Haloalkanes and Haloarenes

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1. In the presence of peroxide hydrogen chloride and hydrogen iodide do not give anti-Markovnikov's addition to alkenes because
    1. Both are highly ionic
    2. One is oxidising and the other is reducing
    3. One of the steps is endothermic in both the cases
    4. All the steps are exothermic in both the reactions
2. On being heated with aniline and KOH, chloroform gives
    1. An almond like smell
    2. A rose-like odor
    3. A smell like oil of wintergreen
    4. An offensive smell
3. Choose the incorrect statement
    1. An SN_1 reaction proceeds with inversion of configuration
    2. An SN_2 reaction proceeds with stereochemical inversion
    3. An SN_2 reaction follows second order kinetics
    4. The reaction of tert-butyl bromide with OH^- follows first order kinetics
4. Which of the statements is not true for the isomeric compounds ethylene chloride and ethylidene chloride?
    1. Both react with aqueous KOH to give the same product
    2. Both react with alcoholic KOH to give the same product
    3. They are derivatives of ethene
    4. They respond to Beilstein's test
5. The reagent for the following conversion is

    1. Alcoholic KOH

    2. Alcoholic KOH followed by $NaNH_2$

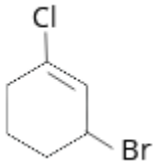
    3. Aqueous KOH followed by $NaNH_2$

    4. Zn/CH_3OH

6. Which of the following halogen exhange reaction will occur?
    1. R-I + NaCl

2. R-F + KCl
3. R-Cl + NaI
4. CH_3-F + AgBr

7. Which of the following groups are ortho and para directing?
    1. -CHO
    2. -$NHCOCH_3$
    3. -CN
    4. -SO_3H
8. The trade name of trochloroethylene is
    1. Freon
    2. Westron
    3. Westrosol
    4. DDT
9. The IUPAC name of the compound shown below is



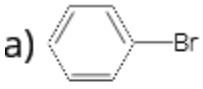
1. 2-bromo-6-chlorocyclohex-1-ene

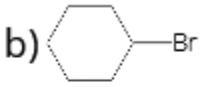
2. 6-bromo-2-chlorocyclohexene

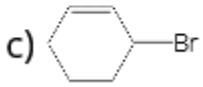
3. 3-bromo-1-chlorocyclohexene

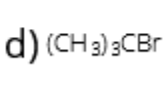
4. 1-bromo-3-chlorocyclohexene

10. The increasing order of hydrolysis of the following compounds is









1 . a < d < b < c 2. a < b < c < d

3. a < b < d < c 4. d < c < b < a

11. On being warmed with silver powder, chloroform gives

1. C_6H_6
2. C_2H_4
3. C_2H_2
4. CH_3Cl

12. The addition of propene with HOCl proceeds via the additions of
    1. H^+ in the first step
    2. Cl^- in the first step
    3. OH^- in the first step
    4. Cl^+ and OH^- in a single step
13. Chlorobenzene can be obtained from benzenediazonium chloride by
    1. Friedel-Crafts reaction
    2. Sandmeyer reaction
    3. Wurtz reaction
    4. Fittig reaction
14. Which of the following reactions cannot be used for the preparation of alkyl halides?
    1. $CH_3CH_2OH + HCl \rightarrow$
    2. $CH_3CH_2OH + HCl + \text{anhy. } ZnCl \rightarrow$
    3. $(CH_3)_3COH + HCl \rightarrow$
    4. $(CH_3)_2CHOH + HCl \rightarrow$
15. Butyronitrile can be prepared by heating
    1. Propyl alcohol with KCN
    2. Butyl alcohol with KCN
    3. Propyl chloride with KCN
    4. Butyl chloride with KCN
16. For a given alkyl group, the boiling point of alkyl halides follows the order
    1. RCl > RBr > RI
    2. RI > RBr > RCl
    3. RI > RCl > RBr
    4. RBr > RI > RCl
17. Which of the following is the most reactive towards nucleophilic substitution reaction?

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

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

1. (a) 2. (b) 3. (c) 4. (d)

18. Addition of HBr gives the same product in the presence or absence of peroxide when alkene is

1. 1-butene
2. 2-methylpropene
3. 1-propene
4. 2-butene

19. Br has a low reactivity in CH_2CHBr because
    1. The C-Br bond has a partial triple bond character
    2. Of the +M effect of bromine
    3. Br is electronegative
    4. None of the above
20. Which of the following is the most suitable for the preparation of n-propylbenzene?
    1. Friedal-Crafts Alkylation
    2. Wurtz Reaction
    3. Wurtz-Fittig Reaction
    4. Grignard Reaction
21. What is the hybridisation of carbon that is attached to chlorine atom in n-primary alkyl halide?
    1. sp^3
    2. sp^2
    3. sp
    4. sp^3d
22. The C-X bond is strongest in
    1. CH_3Cl
    2. CH_3Br
    3. CH_3F
    4. CH_3I
23. IUPAC name for tertiary butyl iodide is
    1. 4-iodobutane
    2. 2-iodobutane
    3. 1-iodo-3-methylpropane
    4. 3-iodo-2-methylpropane
24. Select the incorrect statement
    1. 1,4-dibromobutane react with excess of magnesium in ether to generate di-Grignard reagent
    2. 1,2-dichlorocyclohexane treated with excess of magnesium in ether produces cyclohexane
    3. Vicinal dihalides undergo dehalogenation to give alkene when heated with Zn dust or Mg
    4. 1,3-dichloropropane by treatment with Zn dust or Mg forms cyclopropane
25. The reaction of benzene with chlorine in the presence of iron gives
    1. Benzene hexachloride

2. Chlorobenzene
3. Benzyl chloride
4. Benzoyl chloride

26. Which is used as an anaesthetic during surgery?
    1. Chloroquine
    2. Thyroxine
    3. Halothane
    4. Chloramphenicol

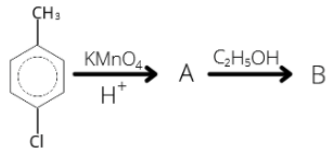
27. Which among the following halides will acquire colour when exposed to light?
    1. R-Br and R-Cl
    2. R-I and R-F
    3. R-Cl and R-Br
    4. R-Br and R-I

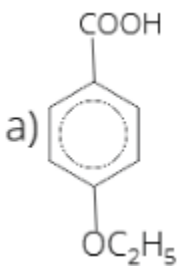
28. Which of the following is used in paint removal?
    1. $CHCl_3$
    2. CH_2Cl_2
    3. CCl_4
    4. CH_3Cl

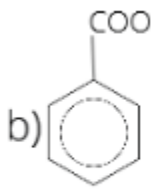
29. Ethyl chloride is converted to butane by
    1. Kolbe's synthesis
    2. Williamson synthesis
    3. Wurtz reaction
    4. Gatterman reaction

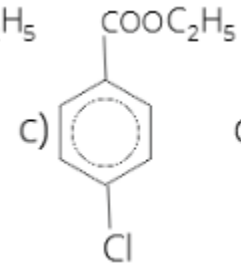
30. Aryl halide is less reactive than alkyl halide towards nucleophilic substitution because
    1. Of less stable carbonium ion
    2. Due to large C-Cl bond energy
    3. Of inductive effect
    4. Of resonance stabilization and sp^3 hybridisation of C attached to halide

31. Identify B in the following reaction



a) 

b) 

c) 

d) None of these

1. (a) 2. (b) 3. (c) 4. (d)

32. Which metal is used in Wurtz synthesis?
    1. Barium
    2. Aluminium
    3. Sodium
    4. Iron
33. The false statement about alkane is
    1. This does not perform polymerisation reaction
    2. This doesn't gives elimination reaction
    3. It doesn't disappear the colour of dilute $KMnO_4$ solution
    4. It does not decolourize bromine water
34. Which of the following is used to decaffeinate coffee?
    1. Iodoform
    2. Carbon tetrachloride
    3. Methylene dichloride
    4. Chloroform
35. Which of the following statements is false about chloroform?
    1. It is a colourless, sweet-smelling liquid
    2. It is almost insoluble in water
    3. It can be used as an inhalational anaesthetic agent
    4. It is highly inflammable
36. Which if the following can not be precipitated with an aqueous solution of $AgNO_3$?
    1. $CHCl_3$
    2. KI
    3. K_2SO_4
    4. KCl
37. Reaction of chlorobenzene with CH_3Cl in presence of $AlCl_3$ gives
    1. Toluene
    2. m-chloro toluene
    3. only o-chloro toluene
    4. Mixture of ortho and para chlorotoluene
38. On nitration, the major product that chlorobenzene gives is
    1. 1-chloro-4-nitrobenzene
    2. 1,4-dinitrobenzene
    3. 1-chloro-3-nitrobenzene
    4. 2,4,6-trinitrobenzene
39. Common name of chloroethane is
    1. Benzyl chloride
    2. Vinyl chloride
    3. Allyl bromide

4. None of these

40. Which if the following has the highest reactivity?
    1. CH_3Br
    2. CH_3CH_2Br
    3. $CH_3CH_2CH_2Br$
    4. $CH_3CH_2CH_2CH_2Br$
41. Which of the following molecules have the highest dipole moment?
    1. CH_3Cl
    2. CH_2Cl_2
    3. $CHCl_3$
    4. CCl_4
42. Which of the following have the highest boiling point?
    1. 1-chloropentane
    2. 2-chloropentane
    3. 3-chloropentane
    4. All have equal boiling point
43. Chlorobenzene and benzene hexachloride are obtained from benzene by the reaction of chlorine, in the presence of
    1. Direct sunlight and anhydrous $AlCl_3$ respectively
    2. Sodium hydroxide and sulphuric acid respectively
    3. Ultraviolet light and anhydrous $FeCl_3$ respectively
    4. Anhydrous $AlCl_3$ and direct sunlight respectively
44. Which of the following can not be prepared by Sandmeyer's reaction?
    1. Chlorobenzene
    2. Bromobenzene
    3. Iodobenzene
    4. All of these
45. Which of the following reagent is used in the conversion of benzene diazonium chloride to chlorobenzene?
    1. $CuCl_2$
    2. Cu_2Cl_2
    3. $FeCl_2$
    4. $FeCl_3$
46. The conversion of ethyl bromide to ethyl iodide using sodium iodide and dry acetone, this reaction is known as
    1. Swarts reaction
    2. Finkelstein reaction
    3. Sandmeyer's reaction
    4. Stephen reaction
47. The vapours of which of the following compound burns with green coloured flame?
    1. CH_3COCH_3

2. C_2H_5OH
3. $CHCl_3$
4. CH_3CHO

48. At normal temperature iodoform is
    1. Thick viscous liquid
    2. Gas
    3. Volatile liquid
    4. Solid

49. Iodoform on reaction with KOH gives
    1. CH3CHO
    2. HCOOK
    3. CH3COOK
    4. HCHO

50. Triiodomethane has antiseptic property because of
    1. Liberation of iodoform
    2. Liberation of free iodide
    3. Formation of phosgene gas
    4. None of these

Answer

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1 . (3)

The addition of Cl and I radicals to alkanes in an anti-Markovnikov's fashion is an endothermic reaction and therefore counterproductive. Without the presence of peroxide, all hydrogen halides will add according to the Markovnikov rule.

2. (4)

Carbylamine reaction takes place

$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_4NC + 3KCl + 3H_2O$

As isocyanide is formed, an offensive smell is given out.

3. (1)

SN_1 reaction proceeds with racemisation and retention of configuration.

4. (1)

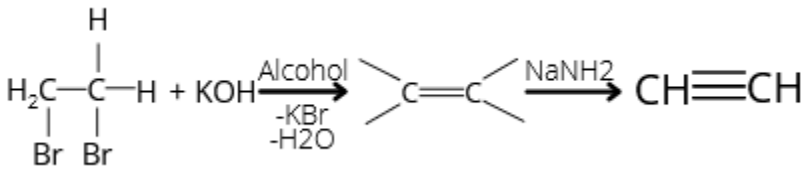
$CH_2(Cl)\text{-}CH_2(Cl) + aq\ KOH \rightarrow CH_2(OH)\text{-}CH_2(OH)$

Ethylene dichloride

$CH_3\text{-}CH(Cl)_2$ + aq KOH → $CH_3\text{-}CHO$

Ethylidene chloride

5. (2)



6. (3)

Bromides and chlorides are insoluble in acetone and hence they can't form a solution with acetone to react with alkyl halides. Sodium iodide, however is soluble in acetone thus forms a solution with acetone and reacts with alkyl halides, thus undergoing Finkelstein reaction

R-X + NaI → R-I + NaX

7. (4)

$-SO_3H$ is an ortho and para directing group.

8. (3)

The trade name of trichloroethylene is westrosol.

9. (3)

3-bromo-1-chlorocyclohexene

10. (2)

a < b < c < d

11. (3)

$2CHCl_4 + 6Ag \rightarrow C_2H_2$ (ethyne) + 6 AgCl

12. (2)

Alkenes undergo electrophilic addition reactions. HOCl on self ionisation produces Cl+ which attacks 1st.

$HOCl + HOCl \rightarrow H_2O + OCl^- + Cl^+$

13. (2)

The formation of chlorobenzene by the reaction of benzene diazonium chloride with Cu_2Cl_2/HCl is known as Sandmeyer's reaction.

14. (1)

Alkyl halide is prepared by the reaction of an alcohol with HCl in which the -OH group is replaced with Cl.

Primary and secondary alcohols require catalysts such as anhydrous zinc chloride.

Tertiary alcohols do not require such catalysts as they are more reactive.

15. (3)

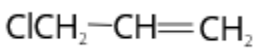
Butyronitrile can be prepared by heating propyl chloride with KCN.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl + KCN \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CN$

16. (2)

Higher the mass of halogen atoms attached with the hydrocarbon part, higher will be the boiling point. Therefore, as I has the highest mass, then Br and then Cl, the boiling point will decrease as : RI > RBr > RCl

17. (4)



18. (4)

2-butene is a symmetric compound and will produce the same product with HBr with or without peroxide.

19. (2)

Br has a low reactivity in CH_2CHBr because of the +M effect of bromine.

20. (3)

The most suitable way for preparing n-propylbenzene is wurtz-fittig reaction.

21. (1)

n primary alkyl halide is R – CH2 – X

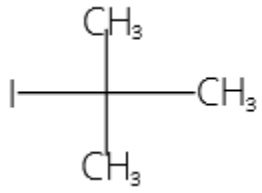
In alkyl halides, halogen is always attached to an sp^3 carbon.

22. (3)

The electron pair is pulled towards the halogen in the carbon-halogen bond as the halogen is more electronegative. As fluorine is the most electronegative element, CH_3F has the strongest bond and has the shortest bond length.

23. (4)

Tertiary butyl iodide is

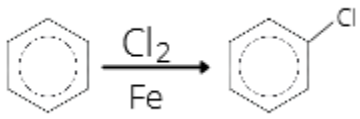


IUPAC Name = 2-iodo-2-methyl propane

24. (3)

Wrong statement – Vicinal dihalides undergo dehalogenation to give alkene when heated with Zn dust or Mg.

25. (2)



26. (3)

Chloroquine – used for malaria

Thyroxine – hormone of thyroid gland

Halothane – anesthetic during surgery

Chloramphenicol – antibiotic for bacterial infections

27. (4)

As we move down the group from fluorine to iodine, molecular size increases.

28. (2)

$CHCl_3$ is used as a solvent and as an anaesthetic.

CCl_4 is used as a fire extinguisher.

CH_2Cl_2 is used as paint removing

CH_3Cl is used as a refrigerator

29. (3)

Wurtz reaction :

$RX + 2Na + RX \rightarrow R\text{-}R + 2NaX$

30. (4)

Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to resonance stabilisation.

Due to resonance, C-Cl bond acquires partial double bond character and becomes shorter and stronger and can't be easily replaced by nucleophiles.

31. (3)

$CH_3\text{-}C_6H_5\text{-}Cl + KMnO_4 \rightarrow COOH\text{-}C_6H_5\text{-}Cl + C_2H_5COOH \rightarrow COOC_2H_5\text{-}C_6H_5\text{-}Cl$

32. (3)

Sodium metal is used in the Wurtz reaction.

33. (2)

Alkanes do show elimination reactions.

34. (3)

Methylene dichloride is used to decaffeinate coffee.

35. (4)

Chloroform is not highly inflammable.

36. (1)

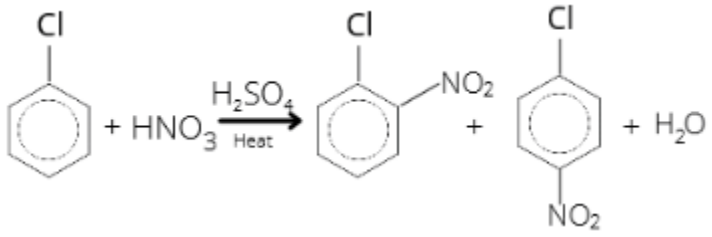
In $CHCl_3$, there are no free Cl^- ions, hence. It doesn't form a precipitate with an aqueous solution of $AgNO_3$.

37. (4)

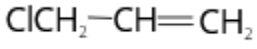
The Cl^- group attached is an ortho-para directing group, therefore, it will form ortho and para chloro toluene.

38. (2)

As Cl- is an ortho-para directing group, it will form ortho-para nitrobenzene.



39. (2)



The substituent group attaches to the double bonded or sp^2 hybridised carbon. Therefore, it is called vinyl chloride.

40. (1)

Br is an electronegative element. The compound is stable if the carbon chain is of more length and thereby inductive effect increases. CH_3Br is less stable and shows higher reactivity because of less inductive effect. Other options have more than one

carbon and hence inductive effect increases, stability increases and reactivity decreases.

41. (1)

Methane has a zero dipole moment. Replacement of one H- atom by Cl atom increases the dipole moment. The increase in dipole moment is because the bond dipole moment of C-H bond and that of C-Cl bond reinforce each other.

Replacement of another H atom by Cl increases the bond angle due to lone pair-lone pair repulsion between Cl- atoms. This reduces the dipole moment and introduces the third Cl- atom. So when the fourth Cl- atom is introduced, the molecule (CCl_4) again becomes symmetrical and the dipole moment reduces to zero. So, CH_3Cl has the highest dipole moment.

42. (1)

The more branched a molecule is, the less will be the surface area to interact through van der waal forces and hence, the boiling point will also decrease. Therefore, 1-chloropentane will have the highest boiling point.

43. (4)

Benzene on substitution reaction with chlorine in the presence of anhydrous AlCl3 will form chlorobenzene. Benzene in addition reaction with chlorine in the presence of sunlight will form benzene hexachloride.

44. (3)

Sandmeyer's reaction is used for the preparation of chlorobenzene and bromobenzene.

45. (2)

Cu_2Cl_2 is used as a reagent and the reaction is called Sandmeyer's reaction.

46. (2)

The conversion of ethyl bromide to ethyl iodide using sodium iodide and dry acetone, this reaction is known as Finkelstein reaction.

C_2H_5-Br + NaI $\rightarrow$ C_2H_5I +NaBr

47. (3)

Chloroform burns with green flames gas.

48. (4)

At room temperature, iodoform is a yellow coloured solid.

49. (2)

$CHI_3 + 4KOH \rightarrow HCOOK + 3KCl + 2H_2O$

50. (2)

Triiodomethane is known as iodoform. As iodoform comes in contact with the matter of skin it decomposes to give free iodine which acts as an antiseptic. It is used for treating skin infection, cuts, boils etc.

Assertion and Reasoning

Codes

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true and but R is not a correct explanation of A

(c) A is true but R is false

(d) A is false, but R is true

1. **Assertion (A)** $(CH_3)_3C\text{-}O\text{-}CH_3$ give $(CH_3)_3C\text{-}I$ and CH_3OH on treatment with HI.

Reason (R) The reaction occurs by SN_1 mechanism.

2. **Assertion (A)** Hydrogen iodide readily reacts with alkenes to form alkyl halides.

Reason (R) Aqueous hydrohalogen acids are used to prepare alkyl halides from alkenes.

3. **Assertion (A)** $CHCI_3$ is stored in dark bottles.

Reason (R) $CHCl_3$ is oxidized in dark.

4. **Assertion (A)** CCI_4 is a fire extinguisher.

Reason (R) CCI_4 is insoluble in water.

5. **Assertion (A)** CH_2-CH-CH_2-X is an example of of a allyl halides.

Reason (R) These are the compounds in which the halogen atom is bonded to an sp^2 hybridised carbon atom.

6. **Assertion (A)** Alkylbenzene is not prepared by Friedel-craft alkylation of benzene.

Reason (R) Alkyl halides are less reactive than aryl halides.

7. **Assertion (A)** Aryl halides cannot be prepared by replacement of of hydroxyl group of phenol by halogen atom.

Reason (R) Phenol react with halogen acids violently.

8. **Assertion (A)** Exposure of ultraviolet rays to human causes the skin cancer, disorder and disrupt the immune system.

Reason (R) Carbon tetrachloride is released into air it rises to atmosphere and deplete the ozone layer.

9. **Assertion (A)** The boiling points of alkyl halides decreases in order: RI > RBr > RCI > RF.

Reason (R) The boiling points of alkyl chloride, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecules mass.

10. **Assertion (A)** Electron withdrawing groups in aryl halides increase the reactivity towards nucleophilic substitution

Reason (R) 2, 4 Dinitrochlorobenzene is less reactive than chlorobenzene

Answer

1. (a)

SN1 reaction occurs in compound that has steric hindrance and $(CH_3)_3$-C-OCH_3 has very much hindrance to attack by reagents.

2. (c)

Dry gaseous hydrohalogenation acids are better electrophiles. In aqueous solution, H_2O acting as nucleophile may produce alcohol.

3. (c)

$CHCl_3$ is stored in dark bottles to avoid reaction in the presence of light. $CHCl_3$ in the presence of light gets oxidised by air.

4. (b)

CCl_4 is carbon tetrachloride and is used in fire extinguisher because it is a heavy non-combustible liquid. CCl_4 in insoluble in water due to absence of hydrogen atom that can form hydrogen bonding with water.

5. (c)

Allyl halides are the compounds in which the halogen atom is bonded to an sp3 hybridised carbon atom next to carbon-carbon double bond.

6. (c)

Aryl halides are more stable and less reactive due to resonance where the lone pair of electron are in conjugation with a pi bond.

7. (c)

Aryl halides can't be prepared by replacing hydroxyl group of phenols because the carbon oxygen bond in phenols because has a partial double bond character and is difficult to break being stronger than a single bond.

8. (b)

The ozone layer is depleted as carbon tetrachloride rises into the atmosphere rises into the atmosphere. As the ozone layer depletes, human being are exposed to more UV radiation, which leads to an

9. (b)

The boiling point of the identical hydrocarbon component is determined by the atomic mass of the halogen atom. The boiling point of a halogen atom increases as its mass increases. As a result, the boiling point of halogen atoms lowers as the atomic mass of the halogen atom decreases.

10. (c)

When electron withdrawing groups are present at the ortho/para position, halobenzenes become reactive to nucleuphile substitution reaction. This is evident by the fact that 2,4-dinitrochlorobenzene requires milder hydrolysis condition than chlorobenzene.