

Haloalkanes and Haloarenes — NEET Chemistry PYQ (2007-2021)

Class 12 Chemistry · 19 real NEET & AIPMT questions, year-tagged · answers checked by RankUp

NEET 2021

1. The major product formed in dehydrohalogenation reaction of 2-Bromo pentane is Pent-2-ene. This product formation is based on ?

- (A) Saytzeff's Rule
- (B) Hund's Rule
- (C) Hofmann Rule
- (D) Huckel's Rule

NEET 2021

2. The correct sequence of bond enthalpy of 'C-X' bond is :

- (A) $\text{CH}_3\text{-F} < \text{CH}_3\text{-Cl} < \text{CH}_3\text{-Br} < \text{CH}_3\text{-I}$
- (B) $\text{CH}_3\text{-F} > \text{CH}_3\text{-Cl} > \text{CH}_3\text{-Br} > \text{CH}_3\text{-I}$
- (C) $\text{CH}_3\text{-F} < \text{CH}_3\text{-Cl} > \text{CH}_3\text{-Br} > \text{CH}_3\text{-I}$
- (D) $\text{CH}_3\text{-Cl} > \text{CH}_3\text{-F} > \text{CH}_3\text{-Br} > \text{CH}_3\text{-I}$

NEET 2020 · Q95

3. Identify compound X in the following sequence of reactions : Toluene ($\text{C}_6\text{H}_5\text{CH}_3$) $\xrightarrow{-\text{Cl}_2/\text{h}\nu}$ X $\xrightarrow{-\text{H}_2\text{O}, 373 \text{ K}}$ Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$)

- (A) Chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$)
- (B) Benzyl chloride ($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$)
- (C) Benzal chloride ($\text{C}_6\text{H}_5\text{CHCl}_2$)
- (D) Benzotrichloride ($\text{C}_6\text{H}_5\text{CCl}_3$)

NEET 2020 · Q114

4. Elimination reaction of 2-Bromo-pentane to form pent-2-ene is : (a) β -Elimination reaction (b) Follows Zaitsev rule (c) Dehydrohalogenation reaction (d) Dehydration reaction

- (A) (a), (b), (c)
- (B) (a), (c), (d)
- (C) (b), (c), (d)
- (D) (a), (b), (d)

NEET 2019 · Q65

5. Among the following, the reaction that proceeds through an electrophilic substitution, is:

- (A) $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \xrightarrow{-\text{Cu}_2\text{Cl}_2} \text{C}_6\text{H}_5\text{Cl} + \text{N}_2$
- (B) $\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow{-\text{AlCl}_3} \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$
- (C) $\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow{-\text{UV light}} \text{C}_6\text{H}_6\text{Cl}_6$ (hexachlorocyclohexane)
- (D) $\text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{HCl} \xrightarrow{-\text{heat}} \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{H}_2\text{O}$

NEET 2018 · Q61

6. The compound C_7H_8 undergoes the following reactions: $\text{C}_7\text{H}_8 \xrightarrow{-(3\text{Cl}_2/\Delta)}$ A $\xrightarrow{-(\text{Br}_2/\text{Fe})}$ B $\xrightarrow{-(\text{Zn}/\text{HCl})}$ C. The product 'C' is

- (A) 3-bromo-2,4,6-trichlorotoluene
- (B) o-bromotoluene
- (C) m-bromotoluene
- (D) p-bromotoluene

NEET 2017 (Gujarati paper) · Q40

7. Which of the following will react faster through $\text{S}_{\text{N}}1$ mechanism?

- (A) $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{Cl}$
- (B) $\text{C}_6\text{H}_5\text{Cl}$ (chlorobenzene)
- (C) $\text{CH}_2=\text{CHCl}$
- (D) $\text{CH}_3\text{CH}_2\text{Cl}$

NEET 2016 Phase 2 · Q76

8. Which of the following can be used as the halide component for Friedel-Crafts reaction?

- (A) Chlorobenzene
- (B) Bromobenzene
- (C) Chloroethene
- (D) Isopropyl chloride

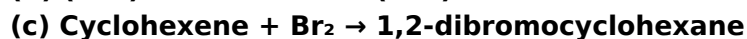
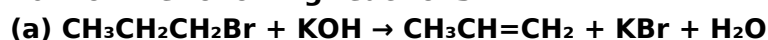
NEET 2016 Phase 2 · Q86

9. Consider the reaction $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{NaCN} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + \text{NaBr}$. This reaction will be the fastest in

- (A) ethanol
- (B) methanol
- (C) N,N'-dimethylformamide (DMF)
- (D) water

NEET 2016 Phase 1 · Q85

10. For the following reactions:



Which of the following statements is correct?

- (A) (a) and (b) are elimination reactions and (c) is addition reaction.
- (B) (a) is elimination, (b) is substitution and (c) is addition reaction.
- (C) (a) is elimination, (b) and (c) are substitution reactions.
- (D) (a) is substitution, (b) and (c) are addition reactions.

AIPMT 2011 Mains

11. Which of the following compounds undergoes nucleophilic substitution reaction most easily?

- (A) p-Chloroanisole ($\text{p-Cl-C}_6\text{H}_4\text{-OCH}_3$)
- (B) Chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$)
- (C) p-Nitrochlorobenzene ($\text{p-Cl-C}_6\text{H}_4\text{-NO}_2$)
- (D) p-Chlorotoluene ($\text{p-Cl-C}_6\text{H}_4\text{-CH}_3$)

AIPMT 2011 Prelims

12. Which one is a nucleophilic substitution reaction among the following?

- (A) $\text{CH}_3\text{CHO} + \text{HCN} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CN}$
- (B) $\text{CH}_3\text{-CH=CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{-CH}(\text{OH})\text{-CH}_3$
- (C) $\text{RCHO} + \text{R}'\text{MgX} \rightarrow \text{R-CH}(\text{OH})\text{-R}'$
- (D) $\text{CH}_3\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-CH}_2\text{Br} + \text{NH}_3 \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-CH}_2\text{NH}_2$

AIPMT 2010 Mains · Q120

13. In the following reaction:

$\text{C}_6\text{H}_5\text{CH}_2\text{Br} \xrightarrow{(1. \text{Mg, ether; 2. H}_3\text{O}^+)} \text{X}$
the product 'X' is

- (A) $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$
- (B) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- (C) $\text{C}_6\text{H}_5\text{CH}_3$
- (D) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$

AIPMT 2010 Prelims · Q90

14. Which is most reactive towards $\text{S}_{\text{N}}1$ reaction?

- (A) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$
- (B) $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$
- (C) $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$
- (D) $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$

15. Which of the following reactions is an example of nucleophilic substitution reaction?

- (A) $2RX + 2Na \rightarrow R-R + 2NaX$
- (B) $RX + H_2 \rightarrow RH + HX$
- (C) $RX + Mg \rightarrow RMgX$
- (D) $RX + KOH \rightarrow ROH + KX$

16. Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces:

- (A) $(p\text{-Cl-C}_6\text{H}_4)_3\text{CH}$
- (B) $(p\text{-Cl-C}_6\text{H}_4)_2\text{C(OH)Cl}$
- (C) $(p\text{-Cl-C}_6\text{H}_4)_2\text{CH-CCl}_3$
- (D) $(p\text{-Cl-C}_6\text{H}_4)_2\text{C(Cl)-CH}_2\text{Cl}$

17. In a SN_2 substitution reaction of the type



Which one of the following has the highest relative rate?

- (A) CH_3CH_2Br
- (B) $CH_3-CH_2-CH_2Br$
- (C) $(CH_3)_2CH-CH_2Br$
- (D) $(CH_3)_3C-CH_2Br$

18. If there is no rotation of plane polarised light by a compound in a specific solvent, though to be chiral, it may mean that

- (A) the compound is certainly meso
- (B) there is no compound in the solvent
- (C) the compound may be a racemic mixture
- (D) the compound is certainly achiral

19. For (i) I^- , (ii) Cl^- , (iii) Br^- , the increasing order of nucleophilicity would be

- (A) $Cl^- < Br^- < I^-$
- (B) $I^- < Cl^- < Br^-$
- (C) $Br^- < Cl^- < I^-$
- (D) $I^- < Br^- < Cl^-$

Answer key and explanations

1. Answer: (A) Saytzeff's Rule

In base-induced dehydrohalogenation, the more substituted (more stable) alkene is the main product, which is Saytzeff's rule. Pent-2-ene is more substituted than pent-1-ene. Hofmann's rule predicts the less substituted alkene and applies to bulky bases or quaternary ammonium bases.

2. Answer: (B) $CH_3-F > CH_3-Cl > CH_3-Br > CH_3-I$

As the halogen gets larger ($F < Cl < Br < I$), the C-X bond becomes longer and overlap poorer, so bond enthalpy decreases: $CH_3-F > CH_3-Cl > CH_3-Br > CH_3-I$. This is why C-I bonds break most easily.

3. Answer: (C) Benzal chloride ($C_6H_5CHCl_2$)

Side-chain chlorination of toluene in light gives benzal chloride, $C_6H_5CHCl_2$; hydrolysis at 373 K gives the gem-diol $C_6H_5CH(OH)_2$, which loses water to form benzaldehyde. Benzyl chloride would hydrolyse to benzyl alcohol and benzotrichloride to benzoic acid.

4. Answer: (A) (a), (b), (c)

HBr is removed from the α -carbon and a β -hydrogen, so it is a β -elimination and a dehydrohalogenation, and the more substituted pent-2-ene is the major product as Zaitsev's rule predicts. No water is lost, so calling it dehydration is wrong.

5. Answer: (B) $\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$

AlCl_3 polarises Cl_2 to generate the electrophile Cl^+ , which attacks the benzene ring: electrophilic aromatic substitution. The Sandmeyer reaction is a radical process, UV chlorination is free-radical addition, and benzyl alcohol with HCl is nucleophilic substitution.

6. Answer: (C) m-bromotoluene

Toluene with Cl_2 under heat (side-chain chlorination) gives $\text{C}_6\text{H}_5\text{CCl}_3$. The $-\text{CCl}_3$ group is electron-withdrawing and meta-directing, so Br_2/Fe gives m-bromobenzotrichloride; Zn/HCl reduces $-\text{CCl}_3$ back to $-\text{CH}_3$, giving m-bromotoluene. Direct bromination of toluene would give the ortho/para products.

7. Answer: (A) $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{Cl}$

$\text{S}_{\text{N}}1$ rate depends on carbocation stability. Allyl chloride ionises to the resonance-stabilised allyl cation, so it reacts fastest. Ethyl chloride would give an unstable primary cation, and vinyl and aryl chlorides have a $\text{C}-\text{Cl}$ bond with partial double-bond character and do not ionise easily.

8. Answer: (D) Isopropyl chloride

Friedel-Crafts alkylation needs a halide that forms a carbocation with AlCl_3 , and isopropyl chloride readily gives the isopropyl cation. In chlorobenzene, bromobenzene and chloroethene the $\text{C}-\text{X}$ bond has partial double-bond character (sp^2 carbon), so aryl and vinyl cations are not formed.

9. Answer: (C) N,N'-dimethylformamide (DMF)

This is an $\text{S}_{\text{N}}2$ reaction of a primary bromide. Polar aprotic solvents such as DMF solvate Na^+ but leave CN^- free and highly nucleophilic, so the rate is greatest. Protic solvents (water, methanol, ethanol) hydrogen-bond to CN^- and slow the reaction.

10. Answer: (B) (a) is elimination, (b) is substitution and (c) is addition reaction.

In (a) HBr is removed to form an alkene (elimination); in (b) $-\text{OH}$ replaces $-\text{Br}$ on the same carbon (substitution); in (c) Br_2 adds across the $\text{C}=\text{C}$ double bond (addition). Calling the second reaction an elimination is wrong because no double bond is formed.

11. Answer: (C) p-Nitrochlorobenzene ($\text{p-Cl-C}_6\text{H}_4\text{-NO}_2$)

Aryl halides undergo nucleophilic substitution only when electron-withdrawing groups at ortho/para positions stabilise the negatively charged intermediate. A para $-\text{NO}_2$ does this strongly, so p-nitrochlorobenzene reacts most easily. $-\text{OCH}_3$ and $-\text{CH}_3$ donate electrons and make substitution harder than in chlorobenzene.

12. Answer: (D) $\text{CH}_3-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2\text{Br} + \text{NH}_3 \rightarrow \text{CH}_3-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2\text{NH}_2$

In the reaction of the primary alkyl bromide with NH_3 , the nucleophile NH_3 replaces Br^- , which is nucleophilic substitution. The cyanohydrin and Grignard reactions are nucleophilic additions to $\text{C}=\text{O}$, and acid-catalysed hydration of propene is electrophilic addition.

13. Answer: (C) $\text{C}_6\text{H}_5\text{CH}_3$

Benzyl bromide with Mg in dry ether forms the Grignard reagent $\text{C}_6\text{H}_5\text{CH}_2\text{MgBr}$, and hydrolysis with H_3O^+ replaces MgBr by H , giving toluene $\text{C}_6\text{H}_5\text{CH}_3$. Benzyl alcohol would need reaction with O_2 or formaldehyde, not plain hydrolysis; bibenzyl is a Wurtz-type side product.

14. Answer: (D) $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$

$\text{S}_{\text{N}}1$ rate depends on carbocation stability. $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$ gives a tertiary carbocation stabilised by two phenyl rings and a methyl group, the most stable of the four. Benzyl bromide gives only a primary benzylic cation.

15. Answer: (D) $\text{RX} + \text{KOH} \rightarrow \text{ROH} + \text{KX}$

In $\text{RX} + \text{KOH}(\text{aq}) \rightarrow \text{ROH} + \text{KX}$ the nucleophile OH^- replaces the halide ion, a nucleophilic substitution. Reaction with Na is the Wurtz coupling, with H_2 is a reduction, and with Mg forms a Grignard reagent.

16. Answer: (C) $(\text{p-Cl-C}_6\text{H}_4)_2\text{CH-CCl}_3$

In conc. H_2SO_4 , chloral condenses with two molecules of chlorobenzene at their para positions, losing water, to give DDT: $(\text{p-Cl-C}_6\text{H}_4)_2\text{CH-CCl}_3$. The CCl_3 group stays intact; it is not replaced by a third ring.

17. Answer: (A) $\text{CH}_3\text{CH}_2\text{Br}$

$\text{S}_{\text{N}}2$ needs backside attack at the carbon bearing Br , so it slows as branching near that carbon increases steric hindrance. Ethyl bromide is the least hindered, so it reacts fastest. The neopentyl-type $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Br}$, though primary, is extremely hindered and reacts slowest.

18. Answer: (C) the compound may be a racemic mixture

A compound believed to be chiral can still show no rotation if it is present as a racemic mixture, where equal amounts of the two enantiomers cancel each other. 'Certainly meso' is too strong: a meso compound is not chiral at all, and a racemate explains the observation equally well.

19. Answer: (A) $\text{Cl}^- < \text{Br}^- < \text{I}^-$

In protic solvents the larger, more polarisable iodide is least solvated and the best nucleophile, so nucleophilicity increases $\text{Cl}^- < \text{Br}^- < \text{I}^-$. The reverse order applies to basicity, not nucleophilicity.

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