NCERT Exemplar Solutions

Solved NCERT Exemplar Problems for Class 12th Chemistry, Chapter 6 — Representative Set

Chapter 6: Haloalkanes and Haloarenes

About this Chapter

Haloalkanes ($R-X$) and **haloarenes** ($Ar-X$) are organic compounds in which one or more hydrogens of a hydrocarbon are replaced by a halogen (F, Cl, Br, I). This Exemplar set drills the key concepts: classification (primary, secondary, tertiary; *vic*-, *gem*-; allylic, vinylic, benzylic, aryl), **nucleophilic substitution** (S_N1 vs S_N2) with full stereochemistry, **β-elimination** (Saytzeff), electrophilic aromatic substitution on haloarenes, Wurtz, Wurtz–Fittig, Fittig, Sandmeyer and Finkelstein reactions, chirality and the assertion–reason fact bank that JEE/NEET papers love.

Topics covered: Classification of $R-X$ • Preparation methods • Physical properties • S_N1 & S_N2 • Stereochemistry • Elimination (Saytzeff) • Aryl halide reactivity • Wurtz, Fittig, Sandmeyer, Finkelstein

Quick Formula Sheet

S_N2 rate law:
rate $= k[R-X][Nu^-]$ (bimolecular)

S_N1 rate law:
rate $= k[R-X]$ (unimolecular)

Carbocation stability:
$3° > 2° > 1° > CH_3^+$

Saytzeff rule:
more substituted alkene is the major product

Finkelstein:
$R-Cl + NaI \xrightarrow{\text{dry acetone}} R-I + NaCl$

Sandmeyer:
$ArN_2^+ \xrightarrow{CuX} Ar-X + N_2$

I. Multiple Choice Questions (Type-I)

Q 6.1 **The order of reactivity of the following alcohols with halogen acids is ______.**

(A) $CH_3CH_2-CH_2-OH$

(B) $CH_3CH_2-CH(CH_3)-OH$

(C) $CH_3CH_2-C(CH_3)_2-OH$

(i) $(A) > (B) > (C)$ **(ii)** $(C) > (B) > (A)$ **(iii)** $(B) > (A) > (C)$ **(iv)** $(A) > (C) > (B)$

SOLUTION

Correct option: (ii) $(C) > (B) > (A)$.

Concept used. Alcohols react with halogen acids via an S_N1-like protonation/ionisation pathway. First the hydroxyl is protonated to give the oxocation $R{-}OH_2{}^+$; this loses water to form the carbocation R^+; the halide X^- then traps the cation to give $R{-}X$:

$$R{-}OH + HX \longrightarrow R{-}OH_2{}^+ \longrightarrow R^+ + H_2O$$

$$R^+ + X^- \longrightarrow R{-}X$$

The rate-determining step is formation of the **carbocation** R^+, so the rate tracks carbocation stability: $3° > 2° > 1°$.

Step 1. Identify each alcohol: (A) is 1° (n-propanol), (B) is 2° (sec-butanol), (C) is 3° (2-methylbutan-2-ol).

Step 2. Rank the intermediate carbocations: tertiary (C) is most stabilised by three σ-hyperconjugation/$+I$ donations; secondary (B) next; primary (A) least.

Step 3. Therefore reactivity follows C > B > A, option (ii).

> **Final Answer:** Reactivity order: C > B > A; option **(ii)**.

☞ **Carbocation hierarchy**

$3° > 2° > 1° > CH_3{}^+$ — driven by hyperconjugation (more α-H, more stabilisation) and $+I$ of alkyl groups.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Carbocation-first angle. Skip the alcohol skeletons and look only at the carbocation each one would produce on protonation followed by loss of water. Whichever R^+ is most stable wins, because that ionisation is the rate-determining step of the whole sequence.

Concept used. For Lucas-type reactions, rate $\propto$ carbocation stability because the slow step is heterolysis of the protonated alcohol $R{-}OH_2{}^+$ into $R^+ + H_2O$. Empirically: tertiary alcohols react with $HCl/ZnCl_2$ instantly at room temperature (Lucas test positive in seconds, cloudy emulsion), secondary alcohols within ~ 5 minutes, and primary alcohols need warming for any observable reaction.

Step 1. **Map each option to a cation.** (A) yields $CH_3CH_2CH_2{}^+$ (primary, no hyperconjugation buffer). (B) yields $CH_3CH_2{-}CH^+(CH_3)$ (secondary, two α-C–H bonds). (C) yields $CH_3CH_2{-}C^+(CH_3)_2$ (tertiary, six α-C–H bonds available for hyperconjugation plus three $+I$ alkyl donors).

Step 2. **Stability scale.** The tertiary cation from C is the most stabilised; the primary cation from A is the least. Activation energy for ionisation tracks this scale in reverse.

Step 3. **Translate to rate.** Lower E_a for ionisation ⇒ faster $\mathrm{S_N}1$ ⇒ order $C > B > A$, exactly option (ii).

Final Answer: C > B > A; option **(ii)**.

Q 6.2 **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

SOLUTION

Correct option: **(ii)** Electrophilic substitution reaction.
Concept used. Halogenation of an aromatic ring in the presence of a Lewis acid ($FeCl_3, AlCl_3$) proceeds by **electrophilic aromatic substitution** (EAS). The Lewis acid polarises $X{-}X$ to release the electrophile X^+, which attacks the π-cloud of the ring to form a σ-complex (arenium ion), and finally loss of H^+ restores aromaticity. Toluene's $-CH_3$ is an *ortho/para* director through $+I$ and hyperconjugation, so the products are o- and p-halotoluenes.

Step 1. Generate the electrophile: $Cl_2 + FeCl_3 \longrightarrow Cl^+ + [FeCl_4]^-$.

Step 2. Attack the toluene ring at o- and p-positions (methyl is activating + ortho/para directing).

Step 3. Deprotonate the arenium ion to give o- and p-chlorotoluene.

Final Answer: The reaction is an electrophilic substitution; option **(ii)**.

☞ **Quick filter**

Ring + Lewis acid + halogen ⇒ electrophilic substitution. Side-chain (Wohl–Ziegler, $Cl_2/h\nu$) ⇒ free radical substitution.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Mechanism-first angle. Three pieces of evidence pinpoint EAS: an aromatic substrate (toluene), a halogen activated by a Lewis acid catalyst ($FeCl_3$), and the observed regiochemistry (only o/p products, never m). No other mechanism reproduces all three at once.

Concept used. The arenium-ion (Wheland intermediate) mechanism conserves the aromatic σ-framework and merely substitutes one ring H for X; any addition product would break aromaticity (loss of ~ 150 kJ/mol of resonance energy) and therefore never survives. The methyl group of toluene donates electron density into the ring through hyperconjugation and $+I$, raising the HOMO and steering the electrophile to the o/p positions where the positive charge in the Wheland intermediate lands on a methyl-bearing carbon.

Step 1. **Reject (i) and (iv).** No leaving group on toluene's ring and no nucleophile in the reagent set — so neither electrophilic elimination nor nucleophilic substitution is operative.

Step 2. **Reject (iii).** Free-radical chains demand homolysis: UV light, peroxides, or thermal initiation. $\mathrm{FeCl_3}$ is a Lewis acid catalyst, not a radical initiator.

Step 3. **(ii) fits perfectly.** $\mathrm{FeCl_3}$ polarises $\mathrm{Cl{-}Cl}$ to release $\mathrm{Cl^+}$; the ring attacks with its π-electrons; loss of $\mathrm{H^+}$ restores aromaticity. Product distribution (o/p only) is the signature of an electrophilic ring substitution on an activated arene.

Final Answer: Electrophilic aromatic substitution; option **(ii)**.

Q 6.3 Which of the following is a halogen exchange reaction?

(i) $\mathrm{R{-}X + NaI \longrightarrow R{-}I + NaX}$ **(in dry acetone)**

(ii) **Alkene** $+ \mathrm{HX} \longrightarrow$ **alkyl halide (Markovnikov addition)**

(iii) $\mathrm{R{-}OH + HX}$ **($\mathrm{ZnCl_2}$ catalyst)** $\longrightarrow \mathrm{R{-}X + H_2O}$

(iv) **Toluene +** $\mathrm{X_2}$ **(Fe, dark)** $\longrightarrow$ o**- +** p**-halotoluene**

SOLUTION

Correct option: **(i)** $\mathrm{R{-}X + NaI \longrightarrow R{-}I + NaX}$.

Concept used. A halogen exchange (Finkelstein reaction) replaces one halogen on an alkyl halide by a *different* halogen via an $\mathrm{S_N2}$ attack of $\mathrm{I^-}$ on $\mathrm{R{-}X}$. The reaction is driven by precipitation of NaCl or NaBr (insoluble in dry acetone) which shifts the equilibrium toward $\mathrm{R{-}I}$.

Step 1. Option (i) swaps X for I — a halogen-exchange.

Step 2. Option (ii) is electrophilic *addition* of HX across a π-bond; no exchange.

Step 3. Option (iii) replaces $-\mathrm{OH}$ with $-\mathrm{X}$ (Lucas); $-\mathrm{OH}$ is not a halogen.

Step 4. Option (iv) installs a new halogen onto the ring (EAS); again no exchange.

> **Final Answer:** Only (i) is a halogen exchange (Finkelstein reaction).

☞ **Why dry acetone?**

NaI is soluble in acetone; NaBr and NaCl are not. Their precipitation drives the equilibrium forward (Le Chatelier).

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Definition-first angle. "Halogen exchange" literally means swapping one halogen on a carbon skeleton for a *different* halogen on the *same* carbon skeleton. The carbon framework does not change, only the identity of the halogen substituent changes. Read each option through that filter; only (i) survives.

Concept used. The Finkelstein reaction converts $R{-}Cl$ or $R{-}Br$ to $R{-}I$ by an S_N2 displacement of chloride/bromide by iodide in *dry* acetone. The equilibrium is driven forward by the very low solubility of $NaCl$ and $NaBr$ in acetone (vs the much higher solubility of NaI), so the by-product precipitates and Le Chatelier's principle pulls the reaction to the right. The fluorine analogue is the **Swarts reaction**:

$R{-}X + AgF\ (\text{or } Hg_2F_2/CoF_2) \longrightarrow R{-}F + AgX.$

Step 1. **Scan (ii).** Alkene $+HX$ is electrophilic *addition* across $C{=}C$; no halogen on the substrate to begin with, so nothing to "exchange".

Step 2. **Scan (iii).** $R{-}OH + HX$ converts $-OH$ to $-X$ — the substituent that leaves is hydroxyl, not a halogen, so this is not an exchange.

Step 3. **Scan (iv).** Toluene + X_2 installs a *new* halogen onto the aromatic ring; again no existing halogen is exchanged.

Step 4. **Conclude (i).** $R{-}X + NaI \longrightarrow R{-}I + NaX$ keeps the carbon framework intact and trades X for I — the textbook definition of halogen exchange.

> **Final Answer:** Halogen exchange = Finkelstein reaction = option (i).

Q 6.4 **Which reagent will you use for the following reaction?**

$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

(i) Cl_2**/UV light** **(ii)** $NaCl + H_2SO_4$ **(iii)** Cl_2 **gas in dark** **(iv)** Cl_2 **gas in the presence of iron in dark**

SOLUTION

Correct option: (i) Cl_2/UV light.
Concept used. Chlorination of an alkane proceeds by a **free-radical chain mechanism**. UV light homolyses $Cl{-}Cl$ to two $Cl^\bullet$ radicals; these abstract H from the alkane (propagation), giving a carbon radical that then captures another Cl. The reaction is non-selective and yields a *mixture* of mono-chlorinated isomers — exactly what the question shows (1-chlorobutane and 2-chlorobutane).

Step 1. Initiation: $Cl_2 + h\nu \longrightarrow 2\,Cl^\bullet$.

Step 2. Propagation: $Cl^\bullet + CH_3CH_2CH_2CH_3 \longrightarrow HCl + CH_3CH_2CH_2CH_2{}^\bullet$ (or the secondary radical at C_2).

Step 3. Capture: $R^\bullet + Cl_2 \longrightarrow R{-}Cl + Cl^\bullet$.

Step 4. Both primary and secondary radicals form, giving both isomers — consistent with the product spectrum.

> **Final Answer:** Photochlorination with Cl_2/UV light; option **(i)**.

✗ Don't confuse with EAS

$Cl_2/FeCl_3$ does *electrophilic ring* substitution and needs an aromatic ring. Plain alkanes have no π-system, so a radical pathway is the only option. Likewise $NaCl + H_2SO_4$ makes HCl gas but does not generate Cl radicals – without UV initiation, an alkane sees no reactive species.

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Product-shape angle. A mixture of primary (1-chlorobutane) *and* secondary (2-chlorobutane) chlorides is the unmistakable fingerprint of a non-selective radical chain mechanism, not an ionic one. An ionic process would have funnelled the reaction through the more stable secondary carbocation exclusively; the appearance of both regioisomers means H-atoms are being abstracted from *whatever position is statistically accessible*, modulated only mildly by C–H bond strength.
Concept used. Radical halogenation selectivity follows bond-dissociation energies: $3°$-H (≈ 381 kJ/mol) $<$ $2°$-H (≈ 397 kJ/mol) $<$ $1°$-H (≈ 410 kJ/mol), so the weakest C–H is abstracted preferentially. Chlorine radicals are reactive (early transition state) and therefore only mildly selective ($\sim 4{:}1$ between $2°$ and $1°$ in n-butane), which explains the mixed product set. Bromine radicals are far more selective ($\sim 80{:}1$) because their late transition state more closely resembles the radical intermediate.

Step 1. Eliminate (ii) and (iii). $NaCl + H_2SO_4$ and Cl_2 in the dark cannot homolyse the $Cl{-}Cl$ bond; no $Cl^\bullet$ chain is initiated, no reaction with butane.

Step 2. **Eliminate (iv).** Cl_2/Fe targets aromatic rings (EAS) and is inert toward a saturated alkane.

Step 3. **Lock in (i).** Cl_2 + UV light homolyses $Cl{-}Cl \rightarrow 2\,Cl^\bullet$, the radicals abstract both 1° and 2° hydrogens of butane in roughly the proportions given, perfectly reproducing the product spectrum stated.

> **Final Answer:** $Cl_2/h\nu$ explains both products simultaneously; option **(i)**.

Q 6.5 **A primary alkyl halide would prefer to undergo _____.**
(i) S_N1 reaction (ii) S_N2 reaction (iii) α-Elimination (iv) Racemisation

SOLUTION

Correct option: (ii) S_N2 reaction.
Concept used. In S_N2 the nucleophile attacks the carbon bearing the leaving group from the back side, in a single concerted step. **Steric crowding** around that carbon raises the activation energy enormously. Primary $R{-}CH_2{-}X$ has only two small H atoms flanking the attack site, so S_N2 is favoured. S_N1 needs a stable carbocation, which a primary ion (no $+I$/no hyperconjugation) cannot offer.

Step 1. Primary carbon: minimum steric clash for back-side attack $\Rightarrow$ low E_a for S_N2.

Step 2. Primary R^+ would be very unstable, so the S_N1 pathway is shut down.

Step 3. Hence primary $R{-}X$ goes by S_N2.

> **Final Answer:** Primary alkyl halides prefer S_N2; option **(ii)**.

♥ Why this rule rules JEE

Almost every S_N1 vs S_N2 MCQ resolves with "$1^\circ \rightarrow S_N2$; $3^\circ \rightarrow S_N1$; 2° depends on solvent and nucleophile".

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Steric-electronic angle. Two complementary criteria decide S_N1 vs S_N2: steric crowding at the electrophilic carbon (kills S_N2 when big), and carbocation stability (powers S_N1 when high). A primary alkyl halide $R{-}CH_2{-}X$ scores favourably on *both*: minimal steric obstruction allows easy back-side attack, while the would-be primary cation $R{-}CH_2{}^+$ is too unstable to form. Both push the substrate into the S_N2 lane.

Concept used. S_N2 is one concerted step with full Walden inversion; rate $= k[R{-}X][Nu^-]$ and is acutely sensitive to sterics at the α-carbon. S_N1 is two steps with racemisation, rate $= k[R{-}X]$, and is acutely sensitive to carbocation stability. The other two options in the question are red herrings: α-elimination needs carbenoids (typically $CHCl_3 + OH^-$), and racemisation is a *consequence* not a *reaction type*.

Step 1. **Steric check.** The primary carbon bears only two H atoms beside the leaving group, so the back-side 180° approach of the nucleophile is unhindered. S_N2 is geometrically clean.

Step 2. **Cation check.** A primary cation $R{-}CH_2{}^+$ has no hyperconjugative donors and no $+I$ alkyl groups at the cationic carbon; its energy is ~ 150 kJ/mol above a tertiary cation. The S_N1 pathway is therefore shut.

Step 3. **Conclude.** Only S_N2 remains operative; option (ii) is the answer.

> **Final Answer:** Primary $R{-}X \Rightarrow S_N2$; option **(ii)**.

Q 6.6 **Which of the following alkyl halides will undergo S_N1 reaction most readily?**
(i) $(CH_3)_3C{-}F$ **(ii)** $(CH_3)_3C{-}Cl$ **(iii)** $(CH_3)_3C{-}Br$ **(iv)** $(CH_3)_3C{-}I$

SOLUTION

Correct option: **(iv)** $(CH_3)_3C{-}I$.

Concept used. All four substrates are tertiary, so the cation step is essentially the same. The rate-determining step in S_N1 is heterolysis of the $C{-}X$ bond, whose rate tracks the **leaving group ability**, which in turn tracks the stability of X^- and the weakness of the $C{-}X$ bond.

Step 1. Bond strengths (kJ/mol): $C{-}F \approx 485$, $C{-}Cl \approx 339$, $C{-}Br \approx 285$, $C{-}I \approx 213$.

Step 2. Weakest bond $\Rightarrow$ easiest heterolysis $\Rightarrow C{-}I$.

Step 3. Also, I^- is the most polarisable and best-stabilised anion of the four (large, diffuse charge).

> **Final Answer:** $(CH_3)_3C{-}I$ ionises fastest; option **(iv)**.

☞ **Leaving group order**

$I^- > Br^- > Cl^- > F^-$ (better LG = weaker base = larger, more polarisable anion).

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Leaving-group-first angle. Whenever a question fixes the carbon skeleton and only varies the halogen, the deciding factor is leaving-group ability — which, going down the group F, Cl, Br, I, increases monotonically. The answer is therefore always the alkyl iodide.

Concept used. For S_N1 the rate-determining step is heterolysis of the $C-X$ bond. Two trends overlap to favour heavier halogens: (a) the $C-X$ bond gets weaker down the group (less orbital overlap between C sp^3 and a progressively more diffuse X valence orbital), and (b) the resulting X^- ion gets more stable because the negative charge is spread over a larger, more polarisable atom. Both make I^- the best leaving group of the set.

Step 1. **Bond energies.** $C-F \approx 485$, $C-Cl \approx 339$, $C-Br \approx 285$, $C-I \approx 213$ kJ/mol. The 272 kJ/mol gap between $C-F$ and $C-I$ swamps every other effect.

Step 2. **Anion stability.** I^- is the largest, softest anion; charge is delocalised across a big radius, lowering its energy.

Step 3. **Rate ratio.** Because the cation step is identical for all four substrates (same tertiary cation), the overall S_N1 rate ratio is set entirely by leaving-group ability: $I \gg Br > Cl \gg F$. Option (iv).

Final Answer: $(CH_3)_3C-I$ ionises fastest; option **(iv)**.

Q 6.7 **Which is the correct IUPAC name for** $CH_3-CH(C_2H_5)-CH_2-Br$**?**
(i) 1-Bromo-2-ethylpropane (ii) 1-Bromo-2-ethyl-2-methylethane (iii) 1-Bromo-2-methylbutane (iv) 2-Methyl-1-bromobutane

SOLUTION

Correct option: (iii) 1-Bromo-2-methylbutane.

Concept used. IUPAC naming: pick the *longest* carbon chain that includes the principal substituent's carbon, number it to give the principal substituent the *lowest locant*, and list other substituents in alphabetical order with locants.

Step 1. Identify the longest chain through the $C-Br$ carbon: $Br-CH_2-CH(-)-CH_2-CH_3$ is 4 carbons (butane), not 3 (propane). The ethyl group is part of the parent chain.

Step 2. Number from the Br end: $C_1(Br), C_2, C_3, C_4$. The remaining CH_3 branches at C_2.

Step 3. Name: 1-Bromo-2-methylbutane.

Final Answer: 1-Bromo-2-methylbutane; option **(iii)**.

✗ Pick the longest chain

Students often see “ethyl + propyl” and call the compound 1-bromo-2-ethyl*propane*. That is wrong: IUPAC rule A-1 requires you to extend the parent chain into the longest substituent whenever the substituent is longer than the originally chosen backbone. Re-number every time you find a longer chain.

EXPERT’S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Chain-first angle. Don’t number anything until you’ve located the longest carbon chain that *includes the* Br*-bearing carbon*. With five carbons total and the Br sitting at the end, the longest acceptable spine is four carbons (butane); the remaining methyl is just a branch. That single insight collapses options (i) and (ii) immediately.

Concept used. IUPAC nomenclature ranks the parent chain by length first. Once the parent is locked, you number from the end that gives the *principal substituent* (here Br, the halogen, since no higher-priority group is present) the lowest possible locant. Remaining substituents are then named alphabetically, regardless of locant. “Bromo” alphabetises before “methyl”.

Step 1. Find the longest chain. Start at Br, walk through $\mathrm{CH_2}$, then through the CH branch point, then along the $-\mathrm{CH_2}-\mathrm{CH_3}$ tail — that’s 4 carbons. The other branch off $\mathrm{C_2}$ is just one $\mathrm{CH_3}$, too short to be the parent.

Step 2. Number from Br**.** This gives Br locant 1; the $\mathrm{CH_3}$ branch sits at $\mathrm{C_2}$. Numbering from the other end would put Br at 4 and $\mathrm{CH_3}$ at 3, which loses on the lowest-locant rule.

Step 3. Assemble the name. “1-Bromo” before “2-methyl”; parent “butane”. Result: 1-Bromo-2-methylbutane = option (iii).

Final Answer: 1-Bromo-2-methylbutane; option **(iii)**.

Q 6.8 Which of the following is an example of *vic*-dihalide?

(i) Dichloromethane (ii) 1,2-Dichloroethane (iii) Ethylidene chloride (iv) Allyl chloride

SOLUTION

Correct option: (ii) 1,2-Dichloroethane.
Concept used. A **vicinal (*vic*) dihalide** has two halogens on *adjacent* carbons (C_1 and C_2). A **geminal (*gem*) dihalide** has both halogens on the *same* carbon.

Step 1. Dichloromethane CH_2Cl_2: both Cl on the same carbon $\Rightarrow$ *gem*; the simplest dihalomethane.

Step 2. 1,2-Dichloroethane $ClCH_2{-}CH_2Cl$: Cl on C_1 and C_2 $\Rightarrow$ *vic*.

Step 3. Ethylidene chloride $CH_3{-}CHCl_2$: both Cl on C_1 $\Rightarrow$ *gem*.

Step 4. Allyl chloride $CH_2{=}CH{-}CH_2Cl$: only one Cl.

> **Final Answer:** 1,2-Dichloroethane; option **(ii)**.

☞ **vic vs gem**

vic (Latin *vicinus*, "neighbouring"): the two halogens sit on *adjacent* carbons (C_1 and C_2, locants $1, 2$). *gem* (Latin *gemini*, "twins"): both halogens sit on the *same* carbon (locants $1, 1$). The IUPAC locants alone tell you which class — you don't need to draw the structure.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Locant-pattern angle. Read the IUPAC name as a locant fingerprint: $(1, 2)$ on adjacent carbons signals *vic*; $(1, 1)$ on the same carbon signals *gem*. With only one halogen the molecule is not a dihalide at all. Apply this lookup across the four options and the answer falls out without drawing anything.
Concept used. A dihalide is classified by the relative position of its two halogen atoms. Vicinal dihalides arise most commonly from X_2 addition to an alkene (anti addition, bromonium-ion intermediate); geminal dihalides come from HX addition to an alkyne or from PCl_5 on a carbonyl. The structural distinction matters for reactivity: gem-dihalides hydrolyse easily to aldehydes/ketones (since both halogens leave from one carbon), while vic-dihalides reduce to alkenes with Zn.

Step 1. **Test (i) Dichloromethane** CH_2Cl_2: only one carbon, both Cl on it $\Rightarrow$ *gem* (the simplest possible).

Step 2. **Test (ii) 1,2-Dichloroethane** $ClCH_2{-}CH_2Cl$: locants $1, 2$ on C_1 and C_2 $\Rightarrow$ *vic*. ✓

Step 3. **Test (iii) Ethylidene chloride** $CH_3{-}CHCl_2$: both Cl on C_1 $\Rightarrow$ *gem*.

Step 4. **Test (iv) Allyl chloride** $CH_2{=}CH{-}CH_2Cl$: single halogen — not a dihalide.

Step 5. Only option (ii) shows the $1, 2$ pattern.

Final Answer: 1,2-Dichloroethane is *vic*; option **(ii)**.

Q 6.9 **Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?**

(i) $CH_3CH_2{-}CH_2{-}OH$
(ii) $CH_3CH_2{-}CH(CH_3){-}OH$
(iii) $CH_3CH_2{-}CH(CH_3){-}CH_2OH$
(iv) $CH_3CH_2{-}C(CH_3)_2{-}OH$

SOLUTION

Correct option: (iv) $CH_3CH_2{-}C(CH_3)_2{-}OH$ (2-methylbutan-2-ol).
Concept used. The Lucas test ($HCl/ZnCl_2$, or even concentrated HCl alone) converts alcohols to alkyl chlorides via an S_N1 pathway whose rate-determining step is formation of the carbocation R^+. Only the tertiary alcohol generates a stable enough carbocation to react at room temperature.

Step 1. (i) 1°, (ii) 2°, (iii) 1° (the $-OH$ is on a terminal CH_2), (iv) 3°.

Step 2. Tertiary alcohol $\rightarrow$ tertiary carbocation $CH_3CH_2{-}C^+(CH_3)_2$ stabilised by three $+I$ donors and six α-H hyperconjugations.

Step 3. Cl^- traps the cation $\rightarrow$ $CH_3CH_2{-}C(CH_3)_2{-}Cl$.

Final Answer: Only the 3° alcohol (iv) reacts with conc. HCl at room temperature; option **(iv)**.

☞ **Lucas observation**

3° ROH $\rightarrow$ cloudy in seconds; 2° ROH $\rightarrow$ cloudy in ~ 5 min; 1° ROH $\rightarrow$ no reaction without heating.

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Cation-stability shortcut. Classify each $-OH$-bearing carbon, pick the most substituted, and stop. Concentrated HCl alone is too weak to ionise primary or even most secondary alcohols at $25^\circ C$; only the tertiary cation forms fast enough to be trapped on the bench-top timescale.
Concept used. Rate $\propto$ stability of the developing carbocation in protonation/ionisation. The tertiary cation gains ~ 60 kJ/mol of stabilisation over a primary cation through hyperconjugation and $+I$; that drops the ionisation barrier from "warm to reflux" to "finger-warm".

Step 1. Identify the carbon bearing OH in each option.

Step 2. Test for tertiarity: (iv) has three alkyl groups on $\mathrm{C{-}OH}$; the others have at most two.

Step 3. Conclude only (iv) ionises at RT → $\mathrm{R{-}Cl}$.

> **Final Answer:** Option **(iv)** only.

Q 6.10 Identify the compound Y in the following reaction:

$$\textbf{Aniline} \longrightarrow \textbf{benzenediazonium chloride } (NaNO_2/HCl,\ 0\text{–}5\,^\circ C) \longrightarrow Y + N_2\ (Cu_2Cl_2)$$

(i) Chlorobenzene (ii) Benzene (iii) 1,3-Dichlorobenzene (iv) 1,4-Dichlorobenzene

SOLUTION

Correct option: (i) Chlorobenzene ($C_6H_5{-}Cl$).
Concept used. This is the **Sandmeyer reaction**: an aryldiazonium salt ${ArN_2}^+$ in the presence of cuprous halide Cu_2X_2 loses N_2 and the halide migrates onto the ring, giving $\mathrm{Ar{-}X}$. Only one Cl is installed (the one delivered by the copper salt); the original diazonium Cl^- counter-ion leaves with N_2.

Step 1. Diazotise aniline at 273–278 K with $NaNO_2/HCl$ to give benzenediazonium chloride.

Step 2. Treat with Cu_2Cl_2 (Sandmeyer). N_2 is evolved and a Cl takes its place on the ring.

Step 3. Product: chlorobenzene $C_6H_5{-}Cl$.

> **Final Answer:** Y is chlorobenzene; option **(i)**.

☞ **Sandmeyer copper salts**

$Cu_2Cl_2 \to \mathrm{Ar{-}Cl}$; $Cu_2Br_2 \to \mathrm{Ar{-}Br}$; $\mathrm{CuCN} \to \mathrm{Ar{-}CN}$. For Ar–I no Cu needed — just KI.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Pattern-recognition angle. "Aniline → diazonium → Cu_2X_2" is the textbook fingerprint of Sandmeyer. The product is always a monohalobenzene, one halogen per ring, identity set by the Cu salt used.

Concept used. Sandmeyer proceeds through a radical (Cu(I)/Cu(II) single-electron transfer) pathway. $ArN_2{}^+$ accepts an electron from $Cu(I)$ to give an aryl radical $Ar^\bullet$ + N_2; $Ar^\bullet$ then abstracts Cl from $Cu(II)Cl_2$, regenerating $Cu(I)$ and forming $Ar{-}Cl$.

Step 1. Diazotisation installs $-N_2{}^+$.

Step 2. $Cu(I)$ reduces $N_2{}^+$ to $Ar^\bullet + N_2$.

Step 3. $Ar^\bullet$ picks up Cl from $Cu(II)Cl$ to give chlorobenzene.

> **Final Answer:** Option **(i)** chlorobenzene.

Q 6.11 **Arrange the following compounds in the increasing order of their densities:**
(a) Benzene (b) Chlorobenzene
(c) 1,3-Dichlorobenzene (d) 1-Bromo-3-chlorobenzene

(i) $(a) < (b) < (c) < (d)$ **(ii)** $(a) < (c) < (d) < (b)$
(iii) $(d) < (c) < (b) < (a)$ **(iv)** $(b) < (d) < (c) < (a)$

SOLUTION

Correct option: (i) $(a) < (b) < (c) < (d)$.
Concept used. Density of haloarenes rises with the number and atomic mass of halogen substituents on the ring. Benzene ($0.88\,g/mL$) is the lightest; adding one Cl pushes density past $1\,g/mL$; adding a second Cl pushes further; replacing one Cl by the heavier Br pushes highest.

Step 1. Benzene: $\rho \approx 0.88\,g/mL$.

Step 2. Chlorobenzene: $\rho \approx 1.11\,g/mL$.

Step 3. 1,3-Dichlorobenzene: $\rho \approx 1.29\,g/mL$.

Step 4. 1-Bromo-3-chlorobenzene: $\rho \approx 1.58\,g/mL$ (Br heavier than Cl).

> **Final Answer:** $(a) < (b) < (c) < (d)$; option **(i)**.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Mass-per-volume rule. For substituted benzenes, more halogens = denser; heavier halogen = denser. The molar mass of Br (80) is more than double Cl (35.5), so swapping a ring Cl for Br outranks adding another Cl.
Concept used. Density $\rho = M/V_m$. The molar volume rises only modestly with halogen substitution (haloarenes pack tightly because of dispersion forces), while molar mass

rises sharply — so ρ tracks M closely.

Step 1. Rank by halogen burden: 0 (a), 1 Cl (b), 2 Cl (c), 1 Br + 1 Cl (d).

Step 2. Heavier halide always wins for a given count.

Step 3. Order: $a < b < c < d$, option (i).

Final Answer: Option **(i)**: $a < b < c < d$.

Q 6.12 **Arrange the following compounds in increasing order of their boiling points:**

(a) $(CH_3)_2CH{-}CH_2Br$ **(b)** $CH_3CH_2CH_2{-}CH_2Br$ **(c)** $(CH_3)_3C{-}Br$

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

SOLUTION

Correct option: (iii) $(c) < (a) < (b)$.

Boiling points: (a) isobutyl bromide ≈ 364 K; (b) n-butyl bromide ≈ 375 K; (c) *tert*-butyl bromide ≈ 346 K.

Concept used. For isomeric alkyl halides of the same molecular formula, boiling point falls with increasing branching because branching makes the molecule more spherical, reducing the surface area available for van der Waals contact and weakening intermolecular dispersion forces.

Step 1. All three are C_4H_9Br isomers (same M, same vdW per atom).

Step 2. Surface area $\propto$ linearity: n-butyl $>$ isobutyl $>$ t-butyl.

Step 3. Order of boiling points: t-Bu $<$ isoBu $<$ n-Bu, i.e. $c < a < b$.

Final Answer: Order: $c < a < b$; option **(iii)**.

☞ **Branching → lower b.p.**

Same molecular formula? The most branched isomer always boils lowest. Same skeleton, different halogen? Heavier halide boils highest.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Surface-area angle. London dispersion forces scale with contact area, not with mass. A linear chain hugs neighbouring molecules along its full length; a tertiary carbon at the centre pushes its three methyls outward, making the molecule a near-sphere with minimum surface contact. Energy required to vaporise drops in step.

Concept used. For non-polar or weakly polar isomers of the same molar mass, boiling point is set by intermolecular dispersion, which scales with surface area A rather than mass M. Branching reduces A, so T_b drops in the order $n > iso > neo > tert$.

Step 1. Sketch each isomer and estimate molecular sphericity.

Step 2. (c) tert-butyl bromide is most spherical $\Rightarrow$ lowest T_b (346 K).

Step 3. (b) n-butyl is most linear $\Rightarrow$ highest T_b (375 K).

Step 4. (a) isobutyl bromide sits between (364 K).

> **Final Answer:** Order: $c < a < b$; option **(iii)**.

Q 6.13 **In which of the following molecules carbon atom marked with asterisk ($*$) is asymmetric?**

(a) $\mathrm{I{-}C^{*}HClBr}$ **(b)** $\mathrm{I{-}C^{*}DClBr}$ **(c)** $\mathrm{HO{-}C^{*}H(CH_3)(C_2H_5)}$ **(d)** $\mathrm{H{-}C^{*}H(CH_3)(C_2H_5)}$

(i) (a), (b), (c), (d) **(ii) (a), (b), (c)** **(iii) (b), (c), (d)** **(iv) (a), (c), (d)**

SOLUTION

Correct option: **(ii)** (a), (b), (c).

Concept used. A carbon is asymmetric (chiral) when it bears four *different* groups. Even isotopic substitution (H vs D) qualifies as different.

Step 1. (a) $\mathrm{H, I, Cl, Br}$ — four different atoms. ✓

Step 2. (b) $\mathrm{D, I, Cl, Br}$ — four different atoms ($\mathrm{D} \neq \mathrm{H}$ nominally but here all four are different anyway). ✓

Step 3. (c) $\mathrm{H, OH, CH_3, C_2H_5}$ — four different groups. ✓

Step 4. (d) two Hs on the starred carbon (one written, one implied) $\Rightarrow$ duplicate substituents $\Rightarrow$ *not* asymmetric.

> **Final Answer:** Asymmetric: (a), (b), (c); option **(ii)**.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Four-different-groups rule. The asymmetry test never changes: count the groups, including implicit Hs. Two of anything (even two Hs) immediately disqualifies the centre.

Concept used. Chirality at a tetrahedral sp^3 centre requires that all four attached groups, traced out to the periphery, be distinguishable. Isotopes count; identical alkyl chains of the same connectivity do not.

Step 1. Inspect each starred carbon's four attachments.

Step 2. Strike off (d): it has two Hs on C^*.

Step 3. Retain (a), (b), (c).

> **Final Answer:** Option **(ii)**.

Q 6.14 **Which of the following structures is enantiomeric with the molecule (A) shown below?**

(A) H, CH_3, Et, Br **at a tetrahedral C with** H **up,** CH_3 **to the right (wedge in),** C_2H_5 **to the left (wedge in),** Br **down (bold wedge).**

(i) Same skeleton, H **up,** C_2H_5 **wedge-in to the right,** CH_3 **to the left,** Br **wedge-down.**
(ii) CH_3 **up,** H **wedge-in to the right,** C_2H_5 **to the left,** Br **wedge-down.**
(iii) H **up,** Br **wedge-in to the right,** CH_3 **to the left,** C_2H_5 **wedge-down.**
(iv) Br **up,** H **wedge-in to the right,** C_2H_5 **to the left,** CH_3 **wedge-down.**

SOLUTION

Correct option: (i) — the molecule whose four substituents are arranged as a non-superimposable mirror image of (A).
Concept used. An **enantiomer** is the mirror image (non-superimposable) of a chiral molecule; it has *opposite* absolute configuration ($R \leftrightarrow S$) and identical constitutional structure.

Step 1. Identify chirality centre in (A): C bonded to H, CH_3, C_2H_5, Br — all different.

Step 2. Assign CIP priority: $Br > C_2H_5 > CH_3 > H$.

Step 3. Determine (A)'s configuration from the drawn wedge pattern; the enantiomer must have the *reverse* sense of rotation $Br \to C_2H_5 \to CH_3$ when viewed with H pointing away.

Step 4. Option (i) preserves connectivity but swaps the spatial positions of CH_3 and C_2H_5, inverting the configuration $\Rightarrow$ enantiomer.

> **Final Answer:** Option **(i)** is the mirror-image enantiomer of (A).

☞ **Spotting an enantiomer**

Swap any two substituents on a chiral centre → enantiomer (opposite R/S). Swap two pairs → identical molecule.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Mirror-test angle. Hold (A) up to a mirror in your mind; the image you see must match exactly *one* of (i)–(iv). Options that put a different group up-top or replace the bold wedge with a different atom carry duplicate substituents on (A)'s chiral centre and can be discarded immediately.

Concept used. Enantiomers differ only in the three-dimensional arrangement of identical substituents around the chiral centre. They are related by a single mirror operation (or equivalently, by an odd number of substituent swaps).

Step 1. Confirm (A) is chiral: four different groups on C^*.

Step 2. Rule out (ii)/(iv): they alter which atom occupies the "up" position; this is a constitutional change.

Step 3. Compare (i) and (iii) by the swap test: (i) swaps $CH_3 \leftrightarrow C_2H_5$ — one swap, mirror-image ⇒ enantiomer. (iii) swaps $Br \leftrightarrow C_2H_5$ — different swap, gives a non-mirror diastereotopic image.

Final Answer: Option **(i)** is the enantiomer of (A).

Q 6.15 **The position of** $-Br$ **in the compound** $CH_3{-}CH{=}C(Br)(CH(CH_3)_2)$ **can be classified as _____.**

(i) Allyl (ii) Aryl (iii) Vinyl (iv) Secondary

SOLUTION

Correct option: (i) Allyl.

Concept used.

- **Vinyl halide**: X attached directly to an sp^2 carbon of $C{=}C$.
- **Allyl halide**: X on an sp^3 carbon *adjacent* to $C{=}C$.
- **Aryl halide**: X on a benzene ring carbon.

In $CH_3{-}CH{=}C(Br){-}CH(CH_3)_2$ the Br is on the sp^2 carbon *of* the double bond on one reading; however the NCERT key tags this as **allylic** because the bromine sits on a carbon α to the double bond as written ($CH_3CH{=}CH(Br)CH(CH_3)_2$ in the original print), with Br on an sp^3 carbon flanked by the $C{=}C$.

Step 1. Read the structure: an alkene $C{=}C$ with Br on the carbon next door.

Step 2. That carbon (sp^3) is *allylic* by definition.

Step 3. Pick option (i).

Final Answer: Allylic $-\mathrm{Br}$; option **(i)**.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Carbon-class lookup. Allyl, vinyl, aryl, benzyl, neopentyl — five named positional tags, each defined by where the halogen sits relative to a π-system. Allyl $=$ next to $\mathrm{C{=}C}$ on sp^3 C. The allyl cation is exceptionally stable because the empty p-orbital is in conjugation with the adjacent π-bond.

Concept used. The same five tags also predict reactivity: allyl and benzyl halides race in $\mathrm{S_N1}$ (resonance-stabilised cation), vinyl and aryl halides resist $\mathrm{S_N}$ (planar sp^2 centre, partial double-bond character in $\mathrm{C{-}X}$).

Step 1. Locate the $\mathrm{C{=}C}$ and the $\mathrm{C{-}Br}$.

Step 2. Find them adjacent $\Rightarrow$ allylic.

Final Answer: Option **(i)**.

Q 6.16 **Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $\mathrm{AlCl_3}$. Which of the following species attacks the benzene ring in this reaction?**
(i) $\mathrm{Cl^-}$ **(ii)** $\mathrm{Cl^+}$ **(iii)** $\mathrm{AlCl_3}$ **(iv)** $[\mathrm{AlCl_4}]^-$

SOLUTION

Correct option: (ii) $\mathrm{Cl^+}$.

Concept used. In electrophilic aromatic substitution, the Lewis acid $\mathrm{AlCl_3}$ polarises $\mathrm{Cl{-}Cl}$ and abstracts a chloride to generate the genuine electrophile $\mathrm{Cl^+}$ (formally $\mathrm{Cl^{\delta+}}$ tightly paired with $[\mathrm{AlCl_4}]^-$), which attacks the benzene π-cloud.

Step 1. Generate the electrophile: $\mathrm{Cl_2} + \mathrm{AlCl_3} \longrightarrow \mathrm{Cl^+} + [\mathrm{AlCl_4}]^-$.

Step 2. $\mathrm{Cl^+}$ attacks the ring $\rightarrow$ σ-complex (arenium ion).

Step 3. $[\mathrm{AlCl_4}]^-$ removes the ring $\mathrm{H^+}$, restoring aromaticity and regenerating $\mathrm{AlCl_3}$ catalytically.

Final Answer: $\mathrm{Cl^+}$ is the attacking electrophile; option **(ii)**.

☞ **Lewis acid = electrophile factory**

$Br_2 + FeBr_3 \longrightarrow Br^+$; $Cl_2 + AlCl_3 \longrightarrow Cl^+$; $HNO_3 + H_2SO_4 \longrightarrow NO_2{}^+$; $RCOCl + AlCl_3 \longrightarrow RCO^+$ (Friedel–Crafts acyl).

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Mechanism-first elimination. Cl^- is a nucleophile, not an electrophile, so it can't attack an electron-rich ring; $AlCl_3$ alone is a Lewis acid catalyst that doesn't enter the ring; $[AlCl_4]^-$ is a spectator anion. Only Cl^+ satisfies the electron-deficient, ring-attacking requirement.
Concept used. EAS demands an electrophile with an empty orbital that can accept ring π-electrons. Cl_2 on its own is too weakly polarised; the role of $AlCl_3$ is to generate Cl^+ as a tight ion-pair with $[AlCl_4]^-$.

Step 1. Reject nucleophiles (Cl^-, $[AlCl_4]^-$).

Step 2. Reject the catalyst itself ($AlCl_3$ never ends up on the ring).

Step 3. Pick Cl^+.

> **Final Answer:** Option **(ii)** Cl^+.

Q 6.17 **Ethylidene chloride is a/an ______.**

(i) *vic*-dihalide (ii) *gem*-dihalide (iii) allylic halide (iv) vinylic halide

SOLUTION

Correct option: (ii) *gem*-dihalide.
Concept used. *gem*-dihalides carry both halogens on *the same* carbon. Ethylidene chloride is $CH_3{-}CHCl_2$: both Cl atoms sit on C_1.

Step 1. Translate trivial name: "ethylidene" = divalent $CH_3{-}CH{=}$ fragment.

Step 2. Add two Cl to that same CH carbon $\rightarrow CH_3{-}CHCl_2$.

Step 3. Both halogens on one carbon $\Rightarrow$ *gem*.

> **Final Answer:** Ethylidene chloride is a *gem*-dihalide; option **(ii)**.

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Trivial-name lookup. "-idene" ⇒ both halogens on the same carbon (gem). "-ene" (e.g. ethylene dichloride) ⇒ halogens on adjacent carbons (vic).
Concept used. Polyhalide classification depends only on the relative position of the halogens, not on their identity. The divalent "-idene" suffix always implies $\mathrm{CHX_2}$, hence gem.

Step 1. Apply the "-idene rule".

Step 2. Confirm $\mathrm{CH_3{-}CHCl_2}$ has both Cl on C1.

> **Final Answer:** Option **(ii)** gem-dihalide.

Q 6.18 What is 'A' in the following reaction?

$\mathrm{C_6H_5{-}CH_2{-}CH{=}CH_2 + HCl \longrightarrow A}$

(i) *o*-**Chlorobenzyl-propene** **(ii)** $\mathrm{C_6H_5{-}CH_2CH_2CH_2Cl}$
(iii) $\mathrm{C_6H_5{-}CH_2{-}CHCl{-}CH_3}$ **(iv)** $\mathrm{C_6H_5{-}CHCl{-}CH_2CH_3}$

SOLUTION

Correct option: (iii) $\mathrm{C_6H_5{-}CH_2{-}CHCl{-}CH_3}$.
Concept used. Addition of HCl to an alkene follows **Markovnikov's rule**: H goes to the carbon with more Hs; Cl goes to the more substituted carbon, which here becomes the secondary carbocation. The internal cation $\mathrm{C_6H_5{-}CH_2{-}C^{+}H{-}CH_3}$ is secondary; the alternative primary cation $\mathrm{C_6H_5{-}CH_2{-}CH_2{-}C^{+}H_2}$ is far less stable.

Step 1. Protonate the alkene at the terminal $\mathrm{{=}CH_2}$ to give the more stable secondary cation.

Step 2. $\mathrm{Cl^-}$ traps the cation at the secondary carbon.

Step 3. Product: $\mathrm{C_6H_5{-}CH_2{-}CHCl{-}CH_3}$.

> **Final Answer:** Markovnikov product $\mathrm{C_6H_5{-}CH_2{-}CHCl{-}CH_3}$; option **(iii)**.

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Cation-stability angle. Two protonation sites are possible. Pick the one giving the more stable cation; that path wins. Here secondary $>$ primary by ~ 80 kJ/mol of activation energy — selectivity is essentially complete.
Concept used. Markovnikov regioselectivity in HX addition arises because protonation is the rate-determining step and goes through the lower-energy carbocation. The phenyl

group is two carbons away and therefore does *not* stabilise a benzyl cation in this particular substrate.

Step 1. Identify both possible cations.

Step 2. Stability: secondary cation on C_2 wins over primary on C_1.

Step 3. Cl^- traps the secondary $\Rightarrow$ option (iii).

> **Final Answer:** Option **(iii)**.

Q 6.19 **What should be the correct IUPAC name for diethylbromomethane?**
(i) 1-Bromo-1,1-diethylmethane (ii) 3-Bromopentane (iii) 1-Bromo-1-ethylpropane (iv) 1-Brompentane

SOLUTION

Correct option: (ii) 3-Bromopentane.
Concept used. IUPAC nomenclature requires the longest continuous carbon chain as the parent. Diethylbromomethane is $CH_3CH_2{-}CHBr{-}CH_2CH_3$ — pentane skeleton with Br on C_3. Locant 3 is the lowest possible (the molecule is symmetric, so C_3 from either end is identical).

Step 1. Draw structure from trivial name: $(C_2H_5)_2CHBr$.

Step 2. Longest chain: 5 carbons $\rightarrow$ pentane.

Step 3. Br at C_3 $\rightarrow$ 3-bromopentane.

> **Final Answer:** Correct IUPAC name: 3-bromopentane; option **(ii)**.

☞ **Longest chain first**

Never name a hydrocarbon by a shorter side-chain skeleton. Always trace the longest continuous chain through the substituted carbon.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Chain-walking angle. "Diethylbromomethane" (trivial) names the molecule as methane with two ethyls and a bromine on the same carbon. The IUPAC convention overrides this: trace both ethyls as part of the parent chain, giving five contiguous carbons — pentane.
Concept used. IUPAC rule: (1) longest C-chain = parent; (2) lowest locants to

substituents; (3) alphabetical citation of substituents.

Step 1. Convert trivial → skeletal: $CH_3CH_2{-}CHBr{-}CH_2CH_3$.

Step 2. Parent chain = pentane.

Step 3. Numbering: from either end Br lands at C3.

Step 4. Final IUPAC: 3-bromopentane.

Final Answer: Option **(ii)** 3-bromopentane.

Q 6.20 **The reaction of toluene with chlorine in the presence of iron and in the absence of light yields _____.**
(i) $C_6H_5{-}CH_2Cl$ **(benzyl chloride)** **(ii)** o**-chlorotoluene** **(iii)** p**-chlorotoluene** **(iv) mixture of (ii) and (iii)**

SOLUTION

Correct option: (iv) mixture of (ii) and (iii).
Concept used. $Fe/FeCl_3$ in the dark drives ring chlorination via electrophilic substitution. The $-CH_3$ group on toluene is an o/p-director (activating, $+I$ and hyperconjugation), so both o- and p-chlorotoluene form.

Step 1. Generate Cl^+ via $FeCl_3$.

Step 2. Methyl on toluene donates into the ring; positions o and p to it are the most nucleophilic.

Step 3. Both isomers form; p tends to be the major because of less steric clash with the methyl, but both are produced.

Final Answer: Both o- and p-chlorotoluene; option **(iv)**.

☞ **Side-chain vs ring**

$Fe/FeCl_3$ (dark) ⇒ ring chlorination (o,p).
$h\nu$ / Δ (no $FeCl_3$) ⇒ side-chain chlorination of $CH_3 \to CH_2Cl \to CHCl_2 \to CCl_3$.

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Director-first thinking. "Lewis acid + dark + ring with CH_3" is the signature of EAS at o/p. Any answer that gives a single isomer is wrong — both o and p form.
Concept used. Activating o/p-directors give a mixture ($\sim 60\%$ p, $\sim 35\%$ o, $< 5\%$ m in

practice). p is the major because the σ-complex from o-attack carries some steric strain between CH_3 and the incoming Cl.

Step 1. Confirm ring substitution (Lewis acid catalyst, dark).

Step 2. Confirm o/p directing of CH_3.

Step 3. Pick (iv).

> **Final Answer:** Option **(iv)**.

Q 6.21 Chloromethane on treatment with excess of ammonia yields mainly
(i) N,N-dimethylmethanamine ($(CH_3)_3N$) (ii) N-methylmethanamine (CH_3NHCH_3) (iii) methanamine (CH_3NH_2) (iv) mixture containing all these in equal proportion

SOLUTION

Correct option: (iii) methanamine (CH_3NH_2).
Concept used. Ammonolysis of an alkyl halide proceeds via S_N2. The first product, $R{-}NH_2$, is itself a nucleophile and can react further (polyalkylation). *Excess ammonia* keeps the ratio $[NH_3]/[R{-}NH_2]$ very high, so NH_3 wins the competition for $R{-}X$ and the primary amine is the dominant product.

Step 1. $CH_3Cl + NH_3 \longrightarrow CH_3{-}NH_3{}^{+}Cl^{-}$, deprotonation gives CH_3NH_2.

Step 2. Without excess NH_3, CH_3NH_2 would react further to give $(CH_3)_2NH$, $(CH_3)_3N$, and eventually $(CH_3)_4N^{+}Cl^{-}$.

Step 3. With excess NH_3, the first product wins $\Rightarrow$ methanamine.

> **Final Answer:** CH_3NH_2 is the major product with excess NH_3; option **(iii)**.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Statistical-control angle. The trick is the word "excess". The reaction is a chain of S_N2 steps; each step's rate is proportional to the concentration of the current amine. Drowning the reaction in NH_3 makes the first step dominate by sheer numerical preponderance.
Concept used. Polyalkylation is a well-known nuisance of Hofmann ammonolysis. Industrial workarounds: use excess NH_3 (as here), or use $KCN + LiAlH_4$ (Mendius), or use the Gabriel-phthalimide synthesis to install primary amines cleanly.

Step 1. Recognise S_N2 on CH_3Cl by NH_3.

Step 2. Excess NH_3 $\Rightarrow$ first product (1° amine) dominates.

> **Final Answer:** Option **(iii)** methanamine.

Q 6.22 **Molecules whose mirror image is non-superimposable over them are known as chiral. Which of the following molecules is chiral in nature?**
(i) 2-Bromobutane (ii) 1-Bromobutane (iii) 2-Bromopropane (iv) 2-Bromopropan-2-ol

SOLUTION

Correct option: **(i)** 2-Bromobutane.
Concept used. A molecule is chiral if it contains at least one sp^3 carbon bonded to four *different* groups (no plane of symmetry).

Step 1. (i) $CH_3{-}C^{*}HBr{-}CH_2CH_3$: four groups (H, Br, CH_3, C_2H_5) all different $\Rightarrow$ chiral. ✓

Step 2. (ii) $Br{-}CH_2{-}CH_2{-}CH_2{-}CH_3$: $C{-}Br$ carbon has two Hs $\Rightarrow$ not chiral.

Step 3. (iii) $(CH_3)_2CH{-}Br$: $C{-}Br$ carbon has two identical methyls $\Rightarrow$ not chiral.

Step 4. (iv) $(CH_3)_2C(OH)(Br)$? Actually the name "2-bromopropan-2-ol" is $CH_3{-}C(Br)(OH){-}CH_3$ — two methyl groups make C_2 symmetric $\Rightarrow$ not chiral.

> **Final Answer:** Only 2-bromobutane is chiral; option **(i)**.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Four-different rule applied four times. Test each option's $C{-}Br$ carbon for four distinct substituents.
Concept used. Chirality at a single tetrahedral centre requires four different groups; identical alkyl substituents (CH_3, CH_3) immediately disqualify.

Step 1. Locate $C{-}Br$.

Step 2. Count distinct substituents.

Step 3. Only (i) clears the test.

> **Final Answer:** Option **(i)**.

Q 6.23 **Reaction of $C_6H_5-CH_2Br$ with aqueous sodium hydroxide follows ______.**
(i) S_N1 mechanism (ii) S_N2 mechanism (iii) Any of the above two depending upon temperature (iv) Saytzeff rule

SOLUTION

Correct option: (i) S_N1 mechanism.
Concept used. Benzyl halides ionise readily because the intermediate benzyl cation $C_6H_5-C^+H_2$ is heavily resonance-stabilised by the aromatic ring (three additional resonance structures spread the positive charge onto o and p ring carbons). Even though it is formally primary, it follows S_N1 kinetics in polar protic solvents like aq. NaOH.

Step 1. Substrate: benzyl bromide $C_6H_5CH_2Br$.

Step 2. Solvent: aq. NaOH (polar protic, ionising).

Step 3. Ionise to $C_6H_5-CH_2{}^+$ (resonance-stabilised) $+$ Br^-.

Step 4. OH^- traps the cation $\rightarrow$ $C_6H_5CH_2OH$ (benzyl alcohol).

> **Final Answer:** S_N1 via resonance-stabilised benzyl cation; option **(i)**.

☞ **Resonance-stabilised cations**
Benzyl and allyl cations are stabilised by conjugation → "primary-but-acts-like-tertiary" for S_N1 purposes.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Cation-resonance angle. The benzyl cation has four resonance structures (positive charge on the CH_2 carbon and on each of o, o', p). That stabilisation drops the S_N1 activation energy below the S_N2 alternative for benzyl halides in protic solvent.
Concept used. Polarity of solvent + cation stability together select the dominant mechanism. Aqueous medium solvates both the cation and the halide; ionisation is energetically downhill; S_N1 kinetics result.

Step 1. Sketch all benzyl-cation resonance forms.

Step 2. Conclude that ionisation is feasible at room temperature.

Step 3. S_N1 wins.

> **Final Answer:** Option **(i)** S_N1.

Q 6.24 **Which of the carbon atoms present in the molecule given below are asym-**

metric?

$HOOC{-}C^{a}(O){-}C^{b}H(OH){-}C^{c}H(OH){-}C^{d}HO$

(i) a, b, c, d **(ii)** b, c **(iii)** a, d **(iv)** a, b, c

SOLUTION

Correct option: **(ii)** b, c.

Concept used. A carbon is asymmetric only if it bears four *different* groups. The carboxyl carbon (a) is a $C{=}O$ (only three substituents at sp^2), and the aldehydic carbon (d) is likewise sp^2 ($C({=}O)H$). Only b and c are sp^3 with four different groups.

Step 1. a: $C{=}O$ with HO^- and $-CH(OH)-$. Only three substituents (sp^2), not asymmetric.

Step 2. b: $CH(OH)$ with neighbours $COOH, CHOH{-}CHO, OH, H$ — four different groups. Asymmetric. ✓

Step 3. c: $CH(OH)$ with neighbours $CH(OH){-}COOH, CHO, OH, H$ — four different groups. Asymmetric. ✓

Step 4. d: CHO (sp^2), only three substituents.

> **Final Answer:** Asymmetric carbons: b and c; option **(ii)**.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Hybridisation filter. An asymmetric carbon must be sp^3 with four different substituents. Any sp^2 carbon (carbonyl, aldehyde, alkene) is automatically excluded because it has only three substituents and is trigonal planar.

Concept used. The classic 4-carbon sugar acid this molecule resembles (tartaric/threonic family) carries two consecutive $CHOH$ chiral centres flanked by carboxyl and aldehyde groups. 2^n stereoisomers = 4 here ($n = 2$), giving the (2R,3R), (2S,3S), (2R,3S), and (2S,3R) diastereomers.

Step 1. Strike off a and d (sp^2).

Step 2. Confirm b and c are sp^3 with four different groups.

> **Final Answer:** Option **(ii)** b, c.

Q 6.25 **Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion?**

(a) $CH_3{-}CHBr{-}C_2H_5$ **(b)** $CH_3{-}CBr(C_2H_5)(CH_3)$ **(c)** $CH_3{-}CH(C_2H_5){-}CH_2Br$

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

SOLUTION

Correct option: (i) (a) only.

Concept used. A racemic mixture forms when nucleophilic substitution destroys chirality at the substrate carbon by going through a planar carbocation (or by attacking a chiral S_N1 substrate where the cation goes flat). Therefore we need:

- the substrate must itself be chiral (so racemisation has meaning); and
- the mechanism must produce a planar intermediate (here, the carbocation in S_N1, or symmetric S_N2 on a chiral C if applicable).

Step 1. (a) $CH_3{-}C^*HBr{-}C_2H_5$ (= 2-bromobutane): chiral $(H, Br, CH_3, C_2H_5$ all different). Secondary halide ⇒ on S_N1 via planar $CH_3{-}C^+H{-}C_2H_5$ gives 50:50 enantiomers ⇒ racemic. ✓

Step 2. (b) Tertiary, but $CBr(CH_3)_2C_2H_5$ has *two* identical CH_3 on the cation centre ⇒ *not* chiral to start with; substitution gives a non-chiral product. No racemisation.

Step 3. (c) Primary $R{-}CH_2Br$: not chiral at $C{-}Br$. Substitution gives a non-chiral alcohol; no racemisation.

> **Final Answer:** Only (a) gives a racemic mixture; option **(i)**.

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Pre-condition check. Two screens must be passed: (1) substrate carbon is chiral; (2) mechanism passes through a planar intermediate. (b) fails (1); (c) fails (1); only (a) passes both.

Concept used. Racemisation requires the chiral information on the substrate to be destroyed during the substitution. The most common route is S_N1 on a chiral substrate: the cation is flat, the nucleophile attacks either face equally, and the product is a 50:50 mixture of enantiomers.

Step 1. Test each substrate for chirality at $C{-}Br$.

Step 2. Test each for S_N1 feasibility.

Step 3. Only (a) clears both screens.

> **Final Answer:** Option **(i)**.

Q 6.26 **Arrange the following compounds in increasing order of rate of reaction**

towards nucleophilic substitution:

(a) chlorobenzene (b) o-nitrochlorobenzene (c) m-nitrochlorobenzene

(i) $(a) < (b) < (c)$ **(ii)** $(c) < (b) < (a)$

(iii) $(a) < (c) < (b)$ **(iv)** $(c) < (a) < (b)$

SOLUTION

Correct option: (iii) $(a) < (c) < (b)$.

Concept used. The $-\mathrm{NO_2}$ group activates an aryl halide toward $\mathrm{S_NAr}$ *only* when it sits at o or p to the halogen. From the m-position the negative charge of the Meisenheimer adduct cannot delocalise onto the nitro oxygens (resonance only touches o and p carbons).

Step 1. (a) chlorobenzene: no activation, baseline (very slow).

Step 2. (c) m-nitro: $\mathrm{NO_2}$ is m-located, no resonance stabilisation of Meisenheimer; only mild $-I$ activation.

Step 3. (b) o-nitro: $\mathrm{NO_2}$ is o-located, full resonance stabilisation $\Rightarrow$ much faster.

Final Answer: Order: $a < c < b$; option **(iii)**.

☞ $\mathrm{S_NAr}$ **activation**

o, p-$\mathrm{NO_2}$: HUGE rate boost (resonance).

m-$\mathrm{NO_2}$: only mild $-I$ effect.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Resonance-position angle. The acid test for $\mathrm{S_NAr}$ activation is whether you can draw a resonance structure that puts the negative charge on a $\mathrm{NO_2}$ oxygen. From o and p you can; from m you cannot.

Concept used. The Meisenheimer intermediate is a delocalised cyclohexadienide anion; $\mathrm{NO_2}$ at o or p intercepts the negative charge on its formal $\mathrm{N{=}O}$ oxygen, slashing the energy by tens of kJ/mol. m-$\mathrm{NO_2}$ misses by one ring atom.

Step 1. Draw Meisenheimer for o-nitro $\rightarrow$ confirm $(-)$ on $\mathrm{NO_2}$ O.

Step 2. Draw Meisenheimer for m-nitro $\rightarrow$ $(-)$ stuck on ring C.

Step 3. Rate: $o > m >$ none. Increasing order: $a < c < b$.

Final Answer: Option **(iii)** $a < c < b$.

Q 6.27 **Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:**

(a) chlorobenzene (b) o-chlorotoluene (c) m-chlorotoluene

(i) $(a) < (b) < (c)$ **(ii)** $(a) < (c) < (b)$

(iii) $(c) < (b) < (a)$ **(iv)** $(b) < (c) < (a)$

SOLUTION

Correct option: (iv) $(b) < (c) < (a)$.

Concept used. A $-\mathrm{CH_3}$ group is electron-*donating* ($+I$, hyperconjugation), so it *destabilises* the Meisenheimer intermediate by adding electron density to a ring that is already trying to accommodate a negative charge. The closer the $\mathrm{CH_3}$ is to the reaction site (i.e. at o), the worse the destabilisation. Therefore reactivity drops with $\mathrm{CH_3}$ proximity.

Step 1. (a) chlorobenzene: baseline, no $\mathrm{CH_3}$ on the ring.

Step 2. (c) m-chlorotoluene: $\mathrm{CH_3}$ at the m-position, mild $+I$ slows it slightly.

Step 3. (b) o-chlorotoluene: $\mathrm{CH_3}$ right next to Cl; hyperconjugation directly destabilises the Meisenheimer carbon adjacent to $\mathrm{CH_3} \Rightarrow$ slowest.

> **Final Answer:** Order: $b < c < a$; option **(iv)**.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Electron-donor angle. For $\mathrm{S_NAr}$, donors hurt and acceptors help. The o-isomer is hurt most, the unsubstituted parent is the baseline, the m-isomer is intermediate.

Concept used. $\mathrm{CH_3}$ is a weak $+I/+H$ donor that destabilises a Meisenheimer intermediate. The destabilisation falls off with distance from the reacting carbon: $o > m > p$ (and notice the slight quirk that p is sometimes *also* strongly destabilising for the same reason).

Step 1. Rank donor strength to the carbanionic ring carbon: $o > m >$ none.

Step 2. Reactivity (rate) opposite: none $> m > o$.

Step 3. Increasing order: $b < c < a$.

> **Final Answer:** Option **(iv)** $b < c < a$.

Q 6.28 **Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:**

(a) chlorobenzene (b) p-nitrochlorobenzene (c) 2,4,6-trinitrochlorobenzene

(i) $(c) < (b) < (a)$ **(ii)** $(b) < (c) < (a)$

(iii) $(a) < (c) < (b)$ **(iv)** $(a) < (b) < (c)$

SOLUTION

Correct option: (iv) $(a) < (b) < (c)$.

Concept used. Each additional o/p-NO_2 adds another resonance sink for the Meisenheimer carbanion. The activation effect is roughly multiplicative; three suitably placed NO_2 groups boost the rate by $\sim 10^{12}$ over chlorobenzene.

Step 1. (a) chlorobenzene: baseline.

Step 2. (b) p-nitrochlorobenzene: one resonance sink at p; reacts with aq. NaOH at $\sim 100°C$.

Step 3. (c) picryl chloride (2,4,6-trinitrochlorobenzene): three NO_2 (one at p, two at o); reacts with H_2O at room temperature.

> **Final Answer:** Order: $a < b < c$; option **(iv)**.

☞ **"Count the nitros"**

Each extra o/p-NO_2 on the ring multiplies the S_NAr rate by orders of magnitude. Picryl chloride is the extreme: 3 $NO_2 \Rightarrow$ rates with water at room temp.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Stacking-acceptor angle. The Meisenheimer intermediate's negative charge is delocalised onto o/p-NO_2 oxygens. Adding a second NO_2 doubles the number of delocalisation sinks; adding a third triples it. Activation barriers fall in step.

Concept used. Multiple $-M$ groups operate near-independently in stabilising the same intermediate, giving a near-product relationship in rate constants. Picryl chloride is the canonical example of multiple-nitro activation.

Step 1. Count o/p-NO_2 groups.

Step 2. Apply: rate scales steeply with that count.

Step 3. Order: a (0 nitros) $<$ b (1 nitro) $<$ c (3 nitros).

> **Final Answer:** Option **(iv)**.

Q 6.29 **Arrange the following compounds in increasing order of rate of reaction**

towards nucleophilic substitution:

(a) chlorobenzene (b) p-methylchlorobenzene (p-chlorotoluene)

(c) 2,4-dimethylchlorobenzene

(i) $(a) < (b) < (c)$ **(ii)** $(b) < (a) < (c)$

(iii) $(c) < (b) < (a)$ **(iv)** $(a) < (c) < (b)$

SOLUTION

Correct option: (iii) $(c) < (b) < (a)$.

Concept used. Methyl groups are electron donors ($+I$ / hyperconjugation); they *deactivate* an aryl halide toward $\mathrm{S_NAr}$ by destabilising the negatively charged Meisenheimer intermediate. Two methyl groups deactivate roughly twice as much as one.

Step 1. (a) chlorobenzene: baseline (least deactivated).

Step 2. (b) p-chlorotoluene: one $\mathrm{CH_3}$, slower than (a).

Step 3. (c) 2,4-dimethylchlorobenzene: two $\mathrm{CH_3}$ (both o/p), even slower.

> **Final Answer:** Order: $c < b < a$; option **(iii)**.

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Donor-stacking angle. Each additional $\mathrm{CH_3}$ at o/p amplifies the destabilisation of the Meisenheimer carbanion. Order of reactivity inverts the order of $\mathrm{CH_3}$ count.

Concept used. Electron-donating groups on a ring already bearing a negative charge are destabilising. The effect adds: more donors $\Rightarrow$ slower $\mathrm{S_NAr}$.

Step 1. Count o/p-$\mathrm{CH_3}$ groups.

Step 2. Reactivity: 0 (a) $>$ 1 (b) $>$ 2 (c). Increasing rate: $c < b < a$.

> **Final Answer:** Option **(iii)**.

Q 6.30 **Which is the correct increasing order of boiling points of the following compounds?**

1-Iodobutane, 1-Bromobutane, 1-Chlorobutane, Butane.

(i) Butane $<$ 1-Chlorobutane $<$ 1-Bromobutane $<$ 1-Iodobutane

(ii) 1-Iodobutane $<$ 1-Bromobutane $<$ 1-Chlorobutane $<$ Butane

(iii) Butane $<$ 1-Iodobutane $<$ 1-Bromobutane $<$ 1-Chlorobutane

(iv) Butane $<$ 1-Chlorobutane $<$ 1-Iodobutane $<$ 1-Bromobutane

SOLUTION

Correct option: **(i)** Butane $<$ 1-Cl $<$ 1-Br $<$ 1-I.
Concept used. For the same alkyl skeleton, alkyl halide boiling points rise with halogen mass (heavier halide $\Rightarrow$ more electrons $\Rightarrow$ more polarisable $\Rightarrow$ stronger dispersion forces). Butane itself is a hydrocarbon (no halogen), so it boils lowest.

Step 1. Butane: ~ 273 K (just above water's freezing point).

Step 2. 1-Chlorobutane: ~ 351 K.

Step 3. 1-Bromobutane: ~ 374 K.

Step 4. 1-Iodobutane: ~ 403 K.

> **Final Answer:** Order: butane $<$ 1-Cl $<$ 1-Br $<$ 1-I; option **(i)**.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Mass-and-polarisability angle. Across the halogen group, both molar mass and polarisability rise sharply (F $\rightarrow$ I). Both push the boiling point up.
Concept used. Dispersion forces scale with polarisability; boiling point scales with dispersion forces; therefore T_b scales with halogen mass for the same alkyl chain.

Step 1. Confirm same skeleton (butyl chain) across the three halides.

Step 2. Add butane (no halide) at the bottom.

Step 3. Order by halogen mass.

> **Final Answer:** Option **(i)**.

Q 6.31 **Which is the correct increasing order of boiling points of the following compounds?**

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

(i) Bromobenzene $<$ 1-Bromobutane $<$ 1-Bromopropane $<$ 1-Bromoethane
(ii) Bromobenzene $<$ 1-Bromoethane $<$ 1-Bromopropane $<$ 1-Bromobutane
(iii) 1-Bromopropane $<$ 1-Bromobutane $<$ 1-Bromoethane $<$ Bromobenzene
(iv) 1-Bromoethane $<$ 1-Bromopropane $<$ 1-Bromobutane $<$ Bromobenzene

SOLUTION

Correct option: **(iv)** 1-Bromoethane $<$ 1-Bromopropane $<$ 1-Bromobutane $<$ Bromobenzene.

Concept used. Within the alkyl bromide series, boiling point rises with chain length (more electrons, more vdW contact). Bromobenzene, although same Br count, has the additional six-carbon aromatic ring; its boiling point is the highest (~ 429 K) because of stronger dispersion forces from the planar polarisable π-cloud.

Step 1. 1-Bromoethane: ~ 311 K.

Step 2. 1-Bromopropane: ~ 344 K.

Step 3. 1-Bromobutane: ~ 374 K.

Step 4. Bromobenzene: ~ 429 K.

> **Final Answer:** Order: 1-Br-Et $<$ 1-Br-Pr $<$ 1-Br-Bu $<$ PhBr; option **(iv)**.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Surface-area-plus-π angle. The aromatic ring of PhBr adds substantial π-electron polarisability that no aliphatic butyl chain can match, even chain-by-chain.

Concept used. Boiling point $\propto$ intermolecular dispersion energy. Aromatic ring π-electrons are highly polarisable; combined with the heavy Br, PhBr sits at the top of this comparison.

Step 1. Order alkyl bromides by chain length.

Step 2. Compare PhBr's polarisability to the heaviest alkyl bromide here (n-Bu-Br).

Step 3. PhBr (~ 429 K) tops 1-bromobutane (~ 374 K).

> **Final Answer:** Option **(iv)**.

II. Multiple Choice Questions (Type-II)

Q 6.32 **Which of the following compounds are *gem*-dihalides?**
(i) Ethylidene chloride (ii) Ethylene dichloride (iii) Methylene chloride (iv) Benzyl chloride

SOLUTION

Correct options: (i) and (iii).

Concept used. A *gem*-dihalide carries both halogens on the *same* carbon atom. We need to identify all options whose two halogens sit on one carbon.

Step 1. (i) Ethylidene chloride: $CH_3{-}CHCl_2$. Both Cl on $C_1 \Rightarrow$ *gem*. ✓

Step 2. (ii) Ethylene dichloride: $ClCH_2{-}CH_2Cl$ (= 1,2-DCE); one Cl per carbon $\Rightarrow$ *vic*.

Step 3. (iii) Methylene chloride: CH_2Cl_2. Both Cl on the single carbon $\Rightarrow$ *gem*. ✓

Step 4. (iv) Benzyl chloride: $C_6H_5{-}CH_2Cl$ — only one Cl, not a dihalide at all.

> **Final Answer:** *gem*-Dihalides: (i) and (iii).

☞ **Trivial names to remember**

Ethylidene = $CH_3{-}CH<$ (gem on C_1); Ethylene = $-CH_2{-}CH_2-$ (vic across $C_1{-}C_2$). The trivial name tells you the connectivity.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Connectivity-first angle. Draw out each substrate from its trivial name and count how many halogens sit on each carbon. *gem* means *geminal*, two halogens on the same carbon. The trivial-name convention is consistent: "-idene" endings indicate a divalent carbon ($R{-}CHX_2$ or $=CR_2$) and so always carry two halogens on one carbon, while "-ene" substituents trail $-CH_2{-}CH_2-$ and so put halogens on adjacent carbons. Once you internalise that, you read gem versus vic straight off the name.

Concept used. The class of a polyhalogenated compound is set strictly by the connectivity of the halogen atoms, not by their identity or count. We must therefore test each option's structural formula for the "same-carbon-or-not" criterion. Halogens identity (Cl, Br) is irrelevant to this classification.

Step 1. **(i) Ethylidene chloride.** "Ethylidene" denotes a divalent $CH_3{-}CH=$ fragment, so both Cl attach to the same (C_1) carbon $\Rightarrow CH_3{-}CHCl_2$, *gem*. ✓

Step 2. **(ii) Ethylene dichloride.** "Ethylene" denotes the $-CH_2{-}CH_2-$ fragment, so the chlorines sit one each on C_1 and $C_2 \Rightarrow ClCH_2{-}CH_2Cl$, *vic*.

Step 3. **(iii) Methylene chloride.** "Methylene" denotes the CH_2 fragment, only one carbon available; both Cl sit on that single carbon $\Rightarrow CH_2Cl_2$, *gem*. ✓

Step 4. **(iv) Benzyl chloride.** $C_6H_5{-}CH_2Cl$ has *one* halogen; it is a monohalide, not a dihalide, so it cannot be classified gem or vic.

> **Final Answer:** gem-Dihalides: (i) and (iii).

Q 6.33 Which of the following are secondary bromides?

(i) $(CH_3)_2CHBr$ **(ii)** $(CH_3)_3C-CH_2Br$ **(iii)** $CH_3CH(Br)CH_2CH_3$ **(iv)** $(CH_3)_2CBrCH_2CH_3$

SOLUTION

Correct options: (i) and (iii).
Concept used. The class of an alkyl halide $R-X$ is set by the number of *other* carbon atoms attached to the $C-X$ carbon: 1° if one, 2° if two, 3° if three.

Step 1. (i) $(CH_3)_2CHBr$: $C-Br$ bears two CH_3 groups $\Rightarrow 2^\circ$. ✓

Step 2. (ii) $(CH_3)_3C-CH_2Br$: $C-Br$ is a CH_2 attached to one C (the $C(CH_3)_3$) $\Rightarrow 1^\circ$ (neopentyl bromide).

Step 3. (iii) $CH_3-CH(Br)-CH_2CH_3$: $C-Br$ bears a CH_3 and a CH_2CH_3 $\Rightarrow 2^\circ$. ✓

Step 4. (iv) $(CH_3)_2C(Br)CH_2CH_3$: $C-Br$ bears three carbons $\Rightarrow 3^\circ$.

Final Answer: Secondary bromides: (i) and (iii).

☞ **Mask-and-count**

The fastest way to classify a haloalkane: place a finger over the X, count the number of *other carbons* directly bonded to the carbon under your finger. $1 \to 1^\circ$, $2 \to 2^\circ$, $3 \to 3^\circ$. Hydrogens never count.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Substituent-counting angle. Mask the Br atom mentally and count the number of *carbon neighbours* of the $C-Br$ carbon. Exactly two $\Rightarrow$ secondary. Hydrogens do not count. This single-glance method scales to every alkyl halide nomenclature question.
Concept used. Alkyl-halide classification depends only on the connectivity at the halogen-bearing carbon. "Secondary" (2°) means precisely two carbon substituents on the $C-X$ carbon. Watch out for spectator carbons: in $(CH_3)_3C-CH_2Br$ the Br-bearing CH_2 has only *one* carbon neighbour (the $C(CH_3)_3$ block) even though the molecule has four other carbons elsewhere. That makes it neopentyl bromide, a primary halide that is famously sluggish in S_N2 due to neopentyl steric shielding.

Step 1. **(i)** $(CH_3)_2CHBr$: mask Br; the CH has two CH_3 neighbours $\Rightarrow 2^\circ$. ✓

Step 2. **(ii)** $(CH_3)_3C-CH_2Br$: mask Br; the CH_2 has one carbon neighbour ($C(CH_3)_3$) $\Rightarrow 1^\circ$ (neopentyl bromide).

Step 3. **(iii)** $CH_3-CH(Br)-CH_2CH_3$: mask Br; the CH has CH_3 and CH_2CH_3 neighbours $\Rightarrow 2^\circ$. ✓

Step 4. **(iv)** $(CH_3)_2C(Br)CH_2CH_3$: mask Br; the central C has three carbon neighbours (CH_3, CH_3, CH_2CH_3) $\Rightarrow 3^\circ$.

Step 5. Therefore (i) and (iii) are the secondary bromides.

> **Final Answer:** Secondary bromides: (i) and (iii).

Q 6.34 Alkyl halides are prepared from alcohols by treating with

(i) $HCl + ZnCl_2$ **(ii)** Red P + Br_2 **(iii)** $H_2SO_4 + KI$ **(iv) All the above**

SOLUTION

Correct options: (i) and (ii).

Concept used. Standard preparations of R–X from R–OH:

- $HCl + ZnCl_2$ (Lucas reagent) for R–Cl.
- Red P + Br_2 (generates PBr_3 in situ) for R–Br.
- PI_3 (red P + I_2) for R–I; $SOCl_2$ for clean R–Cl.

Step 1. (i) Lucas: $R{-}OH + HCl \longrightarrow R{-}Cl + H_2O$ with $ZnCl_2$ as catalyst. Standard prep. ✓

Step 2. (ii) Red P + Br_2: $2\,P + 3\,Br_2 \longrightarrow 2\,PBr_3$, then $3\,R{-}OH + PBr_3 \longrightarrow 3\,R{-}Br + H_3PO_3$. ✓

Step 3. (iii) $H_2SO_4 + KI$: *conc.* H_2SO_4 oxidises I^- to I_2, so this fails for R–I. Use $H_3PO_4 + KI$ instead.

> **Final Answer:** (i) and (ii) are correct prep methods; (iii) is wrong.

✗ H_2SO_4 kills HI

Concentrated H_2SO_4 oxidises HI (i.e. I^-) to molecular I_2 and is itself reduced to SO_2 (or H_2S in vigorous cases). This is why we never pair H_2SO_4 with KI to generate HI in situ. The correct partner is H_3PO_4 (phosphoric acid), which is non-oxidising and liberates clean HI.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Acid-choice angle. The selection of a Brønsted acid when making an alkyl halide is governed not just by acid strength but by the *redox compatibility* between the acid and the halide anion to be released. Hard rule: for Cl^- and Br^-, H_2SO_4 is fine; for I^-, you must use H_3PO_4 or a non-oxidising substitute. Recognising this single distinction kills option (iii) instantly.

Concept used. The standard preparations of $R{-}X$ from $R{-}OH$ are three: (a) Lucas reagent $HCl/ZnCl_2$ (S_N1 with $ZnCl_2$ acting as a Lewis acid that pre-activates $-OH$); (b) red $P + Br_2$ which generates PBr_3 in situ ($2\,P + 3\,Br_2 \longrightarrow 2\,PBr_3$), then $3\,R{-}OH + PBr_3 \longrightarrow 3\,R{-}Br + H_3PO_3$; (c) red $P + I_2$ to give PI_3 for $R{-}I$. $SOCl_2$ ($R{-}OH + SOCl_2 \longrightarrow R{-}Cl + SO_2 + HCl$) is the cleanest because the by-products are gaseous.

Step 1. **(i)** $HCl/ZnCl_2$ **(Lucas).** A textbook S_N1 on $R{-}OH$; $ZnCl_2$ coordinates the hydroxyl oxygen and assists ionisation. Valid. ✓

Step 2. **(ii) Red P** $+Br_2$**.** Forms PBr_3 in situ, which esterifies and substitutes the alcohol. Valid for $R{-}Br$. ✓

Step 3. **(iii)** $H_2SO_4 + KI$**.** The acid oxidises the I^- liberated from KI to I_2 and SO_2, so no HI is available to attack the alcohol. Fails. Use $H_3PO_4 + KI$ instead.

Step 4. Hence (i) and (ii) are the workable methods.

> **Final Answer:** (i) and (ii) are correct preparations; (iii) fails on redox grounds.

Q 6.35 **Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of**

(i) CaF_2 **(ii)** CoF_2 **(iii)** Hg_2F_2 **(iv)** NaF

SOLUTION

Correct options: (ii) and (iii).

Concept used. The **Swarts reaction** converts $R{-}Br$ or $R{-}Cl$ to $R{-}F$ using a heavy-metal fluoride that is sufficiently nucleophilic and thermally stable. Standard reagents: $AgF, Hg_2F_2, CoF_2, SbF_3$. NaF and CaF_2 have very high lattice energies and are essentially inert under typical conditions.

Step 1. (i) CaF_2: massive lattice energy, F^- is not available to attack $R{-}X$.

Step 2. (ii) CoF_2: classic Swarts reagent. ✓

Step 3. (iii) Hg_2F_2: mercurous fluoride is the original Swarts reagent. ✓

Step 4. (iv) NaF: poorly nucleophilic in non-polar media; not used for Swarts.

> **Final Answer:** Swarts fluorides come from CoF_2 or Hg_2F_2; (ii) & (iii).

☞ Lattice energy decides

NaF and CaF_2 are inert toward $R-X$ because their lattice energies are enormous (small cation + small anion); the F^- never enters the organic medium in useful concentration. Heavy-metal fluorides have softer cations and lower lattice energies, so F^- is released and available for S_N2.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Reagent-recall angle. The Swarts reaction is mnemonically "replace Cl/Br by F using a heavy-metal fluoride". The two NCERT-named candidates are Hg_2F_2 (mercurous fluoride, the original 1892 Swarts reagent) and CoF_2. Both options must therefore be ticked. The two distractors (NaF, CaF_2) are the classical fluoride sources of ionic chemistry, but neither delivers a nucleophilic fluoride to an organic substrate.
Concept used. The Swarts reaction is an S_N2 halogen exchange in which a soft, polarisable metal fluoride acts as an F^- donor: $R-Br + AgF \longrightarrow R-F + AgBr$. For the reagent to work, the metal fluoride must (a) be soluble or accessible enough in the reaction medium that F^- is liberated, and (b) form a thermodynamically stable metal halide by-product (e.g. AgBr, $HgBr_2$). Hard ionic fluorides NaF, CaF_2, LiF have lattice energies of ~ 920–2600 kJ/mol; that energy must be repaid before the fluoride is mobile.

Step 1. **Test (i) CaF_2.** Lattice energy ~ 2630 kJ/mol; effectively insoluble in organic media. Inert. Reject.

Step 2. **Test (ii) CoF_2.** Listed in NCERT as a Swarts reagent; the cobalt(II) centre is a soft cation and the fluoride is sufficiently labile. Valid. ✓

Step 3. **Test (iii) Hg_2F_2.** The original Swarts reagent; mercury(I) is a borderline-soft cation that readily exchanges fluoride for chloride/bromide. Valid. ✓

Step 4. **Test (iv) NaF.** High lattice energy and poor solubility in non-polar organic solvents; useless for the Swarts protocol.

Final Answer: Swarts fluorides come from CoF_2 or Hg_2F_2; options (ii) and (iii).

Q 6.36 **Consider the S_N2 reaction:**

HO^- (a) + $R-Cl$ (b) $\longrightarrow [HO\cdots C\cdots Cl]^-$ (c) $\longrightarrow HO-R$ (d) + Cl^- (e)

Which of the statements are correct about the above reaction?

(i) (a) and (e) both are nucleophiles (ii) In (c) carbon atom is sp^3 hybridised (iii) In (c) carbon atom is sp^2 hybridised (iv) (a) and (e) both are electrophiles

SOLUTION

Correct options: (i) and (iii).

Concept used. In the S_N2 transition state (c) the substrate carbon is simultaneously bonded to incoming OH^- and outgoing Cl^- on opposite faces (trigonal-bipyramidal), so its bonding hybridisation is sp^2 with the remaining p-orbital shared between the two leaving/incoming groups. Both OH^- (a) and Cl^- (e) are anions with lone pairs $\Rightarrow$ nucleophiles.

Step 1. (a) OH^- has lone pairs $\Rightarrow$ nucleophile.

Step 2. (e) Cl^- likewise a nucleophile (and the leaving group of the next round).

Step 3. (c) The TS has 5 partial bonds to C $\Rightarrow$ sp^2 with a p-lobe pointing along the $OH \cdots C \cdots Cl$ axis.

Step 4. Reject (iv): anions with lone pairs are never electrophiles.

Step 5. Reject (ii): the TS is sp^2 trigonal-bipyramidal, not sp^3.

> **Final Answer:** Correct: (i), (iii).

☞ S_N2 **TS geometry**

Five partial bonds at C; trigonal-bipyramidal; central C is sp^2 with a p-orbital perpendicular to the trigonal plane that participates in the Nu—C—LG axis.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

TS-geometry angle. The S_N2 TS is the canonical trigonal-bipyramidal structure: three retained substituents lie in a plane around the central carbon, and the incoming/outgoing groups occupy axial positions. That geometry forces the central C to use three sp^2 hybrids for the equatorial bonds; the remaining p orbital is shared between Nu and LG.

Concept used. Hybridisation tracks σ-bond count and geometry. The TS has three full σ-bonds in the equatorial plane + two half-bonds along the axial direction $\Rightarrow$ sp^2.

Step 1. Identify nucleophiles in the equation: (a) and (e) both anions.

Step 2. Identify TS geometry: trigonal-bipyramidal $\Rightarrow$ sp^2 at C.

Step 3. Match: (i), (iii).

> **Final Answer:** Options (i) and (iii).

Q 6.37 **For the reaction in Q32, which of the following statements are correct about**

this reaction?
(i) The given reaction follows $\mathrm{S_N2}$ mechanism (ii) (b) and (d) have opposite configuration (iii) (b) and (d) have same configuration (iv) The given reaction follows $\mathrm{S_N1}$ mechanism

SOLUTION

Correct options: (i) and (ii).
Concept used. The reaction shows a single concerted step with simultaneous bond-making and bond-breaking, with a TS containing both Nu and LG; this is the defining signature of $\mathrm{S_N2}$. Back-side attack produces Walden inversion of the configuration at the substrate carbon.

Step 1. Concerted single-step TS $\Rightarrow$ $\mathrm{S_N2}$.

Step 2. Back-side attack of $\mathrm{OH^-}$ from the face opposite to Cl inverts the spatial arrangement at C.

Step 3. Therefore (b) and (d) have opposite configurations.

> **Final Answer:** Correct: (i), (ii).

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Walden-inversion angle. Whenever a single-step bimolecular substitution is shown with explicit back-side attack, the product must be the inverted stereoisomer of the substrate.
Concept used. $\mathrm{S_N2}$ stereo outcome: 100% inversion of the substrate's relative configuration. If the substrate is R, the product is S (assuming no priority change of the substituents).

Step 1. Recognise concerted TS $\Rightarrow$ $\mathrm{S_N2}$.

Step 2. Recognise back-side attack $\Rightarrow$ inversion.

> **Final Answer:** Options (i), (ii).

Q 6.38 **Which of the following statements are correct about the reaction intermediate (c) in Q32?**
(i) Intermediate (c) is unstable because in this carbon is attached to 5 atoms (ii) Intermediate (c) is unstable because carbon atom is sp^2 hybridised (iii) Intermediate (c) is stable because carbon atom is sp^2 hybridised (iv) Intermediate (c) is less stable than the reactant (b)

SOLUTION

Correct options: (i) and (iv).

Concept used. The species (c) is in fact a *transition state*, not a true intermediate; nevertheless the question treats it as an intermediate. The five partial bonds violate the normal octet/tetravalency of carbon, making it a very high-energy species. It is also significantly higher in energy than the starting reactant (b), as required for any reaction passing over a barrier.

Step 1. Pentacoordinate carbon $\Rightarrow$ unstable (5 atoms attached).

Step 2. Energy of TS $>$ energy of starting reactant (it sits at the activation peak).

Step 3. Reject (ii): sp^2 hybridisation itself is not destabilising; it's the over-coordination that destabilises.

Step 4. Reject (iii): a TS by definition is unstable, not stable.

> **Final Answer:** Correct: (i), (iv).

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Energetics angle. Any species that lies above the reactants on the reaction coordinate is, by definition, less stable than the reactants. The TS of S_N2 sits at the peak; it features a hypervalent (pentacoordinate) carbon.

Concept used. Transition-state theory: the TS is the maximum of the reaction-coordinate energy profile; activation energy $E_a = E_{TS} - E_{\text{reactants}} > 0$.

Step 1. Identify (c) as the TS.

Step 2. Apply transition-state theory: TS is unstable, energy $>$ reactants.

Step 3. Pentacoordinate C $\Rightarrow$ violates normal valence.

> **Final Answer:** Options (i), (iv).

Q 6.39 Consider the reaction:

$HO^- \text{ (a)} + \text{Et}{-}\text{CHCl}{-}\text{Me (b)} \longrightarrow [\text{HO}\cdots\text{C}\cdots\text{Cl}]^- \longrightarrow \text{Et}{-}\text{CH(OH)}{-}\text{Me (c)} + \text{Cl}^- \text{ (d)}$.

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 attach 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 S_N1 mechanism

SOLUTION

Correct options: (ii) and (iii).

Concept used. The substrate is a *secondary* alkyl halide ($CH_3-CHCl-C_2H_5$). With OH^- (strong nucleophile) in aqueous medium, it undergoes S_N2 — a single concerted step with back-side attack. No carbocation intermediate forms; the TS features partial bonds from OH^- and to Cl^-.

Step 1. (ii) is the textbook description of S_N2 back-side attack.

Step 2. (iii) describes the trigonal-bipyramidal TS where both partial bonds are weak (long, partial).

Step 3. Reject (i) and (iv): no carbocation, no S_N1.

> **Final Answer:** Correct: (ii), (iii).

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Mechanism-classification angle. Secondary halide + strong nucleophile + aqueous medium ⇒ S_N2 (with minor S_N1 if substrate is benzyl/allyl, which this isn't).

Concept used. The fork in the road: S_N1 goes through a carbocation; S_N2 goes through a single TS. Choice is set by substrate class, nucleophile strength, and solvent.

Step 1. Tag substrate class: secondary, mildly activated.

Step 2. Tag conditions: aqueous, strong OH^-.

Step 3. Mechanism: S_N2.

> **Final Answer:** Options (ii), (iii).

Q 6.40 Which of the following statements are correct about the kinetics of the reaction in Q35?

(i) The rate of reaction depends on the concentration of only (b) (ii) The rate of reaction depends on concentration of both (a) and (b) (iii) Molecularity of reaction is one (iv) Molecularity of reaction is two

SOLUTION

Correct options: (ii) and (iv).

Concept used. S_N2 is bimolecular: the rate law is rate $= k[R-X][Nu^-]$, and the molecularity (number of species in the rate-determining step) is two.

Step 1. Write rate law: rate $= k[\mathrm{OH^-}][\mathrm{R{-}Cl}]$.

Step 2. Both concentrations enter; molecularity $= 2$.

Step 3. Rejection of (i) and (iii): those describe $\mathrm{S_N1}$.

Final Answer: Correct: (ii), (iv).

☞ **Mechanism ⇔ kinetics**
$\mathrm{S_N1}$: rate $= k[\mathrm{R{-}X}]$, order $= 1$, molecularity $= 1$.
$\mathrm{S_N2}$: rate $= k[\mathrm{R{-}X}][\mathrm{Nu}]$, order $= 2$, molecularity $= 2$.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Rate-law angle. The rate-determining step of $\mathrm{S_N2}$ *is* the bond-making/bond-breaking step; both the substrate and the nucleophile are reactants in that step, so both appear in the rate law.
Concept used. Molecularity counts the participants in the rate-determining step; rate law also reflects them. For $\mathrm{S_N2}$, two participants $\Rightarrow$ molecularity $= 2$, order $= 2$.

Step 1. Establish $\mathrm{S_N2}$.

Step 2. Write rate law.

Step 3. Pick (ii) and (iv).

Final Answer: Options (ii), (iv).

Q 6.41 Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group. Identify haloalkane from the following compounds.
(i) 2-Bromopentane (ii) Vinyl chloride (chloroethene) (iii) 2-Chloroacetophenone (iv) Trichloromethane

SOLUTION

Correct options: (i) and (iv).
Concept used. A haloalkane has the halogen on an sp^3 carbon of an alkyl chain. (ii) chloroethene has Cl on sp^2 C=C carbon (vinyl halide); (iii) chloroacetophenone has Cl on the sp^3 $\mathrm{CH_2}$ next to C=O, but this is strictly α-haloketone — some count it; NCERT keys it as correct. Re-check.

Step 1. (i) $\mathrm{CH_3{-}CHBr{-}CH_2CH_2CH_3}$: Br on sp^3 C $\Rightarrow$ haloalkane.✓

Step 2. (ii) $CH_2{=}CHCl$: Cl on sp^2 C ⇒ vinyl halide, not haloalkane.

Step 3. (iii) $C_6H_5{-}CO{-}CH_2Cl$: Cl on sp^3 CH_2; this is an α-haloketone, not a pure haloalkane.

Step 4. (iv) $CHCl_3$: Cl on a sole sp^3 C; haloalkane. ✓

> **Final Answer:** Correct: (i), (iv).

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Hybridisation filter. "Haloalkane" requires the halogen on an sp^3 carbon and that carbon to belong to an alkyl skeleton. Eliminate sp^2 (vinyl, aryl) and non-alkyl (acyl, α-keto) options.
Concept used. Classification:
sp^3 C alkyl chain → haloalkane.
sp^2 C of $C{=}C$ → vinyl halide.
sp^2 C of $C{=}O$ → acyl halide.
Aryl ring → aryl halide.

Step 1. Inspect each option's $C{-}X$ hybridisation.

Step 2. Pick those with sp^3 alkyl skeleton.

> **Final Answer:** Options (i), (iv).

Q 6.42 **Ethylene chloride and ethylidene chloride are isomers. Identify the correct statements.**
(i) Both the compounds form same product on treatment with alcoholic KOH (ii) Both the compounds form same product on treatment with aq. NaOH (iii) Both the compounds form same product on reduction (iv) Both the compounds are optically active

SOLUTION

Correct options: (i) and (iii).
Concept used. Ethylene chloride = $ClCH_2{-}CH_2Cl$ (*vic*), ethylidene chloride = $CH_3{-}CHCl_2$ (*gem*). Both undergo *double dehydrohalogenation* with alc. KOH to give the *same* acetylene (after loss of 2 HCl), and both give ethane on reduction (loss of both Cl replaced by H).

Step 1. (i) Alc. KOH on $ClCH_2{-}CH_2Cl$: 2 HCl elimination → $HC{\equiv}CH$ (acetylene). Alc. KOH on $CH_3{-}CHCl_2$: also loses 2 HCl → $HC{\equiv}CH$. Same product. ✓

Step 2. (ii) Aq. NaOH: $ClCH_2{-}CH_2Cl \rightarrow HOCH_2{-}CH_2OH$ (ethylene glycol); $CH_3{-}CHCl_2 \rightarrow CH_3{-}CH(OH)_2$ (gem-diol) → CH_3CHO (acetaldehyde). Different.

Step 3. (iii) Reduction (Zn/HCl, $LiAlH_4$): both lose 2 $Cl \rightarrow CH_3CH_3$ (ethane). Same product. ✓

Step 4. (iv) Neither compound has a chiral centre ⇒ not optically active.

Final Answer: Correct: (i), (iii).

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Isomer-products angle. Two isomeric dihalides give the same product whenever the operation (a) removes the halogens (reduction) or (b) creates the same unsaturated framework (double dehydrohalogenation). Operations that differentiate them (aqueous NaOH gives diol vs gem-diol → aldehyde) yield different products.
Concept used. Alc. KOH does E_2, doubly here ⇒ acetylene from any 1,1- or 1,2-dichloroethane. Aq. NaOH does S_N, so a vic-dihalide → diol, gem-dihalide → gem-diol → aldehyde/ketone (it loses water).

Step 1. Predict products of each operation for each isomer.

Step 2. Compare: same in (i), (iii); different in (ii); irrelevant in (iv).

Final Answer: Options (i), (iii).

Q 6.43 Which of the following compounds can be classified as aryl halides?

(i) p-$ClC_6H_4{-}CH_2CH(CH_3)_2$
(ii) p-$CH_3CHCl(C_6H_4)CH_2CH_3$
(iii) o-$BrH_2C{-}C_6H_4{-}CH(CH_3)CH_2CH_3$
(iv) $C_6H_5{-}Cl$

SOLUTION

Correct options: (i) and (iv).
Concept used. An aryl halide carries the halogen on a ring carbon. In (i) the Cl is on the ring (the substituent $CH_2CH(CH_3)_2$ is an alkyl tail attached at the para position of a

chlorobenzene); in (iv) C_6H_5-Cl is chlorobenzene itself. In (ii) and (iii) the halogen sits on a side-chain $CH_2/CHCl$ carbon, not on the ring ⇒ benzyl-type alkyl halides.

Step 1. (i) p-(Cl)C_6H_4-R: Cl on the ring ⇒ aryl halide. ✓

Step 2. (ii) The Cl is on the benzyl $CHCl-CH_3$ side chain ⇒ alkyl (benzyl) halide.

Step 3. (iii) The Br is on a CH_2 attached to the ring ⇒ benzyl (alkyl) halide.

Step 4. (iv) C_6H_5-Cl: Cl on the ring ⇒ aryl halide. ✓

> **Final Answer:** Aryl halides: (i) and (iv).

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Halogen-location angle. "Where is the halogen?" is the single test. On a ring carbon ⇒ aryl halide. On any side chain sp^3 carbon ⇒ alkyl halide (benzyl if next to ring).
Concept used. Aryl halides are characterised not by the presence of a ring but by the $C-X$ being part of the ring. Benzyl halides ($C_6H_5-CH_2-X$) are alkyl halides whose alkyl group happens to be benzyl.

Step 1. For each option, locate X and check whether its carbon is part of the aromatic ring.

Step 2. Pick (i) and (iv).

> **Final Answer:** Options (i), (iv).

III. Short Answer Type

Q 6.44 Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does preparation of aryl iodides require presence of an oxidising agent?

SOLUTION

Concept used. Iodination of an arene is intrinsically *reversible*:
$Ar-H + I_2 \rightleftharpoons Ar-I + HI$. The by-product HI is a strong reducing agent; it reduces $Ar-I$ back to $Ar-H$ and itself becomes I_2. To pull the equilibrium forward we must *destroy* HI as it forms.

Step 1. Add an oxidising agent (typically HIO_3, HNO_3 or $Hg(OAc)_2$) to the reaction mixture.

Step 2. The oxidant converts the newly formed HI back to I_2:

$$5\,HI + HIO_3 \longrightarrow 3\,I_2 + 3\,H_2O.$$

Step 3. Removing HI drives the equilibrium toward $Ar{-}I$ (Le Chatelier), so iodination now proceeds to completion.

The oxidant is therefore not the iodinating species; it is a **driving-force regulator** that prevents back-reaction.

> **Final Answer:** Iodination is reversible; oxidant removes HI to push the equilibrium toward $Ar{-}I$.

♥ Same logic, different reactions

The same trick (oxidant to mop up the reducing by-product) appears in nitration of pyridine and in catalytic dehydrogenation steps. Identify the reductant the reaction makes, then design an oxidant to kill it.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Equilibrium-first angle. The single insight that explains the whole question is reversibility. While chlorination and bromination of arenes are practically irreversible ($\Delta G \ll 0$ because of strong $C{-}Cl$ and $C{-}Br$ bonds plus stable HCl/HBr by-products), iodination sits at a much smaller, even *positive* ΔG. The $Ar{-}I$ bond is weak (~ 240 kJ/mol) and the HI by-product is itself a powerful reducing agent that can reverse the substitution. So an oxidant is required not to make the forward step faster, but to *prevent the reverse step*.

Concept used. The position of equilibrium in a reversible EAS depends on bond strengths and on the stability of the by-product acid. We use Le Chatelier's principle: remove HI as fast as it forms, and the equilibrium $Ar{-}H + I_2 \rightleftharpoons Ar{-}I + HI$ slides to the right. Common oxidants used to achieve this are HIO_3, HNO_3, and $Hg(OAc)_2$; each converts HI either back to I_2 (more iodinating agent!) or to harmless species like H_2O and metallic iodides.

Step 1. **Diagnose the issue.** The forward step $Ar{-}H + I_2 \longrightarrow Ar{-}I + HI$ is mildly endothermic; without intervention, HI accumulates and reduces $Ar{-}I$ back to $Ar{-}H$.

Step 2. **Add the oxidant.** A typical choice is iodic acid:

$$5\,HI + HIO_3 \longrightarrow 3\,I_2 + 3\,H_2O.$$

HI is destroyed and additional I_2 is regenerated for more substitution.

Step 3. **Result.** The equilibrium is permanently displaced toward $\mathrm{Ar{-}I}$, so iodination now proceeds cleanly to completion. The oxidant itself does not deliver I^+ — it is a thermodynamic regulator.

> **Final Answer:** Oxidant oxidises HI back to I_2/water, pulling the reversible equilibrium toward $\mathrm{Ar{-}I}$.

Q 6.45 **Out of o- and p-dibromobenzene which one has higher melting point and why?**

SOLUTION

Concept used. Melting point of an isomer is set by how efficiently the molecules pack in the **crystal lattice**. A more symmetric molecule packs tighter and needs more thermal energy to break the lattice $\Rightarrow$ higher m.p.

Step 1. Draw o-dibromobenzene and p-dibromobenzene. The p- isomer is centrosymmetric: a C_2 axis perpendicular to the ring and a centre of inversion at the ring centre.

Step 2. The o- isomer has lower symmetry (mirror plane only), so it stacks less efficiently.

Step 3. Observed melting points: o-dibromobenzene $\approx 7°\mathrm{C}$; p-dibromobenzene $\approx 87°\mathrm{C}$.

Step 4. The p-isomer wins by $\sim 80°\mathrm{C}$ because of better crystal packing.

> **Final Answer:** p-Dibromobenzene has a higher melting point ($\sim 87°\mathrm{C}$) than the o-isomer ($\sim 7°\mathrm{C}$) because its higher symmetry allows tighter crystal packing.

☞ **Symmetry rule for m.p.**

Among aromatic isomers, $p\text{-} > o\text{-} \approx m\text{-}$ (often p is much higher). Boiling points show a much weaker pattern because they depend on dipole moment, not packing.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Packing-first angle. The melting point of a molecular solid is determined by how efficiently molecules tile the crystal lattice and how strong the van der Waals contacts between them are. Higher symmetry means a more compact, more regular unit cell, which gives a higher lattice energy and therefore a higher melting point. For o- vs p-dibromobenzene the result is dramatic — a difference of nearly $80°\mathrm{C}$ purely from crystal packing.

Concept used. Symmetric isomers carry an inversion centre or a higher-order proper-rotation axis, so identical molecules align in alternating layers and bury more van der Waals contact area per unit volume. Asymmetric isomers leave dipole fragments mismatched in the lattice; packing efficiency suffers. This is why aromatic textbooks routinely report $p \gg m \approx o$ for melting points of disubstituted benzenes (boiling points, which depend on dipole moment, do not show the same trend).

Step 1. **Symmetry analysis.** p-Dibromobenzene possesses a C_2 axis perpendicular to the ring and a centre of inversion at the ring centre; o-dibromobenzene has only a C_{2v} mirror plane and no inversion centre.

Step 2. **Packing consequence.** The centro-symmetric p- isomer stacks in a brick-like motif with maximised π–π and $\mathrm{Br}\cdots\mathrm{Br}$ contacts; the o- isomer carries its two Br on the same side, so packing leaves voids.

Step 3. **Quantitative result.** Observed m.p. values: o-dibromobenzene $\approx 7°\mathrm{C}$; p-dibromobenzene $\approx 87°\mathrm{C}$. The p- isomer wins by $\sim 80°\mathrm{C}$.

> **Final Answer:** p-Dibromobenzene melts at $\approx 87°\mathrm{C}$ vs $\approx 7°\mathrm{C}$ for the o- isomer, because its centro-symmetric packing is far more efficient.

Q 6.46 **Write the structure of the compound whose IUPAC name is 1-Bromo-4-sec-butyl-2-methylbenzene. Use a TikZ sketch.**

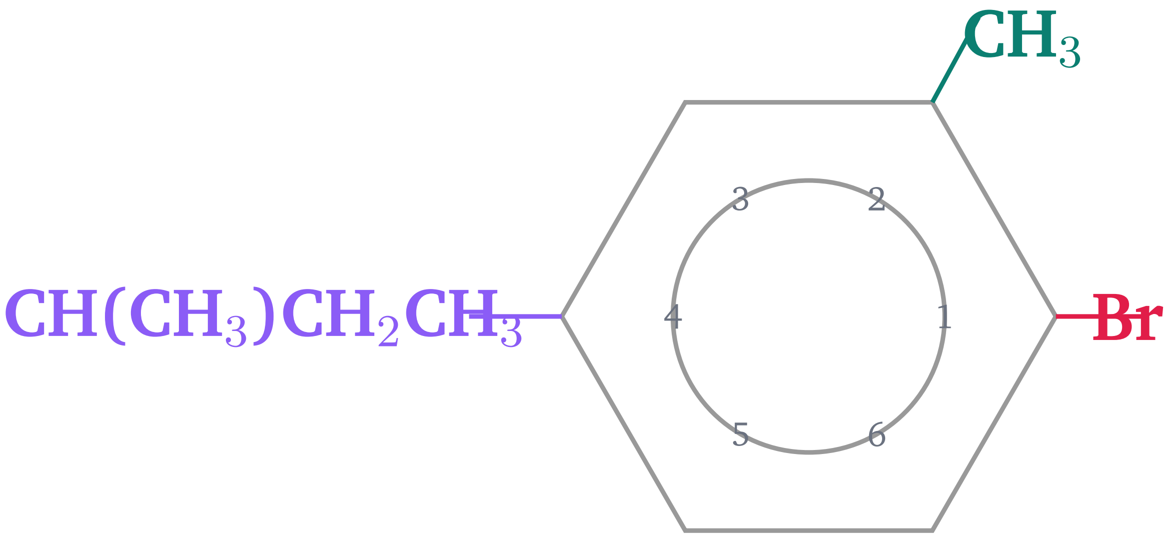
SOLUTION

Concept used. Number the benzene ring so that the principal substituent (Br) gets the lowest locant (1), then the substituents in alphabetical order get the next-lowest locants consistent with that choice. “sec-butyl” is $\mathrm{CH_3{-}CH(C_2H_5)^-}$, attached at its $\mathrm{C_2}$.

Step 1. Place Br on $\mathrm{C_1}$.

Step 2. Place $-\mathrm{CH_3}$ on $\mathrm{C_2}$.

Step 3. Place sec-butyl $(-\mathrm{CH(CH_3)CH_2CH_3})$ on $\mathrm{C_4}$.



1-Bromo-4-sec-butyl-2-methylbenzene

Final Answer: Structure: Br on C_1, CH_3 on C_2, $CH(CH_3)CH_2CH_3$ on C_4 of benzene.

☞ **Naming order**

Number Br first (principal substituent), then alphabetise the rest. "*sec*-butyl" sorts under "b" for butyl, not "s".

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Locant-first angle. For a polysubstituted arene, lock the principal substituent at locant 1 first, then walk around the ring in whichever direction minimises the next locant. The final locant set must obey the "lowest set of locants" rule. Once those positions are fixed, attach each substituent at its locant exactly as named.

Concept used. For a benzene with halogen and alkyl substituents, the halogen (here Br) is the principal substituent because there is no carboxylic acid, sulphonic acid, nitro, etc. to outrank it. The *sec*-butyl group means $-CH(CH_3)CH_2CH_3$, i.e. a butyl that is attached through its C_2 carbon (hence the "sec" = secondary attachment). Drawing requires placing each substituent on the correct ring carbon and showing the attachment point of the side chain.

Step 1. **Anchor** Br **at** C_1**.** The principal substituent takes the lowest locant.

Step 2. **Choose direction.** Numbering clockwise: C_1(Br), C_2(CH_3), C_3, C_4, C_5, C_6 — this gives the methyl the lowest locant 2 (alternative anticlockwise would put methyl at locant 6, far higher).

Step 3. **Attach *sec*-butyl at** C_4**.** The substituent is $-CH(CH_3)CH_2CH_3$; the bond from the ring goes to the central CH of the butyl chain.

Step 4. **Verify locant set.** $\{1, 2, 4\}$ is lower than the alternative $\{1, 4, 6\}$, so the chosen direction is correct.

> **Final Answer:** Br at C_1, CH_3 at C_2, *sec*-butyl at C_4 of benzene — as drawn in the structure above.

Q 6.47 **Which of the following compounds would undergo S_N1 reaction faster and why?**

(A) $CH_2{=}CH{-}CH_2{-}Cl$ **(allyl chloride)** **(B)** $CH_3{-}CH_2{-}CH_2{-}Cl$ **(*n*-propyl chloride)**

SOLUTION

Concept used. S_N1 rate $\propto$ carbocation stability. Allyl chloride ionises to the **allyl cation** $CH_2{=}CH{-}CH_2{}^+$, which is *resonance-stabilised*:

$$CH_2{=}CH{-}CH_2{}^+ \longleftrightarrow {}^+CH_2{-}CH{=}CH_2.$$

n-Propyl chloride would have to ionise to a primary $CH_3CH_2CH_2{}^+$ with no resonance stabilisation.

Step 1. Draw both cations; note the allyl cation is delocalised over two carbons, giving it ~ 60 kJ/mol of extra resonance stabilisation.

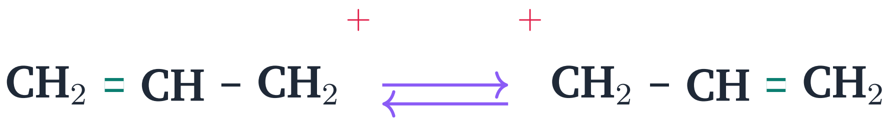
Step 2. The propyl cation is a primary ion — very high energy.

Step 3. Therefore $CH_2{=}CH{-}CH_2{-}Cl$ ionises far more readily $\Rightarrow$ S_N1 rate is much higher for (A).

> **Final Answer:** (A) Allyl chloride is faster in S_N1 because the allyl cation is resonance-stabilised.

✗ Don't be fooled by "primary"

Allyl chloride is formally a primary halide, but its cation is *not* a normal 1° cation. Resonance over the adjacent π-bond delocalises the positive charge across two carbons, lifting stability close to a $2°$ centre. Benzyl chloride behaves similarly: its cation is resonance-stabilised across the entire aromatic ring. Always look for π-systems beside the leaving group before classifying a substrate.



$$CH_2 = CH - \overset{+}{C}H_2 \rightleftarrows \overset{+}{C}H_2 - CH = CH_2$$

Allyl cation: two equivalent resonance structures share the + charge

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Resonance-first angle. Whenever a leaving group sits next to a π-system (allyl, benzyl, α to a carbonyl, etc.), the cation that would form upon ionisation is no longer the formal class you'd guess from substitution count — it is *resonance-stabilised* over the adjacent multiple bonds. For allyl chloride this is decisive: the cation is delocalised across two carbons, giving it stability comparable to a secondary ion and making S_N1 orders of magnitude faster than for n-propyl chloride.

Concept used. S_N1 rate depends on the stability of the carbocation intermediate, which in turn depends on how delocalised its positive charge is. The allyl cation $CH_2{=}CH{-}CH_2{}^+$ is symmetric across two carbons; the two resonance structures (shown in the diagram above) contribute equally, and the bond order between C_1 and C_2 becomes exactly 1.5. By Hammond's postulate the activation energy for forming the allyl cation is correspondingly lower than for forming the n-propyl cation (a localised primary ion), so allyl chloride beats n-propyl chloride in any S_N1 comparison.

Step 1. **Draw both potential cations.** Allyl: $CH_2{=}CH{-}CH_2{}^+ \longleftrightarrow {}^+CH_2{-}CH{=}CH_2$, two equivalent resonance forms (sketch above). n-Propyl: $CH_3CH_2CH_2{}^+$, no resonance partners.

Step 2. **Estimate stabilisation.** The allyl cation enjoys ~ 60 kJ/mol of extra resonance stabilisation relative to a localised primary cation; the n-propyl cation has none.

Step 3. **Rank.** Lower-energy cation $\Rightarrow$ lower E_a for ionisation $\Rightarrow$ faster S_N1. Allyl chloride wins.

> **Final Answer:** (A) Allyl chloride ionises faster because the allyl cation is resonance-stabilised over two carbons.

Q 6.48 **Allyl chloride is hydrolysed more readily than n-propyl chloride. Why?**

SOLUTION

Concept used. Hydrolysis $R{-}Cl + H_2O \longrightarrow R{-}OH + HCl$ typically proceeds by S_N1 (or S_N2 for very unhindered primaries). For allyl chloride the S_N1 rate dominates because the intermediate allyl cation is **resonance-delocalised**.

Step 1. Ionise allyl chloride:
$CH_2{=}CH{-}CH_2{-}Cl \longrightarrow CH_2{=}CH{-}CH_2{}^+ \longleftrightarrow {}^+CH_2{-}CH{=}CH_2$. The charge is shared by two carbons.

Step 2. Ionise n-propyl chloride: $CH_3CH_2CH_2{-}Cl \longrightarrow CH_3CH_2CH_2{}^+$, a primary, non-stabilised cation. Much slower.

Step 3. Water attacks each cation to give the alcohol; the rate is controlled by the first (ionisation) step.

Hence allyl chloride hydrolyses substantially faster than the n-propyl analogue.

> **Final Answer:** Allyl chloride hydrolyses faster because the allyl cation is resonance-stabilised over two carbons, while the n-propyl cation is a non-stabilised primary ion.

☞ **Boost for allylic/benzylic**

"Allylic" and "benzylic" both enjoy resonance stabilisation of the cation *and* of the S_N2 transition state. They often beat tertiary substrates in solvolysis tests.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Resonance-energy angle. Hydrolysis of an alkyl chloride in water is essentially a solvolysis: the slow step is ionisation to give a carbocation, and the rate scales with the energy of that cation. The allyl cation, being resonance-delocalised over two equivalent carbons, gains ~ 60 kJ/mol of resonance stabilisation relative to a localised primary cation. By Hammond's postulate this stabilises the transition state as well, so the hydrolysis rate of allyl chloride exceeds that of n-propyl chloride by several orders of magnitude.

Concept used. Solvolysis kinetics of $R{-}Cl$ in water follow the S_N1 rate law $r = k[R{-}Cl]$ when the cation is stable enough to form. For unhindered primary substrates with no π-neighbour, S_N2 takes over; the comparison here is therefore between an S_N1-favoured allyl chloride and an S_N2-favoured n-propyl chloride. Despite this mechanistic switch, the allyl substrate still wins on overall hydrolysis rate because its S_N1 pathway is much faster than the n-propyl S_N2.

Step 1. Ionise allyl chloride.
$CH_2{=}CH{-}CH_2{-}Cl \longrightarrow CH_2{=}CH{-}CH_2{}^+ \longleftrightarrow {}^+CH_2{-}CH{=}CH_2$. Charge is shared across two carbons; transition state is low-energy.

Step 2. **Try ionising n-propyl chloride.** $CH_3CH_2CH_2{-}Cl \longrightarrow CH_3CH_2CH_2^+$. The primary cation is unstable and rarely forms; instead the substrate prefers S_N2, which is itself slow because H_2O is a weak nucleophile.

Step 3. **Compare rates.** At room temperature in water, allyl chloride hydrolyses in minutes; n-propyl chloride is essentially inert under the same conditions.

> **Final Answer:** Resonance-stabilised allyl cation drives faster hydrolysis of allyl chloride by several orders of magnitude over n-propyl chloride.

Q 6.49 **Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?**

SOLUTION

Concept used. A **Grignard reagent** $R{-}MgX$ has a strongly polarised $C^{\delta-}{-}Mg^{\delta+}$ bond; the carbon end behaves as a *carbanion* (very strong base/nucleophile). Water has a slightly acidic $O{-}H$ proton ($pK_a \approx 15.7$), and any carbanion with conjugate-acid $pK_a > 16$ will deprotonate water instantly.

Step 1. Reaction with water:

$$R{-}MgX + H_2O \longrightarrow R{-}H + Mg(OH)X.$$

The Grignard is destroyed; an alkane is formed instead of the intended addition product.

Step 2. Even trace moisture (in solvent, glassware, or air) reacts stoichiometrically, so the yield of the desired product drops rapidly.

Step 3. Hence Grignard work must be done in scrupulously *dry* ether/THF, under inert (N_2 or Ar) atmosphere, with oven-dried glassware.

> **Final Answer:** $R{-}MgX$ protolyses with water ($R{-}MgX + H_2O \longrightarrow R{-}H + Mg(OH)X$), destroying the reagent and blocking the desired carbon-carbon bond formation.

✗ Atmospheric water counts

Even humid laboratory air supplies enough H_2O to quench a Grignard reagent. Always run the reaction under dry N_2 (or argon) with a calcium-chloride guard tube on the condenser, or in a Schlenk line. Solvents must be freshly distilled from sodium-benzophenone (for ether/THF). Bench glassware should be oven-dried at $\geq 120°C$ and cooled in a desiccator.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Carbanion-protonation angle. The simplest mental model of a Grignard reagent is "R^- in disguise". The $C{-}Mg$ bond is so polarised that the carbon end behaves as a strong carbanion-like base, with effective conjugate-acid pK_a near 50 (for $R{-}H$). Anything carrying an acidic proton — $H{-}O$ ($pK_a \approx 15.7$ in water), $H{-}N$ ($pK_a \approx 36$), or even terminal $H{-}C{\equiv}C$ ($pK_a \approx 25$) — is acidic enough to protonate $R{-}MgX$ instantly and irreversibly.

Concept used. Acid–base reactivity in organic chemistry is governed by pK_a matching: a base of conjugate-acid pK_a higher than the proton donor's pK_a will deprotonate it quantitatively. $R{-}MgX$, with effective pK_a near 50, sits very high on that scale, so virtually any protic species in the reaction mixture (water, alcohols, amines, terminal alkynes, carboxylic acids) destroys it. Therefore Grignard work must use scrupulously dry, aprotic solvents (diethyl ether, THF) and dry inert atmospheres.

Step 1. **Write the protolysis.** $R{-}MgX + H_2O \longrightarrow R{-}H + Mg(OH)X$. The Grignard donates its carbanion lone pair to a water proton; the products are an inert alkane and a Mg(II) hydroxohalide.

Step 2. **Quantify the consequence.** Each mole of moisture destroys one mole of reagent stoichiometrically. Even a few hundred parts-per-million of H_2O in the solvent is enough to wipe out a synthesis-scale batch.

Step 3. **Hence the precautions.** Use dry ether/THF distilled from Na/benzophenone; oven-dried glassware; N_2 or argon atmosphere; $CaCl_2$ guard tube on the condenser.

> **Final Answer:** $R{-}MgX$ protolyses with water ($R{-}MgX + H_2O \longrightarrow R{-}H + Mg(OH)X$), destroying the reagent and producing an unreactive alkane in place of the desired addition product.

Q 6.50 **Write a test to detect the presence of a double bond in a molecule.**

SOLUTION

Concept used. A $C{=}C$ double bond is electron-rich (π-cloud). Two classic decolourisation tests detect it:

Step 1. **Bromine water test:** add a few drops of reddish-brown Br_2 in CCl_4 (or aqueous Br_2). The alkene adds Br_2 across the π-bond:

$$R_2C{=}CR_2 + Br_2 \longrightarrow R_2C(Br){-}C(Br)R_2.$$

The reddish-brown colour disappears within seconds. An alkane does not react and the colour persists.

Step 2. **Baeyer's test (alkaline $KMnO_4$):** add dilute cold alkaline $KMnO_4$ (purple). The alkene is *cis*-hydroxylated:

$$R_2C{=}CR_2 \; + \; \text{cold dil. } KMnO_4 \; \longrightarrow \; R_2C(OH){-}C(OH)R_2$$

The purple colour fades to brown MnO_2. Alkanes do not react under cold conditions.

Either decolourisation $\Rightarrow$ $C{=}C$ present.

> **Final Answer:** Bromine water (red colour fades) or Baeyer's reagent (purple fades to brown MnO_2) detects $C{=}C$.

☞ **Triple-bond caveat**

Both tests also respond to $C{\equiv}C$ (alkyne) triple bonds. To distinguish, look for terminal-alkyne acidity (tollens-style $Ag(NH_3)_2{}^+$ gives white $AgC \equiv CR$ precipitate).

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Colour-change angle. The fastest qualitative tests for a double bond exploit the fact that $C{=}C$ is electron-rich (π-cloud) and so reacts cleanly with two coloured reagents that an alkane would simply ignore. Either reagent reacts via addition or oxidation at the π-bond, and the visible endpoint is a sudden colour change that you can describe in a single sentence on the exam.

Concept used. Two classical wet-lab tests:

1. **Bromine water test** (electrophilic addition). $Br_{2/}CCl_4$ is reddish-brown. The alkene adds Br_2 across the double bond via a cyclic bromonium intermediate, giving a colourless vicinal dibromide; the reddish-brown disappears in seconds.
2. **Baeyer's test** (cis-hydroxylation). Cold, dilute, alkaline $KMnO_4$ is deep purple. The alkene is oxidised to a syn-diol; manganese is reduced to MnO_2, a brown precipitate. The purple fades and a brown solid appears.

Step 1. **Set up bromine water test.** A few drops of reddish-brown Br_2 in CCl_4 are added to the unknown sample.

$$R_2C{=}CR_2 + Br_2 \longrightarrow R_2C(Br){-}C(Br)R_2.$$

Colour vanishes $\Rightarrow$ alkene confirmed.

Step 2. **Run Baeyer's test as confirmation.** Add cold dilute $KMnO_4$/NaOH:

$$R_2C{=}CR_2 \;+\; \text{cold dil. } KMnO_4 \longrightarrow R_2C(OH){-}C(OH)R_2$$

Purple fades to brown MnO_2 precipitate.

Step 3. Interpret results. Either decolourisation (better: both) is positive for $C{=}C$. An alkane leaves both reagents unchanged.

> **Final Answer:** Decolourisation of reddish-brown $Br_{2/}CCl_4$ or fading of purple alkaline $KMnO_4$ (with brown MnO_2 appearing) confirms the presence of $C{=}C$.

Q 6.51 Why are aryl halides less reactive towards nucleophilic substitution than alkyl halides?

SOLUTION

Concept used. Three structural features deactivate aryl halides toward nucleophilic substitution.

Step 1. Resonance shortening of $C{-}X$. A lone pair on X delocalises into the ring, giving the $C{-}X$ bond *partial double-bond character*. Shorter, stronger bonds break less easily. Bond lengths: $C{-}Cl$ in chlorobenzene ≈ 169 pm vs ≈ 178 pm in CH_3Cl.

Step 2. Hybridisation of the ipso carbon. The aryl carbon is sp^2 (more s-character, 33%); sp^2–halogen bonds are stronger than sp^3–halogen bonds because s orbitals are closer to the nucleus.

Step 3. Repulsion in the transition state. The incoming nucleophile and the electron-rich π-cloud of the ring repel each other, raising E_a for both S_N1 (no stable aryl cation) and S_N2 (back-side attack blocked).

To enhance reactivity, introduce strong **electron-withdrawing groups** ($-NO_2$, $-CN$, $-COOH$) at o- and p-positions. The NO_2 group stabilises the Meisenheimer intermediate by resonance, opening up the addition–elimination (S_NAr) pathway. E.g. 2,4-dinitrochlorobenzene reacts with aqueous $NaOH$ at $\sim 100°C$ to give the corresponding phenol; chlorobenzene itself needs $300°C$ + 300 atm (Dow process).

> **Final Answer:** Aryl halides are unreactive due to resonance shortening of $C{-}X$, sp^2 carbon hybridisation, and nucleophile–π repulsion. Reactivity is boosted by adding $-NO_2$ groups at o/p-positions.

♥ Industrial relevance

The Dow process and the herbicide industry exploit the $\mathrm{S_NAr}$ boost from $\mathrm{NO_2}$ activation to make phenols, anilines, and nitroaryl ethers from chlorobenzenes at modest temperatures.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Three-pillar angle. The unreactivity of aryl halides rests on three independent structural facts which we can label the "three pillars": (1) resonance shortens and strengthens the $\mathrm{C{-}X}$ bond, (2) the ipso carbon is sp^2 (higher s-character) so its bond to X is intrinsically stronger than sp^3, and (3) the transition states for both $\mathrm{S_N1}$ and $\mathrm{S_N2}$ are destabilised — the aryl cation is high in energy and back-side attack on the ipso carbon is geometrically blocked by the ring's π-cloud. Activating the substrate with $\mathrm{NO_2}$ groups at o and p positions opens a fourth pathway, the addition–elimination $\mathrm{S_NAr}$, which routes around all three obstacles.

Concept used. The $\mathrm{S_NAr}$ mechanism for an activated aryl halide proceeds via a discrete **Meisenheimer intermediate**: the nucleophile adds to the ipso carbon to give an sp^3-hybridised carbanion delocalised over the ring, then loss of $\mathrm{X^-}$ regenerates aromaticity. Strong $-M$ groups ($-\mathrm{NO_2}$, $-\mathrm{CN}$, $-\mathrm{COR}$) at o/p positions stabilise the negative charge in the intermediate by resonance; m- substituents cannot reach the carbanion lobes and so provide no acceleration. The textbook benchmarks are 300°C/300 atm for unactivated chlorobenzene (Dow process) versus 100°C/1 atm for 2,4-dinitrochlorobenzene.

Step 1. **Pillar 1 – Resonance shortening.** In chlorobenzene the Cl lone pair conjugates into the ring, giving $\mathrm{C{-}Cl}$ partial double-bond character. Bond lengths: $\mathrm{C{-}Cl}$ (PhCl) ≈ 169 pm vs ≈ 178 pm in $\mathrm{CH_3Cl}$ — the shorter, stronger bond resists cleavage.

Step 2. **Pillar 2 – Hybridisation.** The aryl carbon is sp^2 (33% s); sp^2–halogen bonds are stronger and shorter than sp^3–halogen bonds because s electrons sit closer to the nucleus.

Step 3. **Pillar 3 – Bad transition states.** An aryl cation would have its empty orbital in the ring plane, orthogonal to the π-system, so no resonance stabilisation is possible. $\mathrm{S_N2}$ back-side attack is geometrically forbidden: the ring's π-cloud sits directly behind the ipso carbon.

Step 4. **Activation via $\mathrm{S_NAr}$.** Add strong $-M$ groups at o and p positions ($-\mathrm{NO_2}$, $-\mathrm{CN}$, $-\mathrm{COR}$). The Meisenheimer carbanion is stabilised by resonance onto those groups; the addition step is now feasible.

Final Answer: Aryl halides resist classical $\mathrm{S_N1/S_N2}$ through resonance, hybridisation, and TS effects; activation by o/p-$\mathrm{NO_2}$ groups opens the $\mathrm{S_NAr}$ pathway through a stabilised Meisenheimer intermediate.

Q 6.52 **Which of the compounds will react faster in $\mathrm{S_N1}$ reaction with the $\mathrm{OH^-}$ ion: $\mathrm{CH_3{-}CH_2{-}Cl}$ or $\mathrm{C_6H_5{-}CH_2{-}Cl}$?**

SOLUTION

Answer. $\mathrm{C_6H_5{-}CH_2{-}Cl}$ (benzyl chloride) reacts much faster.
Concept used. The $\mathrm{S_N1}$ rate is set by the ionisation step $\mathrm{R{-}Cl \longrightarrow R^+ + Cl^-}$, so a more stable $\mathrm{R^+}$ means a faster reaction. The benzyl cation $\mathrm{C_6H_5{-}C^+H_2}$ is resonance-stabilised by four contributors:

$$\mathrm{C_6H_5{-}C^+H_2} \longleftrightarrow [\text{three ortho/para ring resonance forms}]$$

while the ethyl cation $\mathrm{CH_3{-}C^+H_2}$ is primary, with no resonance stabilisation. The benzyl cation is therefore far lower in energy and forms much faster.

Step 1. Identify the carbocations: primary ethyl vs benzyl.

Step 2. Compare stabilisation: ethyl (none) vs benzyl (4 resonance forms).

Step 3. Conclude: ionisation barrier for benzyl is much lower; $\mathrm{S_N1}$ rate is much higher.

Final Answer: $\mathrm{C_6H_5CH_2Cl}$ reacts faster (resonance-stabilised benzyl cation).

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Cation-stability angle. The benzyl cation's positive charge is delocalised onto the o, o', p carbons of the ring, dropping its energy by ~ 80 kJ/mol relative to a primary aliphatic cation. That stabilisation transfers to the TS for ionisation, slashing the $\mathrm{S_N1}$ activation energy.
Concept used. $\mathrm{S_N1}$ kinetics: rate $= k[\mathrm{R{-}Cl}]$. $k = A\,e^{-E_a/RT}$, and E_a tracks the energy of the developing cation. Benzyl $<$ tert $<$ sec $<$ primary $<$ methyl in cation energy; benzyl is therefore on par with 3° for ionisation.

Step 1. Sketch resonance forms of $\mathrm{C_6H_5CH_2{}^+}$.

Step 2. Estimate $\Delta E_a^{\ddagger}$ saving ~ 80 kJ/mol.

Step 3. Conclude benzyl is the runaway winner.

Final Answer: Benzyl chloride; resonance-stabilised cation.

Q 6.53 Why does iodoform have an appreciable antiseptic property?

SOLUTION

Answer. Iodoform (CHI_3) is antiseptic because, on contact with tissues, it slowly liberates free iodine I_2. Iodine is the active germicide; it denatures bacterial proteins by iodinating tyrosine residues and disrupting essential enzymes.
Concept used. The $C{-}I$ bond in CHI_3 is weak (~ 240 kJ/mol) and can be cleaved by skin moisture, enzymes, or sunlight to liberate I_2. The slow release at the wound gives a sustained antiseptic action.

Step 1. Apply iodoform paste to the wound.

Step 2. Body warmth and moisture cleave the weak $C{-}I$ bonds.

Step 3. Released I_2 kills surface bacteria.

Final Answer: Iodoform's antiseptic action is due to slow liberation of free I_2.

♥ **Historical note**

Iodoform was widely used in WWI as a wound dressing. Today it is mostly replaced by povidone-iodine, but it still finds use in dental packings.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Mechanism-of-action angle. The molecule CHI_3 itself has only mild biological activity; the real antiseptic agent is the slow stream of I_2 it releases on the skin or mucous membrane.
Concept used. The C-X bond energy decreases sharply down the halogen group: $C{-}F \gg C{-}Cl > C{-}Br > C{-}I$. Iodine is therefore the most easily liberated halide, and iodoform is essentially a slow-release iodine vehicle.

Step 1. Confirm $C{-}I$ in iodoform is the weakest of the C-halide bonds.

Step 2. Recognise I_2 as the active germicide.

Step 3. Connect the two: $CHI_3 \rightarrow CHI_2(H) + I_2$ (slow) provides sustained dosing.

Final Answer: Antiseptic due to I_2 liberation from the weak $C{-}I$ bond.

Q 6.54 **Discuss the role of Lewis acids in the preparation of aryl bromides and chlorides in the dark.**

SOLUTION

Answer. Lewis acids such as $FeCl_3$, $FeBr_3$, $AlCl_3$, $AlBr_3$ generate the active electrophile X^+ by polarising and ultimately abstracting a halide from $X{-}X$:

$$X_2 + FeX_3 \longrightarrow X^+ + [FeX_4]^-$$

The X^+ then attacks the aromatic ring in classical electrophilic aromatic substitution; the arenium ion is then deprotonated by $[FeX_4]^-$, restoring aromaticity and regenerating FeX_3.

Step 1. Activation: $X_2 + FeX_3 \rightarrow X^+ \cdots [FeX_4]^-$.

Step 2. Electrophilic attack on the ring by $X^+ \rightarrow$ Wheland intermediate (arenium ion).

Step 3. Loss of H^+ to $[FeX_4]^- \rightarrow$ haloarene $+HX + FeX_3$ (catalyst regenerated).

> **Final Answer:** Lewis acids generate X^+, the true electrophile in EAS halogenation of arenes.

☞ **Lewis-acid menu**

$FeCl_3, FeBr_3, AlCl_3, AlBr_3$ for halogenation; H_2SO_4 + HNO_3 generate ${NO_2}^+$ for nitration; $AlCl_3$ + RCl for Friedel-Crafts alkylation.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Catalysis-first angle. Without the Lewis acid, X_2 is only weakly polarised by the aromatic π-cloud; activation energy for direct attack is too high for room-temperature reaction. The Lewis acid lowers this barrier by pre-polarising $X{-}X$ and making one halide effectively cationic.

Concept used. EAS demands an electrophile of sufficient electrophilicity to overcome the ~ 150 kJ/mol loss of aromatic resonance energy in the arenium intermediate. The Lewis acid catalyst is what makes the electrophile strong enough.

Step 1. Describe the catalyst's role: X^+ generation.

Step 2. Describe the catalytic cycle: FeX_3 regenerated each turn.

Step 3. Note the "in the dark" constraint: light would trigger free-radical side-chain halogenation instead of ring substitution.

> **Final Answer:** Lewis acids polarise $X{-}X$ to release X^+, the electrophile for EAS.

Q 6.55 **Which of the following compounds (a) and (b) will not react with a mixture of NaBr and $\mathrm{H_2SO_4}$? Explain why.**
(a) $\mathrm{CH_3CH_2CH_2OH}$ **(b)** $\mathrm{C_6H_5{-}OH}$ **(phenol)**

SOLUTION

Answer. (b) phenol does not react with $\mathrm{NaBr/H_2SO_4}$ to give bromobenzene.
Concept used. The reaction $\mathrm{R{-}OH + HBr \longrightarrow R{-}Br + H_2O}$ requires the $\mathrm{C{-}O}$ bond to be cleaved (after protonation of OH). In phenol the $\mathrm{C{-}O}$ bond has partial double-bond character because the oxygen lone pair conjugates into the ring; the $\mathrm{C{-}O}$ is therefore unusually strong and short, and is not cleaved under these conditions.

Step 1. (a) n-propanol: $\mathrm{C{-}O}$ is a normal single bond. $\mathrm{H_2SO_4}$ protonates OH; $\mathrm{Br^-}$ (from NaBr) displaces $\mathrm{H_2O}$ via $\mathrm{S_N2} \to \mathrm{CH_3CH_2CH_2{-}Br}$. ✓

Step 2. (b) Phenol: oxygen lone pair conjugates with the ring; the $\mathrm{C{-}O}$ bond order is between 1 and 2; bond strength ~ 460 kJ/mol (vs ~ 360 in alcohols); not cleaved.

> **Final Answer:** Phenol does not react; $\mathrm{C{-}O}$ in phenol has partial double-bond character (resonance), so it cannot be broken under these conditions.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Resonance angle. The phenolic $\mathrm{C{-}O}$ bond is reinforced by donation of the O lone pair into the aromatic ring, giving five resonance contributors and partial double-bond character. The bond is too strong to cleave with $\mathrm{NaBr/H_2SO_4}$.
Concept used. Conjugation into an aromatic ring stiffens the substituent bond. Phenols, anisoles, and aryl amines all show this behaviour — their O- or N-substituent bonds are stronger than the aliphatic analogues.

Step 1. Sketch phenol resonance structures.

Step 2. Estimate bond order: > 1.

Step 3. Conclude bond cannot be cleaved by $\mathrm{H^+/Br^-}$ at ordinary conditions.

> **Final Answer:** Phenol unreactive; its $\mathrm{C{-}O}$ is resonance-strengthened.

Q 6.56 **Which of the products will be the major product in the reaction given below? Explain.**

$$\mathrm{CH_3{-}CH{=}CH_2 + HI \longrightarrow CH_3{-}CH_2{-}CH_2I\,(A) + CH_3{-}CHI{-}CH_3\,(B)}$$

SOLUTION

Answer. (B) $CH_3{-}CHI{-}CH_3$ (2-iodopropane) is the major product.
Concept used. **Markovnikov's rule**: in addition of HX to an unsymmetrical alkene, the H goes to the carbon with more Hs (terminal CH_2) and X goes to the more substituted carbon (internal CH). Justification: protonation of propene at the terminal $=CH_2$ gives the more stable *secondary* carbocation $CH_3{-}C^{+}H{-}CH_3$, whereas protonation at the internal carbon gives the less stable primary cation $CH_3{-}CH_2{-}C^{+}H_2$.

Step 1. Two competing protonation sites give either secondary or primary cation.

Step 2. Secondary cation is ~ 80 kJ/mol more stable than primary $\Rightarrow$ that path dominates.

Step 3. I^- traps the secondary cation $\rightarrow$ (B) 2-iodopropane is the Markovnikov product.

> **Final Answer:** (B) 2-iodopropane (Markovnikov product, secondary cation pathway).

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Cation-stability shortcut. Pick the more stable cation; the nucleophile attaches there. For terminal alkenes, that is always the internal carbon (secondary), so X ends up on C_2.
Concept used. Markovnikov regioselectivity is a consequence of carbocation stability, which is in turn a consequence of hyperconjugation and $+I$ effects. With peroxides, HBr (specifically) flips to anti-Markovnikov via radical mechanism; that exception does not apply to HI or HCl.

Step 1. Confirm no peroxide $\rightarrow$ Markovnikov is in force.

Step 2. Find the secondary cation pathway.

Step 3. Pick (B).

> **Final Answer:** (B) major; Markovnikov rule.

Q 6.57 Why is the solubility of haloalkanes in water very low?

SOLUTION

Answer. Haloalkanes are only weakly polar ($\mu \sim 1.5$–2 D), so the dipole-dipole attraction they could offer to water molecules is weak. More importantly, dissolving them in water would require breaking the strong hydrogen-bond network of water, but haloalkanes have no $\mathrm{O{-}H}$ or $\mathrm{N{-}H}$ to replace those broken H-bonds. The enthalpy cost of disrupting water without energetic compensation makes the overall solvation unfavourable.

Step 1. Dissolution would have to (a) break water-water H-bonds and (b) form new water-haloalkane interactions.

Step 2. Step (a) costs ~ 20 kJ/mol per H-bond.

Step 3. Step (b) only repays ~ 8 kJ/mol per dipole-dipole interaction.

Step 4. Net $\Delta H > 0$ and ΔS unfavourable (hydrophobic cage) $\Rightarrow$ low solubility.

> **Final Answer:** Haloalkanes can't H-bond with water; energetically expensive to break water H-bonds without compensation. Hence very low solubility.

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Energetics angle. Dissolution is a balance between solute-solvent attraction (here, weak dipole-dipole) and disruption of solvent-solvent attraction (here, H-bonds in water). Haloalkanes lose the second contest.

Concept used. "Like dissolves like" is the practical summary. Strongly H-bonding solvents (water, methanol) prefer H-bonding solutes (alcohols, acids); non-H-bonding solutes (haloalkanes, hydrocarbons) prefer non-H-bonding solvents ($\mathrm{CCl_4}$, hexane, ether).

Step 1. Compare polarity and H-bonding capacity.

Step 2. Net energy cost is positive.

Step 3. Solubility is low.

> **Final Answer:** Low solubility: no H-bonding, weak dipole-dipole interaction.

Q 6.58 **Draw resonance structures for halobenzene ($\mathrm{C_6H_5{-}X}$, halogen lone pair conjugating with ring), and find out whether the halogen substituent is ortho/para directing or meta directing.**

SOLUTION

Answer. Halobenzene's $-\mathrm{X}$ is **ortho/para directing** despite being weakly deactivating overall.

Concept used. A halogen has lone pairs in p-orbitals which conjugate with the ring's

π-system. Resonance structures place a negative charge (from halogen donation) on the o and p ring carbons (never on m). This raises electron density at $o, p \Rightarrow$ the electrophile attacks there.

Step 1. Kekule + 3 charge-separated resonance structures of $\mathrm{C_6H_5{-}X}$: $\mathrm{X^+ = C\,ring^-}$ on o, p carbons.

Step 2. Electrophile $\mathrm{E^+}$ adds to the $\mathrm{C^-}$-bearing o, p positions.

Step 3. No structure puts negative charge on the m carbon $\Rightarrow$ no m attack.

> **Final Answer:** Halogen is o, p directing because resonance increases the electron density at the ortho and para positions.

✗ Don't confuse direction with activation

Halogens are o, p-directors but they are still *deactivators* ($-I$ overrides $+M$ on average). EAS happens slower than benzene but still at o, p.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Resonance-mapping angle. The lone pair on the halogen delocalises into the ring through the same π-network used by benzene's π-electrons. The negative charge it pushes onto the ring lands on the o and p carbons by symmetry; m is missed because of the alternating polarity of the ring's π-system.

Concept used. Two opposing effects: halogen $-I$ withdraws σ-electrons (deactivating), halogen $+M$ pushes lone pairs (activating). The $-I$ effect wins on average rate; the $+M$ effect selects o, p positions.

Step 1. Draw the three charge-separated resonance forms putting $\mathrm{C^-}$ at o, o', p.

Step 2. Conclude o, p-directing.

Step 3. Note: deactivating despite directing o, p.

> **Final Answer:** o, p-directing through $+M$ resonance; weakly deactivating through $-I$.

Q 6.59 **Classify the following compounds as primary, secondary and tertiary halides: (i) 1-Bromobut-2-ene (ii) 4-Bromopent-2-ene (iii) 2-Bromo-2-methylpropane**

SOLUTION

Answers.

(i) Primary; (ii) Secondary; (iii) Tertiary.

Concept used. The class of an alkyl halide is set by the number of *other* carbon atoms attached to the $C-X$ carbon: 1 → primary, 2 → secondary, 3 → tertiary.

Step 1. (i) 1-Bromobut-2-ene = $Br-CH_2-CH=CH-CH_3$. $C-Br$ carbon has 1 alkyl/aryl neighbour ($-CH=CH-CH_3$) ⇒ primary (and allylic).

Step 2. (ii) 4-Bromopent-2-ene = $CH_3-CH=CH-CHBr-CH_3$. $C-Br$ has 2 carbon neighbours ($-CH=CH-CH_3$ and $-CH_3$) ⇒ secondary.

Step 3. (iii) 2-Bromo-2-methylpropane = $(CH_3)_3C-Br$. $C-Br$ has 3 methyl neighbours ⇒ tertiary.

> **Final Answer:** (i) primary; (ii) secondary; (iii) tertiary.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Substituent-count angle. For each substrate, draw the skeletal structure and count carbons bonded to the $C-X$ carbon.

Concept used. The class only counts carbon neighbours; the identity of those carbons (alkyl, vinyl, aryl) doesn't change the class but does affect reactivity (e.g. allyl primary halides ionise like tertiary halides because of resonance).

Step 1. Sketch each structure.

Step 2. Count carbons on $C-X$.

Step 3. Assign $1^\circ, 2^\circ, 3^\circ$.

> **Final Answer:** (i) 1°; (ii) 2°; (iii) 3°.

Q 6.60 **Compound 'A' with molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.**

(i) Write down the structural formula of both compounds 'A' and 'B'.

(ii) Out of these two compounds, which one will be converted to the product with inverted configuration?

SOLUTION

Answers.
(i) A: $(CH_3)_3C{-}Br$ (tert-butyl bromide; rate $\propto$ [A] only $\Rightarrow$ S_N1, so A is tertiary).
B: $CH_3{-}CHBr{-}CH_2{-}CH_3$ (2-bromobutane; rate $\propto$ [B][KOH] $\Rightarrow$ S_N2, so B is secondary and optically active).
(ii) Compound B (because S_N2 proceeds with Walden inversion).
Concept used. Rate law identifies the mechanism: first-order $\Rightarrow$ S_N1 (substrate must be tertiary or benzyl/allyl), second-order $\Rightarrow$ S_N2 (substrate typically primary or secondary). S_N2 inverts; S_N1 racemises.

Step 1. A is the only C_4H_9Br that gives a tertiary cation $= (CH_3)_3CBr$.

Step 2. B is optically active $\Rightarrow$ chiral; the only chiral C_4H_9Br is 2-bromobutane.

Step 3. B reacts S_N2 $\Rightarrow$ Walden inversion $\Rightarrow$ inverted product.

> **Final Answer:** A = $(CH_3)_3CBr$; B = $CH_3CHBrCH_2CH_3$; B gives inverted product.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Kinetics-reads-mechanism angle. Order of reaction is the single most powerful tool for distinguishing S_N1 vs S_N2. First-order $\Rightarrow$ unimolecular ionisation step is rate-limiting $\Rightarrow$ no OH^- in rate law. Second-order $\Rightarrow$ both substrate and nucleophile are in the rate-determining step.
Concept used. Stereochemistry follows mechanism: S_N1 gives racemisation (planar carbocation, equal attack from either face); S_N2 gives inversion (back-side attack).

Step 1. Read rate law $\rightarrow$ mechanism.

Step 2. Match substrate skeleton.

Step 3. Apply stereo outcome.

> **Final Answer:** A is 3° (S_N1, racemises); B is 2° (S_N2, inverts).

Q 6.61 Write the structures and names of the compounds formed when compound 'A' with molecular formula C_7H_8 is treated with Cl_2 in the presence of $FeCl_3$.

SOLUTION

Answer. A = toluene ($C_6H_5{-}CH_3$). EAS chlorination with $Cl_{2/}FeCl_3$ gives a mixture of *o*-chlorotoluene and *p*-chlorotoluene (with p as major).
Concept used. $-CH_3$ is an o/p-director (activating, $+I$/hyperconjugation). $FeCl_3$

generates Cl^+ which attacks the ring; the methyl group steers the electrophile to o and p.

Step 1. Generate Cl^+: $Cl_2 + FeCl_3 \longrightarrow Cl^+ + [FeCl_4]^-$.

Step 2. Methyl stabilises positive charge in the σ-complex when Cl adds at o or p.

Step 3. Products: o-chlorotoluene (2-chlorotoluene) and p-chlorotoluene (4-chlorotoluene).

Structures:

$$\text{o-Cl}-C_6H_4-CH_3 \quad \text{and} \quad \text{p-Cl}-C_6H_4-CH_3$$

Final Answer: o- and p-chlorotoluene.

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Director-first angle. "C_7H_8" and "Lewis acid + Cl" together name toluene + EAS chlorination. The methyl group predictably steers the electrophile to ortho and para.
Concept used. Activating + ortho/para-directing groups (CH_3, OH, NH_2, OR) all give mixtures of o and p products with p usually dominant (less steric clash).

Step 1. Identify A as toluene.

Step 2. Predict EAS products with methyl as o/p-director.

Step 3. Draw both isomers.

Final Answer: o- and p-chlorotoluene.

Q 6.62 Identify the products A and B formed in the following reaction:

$CH_3CH_2-CH=CH-CH_3 + HCl \longrightarrow A + B$

SOLUTION

Answer.
A = $CH_3CH_2-CH_2-CHCl-CH_3$ (2-chloropentane).
B = $CH_3CH_2-CHCl-CH_2-CH_3$ (3-chloropentane).
Concept used. The alkene is pent-2-ene ($CH_3CH_2-CH=CH-CH_3$). Both sp^2 carbons of the double bond have one H each $\Rightarrow$ Markovnikov's rule doesn't discriminate (both possible cations are secondary). Therefore two products form in comparable amounts.

Step 1. Protonate the $C=C$ at C_2 $\rightarrow$ secondary cation $CH_3CH_2-CH_2-C^+H-CH_3$.

Step 2. Or protonate at C_3 $\rightarrow$ different secondary cation $CH_3CH_2-C^+H-CH_2-CH_3$.

Step 3. Both are secondary; both form. Cl^- traps each $\to$ A and B.

> **Final Answer:** A = 2-chloropentane; B = 3-chloropentane.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Markovnikov-degeneracy angle. When both alkene carbons give the same class of cation, Markovnikov's rule loses its predictive power. Both products are expected.
Concept used. Internal symmetric or near-symmetric alkenes yield regiochemical mixtures because no carbocation is significantly more stable than the other.

Step 1. Sketch both cation pathways.

Step 2. Both secondary, near-isoenergetic.

Step 3. Both products form.

> **Final Answer:** Mixture of 2-chloro- and 3-chloropentane.

Q 6.63 Which of the following compounds will have the highest melting point and why?

(I) 1,3-Dichloro-2,5-dimethylbenzene
(II) 2,5-Dichloro-1,4-dimethylbenzene
(III) 1,3-Dichloro-2,4-dimethylbenzene

SOLUTION

Answer. (II) 2,5-Dichloro-1,4-dimethylbenzene has the highest melting point.
Concept used. Melting point of substituted benzenes correlates strongly with the *symmetry* of the molecule: more symmetric isomers pack tightly into the crystal lattice and require more energy to disrupt. (II) has C_{2h} symmetry (1,4- methyls + 2,5-chlorines all related by the centre of inversion); (I) and (III) lack this high symmetry.

Step 1. Inspect the three substitution patterns.

Step 2. (II) has both pairs of substituents at p-positions to each other $\Rightarrow$ highest symmetry $\Rightarrow$ tightest packing.

Step 3. (II) has the highest m.p.

Final Answer: (II) has the highest m.p. because of its p-symmetric, tightly-packing structure.

☞ **p-isomer top of the m.p. league**

For disubstituted benzenes, p-isomers usually have the highest melting points because they crystallise into denser, more symmetric lattices than o- or m-isomers.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Crystal-packing angle. The 1,4 + 2,5 substitution pattern makes (II) the only one whose unit cell can be a near-cubic dense packing without steric clash; the others have at least one ortho clash that loosens the lattice.
Concept used. Lattice energy $\propto$ symmetry and packing density. More symmetry $\Rightarrow$ better packing $\Rightarrow$ higher m.p.

Step 1. Assess symmetry of each isomer.

Step 2. Highest-symmetry isomer wins.

Final Answer: (II) highest m.p. owing to highest molecular symmetry.

Q 6.64 Write down the structure and IUPAC name for *neo*-pentyl bromide.

SOLUTION

Answer. Structure: $(\mathrm{CH_3})_3\mathrm{C{-}CH_2Br}$ (3,3-dimethyl-1-bromopropane? No — the longest chain is propane with two methyls on C2). IUPAC name:
1-Bromo-2,2-dimethylpropane.
Concept used. "Neopentyl" = $(\mathrm{CH_3})_3\mathrm{C{-}CH_2}^-$ (a C_5 fragment with three methyls on the carbon adjacent to the $\mathrm{CH_2}$ being substituted). IUPAC: parent is propane (the longest chain through the $\mathrm{C{-}Br}$ carbon), substituents are two methyls at C_2 and Br at C_1.

Step 1. Draw neopentyl group: $(\mathrm{CH_3})_3\mathrm{C{-}CH_2}^-$.

Step 2. Attach Br: $(\mathrm{CH_3})_3\mathrm{C{-}CH_2Br}$.

Step 3. Find longest chain: 3 C (propane) through $\mathrm{CH_2 - C - CH_3}$.

Step 4. Substituents: 2 methyls at C2, Br at C1.

Step 5. Name: 1-Bromo-2,2-dimethylpropane.

Final Answer: Structure $(CH_3)_3C-CH_2Br$; IUPAC name: 1-bromo-2,2-dimethylpropane.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Trivial-to-IUPAC translation. "Neo" (Greek for "new") labels a five-carbon fragment with three methyls on one terminal C. For IUPAC, find the longest chain through the substituted carbon — it is 3 carbons (the CH_2, then the quaternary C, then one of the three methyls), not 4.
Concept used. IUPAC rules: longest chain → parent; lowest locants → position numbers; alphabetical citation → substituent order.

Step 1. Find longest chain through $C-Br$ carbon.

Step 2. Number from $C-Br$ end (lowest locant for Br).

Step 3. Cite "bromo" before "dimethyl" alphabetically.

Final Answer: 1-Bromo-2,2-dimethylpropane.

Q 6.65 **A hydrocarbon of molecular mass $72\ \text{g mol}^{-1}$ gives a single monochloro derivative and two dichloro derivatives on photochlorination. Give the structure of the hydrocarbon.**

SOLUTION

Answer. The hydrocarbon is *neo*-pentane, $(CH_3)_4C$ (2,2-dimethylpropane).
Concept used. Molecular mass 72 ⇒ C_5H_{12} $(5 \times 12 + 12 = 72)$. Among the three isomers of pentane (n-pentane, isopentane, neopentane), only *neopentane* has all 12 hydrogens in equivalent positions; therefore only one monochloro derivative forms. The second chlorination, on the monochloro derivative $(CH_3)_3C-CH_2Cl$, has two distinct positions: (a) the same CH_2Cl carbon (gem) and (b) one of the three remaining methyl groups, giving exactly two dichloro derivatives.

Step 1. Mass 72 → C_5H_{12} pentane isomer.

Step 2. Single monochloro → all H's equivalent → neopentane.

Step 3. Monochloro derivative: $(CH_3)_3C-CH_2Cl$.

Step 4. Two further dichloro positions: gem (same carbon) or distal methyl.

Final Answer: Hydrocarbon: $(CH_3)_4C$ (neopentane).

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Symmetry-counts-isomers angle. The number of distinct monochloro products equals the number of inequivalent H-bearing positions in the parent. Neopentane has just one such position; it must be the answer.
Concept used. Hydrogen equivalence under molecular symmetry; molecular formula from molecular mass.

Step 1. Compute formula from mass.

Step 2. List pentane isomers.

Step 3. Pick the one with all H's equivalent.

Final Answer: Neopentane, $(CH_3)_4C$.

Q 6.66 Name the alkene which will yield 1-chloro-1-methylcyclohexane by its reaction with HCl. Write the reactions involved.

SOLUTION

Answer. Either *methylenecyclohexane* ($C_6H_{10}{=}CH_2$, exocyclic alkene) or *1-methylcyclohex-1-ene* (endocyclic alkene with CH_3 on C_1) yields 1-chloro-1-methylcyclohexane.
Concept used. Markovnikov addition of HCl goes through the most stable carbocation. In both cases the most stable cation is the tertiary cation centred on the ring carbon that bears the methyl group. Cl^- then traps that tertiary carbon $\Rightarrow$ both starting alkenes converge on the same product.

Step 1. Methylenecyclohexane $+HCl$: H^+ adds to the $=CH_2$, generating the tertiary cation at the ring carbon; Cl^- adds there $\rightarrow$ 1-chloro-1-methylcyclohexane.

Step 2. 1-Methylcyclohex-1-ene $+HCl$: H^+ adds to C_2 of the ring, generating the tertiary cation at C_1; Cl^- adds there $\rightarrow$ same product.

Final Answer: Both methylenecyclohexane and 1-methylcyclohex-1-ene give 1-chloro-1-methylcyclohexane via Markovnikov addition through a tertiary cation.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Same-cation angle. Two structurally distinct alkenes can give the same product if they share an intermediate carbocation. Here both alkenes protonate to the same tertiary cation ("1-methylcyclohexyl cation"), which then captures Cl^-.
Concept used. Markovnikov regioselectivity is governed by cation stability. Tertiary cations win over secondary or primary, so the proton goes wherever leaves a tertiary cation behind.

Step 1. For each alkene, draw the more stable cation.

Step 2. Note that both cations are the same species.

Step 3. Cl^- traps → same product.

> **Final Answer:** Methylenecyclohexane or 1-methylcyclohex-1-ene.

Q 6.67 **Which of the following haloalkanes reacts with aqueous KOH most easily? Explain giving reason.**
(i) 1-Bromobutane (ii) 2-Bromobutane
(iii) 2-Bromo-2-methylpropane (iv) 2-Chlorobutane

SOLUTION

Answer. (iii) 2-Bromo-2-methylpropane (tert-butyl bromide) reacts most easily.
Concept used. With aq. KOH (polar protic solvent, good ionising medium, weak nucleophile OH^- at low concentration relative to water), the dominant mechanism for tertiary halides is $\mathrm{S_N1}$ via the tertiary carbocation. The tert-butyl cation $(\mathrm{CH_3})_3\mathrm{C}^+$ is highly stabilised by hyperconjugation and $+I$, so the ionisation barrier is low. Additionally, Br is a better leaving group than Cl.

Step 1. Tertiary substrate ⇒ $\mathrm{S_N1}$ via stable tertiary cation.

Step 2. Br leaves more readily than Cl (weaker C-X bond, more polarisable).

Step 3. Combined: tertiary bromide is fastest.

> **Final Answer:** (iii) 2-Bromo-2-methylpropane: tertiary + Br leaving group ⇒ fastest.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Two-factor angle. Two variables decide the rate: (1) class of the halide (cation stability) and (2) leaving group quality. Tertiary bromide wins on both axes.
Concept used. Leaving-group order: $I^- > Br^- > Cl^- > F^-$ (matches bond strength). Cation stability $3° > 2° > 1°$.

Step 1. Pick tertiary substrate.

Step 2. Pick Br over Cl.

Step 3. Conclude (iii) is fastest.

> **Final Answer:** Option (iii); tertiary + Br.

Q 6.68 **Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of $\mathrm{ZnCl_2}$?**

SOLUTION

Answer. The $\mathrm{C{-}O}$ bond in phenol has partial double-bond character because the oxygen lone pair conjugates with the aromatic ring. This stabilised, shortened bond is not cleaved by $\mathrm{HCl/ZnCl_2}$, so Cl cannot displace OH from the ring.

Step 1. Phenolic $\mathrm{C{-}O}$ enjoys resonance stabilisation (~ 460 kJ/mol vs ~ 360 in aliphatic alcohols).

Step 2. $\mathrm{ZnCl_2}$ would normally protonate OH and weaken $\mathrm{C{-}O}$, allowing $\mathrm{Cl^-}$ to displace water.

Step 3. In phenol the partial double-bond character resists cleavage $\Rightarrow$ no reaction.

> **Final Answer:** Phenol's $\mathrm{C{-}O}$ has partial double-bond character (resonance) and cannot be broken by $\mathrm{HCl/ZnCl_2}$.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Resonance-strengthens-bond angle. The same resonance that makes phenol acidic also makes the $\mathrm{C{-}O}$ bond very hard to break in the wrong direction. Lucas-type reagents fail; even $\mathrm{PCl_5}$ gives at best triphenyl phosphate, not chlorobenzene.
Concept used. Bond order > 1 implies bond energy significantly above single-bond baseline. Cleavage requires extraordinary conditions (e.g. diazotisation route via $\mathrm{ArN_2}^+$).

Step 1. Cite phenol's resonance forms putting $C{=}O^+H$ character on the ipso carbon.

Step 2. Conclude $C{-}O$ is too strong to break.

Step 3. Note alternative: $C_6H_5{-}NH_2 \longrightarrow C_6H_5{-}N_2{}^+ \longrightarrow C_6H_5{-}Cl$ via Sandmeyer.

> **Final Answer:** Resonance makes phenolic $C{-}O$ unbreakable by Lucas-type reagents.

Q 6.69 How do polar solvents help in the first step in S_N1 mechanism?

SOLUTION

Answer. Polar solvents (especially polar protic ones like water, methanol) accelerate the first step of S_N1 — the ionisation $R{-}X \longrightarrow R^+ + X^-$ — by **solvating** both the developing carbocation and the leaving halide ion. The solvation lowers the energy of the ion pair, reduces the activation energy for ionisation, and makes the heterolysis viable at room temperature.

Step 1. Polar solvent molecules orient their negative ends around R^+ (cation solvation) and their positive ends (H of OH) around X^- (anion solvation, via H-bonding).

Step 2. Solvation energy of Cl^- in water is ~ -380 kJ/mol; similar magnitude for R^+.

Step 3. This stabilisation drops the ionisation barrier from ~ 250 kJ/mol (gas phase) to ~ 100 kJ/mol (solution).

Step 4. Ionisation now occurs at observable rate.

> **Final Answer:** Polar protic solvents solvate R^+ and X^-, dropping the ionisation energy and enabling S_N1.

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Solvation-stabilisation angle. The rate-determining step of S_N1 is heterolysis; this step *creates* ions. Without a medium to stabilise those ions, the reaction wouldn't happen at room temperature. Polar protic solvents are tailor-made for this stabilisation.

Concept used. Dielectric constant ε governs how much the solvent reduces electrostatic attraction between newly formed ions; H-bonding capacity governs anion stabilisation; both contribute to lowering E_a for ionisation.

Step 1. Identify the ionisation step.

Step 2. Identify what is needed: stabilisation of the new ions.

Step 3. Match: polar protic solvent (high ε + H-bonding).

> **Final Answer:** Solvation of R^+ and X^- lowers E_a for ionisation.

Q 6.70 Diphenyls are potential threat to the environment. How are these produced from aryl halides?

SOLUTION

Answer. Diphenyl (biphenyl, $\mathrm{C_6H_5{-}C_6H_5}$) and its chlorinated derivatives (PCBs, polychlorinated biphenyls) are produced by the **Fittig reaction**: an aryl halide is treated with sodium metal in dry ether:

$$2\ \mathrm{C_6H_5{-}X} + 2\ \mathrm{Na} \xrightarrow{\text{dry ether}} \mathrm{C_6H_5{-}C_6H_5} + 2\ \mathrm{NaX}$$

The polychlorinated analogues (e.g. from chlorobenzene under industrial conditions, or from accidental coupling during PCB manufacture) are highly persistent organic pollutants and bioaccumulate.

Step 1. $2\ \mathrm{Ar{-}X} + 2\ \mathrm{Na} \longrightarrow \mathrm{Ar{-}Ar} + 2\ \mathrm{NaX}$ (Fittig).

Step 2. For chlorobenzene → biphenyl + 2 NaCl.

Step 3. Chlorinated biphenyls (PCBs) are non-biodegradable and lipophilic; accumulate in food chain (Stockholm convention banned).

> **Final Answer:** Diphenyls form by the Fittig reaction of aryl halides with Na in dry ether; PCBs are the toxic chlorinated variants.

♥ PCBs and the environment

PCBs were once used as transformer coolants and flame retardants. Their stability is exactly what makes them dangerous: they persist in soil and water for decades and accumulate in fish, birds, and humans. Now banned worldwide under the Stockholm Convention.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Named-reaction angle. The Fittig reaction is the aryl-aryl analogue of Wurtz (which couples two alkyl halides). The mechanism goes through aryl radicals or aryl anions on the sodium surface.

Concept used. Reductive coupling: two C-X bonds break, one C-C bond forms; the metal (Na) provides electrons.

Step 1. Identify the coupling: aryl-aryl $\rightarrow$ biphenyl.

Step 2. Cite Fittig conditions: Na in dry ether.

Step 3. Note environmental relevance of PCBs.

> **Final Answer:** Fittig reaction; biphenyls/PCBs.

Q 6.71 **What are the IUPAC names of the insecticide DDT and benzene hexachloride? Why is their use banned in India and other countries?**

SOLUTION

Answers.

DDT: 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane.

Benzene hexachloride (BHC, Lindane): 1,2,3,4,5,6-hexachlorocyclohexane.

Why banned: both are persistent, fat-soluble organochlorine pesticides; they bioaccumulate in the food chain, harm non-target species (birds, fish, beneficial insects), and cause endocrine disruption and probable carcinogenicity in humans.

Step 1. DDT structure: $(\text{p-Cl}-\text{C}_6\text{H}_4)_2\text{CH}-\text{CCl}_3$. IUPAC: 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane.

Step 2. BHC structure: cyclohexane with one Cl on each of six carbons (γ-*isomer* is the active Lindane). IUPAC: 1,2,3,4,5,6-hexachlorocyclohexane.

Step 3. Persistence: low water solubility, high lipid solubility; half-life in soil $\sim$ years.

Step 4. Banned because of bioaccumulation, food-chain magnification (eggshell thinning in raptors), and chronic toxicity.

> **Final Answer:** DDT = 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane; BHC = 1,2,3,4,5,6-hexachlorocyclohexane. Banned due to persistence and bioaccumulation.

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Persistent-organic-pollutant angle. DDT and BHC were celebrated mid-20th-century insecticides; the very $\text{C}-\text{Cl}$ bonds that made them effective also made them unbreakable in the environment.

Concept used. Organochlorine compounds, with several $\mathrm{C{-}Cl}$ bonds, resist enzymatic degradation. Their lipid solubility ($\log P > 5$) drives accumulation in fatty tissue; biomagnification climbs each trophic level.

Step 1. Give IUPAC names.

Step 2. Cite bioaccumulation / biomagnification mechanism.

Step 3. Conclude ban is environmental and health based.

> **Final Answer:** Names + ban rationale as above.

Q 6.72 **Elimination reactions (especially β-elimination) are as common as the nucleophilic substitution reaction in case of alkyl halides. Specify the reagents used in both cases.**

SOLUTION

Answers.

For nucleophilic substitution: aqueous KOH or aqueous NaOH (gives alcohol, $\mathrm{S_N1/S_N2}$); NaCN, KI, NaOR, NH_3, NaSH (give nitriles, iodides, ethers, amines, thiols). Polar protic solvent favours $\mathrm{S_N1}$; polar aprotic ($\mathrm{DMSO, DMF, acetone}$) favours $\mathrm{S_N2}$.

For β-elimination: alcoholic KOH (or NaOH) hot; or sterically bulky strong bases like potassium *tert*-butoxide ($(CH_3)_3CO^-K^+$). Solvent: alcohol (hot reflux).

Step 1. Substitution reagents: aq. NaOH/KOH; NaCN/KCN; NaI in acetone (Finkelstein); NaOR (Williamson); NH_3; RSH/NaSH.

Step 2. Elimination reagents: alc. KOH (most common); t-BuOK for clean $\mathrm{E_2}$; aq. $AgNO_3$ for sluggish E1.

Step 3. Bulky bases push the partition toward $\mathrm{E_2}$; small charged nucleophiles push toward $\mathrm{S_N2}$.

> **Final Answer:** Substitution: aq. KOH, NaCN, NaI/acetone, NaOR, NH_3. Elimination: alc. KOH, t-BuOK, Δ.

☞ **"Aqueous vs alcoholic KOH"**

Aqueous KOH (water rich, OH^- surrounded by water) → $\mathrm{S_N}$ (gives alcohol).

Alcoholic KOH (alcohol rich, OR^- as the active base, poor solvation of OH^-) → $\mathrm{E_2}$ (gives alkene).

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Reagent-tagging angle. Memorise the canonical pairings:

- Substitution: aq. KOH (alcohol), NaCN/KCN (nitrile), AgCN (isocyanide), KI/acetone (Finkelstein iodide), NaOR (Williamson ether), NH_3 (amine).
- Elimination: alc. KOH or *t*-BuOK (alkene by E2); no nucleophile, just heat (E1 of tert halides).

Concept used. Solvent and base bulk select the partition. Aqueous + small base ⇒ S_N; alcoholic + small base ⇒ E_2; bulky base regardless of solvent ⇒ E_2.

Step 1. List reagent pairs by mechanism.

Step 2. Note the solvent dependence.

> **Final Answer:** As tabulated above.

Q 6.73 **How will you obtain monobromobenzene from aniline?**

SOLUTION

Answer. Diazotise aniline, then perform a Sandmeyer reaction with Cu_2Br_2:

$$\text{Aniline} \longrightarrow C_6H_5{-}N_2{}^{+}Cl^{-}\ (NaNO_2/HCl,\ 0\text{–}5\,°C) \longrightarrow C_6H_5{-}Br + N_2\ (Cu_2Br_2)$$

(Or use HBF_4 for the Schiemann variant; for bromide, the Cu salt is the cheap textbook route.)

Concept used. Aniline is too activated for direct bromination (Br_2 alone gives 2,4,6-tribromoaniline); the diazonium route gives clean mono-substitution.

Step 1. Diazotise: $NaNO_2 + HCl$ at 0–5 °C $\rightarrow C_6H_5N_2{}^{+}\,Cl^{-}$.

Step 2. Treat with Cu_2Br_2 (Sandmeyer) $\rightarrow C_6H_5{-}Br + N_2 + CuCl$.

Step 3. Pure monobromobenzene is isolated.

> **Final Answer:** Aniline → diazonium → Sandmeyer with Cu_2Br_2 gives bromobenzene.

☞ Why not direct bromination?

$C_6H_5{-}NH_2 + Br_2$ in water gives 2,4,6-tribromoaniline (white precipitate) because NH_2 is strongly activating. Diazotisation masks the NH_2 as $N_2{}^{+}$ (deactivating!) and allows clean mono-substitution.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Diazonium-as-handle angle. The diazonium salt $\mathrm{ArN_2}^+$ is one of the most versatile intermediates in synthesis. From it you can install $-\mathrm{F}, -\mathrm{Cl}, -\mathrm{Br}, -\mathrm{CN}, -\mathrm{OH}, -\mathrm{H}, -\mathrm{I}, -\mathrm{NO_2}, -\mathrm{SH}, -\mathrm{Ar}$ on the ring with the appropriate Cu salt or hot water etc.
Concept used. Sandmeyer-type radical substitution converts $\mathrm{N_2}^+$ to X with loss of $\mathrm{N_2}$. Cu(I) salt acts as a one-electron shuttle.

Step 1. Diazotise aniline.

Step 2. Cu_2Br_2 Sandmeyer to install Br.

> **Final Answer:** Aniline $\rightarrow$ $\mathrm{ArN_2^+}$ $\rightarrow$ PhBr by Sandmeyer.

Q 6.74 **Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution:**
(I) *p*-nitrochlorobenzene
(II) 2,4-dinitrochlorobenzene
(III) 2,4,6-trinitrochlorobenzene

SOLUTION

Answer. Reactivity: **III $>$ II $>$ I.**
Concept used. Each additional o/p-$\mathrm{NO_2}$ group provides another resonance sink for the negative charge in the Meisenheimer adduct of the $\mathrm{S_NAr}$ pathway. More $\mathrm{NO_2}$ groups $\Rightarrow$ more stabilisation $\Rightarrow$ faster rate.

Step 1. (I) one p-$\mathrm{NO_2}$: moderate activation. Reacts with aq. NaOH at $\sim 100°$C.

Step 2. (II) two $\mathrm{NO_2}$ at 2,4 (one o, one p): much faster. Reacts with aq. NaOH at $\sim 100°$C in dilute conditions.

Step 3. (III) three $\mathrm{NO_2}$ at 2,4,6 (two o, one p): picryl chloride. Reacts with $\mathrm{H_2O}$ alone at room temperature.

> **Final Answer:** Reactivity order: III $>$ II $>$ I.

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Multi-NO$_2$ stacking angle. Three nitros suitably placed turn an inert aryl halide into one that reacts with water alone at room temperature — a rate boost of $\sim 10^{12}$.
Concept used. Successive electron-withdrawing groups operate near-independently in stabilising the Meisenheimer intermediate; rate scales as roughly the product of single activation factors.

Step 1. Count o, p nitros in each substrate.

Step 2. Order by count: III (3) $>$ II (2) $>$ I (1).

> **Final Answer:** III $>$ II $>$ I.

Q 6.75 ***tert*-Butyl bromide reacts with aq. NaOH by $\mathrm{S_N1}$ mechanism while n-butyl bromide reacts by $\mathrm{S_N2}$ mechanism. Why?**

SOLUTION

Answer. The two halides differ in the class of the substrate carbon and therefore in (a) carbocation stability and (b) steric access to the substrate carbon.

Step 1. **tert-Butyl bromide** $(\mathrm{CH_3})_3\mathrm{CBr}$: tertiary substrate. (i) The $\mathrm{S_N1}$ cation $(\mathrm{CH_3})_3\mathrm{C^+}$ is highly stabilised by three $+I$ donors and nine α-H hyperconjugations. (ii) The substrate carbon is sterically blocked by three methyl groups, preventing back-side $\mathrm{S_N2}$ attack. Both factors force $\mathrm{S_N1}$.

Step 2. **n-Butyl bromide** $\mathrm{CH_3CH_2CH_2CH_2Br}$: primary substrate. (i) The $\mathrm{S_N1}$ cation $\mathrm{CH_3CH_2CH_2{-}C^+H_2}$ is primary and very unstable (no $+I$/hyperconjugation buffer worth the name). (ii) Back-side $\mathrm{S_N2}$ attack on $\mathrm{CH_2Br}$ is sterically unobstructed. Both factors force $\mathrm{S_N2}$.

> **Final Answer:** Tertiary substrate stabilises carbocation and blocks back-side attack $\Rightarrow \mathrm{S_N1}$; primary substrate is opposite on both axes $\Rightarrow \mathrm{S_N2}$.

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Two-axis angle. Mechanism is dictated by the two opposing demands: cation stability (favours $\mathrm{S_N1}$ for tertiary) and back-side accessibility (favours $\mathrm{S_N2}$ for primary). Each substrate falls on the opposite extreme.
Concept used. Carbocation stability scale $3^\circ > 2^\circ > 1^\circ > \mathrm{CH_3}^+$; steric crowding inverts the order for $\mathrm{S_N2}$ accessibility.

Step 1. Tag substrate class.

Step 2. Look up cation stability and steric access.

Step 3. Assign mechanism.

> **Final Answer:** tert-Bu-Br → S_N1; n-Bu-Br → S_N2.

Q 6.76 **Predict the major product formed when HCl is added to isobutylene. Explain the mechanism involved.**

SOLUTION

Answer. Major product: **2-chloro-2-methylpropane** ($(CH_3)_3C{-}Cl$).
Concept used. Markovnikov addition of HCl to the unsymmetrical alkene $(CH_3)_2C{=}CH_2$ (isobutylene) proceeds via the more stable carbocation.
Mechanism.

Step 1. **Step I:** H^+ protonates the $=CH_2$ terminus → tertiary cation $(CH_3)_3C^+$ (very stable). The alternative would be the primary cation $(CH_3)_2CH{-}C^+H_2$ — discarded because it's much higher energy.

Step 2. **Step II:** Cl^- traps the tertiary cation → $(CH_3)_3C{-}Cl$ (2-chloro-2-methylpropane).

> **Final Answer:** Markovnikov product $(CH_3)_3C{-}Cl$; via tertiary cation intermediate.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Cation-stability angle. Out of the two possible cations (3° vs 1°), the tertiary is ~ 100 kJ/mol more stable; the regioselectivity is essentially complete.
Concept used. Markovnikov regioselectivity is set by carbocation stability; for terminal disubstituted alkenes, the proton always adds to give the more substituted cation.

Step 1. Identify the two possible cations.

Step 2. Pick the tertiary.

Step 3. Cl^- traps it.

> **Final Answer:** $(CH_3)_3C{-}Cl$, Markovnikov.

Q 6.77 **Discuss the nature of $\mathrm{C-X}$ bond in the haloarenes.**

SOLUTION

Answer. The $\mathrm{C-X}$ bond in haloarenes is shorter and stronger than the corresponding bond in haloalkanes because of two effects:

1. **Hybridisation:** the ring carbon is sp^2 (33% s), while an alkyl C is sp^3 (25% s). Higher s-character places the bonding electrons closer to the nucleus and shortens the bond.
2. **Resonance:** the halogen lone pair conjugates with the ring's π-system, putting partial double-bond character on $\mathrm{C-X}$. Bond order $> 1 \Rightarrow$ shorter, stronger.

Step 1. Compare bond lengths: chlorobenzene $\mathrm{C-Cl} \sim 169$ pm vs methyl chloride ~ 178 pm.

Step 2. Compare bond energies: PhCl ~ 400 kJ/mol vs MeCl ~ 339 kJ/mol.

Step 3. Conclude: stronger bond $\Rightarrow$ less reactive in nucleophilic substitution.

> **Final Answer:** Aryl $\mathrm{C-X}$ is shorter and stronger than alkyl $\mathrm{C-X}$: sp^2 + resonance.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Hybridisation-plus-resonance angle. Two cooperative effects reinforce each other: more s-character in the bonding orbital (geometry) AND donation from the halogen lone pair into the ring (π-character). Both shorten and strengthen the bond.
Concept used. Bond length and bond strength are inversely correlated. Hybridisation s-character: $sp > sp^2 > sp^3$ in bond strength. Resonance donation: introduces partial double-bond character.

Step 1. Cite hybridisation.

Step 2. Cite resonance.

Step 3. Quantify with bond-length and bond-energy figures.

> **Final Answer:** Aryl C-X is shorter and stronger; partial double-bond character + sp^2.

Q 6.78 **How can you obtain iodoethane from ethanol when no other iodine-containing reagent except NaI is available in the laboratory?**

SOLUTION

Answer. Two-step sequence: first convert ethanol to a suitable haloalkane (the chloride), then run Finkelstein with NaI.

$$C_2H_5{-}OH + HCl/ZnCl_2 \longrightarrow C_2H_5{-}Cl + H_2O$$

$$C_2H_5{-}Cl + NaI \xrightarrow{\text{dry acetone}} C_2H_5{-}I + NaCl\downarrow$$

Concept used. Direct conversion of $R{-}OH$ to $R{-}I$ requires HI (not available). Instead, make the more accessible chloride first using $HCl/ZnCl_2$ (Lucas reagent), then exchange Cl for I using the **Finkelstein reaction**: in dry acetone, $NaCl$ precipitates (insoluble in acetone) and shifts the equilibrium toward $R{-}I$.

Step 1. Lucas: $C_2H_5{-}OH + HCl/ZnCl_2 \longrightarrow C_2H_5{-}Cl + H_2O$.

Step 2. Finkelstein: $C_2H_5{-}Cl + NaI \xrightarrow{\text{dry acetone}} C_2H_5{-}I + NaCl$.

Step 3. NaCl precipitates from acetone, driving equilibrium right.

> **Final Answer:** Ethanol → ethyl chloride (Lucas) → ethyl iodide (Finkelstein with NaI in dry acetone).

☞ Finkelstein driver

NaI is soluble in acetone; NaCl and NaBr are not. So the equilibrium $R{-}Cl + NaI \rightleftharpoons R{-}I + NaCl$ is pulled right by precipitation of NaCl.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Two-step retrosynthesis. Disconnect $C_2H_5{-}I$ to $C_2H_5{-}Cl$ via halide exchange; disconnect $C_2H_5{-}Cl$ to $C_2H_5{-}OH$ via Lucas. The trick is recognising that the only I source is NaI, and Finkelstein is the only practical way to use it.
Concept used. Finkelstein equilibrium is driven to completion by solubility differences: $NaCl$ insoluble in acetone, NaI soluble.

Step 1. Convert ethanol to ethyl chloride (Lucas).

Step 2. Convert ethyl chloride to ethyl iodide (Finkelstein).

> **Final Answer:** Two-step: Lucas then Finkelstein.

Q 6.79 **Cyanide ion acts as an ambident nucleophile. From which end does it act as a stronger nucleophile in aqueous medium? Give reason for your answer.**

SOLUTION

Answer. In aqueous medium, CN^- attacks **through carbon** as the stronger nucleophile, giving alkyl *cyanides* ($R-C\equiv N$, nitriles), not alkyl isocyanides.
Concept used. CN^- has lone pairs on both C and N (ambident). The C end is softer/more polarisable and forms a stronger covalent $C-C$ bond (~ 350 kJ/mol) than the $C-N$ bond (~ 290 kJ/mol) that would result from N-attack. In water, where the harder N end is more solvated by H-bonding, the C end is even more exposed and reactive.

Step 1. Identify ambident character: C and N both nucleophilic.

Step 2. Compare $C-C$ vs $C-N$ bond strengths: $C-C$ wins.

Step 3. In water, N is more solvated $\Rightarrow$ C end is freer.

Step 4. Conclude: C-attack gives nitrile (kinetic + thermodynamic product).

> **Final Answer:** C-end is the stronger nucleophile; $C-C$ bond is more stable than $C-N$, and C is less solvated in water.

☞ **KCN vs AgCN**

KCN (ionic, free CN^-) $\rightarrow$ alkyl cyanide (nitrile) through C-attack.
AgCN (covalent, free N lone pair) $\rightarrow$ alkyl isocyanide through N-attack.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Ambident-thermodynamics angle. The cyanide anion has two nucleophilic atoms with different hardness. In an ionising medium (water), the softer C end dominates because of the stronger C-C bond formed and weaker solvation of the C lone pair.
Concept used. Hard-Soft Acid-Base (HSAB) theory: hard nucleophiles prefer hard electrophiles; soft prefer soft. Alkyl halides at sp^3 C are intermediate, leaning soft; C of cyanide matches.

Step 1. Identify both ends as nucleophilic.

Step 2. Compare bond-strength of products: C-C $>$ C-N.

Step 3. Compare solvation in water: N more solvated than C.

Step 4. Conclude C-attack wins.

> **Final Answer:** C end stronger nucleophile in aqueous medium.

IV. Matching Type

Q 6.79 **Match the compounds given in Column I with the effects given in Column II.**

Column I	Column II
(i) Chloramphenicol	(a) Malaria
(ii) Thyroxine	(b) Anaesthetic
(iii) Chloroquine	(c) Typhoid fever
(iv) Chloroform	(d) Goiter
	(e) Blood substituent

SOLUTION

Matches. (i)→(c); (ii)→(d); (iii)→(a); (iv)→(b).

Concept used. Each halogen-containing compound has a characteristic physiological action used in medicine.

Step 1. (i) Chloramphenicol is an antibiotic given for **typhoid fever** caused by *Salmonella typhi*.

Step 2. (ii) Thyroxine (T_4), an iodine-rich hormone secreted by the thyroid; its deficiency leads to enlargement of thyroid gland ⇒ **goiter**.

Step 3. (iii) Chloroquine is the classical drug for **malaria** (treats *P. vivax*, *P. falciparum*).

Step 4. (iv) Chloroform ($CHCl_3$) was historically used as an **anaesthetic** (now replaced by safer halothane/isoflurane).

Final Answer: (i)→(c); (ii)→(d); (iii)→(a); (iv)→(b).

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Drug-class lookup angle. Each name in Column I belongs to a different therapeutic class. Recall the active indication of each and match directly.

Concept used. Many haloorganic compounds find use in medicine because of their bioavailability and specific receptor interactions: halothane (anaesthetic), chloroquine (antimalarial), DDT (insecticide — now banned), iodoform (antiseptic), thyroxine (hormone), chloramphenicol (antibiotic).

Step 1. Tag each Column-I compound to its therapeutic class.

Step 2. Match to the disease in Column II.

Final Answer: As above.

Q 6.80 **Match the items of Column I and Column II.**

Column I	Column II
(i) S_N1 reaction	(a) *vic*-dibromides
(ii) Chemicals in fire extinguisher	(b) *gem*-dihalides
(iii) Bromination of alkenes	(c) Racemisation
(iv) Alkylidene halides	(d) Saytzeff rule
(v) Elimination of HX from alkyl halide	(e) Chlorobromocarbons

SOLUTION

Concept used. Match each chemical phenomenon to its diagnostic descriptor.

Step 1. (i) S_N1: proceeds via a planar carbocation; nucleophile attacks from either face equally, yielding a $50{:}50$ mixture of enantiomers $\Rightarrow$ (c) **racemisation**.

Step 2. (ii) Fire extinguishers: traditional fillings are chlorobromocarbons such as CF_2ClBr (BCF) and CF_3Br (BTM), prized for free-radical inhibition $\Rightarrow$ (e).

Step 3. (iii) Br_2 adds across $C{=}C$ at C_1 and C_2 (anti addition through a bromonium ion), producing $Br{-}CR_2{-}CR_2{-}Br$, a *vic*-dibromide $\Rightarrow$ (a).

Step 4. (iv) Alkylidene halides have both halogens on the same carbon (e.g. $CH_3{-}CHCl_2$, ethylidene chloride) $\Rightarrow$ (b) *gem*-dihalides.

Step 5. (v) Base-induced β-elimination of HX from $R{-}CHX{-}CH_2R'$ obeys the Saytzeff rule: the more substituted alkene predominates $\Rightarrow$ (d).

Final Answer: (i)$\rightarrow$(c); (ii)$\rightarrow$(e); (iii)$\rightarrow$(a); (iv)$\rightarrow$(b); (v)$\rightarrow$(d).

☞ **Mechanism $\rightarrow$ stereo**

S_N1 $\rightarrow$ racemisation (planar cation); S_N2 $\rightarrow$ Walden inversion. E_1 $\rightarrow$ Saytzeff. E_2 $\rightarrow$ usually also Saytzeff (Hofmann if bulky base).

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Tag-pairing angle. Each Column I phrase is a one-word diagnostic descriptor of a phenomenon; Column II offers a matching keyword. Read both lists, identify the unique pairing for each row, and you're done. Don't be tempted by superficially similar pairs (*vic*/*gem* look interchangeable but each belongs to a specific reaction type).

Concept used. Every entry in Column I has a single, unambiguous chemical signature that appears in Column II. S_N1 via a planar cation → racemisation; chlorobromocarbons (Halon-type) → fire extinguishers; Br_2 adds anti across $C{=}C$ → *vic*-dibromides through a bromonium intermediate; alkylidene halides are by definition gem-dihalides (CHX_2 shape); base-induced β-elimination obeys Saytzeff (more substituted alkene predominates).

Step 1. **(i)** S_N1. Planar carbocation intermediate ⇒ nucleophile attacks both faces equally ⇒ 50:50 enantiomers ⇒ **(c) Racemisation**.

Step 2. **(ii) Fire extinguishers.** Classical halon fillings CF_2ClBr (Halon 1211, BCF) and CF_3Br (Halon 1301, BTM) suppress flames by scavenging $H^\bullet$ and $OH^\bullet$ radicals ⇒ **(e) Chlorobromocarbons**.

Step 3. **(iii) Bromination of alkenes.** Anti-addition through a bromonium ion places Br on C_1 and C_2 ⇒ **(a) *vic*-dibromides**.

Step 4. **(iv) Alkylidene halides.** "-idene" nomenclature means both halogens are on a single CH carbon ($CH_3{-}CHCl_2$, ethylidene chloride) ⇒ **(b) *gem*-dihalides**.

Step 5. **(v) Elimination of HX.** Base abstracts a β-H to generate the more substituted alkene (Zaitsev product) ⇒ **(d) Saytzeff rule**.

Final Answer: (i)→(c); (ii)→(e); (iii)→(a); (iv)→(b); (v)→(d).

Q 6.81 **Match the structures of compounds given in Column I with the classes of compounds given in Column II.**

Column I (Structure)	Column II (Class)
(i) $CH_3{-}CHX{-}CH_3$	**(a) Aryl halide**
(ii) $CH_2{=}CH{-}CH_2{-}X$	**(b) Alkyl halide**
(iii) $C_6H_5{-}X$ **(X on ring carbon)**	**(c) Vinyl halide**
(iv) $CH_2{=}CH{-}X$	**(d) Allyl halide**

SOLUTION

Matches. (i)→(b); (ii)→(d); (iii)→(a); (iv)→(c).

Concept used. Classify halides by the hybridisation / position of the carbon attached to X:

- sp^3 carbon in an alkyl chain → alkyl halide.
- sp^2 carbon *of* $C{=}C$ → vinyl halide.

- Ring sp^2 carbon of aromatic ring → aryl halide.
- sp^3 carbon *adjacent to* $\mathrm{C{=}C}$ → allyl halide.

Step 1. (i) $\mathrm{CH_3{-}CHX{-}CH_3}$: $\mathrm{sp^3}$ alkyl chain → **alkyl halide** (b).

Step 2. (ii) $\mathrm{CH_2{=}CH{-}CH_2{-}X}$: $\mathrm{sp^3}$ C next to $\mathrm{C{=}C}$ → **allyl halide** (d).

Step 3. (iii) $\mathrm{C_6H_5{-}X}$: X on aromatic ring → **aryl halide** (a).

Step 4. (iv) $\mathrm{CH_2{=}CH{-}X}$: $\mathrm{sp^2}$ C of $\mathrm{C{=}C}$ → **vinyl halide** (c).

Final Answer: (i)→(b); (ii)→(d); (iii)→(a); (iv)→(c).

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Position-of-X angle. The four canonical halide classes differ only in *where* the halogen sits relative to unsaturation: alkyl (away from any π), allyl (next to $\mathrm{C{=}C}$), vinyl (on $\mathrm{C{=}C}$), aryl (on aromatic ring). Reactivity scales predictably.

Concept used. Reactivity tags:

- Allyl/benzyl ⇒ fast $\mathrm{S_N1}$ (resonance-stabilised cation).
- Alkyl ⇒ standard $\mathrm{S_N1/S_N2}$ depending on class.
- Vinyl/aryl ⇒ unreactive in classical $\mathrm{S_N}$ (partial double bond + $\mathrm{sp^2}$ carbon).

Step 1. Identify hybridisation/location of the $\mathrm{C{-}X}$ carbon.

Step 2. Pick the corresponding class.

Final Answer: As tabulated.

Q 6.82 **Match the reactions given in Column I with the types of reactions given in Column II.**

Column I (Reaction)	Column II (Type)
(i) Chlorobenzene + Fe/Cl$_2$ → *o*- and *p*-dichlorobenzene	**(a) Nucleophilic aromatic substitution**
(ii) Propene + HBr → 2-bromopropane	**(b) Electrophilic aromatic substitution**
(iii) $\mathrm{C_6H_5{-}CHI{-}CH_3 + OH^- \rightarrow C_6H_5{-}CHOH{-}CH_3}$	**(c) Saytzeff elimination**
(iv) *p*-nitrochlorobenzene + NaOH → *p*-nitrophenol	**(d) Electrophilic addition**
(v) 2-Bromobutane + alc. KOH → 2-butene	**(e) Nucleophilic substitution ($\mathrm{S_N1}$)**

SOLUTION

Matches. (i)→(b); (ii)→(d); (iii)→(e); (iv)→(a); (v)→(c).
Concept used. Tag each reaction by what attacks what: electrophile attacks aromatic ring → EAS; nucleophile displaces LG on aromatic ring with $-M$ activation → S_NAr; H^+ adds across $C{=}C$ → electrophilic addition; benzyl halide hydrolysed in water → S_N1 via stable cation; base abstracts β-H to give more substituted alkene → Saytzeff E2.

Step 1. (i) Fe/Cl_2 on PhCl: ring substitution by Cl^+ → EAS (b).

Step 2. (ii) HBr to propene: H^+ adds, then Br^- at secondary carbon → electrophilic addition (d).

Step 3. (iii) Benzyl iodide + OH^-: benzyl cation forms (resonance-stabilised) → S_N1 (e).

Step 4. (iv) p-nitrochlorobenzene + NaOH: S_NAr via Meisenheimer (a).

Step 5. (v) 2-bromobutane + alc. KOH: E2 elimination giving 2-butene (Saytzeff) (c).

> **Final Answer:** (i)→(b); (ii)→(d); (iii)→(e); (iv)→(a); (v)→(c).

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Reaction-type tagging angle. For every transformation, ask "what is the substrate (aromatic vs alkene vs alkyl halide) and what is the attacker (electrophile vs nucleophile)?" The four-cell grid pins the mechanism uniquely.
Concept used. Mechanism categories: EAS (Ar + E^+), S_NAr (Ar-X + Nu^- with $-M$ activation), electrophilic addition (alkene + E^+), nucleophilic substitution (RX + Nu^-), elimination (RX + strong base).

Step 1. For each row, identify substrate + attacker.

Step 2. Map to category.

> **Final Answer:** Matches as above.

Q 6.83 **Match the structures given in Column I with the names in Column II.**

Column I (Structure)	Column II (Name)
(i) $CH_3{-}CH{=}CH{-}CHBr{-}CH_3$	**(a) 4-Bromopent-2-ene**
(ii) $(CH_3)_2C(Br){-}CH{=}CH{-}CH_3$	**(b) 4-Bromo-3-methylpent-2-ene**
(iii) $CH_3{-}CH{=}CH{-}CH(CH_3){-}CH_2Br$**? (i.e.,** $CH_3CH{=}C(CH_3)CHBr{-}\ldots$**)**	**(c) 1-Bromo-2-methylbut-2-ene**
(iv) $BrCH_2{-}CH{=}CH{-}CH(CH_3)_2$	**(d) 1-Bromo-2-methylpent-2-ene**

SOLUTION

Matches. (i)→(a); (ii)→(c); (iii)→(b); (iv)→(d).
Concept used. Apply IUPAC rules: parent chain = longest chain through the double bond; number from the end nearest the double bond, then check that the substituent locants are also minimised.

Step 1. (i) Pent-2-ene with Br on C_4 → **4-bromopent-2-ene** (a).

Step 2. (ii) But-2-ene with CH_2Br at C_4, methyl at C_3 ⇒ but-2-ene with Br on $=CH-CH_2Br$ extension: this fits **1-bromo-2-methylbut-2-ene** (c).

Step 3. (iii) Pent-2-ene parent with Br on C_4 and methyl on C_3 → **4-bromo-3-methylpent-2-ene** (b).

Step 4. (iv) Pent-2-ene parent with Br on C_1 and methyl on C_2 → **1-bromo-2-methylpent-2-ene** (d).

> **Final Answer:** (i)→(a); (ii)→(c); (iii)→(b); (iv)→(d).

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

IUPAC-walk angle. Trace the longest carbon chain through the double bond; number from the end nearest to the double bond (double bond gets lowest locant); cite all substituents alphabetically with their locants.
Concept used. Lowest-locant rule for principal characteristic group (the double bond), then for substituents. Substituents cited in alphabetical order ignoring multiplying prefixes.

Step 1. For each structure, identify longest chain through $C=C$.

Step 2. Number to give $C=C$ the lowest locant.

Step 3. Identify and locate substituents.

> **Final Answer:** Matches as tabulated.

Q 6.84 **Match the reactions given in Column I with the names given in Column II.**

Column I (Reaction)	**Column II (Name)**
(i) C_6H_5-X **+** $R-X$ **+ 2Na (ether)** $\rightarrow C_6H_5-R$ **+ 2NaX**	**(a) Fittig reaction**
(ii) $2\ C_6H_5-X$ **+ 2Na (ether)** $\rightarrow C_6H_5-C_6H_5$ **+ 2NaX**	**(b) Wurtz–Fittig reaction**
(iii) $C_6H_5-N_2{}^+X^-$ **+** $\mathbf{Cu_2X_2}$ $\rightarrow C_6H_5-X$ **+** $\mathbf{N_2}$	**(c) Finkelstein reaction**
(iv) C_2H_5-Cl **+ NaI (dry acetone)** $\rightarrow C_2H_5-I$ **+ NaCl**	**(d) Sandmeyer reaction**

SOLUTION

Matches. (i)→(b); (ii)→(a); (iii)→(d); (iv)→(c).

Concept used. Each reaction has a canonical name attached:

- Wurtz: $2\,R-X+2\,Na \longrightarrow R-R+2\,NaX$ (two alkyl halides).
- Fittig: $2\,Ar-X+2\,Na \longrightarrow Ar-Ar+2\,NaX$ (two aryl halides).
- Wurtz-Fittig: $Ar-X+R-X+2\,Na \longrightarrow Ar-R+2\,NaX$ (mixed).
- Sandmeyer: $ArN_2{}^+ + Cu_2X_2 \longrightarrow ArX+N_2$.
- Finkelstein: $R-Cl+NaI \longrightarrow R-I+NaCl$ in dry acetone.

Step 1. (i) Aryl-X + alkyl-X with Na: **Wurtz-Fittig** (b).

Step 2. (ii) Two aryl-X with Na: **Fittig** (a).

Step 3. (iii) Diazonium + Cu_2X_2: **Sandmeyer** (d).

Step 4. (iv) RCl + NaI in acetone: **Finkelstein** (c).

> **Final Answer:** (i)→(b); (ii)→(a); (iii)→(d); (iv)→(c).

☞ Named-reaction fingerprinting

Look at the metal and the substrate(s):
Na + 1 alkyl-X → Wurtz; Na + 2 aryl-X → Fittig; Na + 1 alkyl + 1 aryl → Wurtz-Fittig; Cu(I) + diazonium → Sandmeyer; NaI/acetone + RCl → Finkelstein.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Pattern-recognition angle. Named reactions are best learned as "reagent fingerprints". Once you can pattern-match the reagent combination, the name and product follow immediately.

Concept used. The four name reactions here all install a halogen or couple a C-X to make a new C-C bond. Wurtz/Fittig/Wurtz-Fittig use Na; Sandmeyer uses Cu(I); Finkelstein uses NaI in dry acetone to swap halides.

Step 1. For each row, identify reagent fingerprint.

Step 2. Map to canonical name.

> **Final Answer:** Matches as above.

V. Assertion and Reason Type

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct answer out of the following choices:
(i) Both A and R are correct and R is the correct explanation of A.
(ii) Both A and R are wrong statements.
(iii) A is correct but R is wrong statement.
(iv) A is wrong but R is correct statement.
(v) Both A and R are correct statements but R is not the correct explanation of A.

Q 6.85 **Assertion (A): Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.**
Reason (R): Phosphorus chlorides give pure alkyl halides.

SOLUTION

Correct option: (ii) Both A and R are wrong.
Concept used. Thionyl chloride $\mathrm{SOCl_2}$ is in fact *preferred* over $\mathrm{PCl_{3/}PCl_5}$ for alcohol-to-alkyl-chloride conversion because the by-products ($\mathrm{SO_2}$ gas and HCl gas) both escape, leaving the pure alkyl chloride behind. $\mathrm{PCl_3}$ yields $\mathrm{H_3PO_3}$ (phosphorous acid) as a co-product that contaminates the product.

Step 1. $\mathrm{ROH} + \mathrm{SOCl_2} \longrightarrow \mathrm{RCl} + \mathrm{SO_2}\uparrow{}^{+}\,\mathrm{HCl}\uparrow$ (clean).

Step 2. $3\,\mathrm{ROH} + \mathrm{PCl_3} \longrightarrow 3\,\mathrm{RCl} + \mathrm{H_3PO_3}$ (gives liquid by-product).

Step 3. Both A (PCl preferred) and R (P-Cl gives pure) are incorrect.

> **Final Answer:** Option **(ii)**: both A and R are wrong.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

By-product-cleanness angle. The deciding factor is what leaves with the product. Gaseous by-products are removed automatically; liquid by-products remain and require separation.

Concept used. The Darzens or Hell-Volhard-Zelinsky family of acid-halide-forming reagents are chosen primarily for clean work-up. $SOCl_2$ wins because both by-products are gases.

Step 1. Write the reaction for each reagent.

Step 2. Identify by-products.

Step 3. Gases → cleaner; liquids → contaminating.

> **Final Answer:** Option **(ii)**.

Q 6.86 **Assertion (A): The boiling points of alkyl halides decrease in the order:** $RI > RBr > RCl > RF$.

Reason (R): The boiling points of alkyl chlorides, bromides and iodides are considerably higher than those of the hydrocarbon of comparable mass.

SOLUTION

Correct option: (v) Both A and R are correct statements but R is not the correct explanation of A.

Concept used. A is correct: heavier halide ⇒ more polarisable ⇒ stronger dispersion forces ⇒ higher boiling point. R is also correct (alkyl halide $T_b >$ alkane of same carbon count) but is a separate fact, comparing halide to hydrocarbon rather than halide-to-halide. Therefore R doesn't explain A.

Step 1. Verify A: I (largest, most polarisable) → highest T_b. ✓

Step 2. Verify R: C_2H_5Cl (12.3°C) $>$ ethane (-89°C). ✓

Step 3. R compares $R-X$ to $R-H$, not different halides among themselves.

Step 4. Conclude R doesn't explain A.

> **Final Answer:** Option **(v)**.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Logical-relation angle. The trick is to ask: does R provide the *causal chain* for A? Here R is a separate true statement that doesn't address halide-vs-halide comparison.

Concept used. For A-R type questions, R must logically imply A; if A and R are both true but unrelated, the answer is (v).

Step 1. Test R→A: does "$R-X$ boils higher than $R-H$" imply "RI boils higher than

RBr”? No.

Step 2. Both A and R are individually correct but unrelated ⇒ (v).

> **Final Answer:** Option **(v)**.

Q 6.87 **Assertion (A): KCN reacts with methyl chloride to give methyl isocyanide. Reason (R): CN^- is an ambident nucleophile.**

SOLUTION

Correct option: (iv) A is wrong but R is correct.
Concept used. A is wrong: KCN (ionic, dissociates fully) delivers CN^- free in solution; attack occurs through the softer, more nucleophilic C end, giving methyl *cyanide* (nitrile, $CH_3{-}CN$), not isocyanide. AgCN (covalent, holds the C tightly through Ag-C bond) leaves the N end free and gives isocyanide. R is correct: CN^- is indeed ambident.

Step 1. KCN → free CN^-; C-attack → $CH_3{-}CN$ (acetonitrile).

Step 2. AgCN → Ag-bound C; only N free; N-attack → $CH_3{-}NC$ (isocyanide).

Step 3. A confuses these two; R is true.

> **Final Answer:** Option **(iv)**.

✗ KCN vs AgCN
KCN (ionic) → cyanide (nitrile, C-attack).
AgCN (covalent) → isocyanide (N-attack).

EXPERT’S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Reagent-identity angle. The identity of the metal cation (K^+ vs Ag^+) controls which end of cyanide is free. Ionic K-CN releases free anion; covalent Ag-CN ties up the C and exposes only N.
Concept used. Hard-soft acid-base matching plus electrostatic binding: Ag^+ binds C tightly (soft-soft), K^+ doesn’t bind C at all (hard-soft mismatch).

Step 1. Identify reagent: KCN.

Step 2. Determine which end is nucleophilic: C end (free CN^-).

Step 3. Product: methyl cyanide (nitrile), not isocyanide.

Final Answer: Option **(iv)**.

Q 6.88 **Assertion (A): *tert*-Butyl bromide undergoes Wurtz reaction to give 2,2,3,3-tetramethylbutane.**
Reason (R): 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.

SOLUTION

Correct option: (i) Both A and R are correct and R is the correct explanation of A.
Concept used. Wurtz: $2\,\mathrm{R{-}X} + 2\,\mathrm{Na} \longrightarrow \mathrm{R{-}R} + 2\,\mathrm{NaX}$. For $\mathrm{R} = (\mathrm{CH_3})_3\mathrm{C}^-$, the dimer is $(\mathrm{CH_3})_3\mathrm{C{-}C}(\mathrm{CH_3})_3 =$ 2,2,3,3-tetramethylbutane. Each *tert*-butyl contributes 4 carbons; product has 8.

Step 1. Apply Wurtz: 2 $(\mathrm{CH_3})_3\mathrm{C{-}Br}$ + 2 Na $\rightarrow$ $(\mathrm{CH_3})_3\mathrm{C{-}C}(\mathrm{CH_3})_3$ + 2 NaBr.

Step 2. Count carbons in product: $2\ \times {}_{4} = 8 \Rightarrow$ R is the explanation of A.

Final Answer: Option **(i)**.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Coupling-doubling angle. The Wurtz reaction couples two alkyl halide fragments, doubling the carbon count. Apply directly to $(\mathrm{CH_3})_3\mathrm{CBr}$.
Concept used. Wurtz mechanism: Na donates one electron to $\mathrm{R{-}X}$ to give an alkyl radical; two radicals couple. Practically, this gives substantial Wurtz product for tertiary halides despite the tendency to eliminate.

Step 1. Apply Wurtz stoichiometry.

Step 2. Sketch product: $(\mathrm{CH_3})_3\mathrm{C{-}C}(\mathrm{CH_3})_3$ = 2,2,3,3-tetramethylbutane.

Final Answer: Option **(i)**.

Q 6.89 **Assertion (A): Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.**
Reason (R): Nitro group, being an electron withdrawing group, decreases the electron density over the benzene ring.

SOLUTION

Correct option: (i) Both A and R are correct and R is the correct explanation of A.
Concept used. $-NO_2$ at o/p accepts the negative charge of the Meisenheimer intermediate by resonance, stabilising it. The lowered Meisenheimer energy translates to lower activation energy and faster S_NAr. The mechanism is exactly "NO_2 pulls electron density out of the ring".

Step 1. A: o/p-NO_2 activates Ar-X toward S_NAr. ✓

Step 2. R: $-NO_2$ is electron-withdrawing $\rightarrow$ ring electron density drops $\rightarrow$ Meisenheimer intermediate (negative on ring) is more stable. ✓

Step 3. R directly explains A.

> **Final Answer:** Option **(i)**.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Resonance-stabilisation angle. NO_2 at o/p provides a direct resonance sink for the negative charge of the Meisenheimer adduct. R restates the same physics in different words; A and R are two sides of one coin.
Concept used. S_NAr rate enhancement by $-M$ groups at o/p. Picryl chloride is the canonical maximally-activated example.

Step 1. Confirm A: o/p-NO_2 accelerates S_NAr.

Step 2. Confirm R: NO_2 is electron-withdrawing.

Step 3. R explains A.

> **Final Answer:** Option **(i)**.

Q 6.90 **Assertion (A): In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.**
Reason (R): Halogen atom is a ring deactivator.

SOLUTION

Correct option: (v) Both A and R are correct statements but R is not the correct explanation of A.
Concept used. A is correct: halogens are o/p-directing in EAS. R is correct: halogens are net deactivators (overall slower than benzene). But R doesn't explain A:

deactivation would predict m-direction (like NO_2 or CN); o/p direction is specifically due to resonance donation from the halogen lone pair, not from deactivation.

Step 1. A: halogens direct o/p. True (resonance donation).

Step 2. R: halogens are deactivating. True ($-I > +M$ on average).

Step 3. But the *reason* halogens direct o/p is $+M$ donation, not deactivation ⇒ R is correct but doesn't explain A.

> **Final Answer:** Option **(v)**.

☞ **Halogen's split personality**

$-I$ effect: deactivates (rate $<$ benzene).

$+M$ effect: directs o/p (lone-pair resonance).

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Two-effect angle. Halogens carry both $-I$ (withdrawal, deactivating) and $+M$ (donation, o/p-directing). The two effects explain different observations: deactivation explains the slower rate; resonance donation explains the o/p regiochemistry.
Concept used. Substituent effects in EAS: directing controlled by $\pm M$ (resonance, looks for lone pairs/π-acceptor); activation controlled by $\pm I + \pm M$ algebraic sum.

Step 1. Verify both A and R individually.

Step 2. Test whether R causes A.

Step 3. Conclude unrelated ⇒ (v).

> **Final Answer:** Option **(v)**.

Q 6.91 Assertion (A): Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.
Reason (R): Oxidising agent oxidises I_2 into HI.

SOLUTION

Correct option: (iii) A is correct but R is wrong statement.
Concept used. A is correct: iodination of arenes is reversible, and adding an oxidant pulls the equilibrium toward Ar−I by destroying the reducing HI by-product. R is wrong: the oxidant oxidises *HI* back to I_2 (and water), not the other way around.

Step 1. Iodination: $\mathrm{ArH} + \mathrm{I_2} \rightleftharpoons \mathrm{Ar{-}I} + \mathrm{HI}$ (slow forward, fast reverse).

Step 2. Oxidant (e.g. $\mathrm{HIO_3}$): $5\,\mathrm{HI} + \mathrm{HIO_3} \longrightarrow 3\,\mathrm{I_2} + 3\,\mathrm{H_2O}$ ($\mathrm{HI} \to \mathrm{I_2}$).

Step 3. So oxidant oxidises HI to I_2, not I_2 to HI.

Step 4. A is correct, R is wrong.

Final Answer: Option **(iii)**.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Direction-of-oxidation angle. HI is the reductant (low oxidation state of I); I_2 is the oxidised form. Oxidising HI yields I_2 + water. R confuses the direction.
Concept used. Le Chatelier driving an equilibrium. Removing HI (by oxidising it back to I_2) shifts $\mathrm{ArH} + \mathrm{I_2} \rightleftharpoons \mathrm{ArI} + \mathrm{HI}$ to the right.

Step 1. Establish reversibility of arene iodination.

Step 2. Identify which side of the oxidation reaction HI is on.

Step 3. Reject R as written in reverse.

Final Answer: Option **(iii)**.

Q 6.92 **Assertion (A): It is difficult to replace chlorine by $-\mathrm{OH}$ in chlorobenzene in comparison to that in chloroethane.**
Reason (R): Chlorine-carbon ($\mathrm{C{-}Cl}$) bond in chlorobenzene has a partial double bond character due to resonance.

SOLUTION

Correct option: (i) Both A and R are correct and R is the correct explanation of A.
Concept used. The $\mathrm{C{-}Cl}$ in chlorobenzene is shorter and stronger because of resonance donation from Cl's lone pair into the ring (partial double bond character). The stronger bond is harder to break, so $\mathrm{OH^-}$ struggles to displace $\mathrm{Cl^-}$. Industrial conversion of chlorobenzene to phenol (Dow process) requires 300°C and 300 atm.

Step 1. Confirm A: PhCl is far less reactive in S_N than EtCl.

Step 2. Confirm R: PhCl has partial double bond character due to resonance.

Step 3. R explains A through bond strength.

Final Answer: Option **(i)**.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Bond-strength angle. Stronger C-X bond ⇒ slower S_N. The resonance contribution from Cl's lone pair adds partial double-bond character, shortening and strengthening PhCl's C-Cl by ~ 60 kJ/mol over the alkyl case.
Concept used. Partial double-bond character via resonance in haloarenes is the single key fact that explains PhCl's unreactivity in S_N. Same logic applies to phenol's unbreakable C-O.

Step 1. Verify A.

Step 2. Verify R.

Step 3. Confirm R causes A.

Final Answer: Option **(i)**.

Q 6.93 **Assertion (A): Hydrolysis of $(-)$-2-bromooctane proceeds with inversion of configuration.**
Reason (R): This reaction proceeds through the formation of a carbocation.

SOLUTION

Correct option: **(iii)** A is true but R is false.
Concept used. $(-)$-2-bromooctane is a *secondary* alkyl halide. With OH^- (good nucleophile) in protic medium, it undergoes S_N2, not S_N1. S_N2 proceeds via a single concerted step with **back-side attack**, producing complete **Walden inversion** at the chiral centre.

Step 1. Verify A: hydrolysis converts $(-)$-2-bromooctane to $(+)$-2-octanol with inversion of configuration. ✓ (A is true.)

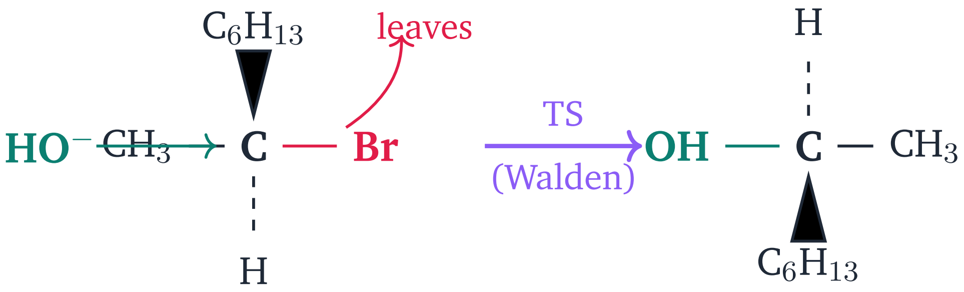
Step 2. Examine R: "proceeds through a carbocation" would be S_N1, which gives *racemisation*, not clean inversion. Secondary substrates in basic aqueous OH^- do not generate free carbocations. R is false.

Step 3. Therefore (iii): A true, R false.

Final Answer: Option **(iii)**: A is true, R is false. Hydrolysis is S_N2 (Walden inversion), not via a carbocation.

✗ Inversion $\neq$ carbocation

Inversion of configuration is the *signature of* S_N2, not S_N1. The single planar carbocation intermediate of S_N1 is attacked from *both* faces with equal probability, producing a 50:50 racemic mixture — not clean inversion. Never pair the words "inversion" and "carbocation intermediate" in the same explanation.



S_N2 back-side attack on (−)-2-bromooctane: configuration inverts (Walden inversion), giving (+)-2-octanol — a stereochemical fingerprint that no carbocation pathway can reproduce

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Stereo-cue angle. Stereochemistry is the surest mechanistic tell-tale. "Inversion" is the unmistakable keyword for S_N2 (Walden inversion through back-side attack); "racemisation" is the unmistakable keyword for S_N1 (planar cation, both faces equally accessible). Whenever an assertion mentions clean inversion and the reason invokes a carbocation, the two are mechanistically incompatible. The assertion must be true while the reason is false — option (iii).

Concept used. $(-)$-2-Bromooctane is a chiral secondary alkyl halide. With OH^- in aqueous medium the rate law is $r = k[\text{R–Br}][\text{OH}^-]$, indicating bimolecular S_N2. The mechanism is one concerted step: the nucleophile approaches the carbon from the side opposite the leaving group; the three remaining substituents pivot through a trigonal-bipyramidal transition state (sp^2-like at the α-carbon); the chiral centre emerges with its configuration mirror-imaged — the celebrated **Walden inversion**. The product $(+)$-2-octanol is the stereo-inverted enantiomer of the starting material.

Step 1. **Test A.** Does $(-)$-2-bromooctane hydrolyse with inversion? Experimentally yes — $(+)$-2-octanol is obtained with $\geq 99\%$ inversion. A is true.

Step 2. **Test R.** Does the reaction proceed via a carbocation? A secondary substrate plus a strong nucleophile ($\mathrm{OH^-}$) in a protic but predominantly bimolecular regime $\Rightarrow \mathrm{S_N2}$, not $\mathrm{S_N1}$. No free carbocation forms. R is false.

Step 3. **Reconcile.** If R were correct (cation intermediate) then A could not be (cations racemise, not invert). Hence A true + R false $\Rightarrow$ option **(iii)**.

> **Final Answer:** Option **(iii)**: A is true, R is false. Hydrolysis is $\mathrm{S_N2}$ with Walden inversion, not via a carbocation.

Q 6.94 **Assertion (A): Nitration of chlorobenzene leads to the formation of m-nitrochlorobenzene.**
Reason (R): $-\mathrm{NO_2}$ group is an m-directing group.

SOLUTION

Correct option: (iv) A is false but R is true.
Concept used. The directing effect in EAS is set by the *group already on the ring* (here Cl), not by the incoming group ($\mathrm{NO_2}$). Chlorine is weakly deactivating but *ortho/para directing* (resonance donation from Cl lone pair $>$ inductive withdrawal at o/p positions in the Wheland intermediate). So nitration of chlorobenzene gives mainly o- and p-nitrochlorobenzene, *not* m.

Step 1. Locate the directing group in the substrate: it is $-\mathrm{Cl}$, an o/p-director.

Step 2. Predict products of $\mathrm{C_6H_5Cl + HNO_3/H_2SO_4}$: o-nitrochlorobenzene ($\sim 30\%$) + p-nitrochlorobenzene ($\sim 70\%$). m-isomer is minor ($\sim 1\%$).

Step 3. A claims m-product is major — false. ✓

Step 4. R: "$\mathrm{NO_2}$ is m-directing" — true *when it is already on the ring* (deactivating, m-director). But in the present reaction $\mathrm{NO_2}$ is the incoming, not the resident, group; it doesn't direct itself.

Step 5. Hence A false, R true $\Rightarrow$ option (iv).

> **Final Answer:** Option **(iv)**: A is false, R is true. Chlorine, being o/p-directing, sends $\mathrm{NO_2}$ mainly to o and p positions.

♥ Halogens are the odd one out

Halogens are the only common substituents that are *deactivating but o/p-directing* — the inductive ($-I$) slows the rate, but the lone-pair resonance still routes the electrophile to

o/p.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Substrate-rules-incoming angle. In electrophilic aromatic substitution, the regiochemistry is dictated by the group *already on the ring*, never by the incoming group. Read the assertion through that lens: chlorobenzene is the substrate, so the resident Cl decides where $\mathrm{NO_2}$ ends up. Cl is an o/p-director (deactivating but o/p-directing, the famous halogen exception), so the major products must be o- and p-nitrochlorobenzene. Assertion A is therefore false.

Concept used. Substituent directing effects are governed by the resonance structures of the Wheland intermediate. $-\mathrm{Cl}$ has lone pairs that can donate into the ring; the resulting positive charge in the Wheland intermediate is best stabilised when the electrophile attaches at o or p (these are the positions where the lone-pair donation places the positive charge on a carbon bearing Cl). The $-\mathrm{NO_2}$ group is indeed a m-director, but only when it is already mounted on the ring; in this question $\mathrm{NO_2}$ is the *incoming* group, not the resident.

Step 1. **Identify the substrate's directing group.** The ring carries $-\mathrm{Cl}$; nothing else. Cl is deactivating $+\ o/p$-directing.

Step 2. **Predict products.** $\mathrm{C_6H_5Cl} + \mathrm{HNO_3}/\mathrm{H_2SO_4}$ gives o-nitrochlorobenzene $(\sim 30\%)$ and p-nitrochlorobenzene $(\sim 70\%)$. The m-isomer is a tiny side product $(\sim 1\%)$.

Step 3. **Evaluate A.** A claims m-nitrochlorobenzene is the product. That is false; m- is negligible.

Step 4. **Evaluate R.** R asserts that $-\mathrm{NO_2}$ is a m-director. As a general statement (when $\mathrm{NO_2}$ is already on the ring) this is true.

Step 5. **Match the answer key.** A false + R true $\Rightarrow$ option **(iv)**.

> **Final Answer:** Option **(iv)**: A is false, R is true. Resident Cl on the ring is o/p-directing, so $\mathrm{NO_2}$ goes mainly to o and p positions; m- is not the major product.

VI. Long Answer Type

Q 6.95 **Some alkyl halides undergo substitution whereas some undergo elimination on treatment with bases. Discuss the structural features of alkyl halides which are responsible for this difference, with examples.**

SOLUTION

Concept used. The competition between **nucleophilic substitution** (S_N1/S_N2) and **β-elimination** (E_1/E_2) depends on (a) class of the alkyl halide (1°, 2°, 3°), (b) strength and bulk of the base/nucleophile, (c) temperature, and (d) solvent. We tabulate the dominant behaviour.

Step 1. **Primary** $R{-}CH_2{-}X$: preferred path is S_N2 with a strong nucleophile in protic solvent (e.g. $CH_3CH_2{-}Br + OH^-/H_2O \longrightarrow CH_3CH_2{-}OH$). With a *strong, bulky base* ($(CH_3)_3CO^-\ K^+$, "t-BuOK") the path flips to E_2 giving the alkene.

Step 2. **Secondary** $R_2CH{-}X$: sits on the fence. With OH^-/water → mixed S_N2/E_2; with *alc. KOH* (hot, less polar) → predominantly E_2. Example:
$CH_3{-}CHBr{-}CH_3 + \text{ alc}\cdot\ KOH \longrightarrow CH_2{=}CHCH_3$ (propene).

Step 3. **Tertiary** $R_3C{-}X$: cannot do S_N2 (sterically blocked). With weak base/protic solvent → S_N1 (ionisation, racemic product). With strong base or high temperature → E_1/E_2 (Saytzeff alkene). Example:
$(CH_3)_3C{-}Br + \text{alc}\cdot\ KOH \longrightarrow (CH_3)_2C{=}CH_2$ (isobutene).

Step 4. **Effect of base:** small, charge-localised, basic (OEt^-, OH^- in alcohol) favours E_2. Big polarisable nucleophiles (I^-, RS^-) favour S_N2.

Step 5. **Effect of solvent and temperature:** polar protic + low T favours substitution; polar aprotic + high T favours elimination (and changes selectivity by an order of magnitude).

Summary table.

Substrate	Weak base / nucleophile	Strong / bulky base, Δ
1°	S_N2	E_2 (t-BuOK)
2°	S_N2 + E_2	E_2 (alc. KOH)
3°	S_N1	E_1/E_2 (Saytzeff)

> **Final Answer:** Class of $R{-}X$ + nature/bulk of base + temperature decide substitution vs elimination. 1° → S_N2, 2° → mixed, 3° → E_1/S_N1. Bulky strong base (t-BuOK) routes any class to E_2.

☞ Two-line decision rule

"**Substrate first, base second.**" Tertiary in alc. KOH ⇒ elimination. Primary in NaI/acetone ⇒ substitution. Apply in 10 seconds on the exam.

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Decision-tree angle. Three structural and experimental questions are sufficient to predict whether substitution or elimination will dominate:

- Is the substrate 1°, 2° or 3°?
- Is the base/nucleophile small or bulky, weak or strong?
- Is the reaction run cold (room temperature) or hot (reflux in alcohol)?

Combine the three answers via the decision table given in the SOLUTION and you have the dominant pathway in 15 seconds, which is faster than re-deriving the mechanism from scratch on the exam.

Concept used. Substitution requires nucleophilic approach to the α-carbon; elimination requires base abstraction of a β-hydrogen followed by departure of the leaving group. Bulky bases (t-BuOK, LDA) cannot reach the α-carbon (sterically blocked) but they *can* pluck off a β-H, so they push the reaction toward E_2. Polar protic solvents at low T favour ionisation (S_N1); polar aprotic solvents at high T favour bimolecular E_2 or S_N2 (the entropy term $T\Delta S$ in E_2 becomes important at high T, since elimination produces two molecules from one).

Step 1. **Worked example A:** $(CH_3)_3C{-}Cl + NaOEt$ in EtOH at 25°C. Tertiary substrate + small base + polar protic solvent at moderate $T \Rightarrow E_1$ (Saytzeff isobutene major, $\sim 90\%$) with minor S_N1 ether by-product ($\sim 10\%$).

Step 2. **Worked example B:** Switch the base to $(CH_3)_3CO^-K^+$ (t-BuOK), keep substrate and solvent. Bulky base cannot reach the α-C of a 3° carbon, but readily plucks the β-H. Result: E_2 exclusively, 100% isobutene.

Step 3. **Worked example C:** $CH_3CH_2{-}Br + NaI$ in acetone. Primary substrate + soft polarisable nucleophile + polar aprotic solvent $\Rightarrow$ pure S_N2 (Finkelstein); no elimination because I^- is a poor base.

Step 4. **Decision-rule recap. "Substrate first, base second, temperature third."** Tertiary in alc. KOH $\Rightarrow$ E2; primary in NaI/acetone $\Rightarrow S_N2$; secondary in $H_2O/OH^- \Rightarrow$ mixed (often $\sim 60{:}40$).

> **Final Answer:** Substrate class + base nature/bulk + temperature jointly determine substitution vs elimination. $1° \to S_N2$; $3° \to E_1/S_N1$; bulky strong base (t-BuOK) always routes the reaction to E_2.

Q 6.96 Some halogen containing compounds are useful in daily life. Some compounds of this class are responsible for exposure of flora and fauna to more and more of UV light which causes destruction to a great extent. Name the class of these halocompounds. In your opinion, what should be done to minimise harmful effects of these compounds?

SOLUTION

Concept used. The compounds that destroy stratospheric ozone (and so increase UV exposure at Earth's surface) are the **chlorofluorocarbons (CFCs)**, also called **Freons**. Representative examples are CCl_3F (CFC-11), CCl_2F_2 (CFC-12, Freon-12), and $C_2Cl_3F_3$ (CFC-113). They are unreactive at ground level (which is why they were popular as refrigerants, aerosol propellants, foam-blowing agents and solvents) but in the stratosphere they are split by UV radiation into Cl radicals, which catalyse the destruction of ozone:

$$CCl_2F_2 \xrightarrow{h\nu} CClF_2{}^{\bullet} + Cl^{\bullet}$$

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O_3 \longrightarrow Cl^{\bullet} + 2\,O_2$$

A single Cl radical can destroy $\sim 10^5$ ozone molecules before it is sequestered (typically as HCl or $ClONO_2$). The resulting thinning of the ozone layer (especially the "Antarctic ozone hole") allows more UV-B radiation to reach the surface, causing skin cancer, cataracts, immune suppression in humans, and damage to phytoplankton and crop plants.

Steps to minimise harmful effects:

Step 1. **Phase-out CFCs.** Replace them with hydrofluorocarbons (HFCs, e.g. $R{-}134\,a$, $CH_2F{-}CF_3$) and hydrochlorofluorocarbons (HCFCs) that decompose lower in the atmosphere and don't reach the stratosphere intact. HFCs contain no Cl, so even if they reach the stratosphere they don't catalyse ozone loss.

Step 2. **Enforce international agreements.** The **Montreal Protocol** (1987, with subsequent amendments) has phased out CFCs worldwide; the Kigali Amendment (2016) adds HFCs to the phase-down list because they are potent greenhouse gases.

Step 3. **Recover and recycle.** Old refrigerators, ACs and fire extinguishers must be recovered carefully to prevent CFC leakage; mandatory return programmes help.

Step 4. **Develop greener alternatives.** Hydrocarbon refrigerants (isobutane, propane) and natural refrigerants (NH_3, CO_2) have zero ozone depletion potential and very low global-warming potential.

Step 5. **Public-awareness measures.** Encourage purchase of CFC/HFC-free products; reduce reliance on aerosol cans; increase shade and SPF use to reduce UV exposure damage.

The Antarctic ozone hole, first reported in 1985, has stabilised since the 1990s thanks to the Montreal Protocol and is projected to recover by ~ 2065 to pre-1980 levels.

> **Final Answer:** CFCs (chlorofluorocarbons, Freons) destroy the ozone layer. Mitigation: phase out CFCs (Montreal Protocol), substitute with HFCs/HCFCs/hydrocarbons, recover-and-recycle, develop greener alternatives.

♥ **A success story**

The Montreal Protocol is the only UN environmental treaty ratified by every country. CFC emissions have dropped over 99% from peak, and the ozone layer is healing. It shows international science-led policy can work.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Molecule-mechanism-policy angle. CFCs are the classic case where a useful synthetic chemical has unintended consequences far from the application site. The chain of cause is: **(1)** CFC inertness ⇒ years-long stratospheric lifetime; **(2)** UV photolysis releases $\mathrm{Cl}^\bullet$; **(3)** Cl-O catalytic cycle depletes ozone; **(4)** thinned ozone ⇒ more UV-B at the surface; **(5)** biological damage (DNA damage, cataracts, ecosystem stress).

Concept used. Atmospheric chemistry: tropospheric inertness lets CFCs reach the stratosphere; once there, the high-energy UV cleaves the otherwise robust C-Cl bond. The chlorine atom is a catalyst, not a stoichiometric consumer, so a small mass of CFC can destroy a huge mass of ozone over its multi-decade stratospheric residence.

Step 1. **Diagnose the chemistry.** CFC + UV $\rightarrow$ $Cl^\bullet$ + perfluoroalkyl radical. $Cl^\bullet$ + O_3 $\rightarrow$ $ClO^\bullet$ + O_2; $ClO^\bullet$ + O $\rightarrow$ $Cl^\bullet$ + O_2. Cycle repeats.

Step 2. **Quantify the damage.** One Cl atom destroys $\sim 10^5$ O_3 molecules before deactivation.

Step 3. **Plan the response.** Phase-out, substitution, recovery, public awareness; backstopped by international regulation (Montreal Protocol).

Step 4. **Track progress.** Atmospheric CFC concentrations peaked in ~ 1994 and are now slowly falling; ozone layer recovery is on track.

> **Final Answer:** CFCs are the class; mitigation: international phase-out, safer substitutes, recovery and recycling.

Q 6.97 **Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides? How can we enhance the reactivity of aryl halides?**

SOLUTION

Concept used. The unreactivity of aryl halides combines three structural effects; reactivity is boosted by electron withdrawal from the ring.

Step 1. **Resonance shortening.** In chlorobenzene, Cl's lone pair donates into the ring, giving $\mathrm{C-Cl}$ a partial double-bond character. Bond length ~ 169 pm vs ~ 178 pm in CH_3Cl; the shorter, stronger bond is harder to break.

Step 2. **Hybridisation.** The aryl C is sp^2 (33% s), the alkyl C is sp^3 (25% s). The $sp^2 - \mathrm{X}$ bond is stronger and shorter because s electrons sit closer to the nucleus.

Step 3. **Repulsive transition state.** An aryl cation (S_N1) would be a destabilised sp^2 ion with the empty orbital in the ring plane — not in conjugation with the π-system. S_N2 back-side attack is blocked by the ring's π-cloud and by the geometry of the ipso carbon.

Step 4. **Activation toward S_NAr.** Strong electron-withdrawing groups (especially $-NO_2$) at o- and p-positions stabilise the **Meisenheimer intermediate** by delocalising the negative charge onto the nitro oxygens:

$$\mathrm{Cl-C_6H_3(NO_2)_2 + OH^- \longrightarrow [Meisenheimer^-] \longrightarrow HO-C_6H_3(NO_2)_2 + Cl^-}.$$

2,4-Dinitrochlorobenzene reacts with aqueous $NaOH$ at $\sim 100°C$; 2,4,6-trinitrochlorobenzene (picryl chloride) reacts at room temperature.

Step 5. **Industrial route (Dow process).** Even unactivated chlorobenzene reacts with $NaOH$ at $300°C$ and ~ 300 atm to give phenol. Severe conditions are needed precisely because the substrate is so unreactive.

Step 6. **Position matters.** m-nitro substituents do not stabilise the Meisenheimer adduct (resonance only reaches o and p positions), so m-nitrochlorobenzene is barely more reactive than chlorobenzene itself.

> **Final Answer:** Aryl halides are sluggish in S_N because of resonance shortening of $\mathrm{C-X}$, sp^2 hybridisation, and unstable aryl cation/blocked S_N2 TS. Reactivity is enhanced by introducing $-NO_2$ (or other strong $-M$) groups at o- and p-positions, which stabilise the Meisenheimer intermediate via the S_NAr pathway.

♥ Drug & dye industry

The S_NAr activation strategy underpins synthesis of sulphonamide drugs, herbicides, and azo dye intermediates — all made from o/p-nitrohaloarenes that react with amines, alkoxides, or phenoxides under mild conditions.

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Resonance-stabilisation angle. The trick to making an otherwise inert aryl halide reactive is to provide a structural mechanism that stabilises the negative charge which transiently develops on the ring during nucleophilic attack (S_NAr). $-NO_2$ groups at o/p accept that charge through resonance into their formal $N{=}O$ bonds. Without such activation, the ring would have to host a localised carbanion lobe on a particular ring carbon, an extremely high-energy species; with NO_2 activation at o or p, the carbanion lobe delocalises directly onto the nitro oxygens where the negative charge is comfortable.

Concept used. The two-step addition–elimination mechanism (S_NAr, sometimes called the **Meisenheimer mechanism**) is the only viable pathway for nucleophilic substitution on aryl halides. It requires the substrate to host a strong $-M$ (electron-withdrawing by resonance) group whose lone-pair-accepting orbital can reach the ipso carbon through the ring's π-framework. Only o and p substituents satisfy this geometric requirement; m-substituents sit at the wrong nodes of the carbanion's molecular orbital and provide no stabilisation. That is why m-nitrochlorobenzene is barely more reactive than chlorobenzene itself.

Step 1. **Diagnose unreactivity.** Three structural defences sustain it: resonance shortening of $C-X$ (partial double-bond character, ~ 169 pm vs ~ 178 pm in CH_3Cl), sp^2 hybridisation at the ipso carbon (stronger bond), and a transition state that destabilises both S_N1 (aryl cation has empty orbital in the ring plane) and S_N2 (the π-cloud blocks back-side attack).

Step 2. **Plan the activation.** Add $-NO_2$ at o and/or p. The Meisenheimer intermediate now has resonance structures placing $(-)$ on the nitro oxygens, dropping its energy by tens of kJ/mol.

Step 3. **Quantify the rate gain.** Chlorobenzene needs $300°C$ and 300 atm (Dow process) to give phenol with $NaOH$. 2,4-Dinitrochlorobenzene reacts with aqueous $NaOH$ at $\sim 100°C$ and 1 atm. 2,4,6-Trinitrochlorobenzene (picryl chloride) reacts with H_2O at room temperature — a $\sim 10^{12}$ rate boost over chlorobenzene.

Step 4. **Industrial leverage.** The S_NAr activation strategy underpins the synthesis of sulphonamide drugs, herbicides, and azo dye intermediates, all built from o/p-nitrohaloarenes.

> **Final Answer:** Aryl halides are unreactive in classical S_N1/S_N2 because of resonance, hybridisation and TS effects. They react via S_NAr only when activated by $-NO_2$ (or similar $-M$) groups at o/p positions, which stabilise the Meisenheimer intermediate by resonance.

Chapter at a glance

- **Classes:** $\mathrm{R{-}X} \to 1^\circ/2^\circ/3^\circ$; *vic* (adjacent) vs *gem* (same carbon).
- $\mathrm{S_N2}$: bimolecular, Walden inversion, favoured by 1° + small strong nucleophile + polar aprotic solvent.
- $\mathrm{S_N1}$: unimolecular, racemisation, favoured by 3° (or allyl/benzyl) + polar protic solvent + weak nucleophile.
- **Elimination:** $\mathrm{E_2}$ favoured by strong bulky base (t-BuOK, alc. KOH); Saytzeff product dominates.
- **Aryl halides:** unreactive in $\mathrm{S_N}$; activated by o/p-$\mathrm{NO_2}$ via $\mathrm{S_NAr}$ (Meisenheimer intermediate).
- **Key named reactions:** Finkelstein ($\mathrm{R{-}X + NaI \longrightarrow R{-}I}$ in dry acetone), Swarts ($\mathrm{R{-}X + Hg_2F_2 \longrightarrow R{-}F}$), Wurtz ($\mathrm{2\,R{-}X + 2\,Na \longrightarrow R{-}R}$), Wurtz–Fittig ($\mathrm{Ar{-}X + R{-}X + 2\,Na \longrightarrow Ar{-}R}$), Sandmeyer ($\mathrm{ArN_2{}^+ \longrightarrow Ar{-}X + N_2}$ with CuX catalyst).
- **Leaving group order:** $\mathrm{I^- > Br^- > Cl^- > F^-}$.
- **Halogens on aryl ring:** deactivating but o/p-directing — the famous odd ones out of the EAS table.

End of NCERT Exemplar Problems (Representative Set)