CH_2 \mathring{C}H_2 OAc$

(c) OAc

- (d) Both (a) & (b)
- **68.** Anisole  $\xrightarrow{\text{excess HI (conc.)}} \text{Product}$ 
  - (a)  $\langle O \rangle$  + CH<sub>3</sub>I
- (p) (D)—I + CH3OH
- (c) OH + CH<sub>3</sub>I
- (d) OH + CH<sub>3</sub>CH<sub>2</sub>I
- **69.** Which of the following compounds would react faster with NaCN in an  $S_{N^2}$  reaction?
  - (a) J
- (b) OT:
- (c) MeO
- (d)  $\sim$ OTs

70. HC 
$$\equiv$$
 CNa + Cl - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - I  $\longrightarrow$  (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)  $H C \equiv C CH_2 CH_2 CH_2 CI$
- (d)  $CH_2 = CH CH_2 Cl$
- 71. What is the major product obtained in the following reaction?

$$\sim$$
 SNa + CH<sub>3</sub> — Br  $\xrightarrow{\text{Et}_2\text{O}}$  Product

- (a)
- (b) Br
- (c)  $\sim$  S<sub>CH<sub>3</sub></sub> (d)  $\sim$
- 72. Br  $CH_3 + OH^- \xrightarrow{S_{N^2}} A$ ; The product A is:
  - (a) HOCH<sub>3</sub>

- (b) HO CH<sub>3</sub>
- (c) Both (a) and (b) are correct
- (d) None is correct
- **73.**  $Me_2C = CH CH_2 CH_2 CI \xrightarrow{H_2O} (X)$ ; Major product of the reaction is :

(b) 
$$Me_2C = CH - CH_2 - CH_2 - OH$$

(c)  $Me_2C = CH - CH - CH_2 - OH$ 

74.  $OH \xrightarrow{HBr \atop \Delta} (A)$ 

$$OH \xrightarrow{\text{HBr}} OB$$

$$OCH_3$$

Product (A) and (B) respectively are:

(a) 
$$OH$$
 and  $OH$  (b)  $OH$  and  $OH$   $OH$   $OH$ 

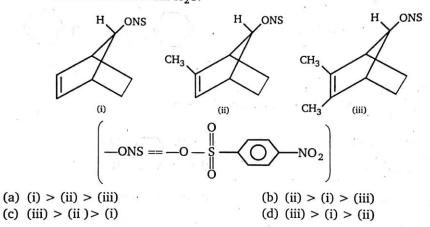
### 280

# ORGANIC Chemistry for IIT-JEE

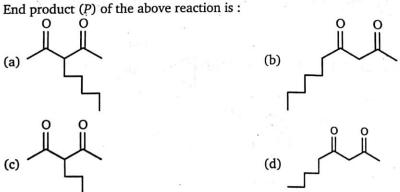
(c) 
$$OH$$
 and  $OH$  (d)  $OH$  and  $OCH_3$   $OCH_3$ 

**75.** Relative rate of reaction with  $H_2O$ .

00,00,00,00



2 eq. KNH<sub>2</sub> 76.  $NH_3(l)$ 



Which of the following statements is correct regarding the rate of hydrolysis of the compounds (A) and (B) by  $S_{N^1}$  reaction? 77.

$$A$$
 Br  $O$   $B$ 

- (a) A reacts faster than B
- (b) B reacts faster than A
- (c) Both A and B reacts at the same rate
- (d) Neither A nor B reacts
- **78.** What are reactant X and product Y in the following sequence of reactions?

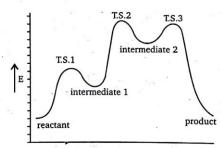
**79.** Transition state of given  $S_{N_2}$  is:

$$(a) \begin{bmatrix} \delta \Theta \\ OR \\ OR \\ H \\ Br \\ \delta \Theta \end{bmatrix}^{\ddagger} \qquad (b) \begin{bmatrix} CH_2 - O - R \\ OR \\ OR \\ H \\ Br \\ \delta(+) \end{bmatrix}^{\ddagger}$$

(c) 
$$\begin{bmatrix} \delta \oplus & \\ OR & \\ & H \\ & Br \\ \delta \ominus & \end{bmatrix}$$

(d) 
$$\begin{bmatrix} \delta(-) \\ OR \\ H \\ Br \\ \delta(-) \end{bmatrix}^{\ddagger}$$

- **80.**  $C_6H_{13}Br + OH^- \longrightarrow C_6H_{13}OH + Br^-$  is an example of:
  - (a) Nucleophilic addition
- (b) Nucleophilic substitution
- (c) Electrophilic addition
- (d) Electrophilic substitution
- (e) Free radical substitution
- **81.** Transition state 2 is structurally most likely as:

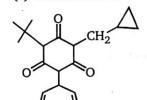


(a) intermediate 1

(b) transition state 3

(c) intermediate 2

(d) product



x = Number of aromatic compound obtained when above compound undergo complete acidic hydrolysis.

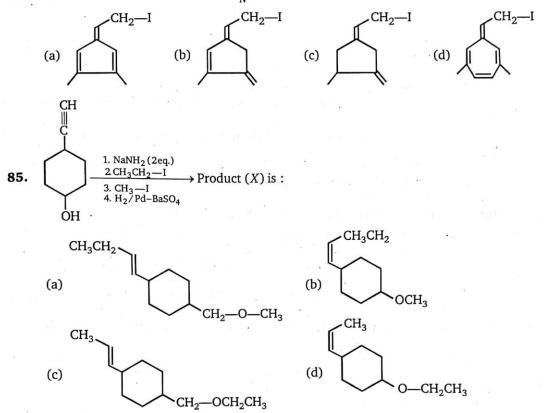
(a) 1

82.

- (b) 2
- (c) 3
- (d) 4

- 83.  $S_N 1$  and  $S_N 2$  reactions are
  - (a) Both stereospecific
  - (b) Both stereoselective
  - (c) Stereoselective and stereospecific respectively
  - (d) Stereospecific and stereoselective respectively

**84.** Most reactive compound toward  $S_{N^1}$  is :



						ANSV	VERS	— LE	VEL 1						
1.	(a)	2.	(b)	3.	(c)	4.	(a)	5.	(b)	6.	(b)	7.	(b)	8.	(d)
9.	(b)	10.	(a)	11.	(c)	12.	(a)	13.	(d)	14.	(d)	15.	(b)	16.	(c)
17.	(a)	18.	(a)	19.	(c)	20.	(d)	21.	(b)	22.	(a)	23.	(c)	24.	(c)
25.	(d)	26.	(d)	27.	(d)	28.	(a)	29.	(a)	30.	(d)	31.	(b)	32.	(d)
33.	(d)	34.	(c)	35.	A(a)	35.	B(b)	36.	(d)	37.	(b)	38.	(d)	39.	(b)
40.	(d)	41.	(d)	42.	(a)	43.	(c)	44.	(b)	45.	(c)	46.	(d)	47.	(a)
48.	(b)	49.	(b)	50.	(d)	51.	(b)	52.	(d)	53.	(a)	54.	(b)	55.	(a)
56.	(a)	57.	(b)	58.	(c)	59.	(c)	60.	(b)	61.	(c)	62.	(d)	63.	(a)
64.	(b)	65.	(c)	66.	(d)	67.	(d)	68.	(c)	69.	(d)	70.	(c)	71.	(c)
72.	(b)	73.	(d)	74.	(b)	75.	(c)	76.	(d)	77.	(b)	78.	(b)	79.	(d)
80.	(b)	81.	(c)	82.	(b)	83.	(b,c)	84.	(d)	85.	(b)				



1. Statement-1: Nucleophilicity order in polar-protic solvent is  $I^- < Br^- < Cl^- < F^-$ 

**Statement-2**: Due to bigger size of I<sup>-</sup> it is less solvated in polar-protic solvent.

- (a) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (b) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (c) Statement-1 is true, statement-2 is false.
- (d) Statement-1 is false, statement-2 is true.

# 2. Statement - 1 : $CH_3 - CH_2 - Cl + NaI \xrightarrow{Acetone} CH_3 - CH_2 - I + NaCl \downarrow$

**Statement- 2:** Acetone is polar-protic solvent and solubility order of sodium halides decreases dramatically in order NaI > NaBr > NaCl. The last being virtually insoluble in this solvent and a 1° and 2° chloro alkane in acetone is completely driven to the side of Iodoalkane by the precipitation reaction.

- (a) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for statement-1.
- (b) Statement-1 is true, Statement-2 is true and Statement-2 is Not the correct explanation for statement-1.
- (c) Statement-1 is true, Statement-2 is false.
- (d) Statement-1 is false, Statement-2 is true.
- 3. Encircle whichever of the following:
  - (a) is the stronger nucleophile (aprotic solvent): F or I
  - (b) is the stronger nucleophile (protic solvent): F or I
  - (c) is the stronger base: For I
  - (d) is the stronger nucleophile (protic solvent): NH3 or NH2NH2
  - (e) is the better leaving group : CH<sub>3</sub>COO or CH<sub>3</sub>SO<sub>3</sub>
- 4. Encircle whichever of the following:

(a) undergoes an 
$$S_{N^2}$$
 reaction more rapidly,  $CH_3 - Br$  or  $CH_3 - CH - CH_3$ 

(b) undergoes an  $S_{N^1}$  reaction more rapidly,  $CH_3 - Br$  or  $CH_3 - CH - CH_3$ 

(c) undergoes an 
$$E_2$$
 reaction to give (Z)-1,2-diphenylpropene:

# (d) reacts with NaI to give (Z)-1,2-diphenylpropene :

(e) undergoes an  $S_{N^1}$  reaction more rapidly,

## **5.** Encircle whichever of the following:

(a) undergoes an  $S_{N^2}$  reaction more rapidly:  $CH_2$ -Br or  $CH_2$ -Br

(b) undergoes an 
$$E_1$$
 reaction more rapidly :  $\begin{array}{c} CH_3 \\ CH-CH_2-CH_2 \\ Br \end{array}$  or  $\begin{array}{c} CH_3 \\ C-CH_2-CH_3 \\ Br \end{array}$ 

(c) undergoes an  $S_{N^1}$  reaction more rapidly:

(d) undergoes an  $S_{N^2}$  reaction more rapidly:

(e) undergoes an  $\rm E_2$  reaction more rapidly :

$$\int_{Cl} \text{or} \int_{C} C$$

# 6. Match the column:

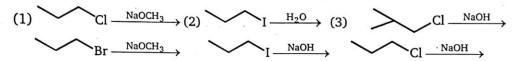
	Alkyl halide		Relative ra	ate	Relative rate (S <sub>N<sup>2</sup></sub> )
(a)	CH <sub>3</sub> – Br	(p)	1	(w)	1200
(b)	CH <sub>3</sub> -CH <sub>2</sub> - Br	(q)	1.05	(x)	40
(c)	CH <sub>3</sub> -CH -Br	(r)	11	(y)	16
(d)	$\begin{array}{c} \text{CH}_3 \\ \mid \\ \text{CH}_3 - \text{C} - \text{Br} \\ \mid \\ \text{CH}_3 \end{array}$	(s)	1,200000	(z)	1

# 7. Matrix:

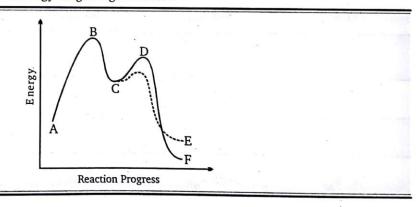
	Column (I)		Column (II)	
	Compound	Type of reaction		
(a)	CI CI	(p)	S <sub>N</sub> <sup>1</sup> reaction can take place	
(b)	CI	(q)	S <sub>N<sup>2</sup></sub> reaction can take place	
(c)	CI	(r)	$S_{N^1}$ is not possible	
(d)	CI	(s)	S <sub>N<sup>2</sup></sub> is not possible	

#### ALKYL HALIDES (SUBSTITUTION)

- 8. Encircle whichever of the following:
  - (a) undergoes an  $S_{N^2}$  reaction more rapidly, O
  - (b) undergoes an S  $_{N^1}$  reaction more rapidly,  $(CH_3)_3C-Br$  or  $(CH_3)_3C-I$
  - (c) undergoes an  $S_{N^1}$  reaction more rapidly, P or P or
- **9.** Reactivity: Circle the reaction that reacts FASTER by  $S_{N^2}$  in each pair:



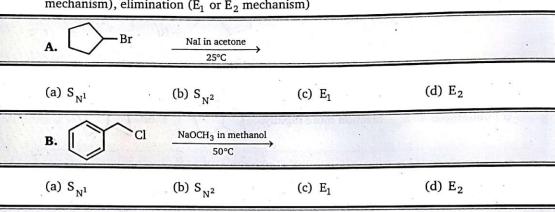
10. Consider the potential energy diagram given below

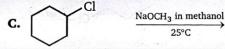


- (X) Name the positions A-D
- (Y) Answer the following questions.
  - (i) Both reaction pathways are: EXOTHERMIC or ENDOTHERMIC
  - (ii) Which step is the rate determining step (RDS)?
    - B or D
  - (iii) Which product is most stable?

- E or F
- (iv) In accordance with Hammonds postulate, exothermic reactions tend to have
  - (a) early transition states that are reactant like
  - (b) late transition states that are reactant-like
  - (c) early transition states that are product-like
  - (d) late transition states that are product-like.

11. Select whether the following combinations of reactants will react by substitution (S $_{N^1}$  or S $_{N^2}$  mechanism), elimination (E $_1$  or E $_2$  mechanism)





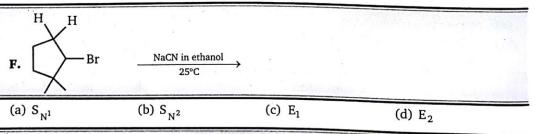
(a) 
$$S_{N^1}$$
 (b)  $S_{N^2}$ 
**D.**  $(CH_3)_3C - OH \xrightarrow{BBr 48\% \text{ in } H_2O}$ 

- (a)  $S_{N^1}$  (b)  $S_{N^2}$ 
  - (b)  $S_{N^2}$  (c)  $E_1$  (d)  $E_2$

(c) E<sub>1</sub>

- E.  $(CH_3)_2CH Br$ NaCN in ethanol
  25°C
- 25°C
- (a)  $S_{N^1}$  (b)  $S_{N^2}$
- (c) E<sub>1</sub>
- (d) E<sub>2</sub>

(d) E<sub>2</sub>



- **G.**  $(CH_3)_2CHCH_2CH_2 OH$  HBr 48% in  $H_2O$  50°C
- (a) S<sub>N1</sub>
- (b)  $S_{N^2}$
- (c) E<sub>1</sub>
- (d) E<sub>2</sub>

### ALKYL HALIDES (SUBSTITUTION)

**12.** Examine the ten structural formulas shown in fig. & select that satisfy each of the following conditions. Write one or more (a through j) in each answer box.

(a)	Br	(ъ)	$\begin{array}{c} \operatorname{CH}_3 \\ \mid \\ \operatorname{H}_3\operatorname{C} - \operatorname{C} - \operatorname{Cl} \\ \mid \\ \operatorname{CH}_3 \end{array}$	(c)	CH <sub>2</sub> – Br
(d)	CH <sub>3</sub> –I	(e)	CH <sub>2</sub> – Br	<b>(f)</b>	CI
(g)	$\begin{array}{c} \operatorname{CH_3} \\ \operatorname{H_3C} - \operatorname{C} - \operatorname{CH_2} - \operatorname{Cl} \\ \operatorname{CH_3} \end{array}$	(h)	$\begin{array}{c} {\rm H_2C} {\rm CH_2-CI} \\ {\rm CH_3} \end{array}$	(i)	Br
(j)	Cl				

- A. Which compounds give an  $S_{N^2}$  substitution reaction on treatment with alcoholic NaSH?
- **B.** Which compounds give an E<sub>2</sub> elimination reaction on treatment with alcoholic KOH?
- C. Which compounds do not react under either of the previous reaction conditions?

13. Select which reaction from the following reaction pairs will occur faster.

Select Which	reaction from the following reaction pairs will occur faster.
	PART - 1
Reaction A	$CH_3 \xrightarrow{H_2O} CH_3$
Reaction B	$ \begin{array}{c} I \\ H_{2O} \\ \hline DMSO \end{array} $ $ \begin{array}{c} OH \\ H \end{array} $
	PART - 2
Reaction C	$Cl$ $CH_3 \xrightarrow{Nal} CH_3$
Reaction D	$CH_2CI \longrightarrow CH_2I$ $\xrightarrow{NaI} \longrightarrow DMSO$
	PART - 3
Reaction E	$ \begin{array}{c c} I & & Cl \\ H & \underline{\text{NaCl}} & & H \end{array} $
Reaction F	$\begin{array}{c c} I & & \\ H & \xrightarrow{NaCl} & H \end{array}$
	PART - 4
Reaction G	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
Reaction H	$\begin{array}{c} \text{Br} \\ \text{H} & \xrightarrow{\text{NaN}_3} \\ \text{DMSO} \end{array}$

	PART - 5
Reaction I	$\begin{array}{c c} CH_2-CI & CH_2-I \\ \hline & \\ \hline \end{array}$
Reaction J	$ \begin{array}{c c} \text{Br} & I \\ \hline \\ NaI \\ \text{acetone} \end{array} $ $ \begin{array}{c} \text{CH}_3 \end{array} $ $ \begin{array}{c} \text{CH}_3 \end{array} $

## 14. Tick your answer in the given box.

	Alkyl Halide	2-D Structure	Expect S <sub>N</sub> <sup>2</sup> (at a reasonable rate)
(a)	1-Bromobutane	Br	Yes
(b)	1- Chlorobutane	CI	Yes
(c)	2-Bromobutane	Br	Yes
(d)	2-Chlorobutane	CI	Yes
(e)	2-Chloro-2-methyl propane	CI	Yes

(f)		Br	Yes
	Bromocyclohexane		No
(-)		Br	Yes
(g)	Bromobenzene		No
(h)	Benzyl bromide	CH <sub>2</sub> -Br	Yes
		0	No
(i)	1-Bromo-2,2-dimethyl propane	Br	Yes
		~\	No
Ø	District the second		Yes
U)	Bicyclo compound	Br	No
(k)	1-bromotriptycene	Br	Yes
(AL)	1-ыонопрусене		No

#### 15. Match the column

	Column-I		Column-II
(a)	CI	(p)	It will undergo Nucleophilic Substitution reaction
(ъ)	CH <sub>2</sub> —Cl	(q)	It will undergo $E_2$ reaction
(c)	CH <sub>3</sub> C—Cl	(r)	It will undergo $E_1$ reaction
(d)	NO <sub>2</sub>	(s)	It will undergo $S_{N^2}$ reaction
		(t)	It will undergo $S_{N^1}$ reaction

16.

17.

marks and	Column (I)		Column (II)
(a)	$Ph \xrightarrow{\qquad} Cl \xrightarrow{\qquad H_2O \qquad}$	(p)	$S_{N^1}$
(b)	$\sim$	(q)	$S_{N^2}$
(c)	$ \begin{array}{c}                                     $	(r)	Carbocation is intermediate
(d)		(s)	Carbanion is intermediate

18.

	Column (I)		Column (II)
	(Reaction sequence)		(Reagent required)
(a)	$\rightarrow$ OEt	(p)	EtO <sup>⊖</sup>
(b)	$\rightarrow$ Br $\rightarrow$	(q)	EtBr
(c)	$\rightarrow$ OEt	(r)	EtOH∕H <sup>⊕</sup>
(d) E	$Et - Cl \longrightarrow /$	(s)	Et-Cl/Na ether

ALKYL HALIDES

295

**19.** Choose the one compound within each set that meets the indicated criterion :

	Column (I)	A Death	Column (II)
(a)	The compound that reacts with alcoholic KOH to liberate Halide ion through substitution reaction.	(p)	$O_2N$ $CH_3$
(b)	The compound that cannot be prepared by a Williamson ether synthesis.	(q)	$\bigcirc$ OC <sub>2</sub> H <sub>5</sub>
(c)	The compound that gives an acidic solution when allowed to stand in aqueous ethanol.	(r)	o
(d)	The ether that cleaves more rapidly in HI.	(s)	$ \begin{array}{c}  & \text{Br} \\  & \text{I} \\  & \text{C} \\  & \text{CH}_3 \end{array} $

#### ANSWERS -

- 1.
- c The reaction is Finkelstein reaction. 2.

- (b)  $(\Gamma)$ ; (c)  $(\Gamma)$ ; (d)  $(NH_2-NH_2)$
- (e) CH<sub>3</sub>SO<sub>2</sub>

- (a)  $CH_3 Br$
- (b) CH<sub>3</sub> -CH-CH<sub>3</sub>
- (c)

- a p, w; b q, x; c r, y; d s, z
- a-r, s; b-p, q; c-r, s; d-r, s



- 9.

- (X) A- reactants, B-transition state, C-Inter mediate, D- transition state 10.
  - (Y) (i) exothermic (ii) B (iii) F (iv) a

**11.** A - b; B - b; C - d; D - a; E - b; F - b; G - b

**12.** 
$$A - c$$
,  $d$ ,  $e$ ,  $f$ ,  $h$ ;  $B - b$ ,  $c$ ,  $f$ ,  $i$ ;  $C - a$ ,  $g$ ,  $j$ 

**14.** Yes – a, b, c, d, f, h, 
$$No - e$$
, g, i, j, k

17. 
$$a-p, r$$
;  $b-q$ ;  $c-s$ ;  $d-r$ 

**18.** 
$$a-q$$
;  $b-p$ ;  $c-r$ ;  $d-q$ 

19. 
$$a-p$$
;  $b-r$ ;  $c-s$ ;  $d-q$