St Andrew's Scot Sr Sec School

CH-6, Ch-7

ASSIGNMENT QUESTION.

Class XII Chemistry • Chapters: Haloalkanes & Haloarenes | Alcohols, Phenols & Ethers **Ref:** 12th New NCERT & MTG • **CBSE 2026 Pattern**

General Instructions: This assignment contains 50 uniquely curated questions conforming strictly to the latest CBSE 2025–26 curriculum and premier competitive examinations (JEE / NEET). Questions are graded by conceptual depth, concluding with 10 comprehensive multi-step structural word problems in Section E.

SECTION A: Multiple Choice Questions (Single Correct Option) *[1 Mark Each • Level: Foundational to Moderate]*

1. The correct decreasing order of reactivity of the following alkyl halides towards S_N2 displacement reaction is:

(a) 1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylpropane > 2-Bromo-2-methylpropane

(b) 1-Bromobutane > 1-Bromo-2-methylpropane > 1-Bromo-3-methylbutane > 2-Bromo-2-methylpropane

(c) 2-Bromo-2-methylpropane > 1-Bromo-2-methylpropane > 1-Bromo-3-methylbutane > 1-Bromobutane

(d) 1-Bromo-3-methylbutane > 1-Bromobutane > 1-Bromo-2-methylpropane > 2-Bromo-2-methylpropane

2. Which of the following aryl halides undergoes nucleophilic aromatic substitution (S_NAr) with aqueous **NaOH** under the mildest conditions (lowest temperature)?

(a) Chlorobenzene

(b) 4-Nitrochlorobenzene

(c) 2,4-Dinitrochlorobenzene

(d) 2,4,6-Trinitrochlorobenzene

3. An unknown monohydric alcohol produces an immediate turbidity at room temperature upon addition of Lucas reagent (conc. **HCl** + anhydrous **$ZnCl_2$**). The alcohol is most likely:

(a) Butan-1-ol

(b) Butan-2-ol

(c) 2-Methylpropan-2-ol

(d) 2-Methylpropan-1-ol

4. The correct increasing order of acidic strength for the following compounds is:

Ethanol (I), Phenol (II), *p*-Nitrophenol (III), *p*-Cresol (IV)

(a) I < IV < II < III

(b) I < II < IV < III

(c) IV < I < II < III

(d) III < II < IV < I

5. Reaction of *tert*-butyl methyl ether with one equivalent of concentrated hydriodic acid (**HI**) at room temperature yields:

(a) *tert*-Butyl alcohol + Iodomethane

(b) *tert*-Butyl iodide + Methanol

(c) *tert*-Butyl iodide + Iodomethane

(d) Isobutylene + Methanol

6. Haloalkanes react with **KCN** to form alkyl cyanides as major products, whereas with **AgCN** they form alkyl isocyanides as major products. This is because:

(a) **KCN** is covalent while **AgCN** is predominantly ionic

(b) Cyanide ion is an ambident nucleophile; ionic **KCN** allows attack through carbon, whereas covalent **AgCN** leaves nitrogen lone pair free to attack

(c) Nitrogen is more electronegative than carbon

(d) Silver forms coordinate bond preferentially with alkyl groups

7. The major monobromo derivative obtained upon treating anisole ($C_6H_5OCH_3$) with bromine in ethanoic acid (Br_2 / CH_3COOH) is:

(a) 2-Bromoanisole
(b) 4-Bromoanisole
(c) 3-Bromoanisole
(d) 2,4-Dibromoanisole

8. Which of the following reagent sequences converts propene into propan-1-ol with anti-Markovnikov regioselectivity?

(a) H_2O / H^+ (Acid-catalysed hydration)
(b) B_2H_6 followed by alkaline H_2O_2
(c) Alkaline $KMnO_4$
(d) O_3 followed by Zn / H_2O

9. Oxidation of phenol with acidified sodium dichromate ($Na_2Cr_2O_7$ / H_2SO_4) produces a conjugated diketone known as:

(a) Resorcinol
(b) Catechol
(c) *p*-Benzoquinone
(d) Salicylic acid

10. The active electrophilic intermediate involved in the Reimer-Tiemann reaction of phenol with chloroform in aqueous NaOH is:

(a) Dichlorocarbocation ($^+CHCl_2$)
(b) Neutral Dichlorocarbene ($:CCl_2$)
(c) Trichlorocarbanion ($^-CCl_3$)
(d) Formyl cation (^+CHO)

11. Dehydration of ethanol with concentrated H_2SO_4 at **413 K** and **443 K** gives, respectively:

(a) Ethoxyethane and Ethene
(b) Ethene and Ethoxyethane
(c) Diethyl sulphate and Ethene
(d) Ethyl hydrogen sulphate and Ethoxyethane

12. Which of the following compounds gives a yellow precipitate of triiodomethane (iodoform) on warming with I_2 and aqueous NaOH?

(a) Pentan-3-ol
(b) 3-Methylbutan-2-ol
(c) Methanol
(d) 2-Methylpropan-1-ol

13. The industrial preparation of phenol from chlorobenzene by heating with aqueous NaOH at **623 K** and **300 atm** pressure followed by acidification is:

(a) Dow's process
(b) Raschig process
(c) Kolbe's process
(d) Williamson synthesis

14. Heating 2-bromopentane with alcoholic KOH predominantly yields pent-2-ene instead of pent-1-ene. This elimination regioselectivity is governed by:

(a) Markovnikov's rule
(b) Saytzeff's (Zaitsev's) rule
(c) Hofmann's elimination rule
(d) Kharasch peroxide effect

15. Treatment of sodium phenoxide with carbon dioxide at **400 K** under **4–7 atm** pressure followed by acid hydrolysis yields:

(a) Salicylaldehyde
(b) Salicylic acid (2-Hydroxybenzoic acid)
(c) Benzoic acid
(d) Methyl salicylate

SECTION B: Assertion - Reason Type Questions *[1 Mark Each • Level: Moderate]*

Directions (Q16–Q20): In each question, a statement of Assertion (A) is followed by a statement of Reason (R). Choose the correct option:
(A) Both (A) and (R) are true, and (R) is the correct explanation of (A). | **(B)** Both (A) and (R) are true, but (R) is NOT the correct explanation of (A).
(C) (A) is true, but (R) is false. | **(D)** (A) is false, but (R) is true.

16. **Assertion (A):** Haloarenes are extremely less reactive towards nucleophilic aromatic substitution than haloalkanes.
Reason (R): In haloarenes, the lone pair of electrons on halogen delocalises with the π-electrons of the benzene ring, imparting partial double bond character to the C—X bond.

17. **Assertion (A):** The boiling point of ethanol (351 K) is much higher than that of isomeric methoxymethane (249 K) and propane (231 K).
Reason (R): Molecules of ethanol undergo extensive intermolecular hydrogen bonding resulting in strong molecular association.

18. **Assertion (A):** Reaction of 2-bromo-2-methylpropane with sodium methoxide (**CH_3ONa**) predominantly gives 2-methylpropene rather than *tert*-butyl methyl ether.
Reason (R): Alkoxides are not only powerful nucleophiles but also strong bases; with tertiary alkyl halides, elimination preferentially outcompetes substitution.

19. **Assertion (A):** *o*-Nitrophenol is steam volatile and can be separated from *p*-nitrophenol by steam distillation.
Reason (R): *o*-Nitrophenol exhibits intramolecular hydrogen bonding (chelation), whereas *p*-nitrophenol exhibits intermolecular hydrogen bonding leading to association.

20. **Assertion (A):** The dipole moment of chlorobenzene (1.69 D) is lower than that of cyclohexyl chloride (1.86 D).
Reason (R): The C—Cl carbon in chlorobenzene is sp^2 hybridised with greater s-character, which is more electronegative and releases less electron density towards chlorine compared to the sp^3 carbon of cyclohexyl chloride.

SECTION C: Conceptual & Scientific Reasoning Questions
[2 & 3 Marks • Level: Conceptual & Application-Oriented]

21. Alkyl halides are polar molecules with significant dipole moments, yet they are practically insoluble (immiscible) in water. Explain this physical anomaly on the basis of intermolecular energetics.

22. An equimolar racemic mixture of (±)-butan-2-ol is optically inactive. Justify this optical inactivity and explain the fundamental principle of 'external compensation'.

23. Account for the structural differences in bond angles:

(a) Why is the C—O—H bond angle in methanol (108.9°) slightly less than the tetrahedral angle (109.5°)?

(b) Why is the C—O—C bond angle in methoxymethane (111.7°) slightly greater than the tetrahedral angle?

24. Thionyl chloride (**$SOCl_2$**) is the most preferred laboratory reagent for converting primary and secondary aliphatic alcohols into alkyl chlorides. Justify this preference with a balanced chemical equation.

25. Give concise scientific reasoning for the following:

(a) Phenol has a higher acid dissociation constant ($pK_a \approx 10$) than ethanol ($pK_a \approx 16$).

(b) A nitro group attached at the *ortho* or *para* position increases the acidity of phenol drastically, whereas at the *meta* position the increase is much less pronounced.

26. Why cannot aryl halides (e.g., chlorobenzene) or vinyl halides (e.g., vinyl chloride) be used as electrophilic alkylating substrates in Williamson ether synthesis?

27. Predict the product(s) formed and explain the chemical rationale when phenol is treated with:

(a) Bromine water (**Br_2 / H_2O**) at room temperature.

(b) Bromine in non-polar solvent (**Br_2 / CS_2**) at low temperature (273 K).

28. Grignard reagents (**RMgX**) are extremely versatile synthetic tools in organic synthesis, yet they must always be prepared and stored under strictly anhydrous conditions. Explain with a suitable chemical reaction.

29. When anisole (**$C_6H_5OCH_3$**) is cleaved with concentrated hydriodic acid (**HI**), the products are phenol and iodomethane, but never iodobenzene and methanol. Explain this regioselectivity mechanistically.

30. Explain the following physical and chemical phenomena:

(a) *p*-Dichlorobenzene possesses a significantly higher melting point and lower organic solubility than its corresponding *ortho* and *meta* isomers.

(b) Allyl chloride (**CH_2=CH—CH_2Cl**) undergoes solvolytic hydrolysis via S_N1 mechanism much faster than *n*-propyl chloride (**$CH_3CH_2CH_2Cl$**).

SECTION D: Mechanisms, Conversions & Distinguishing Tests *[3 & 5 Marks • Level: Intermediate to Advanced Problem Solving]*

31. Write the stepwise reaction mechanism for the acid-catalysed hydration of ethene to yield ethanol. Clearly identify the electrophile, the carbocation intermediate, and the rate-determining step (RDS).

32. Outline the complete two-step mechanism for the alkaline hydrolysis of 2-bromo-2-methylpropane (*tert*-butyl bromide) via the S_N1 pathway. Why does an S_N1 reaction on an optically active tertiary alkyl halide lead to partial or complete racemisation?

33. Write the complete stepwise mechanism for the bimolecular dehydration of ethanol to form diethyl ether in the presence of concentrated sulphuric acid at **413 K** (S_N2 pathway).

34. Show how the following multi-step synthetic conversions can be carried out cleanly:

(a) Propene ⟶ Propan-1-ol (via Hydroboration-Oxidation and via Peroxide addition/hydrolysis)

(b) Ethanol ⟶ But-1-yne

35. Devise efficient reaction sequences for the following transformations:

(a) Chlorobenzene ⟶ *p*-Nitrophenol

(b) Aniline ⟶ Chlorobenzene (via Diazotisation and Sandmeyer reaction)

36. Write balanced chemical equations along with specific reaction conditions for each of the following named organic reactions:

(a) Kolbe's Reaction (conversion of sodium phenoxide to salicylic acid)

(b) Williamson Ether Synthesis (formation of *tert*-butyl ethyl ether)

(c) Finkelstein Reaction and Swarts Reaction

37. How will you carry out the following syntheses?

(a) Phenol ⟶ Aspirin (Acetylsalicylic acid)

(b) Cumene (isopropylbenzene) ⟶ Phenol and Acetone (Industrial preparation)

38. Give one simple and distinctive chemical test to distinguish between each of the following pairs of compounds, stating the reagent used and the visible observation:

(a) Propan-1-ol and Propan-2-ol

(b) Chlorobenzene and Benzyl chloride

(c) Phenol and Benzoic acid

39. Predict the major organic product(s) formed in each of the following chemical reactions:

(a) $\mathbf{CH_3—CH=CH_2 + HBr \longrightarrow}$ [in presence of Benzoyl Peroxide]

(b) $\mathbf{(CH_3)_3C—O—CH_3 + excess\ HI\ \ \&xrightarrow\{\;\Delta\;\}}$?

(c) **Phenol + Zn (dust)** $\mathbf{\ \&xrightarrow\{\;\Delta\;\}}$?

(d) **2-Bromobutane + alc. KOH** $\mathbf{\ \&xrightarrow\{\;\Delta\;\}}$?

40. An optically active haloalkane **'X'** ($\mathbf{C_4H_9Cl}$) undergoes bimolecular nucleophilic substitution (S_N2) with aqueous **NaOH**.

(a) Give the IUPAC name and draw the 3D flying-wedge structure of **'X'**.

(b) Illustrate the transition state and explain why the reaction proceeds with complete inversion of stereochemical configuration (Walden Inversion).

SECTION E: Multi-Step Structural Elucidation & Word Problems *[Word Problems • 4 & 5 Marks • Comprehensive Board & Competition Focus]*

41. An organic compound **[A]** with molecular formula $\mathbf{C_4H_9Br}$ reacts with aqueous **KOH** via first-order kinetics (S_N1) at an extremely rapid rate to form compound **[B]** ($\mathbf{C_4H_{10}O}$). When compound **[A]** is heated with alcoholic **KOH**, it undergoes dehydrohalogenation to yield an alkene **[C]** ($\mathbf{C_4H_8}$). Alkene **[C]** on reductive ozonolysis ($\mathbf{O_3}$ **/ Zn–**$\mathbf{H_2O}$) gives acetone ($\mathbf{CH_3COCH_3}$) and formaldehyde (**HCHO**).

(a) Identify compounds **[A]**, **[B]**, and **[C]**.

(b) Write all chemical equations involved in each step.

42. An aromatic organic compound **[A]** ($\mathbf{C_7H_8O}$) is insoluble in aqueous $\mathbf{NaHCO_3}$ but dissolves readily in aqueous **NaOH**. When **[A]** is treated with neutral $\mathbf{FeCl_3}$ solution, it develops a characteristic violet coloration. On bromination with bromine water, **[A]** rapidly forms a white precipitate of a tribromo derivative **[B]** ($\mathbf{C_7H_5Br_3O}$).

(a) Deduce the structural formulae and IUPAC names of compounds **[A]** and **[B]**.

(b) Write the balanced chemical equation for the conversion of **[A]** to **[B]**.

43. A primary alkyl halide **[A]** ($\mathbf{C_4H_9Br}$) on reaction with alcoholic **KOH** gives an alkene **[B]** ($\mathbf{C_4H_8}$). Compound **[B]** reacts with **HBr** in the absence of peroxides to give compound **[C]**, which is a positional isomer of **[A]**. When compound **[A]** is treated with sodium metal in dry ether (Wurtz reaction), it yields an alkane **[D]** ($\mathbf{C_8H_{18}}$) containing two tertiary carbon atoms (2,5-dimethylhexane).

(a) Identify compounds **[A]**, **[B]**, **[C]**, and **[D]**.

(b) Write the reaction equations for the formation of **[B]**, **[C]**, and **[D]**.

44. An aromatic compound **[A]** on treatment with chloroform and aqueous **NaOH** at **340 K** followed by acidification yields two isomeric products **[B]** and **[C]** with molecular formula $\mathbf{C_7H_6O_2}$. Compound **[B]** is steam-volatile and exhibits intramolecular hydrogen bonding, whereas **[C]** is non-steam-volatile. When compound **[B]** is distilled with zinc dust, it gives an aromatic aldehyde **[D]**.

(a) Identify compounds **[A]**, **[B]**, **[C]**, and **[D]**.

(b) Name the chemical reaction converting **[A]** to **[B]** and **[C]**, and state the active electrophile involved.

45. An alkyl halide **[A]** ($C_5H_{11}Cl$) on dehydrohalogenation with hot alcoholic **KOH** predominantly yields alkene **[B]** (C_5H_{10}). Alkene **[B]** upon ozonolysis followed by reductive cleavage with **Zn / H_2O** produces an equimolar mixture of propanone (CH_3COCH_3) and ethanal (CH_3CHO).

(a) Deduce the structural formula and IUPAC name of **[A]** and **[B]**.

(b) Write the chemical reactions and state the empirical rule governing the preferential formation of alkene **[B]**.

46. An ether **[A]** ($C_5H_{12}O$) on cleavage with one equivalent of hot concentrated hydriodic acid (**HI**) yields an alkyl iodide **[B]** and an alcohol **[C]**. Compound **[B]** on hydrolysis with aqueous **NaOH** gives an alcohol that produces a yellow precipitate of iodoform on warming with **I_2 / NaOH**. Alcohol **[C]** when treated with Lucas reagent produces turbidity after approximately 5 minutes at room temperature.

(a) Identify the structural formulae and IUPAC names of compounds **[A]**, **[B]**, and **[C]**.

(b) Write the chemical equations for the cleavage of **[A]** with **HI** and the subsequent test reactions.

47. A hydrocarbon **[A]** (C_4H_8) decolourises bromine in **CCl_4**. Addition of **HBr** to **[A]** in the presence of benzoyl peroxide gives compound **[B]** (C_4H_9Br). When **[B]** is heated with aqueous **KOH**, it forms compound **[C]** ($C_4H_{10}O$), which on oxidation with alkaline **$KMnO_4$** gives a carboxylic acid **[D]** ($C_4H_8O_2$). However, direct acid-catalysed hydration of **[A]** yields compound **[E]** ($C_4H_{10}O$), which is an isomer of **[C]** and is resistant to mild oxidation.

(a) Identify compounds **[A]**, **[B]**, **[C]**, **[D]**, and **[E]**.

(b) Write the complete reaction sequence from **[A]** to **[D]** and **[A]** to **[E]**.

48. An aromatic hydrocarbon **[A]** (C_7H_8) reacts with chlorine gas in the presence of sunlight at boiling temperature to give compound **[B]** (C_7H_7Cl). Compound **[B]** upon boiling with aqueous **NaOH** gives an organic compound **[C]** (C_7H_8O). Compound **[C]** on oxidation with pyridinium chlorochromate (PCC) in dichloromethane yields **[D]** (C_7H_6O). When compound **[D]** is heated with 50% aqueous **NaOH** (Cannizzaro reaction), it regenerates compound **[C]** alongside the sodium salt of benzoic acid.

(a) Identify compounds **[A]**, **[B]**, **[C]**, and **[D]**.

(b) Write the reaction of compound **[B]** with alcoholic **KCN** followed by complete acidic hydrolysis.

49. An aryl halide **[A]** (C_6H_5Cl) is heated with chloromethane in the presence of anhydrous **$AlCl_3$** to yield two isomeric products **[B]** and **[C]** (C_7H_7Cl). Compound **[C]** (major isomer) on vigorous oxidation with hot alkaline **$KMnO_4$** followed by acidification yields 4-chlorobenzoic acid. When **[A]** is treated with sodium metal in dry ether (Fittig reaction), it produces a symmetrical biaryl compound **[D]** ($C_{12}H_{10}$).

(a) Identify compounds **[A]**, **[B]**, **[C]**, and **[D]**.

(b) Explain why compound **[C]** is formed as the major product over isomer **[B]** during the Friedel-Crafts alkylation.

50. An optically active alcohol **[A]** ($C_6H_{14}O$) reacts with Lucas reagent slowly and undergoes dehydration when heated with concentrated **H_2SO_4** at **443 K** to yield predominantly an alkene **[B]** (C_6H_{12}). Alkene **[B]** exhibits geometrical (*cis–trans*) isomerism. Alkene **[B]** on ozonolysis followed by reductive cleavage with **Zn / H_2O** produces an equimolar mixture of ethanal (CH_3CHO) and butan-2-one ($CH_3COCH_2CH_3$).

(a) Deduce the structural formula and IUPAC name of the chiral alcohol **[A]**.

(b) Draw the structures of both geometrical stereoisomers (*cis* and *trans*) of alkene **[B]**.

(c) Write the complete reaction sequence for the dehydration of **[A]** and the ozonolysis of **[B]**.