

HALOALKANES AND HALOARENES

CHEMICAL PROPERTIES OBJECTIVES

ASSERTION-REASON TYPE OF QUESTIONS

The question given below consist of an assertion and a reason use the following key to choose appropriate answer

- Both assertion and reason are correct and reason is the correct explanation of the assertion
- Both assertion and reason are correct and reason is not the correct explanation of the assertion
- Assertion is correct but reason is incorrect
- Assertion is wrong Reason is correct.

1) **Assertion:** Alkyl halides are insoluble in water

Reason: Energy is required to break H bonds in water

2) **Assertion:** Para chloro-benzene is having higher melting point than other two isomers

Reason: Due to symmetry molecule is well fit in to the lattice.

3) **Assertion:** Tertiary alkyl halides are least reactive in S_N2 reactions

Reason: Steric hindrance is minimum in tertiary Alkyl halides

4) **Assertion:** Only achiral molecules when undergo substitution, optical rotation changes

Reason: When molecule and its mirror images are non superimposable, they show optical activity.

5) **Assertion:** Alkyl iodides are more reactive towards nucleophilic substitution reaction

Reason: C-I bond is stronger than any other carbon halogen bond

6) **Assertion:** The reaction of Arenes and iodine is carried out in presence of HIO_4

Reason: HIO_4 Oxidises HI formed during the reaction to I_2 and prevents backward reaction.

7) **Assertion:** During Finkelstein reaction alkyl chloride is treated with NaI in presence of Acetone

Reason: Acetone is a very good organic solvent

8) **Assertion:** Boiling points of alkyl iodides are lower than that of Alkyl chlorides

Reason: Vander force is more in alkyl iodides due to large size of iodine

9) **Assertion:** Among isomeric alkyl halides straight chain alkyl halides have highest boiling point

Reason: Dispersion force is minimum in branched chain alkyl halides.

10) **Assertion:** Alkyl halides mainly form alkyl cyanides when treated with AgCN

Reason: Due to covalent nature of AgCN attack takes place through Nitrogen.

11) **Assertion:** Alkyl halides forms Nitriles when treated with KCN

Reason: CN^- is an ambident nucleophile

12) **Assertion:** In Mono haloarenes further electrophilic substitution takes place at ortho and para position.

Reason: The lone pair of electrons on Cl is in conjugation with benzene ring, increasing electron density at ortho and para position...

- 13) **Assertion:** Nitration of chloro benzene leads to the formation of Meta nitro chlorobenzene.
Reason: NO₂ group is Meta directing towards electrophilic substitution reaction.
- 14) **Assertion:** Allyl halides react faster in SN₁ reaction
Reason: Allyl cations are stabilized by resonance
- 15) **Assertion:** Among different halogens alkyl chlorides are more reactive than iodides towards substitution reaction .
Reason: C-Cl bond is stronger than C-I bond
- 16) **Assertion:** Hydrolysis of (-) 2-bromo octane Proceeds with the inversion of configuration
Reason: This reaction proceeds via the formation of carbocation.
- 17) **Assertion:** Benzyl halides react faster in SN₁ reaction.
Reason: Benzyl cations formed is stabilized by resonance.
- 18) **Assertion:** When 2-bromo butane is treated with alcoholic KOH But-1-ene is the major product
Reason: During dehydrohalogenation reactions more alkylated alkene is the major product.
- 19) **Assertion:** During the reaction between Tertiary butyl bromide and C₂H₅ONa Alkene is the major product.
Reason: In presence of strong base Elimination competes over substitution.
- 20) **Assertion:** It is necessary to avoid even traces of water from Grignard reagent.
Reason: Grignard reagent is used in preparing alcohols
- 21) **Assertion:** It is difficult to break C-X bond in alkyl halides
Reason: C-X bond in aryl halides have partial double character
- 22) **Assertion:** Propene when treated with HBr form 1- bromo propane as the major product
Reason: During the addition of HBr a secondary carbocation is formed.
- 23) **Assertion:** The presence of NO₂ group at ortho position of aryl halides increases reactivity of haloarenes towards nucleophilic substitution reaction
Reason: Presence of NO₂ group at ortho and para position of aryl halides reduces the electron density in benzene and hence facilitates the attack.
- 24) **Assertion:** Alkyl halides are more reactive towards nucleophilic substitution reaction compared to aryl halides
Reason: In alkyl halides halogen is connected to sp³ hybridised carbon.
- 25) **Assertion:** SN reaction are generally carried out in presence polar protic solvents such as water
Reason: The energy needed to break C-X bond is obtained through solvation of halide ion with proton of protic solvent.
- 26) **Assertion:** Thionyl chloride are preferred over Phosphorus chlorides (tri and penta) for the preparation of alkyl chlorides from alcohols.
Reason: Phosphorus chlorides give pure alkyl halides.

27. **Assertion:** The boiling points of alkyl halides decrease in the order : $RI > RBr > RCl > RF$

Reason : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

28. **Assertion:** KCN reacts with methyl chloride to give methyl isocyanide

Reason: CN – is an ambident nucleophile.

29. **Assertion :** tert-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

Reason: In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

30. **Assertion:** Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.

Reason: Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

31. **Assertion:** In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.

Reason: Halogen atom is a ring deactivator.

32. **Assertion:** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidizing agent.

Reason: Oxidizing agent oxidizes I_2 into HI .

33. **Assertion:** It is difficult to replace chlorine by $-OH$ in chlorobenzene in comparison to that in chloroethane.

Reason: Chlorine-carbon ($C-Cl$) bond in chlorobenzene has a partial double bond character due to resonance.

34. **Assertion:** Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.

Reason: This reaction proceeds through the formation of a carbocation.

35. **Assertion:** Nitration of chlorobenzene leads to the formation of m-nitro chlorobenzene

Reason: $-NO_2$ group is a m-directing group.

ANSWER KEY

1) b 2) a 3) c 4) d 5) c 6) a 7) b 8) d 9) b 10) d 11) b 12) a 13) d 14) a 15) d 16) c 17) a 18) d 19) a 20) b 21) d 22) d 23) a 24) b 25) a 26) c 27) b 28) d 29) a 30) a 31) b 32) c 33) a 34) c 35) d

1. Fluorobenzene can be synthesized in laboratory

(i) by heating phenol with HF and KF (ii) by heating the diazonium salt with HF_4

(iii) by direct fluorination of benzene with F_2 gas

(iv) by heating 1-Bromobenzene with NaF solution

Ans: (ii) by heating the diazonium salt with HF_4

2. Toluene reacts with chlorine in the presence of iron (III) chloride gives X and in presence of light gives Y then X and Y are

(i) X= m-Chlorotoluene, Y= p-Chlorotoluene

(ii) X= o and p-Chlorotoluene, Y= Trichloromethyl benzene

(iii) X= Benzyl chloride, Y= m-Chlorotoluene

(iv) X= Benzyl chloride, Y= o-Chlorotoluene

Ans: (ii) X= o and p-Chlorotoluene, Y= Trichloromethylbenzene

3. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction?

(i) Cl^- (ii) Cl^+ (iii) $AlCl_3$ (iv) $[AlCl_4]^-$

Ans: (ii) Cl^+

4. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

- (i) Electrophilic elimination reaction (ii) Electrophilic substitution reaction
(iii) Free radical addition reaction (iv) Nucleophilic substitution reaction

Ans: (ii) Electrophilic substitution reaction

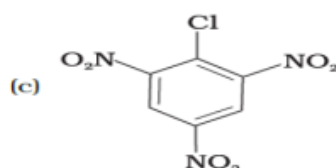
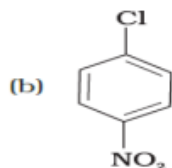
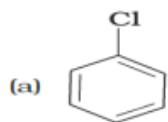
5 Which of the following is not chiral?

- (i) 2-Hydroxypropanoic acid (ii) 2-Butanol (iii) 2,3-Dibromobutane (iv) 3-Bromopentane

Ans: (iv) 3-Bromopentane

6.

Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:



(i) (c) < (b) < (a)

(ii) (b) < (c) < (a)

(iii) (a) < (c) < (b)

(iv) (a) < (b) < (c)

Ans: (iv) (a) < (b) < (c)

7. Which of the following statements are correct about the mechanism of this reaction?



(i) A carbocation will be formed as an intermediate in the reaction.

(ii) OH⁻ will attack the substrate (b) from one side and Cl⁻ will leave it simultaneously from other side.

(iii) An unstable intermediate will be formed in which OH⁻ and Cl⁻ will be attached by weak bonds

(iv) Reaction proceeds through SN₂ mechanism

Ans: (i) A carbocation will be formed as an intermediate in the reaction

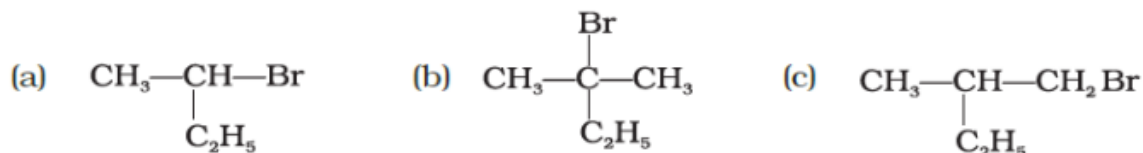
8. Phosgene is a common name of

- a) Phosphoryl chloride b) Thionyl chloride c) Carbonyl chloride d) carbon dioxide

Ans. C

9.

Which of the following compounds will give racemic mixture on nucleophilic substitution by OH⁻ ion?



(i) (a)

(ii) (a), (b), (c)

(iii) (b), (c)

(iv) (a), (c)

Ans: (i) (a)

10. Reaction of C₆H₅CH₂Br with aqueous sodium hydroxide follows:

(i) S_N1 mechanism

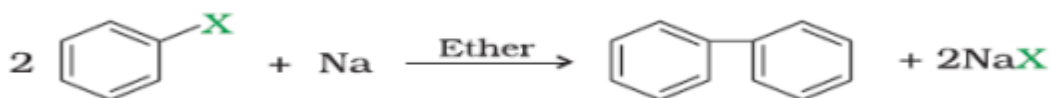
(ii) S_N2 mechanism

(iii) Any of the above two depending upon the temperature of reaction

(iv) Saytzeff rule

Ans: (i) S_N1 mechanism

11. What is name of following reaction:



(i) Wurtz Reaction

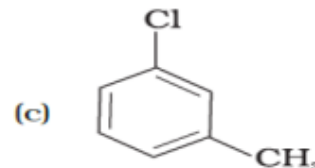
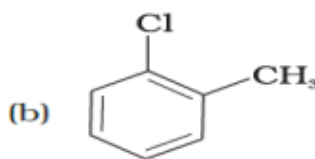
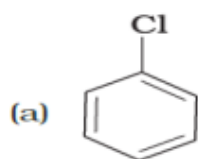
(ii) Fitting Reaction

(iii) Wurtz- Fitting Reaction

(iv) swartz reaction

Ans: (ii) Fitting Reaction

12. Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:



(i) (a) < (b) < (c) (ii) (a) < (c) < (b) (iii) (c) < (b) < (a) (iv) (b) < (c) < (a)

Ans iv)

13. Which one of the following compounds is more reactive towards S_N1 reaction?

a. $\text{CH}_2=\text{CHCH}_2\text{Br}$ b. $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ c. $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ d. $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$

Ans: c. $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$

14. Which of the following isomer has the highest melting point:

- (a) 1,2-dichlorobenzene (b) 1,3-dichlorobenzene
(c) 1,4-dichlorobenzene (d) all isomers have same melting points

Ans: (c) 1,4-dichlorobenzene

15. Major product obtained on reaction of 3-Phenyl propene with HBr in presence of organic peroxide

- (a) 3-Phenyl 1-bromopropane (b) 1-Phenyl-3-bromopropane
(c) 1-Phenyl-2-bromopropane (d) 3-Phenyl-2-bromopropane

Ans: (b) 1-Phenyl-3-bromopropane

16. Which is the correct increasing order of boiling points of the following compounds?

1-Bromoethane, 1-Bromopropane, 1-Bromobutane, Bromobenzene

- (a) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane
(b) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane
(c) 1-Bromopropane < 1-Bromobutane < 1-Bromoethane < Bromobenzene
(d) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

Ans: 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

17. Which of the following is a correct statement for $\text{C}_2\text{H}_5\text{Br}$?

- (a) It reacts with metallic Na to give butane.
(b) It gives nitroethane on heating with aqueous solution of KNO_2
(c) It gives $\text{C}_2\text{H}_5\text{OH}$ on boiling with alcoholic potash.
(d) It forms diethyl thioether on heating with alcoholic KSH

Ans: (a) It reacts with metallic Na to give butane.

18. Which of the following alkyl halides will undergo SN_1 reaction most readily?

- (i) $(\text{CH}_3)_3\text{C}-\text{F}$ (ii) $(\text{CH}_3)_3\text{C}-\text{Cl}$ (iii) $(\text{CH}_3)_3\text{C}-\text{Br}$ (iv) $(\text{CH}_3)_3\text{C}-\text{I}$

Ans: (iv) $(\text{CH}_3)_3\text{C}-\text{I}$

19. The reagent for following conversion is (are) $\text{CH}_2\text{Br}-\text{CH}_2\text{Br} \rightarrow \text{CH}\equiv\text{CH}$

- (i) Alcoholic KOH (ii) Alcoholic KOH followed by NaNH_2
(iii) Aqueous KOH followed by NaNH_2 (iv) Zn/methanol

Ans: (ii) Alcoholic KOH followed by NaNH_2

19. The organic choro compound, which shows complete stereo chemical inversion during a SN_2 reaction, is

- (i) $(\text{C}_2\text{H}_5)_2\text{CHCl}$ (ii) $(\text{CH}_3)_3\text{CCl}$
(iii) $(\text{CH}_3)_2\text{CHCl}$ (iv) CH_3Cl

Ans: (iv) CH_3Cl

20. SN_1 reaction of alkyl halides lead to

- (a) Retention of configuration (b) Racemisation (c) Inversion of configuration (d) None of these
Ans b)

21. Fitting reaction can be used to prepare

- (a) Toluene (b) Acetophenone (c) Diphenyl (d) Chlorobenzene

Ans, c

22. Methyl bromide reacts with AgF to give methyl fluoride and silver bromide. This reaction is called

- (a) Fittig reaction (b) Swartz reaction (c) Wurtz reaction (d) Finkelstein reaction

Ans. b

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

- (a) $\text{ClCH}_2\text{-CH}=\text{CH}_2$ (b) $\text{CH}_2=\text{CH-Cl}$
(c) $\text{CH}_3\text{CH}=\text{CH-Cl}$ (d) $\text{C}_6\text{H}_5\text{Cl}$

Ans a

24. Compound A reacts with PCl_5 to give B which on treatment with KCN followed by hydrolysis gave propanoic acid. What are A and B respectively

- (a) C_3H_8 and $\text{C}_3\text{H}_7\text{Cl}$ (b) C_2H_6 and $\text{C}_2\text{H}_5\text{Cl}$
(c) $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{Cl}$ (d) $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_4\text{Cl}_2$

Ans. c)

25. Most reactive halide towards SN_1 reaction is

- (a) n- Butyl chloride (b) sec- Butyl chloride (c) tert-Butyl chloride (d) Allyl chloride

Ans d)

26. Tertiary alkyl halides are practically inert to substitution by SN_2 mechanism because of

- (a) Insolubility (b) Inductive effect (c) Instability (d) Steric hinderance

Ans d)

27. Which of the following compounds is optically active?

- (a) $(\text{CH}_3)_2\text{CHOH}$ (b) $\text{CH}_3\text{CHClCOOH}$
(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (d) $(\text{CH}_3)_3\text{CCl}$

Ans. b)

28. An alkyl halide forms its Grignard reagent followed by treating with water yields propane. The original alkyl halide is

- (a) Methyl iodide (b) Ethyl bromide (c) Propyl bromide (d) Butyl bromide

Ans. c)

29. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

- (i) Electrophilic elimination reaction (ii) Electrophilic substitution reaction
(iii) Free radical addition reaction (iv) Nucleophilic substitution reaction

Ans. (ii)

30. The order of reactivities of the following alkyl halides for a SN_2 reaction is

- (a) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$ (b) $\text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3\text{-I}$
(c) $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{F} > \text{CH}_3\text{I}$ (d) $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3\text{F}$

Ans d

31. The stereochemistry of the product formed if optically active alkyl halide undergoes substitution reaction by SN_1 mechanism is -

- (a) Optically active inverted product (b) Optically active retention product
(c) Racemic mixture (d) None of the above

Ans , C

32. Which one is most reactive towards SN1 reaction ?

(a) $\text{CH}_3\text{CH}_2\text{Br}$ (b) $\text{CH}_3\text{CH}(\text{CH}_3)\text{Br}$ (c) $(\text{CH}_3)_3\text{CBr}$ (d) CH_3Br

Ans C

33. n-propyl bromide on treatment with ethanolic potassium hydroxide produces

(a) propane (b) propene (c) propyne (d) propanol

Ans b

34. Reaction used to prepare alkyl iodide from alkyl bromide by using NaI in acetone is

(a) Williamson's reaction (b) Swart reaction

(c) Finkelstein reaction (d) Wurtz reaction

Ans, C

35. Which of the following group at para position increase the reactivity of aryl halides towards nucleophilic substitution?

(A) $-\text{CH}_3$ (B) $-\text{OCH}_3$ (C) $-\text{NH}_2$ (D) $-\text{NO}_2$

Ans. D