# Chapter 24

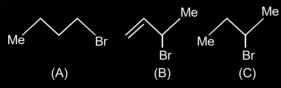
# **Haloalkanes and Haloarenes**

- 1. The number of stereoisomers possible for a compound of the molecular formula CH<sub>2</sub> - CH = CH -CH(OH)-Me is [AIEEE-2009]
  - (1) 2

(2) 4

(3) 6

- (4) 3
- 2. Consider the following bromides



The correct order of S<sub>N</sub>1 reactivity is [AIEEE-2010]

- (1) A > B > C
- (2) B > C > A
- (3) B > A > C
- (4) C > B > A
- Out of the following, the alkene that exhibits optical isomerism is [AIEEE-2010]
  - (1) 2-methyl-2-pentene
- (2) 3-methyl-2-pentene
- (3) 4-methyl-1-pentene (4) 3-methyl-1-pentene
- The change in the optical rotation of freshly prepared solution of glucose is known as

### [AIEEE-2011]

- (1) Mutarotation
- (2) Tautomerism
- (3) Racemisation
- (4) Specific rotation
- Consider thiol anion (RS<sup>O</sup>) and alkoxy anion 5. (RO<sup>O</sup>). Which of the following statement is correct? [AIEEE-2011]
  - (1) RS<sup>O</sup> is more basic but less nucleophilic than RO
  - (2) RS<sup>O</sup> is less basic and less nucleophilic than RO<sup>⊖</sup>
  - (3) RS<sup>O</sup> is less basic but more nucleophilic than RO<sup>⊖</sup>
  - (4) RS<sup>O</sup> is more basic and more nucleophilic than RO

6. How many chiral compounds are possible on monochlorination of 2-methyl butane?

[AIEEE-2012]

(1) 2

(2) 4

(3) 6

- (4) 8
- 7. What is DDT among the following? [AIEEE-2012]
  - (1) A fertilizer
  - (2) Biodegradable pollutant
  - (3) Non-Biodegradable pollutant
  - (4) Greenhouse gas
- A solution of (-) 1 chloro 1 phenylethane 8. in toluene racemises slowly in the presene of a small amount of SbCl<sub>5</sub>, due to the formation of

# [JEE (Main)-2013]

- (1) Carbanion
- (2) Carbene
- (3) Carbocation
- (4) Free radical
- 9. Compound (A), C<sub>8</sub>H<sub>o</sub>Br, gives a white precipitate when warmed with alcoholic AgNO<sub>3</sub>. Oxidation of (A) gives an acid (B), C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>. (B) easily forms anhydride on heating. Identify the compound (A).

[JEE (Main)-2013]

 $C_2H_5$ 

(1) 
$$CH_2Br$$
 $CH_3$ 
 $CH_3Br$ 

$$(4) \bigcirc CH_2Br \\ CH_3$$

In S<sub>N</sub>2 reactions, the correct order of reactivity for the following compounds

CH<sub>3</sub>CI, CH<sub>3</sub>CH<sub>2</sub>CI, (CH<sub>3</sub>)<sub>3</sub>CHCl and (CH<sub>3</sub>)<sub>3</sub>CCl is

# [JEE (Main)-2014]

- (1)  $CH_3CI > (CH_3)_3CHCI > CH_3CH_3CI > (CH_3)_3CCI$
- (2)  $CH_3CI > CH_3CH_2CI > (CH_3)_2CHCI > (CH_3)_3CCI$
- (3)  $CH_3CH_2CI > CH_3CI > (CH_3)_2CHCI > (CH_3)_3CCI$
- (4)  $(CH_3)_2CHCI > CH_3CH_2CI > CH_3CI > (CH_3)_3CCI$

- 11. The synthesis of alkyl fluorides is best accomplished by [JEE (Main)-2015]
  - (1) Free radical fluorination
  - (2) Sandmeyer's reaction
  - (3) Finkelstein reaction
  - (4) Swarts reaction
- 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields: [JEE (Main)-2016]

(b) 
$$C_2H_5CH_2C - CH_2$$
  
 $CH_3$ 

- (1) (a) and (c)
- (2) (c) only
- (3) (a) and (b)
- (4) All of these
- 13. The absolute configuration of

is

[JEE (Main)-2016]

- (1) (2S, 3R)
- (2) (2S, 3S)
- (3) (2R, 3R)
- (4) (2R, 3S)
- 14. The product of the reaction given below is



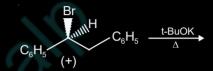
[JEE (Main)-2016]







- The increasing order of the reactivity of the following halides for the S<sub>N</sub>1 reaction is [JEE (Main)-2017]
  - . CH₃CHCH₂CH₃ | | CI
  - II. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CI
  - III.  $p-H_3CO-C_6H_4-CH_2CI$
  - (1) (I) < (III) < (II)
  - (2) (II) < (III) < (I)
  - (3) (III) < (II) < (I)
  - (4) (II) < (I) < (III)
- 16. The major product obtained in the following reaction is [JEE (Main)-2017]

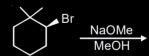


- (1)  $(+)C_6H_5CH(O^tBu)CH_2C_6H_5$
- (2)  $(-)C_6H_5CH(O^tBu)CH_2C_6H_5$
- (3)  $(\pm)C_6H_5CH(O^tBu)CH_2C_6H_5$
- (4)  $C_6H_5CH = CHC_6H_5$
- 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product.
   The number of possible stereoisomers for the product is
   [JEE (Main)-2017]
  - (1) Two

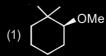
(2) Four

(3) Six

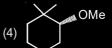
- (4) Zero
- 18. The major product of the following reaction is



[JEE (Main)-2018]







19. The major product of the following reaction is

The major product of the following reaction is

$$\begin{array}{c} \text{Br} \\ \text{Ph} \\ \end{array} \begin{array}{c} \text{KOH alc (excess)} \\ \Delta \end{array}$$

[JEE (Main)-2019]

.Br

21. The major product of the following reaction is

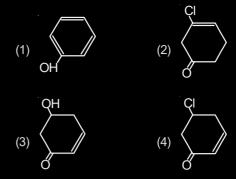
$$(1) \xrightarrow{\text{CH}_3} \text{OH} \xrightarrow{\text{(i) aq.NaOH}} \text{[JEE (Main)-2019]}$$

$$(2) \xrightarrow{\text{CH}_3} \text{OH}$$

$$(3) \xrightarrow{\text{CH}_3} \text{OH}$$

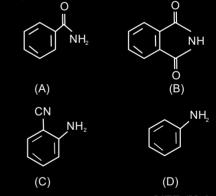
$$(4) \xrightarrow{\text{CH}_3} \text{OH}$$

22. The major product of the following reaction is



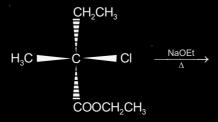
23. Which of the following compounds will produce a precipitate with AgNO<sub>3</sub>? [JEE (Main)-2019]

24. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is

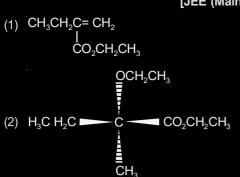


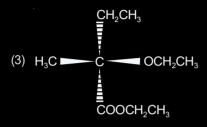
[JEE (Main)-2019]

- (1) (A) < (B) < (C) < (D) (2) (B) < (A) < (C) < (D)
- (3) (B) < (A) < (D) < (C) (4) (A) < (C) < (D) < (B)
- 25. The major product of the following reaction is



[JEE (Main)-2019]





$$CO_2CH_2CH_3$$

$$(4) CH_3C = CHCH_3$$

26. The major product of the following reaction is:

$$(1) Cl_2/hv$$

$$(2) H_2O, \Delta$$

$$(2) Cl$$

$$(2) Cl$$

$$(3) Cl$$

$$(4) Cl$$

$$(4) Cl$$

27. The major product of the following reaction is

(3) (4) (1) \*BuOK (2) Conc.H<sub>2</sub>SO<sub>d</sub>/
$$\Delta$$

[JEE (Main)-2019]

28. The major product of the following reaction is

29. The major products A and B for the following reactions are, respectively

$$\frac{\text{KCN}}{\text{DMSO}}[A] \xrightarrow{\text{H}_2/\text{Pd}} [B]$$

[JEE (Main)-2019]

(1) 
$$CN$$
;  $CH_2NH_2$ 

(3) 
$$HO$$
  $CN$   $HO$   $CH_2-NH_2$   $H$ 

$$\begin{array}{c}
O \\
CN
\end{array};
\begin{array}{c}
OH \\
CH_2NH_2
\end{array}$$

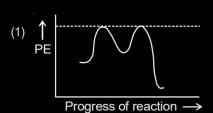
30. Increasing order of reactivity of the following compounds for  $\rm S_N 1$  substitution is

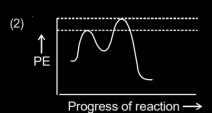
[JEE (Main)-2019]

(3) 
$$(B) < (A) < (D) < (C)$$
  $(4)$   $(A) < (B) < (D) < (C)$ 

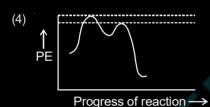
31. Which of the following potential energy (PE) diagrams represents the  $S_N1$  reaction?

# [JEE (Main)-2019]









32. The major product of the following reaction is:

33. Increasing rate of  $S_N$ 1 reaction in the following compounds is :

[JEE (Main)-2019]

(1) 
$$(B) < (A) < (C) < (D)$$
 (2)

(2) 
$$(A) < (B) < (D) < (C)$$

(3) 
$$(B) < (A) < (D) < (C)$$
  $(4)$   $(A) < (B) < (C) < (D)$ 

34. The major product 'Y' in the following reaction is:

[JEE (Main)-2019]

- 35. The increasing order of nucleophilicity of the following nucleophiles is :
  - (a) CH<sub>3</sub>CO<sub>2</sub><sup>©</sup>
- (b) H<sub>2</sub>O
- (c) CH<sub>3</sub>SO<sub>3</sub><sup>©</sup>
- (d) OH

# [JEE (Main)-2019]

(1) 
$$(d) < (a) < (c) < (b)$$

(2) 
$$(b) < (c) < (d) < (a)$$

(3) 
$$(a) < (d) < (c) < (b)$$

36. The major product(s) obtained in the following reaction is/are

[JEE (Main)-2019]

37. An 'Assertion' and a 'Reason' are given below. Choose the correct answer from the following options:

**Assertion (A):** Vinyl halides do not undergo nucleophilic substitution easily.

Reason (R): Even though the intermediate carbocation is stabilized by loosely held  $\pi$ -electrons, the cleavage is difficult because of strong bonding. [JEE (Main)-2019]

- (1) Both (A) and (R) are correct statements and (R) is the correct explanation of (A).
- (2) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A).
- (3) Both (A) and (R) are wrong statements.
- (4) (A) is a correct statement but (R) is a wrong statement.
- 38. Which one of the following is likely to give a precipitate with AgNO<sub>3</sub> solution?

[JEE (Main)-2019]

- (1)  $CH_2 = CH CI$
- (2) CHCl<sub>3</sub>

(3) CCI<sub>4</sub>

- (4) (CH<sub>3</sub>)<sub>3</sub>CCI
- 39. Consider the following reactions:

(a) 
$$(CH_3)_3 CCH(OH)CH_3 \frac{\text{conc.H}_2SO_4}{}$$

(b) 
$$(CH_3)_2 CHCH(Br)CH_3 - alc.KOH$$

(c) 
$$(CH_3)_2 CHCH(Br)CH_3 \xrightarrow{(CH_3)_3 O^{\ominus} K^{\oplus}}$$

(d) 
$$(CH_3)_2C - CH_2 - CHO \xrightarrow{\Delta}$$
  
OH

Which of these reaction(s) will not produce Saytzeff product? [JEE (Main)-2020]

- (1) (a), (c) and (d)
- (2) (c) only
- (3) (b) and (d)
- (4) (d) only
- 40. The major product of the following reaction is

41. For the following reactions

$$CH_{3}CH_{2}CH_{2}Br + Z \xrightarrow{K_{3}} CH_{3}CH_{2}CH_{2}Z + Br^{\Theta}$$

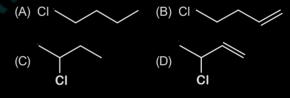
$$CH_{3}CH_{2}CH_{2}Br + Z \xrightarrow{e_{H_{1}H_{1}}} \frac{k_{5}}{e_{H_{1}H_{1}}} CH_{3}CH = CH_{2} + HZ + Br^{\Theta}$$

where.

$$Z^{\Theta} = CH_{3}CH_{2}O^{\Theta}$$
 (A) or  $H_{3}C - C - O^{\Theta}$  (B),

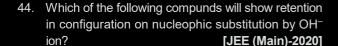
 $k_s$  and  $k_e$ , are, respectively, the rate constants for substitution and elimination, and  $\mu = \frac{k_s}{k_e}$ , the correct option is

- (1)  $\mu_B > \mu_A$  and  $k_e(A) > k_e(B)$
- (2)  $\mu_{\Delta} > \mu_{B}$  and  $k_{a}(A) > k_{a}(B)$
- (3)  $\mu_{B} > \mu_{A}$  and  $k_{e}(B) > k_{e}(A)$
- (4)  $\mu_{\Delta} > \mu_{B}$  and  $k_{A}(B) > k_{A}(A)$
- 42. The decreasing order of reactivity towards dehydrohalogenation (E<sub>1</sub>) reaction of the following compounds is



[JEE (Main)-2020]

- (1) B > A > D > C
- (2) B > D > A > C
- (3) B > D > C > A
- (4) D > B > C > A
- 43. Which of the following reactions will not produce a racemic product? [JEE (Main)-2020]
  - (1)  $CH_3CH_2CH=CH_2 \xrightarrow{HBr} \rightarrow$



(1) 
$$CH_3 - CH_3 - Br$$

(3) 
$$CH_3 - CH - CH_2Br$$
 (4)  $CH_3 - C - H$   $C_6H_{13}$ 

45. The major product obtained from  $E_2$  – elimination of 3-bromo-2-fluoropentane is [JEE (Main)-2020]

Br 
$$|$$
 (4)  $CH_3 - CH_2 - C = CH - CH_3$ 

46. The mechanism of S<sub>N</sub>1 reaction is given as

$$R-X \rightarrow R^{\Theta} X^{\Theta} \rightarrow R^{\Theta} \parallel X^{\Theta} \xrightarrow{Y^{\Theta}} R-Y+X^{\Theta}$$
lon pair
Solvent
Separated ion

A student writes general characteristics based on the given mechanism as

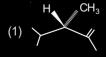
- (a) The reaction is favoured by weak nucleophiles.
- (b) R<sup>®</sup> would be easily formed if the substituents are bulky.
- (c) The reaction is accompanied by racemization.
- (d) The reaction is favoured by non-polar solvents. Which observations are correct?

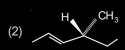
# [JEE (Main)-2020]

- (1) (b) and (d)
- (2) (a) and (c)
- (3) (a) and (b)
- (4) (a), (b) and (c)

47. Which of the following compounds produces an optically inactive compound on hydrogenation?

### [JEE (Main)-2020]





$$(3) \qquad H \qquad CH_3 \qquad (4) \qquad H \qquad CH_3$$

The decreasing order of reactivity of the following compounds towards nucleophilic substitution (S<sub>N</sub>2)

$$\begin{array}{c}
CH_2CI \\
O \\
(I)
\end{array}$$

$$\begin{array}{c}
CH_2CI \\
O \\
NO_2
\end{array}$$

$$(II)$$

$$\begin{array}{c}
CH_2CI \\
O\\
NO_2\\
(III)
\end{array}$$

$$\begin{array}{c}
CH_2CI \\
O_2N
\end{array}$$

$$\begin{array}{c}
O_2N
\end{array}$$

$$\begin{array}{c}
NO
\end{array}$$

### [JEE (Main)-2020]

(1) 
$$(II) > (III) > (IV) > (I)$$
 (2)  $(II) > (III) > (I) > (IV)$ 

$$(2)$$
  $(II) > (III) > (I) > (IV)$ 

(3) 
$$(|II|) > (|I|) > (|V|) > (|I|) >$$

The major product in the following reaction is

# [JEE (Main)-2020]

50. The decreasing order of reactivity of the following organic molecules towards AgNO<sub>3</sub> solution is



[JEE (Main)-2020]

(1) 
$$(B) > (A) > (C) > (D)$$

(2) 
$$(A) > (B) > (D) > (C)$$

(3) 
$$(A) > (B) > (C) > (D)$$

$$(4)$$
  $(C) > (D) > (A) > (B)$ 

51. Which of the following compounds will form the precipitate with aq. AgNO<sub>3</sub> solution most readily?

[JEE (Main)-2020]

$$(1) \bigcirc O \bigcirc Br \qquad (2) \bigcirc N$$

(3) 
$$(4)$$
  $OCH_3$ 

52. The number of chiral carbons present in the molecule given below is \_\_\_\_\_.

[JEE (Main)-2020]

53. The total number of monohalogenated organic products in the following (including stereoisomers) reaction is \_\_\_\_\_.

Α

$$\frac{\text{(i) } H_2/\text{Ni}/\Delta}{\text{(ii) } X_2/\Delta}$$

(Simplest optically active alkene)

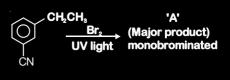
[JEE (Main)-2020]

54. The product formed in the first step of the reaction

 $Mg/Et_2O(Et = C_2H_5)$  is:

[JEE (Main)-2021]

55. For the given reaction:



What is 'A'?

[JEE (Main)-2021]

56. Identify A in the given reaction,

[JEE (Main)-2021]

57. Match List-I with List-II

List-I

reaction

List-II

(c) 2CH<sub>3</sub>CH<sub>2</sub>Cl+2Na

(iii) Fittig reaction

$$\xrightarrow{\text{Ether}}$$
  $C_2H_5 - C_2H_5 + 2\text{NaCl}$ 

(d)  $2C_6H_5CI + 2Na$ 

(iv) Gatterman

 $\underbrace{\text{Ether}}_{\text{C}_6} \text{H}_5 - \text{C}_6 \text{H}_5 + 2 \text{NaCl}$ 

reaction

Choose the correct answer from the options given below [JEE (Main)-2021]

(1) (a)-(iii); (b)-(iv); (c)-(i); (d)-(ii)

(2) (a)-(ii); (b)-(iv); (c)-(i); (d)-(iii)

(3) (a)-(iii); (b)-(i); (c)-(iv); (d)-(ii)

(4) (a)-(ii); (b)-(i); (c)-(iv); (d)-(iii)

58.  $H_3C$  OH  $\begin{array}{c}
 & \xrightarrow{20\% \ H_3PO_4} \\
 & \xrightarrow{358 \ K}
\end{array}$ (Major Product)

$$H_3C$$
  $CI$ 

$$\xrightarrow{(CH_3)_3CO^-K^+} \text{"B"}$$
(Major Product)

The products "A" and "B" formed in above reactions are [JEE (Main)-2021]

(1) 
$$A - \bigcirc$$
  $B - \bigcirc$ 

$$\begin{array}{c} CH_2 \\ \parallel \\ (2) \\ A - \end{array} \qquad B - \begin{array}{c} CH_2 \\ \parallel \\ \end{array}$$

- 59. The correct pair(s) of the ambident nucleophiles is (are): [JEE (Main)-2021]
  - (A) AgCN/KCN
  - (B) RCOOAg/RCOOK
  - (C) AgNO<sub>2</sub>/KNO<sub>2</sub>
  - (D) Agl/KI
  - (1) (B) and (C) only
  - (2) (B) only
  - (3) (A) only
  - (4) (A) and (C) only

60. Given below are two statements:

**Statement I**: C<sub>2</sub>H<sub>5</sub>OH and AgCN both can generate nucleophile.

**Statement II**: KCN and AgCN both will generate nitrile nucleophile with all reaction conditions.

Choose the **most appropriate** option.

# [JEE (Main)-2021]

- (1) Statement I is true but statement II is false
- (2) Statement I is false but statement II is true
- (3) Both statement I and statement II are true
- (4) Both statement I and statement II are false
- 61. In the given reaction 3-Bromo-2,2-dimethyl butane  $C_2H_5OH \longrightarrow (Major Product)$

# [JEE (Main)-2021]

- (1) 1-Ethoxy-3,3-dimethyl butane.
- (2) 2-Hydroxy-3,3-dimethyl butane.
- (3) 2-Ethoxy-2,3-dimethyl butane.
- (4) 2-Ethoxy-3,3-dimethyl butane.

62. 
$$\frac{\text{(i) } (C_eH_eCO)_2O_2, HBr}{\text{(ii) } CoF_2} \xrightarrow{\text{(major product)}} P$$

Major product P of above reaction, is

### [JEE (Main)-2021]

63. Presence of which reagent will affect the reversibility of the following reaction, and change it to a irreversible reaction

$$CH_4 + I_2 \xrightarrow{hv} CH_3 - I + HI$$

# [JEE (Main)-2021]

- (1) Dilute HNO<sub>2</sub>
- (2) Liquid NH<sub>3</sub>
- (3) HOCI
- (4) Concentrated HIO<sub>2</sub>

64. Among the following compounds I-IV, which one forms a yellow precipitate on reacting sequentially with (i) NaOH (ii) dil. HNO<sub>3</sub> (iii) AgNO<sub>3</sub>?

# [JEE (Main)-2021]

(1) III

(2) II

(3) IV

- (4) I
- 65. The number of stereoisomers possible for 1, 2-dimethyl cyclopropane is : [JEE (Main)-2021]
  - (1) Two

(2) Three

(3) One

(4) Four

66. In the following sequence of reactions the P is:

$$\begin{array}{c}
CI \\
+ Mg \xrightarrow{dry} [A] \xrightarrow{ethanol} P \\
(Major Product)
\end{array}$$

# [JEE (Main)-2021]

(1)



67. The major product (A) formed in the reaction given below is : [JEE (Main)-2021]

$$\begin{array}{c} \mathsf{CH_3} - \mathsf{CH_2} - \mathsf{CH} - \mathsf{CH_2} - \mathsf{Br} \\ \\ & + \mathsf{CH_3O}^{\Theta} \xrightarrow{\mathsf{CH_3OH}} \mathsf{A} \\ & & \mathsf{(Major\ product)} \end{array}$$

$$CH_3 - CH_2 - CH - CH_2Br$$
(1)
$$OCH_3$$

$$CH_3 - CH_2 - C = CH_2$$
(2)

$$CH_3 - CH_2 - CH - CH_2 - OCH_3$$
(4)

68. The correct order of reactivity of the given chlorides with acetate in acetic acid is: [JEE (Main)-2021]

$$(1) \begin{array}{c} CH_3 \\ CI \\ CH_3 \end{array}$$

(2) 
$$CH_3$$
  $CH_3$   $CH_$ 

$$(3) \begin{array}{c} CH_3 \\ CH_2 \\ CH_3 \end{array}$$

$$(4) \qquad CH_2CI \qquad CH_3 \qquad CI \qquad CI \qquad CH_3$$

69. The major product of the following reaction is

$$CH_3$$
 $CI$ 
 $NaOH$ 
 $C_2H_5OH$ 
 $Major product$ 

[JEE (Main)-2021]



70. For the following sequence of reactions, the correct products are :

1. Br<sub>2</sub>/Fe/
$$\Delta$$
2. Mg/dy ether
3. CH<sub>3</sub>OH Products

[JEE (Main)-2021]

71. The stereoisomers that are formed by electrophilic addition of bromine to *trans*-but-2-ene is/are :

### [JEE (Main)-2021]

- (1) 1 racemic and 2 enantiomers
- (2) 2 identical mesomers
- (3) 2 enantiomers
- (4) 2 enantiomers and 2 mesomers

72. The correct order of the following compounds showing increasing tendency towards nucleophilic substitution reaction is: [JEE (Main)-2021]

- (1) (iv) < (i) < (ii) < (iii)
- (2) (iv) < (i) < (iii) < (ii)
- (3) (iv) < (iii) < (ii) < (i)
- (4) (i) < (ii) < (iii) < (iv)
- 73. The major product of the following reaction is:

[JEE (Main)-2022]

(3) 
$$SPh$$
  $SPh$   $SPh$   $SPh$   $SPh$   $SPh$   $SPh$ 

74. Product 'A' of following sequence of reactions is

Ethylbenzene 
$$\xrightarrow{\text{(a) Br}_2, Fe}$$
  $\xrightarrow{\text{(b) Cl}_2, \Delta}$   $\xrightarrow{\text{Major Product}}$ 

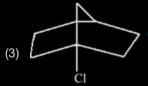
[JEE (Main)-2022]

(1) 
$$CI$$
 $C=CH_2$ 
 $C=CH_2$ 
(2)  $C=CH_2$ 

(3) 
$$CH = CH_2$$

$$(4) \qquad Br$$

75. Which one of the following compounds is inactive towards  $S_N 1$  reaction? [JEE (Main)-2022]



76. The major product of the following reaction contains bromine atom(s).

$$\xrightarrow{\text{Br}_2} \text{Major Product}$$

[JEE (Main)-2022]

77. Two isomers (A) and (B) with Molar mass 184 g/mol and elemental composition C, 52.2%; H, 4.9 % and Br 42.9% gave benzoic acid and p-bromobenzoic acid, respectively on oxidation with KMnO<sub>4</sub>. Isomer 'A' is optically active and gives a pale yellow precipitate when warmed with alcoholic AgNO<sub>3</sub>. Isomers 'A' and 'B' are, respectively

[JEE (Main)-2022]

(1) 
$$H_3C - CHBr - C_6H_5$$
 and  $CH_2Br$   $CH_3$ 

(3) 
$$H_3C - CHBr - C_6H_5$$
 and  $Br$ 

(4) 
$$CH_2CH_3$$
 and  $H_3C - CHBr - C_6H_5$ 

78. The total number of monobromo derivatives formed by the alkanes with molecular formula C<sub>5</sub>H<sub>12</sub> is (excluding stereo isomers)\_\_\_\_.

[JEE (Main)-2022]

79. Total number of isomers (including stereoisomers) obtained on monochlorination of methylcyclohexane is .

[JEE (Main)-2022]

80. 
$$CH_2OH + HCI \xrightarrow{\Delta} A \xrightarrow{Nal} B$$

In the above reaction product B is:

Product B is

[JEE (Main)-2022]

83.

(3) 
$$CH_2CI$$
  $CH_2C$ 

- 81. Optical activity of an enantiomeric mixture is +12.6° and the specific rotation of (+) isomer is +30°. The optical purity is \_\_\_\_\_
  - [JEE (Main)-2022]
- Identify the correct statement for the below given 82. transformation.

$$\begin{array}{c}
\mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{CH}_1 - \mathsf{CH}_3 \xrightarrow{C_2\mathsf{H}_5\mathsf{ONa}} \mathsf{A} + \mathsf{B} \\
\oplus \mathsf{N}(\mathsf{CH}_3)_3
\end{array}$$

# [JEE (Main)-2022]

- (1) A-CH<sub>2</sub>CH<sub>2</sub>CH=CH-CH<sub>3</sub>, B-CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH= CH<sub>a</sub>, Saytzeff products
- (2) A-CH,CH,CH=CH-CH, B-CH,CH,CH,CH= CH<sub>3</sub>, Hofmann products
- (3) A-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>, B-CH<sub>3</sub>CH<sub>2</sub>CH= CHCH<sub>2</sub>, Hofmann products
- (4) A-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>, B-CH<sub>3</sub>CH<sub>2</sub>CH= CHCH<sub>3</sub>, Saytzeff products

$$(Major Product) \xrightarrow{C_2H_5OH-H_2O} CI$$

$$\frac{NaCN}{C_2H_5OH-H_2O} \xrightarrow{(B')} (Major Product)$$

Considering the above reactions, the compound 'A' and compound 'B' respectively are:

[JEE (Main)-2022]

$$(3) \qquad \stackrel{\oplus}{\underset{N \equiv C}{\otimes}} \qquad \stackrel{\bigcirc}{\underset{C \equiv N}{\otimes}}$$

(4) 
$$C \equiv N$$
,  $M \equiv C$ 

84. Compound 'A' undergoes following sequence of reactions to give compound 'B'. The correct structure and chirality of compound 'B' is

[where Et is -C2H2]

$$\longrightarrow \left( \begin{array}{c} \text{(i)Mg.Et}_2O \\ \text{(ii)D}_2O \end{array} \right) B$$

Compound 'A'

[JEE (Main)-2022]

85. The correct order of nucleophilicity is

[JEE (Main)-2022]

(1) 
$$F^- > OH^-$$

(2) H<sub>2</sub> 
$$\ddot{O}$$
 > OH

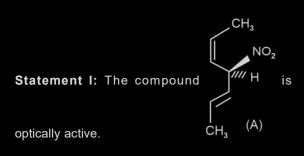
(3) 
$$R\ddot{O}H > RO^-$$
 (4)  $NH_2^- > NH_3$ 

(4) 
$$NH_2^- > NH_3$$

36.	Total number of possible stereoisomers of dimethyl		
	cyclopentane is	CH₃	
	[JEE (Main)-2022]	Statement II: O <sub>2</sub> N is mirror image	
37.	The number of chiral alcohol(s) with molecular	Statement II:	is mirror image
	formula C H O is	H ''''	

[JEE (Main)-2022]

88. Given below are two statements.



of above compound A.

In the light of the above statement, choose the **most appropriate** answer from the options given below. [JEE (Main)-2022]

- (1) Both Statement I and Statement II are correct.
- (2) Both **Statement I** and **Statement II** are incorrect.
- (3) Statement I is correct but Statement II is incorrect.
- (4) **Statement I** is incorrect but **Statement II** is correct.

# **Haloalkanes and Haloarenes**

#### 1. Answer (2)

 $CH_3CH = CH - CH(OH)Me$  has

$$CH_3$$
 + its enantiomer

$$H$$
  $C = C$   $H$  + its enantiomer  $CH_3$ 

H 
$$C = C$$
  $Me$   $Me - C$   $Me$   $H$   $H$ 

### 2. Answer (2)

Formation of carbocation is rate determining step in  $S_{\rm N}1$  reaction. Hence alkyl halide which gives more stable carbocation is more reactive towards  $S_{\rm N}1$  reaction

decreasing order of S<sub>N</sub>1 reactivity

# 3. Answer (4)



4. Answer (1)

Fact.

5. Answer (3)

On moving down a group basicity decreases but nucleophilicity increases.

- 6. Answer (2)
- 7. Answer (3)
- 8. Answer (3)

$$CH_3 \qquad CH_3$$

$$\rightarrow H - C - CI + CI - C - H$$

$$C_6H_5 \qquad C_6H_5$$
(Racemic mix.)

# 9. Answer (4)

$$CH_{2}Br \xrightarrow{\text{alc. AgNO}_{3}} O CH_{2}NO_{3}^{\ominus} + AgBr \downarrow CH_{3} \text{ (Light yellow ppt.)}$$

$$O COOH O COO + H_{2}O$$

Note: Compound (A) reacts with alc. AgNO<sub>3</sub> to give light yellow ppt. of AgBr and not white ppt. as given in the question.

#### 10. Answer (2)

Rate of  $S_N^2$  reaction depends on steric crowding of alkyl halide. So order is

$$CH_3CI > (CH_3)CH_2 - CI > (CH_3)_2CH - CI > (CH_3)_3CCI$$

11. Answer (4)

Swart's reaction

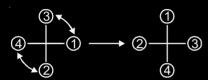
$$CH_3 - CI + AgF \xrightarrow{\Delta} CH_3F + AgCI$$

12. Answer (4)

$$CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{3}-$$

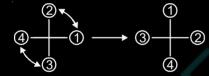
13. Answer (1)

At (1),



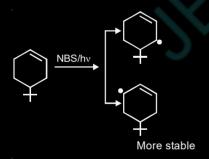
It is 'S' configurated.

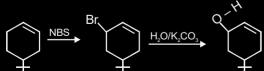
At (2),



It is 'R' configurated.

#### 14. Answer (1)





15. Answer (4)

Rate of  $S_N 1$  reaction  $\infty$  stability of carbocation

I. 
$$CH_3 - CH - CH_2 - CH_3 \longrightarrow CH_3 - \overset{\dagger}{C}H - CH_2 - CH_3$$

II. 
$$CH_3 - CH_2 - CH_2 - CI \longrightarrow CH_3 - CH_2 - \overset{\dagger}{C}H_2$$

So, II < I < III

Increase stability of carbocation and hence increase reactivity of halides.

16. Answer (4)

$$C_6H_5 \xrightarrow{(+)} C_6H_5 \xrightarrow{\text{t-BuOK}} C_6H_5$$

17. Answer (2)

$$CH_3$$
 $CH_3 - CH = C - CH_2 - CH_3 \xrightarrow{R_2O_2}$ 
3-methyl pent-2-ene

Since product (X) contains two chiral centres and it is unsymmetrical.

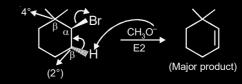
So, its total stereoisomers =  $2^2 = 4$ .

18. Answer (2)

 ${\rm CH_3O^-}$  is a strong base and strong nucleophile, so favourable condition is  ${\rm S_N2/E2}$ .

Given alkyl halide is 2° and  $\beta$  C's are 4° and 2°, so sufficiently hindered, therefore, E2 dominates over S<sub>N</sub>2.

Also, polarity of  $CH_3OH$  (solvent) is not as high as  $H_2O$ , so E1 is also dominated by E2.



19. Answer (4)

20. Answer (2)

21. Answer (1)

$$\begin{array}{c}
CH_3 \\
OH_{AOH}
\end{array}$$

$$\begin{array}{c}
CH_3 \\
O^{-}Na^{+}
\end{array}$$

$$\begin{array}{c}
CH_3 \\
CH_3 \\
\end{array}$$

$$\begin{array}{c}
CH_3 \\
\end{array}$$

$$\begin{array}{c}
+NaI
\end{array}$$

22. Answer (1)

23. Answer (4)

24. Answer (2)

Reactivity of compounds (nucleophiles) with alkyl halides will depend upon the availability of lone pair of electrons on nitrogen (amines or acid amides)

25. Answer (4)

High temperature and strong base favours elimination reaction forming more stable alkene according to Saytzeff rule.

26. Answer (3)

$$\begin{array}{c|c} CH_3 & CHCI_2 \\ \hline \\ O & CI \\ \hline \\ CI & CHO \\ \hline \\ CI & CHO$$

27. Answer (2)

28. Answer (2)

More stable product due to conjugation

29. Answer (4)

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30. Answer (3)

S<sub>N</sub>1 reaction proceeds via formation of carbocation.

On comparing (A) and (B), in (A) there is formation of tertiary carbocation  $CH_3-C_{\bigoplus}^{CH_3}$  after rearrangement while (B) is primary.

So, 
$$(C) > (D) > (A) > (B)$$
.

31. Answer (4)

In S<sub>N</sub>1 reaction, formation of carbocation (1<sup>st</sup> step) is rate determining step (RDS)

.. Correct graph is given in option-4.

32. Answer (1)

$$CH_{3} - CH - CH - CH_{3} \xrightarrow{CH_{3}OH} CH_{3} - C - CH - CH_{3} + Br^{-}$$

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

33. Answer (1)

The rate of  $S_N 1$  is decided by the stability of carbocation formed in the rate determining step.

(A) 
$$CH - CH_3$$
  $CH - CH_3$ 

Carbocation (D) is most stable due to +R effect of  $CH_3O$  group, (C) is stabilised by +I and +H effect of  $CH_3$  group; (B) is least stable due to -I effect of MeO group. So increasing order of rate of  $S_N1$  is  $S_N1$  is  $S_N1$  is  $S_N1$  is  $S_N1$ 0.

34. Answer (3)

35. Answer (4)

Greater the negative charge Present on a nucleophilic centre greater would be its nucleophilicity.

36. Answer (1)

37. Answer (4)

$$CH_2 = CH - CI CH_2 = C - H \text{ or } H - C - C - H$$

Fig. (1)

Fig. (2)

Fig. (3)

Also.

$$\overrightarrow{CH_1} = CH \stackrel{\checkmark}{-} \overrightarrow{CI} \longleftrightarrow \stackrel{\Theta}{CH_2} - CH = \overrightarrow{CI}$$

Due to partial double bond character of C – Halogen bond, Halogen leaves with great difficulty, if at all it does. Hence, vinyl halides do not undergo nucleophilic substitution easily.

Assertion is correct.

Intermediate carbocation is not stabilised by loosely held  $\pi$ -electrons because empty orbital (see Fig. (3)), being at 90°, cannot overlap with porbitals of  $\pi$  bond. Reason is wrong.

38. Answer (4)

Carbocation is formed on reaction with Ag+

$$R \longrightarrow CI + Ag^{+} \longrightarrow R^{+} + \underset{ppt.}{AgCI} \downarrow$$

The more the stability of  $R^+$ , the more R — CI is likely to give precipitate

CH₃

CH₃ — C⊕ is most stable carbocation compared

CH₃

to other options:

$$CH_2 = \overset{\oplus}{C}H, \overset{\oplus}{C}HCl_2, \overset{\oplus}{C}Cl_3$$

39. Answer (2)

Tertiary butoxide is a bulky base and it extracts the least hindered hydrogen

$$\begin{array}{c|c} CH_3 & CH - CH - CH_3 & \xrightarrow{tBuO} & CH_3 \\ CH_3 & & CH - CH = CH_2 \\ CH_3 & & CH_3 \end{array}$$

40. Answer (4)

41. Answer (4)

$$CH_3 - CH_2 - CH_2 - Br + Z - \underbrace{\begin{matrix} k_s \\ k \end{matrix}}_{k} \mu = \frac{k_s}{k_e}$$

when

$$Z^{\Theta} = CH_3CH_2O^-$$
 (A)  
 $Z^{\Theta} = O^-$  (B)  
 $\Rightarrow \mu_A > \mu_B \text{ and } k_e(B) > k_e(A)$ 

42. Answer (4)

Dehydrohalogenation of the given halides by E<sub>1</sub> mechanism is decided by the stability of carbocation formed in the first step. The correct decreasing order of the given halides towards dehydrohalogenation by E<sub>1</sub> mechanism is

43. Answer (3)

44. Answer (3)

$$\begin{array}{ccc}
CH_3 - \overset{\star}{C}H - CH_2Br & \xrightarrow{OH^{\ominus}} & CH_3 - \overset{\star}{C}H - CH_2OH_2OH_3 \\
C_2H_5 & & C_2H_5
\end{array}$$

Here, no bond to the stereocenter is broken, so the product will have the same configuration of groups around the stereocenter as that of reactant. This is a case of retention of configuration.

(Reference → NCERT Page 308)

Br (Racemic mixture)

# 45. Answer (3)

Base abstracts most acidic hydrogen and departure of better leaving group takes place simultaneously.

Br F F F 
$$CH_3 - CH_2 - CHCHCH_3 \xrightarrow{Base} CH_3 - CH_2 - CH = C - CH_3$$

46. Answer (4)

S<sub>N</sub>1 reaction mechanism is favoured by polar solvents, weak nucleophiles, bulky substituents and the reaction is accompanied by racemization.

47. Answer (1)

optically inactive as no chiral centre is there

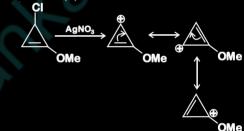
48. Answer (3)

 $-{\rm NO}_2$  group present at ortho and para position deactivate the benzene ring and making the carbon attached to ring ( $-{\rm CH}_2$  - CI) group more

electrophilic for the incoming nucleophile to give  $S_N 2$  reaction but rate of  $S_N 2$  reaction decreases as hindrence increases around the electrophilic carbon. Hence correct order of nucleophilic substitution reaction ( $S_N 2$ ) will be

49. Answer (3)

50. Answer (1)



aromatic as well as stabilized by lone pair of -OMe

So the order is

CI

CI

CH<sub>3</sub>-CH-CH<sub>3</sub>

OMe Aromatic

CI

2° carbocation

V

CH<sub>3</sub>-CH-CH<sub>2</sub>-NO<sub>2</sub>

CI

-I effect of NO<sub>2</sub>

51. Answer (2)

Ease of precipitation of AgBr depends upon the rate of formation of carbocation

Most stable carbocation due to +R effect of N.

52. Answer (5)

Chiral carbon atom is bonded to 4 different atoms or group of atoms. The given structure has 5 chiral carbon-atoms.

#### 53. Answer (8)

The simplest optically active alkene is

# 54. Answer (1)

Intramolecular substitution reaction

#### 55. Answer (4)

So the correct option should be (4)

56. Answer (4)

57. Answer (2)

- (a) Sandmeyer reaction
- (b) Gatterman reaction
- (c) Wurtz reaction
- (d) Fittig reaction
- (a)-(ii); (b)-(iv); (c)-(i); (d)-(iii)
- 58. Answer (3)

$$H_3C \xrightarrow{CI} \xrightarrow{(CH_3)_3CO^-K^+} \xrightarrow{CH_2} (B)$$

59. Answer (4)

AgCN/KCN → ambident nucleophile

Nucleophilic site is N and C in the above two case.

AgNO₂/KNO₂ → ambident nucleophiles

N and O are the nucleophilic site in these two cases

While in B and D, there is only one nucleophilic site.

60. Answer (1)

Both C<sub>2</sub>H<sub>5</sub>OH and AgCN can generate nucleophile.

KCN generates nitriles on substitution reactions with haloalkanes where AgCN generates isonitriles on substitution reactions with haloalkanes. Because KCN is ionic and has 'C' nucleophilic centre whereas AgCN is covalent and has 'N' nucleophilic centre.

61. Answer (3)

$$CH_3 CH_3$$

$$C_2H_5OH H_3C$$

$$Rearrangement (methyl shift)$$

$$C_2H_5OH CH_3$$

$$CH_3 CH_3$$

$$Rearrangement (methyl shift)$$

62. Answer (3)

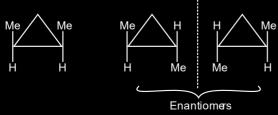
63. Answer (4)

lodination is very slow and a reversible reaction. It can be carried out in the presence of oxidizing agents like HIO<sub>3</sub> or HNO<sub>3</sub>.

$$CH_4 + I_2 \longrightarrow CH_3I + HI$$
  
 $HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$ 

64. Answer (3)

65. Answer (2)



Total three stereoisomers

66. Answer (3)

The alkyl part of Grignard's reagent [A] picks up proton from ethanol forming cyclopentane as major product.

67. Answer (2)

$$CH_3 - CH_2 - C = CH_2$$

$$CH_3 - CH_2 - C = CH_2$$

$$CH_3 - CH_2 - C = CH_2$$

68. Answer (3)

Acetate in acetic acid with R-X cause S<sub>N</sub>1

Allylic halides undergo faster S<sub>N</sub>1

Correct order is

69. Answer (1)

70. Answer (1)

(i) Br<sub>2</sub>/Fe/
$$\Delta$$

Mg/dry ether

MgBr

CH<sub>3</sub>OH

H

OCH<sub>3</sub>

71. Answer (2)

$$H_{3}C = C \xrightarrow{CH_{3}} H + Br_{2} \xrightarrow{CH_{3}} H \xrightarrow{CH_{3}} H$$

anti-addition on trans 2-butene will form mesomer

### 72. Answer (4)

More the number of EWG attached to benzene ring, more will be the tendency towards nucleophilic substitution reaction

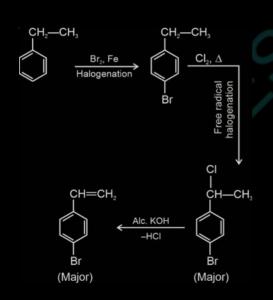
$$\begin{array}{c|c}
CI & CI & CI & CI \\
O_2N & NO_2 & NO_2 & NO_2 \\
NO_2 & NO_2 & NO_2 \\
iv > iii > ii > i
\end{array}$$

# 73. Answer (1)

$$\begin{array}{c|c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

Rate of  $S_N 2 > S_N 2$  (AR)

# 74. Answer (4)



### 75. Answer (3)

is inactive towards 
$$S_{N}1$$
 as

halogen is attached to bridge head carbon atom, where formation of carbocation is not possible.

# 76. Answer (1)

#### 77. Answer (3)

moles relative ratio simplest ratio C 52.2 =  $52.2/12 = 4.35 \rightarrow 8.7$  H  $4.9 = 4.9/1 = 4.9 \rightarrow 9.8$  Br  $42.9 = 42.9/80 = 0.5 \rightarrow 1$ 

 $C_8H_0Br$ 

A is optically active

$$\begin{array}{c} \operatorname{Br} \\ | \\ \operatorname{CH}_3 - \operatorname{CH} - \operatorname{C}_6 \operatorname{H}_5 \end{array}$$

B forms para bromo benzoic acid on reaction with KMnO<sub>4</sub>.

#### 78. Answer (8)

Total monobromo derivatives = 8

$$\mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{Br},$$

$$\mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{CH} - \mathsf{CH}_3 \\ | \\ \mathsf{Br}$$

$$\begin{array}{c} \mathsf{CH_3} - \mathsf{CH_2} - \mathsf{CH} - \mathsf{CH_2} - \mathsf{CH_3}, \\ | \\ \mathsf{Br} \end{array}$$

$$\begin{array}{c} \operatorname{CH_3} - \operatorname{CH_2} - \operatorname{CH} - \operatorname{CH_2} - \operatorname{Br}, \\ | \\ \operatorname{CH_3} \end{array}$$

## 79. Answer (12.00)

Compounds formed on mono-chlorination of methylcyclohexane are :

∴ Total mono-chlorinated products formed = 12

#### 80. Answer (1)

$$CH_2OH$$
  $CH_2-CI$   $CH_2-I$ 
 $CH_2OH$   $CH_2OH$ 
 $CH_2OH$   $CH_2OH$ 
 $CH_2OH$   $CH_2OH$ 
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Product B is 4-iodomethylphenol.

# 81. Answer (42)

Optical purity = 
$$\frac{\text{Total rotation}}{\text{Specific rotation}} \times 100$$
  
=  $\frac{12 \cdot 6}{30} \times 100$   
= 42%

#### 82. Answer (3)

$$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{(A)}{\text{CH}_3}-\overset{(A)}{\text{CH}_3}-\overset{(A)}{\text{CH}_3}-\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH},\\ \overset{(A)}{\text{CH}_3}-\overset{(A)}{\text{$$

83. Answer (3)

$$CI \xrightarrow{AgCN} \bigvee_{EtOH-H,O} \bigvee_{N=C}^{\oplus} \bigvee_{N=C}^{\ominus}$$

$$Product - 'A'$$

$$CI \xrightarrow{EtOH-H,O} \bigvee_{C=N}^{\otimes} C=N$$

$$Product - 'B'$$

KCN is ionic so  $\stackrel{\Theta}{\mathsf{CN}}$  attacks through 'C' – atom.

AgCN is covalent so CN attacks through 'N' - atom.

84. Answer (3)

85. Answer (4)

$$NH_3 \longrightarrow NH_2^- + H$$
Acid Conjugate base

Conjugate base of acid is always a stronger nucleophile.

86. Answer (Bonus)

Position of methyl groups not mentioned.

87. Answer (1)

88. Answer (3)

Compound (A) in Statement-I and compound in Statement-II is not the mirror image of (I).