collegedunia

Collegedunia NCERT Solutions

Step-by-step solutions, alternate methods & exam tips for Class 12 Chemistry

Chapter 6: Haloalkanes and Haloarenes

About this Chapter

Haloalkanes and haloarenes are hydrocarbons in which one or more hydrogen atoms have been replaced by halogen (F, Cl, Br, I). This chapter develops their **IUPAC nomenclature**, methods of preparation from alcohols, alkanes and alkenes, the S_N1 **and** S_N2 mechanisms with full stereochemistry, elimination ($E1/E2$) following **Saytzeff's rule**, and the contrasting low reactivity of haloarenes towards nucleophilic substitution. Optical activity, Walden inversion, Grignard reagents and major industrial halocompounds (DDT, freons, iodoform) are also covered.

Topics covered: Classification & IUPAC names • Preparation from alcohols, alkanes, alkenes • S_N1 vs S_N2 • Walden inversion • Chirality • Elimination ($E1/E2$) • Haloarenes • Grignard reagents • Wurtz & Wurtz–Fittig • Polyhalogen compounds (CCl_4, CHI_3, DDT, freons)

Quick Formula Sheet

S_N2 rate law:
rate $= k\,[\text{R–X}][\text{Nu}^-]$, one step, backside attack, inversion

S_N1 rate law:
rate $= k\,[\text{R–X}]$, two steps, carbocation, racemisation

Reactivity order S_N2:
$1^\circ > 2^\circ > 3^\circ$; R–I > R–Br > R–Cl > R–F

Reactivity order S_N1:
$3^\circ > 2^\circ > 1^\circ$ (carbocation stability)

Saytzeff's rule:
Major alkene = more highly substituted (more stable) one.

Finkelstein:
$\text{R–Cl} + \text{NaI} \xrightarrow{\text{dry acetone}} \text{R–I} + \text{NaCl}\,(s)$

Wurtz:
$2\,\text{R–X} + 2\,\text{Na} \xrightarrow{\text{dry ether}} \text{R–R} + 2\,\text{NaX}$

Grignard formation:
$\text{R–X} + \text{Mg} \xrightarrow{\text{dry ether}} \text{R–Mg–X}$

Exercise

Q 6.1 **Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:**

(i) $(CH_3)_2CHCH(Cl)CH_3$

(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

(iii) $CH_3CH_2C(CH_3)_2CH_2I$

(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$

(v) $CH_3CH(CH_3)CH(Br)CH_3$

(vi) $CH_3C(C_2H_5)_2CH_2Br$

(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$

(viii) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$

(ix) $CH_3CH{=}CHC(Br)(CH_3)_2$

(x) $p\text{-}ClC_6H_4CH_2CH(CH_3)_2$

(xi) $m\text{-}ClCH_2C_6H_4CH_2C(CH_3)_3$

(xii) $o\text{-}Br\text{-}C_6H_4CH(CH_3)CH_2CH_3$

SOLUTION

Concept used. The IUPAC name of a haloalkane is built from four pieces, in order:

(a) **Parent chain**: the longest continuous carbon chain that contains the carbon carrying the halogen.

(b) **Numbering**: number the parent chain from the end that gives the *lowest locant* to the first point of difference (halogen *vs.* alkyl substituents are treated equally; the lower set wins).

(c) **Substituent prefixes**: name halogens as *fluoro-, chloro-, bromo-, iodo-*, alkyls as *methyl, ethyl, . . .*, alphabetically (di-, tri- do not count for alphabetisation).

(d) **Suffix**: $-ane$ for the parent alkane, $-ene/-yne$ for unsaturated chains, and the locants of double/triple bonds get the lowest set after substituent locants are tied.

Classification rules.

- **Alkyl halide**: X on an sp^3 carbon of an open chain. It is **primary** (1°) if the carbon carrying X is bonded to one other carbon, **secondary** (2°) if bonded to two, **tertiary** (3°) if bonded to three.
- **Allyl halide**: X on an sp^3 carbon *next to* C=C (i.e. on the allylic carbon).
- **Benzyl halide**: X on the sp^3 carbon directly attached to a benzene ring.
- **Vinyl halide**: X on an sp^2 carbon of C=C.
- **Aryl halide**: X attached directly to an aromatic sp^2 ring carbon.

> ☞ **The "lowest locant" rule**
> If both numbering directions give the same first locant, compare the second, then third, etc. If all locants are equal, the alphabetically earlier substituent gets the smaller number.

Step 1. **(i) $(CH_3)_2CHCH(Cl)CH_3$.** Expand: $CH_3-CH(CH_3)-CH(Cl)-CH_3$. Longest chain through the C–Cl carbon = 4 carbons (butane). Numbering from the right gives Cl at C_2 and CH_3 substituent at C_3; *chloro* alphabetises before *methyl*, so chloro gets the smaller locant. Name: **2-chloro-3-methylbutane**. The Cl-bearing carbon is attached to two other carbons, hence **secondary (2°) alkyl halide**.

Step 2. **(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$.** The longest chain through C–Cl runs through the ethyl branch: $CH_3-CH_2-CH(CH_3)-CH(Cl)-CH_2-CH_3$ (6 C, hexane). Numbering from the Cl end gives Cl at C_3 and CH_3 at C_4. Name: **3-chloro-4-methylhexane**. The Cl-bearing carbon is bonded to two other carbons, hence **secondary (2°) alkyl halide**.

Step 3. **(iii) $CH_3CH_2C(CH_3)_2CH_2I$.** Longest chain = $I-CH_2-C(CH_3)_2-CH_2-CH_3$ (4 C through I; the second CH_3 on the quaternary carbon becomes a methyl substituent). Numbering from the I end gives I at C_1 and two methyls at C_2. Name: **1-iodo-2,2-dimethylbutane**. The I-carbon is bonded to one other carbon, hence **primary (1°) alkyl halide**.

Step 4. **(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$.** The Br sits on an sp^3 carbon directly attached to a benzene ring. Choose the benzene ring as the parent. Substituent: $-CH(Br)CH_2C(CH_3)_3$ which is 1-bromo-3, 3-dimethylbutyl. Name: **(1-bromo-3,3-dimethylbutyl)benzene**. Because Br is on the carbon directly attached to Ph, this is a **secondary (2°) benzyl halide**.

Step 5. **(v) $CH_3CH(CH_3)CH(Br)CH_3$.** Longest chain through C–Br = 4 C (butane). Numbering from the right gives Br at C_2 and CH_3 at C_3. *Bromo* alphabetises before *methyl*, so bromo gets the smaller locant. Name: **2-bromo-3-methylbutane**. The Br-carbon is bonded to two other carbons, hence **secondary (2°) alkyl halide**.

Step 6. **(vi) $CH_3C(C_2H_5)_2CH_2Br$.** Choose the longest chain through C–Br: $Br-CH_2-C(CH_3)(C_2H_5)-C_2H_5$ (4 C, butane). The remaining C_2H_5 and CH_3 become substituents at C_2. Name: **1-bromo-2-ethyl-2-methylbutane**. Br-carbon bonded to one other carbon, hence **primary (1°) alkyl halide**.

Step 7. **(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$.** Longest chain through C–Cl = 5 C (pentane). Numbering puts Cl at C_3 with a CH_3 also at C_3. Name: **3-chloro-3-methylpentane**. The Cl-carbon is bonded to three other carbons, hence **tertiary (3°) alkyl halide**.

Step 8. **(viii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$.** Parent chain = 6 C with one C=C.

Numbering from the left puts C=C between C_2 and C_3, Cl at C_3, CH_3 at C_5. Name: **3-chloro-5-methylhex-2-ene**. The Cl sits on an sp^2 carbon of C=C, hence **vinyl halide**.

Step 9. **(ix) $CH_3CH=CHC(Br)(CH_3)_2$.** Parent chain = 5 C with one C=C. Numbering must give the C=C (the principal characteristic) the lowest locant, so number from the left: $CH_3(C1)-CH(C2)=CH(C3)-C(Br)(CH_3)(C4)-CH_3(C5)$. C=C between C2 and C3 (locant 2 beats 3), Br at C4 and a methyl substituent at C4. Name: **4-bromo-4-methylpent-2-ene**. The Br-carbon is sp^3 and adjacent to C=C, hence **allyl halide** (and a **tertiary** one, since it is bonded to three other carbons).

Step 10. **(x) $p-ClC_6H_4CH_2CH(CH_3)_2$.** Parent: benzene ring; the substituent $-CH_2-CH(CH_3)_2$ is *2-methylpropyl* (isobutyl). Name: **1-chloro-4-(2-methylpropyl)benzene**. The Cl is on an aromatic ring carbon, hence **aryl halide**.

Step 11. **(xi) $m-ClCH_2C_6H_4CH_2C(CH_3)_3$.** The Cl sits on a benzylic $-CH_2-$ group. Substituents on the ring: $-CH_2Cl$ (chloromethyl) and $-CH_2C(CH_3)_3$ (2,2-dimethylpropyl). *meta* relationship = 1,3. Name: **1-(chloromethyl)-3-(2,2-dimethylpropyl)benzene**. Cl on a carbon directly bonded to the ring, hence **primary (1°) benzyl halide**.

Step 12. **(xii) $o-Br-C_6H_4CH(CH_3)CH_2CH_3$.** The side chain is *butan-2-yl* (*sec*-butyl) and the ring carries Br *ortho* (1,2) to it. Name: **1-bromo-2-(butan-2-yl)benzene**. Br on the aromatic ring, hence **aryl halide**.

Final Answer: See the bold IUPAC name and class type stated in each step above.

☞ Exam Tip

For aliphatic structures, draw the carbon skeleton first, mark the X, then count chains *through* X. For aromatic compounds with one short side chain, the side chain is usually a substituent on benzene (parent = benzene), but if the chain is long, switch the parent.

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

Structural observation. Treat naming as a two-pass problem: first pick the parent (longest chain through the halogen for aliphatics, the ring for aromatics with short branches), then assign locants. Classification is independent of the IUPAC name: just look at the hybridisation of the C attached to X and what else is on it.

- *Alkyl/Benzyl/Allyl*: X is on an sp^3 carbon.
- *Vinyl/Aryl*: X is on an sp^2 carbon.

- Further split sp^3 into $1^\circ/2^\circ/3^\circ$ by counting carbons on the C–X carbon.

Alternative approach: classification first. A useful shortcut for board questions is to do classification *before* naming. Drawing the carbon skeleton already tells you the hybridisation of the C– –X carbon, and one glance gives $1^\circ/2^\circ/3^\circ$, allyl, benzyl, vinyl or aryl. Once classified, the IUPAC name becomes almost mechanical: aryl/vinyl need the unsaturation/ring in the parent, allyl/benzyl give either choice of parent, and alkyl is always named as an alkane.

Step 1. Group the questions: (i), (ii), (v), (vii) are open-chain sp^3 halides, so they are named as substituted alkanes. (iii), (vi) have a quaternary carbon adjacent to CH_2X; the longest chain runs through one of the long arms, the other becomes a substituent.

Step 2. (iv), (xi) have the halogen on the benzylic CH_2 or CHR: *benzyl* class. Their names use benzene as the parent because the side chain is short.

Step 3. (viii) has Cl on sp^2 C=C carbon, so *vinyl*. (ix) has Br on an sp^3 carbon directly attached to C=C, so *allyl*. Watch the distinction: it is not the geometry of the bond, it is which carbon (allylic = next-door to C=C; vinylic = part of C=C).

Step 4. (x), (xii) have X on the ring carbon itself, so *aryl*. The chains hanging off the ring are substituents, named as *isobutyl* (= 2-methylpropyl) and *sec-butyl* (= butan-2-yl).

Step 5. Re-read every assigned name to check alphabetical order of prefixes, lowest locants, correct −ene/−yne for unsaturated chains.

Step 6. **Reactivity preview (concept linkage).** The class label tells you how the molecule will behave later in the chapter: 3° alkyl and benzyl/allyl tertiary go through S_N1; 1° alkyl go through S_N2; vinyl and aryl halides are nearly unreactive toward nucleophilic substitution because the C–X carbon is sp^2 and the bond has partial double-bond character.

Why this matters. The two questions “what is the IUPAC name?” and “what type of halide is it?” are independent and need two passes over the structure. JEE/NEET routinely test the *allyl vs. vinyl* and *benzyl vs. aryl* distinction because one carbon shift changes everything (reactivity, stability, mechanism). A typical 2-mark CBSE question asks “classify the following halide and write its IUPAC name” — both parts get full marks only if the class label matches what you draw.

Final Answer: (i) 2-chloro-3-methylbutane, 2° alkyl; (ii) 3-chloro-4-methylhexane, 2° alkyl; (iii) 1-iodo-2,2-dimethylbutane, 1° alkyl; (iv) (1-bromo-3,3-dimethylbutyl)benzene, 2° benzyl; (v) 2-bromo-3-methylbutane, 2° alkyl; (vi) 1-bromo-2-ethyl-2-methylbutane, 1° alkyl; (vii) 3-chloro-3-methylpentane, 3° alkyl; (viii) 3-chloro-5-methylhex-2-ene, vinyl; (ix) 4-bromo-4-methylpent-2-ene, 3° allyl; (x) 1-chloro-4-(2-methylpropyl)benzene, aryl; (xi) 1-(chloromethyl)-3-(2,2-dimethylpropyl)benzene, 1° benzyl; (xii) 1-bromo-2-(butan-2-yl)benzene, aryl.

Q 6.2 **Give the IUPAC names of the following compounds:**

(i) $CH_3CH(Cl)CH(Br)CH_3$

(ii) $CHF_2CBrClF$

(iii) $ClCH_2C{\equiv}CCH_2Br$

(iv) $(CCl_3)_3CCl$

(v) $CH_3C(p-ClC_6H_4)_2CH(Br)CH_3$

(vi) $(CH_3)_3CCH{=}CClC_6H_4I-p$

SOLUTION

Concept used. For polyhalogenated compounds, treat each halogen as a separate substituent and list them alphabetically (*bromo, chloro, fluoro, iodo*). For chains with multiple halogens, give the *lowest set of locants* to the substituents collectively. When the parent has a triple bond, use the suffix $-yne$.

Step 1. **(i)** $CH_3CH(Cl)CH(Br)CH_3$**.** Parent: butane (4 C). Numbering from either end gives substituents at C2 and C3, a tie. *Bromo* alphabetises before *chloro*, so Br must get the smaller locant. Number from the right. Name: **2-bromo-3-chlorobutane**.

Step 2. **(ii)** $CHF_2CBrClF$**.** Parent: ethane (2 C). Number from the right so the larger cluster of substituents gets the lower locant. C1 carries Br, Cl, F; C2 carries F, F. Name: **1-bromo-1-chloro-1,2,2-trifluoroethane**.

Step 3. **(iii)** $ClCH_2C{\equiv}CCH_2Br$**.** Parent: 4 C with a triple bond, i.e. but-2-yne. *Bromo* alphabetises before *chloro*, so Br gets locant 1. Name: **1-bromo-4-chlorobut-2-yne**.

Step 4. **(iv)** $(CCl_3)_3CCl$**.** The central carbon is bonded to three CCl_3 groups and one Cl. The longest chain through it is 2 C (ethane). Substituents: three Cl on C2 (2,2,2-trichloro), one Cl on C1 and two CCl_3 (trichloromethyl) on C1. Alphabetise on the substituent root: *chloro* (c) before *trichloromethyl* (t). Name: **1,2,2,2-tetrachloro-1,1-bis(trichloromethyl)ethane**.

Step 5. **(v) $CH_3C(p-ClC_6H_4)_2CH(Br)CH_3$.** Parent: butane. From the right, Br at C_2; two *p*-chlorophenyl groups at C_3. Name: **2-bromo-3,3-bis(4-chlorophenyl)butane**.

Step 6. **(vi) $(CH_3)_3CCH=CClC_6H_4I-p$.** The longest chain through C=C runs through the *tert*-butyl carbon out to the =CCl: 4 C (but-1-ene). The *p*-iodophenyl sits on C1, Cl on C1, and the *tert*-butyl's three methyls put two more methyls and the chain end on C3. Name: **1-chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene**.

Final Answer: (i) 2-bromo-3-chlorobutane; (ii) 1-bromo-1-chloro-1,2,2-trifluoroethane; (iii) 1-bromo-4-chlorobut-2-yne; (iv) 1,2,2,2-tetrachloro-1,1-bis(trichloromethyl)ethane; (v) 2-bromo-3,3-bis(4-chlorophenyl)butane; (vi) 1-chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene.

✗ Common Mistake

Students often forget that multiplying prefixes (*di-, tri-, bis-*) do not count for alphabetising. Alphabetise the substituent root: *trichloromethyl* sits under "t", not "b".

EXPERT'S SOLUTION *: Sneha Iyer, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Polyhalogen names are a discipline problem, not a chemistry problem. Step through three checks: (a) identify the parent chain, (b) number so the substituents take the lowest set, (c) write substituents alphabetically.

Alphabetisation rule, expanded. When two substituents tie for the locant, the *first letter of the substituent root* (not the multiplying prefix) decides which gets the smaller number. So *di*methyl alphabetises as "m"; *tri*chloromethyl alphabetises as "t"; *bis*(4-chlorophenyl) alphabetises as "c" (chlorophenyl). For (iv), the substituent *trichloromethyl* comes after *chloro* alphabetically, so *chloro* locants are written first.

Step 1. For (i), the chain is short and the two halogens differ: *bromo* alphabetises before *chloro*, so it must take the smaller locant. Number from the right.

Step 2. For (ii), the parent is ethane. Pick the end with the larger substituent cluster. 1-Br + 1-Cl + 1-F + 2,2-(F,F) gives three F atoms, so the trifluoro prefix is 1,2,2.

Step 3. For (iii), the locant of the triple bond and the locant of the lowest-set substituents are both 2: tie. Use alphabet: bromo < chloro, so bromo gets the 1 position.

Step 4. For (iv), the chain is just two carbons. Three CCl_3 groups become three *trichloromethyl* substituents. Locants: 1,2,2,2-tetrachloro plus 1,1-bis(trichloromethyl). Note "bis" (not "di") because the substituent name

trichloromethyl is itself a compound name.

Step 5. For (v) and (vi), the aryl groups go in parentheses with their substitution locant: *4-chlorophenyl*, *4-iodophenyl*. In (vi) the C=C is between C1 and C2 of a but-1-ene chain.

Step 6. **Cross-check.** Re-read each name and rebuild the structure on paper; if you can recover the input formula unambiguously, the name is correct. This back-translation is the surest way to catch wrong locants.

Why this matters. The 2026–27 syllabus emphasises modern IUPAC formatting (locants attached to the suffix, e.g. "but-2-ene" not "2-butene"), and numbering questions appear every year in board papers as 1- and 2-mark questions.

Final Answer: Same six names as in the main solution.

☞ **Multiplying prefixes *do not* alphabetise**

di-, tri-, tetra- are ignored for alphabetisation, but *iso-, sec-, tert- are* included (they are part of the substituent name). So *isopropyl* alphabetises under "i", not "p".

Q 6.3 **Write the structures of the following organic halogen compounds:**

(i) 2-Chloro-3-methylpentane

(ii) p-Bromochlorobenzene

(iii) 1-Chloro-4-ethylcyclohexane

(iv) 2-(2-Chlorophenyl)-1-iodooctane

(v) 2-Bromobutane

(vi) 4-tert-Butyl-3-iodoheptane

(vii) 1-Bromo-4-sec-butyl-2-methylbenzene

(viii) 1,4-Dibromobut-2-ene

SOLUTION

Concept used. To turn a name into a structure we work *backwards* through the IUPAC rules: read the parent (chain length, saturated/unsaturated, cyclic), then place substituents at their locants, then check that the locants are the lowest possible set.

Step 1. **(i) 2-Chloro-3-methylpentane.** Pentane = 5 C chain. Place Cl at C2 and CH_3 at C3:

$$CH_3-CH(Cl)-CH(CH_3)-CH_2-CH_3.$$

Step 2. **(ii) *p*-Bromochlorobenzene.** *para* means 1,4 disubstitution on a benzene ring;

place Br at C1 and Cl at C4:

$$\mathrm{Br{-}C_6H_4{-}Cl}\ (1,4).$$

Step 3. **(iii) 1-Chloro-4-ethylcyclohexane.** Cyclohexane has 6 ring carbons; place Cl at C1 and C_2H_5 at C4 (across the ring).

Step 4. **(iv) 2-(2-Chlorophenyl)-1-iodooctane.** Octane = 8 C chain; I at C1, and at C2 we attach *2-chlorophenyl* (a benzene ring with Cl at its *ortho* position relative to the link):

$$\mathrm{I{-}CH_2{-}CH(o{-}ClC_6H_4){-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}.$$

Step 5. **(v) 2-Bromobutane.** Butane = 4 C; Br at C2:

$$\mathrm{CH_3{-}CH(Br){-}CH_2{-}CH_3}.$$

Step 6. **(vi) 4-tert-Butyl-3-iodoheptane.** Heptane = 7 C; I at C3 and $-\mathrm{C(CH_3)_3}$ at C4:

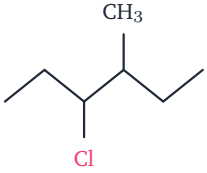
$$\mathrm{CH_3CH_2{-}CH(I){-}CH(C(CH_3)_3){-}CH_2{-}CH_2{-}CH_3}.$$

Step 7. **(vii) 1-Bromo-4-*sec*-butyl-2-methylbenzene.** Benzene ring; Br at C1, CH_3 at C2, *sec*-butyl ($= \mathrm{CH(CH_3)CH_2CH_3}$) at C4.

Step 8. **(viii) 1,4-Dibromobut-2-ene.** But-2-ene means a 4 C chain with C=C between C2 and C3; place Br at C1 and C4:

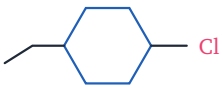
$$\mathrm{BrCH_2{-}CH{=}CH{-}CH_2Br}.$$

(i) 2-chloro-3-methylpentane

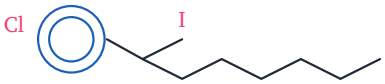


(ii) *p*-bromochlorobenzene

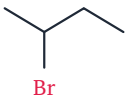
(iii) 1-chloro-4-ethylcyclohexane



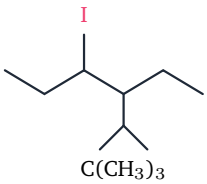
(iv) 2-(2-chlorophenyl)-1-iodooctane



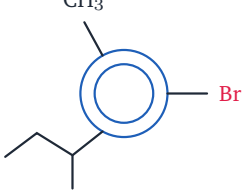
(v) 2-bromobutane



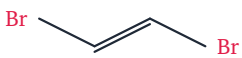
(vi) 4-*tert*-butyl-3-iodoheptane



(vii) 1-bromo-4-*sec*-butyl-2-methylbenzene



(viii) 1,4-dibromobut-2-ene



Final Answer: Structures drawn step-by-step above.

EXPERT'S SOLUTION *: Riya Banerjee, Ph.D Organic Chemistry, IISc Bangalore*

Picture-first. Name → structure is the inverse of naming. Read the parent first (chain length and saturation), then walk through the locants and attach substituents at the named positions. Treat aryl substituents like *2-chlorophenyl* as sub-named groups: a phenyl ring with a chloro at the *ortho* (2-) position.

Decoding nested substituent names. When a name has a substituent in parentheses, *both* the name outside and inside need parsing. "2-(2-chlorophenyl)-1-iodooctane" decodes as: parent = octane (8 C); at C1 attach iodine; at C2 attach "2-chlorophenyl" (a phenyl ring where its own C2 carries Cl). The parenthesised number always refers to the substituent's own numbering, not the parent chain's.

Step 1. For (i), (v), (vi), (viii) the parent is an open-chain alkane/alkene. Draw the chain, number left to right by default, drop substituents at the listed locants.

Step 2. For (ii), (vii) the parent is benzene. Reduce the substituent names to fragments (Br, Cl, CH_3, *sec*-butyl). Place at the listed ring positions. Remember *para* = 1,4 and *ortho* = 1,2.

Step 3. For (iii) the parent is a 6-membered ring (cyclohexane); place substituents diametrically.

Step 4. For (iv) the parent is an 8-C chain (octane). The phrase "2-(2-chlorophenyl)" attaches a benzene ring at C2 of the octane chain, and the benzene ring itself carries a Cl at its own C2 (the ring carbon adjacent to the link).

Step 5. For (vi) the common-name fragment *tert*-butyl = $-C(CH_3)_3$ attaches like any other substituent; *sec*-butyl in (vii) is $-CH(CH_3)CH_2CH_3$. Memorise the four C_4 substituent fragments (n-, iso-, sec-, tert-) since they recur in CBSE questions.

Step 6. Sanity-check: re-derive the IUPAC name from each drawn structure to confirm it matches. If the recovered name differs in any locant, your placement is wrong.

Why this matters. Reversibility (name ↔ structure) is a key NCERT exam ask. Practising both directions on the same compound trains the eye. In the 2-mark NCERT format, half marks are for the structure and half for showing the locant assignment; neat structural drawings get full marks even without a re-derivation step.

Final Answer: Structures as drawn in the main solution.

☞ Exam Tip

When you must draw a structure from a name, sketch the parent backbone first as a zigzag and *number every carbon*. Only then attach the substituents. Drawing in this order eliminates "where does locant 3 sit?" confusion in (iv), (vi), (vii).

Q 6.4 **Which one of the following has the highest dipole moment?**

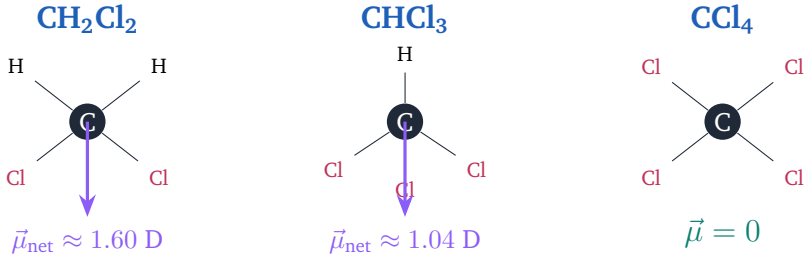
(i) CH_2Cl_2

(ii) $CHCl_3$

(iii) CCl_4

SOLUTION

Concept used. The molecular dipole moment ($\vec{\mu}$) is the vector sum of the individual bond dipoles. In a symmetric molecule, equal and opposite bond dipoles cancel, giving $\vec{\mu} = 0$. In an asymmetric molecule, the cancellation is incomplete, so the molecule has a net dipole. The magnitude depends on (i) the orientation of bond dipoles and (ii) whether C–H contributions reinforce or oppose the C–Cl contributions.



Step 1. **Identify the geometry.** All three molecules are tetrahedral (the central C is sp^3). Bond angles are close to $109.5°$.

Step 2. **CCl_4.** Four identical C–Cl bonds at tetrahedral angles. By symmetry, the four bond dipoles cancel exactly: $\vec{\mu}_{CCl_4} = 0$ D.

Step 3. **CH_2Cl_2.** Two C–Cl dipoles point "downwards" (towards the chlorines), and two C–H dipoles point "upwards" (towards the hydrogens, because C is more electronegative than H so the bond dipole points C $\rightarrow$ H, i.e. outward at H). The two pairs of dipoles point in the *same* general direction along the bisector axis, so they *add*. The measured value is $\mu \approx 1.60$ D.

Step 4. **$CHCl_3$.** One C–H dipole and three C–Cl dipoles. The three C–Cl dipoles partially cancel each other; their axial components point opposite to the C–H dipole. The two contributions therefore *partially oppose*: the net is $\mu \approx 1.04$ D.

Step 5. **Compare.**

$$\mu(CH_2Cl_2) > \mu(CHCl_3) > \mu(CCl_4) = 0.$$

So CH_2Cl_2 has the largest dipole moment.

Final Answer: **CH_2Cl_2** has the highest dipole moment (~ 1.60 D), because the C–H and C–Cl bond dipoles add constructively, whereas in $CHCl_3$ they partly oppose, and in CCl_4 they cancel entirely.

★ Why the textbook value of $CHCl_3$ is smaller than CH_2Cl_2

Even though $CHCl_3$ has more polar C–Cl bonds, the three C–Cl bond moments have a resultant pointing opposite to the C–H bond moment, so part of the dipole is cancelled. In CH_2Cl_2 the resultants reinforce.

EXPERT'S SOLUTION *: Aditya Verma, Ph.D Organic Chemistry, IISc Bangalore*

Picture-first. Draw the tetrahedron and add bond-dipole vectors from C toward the more electronegative end of each bond. The *vector sum* is the molecular dipole.
Vector intuition. Treat each bond dipole as a vector of length μ_{bond} pointing from the less- to the more-electronegative atom. For symmetric arrangements (tetrahedral, trigonal-planar, linear) where all four bonds are equal, the resultant is zero. The moment a single atom is swapped (say Cl for H), one of the cancelling vectors is replaced by a different vector, and the resultant becomes non-zero. The size of the resultant depends on the *angle* between the surviving cluster vectors.

Step 1. CCl_4: four equal C–Cl vectors arranged tetrahedrally. The sum of vectors from the centre of a regular tetrahedron to its four vertices is the zero vector. Hence $\mu = 0$ D.

Step 2. $CHCl_3$: replace one Cl of CCl_4 with H. The C–H bond dipole points toward C (since $\chi_C > \chi_H$), opposite to the C–Cl dipole that was removed. The single C–H dipole partly opposes the net C–Cl dipole, so the molecule has a small net moment, ~ 1.04 D.

Step 3. CH_2Cl_2: two C–Cl dipoles and two C–H dipoles, with the two halves on opposite faces of the tetrahedron. The vector sums of the two C–Cl dipoles and of the two C–H dipoles point in the *same* direction, so they add. Net $\mu \approx 1.60$ D, the largest of the three.

Step 4. Experimental dipole moments (NCERT Table 6.2): $CH_3Cl = 1.86$ D, $CH_2Cl_2 = 1.60$ D, $CHCl_3 = 1.04$ D, $CCl_4 = 0$ D. The trend $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$ is governed by symmetry, not by the count of polar bonds.

Step 5. **Common pitfall to avoid.** "More C–Cl bonds means higher dipole" is wrong. The dipole of CH_3Cl is even larger than CH_2Cl_2 although it has fewer Cl atoms, because in CH_3Cl all three C–H dipoles add constructively with the single C–Cl along the C–Cl axis.

Step 6. **Numerical cross-check.** A back-of-envelope estimate for CH_2Cl_2: each C–Cl bond moment is about 1.5 D; with a Cl–C–Cl angle of $\sim 109.5°$ the resultant of the two C–Cl dipoles is $2 \times 1.5 \cos(54.7°) \approx 1.73$ D, then add the two C–H contributions (~ 0.4 D each, in the same direction) and you reach the observed ~ 1.6 D.

Why this matters. Counting polar bonds is a beginner's trap. Always sketch the

geometry and add vectors. The same vector logic explains why *p*-dichlorobenzene has $\mu = 0$ while *o*- and *m*-isomers do not (Q 6.18), why NH_3 and NF_3 differ in dipole sign, and why CO_2 ($\mu = 0$) and H_2O ($\mu \neq 0$) behave so differently.

Final Answer: CH_2Cl_2 has the highest dipole moment.

♥ Symmetry → dipole → physical properties

A zero dipole molecule like CCl_4 has no permanent dipole-dipole interactions, so its boiling point (77°C) is governed only by London forces (large because of four heavy Cl atoms). CH_2Cl_2 has $\mu = 1.60$ D and boils at 40°C: lower because the molecule is smaller, despite the higher dipole. Boiling-point predictions need *both* dipole and dispersion considered.

Q 6.5 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

SOLUTION

Concept used. The degree of unsaturation Ω for a hydrocarbon $C_n H_m$ is

$$\Omega = \frac{2n + 2 - m}{2}.$$

Ω counts the total number of rings + double bonds + triple bonds (each double = 1, each triple = 2, each ring = 1). For C_5H_{10}, $\Omega = (10 + 2 - 10)/2 = 1$, so the molecule has exactly one ring or one C=C.

☞ Why "no reaction in the dark" rules out an alkene

Alkenes react with Cl_2 in the dark by electrophilic addition across the C=C (no light needed). If a C_5H_{10} compound does *not* react with Cl_2 in the dark, it cannot contain a C=C. So $\Omega = 1$ must come from a ring: the compound is a cycloalkane.

Step 1. Compute Ω for C_5H_{10}: $\Omega = (2 \cdot 5 + 2 - 10)/2 = 2/2 = 1$. One ring or one double bond.

Step 2. "Dark + no reaction" rules out a C=C. The compound is a cyclopentane (C_5H_{10}, one ring).

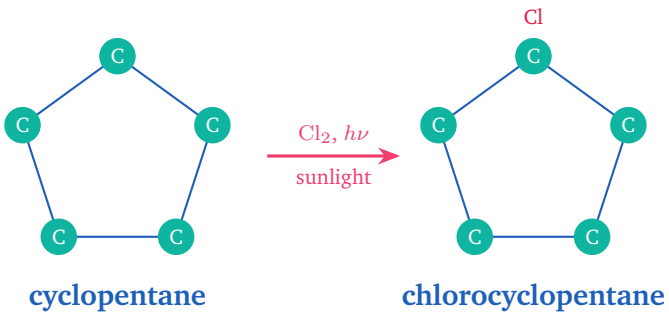
Step 3. Alkanes and cycloalkanes react with Cl_2 in *sunlight* by a free-radical chain: initiation $Cl_2 \xrightarrow{h\nu} 2\,Cl^{\bullet}$, propagation $Cl^{\bullet} + R{-}H \longrightarrow H{-}Cl + R^{\bullet}$ and $R^{\bullet} + Cl_2 \longrightarrow R{-}Cl + Cl^{\bullet}$.

Step 4. "One single monochloride" means *all the C–H bonds in the molecule are equivalent*. Among the C_5H_{10} cycloalkanes, only **cyclopentane** has every hydrogen equivalent (a 5-membered ring with all $-CH_2-$ groups chemically

identical).

Step 5. Verify: chlorination of cyclopentane gives only chlorocyclopentane:

$$C_5H_{10} + Cl_2 \xrightarrow{h\nu} C_5H_9Cl + HCl.$$



cyclopentane **chlorocyclopentane**

Final Answer: The hydrocarbon is **cyclopentane**, C_5H_{10}. Its monochloride is **chlorocyclopentane**.

☞ Exam Tip

"Single product on photochlorination" is a strong NCERT-style hint: it means every C–H bond in the parent is equivalent. For C_5H_{10} this immediately picks out cyclopentane; for C_5H_{12} it picks out neopentane (2,2-dimethylpropane).

EXPERT'S SOLUTION *: Arjun Singh, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Two clues, two filters: "no dark reaction with Cl_2" eliminates alkenes; "single monochloride" demands all-equivalent hydrogens.

Symmetry counting in detail. To check whether all H's in a cycloalkane are equivalent, draw the ring and mark each ring carbon. Use the ring's rotational and mirror symmetry to test if any two H's can be carried into each other by a symmetry operation. For cyclopentane, the D_{5h} symmetry has C_5 rotational axis: any ring CH_2 can be carried onto any other by a 72° rotation, and the two H's on each CH_2 are related by the in-plane mirror. All 10 H's are equivalent.

Step 1. Filter 1: "no reaction in dark with Cl_2" means no C=C. Since the formula C_5H_{10} has one degree of unsaturation, that unsaturation must be a ring.

Step 2. Filter 2: "single monochloride" means there is only one kind of C–H. For five-carbon cycloalkanes, the candidates are cyclopentane (all 10 H's equivalent), methylcyclobutane (4 kinds of H), and ethylcyclopropane (5 kinds of H). Only cyclopentane survives.

Step 3. Reaction is photochemical ($Cl_2 \xrightarrow{h\nu} 2\,Cl^\bullet$); the $Cl^\bullet$ radical abstracts an H to give

a 5-membered radical, which reacts with Cl_2 to give the monochloride. The overall stoichiometry is $C_5H_{10} + Cl_2 \longrightarrow C_5H_9Cl + HCl$.

Step 4. Confirm by counting hydrogens: cyclopentane has 10 equivalent C–H bonds, so abstracting any of them gives the same radical and the same product.

Step 5. **Common pitfall to avoid.** Don't forget that methylcyclobutane and ethylcyclopropane also satisfy C_5H_{10} and have one ring (so $\Omega = 1$, no C=C). It is the "single monochloride" clue that rules them out, not the dark-test clue.

Step 6. **Concept linkage.** The same reasoning identifies neopentane (2,2-dimethylpropane, C_5H_{12}) from radical bromination giving a single monobromide; both compounds have T_d-related symmetry that puts all C–H's in one equivalence class.

Why this matters. Substitution-selectivity problems on hydrocarbons reduce to symmetry counting. Practice on C_4H_{10} (only n-butane and isobutane), C_5H_{12} (the three pentanes), and C_5H_{10}. In JEE-Mains the question is often phrased "which hydrocarbon gives only one monobromide?" — the answer is always the most symmetric one.

Final Answer: Cyclopentane.

Q 6.6 Write the isomers of the compound having formula C_4H_9Br.

SOLUTION

Concept used. "Isomers of C_4H_9Br" means all structures consistent with the molecular formula. We enumerate the carbon skeletons of C_4H_{10} (namely n-butane and isobutane) and substitute one H by Br in every non-equivalent position.

Step 1. **n-Butane skeleton** $CH_3-CH_2-CH_2-CH_3$: the two terminal CH_3 groups are equivalent (one kind of H); the two internal CH_2 groups are equivalent (a second kind of H). Substituting gives:

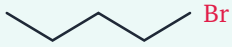
- **1-Bromobutane**: $CH_3-CH_2-CH_2-CH_2Br$ (primary, 1°).
- **2-Bromobutane**: $CH_3-CH_2-CH(Br)-CH_3$ (secondary, 2°). This carbon has four different groups (H, Br, CH_3, CH_2CH_3), so it is a **stereocentre**; the compound exists as a pair of enantiomers (R and S).

Step 2. **Isobutane skeleton** $(CH_3)_3CH$: the three CH_3 groups are equivalent (one kind of H); the lone central CH is a second kind of H. Substituting gives:

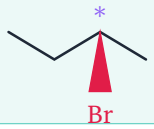
- **1-Bromo-2-methylpropane (isobutyl bromide)**: $(CH_3)_2CH-CH_2Br$ (1°).
- **2-Bromo-2-methylpropane (*tert*-butyl bromide)**: $(CH_3)_3C-Br$ (3°).

Step 3. Therefore there are **four constitutional isomers** of C_4H_9Br, namely 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. Counting the enantiomeric pair of 2-bromobutane, **five total stereoisomers** exist.

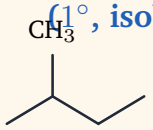
(a) 1-bromobutane (1°)



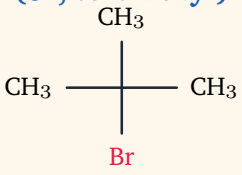
(b) 2-bromobutane (2°, chiral)



(c) 1-bromo-2-methylpropane (1°, isobutyl)



(d) 2-bromo-2-methylpropane (3°, *tert*-butyl)



Final Answer: Four constitutional isomers: 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. 2-Bromobutane itself comes as a pair of enantiomers (R and S), giving five total stereoisomers.

EXPERT'S SOLUTION *: Pranav Nair, M.Sc Chemistry, IIT Kanpur*

Structural observation. C_4H_9Br is saturated with no rings: enumerate by carbon skeleton, then by H-replacement position.

Two-step enumeration recipe. For any $C_n H_{2n+1} X$: (1) list all carbon skeletons of $C_n H_{2n+2}$; for $n = 4$ that is 2 (n-butane, isobutane); for $n = 5$ that is 3 (n-pentane, isopentane, neopentane). (2) On each skeleton, identify each set of equivalent H's and substitute one at a time. The number of constitutional isomers equals the sum of inequivalent H sets across skeletons.

Step 1. For C_4 the two carbon skeletons are n-butane (linear) and isobutane (branched).

Step 2. In n-butane, two non-equivalent H positions exist (terminal CH_3 and internal CH_2): 1-bromobutane and 2-bromobutane.

Step 3. In isobutane, two non-equivalent H positions exist (terminal CH_3 on any of the three equivalent arms, and the central CH): 1-bromo-2-methylpropane and 2-bromo-2-methylpropane.

Step 4. 2-Bromobutane has a stereocentre at C2 (four different groups: H, Br, methyl, ethyl): it is chiral and exists as a pair of enantiomers.

Step 5. **Identity check.** Confirm each isomer by counting H's: 1-Br-butane $= C_4H_9Br$ (3+2+2+2 H + 0 on Br C $= 9$ H, ✓); 2-Br-butane $= 3+2+1+3 = 9$ H ✓; isobutyl bromide $= 6+1+2 = 9$ H ✓; t-butyl bromide $= 9+0 = 9$ H ✓. All match the molecular formula.

Step 6. **Class of each.** 1-Br-butane (1°), 2-Br-butane (2°), isobutyl bromide (1°), t-butyl bromide (3°). The two primaries give slow S_N1; the secondary mixes S_N1/S_N2; the tertiary gives only S_N1 (and $E1$).

Why this matters. Counting isomers is a common JEE/CBSE Q. The recipe (skeletons × non-equivalent H sites) generalises to any $C_n H_{2n+1} X$. The same enumeration template also produces all isomers of C_5H_{12} (3), $C_5H_{11}Br$ (8), and other simple haloalkane problems.

> **Final Answer:** Four constitutional isomers; 2-bromobutane adds an R/S pair for a total of five stereoisomers.

✗ Common Mistake

A common slip is to count R- and S-2-bromobutane as two *constitutional* isomers. They are not — they are *stereoisomers* of the same constitutional isomer. The four constitutional isomers are unambiguous; the count rises to five only when stereoisomers are explicitly included.

Q 6.7 Write the equations for the preparation of 1-iodobutane from
(i) 1-butanol
(ii) 1-chlorobutane
(iii) but-1-ene.

SOLUTION

Concept used. 1-Iodobutane ($CH_3CH_2CH_2CH_2I$) can be prepared from each precursor by a different route:

- *From an alcohol*: convert $-$OH to $-$I using red phosphorus and iodine, which generates HI *in situ*.
- *From a chloroalkane*: a **Finkelstein reaction** in dry acetone: NaI dissolves in acetone whereas NaCl does not. Precipitation of NaCl drives the equilibrium toward the iodide.
- *From an alkene*: anti-Markovnikov addition of HBr with peroxide (Kharasch effect)

gives 1-bromobutane, which is converted to 1-iodobutane by Finkelstein exchange. Peroxide effect does not work for HI, so we cannot go directly from but-1-ene to 1-iodobutane.

Step 1. **(i) From 1-butanol.**

$$\mathrm{CH_3CH_2CH_2CH_2OH + HI \xrightarrow{\Delta} CH_3CH_2CH_2CH_2I + H_2O.}$$

The HI is generated from red P and I_2:

$$\mathrm{3\,CH_3CH_2CH_2CH_2OH + P + \frac{3}{2}\,I_2 \longrightarrow 3\,CH_3CH_2CH_2CH_2I + H_3PO_3.}$$

Mechanism: HI protonates the alcohol O to give the oxonium $\mathrm{R-OH_2^+}$, which is attacked by I^- in an S_N2 step (backside attack on C, water leaves).

Step 2. **(ii) From 1-chlorobutane (Finkelstein).**

$$\mathrm{CH_3CH_2CH_2CH_2Cl + NaI \xrightarrow{dry\,acetone} CH_3CH_2CH_2CH_2I + NaCl\,(s).}$$

Mechanism is S_N2: I^- attacks the primary C–Cl carbon from the back, displacing Cl^-. The reaction is driven by precipitation of NaCl (insoluble in acetone).

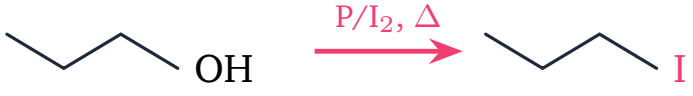
Step 3. **(iii) From but-1-ene.** Two-step sequence. *Step (a): anti-Markovnikov addition of HBr with peroxide* (Kharasch effect):

$$\mathrm{CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{peroxide} CH_3CH_2CH_2CH_2Br.}$$

Mechanism: peroxide initiates $Br^\bullet$, which adds to the terminal C (giving the more stable secondary radical); chain transfer with HBr gives 1-bromobutane. *Step (b): Finkelstein exchange*:

$$\mathrm{CH_3CH_2CH_2CH_2Br + NaI \xrightarrow{dry\,acetone} CH_3CH_2CH_2CH_2I + NaBr\,(s).}$$

Route (i): from 1-butanol



Route (ii): Finkelstein

Route (iii): from but-1-ene

Final Answer: (i) $CH_3CH_2CH_2CH_2OH \xrightarrow{HI,\,\Delta} CH_3CH_2CH_2CH_2I$;
(ii) $CH_3CH_2CH_2CH_2Cl + NaI \xrightarrow{acetone} CH_3CH_2CH_2CH_2I + NaCl$;
(iii) $CH_3CH_2CH{=}CH_2 \xrightarrow{HBr/peroxide} CH_3CH_2CH_2CH_2Br \xrightarrow{NaI,acetone}$
$CH_3CH_2CH_2CH_2I$.

★ Peroxide effect (Kharasch)

HBr adds anti-Markovnikov to an asymmetric alkene *only in the presence of peroxides*, because the chain runs via radicals: peroxide gives $Br^{\bullet}$; $Br^{\bullet}$ adds to the alkene to form the more stable secondary radical; that radical abstracts H from HBr to give the anti-Markovnikov product. HCl and HI do not follow this because their corresponding chain steps are endothermic.

EXPERT'S SOLUTION *: Karan Reddy, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Aim at the same end product $CH_3CH_2CH_2CH_2I$ from three different starting points: a hydroxyl, a chloride, and an alkene.

Alternative reagents (board-friendly substitutes). For (i), $SOCl_2$ then NaI/acetone is a longer but equally valid two-step route to the chloride first, then Finkelstein. PCl_5 or PCl_3 would give the chloride from the alcohol if you prefer working through 1-chlorobutane. NCERT explicitly mentions P + I_2/red P for direct conversion to the iodide.

Step 1. For *1-butanol*, the practical lab reagent is P + I_2, which yields HI *in situ*. The overall stoichiometry is $3\,ROH + P + \frac{3}{2}\,I_2 \longrightarrow 3\,RI + H_3PO_3$. Each ROH gets attacked by HI in two steps: protonate OH, then S_N2 by I^-.

Step 2. For *1-chlorobutane*, Finkelstein. The driving force is differential solubility: NaI is soluble in dry acetone, but the product NaCl is not. Le Chatelier pulls the equilibrium fully to the right.

Step 3. For *but-1-ene*, do not try direct HI addition (it gives 2-iodobutane, not the desired 1-iodobutane). Instead, Kharasch-add HBr/peroxide to get 1-bromobutane (anti-Markovnikov), then Finkelstein to swap Br for I.

Step 4. Confirm regioselectivity in step (iii): $Br^{\bullet}$ adds to the terminal CH_2 (less substituted carbon) because that puts the radical on the more substituted (more stable) secondary carbon.

Step 5. **Why HI peroxide doesn't work.** The H–I bond (~ 297 kJ/mol) is much weaker than C–I (~ 234 kJ/mol), so the chain-transfer step $R^{\bullet} + HI \longrightarrow R{-}H + I^{\bullet}$ is exothermic (favourable) but the alkene-addition step $I^{\bullet} + C{=}C \longrightarrow I{-}C{-}C^{\bullet}$ is too endothermic to sustain a chain. So peroxide effect runs cleanly only for

HBr, not HI or HCl.

Step 6. **Concept linkage.** This question previews retrosynthesis: every chain-modifying disconnection in organic chemistry comes back to one of these named transformations (alcohol → halide → Finkelstein, alkene → Markovnikov/anti-Markovnikov HX).

Why this matters. These three routes summarise the three canonical disconnections to a primary alkyl iodide. In a CBSE board question, examiners explicitly state "write three different conversions" to test whether students can pick the correct reagent for each starting material.

> **Final Answer:** (i) P/I_2 on 1-butanol; (ii) NaI/acetone on 1-chlorobutane; (iii) HBr/peroxide on but-1-ene, then NaI/acetone.

☞ **Memorise the Finkelstein driving force**

NaCl (and NaBr) are *insoluble* in dry acetone; NaI is soluble. So $\mathrm{R{-}Cl + NaI \xrightarrow{acetone} R{-}I + NaCl(s)}$ removes one product from solution and pulls the equilibrium fully right — works even when C−I vs C−Cl thermodynamics are nearly even.

Q 6.8 What are ambident nucleophiles? Explain with an example.

SOLUTION

Concept used. A nucleophile is a species with a lone pair (or π-electrons) that attacks an electrophilic centre. An **ambident nucleophile** (Latin *ambi-* = both, *dent* = tooth) has *two* different reactive sites; either can serve as the donor. Which site attacks depends on:

- the hardness/softness of the nucleophile and electrophile (HSAB principle: hard prefers hard, soft prefers soft);
- the mechanism (S_N2 vs S_N1);
- the solvent, the temperature, and the kinetic-vs- thermodynamic control.

☞ **The classical example: cyanide ion CN^-**

CN^- has lone pairs on both C and N. Attack via C gives an **alkyl cyanide** (nitrile) R−C≡N; attack via N gives an **alkyl isocyanide** R−N≡C.

Step 1. **Cyanide ion** CN^- has lone pairs on both C and N (resonance pushes negative charge between the two ends). Both ends are nucleophilic.

Step 2. With KCN (ionic salt, polar solvent), the C end is the more nucleophilic end and

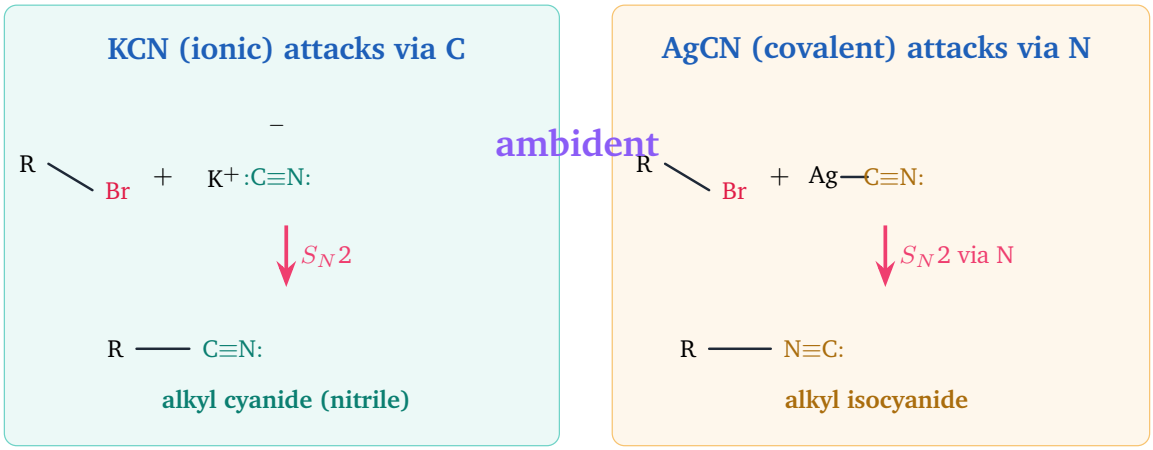
attacks the alkyl halide:

$$\mathrm{R{-}X + K^{+}CN^{-} \longrightarrow R{-}C{\equiv}N + K^{+}X^{-}} \quad \text{(alkyl cyanide)}.$$

Step 3. With AgCN (more covalent salt with the Ag–C bond locking the C lone pair), the lone pair on N is more available; the N end attacks:

$$\mathrm{R{-}X + Ag{-}C{\equiv}N \longrightarrow R{-}N{\equiv}C + AgX\,(s)} \quad \text{(alkyl isocyanide)}.$$

Step 4. **Other ambident nucleophiles**: nitrite NO_2^- (gives nitro R–NO_2 via N, or nitrite ester R–O–N=O via O); thiocyanate SCN^- (gives R–SCN or R–NCS); enolate (*C*-alkylation or *O*-alkylation).



Final Answer: An ambident nucleophile has two different reactive sites. *Example*: cyanide ion CN^- attacks via C (giving R–CN) when paired with KCN, and via N (giving R–NC) when paired with AgCN.

♥ Why care about ambident behaviour

The same nucleophile produces two structurally and functionally different products depending on conditions. In synthesis, controlling this lets us pick which functional group to install.

EXPERT'S SOLUTION *: Vivaan Bhat, Ph.D Organic Chemistry, IISc Bangalore*

Structural observation. Whenever you see a nucleophile written with delocalised charge over two atoms (O/N, C/N, S/N), suspect ambident behaviour.

- CN^-: C or N.
- NO_2^-: N or O.
- SCN^-: S or N.

HSAB applied carefully. Hard nucleophiles (small, electronegative, weakly polarisable)

prefer hard electrophiles (small, positive). Soft nucleophiles (large, polarisable, often neutral) prefer soft electrophiles (large, partial positive). In CN^-, the N end is harder (more electronegative); the C end is softer (more polarisable). For an alkyl halide with δ^+ on a soft carbon, C attack dominates. For early (S_N1-like) transition states with a more localised charge, the N attack route opens up.

Step 1. For CN^- with KCN, the ionic K–C bond is fully ionised; the C lone pair is free and attacks R–X in S_N2, producing the nitrile.

Step 2. For CN^- with AgCN, Ag forms a covalent Ag–C bond, locking the C lone pair and freeing the N lone pair to attack, producing the isocyanide.

Step 3. HSAB explains it: hard N^- prefers harder electrophiles (early transition states, S_N1-like), soft C prefers softer electrophiles (later transition states, S_N2).

Step 4. Selectivity also depends on solvent: protic solvents hydrogen-bond the more electronegative end, slowing it down and shifting attack to the other end.

Step 5. **Exam-tip framing.** In NCERT exercise answers, always cite the *example* as CN^- with KCN *vs.* AgCN — this is the textbook canonical pair and is the one CBSE markers expect. Mention NO_2^-, SCN^- as additional examples for the 3-mark variant.

Step 6. **Concept linkage.** Ambident nucleophiles appear again in chapter 7 (Alcohols, Phenols, Ethers): the phenoxide $C_6H_5O^-$ is ambident between O and the *ortho/para* ring carbons, leading to Kolbe–Schmidt and Reimer–Tiemann reactions where C- rather than O-attack dominates.

Why this matters. Same starting material plus the same nucleophile, two different products. NCERT exam writes this as a one-mark or short-answer question. The deeper idea — that delocalised charge enables more than one nucleophilic site — recurs through enolates, phenoxides, carboxylates and is foundational for much of the rest of class 12 organic chemistry.

Final Answer: Same conclusion: CN^- (and NO_2^-, SCN^-) is ambident; R–X + KCN $\longrightarrow$ R–CN but R–X + AgCN $\longrightarrow$ R–NC.

Q 6.9 **Which compound in each of the following pairs will react faster in S_N2 reaction with OH^-?**

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl

SOLUTION

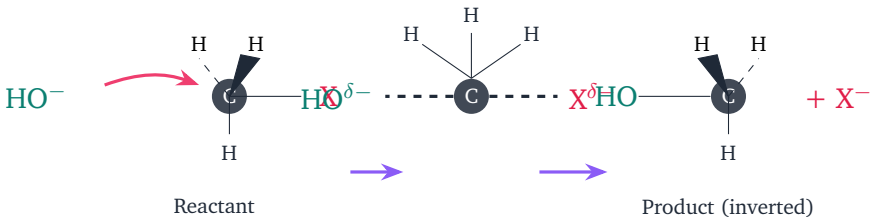
Concept used. The S_N2 (*bimolecular nucleophilic substitution*) rate law is

$$\text{rate} = k\,[\text{R–X}]\,[\text{Nu}^-].$$

The nucleophile attacks the carbon from the side opposite to the leaving group (backside attack), through a single trigonal-bipyramidal transition state in which the C is partially bonded to both Nu and X. The reaction is fastest when

- the leaving group is a good leaving group (weakest base, best polarisable: $I^- > Br^- > Cl^- > F^-$);
- the substrate is sterically unhindered (methyl $> 1^\circ > 2^\circ > 3^\circ$);
- the nucleophile is strong and the solvent is polar aprotic.

S_N2: backside attack with Walden inversion
Transition state



Step 1. **(i) CH_3Br vs CH_3I.** The two have the same carbon framework (methyl, no steric difference), so the rate is decided by the leaving group. I^- is larger and more polarisable than Br^-, and is a weaker base (HI is a stronger acid than HBr), so I^- is a **better leaving group**. The C–I bond (~ 234 pm) is also weaker than the C–Br bond (~ 194 pm), so it breaks more easily. Therefore CH_3I reacts faster than CH_3Br in S_N2.

Step 2. **(ii) $(CH_3)_3CCl$ vs CH_3Cl.** The leaving group is Cl^- in both, so the rate is decided by *steric crowding* at the electrophilic C. CH_3Cl is methyl (no β-substituents), so the backside is wide open. $(CH_3)_3CCl$ is tertiary, with three CH_3 groups crowding the backside; the transition state is destabilised by steric repulsion and the rate is essentially zero. Therefore CH_3Cl reacts much faster than $(CH_3)_3CCl$ in S_N2.

Final Answer: (i) CH_3I reacts faster (better leaving group). (ii) CH_3Cl reacts faster (no steric hindrance at C).

✗ Common Mistake

Do not mix up S_N1 and S_N2 trends. In S_N1 the rate-determining step is ionisation of R–X, so 3° alkyl halides are fastest because they form the most stable carbocation. In S_N2

the rate-determining step is backside attack, so 1° alkyl halides (no steric crowding) are fastest.

EXPERT'S SOLUTION *: Aanya Joshi, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Two single-question filters: leaving-group ability for (i), steric accessibility for (ii).

Quantitative perspective. Relative S_N2 rates with OH^- (taking $CH_3I = 1$): $CH_3I \approx 1.0$, $CH_3Br \approx 0.02$ — a $\sim 50\times$ rate difference. For the steric pair: $CH_3Cl/(CH_3)_3CCl \approx 10^6$ — six orders of magnitude. These ratios underline how different the two controlling factors are in magnitude.

Step 1. Leaving-group ability for halides follows $I^- > Br^- > Cl^- > F^-$. The rule of thumb: the weaker the conjugate base, the better the leaving group, and HI ($pK_a \approx -10$) is much more acidic than HBr ($pK_a \approx -9$).

Step 2. For (i), same carbon, different X: CH_3I wins because the C–I bond is weaker and I^- is a better leaving group.

Step 3. Steric hindrance to backside attack scales as $3^\circ \gg 2^\circ > 1^\circ \approx$ methyl. The S_N2 transition state has a crowded 5-coordinate C; more substituents means worse crowding.

Step 4. For (ii), same X, very different steric situation: methyl chloride is essentially fully exposed; *tert*-butyl chloride has three methyls blocking the backside. Methyl chloride wins by orders of magnitude.

Step 5. **Alternative perspective: bond strength.** The C–X bond strengths (kJ/mol) are roughly C–F (485), C–Cl (327), C–Br (285), C–I (213). Weaker bond = easier breaking = better leaving group. This trend *reinforces* (does not contradict) the basicity argument.

Step 6. **Concept linkage.** The same orderings carry into $E2$ eliminations (I^- fastest, F^- slowest leaving) and into haloarene reactivity (where F on benzene is actually fastest in the addition-elimination mechanism of nucleophilic aromatic substitution — the opposite of the S_N2 trend! See chapter 6 sections on aryl halides).

Why this matters. A two-line answer per pair is enough for NCERT marking; the underlying reasoning (LG ability + steric access) is universal across S_N2 questions. CBSE markers expect both the *order* and one *reason* (LG ability OR steric) for full marks.

Final Answer: (i) CH_3I; (ii) CH_3Cl.

☞ Exam Tip

For S_N2 comparison questions, always check *which factor varies* between the two structures. If the C is the same, the leaving group decides; if X is the same, the substrate's steric crowding decides. If *both* differ, evaluate each separately and let the larger effect win.

Q 6.10 **Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:**
(i) 1-Bromo-1-methylcyclohexane
(ii) 2-Chloro-2-methylbutane
(iii) 2,2,3-Trimethyl-3-bromopentane.

SOLUTION

Concept used. **Dehydrohalogenation** (also called β-elimination or $E2$) removes one H from a β-carbon (the carbon next to the one bearing X) and X from the α-carbon, giving an alkene. Strong bases like **sodium ethoxide** ($C_2H_5O-Na^+$) favour $E2$ over substitution. According to **Saytzeff's rule**, the *major* alkene is the *most substituted* one (more alkyl groups stabilise the C=C via hyperconjugation).

Step 1. **(i) 1-Bromo-1-methylcyclohexane.** The Br sits on a ring carbon that also carries a CH_3. β-positions: two ring carbons adjacent to the C–Br, both $-CH_2-$ (equivalent by symmetry), and the methyl group (which contributes β-H's, giving an exocyclic $=CH_2$).

Possible alkenes:

- Loss of H from a ring CH_2: gives **1-methylcyclohex-1-ene** (trisubstituted).
- Loss of H from the methyl: gives **methylenecyclohexane** (disubstituted).

Saytzeff: trisubstituted > disubstituted; the major product is **1-methylcyclohex-1-ene**.

Step 2. **(ii) 2-Chloro-2-methylbutane.** The Cl sits on C2 of the chain $CH_3-C(Cl)(CH_3)-CH_2-CH_3$. β-carbons: C1 (a CH_3, terminal), C3 (a CH_2, internal), and the methyl substituent on C2.

Possible alkenes:

- Loss of H from C3 CH_2: gives **2-methylbut-2-ene** (trisubstituted).
- Loss of H from C1 CH_3 or from the methyl substituent: gives **2-methylbut-1-ene** (disubstituted).

Major: **2-methylbut-2-ene**.

Step 3. **(iii) 2,2,3-Trimethyl-3-bromopentane.** $(CH_3)_3C-C(Br)(CH_3)-CH_2-CH_3$. The Br is on C3. β-carbons: C2 (a quaternary $C(CH_3)_3$, no H, so no elimination

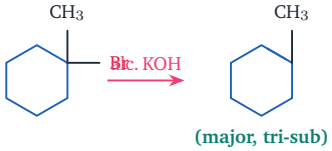
there), C4 (a CH_2), and the methyl substituent on C3.

Possible alkenes:

- Loss of H from C4: gives **3,4,4-trimethylpent-2-ene** (trisubstituted).
- Loss of H from the methyl substituent on C3: gives **2,3,3-trimethylpent-1-ene** (disubstituted).

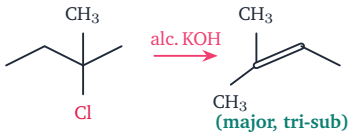
Major: **3,4,4-trimethylpent-2-ene**.

(i) 1-bromo-1-methylcyclohexane → 1-methylcyclohex-1-ene



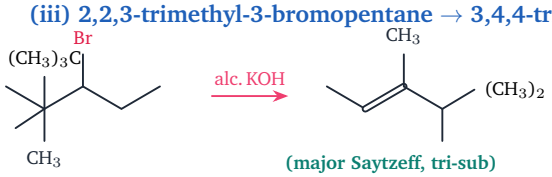
(major, tri-sub)

(ii) 2-chloro-2-methylbutane → 2-methylbut-2-ene



(major, tri-sub)

(iii) 2,2,3-trimethyl-3-bromopentane → 3,4,4-trimethylpent-2-ene



(major Saytzeff, tri-sub)

Final Answer: (i) Major: 1-methylcyclohex-1-ene; minor: methylenecyclohexane. (ii) Major: 2-methylbut-2-ene; minor: 2-methylbut-1-ene. (iii) Major: 3,4,4-trimethylpent-2-ene; minor: 2,3,3-trimethylpent-1-ene.

★ Saytzeff vs Hofmann

Saytzeff (Zaitsev) product: most substituted alkene, favoured by small bases (EtO^-, HO^-).
Hofmann product: least substituted alkene, favoured by bulky bases ($tBuO^-$, $(iPr)_2N^-$).
NCERT exercises usually assume small base, hence Saytzeff.

EXPERT'S SOLUTION *: Ananya Kapoor, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Identify every β-hydrogen on a distinct β-carbon, draw the alkene formed by removing each in turn, then rank by alkene substitution (Saytzeff).
Mechanism perspective. $E2$ is concerted: the C–H bond, the C–C bond and the C–X bond all move together in one transition state. The base (EtO^-) abstracts H as X^- leaves; the two carbons rehybridise from sp^3 to sp^2. A key geometric requirement is that the H and X sit *antiperiplanar* (dihedral $\approx 180°$). In open-chain systems this is achieved by rotation; in cyclic systems it constrains which H can be removed (this matters for ring systems with conformational locks like methylcyclohexane derivatives).

Step 1. For (i), the two ring CH_2 are equivalent: they give one product (1-methylcyclohex-1-ene). The methyl β-H gives methylenecyclohexane. Trisubstituted vs disubstituted; major is the trisubstituted ring alkene.

Step 2. For (ii), the C1 methyl and the C2-methyl substituent give the same terminal alkene 2-methylbut-1-ene; the C3 CH_2 gives 2-methylbut-2-ene. Major: 2-methylbut-2-ene (trisubstituted).

Step 3. For (iii), the quaternary C2 has no β-H. The C4 CH_2 gives an internal trisubstituted alkene; the methyl on C3 gives a terminal disubstituted alkene. Major: 3,4,4-trimethylpent-2-ene.

Step 4. Count the substitution: trisubstituted has 3 alkyl groups on C=C; disubstituted has 2. Saytzeff says "more".

Step 5. **Numerical check (alkene stability).** Heats of hydrogenation (kJ/mol, smaller = more stable alkene): monosubstituted ≈ -126, disubstituted ≈ -116, trisubstituted ≈ -113, tetrasubstituted ≈ -111. The ~ 5 kJ/mol difference per added substituent is the energetic basis of Saytzeff's rule.

Step 6. **Common pitfall in (i).** Students sometimes count only the ring CH_2 groups and forget the methyl. The methyl is itself a β-position (carbons one bond from C–Br), and removing one of its H's gives the terminal alkene methylenecyclohexane. Both products are valid; only the relative *amount* differs.

Step 7. **Concept linkage.** Saytzeff governs $E1$ as well (carbocation $\rightarrow$ most substituted alkene). When the base is *bulky* (like t-BuO^-, hindered amines), Hofmann elimination kicks in and the *least* substituted alkene becomes major because the bulky base can only reach the least crowded β-H.

Why this matters. Saytzeff vs Hofmann is a one-mark selection problem in NCERT/JEE. The recipe: list β-H sites, count alkene substitution, pick the most substituted (with a small base). For 3-mark questions, also draw the alkenes' structural formulae and label the substitution pattern.

> **Final Answer:** Same Saytzeff majors as in main solution.

☞ β-H definition

The β-carbon is any carbon *adjacent* (one bond away) from the C bearing X. The β-hydrogens are the H's on those β-carbons. *Every* β-carbon with at least one H is a candidate for elimination — including methyl substituents on the α-C.

Q 6.11 How will you bring about the following conversions?

(i) Ethanol to but-1-yne; (ii) Ethane to bromoethene; (iii) Propene to 1-nitropropane; (iv) Toluene to benzyl alcohol; (v) Propene to propyne; (vi) Ethanol to ethyl fluoride; (vii) Bromomethane to propanone; (viii) But-1-ene to but-2-ene; (ix) 1-Chlorobutane to n-octane; (x) Benzene to biphenyl.

SOLUTION

Concept used. Each conversion uses a small set of named transformations: *halogenation*, *elimination*, *nucleophilic substitution*, *Wurtz coupling*, *Grignard chemistry*, etc.

Step 1. **(i) Ethanol $\rightarrow$ but-1-yne.**

$$\mathrm{CH_3CH_2OH} \xrightarrow{conc.\ H_2SO_4,\ \Delta} \mathrm{CH_2{=}CH_2} \xrightarrow{Br_2,\ CCl_4} \mathrm{CH_2BrCH_2Br}$$

$$\mathrm{CH_2BrCH_2Br} \xrightarrow{NaNH_2,\ liq.\ NH_3} \mathrm{HC{\equiv}CH} \xrightarrow{NaNH_2;\ EtBr} \mathrm{HC{\equiv}C{-}CH_2CH_3}.$$

Step 2. **(ii) Ethane $\rightarrow$ bromoethene.**

$$\mathrm{CH_3CH_3} \xrightarrow{Br_2,\ h\nu} \mathrm{CH_3CH_2Br} \xrightarrow{alc.\ KOH} \mathrm{CH_2{=}CH_2}$$

$$\mathrm{CH_2{=}CH_2} \xrightarrow{Br_2,\ CCl_4} \mathrm{CH_2BrCH_2Br} \xrightarrow{alc.\ KOH,\ 1eq.} \mathrm{CH_2{=}CHBr}.$$

Step 3. **(iii) Propene $\rightarrow$ 1-nitropropane.**

$$\mathrm{CH_3CH{=}CH_2} \xrightarrow{HBr,\ peroxide} \mathrm{CH_3CH_2CH_2Br} \xrightarrow{AgNO_2} \mathrm{CH_3CH_2CH_2NO_2}.$$

($\mathrm{AgNO_2}$ gives nitroalkane.)

Step 4. **(iv) Toluene $\rightarrow$ benzyl alcohol.**

$$\mathrm{C_6H_5CH_3} \xrightarrow{Cl_2,\ h\nu} \mathrm{C_6H_5CH_2Cl} \xrightarrow{aq.\ NaOH} \mathrm{C_6H_5CH_2OH}.$$

Step 5. **(v) Propene $\rightarrow$ propyne.**

$$\mathrm{CH_3CH{=}CH_2} \xrightarrow{Br_2,\ CCl_4} \mathrm{CH_3CHBrCH_2Br} \xrightarrow{KOH(alc.),\ 2eq.} \mathrm{CH_3C{\equiv}CH}.$$

Step 6. **(vi) Ethanol $\rightarrow$ ethyl fluoride.**

$$\mathrm{CH_3CH_2OH} \xrightarrow{HBr\ or\ PBr_3} \mathrm{CH_3CH_2Br} \xrightarrow{Hg_2F_2\ or\ AgF} \mathrm{CH_3CH_2F}.$$

Step 7. **(vii) Bromomethane $\rightarrow$ propanone.**

$$\mathrm{CH_3Br} \xrightarrow{KCN} \mathrm{CH_3CN} \xrightarrow{CH_3MgBr;\ H_3O^+} \mathrm{CH_3{-}CO{-}CH_3}.$$

(Grignard attacks the nitrile carbon; the imine salt hydrolyses to a ketone.)

Step 8. **(viii) But-1-ene → but-2-ene.**

$$CH_3CH_2CH{=}CH_2 \xrightarrow{HBr(no\,peroxide)} CH_3CH_2CHBrCH_3$$

$$CH_3CH_2CHBrCH_3 \xrightarrow{alc.\,KOH,\,Saytzeff} CH_3CH{=}CHCH_3.$$

Step 9. **(ix) 1-Chlorobutane → n-octane (Wurtz).**

$$2\,CH_3CH_2CH_2CH_2Cl + 2\,Na \xrightarrow{dry\,ether} CH_3(CH_2)_6CH_3 + 2\,NaCl.$$

Step 10. **(x) Benzene → biphenyl.**

$$C_6H_6 \xrightarrow{Br_2,\,FeBr_3} C_6H_5Br; \quad 2\,C_6H_5Br + 2\,Na \xrightarrow{dry\ ether} C_6H_5{-}C_6H_5 + 2\,NaBr.$$

Final Answer: Ten conversions answered above with full reagent sequences and stepwise equations.

EXPERT'S SOLUTION *: Diya Chatterjee, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Each conversion is a retrosynthesis. Walk backward from the target to the starting material; identify the disconnection(s); pick standard reagents.

Step 1. For (i) but-1-yne, the disconnection C–C between an ethyl and the terminal alkyne gives ethyne + CH_3CH_2Br. Ethyne is built from ethanol via ethylene, dibromide, double elimination.

Step 2. For (ii) bromoethene, the disconnection at C=C–Br suggests $CHBr{=}CH_2$ from $CH_2Br{-}CH_2Br$ by single elimination. Build the dibromide from ethylene; ethylene from bromoethane (radical bromination of ethane).

Step 3. For (iii), $R{-}NO_2$ from R–Br + $AgNO_2$. The R–Br is from propene by Kharasch addition of HBr with peroxide.

Step 4. For (iv), $Ph{-}CH_2OH$ from $Ph{-}CH_2Cl$ via hydrolysis. Get $Ph{-}CH_2Cl$ from toluene by photochemical side-chain chlorination.

Step 5. For (v), double dehydrohalogenation of a vicinal dibromide. Build the dibromide from propene and Br_2.

Step 6. For (vi), since HF cannot substitute –OH directly, route through bromide and swap to fluoride with AgF.

Step 7. For (vii), nitrile-to-ketone sequence: $CH_3Br \longrightarrow CH_3CN \longrightarrow CH_3{-}CO{-}CH_3$ via Grignard addition and hydrolysis.

Step 8. For (viii), Markovnikov HBr gives 2-bromobutane; alc. KOH gives Saytzeff

but-2-ene.

Step 9. For (ix), Wurtz couples two molecules of R–Cl with Na in dry ether to give the R-R dimer.

Step 10. For (x), Wurtz–Fittig couples two Ph–Br with Na in dry ether to give biphenyl.

Why this matters. These ten conversions span the major named reactions of this chapter (Wurtz, Wurtz–Fittig, Finkelstein, Saytzeff, Kharasch, Grignard). Multi-mark CBSE questions sometimes recombine 4–5 of them as a single "starting from X, give Y" chain; practising all ten in advance puts you in a position to recognise any sub-chain instantly.

Concept linkage. Notice that conversions (i), (ii), (iv) all use a haloalkane intermediate; (v) uses two elimination steps in sequence. Most multistep retrosynthesis in class 12 organic chemistry passes through one or more haloalkanes — they are the chapter's pivot point because every C–X bond breaks (substitution) or its β-H leaves (elimination) under known conditions.

Final Answer: Same ten sequences with same reagents.

✗ Common Mistake

For conversion (i) Ethanol $\rightarrow$ but-1-yne, students often write a *single*-step reagent or stop at ethyne. The correct chain is four operations: dehydration to ethylene, bromination, double elimination to ethyne, then alkylation with EtBr via the acetylide. Skipping any step loses the route entirely.

Q 6.12 **Explain why**

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

SOLUTION

Concept used.

- Dipole moment $\mu = q \cdot d$ depends on the partial charge q and the bond length d. Hybridisation and π-donation affect q; bond length affects d.
- Miscibility depends on whether mixing breaks more strong H-bonds than it forms.
- A Grignard reagent (R–Mg–X) is a strongly polar organometallic with δ^- on C, behaving as a strong base/nucleophile.

Step 1. **(i)** μ(**chlorobenzene**) $<$ μ(**cyclohexyl chloride**)**.** Two reasons:

(a) *Hybridisation of carbon*: in chlorobenzene, the C attached to Cl is sp^2 (s-character $\sim 33\%$); in cyclohexyl chloride, sp^3 ($\sim 25\%$). Higher s-character means a more electronegative C, smaller electronegativity difference with Cl, and a smaller μ for chlorobenzene.

(b) *Resonance ($+M$ donation)*: in chlorobenzene, lone pairs on Cl delocalise into the ring, giving Cl partial positive character and the ring partial negative. This opposes the C–Cl σ dipole, reducing μ.

Combined: $\mu_{C_6H_5Cl} \approx 1.69$ D, $\mu_{C_6H_{11}Cl} \approx 2.05$ D.

Step 2. **(ii) Alkyl halides are immiscible with water.** Water dissolves a solute only if the energy released by forming solute–water attractions (∼H-bonds) compensates for breaking water–water H-bonds. Alkyl halides cannot donate H-bonds (no O–H or N–H) and accept very weakly. Mixing them into water would require breaking a network of strong water–water H-bonds (each ~ 20 kJ/mol) in exchange for weak van der Waals/halide dipole interactions. The free-energy change is positive, so the two phases stay separate.

Step 3. **(iii) Anhydrous conditions for Grignard.** The C–Mg bond in R–Mg–X is strongly polarised: $R^{\delta-}-Mg^{\delta+}$, with R acting as a carbanion equivalent. Water has an acidic O–H ($pK_a \approx 15.7$); the conjugate acid of R^- (which is R–H) has $pK_a \approx 50$. So R^- is ~ 35 pK units more basic than OH^-, and the deprotonation is essentially irreversible:

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

The Grignard is destroyed before it can react with the intended electrophile.

Final Answer: (i) sp^2 hybridisation + resonance reduce μ of chlorobenzene below that of cyclohexyl chloride; (ii) no H-bonding from alkyl halides to water; mixing demands breaking water's own H-bond network; (iii) Grignard reagent is a strong base toward water and is destroyed instantly by moisture.

EXPERT'S SOLUTION *: Krishna Pillai, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Three short "why?" questions, three named effects: hybridisation + resonance; H-bond mismatch; acid–base reactivity.
Diagram thinking for (i). Sketch chlorobenzene with the Cl lone pair drawn as an arrow into the ring (the $+M$ resonance contributor); the partial negative on the ring carbons opposes the C–Cl dipole. Add the C–Cl bond-length annotation: ~ 169 pm (chlorobenzene) vs ~ 177 pm (cyclohexyl chloride). Both shorter bond and weaker partial charge reduce $\mu = q \cdot d$.

Step 1. For (i), pair the two factors. Higher s-character at the sp^2 ring C makes it more electronegative; the C–Cl bond is also shorter (~ 169 pm vs ~ 177 pm for sp^3). Combined with $+M$ donation from Cl, the net dipole is reduced.

Step 2. For (ii), break down miscibility into ΔH_{soln} and ΔS_{soln}. The positive ΔH from breaking water H-bonds dominates over the small ion–dipole attractions an alkyl halide can offer. Two phases is the lower-energy state.

Step 3. For (iii), use a $\text{p}K_a$ argument. The carbanion derived from a Grignard is the conjugate base of an alkane ($\text{p}K_a \approx 50$). Water ($\text{p}K_a = 15.7$) is a much stronger acid. The protonation lies $\sim 10^{34}$ to the right toward R–H.

Step 4. **Numerical reinforcement for (i).** Even though chlorobenzene has higher s-character at C (so the C–Cl bond is more polar in some sense), the resonance donation reduces the partial negative on Cl. Both effects together drop μ from ~ 2.05 D (cyclohexyl chloride) to ~ 1.69 D (chlorobenzene) — an 18% decrease.

Step 5. **Practical note on (iii).** The Grignard rule "no moisture" extends to apparatus: glassware must be flame-dried; solvents (dry ether or THF) must be distilled over Na/benzophenone; Mg turnings should be activated with a tiny crystal of I_2 to remove surface oxide. A single drop of water can quench a Grignard run that took hours to set up.

Step 6. **Concept linkage.** The same protic-incompatibility of Grignards extends to alcohols (ROH also kills Grignards), amines (R_2NH), terminal alkynes (HC≡CR), and acids — any O–H, N–H, S–H, or terminal sp-CH with $\text{p}K_a < 50$ will protonate R–MgX.

Why this matters. Each of these three explanations is a self-contained one-mark answer NCERT loves to ask. The reasoning templates (resonance + hybridisation; energetics of solvation; $\text{p}K_a$ logic) recur in chapters on Alcohols, Amines and Carbonyls.

Final Answer: Same three explanations, with the quantitative arguments above.

♥ Grignard's exclusion rule generalises

The "anhydrous conditions" requirement isn't unique to R–MgX: every organometallic species with a polarised C–metal bond (n-BuLi, R_3Al, R_2Zn, R–Na, R–K) is destroyed by trace water. In synthesis labs, "Schlenk technique" (dry inert atmosphere) is the standard infrastructure for handling these reagents.

Q 6.13 Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

SOLUTION

Concept used. Polyhalogenated compounds find use because of their high density, low flammability, low chemical reactivity, high boiling points (chlorinated solvents); insecticidal action (chlorinated aromatics); pharmaceutical antiseptic action (CHI_3); and refrigerant properties (volatile fluorochlorocarbons).

Step 1. **Freon-12 (CCl_2F_2, dichlorodifluoromethane).**

- Refrigerant in domestic and industrial refrigeration and air-conditioning.
- Aerosol propellant in spray cans.
- *Phased out under the Montreal Protocol; CFCs deplete stratospheric ozone.*

Step 2. **DDT (*p,p'*-dichlorodiphenyltrichloroethane).**

- First synthetic chlorinated insecticide; effective against malaria-carrying mosquitoes and lice.
- Banned for agriculture in many countries because of bioaccumulation, persistence, and toxicity to non-target species.

Step 3. **Carbon tetrachloride (CCl_4).**

- Industrial solvent for fats, oils, resins.
- Earlier used in fire extinguishers (Pyrene-type); discontinued because hot CCl_4 can generate phosgene ($COCl_2$, toxic).
- Feedstock for CCl_2F_2 (freon-12) synthesis.

Step 4. **Iodoform (CHI_3).**

- Antiseptic for dressing wounds (the antiseptic action comes from liberated free I_2, not from CHI_3 itself).
- Largely replaced by modern antiseptics because of its unpleasant smell and irritation potential.

Final Answer: Freon-12: refrigerant + aerosol propellant; DDT: insecticide (now restricted); CCl_4: industrial solvent, formerly fire extinguisher; CHI_3: antiseptic for wound dressings.

♥ Environmental footnote

The properties that made these compounds useful (chemical inertness, volatility, lipophilicity) also make them long-lived pollutants. The Montreal Protocol (1987) regulates CFCs; the Stockholm Convention regulates DDT.

EXPERT'S SOLUTION *: Ishaan Desai, M.Sc Chemistry, IIT Kanpur*

Quick reading. Four common polyhalogen compounds, four common uses, four corresponding environmental footnotes.

Structure → property logic. Each compound's utility comes from a structural feature you can read off the formula: freon-12 (CCl_2F_2) has small molecular mass and zero net H-bonding → low b.p., volatile, good refrigerant. CCl_4 is heavy and symmetric (zero dipole, no H-bond) → dense solvent for non-polar oils. CHI_3 is heavy (low volatility) yet hydrolytically unstable → slow I_2 release. DDT's chlorinated aromatic core is lipophilic and persistent → long-lasting insecticide.

Step 1. Freon-12: refrigerant. Property used: low boiling ($-29.8°C$), non-flammable.

Step 2. DDT: insecticide, especially anti-malarial vector control. Property used: lipophilic, neurotoxic to insects.

Step 3. CCl_4: solvent for fats/oils, formerly a fire extinguisher. Property used: dense, non-flammable.

Step 4. CHI_3: antiseptic (releases I_2, which is the actual germicide). Property used: slow I_2 release.

Step 5. Environmental caveats (board-asked). CFCs catalytically destroy stratospheric O_3 (Rowland–Molina mechanism). DDT bioaccumulates (lipid-soluble, long biological half-life). CCl_4 is hepatotoxic and forms $COCl_2$ (phosgene) in heat. CHI_3 causes skin irritation and has an unpleasant odour.

Step 6. Replacements (modern chemistry). Freon-12 has been replaced by HFCs (e.g. CH_2FCF_3) and HFOs that contain no Cl (so no ozone depletion). CCl_4 in fire-fighting has been replaced by CO_2 and dry chemical extinguishers. DDT use is heavily restricted but the WHO still permits indoor residual spraying against malaria mosquitoes in some regions.

Why this matters. NCERT pairs the use with an environmental caveat in each case; expect a one-mark question or a part of a multi-mark question asking "write one use and one disadvantage". The Montreal Protocol (1987) and Stockholm Convention (2001) are international agreements students should be aware of for the 2-mark "mention one international protocol" extension.

Final Answer: Same uses as the main solution.

☞ Exam Tip

For "uses of X" board questions, write *two* uses if the question asks for one, and *three* if it asks for two — markers give marks only when uses are distinct (different application domains). Pair each use with an environmental footnote for full marks on the 3-mark variant.

Q 6.14 **Write the structure of the major organic product in each of the following reactions:**

(i) $CH_3CH_2CH_2Cl + NaI \longrightarrow$

(ii) $(CH_3)_3CBr + KOH \longrightarrow$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \longrightarrow$

(iv) $CH_3CH_2Br + KCN \longrightarrow$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(vii) $CH_3CH_2CH{=}CH_2 + HBr \longrightarrow$

(viii) $CH_3CH{=}C(CH_3)_2 + HBr \longrightarrow$

SOLUTION

Concept used.

- Finkelstein exchange: $\mathrm{R{-}Cl + NaI \xrightarrow{acetone} R{-}I + NaCl(s)}$.
- 3° halide + alcoholic KOH $\rightarrow E2$; 2° halide + aqueous KOH $\rightarrow$ substitution.
- Williamson ether synthesis: alkoxide + primary halide $\rightarrow$ ether.
- Thionyl chloride: alcohol $\rightarrow$ chloride with SO_2 + HCl as by-products (clean, gas escapes).
- Markovnikov: in HX addition to an asymmetric alkene, the H goes to the carbon with more H's, X to the more substituted C.

Step 1. **(i)** $\mathrm{CH_3CH_2CH_2Cl + NaI \xrightarrow{dry\,acetone} CH_3CH_2CH_2I + NaCl(s)}$. *Finkelstein* (primary chloride; NaCl precipitates in acetone).

Step 2. **(ii)** $\mathrm{(CH_3)_3CBr + KOH(alc\cdot) \xrightarrow{\Delta} (CH_3)_2C{=}CH_2 + KBr + H_2O}$. 3° substrate + alcoholic KOH $\rightarrow E2$ to give isobutylene (2-methylprop-1-ene).

Step 3. **(iii)** $CH_3CH(Br)CH_2CH_3 + NaOH(aq\cdot) \longrightarrow CH_3CH(OH)CH_2CH_3 + NaBr$. 2° substrate + aqueous NaOH $\rightarrow$ substitution to give butan-2-ol.

Step 4. **(iv)** $CH_3CH_2Br + KCN \longrightarrow CH_3CH_2CN + KBr$. *Ambident nucleophile* CN^-; with KCN the C end attacks to give propanenitrile.

Step 5. **(v)** $C_6H_5O^-Na^+ + C_2H_5Cl \longrightarrow C_6H_5{-}O{-}C_2H_5 + NaCl$. *Williamson ether synthesis*: phenoxide + ethyl chloride $\rightarrow$ phenetole (ethoxybenzene).

Step 6. **(vi)** $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2(g) + HCl(g)$. Clean chlorination of 1° alcohol.

Step 7. **(vii)** $CH_3CH_2CH{=}CH_2 + HBr \longrightarrow CH_3CH_2CH(Br)CH_3$. *Markovnikov* addition of HBr to but-1-ene gives 2-bromobutane.

Step 8. **(viii)** $CH_3CH{=}C(CH_3)_2 + HBr \longrightarrow CH_3CH_2C(Br)(CH_3)_2$. *Markovnikov*: H adds to C2 (less substituted), Br adds to C3 (more substituted), giving 2-bromo-2-methylbutane.

(i) Finkelstein $CH_3CH_2CH_2Cl \xrightarrow{NaI,\ dry\ acetone} CH_3CH_2CH_2I + NaCl\ (s)$

(ii) $E2$ **on** 3° $(CH_3)_3CBr \xrightarrow{KOH/EtOH,\ \Delta} (CH_3)_2C{=}CH_2 + KBr + H_2O$

(iii) S_N **on** 2° $CH_3CH(Br)CH_2CH_3 \xrightarrow{NaOH\ (aq.)} CH_3CH(OH)CH_2CH_3 + NaBr$

(iv) Kolbe nitrile $CH_3CH_2Br \xrightarrow{KCN} CH_3CH_2CN + KBr$

(v) Williamson $C_6H_5O^-Na^+ + C_2H_5Cl \longrightarrow C_6H_5OC_2H_5 + NaCl$

(vi) $SOCl_2$ $CH_3CH_2CH_2OH \xrightarrow{SOCl_2} CH_3CH_2CH_2Cl + SO_2\ (g) + HCl\ (g)$

(vii) Markovnikov $CH_3CH_2CH{=}CH_2 \xrightarrow{HBr} CH_3CH_2CH(Br)CH_3$ (2-bromobutane)

(viii) Markovnikov $CH_3CH{=}C(CH_3)_2 \xrightarrow{HBr} CH_3CH_2C(Br)(CH_3)_2$ (2-bromo-2-methylbutane)

Final Answer: (i) 1-iodopropane; (ii) 2-methylprop-1-ene (isobutylene); (iii) butan-2-ol; (iv) propanenitrile; (v) ethoxybenzene (phenetole); (vi) 1-chloropropane; (vii) 2-bromobutane; (viii) 2-bromo-2-methylbutane.

☞ Exam Tip

Read the base/solvent carefully. *Alcoholic* KOH = elimination ($E2$). *Aqueous* KOH = substitution (S_N). KCN → nitrile; AgCN → isocyanide.

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

Strategic angle. Eight one-line transformations, each matching a named reaction. Identify the reaction class, write the product directly.

Reaction-class index. Build a mental table: (i) Finkelstein (halide exchange); (ii) $E2$ (tertiary + alcoholic base); (iii) S_N (secondary + aqueous base); (iv) S_N with ambident nucleophile (CN^- via C end); (v) Williamson ether synthesis; (vi) $SOCl_2$ clean chlorination; (vii), (viii) Markovnikov HX addition. Reading the reagent first makes the answer "write itself".

Step 1. (i) Finkelstein in dry acetone; primary chloride → iodide.

Step 2. (ii) 3° bromide + alcoholic KOH → $E2$; only one Saytzeff alkene possible.

Step 3. (iii) 2° bromide + aqueous NaOH → substitution to give the secondary alcohol.

Step 4. (iv) KCN's C end attacks primary bromide → nitrile.

Step 5. (v) Williamson: phenoxide + primary alkyl halide → ether.

Step 6. (vi) $SOCl_2$ converts 1° alcohol to 1° chloride; gaseous by-products.

Step 7. (vii) Markovnikov HBr addition to but-1-ene; Br to the more substituted C.

Step 8. (viii) Markovnikov HBr addition to 2-methylbut-2-ene; Br to the C with two methyl substituents.

Step 9. **Common pitfall in (ii).** A tertiary halide with *aqueous* KOH would also give some elimination because of the substrate's steric crowding; the textbook answer focuses on *alcoholic* KOH where the elimination channel dominates cleanly. Always read the solvent specification.

Step 10. **Why $SOCl_2$ is preferred over HCl/PCl5 in (vi).** The by-products are gases (SO_2, HCl) which escape; no separation step needed, and the product is high-purity alkyl chloride. PCl_5 leaves $POCl_3$ as a liquid contaminant.

Why this matters. A perfect drill on S_N2 vs $E2$ vs addition, plus the Williamson and $SOCl_2$ shortcuts. Many of these reactions are the building blocks for the multistep conversions in Q 6.11 and Q 6.19, so mastering them in isolation lets you handle the chains downstream.

Final Answer: Same eight products as in main solution.

✗ Common Mistake

For (vii) and (viii), do not confuse Markovnikov with *anti*-Markovnikov. The bare reagent "HBr" (no peroxide, no ROOR) follows Markovnikov: Br adds to the carbon with more carbon substituents. Anti-Markovnikov needs an explicit peroxide indicator like ROOR or *benzoyl peroxide*.

Q 6.15 Write the mechanism of the following reaction:

$$\mathrm{n-BuBr} + \mathrm{KCN} \xrightarrow{ethanol/water} \mathrm{n-BuCN}.$$

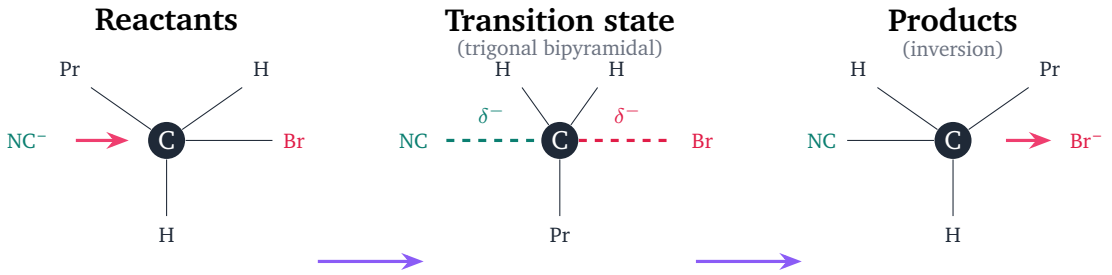
SOLUTION

Concept used. S_N2 **mechanism** for a primary alkyl halide reacting with a strong nucleophile:

$$\text{rate} = k\,[\mathrm{R\text{–}X}][\mathrm{Nu}^-].$$

The nucleophile attacks the C bearing X from the side directly opposite X (**backside attack**). The three other groups on that C transition from a tetrahedral geometry

through a planar trigonal-bipyramidal (TS) and re-pyramidalise on the opposite face (**Walden inversion**). Single concerted step, no intermediate.
For our system: n-butyl bromide is a 1° halide with no β-branching, so the backside is unhindered; CN^- is a strong nucleophile (from KCN dissociation in ethanol/water).



Step 1. **Step 1 (only step).** CN^- (specifically its carbon end) approaches the C of n-BuBr from the side opposite to Br. A new C–CN bond starts to form while the C–Br bond starts to break, in concert.

Step 2. **Transition state.** The C is sp^2-like; the three remaining groups (one H from each C–H, and the propyl chain) lie in a plane through the C; CN and Br sit on either side along the reaction axis. Both partial bonds carry partial negative charge.

Step 3. **Products.** The Br^- ion departs with the bond pair; the C re-pyramidalises on the opposite face. The result is n-butyl cyanide (pentanenitrile) with the C's stereochemistry *inverted*.

Step 4. **Rate law.**

$$\text{rate} = k\,[\mathrm{C_4H_9Br}][\mathrm{CN^-}].$$

First order in each, hence "bimolecular nucleophilic substitution", S_N2.

Step 5. **Why S_N2 and not S_N1?** n-butyl bromide is a primary halide; the primary carbocation $CH_3CH_2CH_2CH_2^+$ is highly unstable, so the S_N1 pathway does not compete.

> **Final Answer:** S_N2 mechanism: single concerted step, backside attack of CN^- on the 1° C, Walden inversion, rate $= k\,[\mathrm{RBr}][\mathrm{CN^-}]$.

★ Solvent in this NCERT example

NCERT writes "ethanol/water" as the solvent. KCN dissociates fully in this mixture; the CN^- is partially solvated by hydrogen bonds from OH but is still a strong nucleophile, and the primary substrate keeps the rate S_N2.

EXPERT'S SOLUTION *: Rohit Gupta, Ph.D Organic Chemistry, IISc Bangalore*

Picture-first. Walden's inversion is the visual signature of S_N2: think "umbrella inversion" at the carbon. The three non-leaving groups pass through a planar arrangement and emerge on the opposite side.

Energy-profile perspective. Plot energy vs. reaction coordinate: starts at the reactant level (R–Br + CN^-), rises smoothly to a single transition state (the trigonal-bipyramidal arrangement with partial bonds to both Nu and LG), and falls to the product level (R–CN + Br^-). *Only one* maximum, no intermediate. Contrast with S_N1 (two maxima, a carbocation valley between them).

Step 1. Identify the substrate as primary, the nucleophile as strong (CN^-); both push toward S_N2.

Step 2. Draw the curly arrow from the C of CN^- to the C bearing Br; simultaneously draw the curly arrow from the C–Br bond out onto Br.

Step 3. In the transition state, show the three remaining substituents (C_3H_7, H, H) flattened in a plane through C, with partial bonds to both incoming CN and outgoing Br.

Step 4. Complete the inversion: the CN group is now on the opposite side from where Br was. Since the C in this substrate is not a stereocentre (two H's on it), the inversion is not observable here, but in a chiral case it would invert configuration.

Step 5. Confirm by the rate law: rate $= k[\text{RBr}][CN^-]$ is bimolecular.

Step 6. **Alternative mechanism check.** An S_N1 pathway would require n-BuBr to ionise to n-Bu^+ first. Primary carbocation $CH_3CH_2CH_2CH_2{}^+$ has no π-stabilisation and lies ~ 280 kJ/mol above the ionised state of a tertiary carbocation. The ionisation step is forbiddingly slow, so S_N1 does not compete.

Step 7. **Stereochemistry test for S_N2.** If the substrate were chiral (e.g. (R)-2-bromobutane), S_N2 would invert the configuration to give (S)-2-cyanobutane. This single observation (inversion, not retention, not racemisation) is what distinguishes S_N2 from S_N1 experimentally.

Why this matters. Backside attack with Walden inversion is one of the most diagnostically clean reactions in organic chemistry. It generalises: *any* bimolecular nucleophilic substitution at sp^3 C inverts the configuration. Modern synthesis uses this for stereocontrolled construction of stereocentres (Mitsunobu reaction, S_N2 ring-opening of epoxides with full inversion).

> **Final Answer:** Same: S_N2, single step, backside attack, inversion, rate $= k[\text{RBr}][CN^-]$.

♥ Walden inversion as a synthetic tool

The stereochemical outcome of S_N2 is a *tool*, not a quirk. Want to flip the configuration of an alcohol? Convert to a tosylate or mesylate (a good leaving group), then S_N2 with a nucleophile (e.g. acetate, then hydrolyse). The product alcohol has inverted stereochemistry. The Mitsunobu reaction exploits exactly this sequence in one pot.

Q 6.16 Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane;

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane;

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

SOLUTION

Concept used. S_N2 reactivity correlates with steric accessibility of the C bearing X. The order is:

$$\text{methyl} > 1^\circ > 2^\circ > 3^\circ.$$

Among 1° halides, branching at the β-carbon further slows the reaction. A *neopentyl*-type β-branch is the slowest of all primary substrates because it blocks the backside.

Step 1. **(i)** Identify the class of each:

- 1-Bromopentane: 1°.
- 2-Bromopentane: 2°.
- 2-Bromo-2-methylbutane: 3°.

Order: $1^\circ > 2^\circ > 3^\circ$. So:

$$\text{1-Bromopentane} > \text{2-Bromopentane} > \text{2-Bromo-2-methylbutane}.$$

Step 2. **(ii)** Identify the class:

- 1-Bromo-3-methylbutane: 1°.
- 2-Bromo-3-methylbutane: 2°.
- 2-Bromo-2-methylbutane: 3°.

Order:

$$\text{1-Bromo-3-methylbutane} > \text{2-Bromo-3-methylbutane} > \text{2-Bromo-2-methylbutane}.$$

Step 3. **(iii)** All four are primary, so the discriminator is β-branching:

- 1-Bromobutane: β-C is a CH_2 (no branching).
- 1-Bromo-3-methylbutane: β-C is a CH_2; the branch is at γ.
- 1-Bromo-2-methylbutane: β-C carries a methyl.
- 1-Bromo-2,2-dimethylpropane (neopentyl bromide): β-C is $C(CH_3)_3$, heavily hindering backside attack.

Order:

$$\text{1-Bromobutane} > \text{1-Bromo-3-methylbutane} > \text{1-Bromo-2-methylbutane} > \text{1-Bromo-2,2-dimethylpropane}.$$

Final Answer: (i) 1-Br-pentane > 2-Br-pentane > 2-Br-2-methylbutane; (ii) 1-Br-3-methylbutane > 2-Br-3-methylbutane > 2-Br-2-methylbutane; (iii) 1-Br-butane > 1-Br-3-methylbutane > 1-Br-2-methylbutane > 1-Br-2,2-dimethylpropane.

★ Why β-branching matters so much

In the S_N2 transition state, the nucleophile, the C and the leaving group are colinear. The three remaining substituents on the α-C are pushed flat into a plane. Bulky groups on the β-C poke into that plane and the incoming Nu has to squeeze past them. Methyl groups at β cause noticeable rate drops; tBu at β (i.e. neopentyl) shuts S_N2 down.

EXPERT'S SOLUTION *: Yash Rao, M.Sc Chemistry, IIT Kanpur*

Structural observation. Reactivity in S_N2 is a steric contest. Rank by (a) class of substrate at α, (b) crowding at β for ties.
Quantitative scale. Relative S_N2 rates (typical C–Br, NaOEt in EtOH, set methyl $= 1$): methyl ≈ 1, ethyl (1°) ≈ 0.03, 1° with β-methyl (isobutyl) $\approx 4 \times 10^{-4}$, neopentyl (β-tBu) $\approx 4 \times 10^{-6}$. The drop is dramatic — neopentyl is slower than the corresponding tertiary halide for S_N2!

Step 1. Class hierarchy: methyl > 1° > 2° > 3°. Three classes in (i), three in (ii); rank as is.

Step 2. In (iii), all are 1°, so move to the β-C. Count methyl substituents on β: 1-Br-butane has 0; 1-Br-3-methylbutane has 0 at β (branch at γ); 1-Br-2-methylbutane has 1 methyl at β; neopentyl has 3 at β. Order is the reverse of β-substitution.

Step 3. Confirm by mental drawing of the TS for each: more substituents on the β-C means more atoms in the way of the incoming Nu.

Step 4. **Visualisation.** Picture the S_N2 transition state as a hand reaching from behind

the C, while the other three substituents lie flat. For methyl, only three small H's are flat — easy. For neopentyl, three methyls hang off the C next to the planar layer and actively block the approach path of the incoming Nu.

Step 5. **γ-branching is fine.** 1-Bromo-3-methylbutane has a branch at γ (two carbons from Br), which is far enough that it does not crowd the backside; its rate is essentially the same as that of n-pentyl bromide. Only β (and α) branching matters.

Step 6. **Concept linkage.** The same steric reasoning *reverses sign* for S_N1: tertiary halides ionise fastest because the more substituted carbocation is more stable. Reactivity scales opposite to S_N2: $3^\circ > 2^\circ > 1^\circ >$ methyl.

Why this matters. Steric reasoning is the only tool you need to rank S_N2 rates within a homologous series. The same "count substituents at β" technique solves any JEE/CBSE ranking question on S_N2 within a closed family of primary halides.

Final Answer: Same three orderings as the main solution.

☞ **The $\alpha/\beta/\gamma$ labels**

α-C = the carbon bonded to X. β-C = any carbon bonded to the α-C. γ-C = any carbon bonded to a β-C. For S_N2, only α and β branching slows the rate; γ branching is too far to matter.

Q 6.17 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

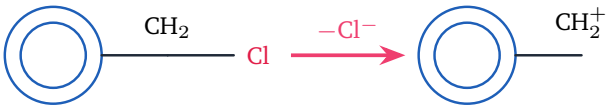
SOLUTION

Concept used. Both substrates are benzyl-type chlorides: the C bearing Cl is benzylic. Hydrolysis with aqueous KOH on a benzyl-type halide can proceed by either S_N1 or S_N2; we expect S_N1 character to grow with stabilisation of the resulting benzylic carbocation.

- $C_6H_5CH_2Cl$: *benzyl chloride*, 1° benzyl. Carbocation $PhCH_2^+$ is monobenzylic.
- $C_6H_5CHClC_6H_5$: *benzhydryl chloride* (diphenylmethyl chloride), 2° benzyl. Carbocation Ph_2CH^+ is dibenzylic.

The cation Ph_2CH^+ is stabilised by resonance into both phenyl rings (extensive $+M$ donation); the cation $PhCH_2^+$ is stabilised by resonance into one phenyl. The dibenzylic cation is therefore *much more stable*.
Since S_N1 rate $\propto$ rate of ionisation $\propto$ stability of the resulting cation, $C_6H_5CHClC_6H_5$ should hydrolyse faster than $C_6H_5CH_2Cl$.

Benzyl chloride → benzyl cation (mono-benzylic)

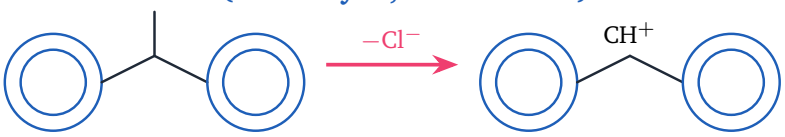


~3 resonance forms (one ring delocalises +)

benzhydryl wins

(faster S_N1)

Benzhydryl chloride → benzhydryl cation (di-benzylic, more stable)



~5 resonance forms (TWO rings delocalise +)

Step 1. Draw the resonance structures of $PhCH_2^+$: positive charge delocalises into the *ortho* and *para* positions of the phenyl ring.

Step 2. Draw the resonance structures of Ph_2CH^+: positive charge delocalises into *both* rings, doubling the stabilisation.

Step 3. Greater delocalisation gives a lower-energy cation, smaller $\Delta G^\ddagger$ for ionisation, and a faster S_N1 hydrolysis.

Step 4. Conclude: Ph_2CHCl (benzhydryl chloride) is hydrolysed more easily than $PhCH_2Cl$ (benzyl chloride).

Final Answer: **$C_6H_5CHClC_6H_5$ (benzhydryl chloride)** is more easily hydrolysed: the resulting carbocation Ph_2CH^+ is stabilised by resonance into *two* phenyl rings, lowering the activation barrier for S_N1 ionisation.

EXPERT'S SOLUTION *: Ishita Nair, M.Sc Chemistry, IIT Kanpur*

Strategic angle. The fast-hydrolysis question on benzyl-type halides is always answered by counting cation resonance forms.

Resonance counting recipe. For each candidate carbocation, draw the structure with + on C, then push every adjacent π system or lone pair toward the +. Count distinct contributors that place + on different atoms. For $PhCH_2^+$: + on the benzylic C, then + on o (2 of these), then + on p, then back to benzylic — *4 contributors*. For Ph_2CH^+: + on the central C, then on o/p of *each* of the two phenyl rings — *7 contributors*. Roughly twice the delocalisation, much more stable.

Step 1. In aqueous KOH, polar protic solvent stabilises the ionisation intermediate. Both substrates can in principle undergo S_N1.

Step 2. $PhCH_2^+$ has one phenyl ring to delocalise into; the resonance contributors place positive charge at the *ortho* (2 positions) and *para* of the ring.

Step 3. Ph_2CH^+ has two phenyl rings; positive charge delocalises across both, doubling the stabilising resonance.

Step 4. Lowering the carbocation energy lowers $\Delta G^\ddagger$ for ionisation; rate goes up.

Step 5. Hence Ph_2CHCl reacts faster than $PhCH_2Cl$ with aqueous KOH.

Step 6. **Mechanism perspective.** Hydrolysis proceeds via S_N1: rate-determining ionisation gives the carbocation, which is then trapped by H_2O (or OH^-) in a fast step. So the *rate* depends only on [RCl], not on [OH-]. This means the rate ratio $Ph_2CHCl/PhCH_2Cl$ would be the same in pure water or in dilute KOH.

Step 7. **Triphenyl extension.** For triphenylmethyl (trityl) chloride Ph_3CCl, the cation is stabilised by *three* rings — exceptionally stable. Trityl chloride hydrolyses in pure water at room temperature, whereas $PhCH_2Cl$ needs warm aqueous KOH.

Step 8. **Concept linkage.** The same logic explains why allyl, benzyl, and especially diphenyl/triphenyl methyl substrates react via S_N1 even when they are primary or secondary — substantial cation π-stabilisation overrides the standard $1^\circ < 2^\circ < 3^\circ$ progression based purely on inductive effects.

Why this matters. The trick is to spot that we are comparing carbocation stabilities, not steric accessibilities; benzhydryl wins decisively because of double resonance. CBSE short-answer questions on "which halide hydrolyses faster?" are almost always carbocation stability problems in disguise.

Final Answer: $C_6H_5CHClC_6H_5$ (benzhydryl chloride) hydrolyses faster.

✗ Common Mistake

A frequent error is to count steric crowding: "Ph_2CHCl has two phenyl groups, more crowding, so slower". This logic applies to S_N2 but *not* to S_N1. In S_N1, the rate-determining step is ionisation — steric strain in the substrate actually *helps* (relieves on going to a planar carbocation).

Q 6.18 p-Dichlorobenzene has higher m.p. than those of o- and m-isomers. Discuss.

SOLUTION

Concept used. For molecules of comparable polarity and molar mass, the *melting point* is governed primarily by *crystal packing*: how efficiently the molecules stack in the solid

state. **High symmetry** allows molecules to pack tightly into the unit cell, increasing intermolecular contact and lattice energy, and raising the melting point. The boiling point, by contrast, depends mostly on the dipole moment and van der Waals attractions in the liquid.

Step 1. **Symmetry argument.** *p*-Dichlorobenzene has a C_{2h} symmetry: the molecule is *centrosymmetric*. The two C–Cl dipoles are antiparallel and cancel ($\mu = 0$ D). Molecules are flat, linear-shaped and pack into a highly ordered, dense crystal.

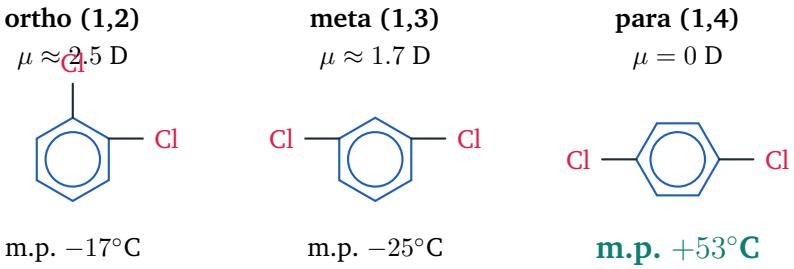
The *o*- and *m*-isomers are not centrosymmetric and have non-zero μ (*o*- $\mu \approx 2.5$ D, *m*- $\mu \approx 1.7$ D). Their less symmetric shapes pack less efficiently in the solid state.

Step 2. **Numerical comparison.**

- *o*-dichlorobenzene: m.p. $\approx -17^\circ$C, b.p. $\approx 180^\circ$C.
- *m*-dichlorobenzene: m.p. $\approx -25^\circ$C, b.p. $\approx 173^\circ$C.
- *p*-dichlorobenzene: m.p. $\approx 53^\circ$C, b.p. $\approx 174^\circ$C.

The *p*-isomer's m.p. is dramatically higher.

Step 3. **Why b.p. doesn't follow the m.p. trend.** *o*-Dichlorobenzene has the highest dipole moment and therefore the highest b.p. *p*-Dichlorobenzene's $\mu = 0$ D, so its b.p. is among the lowest. The discrepancy between b.p. and m.p. trends is precisely the "packing vs. dipole" distinction.



Final Answer: *p*-dichlorobenzene's high symmetry and zero dipole let its molecules pack into a tighter, more ordered crystal lattice, giving the highest melting point of the three isomers.

♥ Symmetry & packing in molecular solids

The same idea explains why n-alkanes with an even number of C's melt higher than the next-odd one, why benzene's m.p. is 5.5°C while toluene's is -95°C, etc.

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

Structural observation. M.p. is a *crystal* property; b.p. is a *liquid–gas* property. They can move in opposite directions when symmetry and dipole disagree.

Sketch of the crystal-packing argument. In a molecular crystal, the lattice energy comes from (a) dispersion (London) forces between heavy atoms, (b) dipole–dipole alignment, and (c) shape complementarity (how snugly the molecules fit). Higher shape symmetry = more efficient packing density = more neighbouring contacts per molecule = larger total lattice attraction. Even though *p*-dichlorobenzene has *zero* dipole, its shape (linear-rod) packs into a denser unit cell than the bent shapes of *o*- and *m*-isomers.

Step 1. Sketch each isomer; mark the two C–Cl dipoles and the molecular symmetry axis.

Step 2. Only the *para*-isomer is centrosymmetric; its $\mu = 0$ and it has the highest symmetry.

Step 3. In the solid, high symmetry means molecules stack like flat coins into close-packed columns. Lattice energy is therefore largest for the *para*-isomer.

Step 4. Heating breaks the lattice; the *para* lattice requires the most heat to disrupt, hence the highest m.p.

Step 5. The *o*- and *m*-isomers have higher dipole moments but poorer packing; net result is a lower m.p. but a competitive (sometimes higher) b.p.

Step 6. **Boiling-point cross-check.** *o*-dichlorobenzene: b.p. 180°C ($\mu \approx 2.5$ D, highest); *m*-: b.p. 173°C ($\mu \approx 1.7$ D); *p*-: b.p. 174°C ($\mu = 0$ D). B.p. correlates with dipole moment, not with crystal packing — exactly the opposite trend to m.p.

Step 7. **Concept linkage.** The same idea generalises to n-alkanes (even-numbered alkanes pack better than adjacent odd ones, so their m.p. is locally higher), to symmetric vs. asymmetric isomers of disubstituted aromatics in general, and to fullerenes (C_{60} packs like a sphere, very high m.p.).

Step 8. **Exam-tip.** If asked "why is the m.p. of A higher than that of B?", invoke crystal-packing/symmetry. If asked "why is the b.p. of A higher than that of B?", invoke dipole moment and/or molecular mass (dispersion).

Why this matters. A classic two-mark NCERT question. Use symmetry + packing for m.p.; dipole + vdW for b.p. The counter-intuitive result that the most symmetric (zero-dipole) isomer has the highest m.p. trains the eye to separate "melting" (crystal → liquid) from "boiling" (liquid → gas) in problems on physical properties.

Final Answer: Higher symmetry → tighter crystal → higher m.p. of *p*-dichlorobenzene compared with the *o*- and *m*-isomers.

☞ Naphtalene moth-balls swapped for *p*-DCB

p-Dichlorobenzene (m.p. 53°C, b.p. 174°C) is the active ingredient in modern moth-balls and air-freshener cubes because it *sublimes* slowly at room temperature, releasing a mild odour that repels insects. The crystal packing efficiency we described is exactly what makes it solid at room temperature in the first place.

Q 6.19 How can the following conversions be carried out?

(i) Propene to propan-1-ol; (ii) Ethanol to but-1-yne; (iii) 1-Bromopropane to 2-bromopropane; (iv) Toluene to benzyl alcohol; (v) Benzene to 4-bromonitrobenzene; (vi) Benzyl alcohol to 2-phenylethanoic acid; (vii) Ethanol to propanenitrile; (viii) Aniline to chlorobenzene; (ix) 2-Chlorobutane to 3,4-dimethylhexane; (x) 2-Methyl-1-propene to 2-chloro-2-methylpropane; (xi) Ethyl chloride to propanoic acid; (xii) But-1-ene to n-butyliodide; (xiii) 2-Chloropropane to 1-propanol; (xiv) Isopropyl alcohol to iodoform; (xv) Chlorobenzene to p-nitrophenol; (xvi) 2-Bromopropane to 1-bromopropane; (xvii) Chloroethane to butane; (xviii) Benzene to diphenyl; (xix) tert-Butyl bromide to isobutyl bromide; (xx) Aniline to phenylisocyanide.

SOLUTION

Concept used. Twenty conversions, each a chain of named reactions: hydroboration–oxidation, Wurtz, Sandmeyer, hydrolysis, Williamson, Kolbe nitrile, carbylamine, etc.

Step 1. **(i) Propene → propan-1-ol** (anti-Markovnikov):

$$CH_3CH{=}CH_2 \xrightarrow{B_2H_6} (CH_3CH_2CH_2)_3B \xrightarrow{H_2O_2/OH^-} CH_3CH_2CH_2OH.$$

Step 2. **(ii) Ethanol → but-1-yne**:

$$EtOH \xrightarrow{conc.\ H_2SO_4} C_2H_4 \xrightarrow{Br_2} CH_2BrCH_2Br$$

$$CH_2BrCH_2Br \xrightarrow{NaNH_2} HC{\equiv}CH \xrightarrow{NaNH_2;\ EtBr} HC{\equiv}CCH_2CH_3.$$

Step 3. **(iii) 1-Bromopropane → 2-bromopropane**:

$$CH_3CH_2CH_2Br \xrightarrow{alc.\ KOH} CH_3CH{=}CH_2 \xrightarrow{HBr,Markov.} CH_3CHBrCH_3.$$

Step 4. **(iv) Toluene → benzyl alcohol**:

$$C_6H_5CH_3 \xrightarrow{Cl_2,\ h\nu} C_6H_5CH_2Cl \xrightarrow{aq.\ NaOH} C_6H_5CH_2OH.$$

Step 5. **(v) Benzene → 4-bromonitrobenzene**: brominate first (so Br directs the NO_2 to para): $C_6H_6 \xrightarrow{Br_2,\ FeBr_3} C_6H_5Br \xrightarrow{HNO_3/H_2SO_4} p{-}BrC_6H_4NO_2$.

Step 6. **(vi) Benzyl alcohol → 2-phenylethanoic acid**:

$$C_6H_5CH_2OH \xrightarrow{SOCl_2} C_6H_5CH_2Cl \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow{H_3O^+} C_6H_5CH_2COOH.$$

Step 7. **(vii) Ethanol → propanenitrile**:
$\mathrm{EtOH} \xrightarrow{HBr/PBr_3} \mathrm{CH_3CH_2Br} \xrightarrow{KCN} \mathrm{CH_3CH_2CN}.$

Step 8. **(viii) Aniline → chlorobenzene** (Sandmeyer):
$\mathrm{C_6H_5NH_2} \xrightarrow{NaNO_2, HCl, 0\text{–}5^\circ C} \mathrm{C_6H_5N_2{}^+Cl^-} \xrightarrow{CuCl} \mathrm{C_6H_5Cl} + \mathrm{N_2}.$

Step 9. **(ix) 2-Chlorobutane → 3,4-dimethylhexane** (Wurtz): $2\,\mathrm{CH_3CHClCH_2CH_3} + 2\,\mathrm{Na} \longrightarrow \mathrm{CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3} + 2\,\mathrm{NaCl}.$

Step 10. **(x) 2-Methyl-1-propene → 2-chloro-2-methylpropane** (Markovnikov HCl):
$\mathrm{(CH_3)_2C{=}CH_2} + \mathrm{HCl} \longrightarrow \mathrm{(CH_3)_3C{-}Cl}.$

Step 11. **(xi) Ethyl chloride → propanoic acid**:
$\mathrm{C_2H_5Cl} \xrightarrow{KCN} \mathrm{C_2H_5CN} \xrightarrow{H_3O^+} \mathrm{CH_3CH_2COOH}.$

Step 12. **(xii) But-1-ene → *n*-butyl iodide**:

$$\mathrm{CH_3CH_2CH{=}CH_2} \xrightarrow{HBr/peroxide} \mathrm{CH_3CH_2CH_2CH_2Br} \xrightarrow{NaI, acetone} \mathrm{CH_3CH_2CH_2CH_2I}.$$

Step 13. **(xiii) 2-Chloropropane → 1-propanol**:
$\mathrm{CH_3CHClCH_3} \xrightarrow{alc.\,KOH} \mathrm{CH_3CH{=}CH_2} \xrightarrow{B_2H_6;\, H_2O_2/OH^-} \mathrm{CH_3CH_2CH_2OH}.$

Step 14. **(xiv) Isopropyl alcohol → iodoform** (haloform):
$\mathrm{(CH_3)_2CHOH} \xrightarrow{I_2,\, NaOH} \mathrm{CHI_3} + \mathrm{CH_3COO^-Na^+}.$

Step 15. **(xv) Chlorobenzene → p-nitrophenol**: nitrate first, then hydrolyse the activated Cl:
$\mathrm{C_6H_5Cl} \xrightarrow{HNO_3/H_2SO_4} \mathrm{p{-}O_2NC_6H_4Cl} \xrightarrow{NaOH(aq);\, H_3O^+} \mathrm{p{-}O_2NC_6H_4OH}.$

Step 16. **(xvi) 2-Bromopropane → 1-bromopropane**:
$\mathrm{CH_3CHBrCH_3} \xrightarrow{alc.\,KOH} \mathrm{CH_3CH{=}CH_2} \xrightarrow{HBr/peroxide} \mathrm{CH_3CH_2CH_2Br}.$

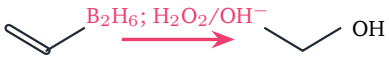
Step 17. **(xvii) Chloroethane → butane** (Wurtz): $2\,\mathrm{CH_3CH_2Cl} + 2\,\mathrm{Na} \longrightarrow \mathrm{CH_3CH_2CH_2CH_3} + 2\,\mathrm{NaCl}.$

Step 18. **(xviii) Benzene → diphenyl**: $\mathrm{C_6H_6} \xrightarrow{Br_2,\, FeBr_3} \mathrm{C_6H_5Br}$; $2\,\mathrm{C_6H_5Br} + 2\,\mathrm{Na} \longrightarrow \mathrm{C_6H_5{-}C_6H_5} + 2\,\mathrm{NaBr}$ (Wurtz–Fittig).

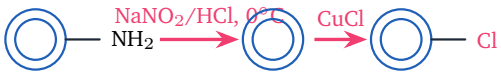
Step 19. **(xix) *tert*-Butyl bromide → isobutyl bromide**:
$\mathrm{(CH_3)_3CBr} \xrightarrow{alc.\,KOH} \mathrm{(CH_3)_2C{=}CH_2} \xrightarrow{HBr/peroxide} \mathrm{(CH_3)_2CHCH_2Br}.$

Step 20. **(xx) Aniline → phenylisocyanide** (carbylamine):
$\mathrm{C_6H_5NH_2} + \mathrm{CHCl_3} + 3\,\mathrm{KOH} \xrightarrow{\Delta} \mathrm{C_6H_5NC} + 3\,\mathrm{KCl} + 3\,\mathrm{H_2O}.$

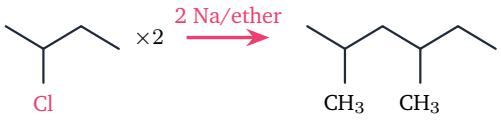
(i) Hydroboration: propene → propan-1-ol



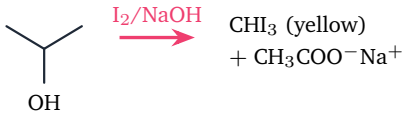
(viii) Sandmeyer: aniline → PhCl



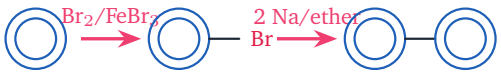
(ix) Wurtz: 2 (2-ClBu) → 3,4-dimethylhexane



(xiv) Haloform: i-PrOH → CHI_3



(xviii) Wurtz–Fittig: benzene → biphenyl



(xx) Carbylamine: aniline → PhNC

Final Answer: Twenty conversions with full reagent sequences as above.

EXPERT'S SOLUTION *: Aanya Verma, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. A pattern recognition drill. Group by the reaction type and write reagents from memory.

- Hydroboration–oxidation: (i), (xiii).
- Multistep alkyne building: (ii).
- Wurtz / Wurtz–Fittig: (ix), (xvii), (xviii).
- Sandmeyer / diazonium: (viii).
- Kolbe nitrile: (vi), (vii), (xi).
- Carbylamine: (xx).
- Haloform: (xiv).
- Halide-shift through alkene + Kharasch: (iii), (xii), (xvi), (xix).
- Markovnikov: (x).
- EAS sequence on benzene: (v), (xv).
- Free-radical side-chain chlorination + hydrolysis: (iv).

Halide-shift pattern explained. Conversions (iii), (xvi), (xix) all involve relocating a halogen from one carbon to a neighbouring carbon. The universal recipe is: (1) eliminate to the alkene with alc. KOH, (2) re-add HX. If Markovnikov gives the desired product, use plain HX; if anti-Markovnikov is needed, use HX/peroxide. This two-step "halide-shift" is the only way to relocate a halogen in NCERT-level chemistry.

Step 1. Walk through each in ~ 1 minute: identify the functional group change, pick the standard reagent.

Step 2. Pay attention to directing effects in aromatic substitutions (Cl, Br are *o,p*-directors; NO_2 is a *m*-director).

Step 3. For halide-shift problems (xiii, xvi, xix), the recipe is always: $E2$ to give alkene, then add HX with peroxide if you want anti-Markovnikov.

Step 4. **Order of operations in (v) and (xv).** For $C_6H_6 \rightarrow$ 4-bromonitrobenzene, brominate *before* nitrating because Br is *o,p*-directing but NO_2 is *m*-directing — the order determines which isomer dominates. For chlorobenzene $\rightarrow$ 4-nitrophenol, nitrate first to activate the ring toward nucleophilic substitution of Cl; without the *para* NO_2 the Cl would not be hydrolysed under reasonable conditions.

Step 5. **Wurtz vs. Wurtz–Fittig in (ix), (xvii), (xviii).** Wurtz: $R-X + R-X + 2\,Na \longrightarrow R-R + 2\,NaX$ (alkyl coupling). Wurtz–Fittig: $Ar-X + R-X + 2\,Na \longrightarrow Ar-R + 2\,NaX$ (mixed alkyl-aryl) or $2\,Ar-X + 2\,Na \longrightarrow Ar-Ar + 2\,NaX$ (aryl-aryl). For (xviii) we use the latter on PhBr to give biphenyl.

Step 6. **Spotting Sandmeyer in (viii).** Aniline ($ArNH_2$) $\rightarrow$ aryl halide requires the diazonium intermediate $Ar-N_2^+X^-$, which is then displaced by CuX (Sandmeyer) or by aqueous HCl boil (Gattermann). Aniline can never be converted directly to chlorobenzene with HCl or NaCl.

Why this matters. Master the table of "reaction class $\rightarrow$ reagent" and you can produce these from a clean slate. NCERT Q 6.19 with its twenty parts is the chapter's flagship pattern-drill; working through it builds the foundation for organic-chemistry retrosynthesis throughout class 12. JEE-Advanced 1-mark MCQs are nearly always drawn from this list of named transformations.

> **Final Answer:** Same twenty reagent sequences.

☞ Exam Tip

For the 5-mark CBSE "how will you carry out the following conversions" question, write *both* the reagent above each arrow *and* the intermediate structure below. Markers deduct for missing intermediates even if the final product is correct.

✗ Common Mistake

For (viii), do not jump from $C_6H_5NH_2$ directly to C_6H_5Cl with HCl — that gives the ammonium salt $C_6H_5NH_3^+Cl^-$, not the aryl chloride. The diazonium step is *required*.

Q 6.20 **The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.**

SOLUTION

Concept used. Aqueous KOH and alcoholic KOH differ in two key ways:

- **Active species.** In aqueous KOH, the dominant species is OH^- (a strong nucleophile, small/hard). In alcoholic KOH (KOH dissolved in ethanol), the active species is $C_2H_5O^-$ (ethoxide), which is a *bulkier and stronger base* than OH^-.
- **Solvent.** Water is a polar protic solvent that stabilises OH^- and the charge build-up in the substitution transition state; ethanol is also protic but less so, and it solvates ethoxide less tightly.

The two channels are:

$$\begin{aligned} \text{Substitution } (S_N2 \text{ or } S_N1): &\quad \mathrm{R{-}Cl + OH^- \longrightarrow R{-}OH + Cl^-}, \\ \text{Elimination } (E2 \text{ or } E1): &\quad \mathrm{R{-}CHR\prime{-}CH_2{-}Cl + OEt^-} \\ &\qquad \longrightarrow \mathrm{R{-}CH{=}CH{-}R\prime + EtOH + Cl^-}. \end{aligned}$$

Substitution wins when the base is a good nucleophile (small, unhindered) and the substrate is unhindered; elimination wins when the base is bulky/stronger and the substrate has accessible β-H's.

Step 1. **Aqueous KOH.** The reactive species is OH^-, a small, strong nucleophile and a weaker base than ethoxide. Attack on the C–Cl carbon is fast, giving an alcohol via S_N pathway. Water-mediated stabilisation of the polar transition state pushes the system toward substitution.

Step 2. **Alcoholic KOH.** The reactive species is $C_2H_5O^-$ (ethoxide), bulkier and stronger as a base than hydroxide. It preferentially abstracts a β-H from R–Cl in a concerted $E2$ step:

$$\mathrm{H{-}C{-}C{-}Cl \xrightarrow{EtO^-} C{=}C + EtO{-}H + Cl^-}.$$

Because EtO^- is bulky, it is less efficient at the crowded backside attack on C, so it abstracts the more accessible β-H instead.

Step 3. **Saytzeff vs Hofmann.** EtO^- is not bulky enough to enforce Hofmann; the elimination still gives the Saytzeff (most substituted) alkene as the major product.

Step 4. **Summary.**

- Aqueous KOH $\rightarrow$ alcohol (substitution dominates).
- Alcoholic KOH $\rightarrow$ alkene (elimination dominates).

Final Answer: Aqueous KOH provides OH^-, a strong but *small* nucleophile that prefers substitution to give R–OH. Alcoholic KOH provides ethoxide ($C_2H_5O^-$), a *bulkier* and stronger base that prefers elimination to give the alkene.

☞ Exam Tip

The mnemonic "aqueous = alcohol; alcoholic = alkene" is worth memorising.

EXPERT'S SOLUTION *: Siddharth Chatterjee, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Same reagent, two different solvents, two different products. The discriminator is which species is solvated vs. free.

Acid–base picture of solvent effect. In water, the equilibrium $\mathrm{KOH(aq)} \rightleftharpoons \mathrm{K^+ + OH^-}$ favours the right completely; $\mathrm{OH^-}$ is the only meaningful nucleophile. In ethanol, KOH dissolves and *also* establishes $\mathrm{OH^- + C_2H_5OH} \rightleftharpoons \mathrm{C_2H_5O^- + H_2O}$, which has $K_{\mathrm{eq}} \approx 1$ because $\mathrm{p}K_a(\mathrm{H_2O}) \approx 15.7$ and $\mathrm{p}K_a(\mathrm{EtOH}) \approx 16$. So a mixture of $\mathrm{OH^-}$ and $\mathrm{C_2H_5O^-}$ is present in alcoholic KOH. Ethoxide, being slightly bulkier and slightly stronger, dominates the elimination channel.

Step 1. In water, $\mathrm{OH^-}$ is the active species: small, strong nucleophile, moderate base. With a primary or secondary alkyl chloride, it does S_N to give the alcohol.

Step 2. In ethanol, KOH dissolves with deprotonation of ethanol and $\mathrm{C_2H_5O^-}$ (ethoxide) becomes the active species. Ethoxide is bulkier and a stronger base, so it abstracts a β-H ($E2$) in preference to attacking the C.

Step 3. Polar protic solvents (water more so than ethanol) stabilise the build-up of charge in the substitution TS; less polar protic solvents (ethanol) tilt the balance toward elimination.

Step 4. Hence: R–Cl + KOH(aq) gives R–OH (substitution); R–Cl + KOH(alc·) gives alkene (elimination).

Step 5. **Temperature also matters.** Heating (Δ) favours elimination over substitution because $E2$ has a higher activation entropy (more degrees of freedom in the TS) and is favoured at higher T. So *warm* alcoholic KOH gives the cleanest alkene yield.

Step 6. **Substrate sensitivity.** The substitution-vs- elimination balance also depends on substrate class: 1° halides prefer S_N2 even with bulky bases; 3° halides prefer $E2$ even with small bases; 2° halides are in the borderline zone where solvent choice dictates the outcome.

Why this matters. The same idea generalises: choose *aqueous* for substitution, *alcoholic* for elimination, *bulky alkoxide* (t-BuOK) for Hofmann elimination. The trio "aqueous KOH, alcoholic KOH, t-BuOK" covers nearly every substitution–elimination scenario in class 12 organic chemistry.

Final Answer: Aqueous KOH gives R–OH; alcoholic KOH gives alkene.

☞ Three bases ranked by bulk

OH^- (smallest, mild base, good Nu) → favours substitution. EtO^- (mid-size, stronger base) → favours elimination, Saytzeff. *tert*-butoxide $(CH_3)_3CO^-$ (very bulky, very strong base) → forces elimination, often Hofmann.

Q 6.21 Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18}, which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

SOLUTION

Concept used.

- Primary C_4H_9Br candidates: 1-bromobutane (n-BuBr) and 1-bromo-2-methylpropane (isobutyl bromide).
- Wurtz on n-BuBr gives n-octane. The problem says (d) is *different* from what n-BuBr gives, so (a) cannot be n-BuBr. Hence (a) = isobutyl bromide.
- Alcoholic KOH on isobutyl bromide eliminates to give 2-methylpropene (isobutylene).
- HBr Markovnikov on 2-methylpropene gives $(CH_3)_3CBr$, the 3° tert-butyl bromide. This is a constitutional isomer of (a).
- Wurtz on isobutyl bromide gives 2,5-dimethylhexane, a C_8H_{18} compound different from n-octane.

Step 1. **Identify (a).** (a) is primary, and Wurtz on (a) gives a C_8H_{18} hydrocarbon different from n-octane. So (a) = **isobutyl bromide, $(CH_3)_2CHCH_2Br$**.

Step 2. **(a) → (b) with alc. KOH.**

$$(CH_3)_2CHCH_2Br + KOH(alc\cdot) \xrightarrow{\Delta} (CH_3)_2C{=}CH_2 + KBr + H_2O.$$

(b) = **2-methylprop-1-ene (isobutylene)**.

Step 3. **(b) → (c) with HBr** (Markovnikov):

$$(CH_3)_2C{=}CH_2 + HBr \longrightarrow (CH_3)_3C{-}Br.$$

(c) = **2-bromo-2-methylpropane (*tert*-butyl bromide)**, an isomer of (a).

Step 4. **(a) → (d) with Na** (Wurtz):

$$2\,(CH_3)_2CHCH_2Br + 2\,Na \xrightarrow{dry\,ether} (CH_3)_2CHCH_2{-}CH_2CH(CH_3)_2 + 2\,NaBr.$$

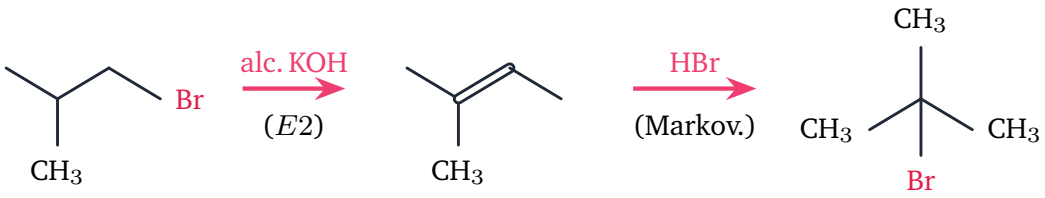
(d) = **2,5-dimethylhexane**.

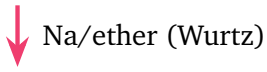
Step 5. Compare with n-octane (Wurtz on n-BuBr):

$$2\,CH_3CH_2CH_2CH_2Br + 2\,Na \longrightarrow CH_3(CH_2)_6CH_3 + 2\,NaBr.$$

Confirmed: 2,5-dimethylhexane is different from n-octane.

(a) isobutyl bromide (b) 2-methylprop-1-ene (c) *tert*-butyl bromide





(d) 2,5-dimethylhexane Compare: n-BuBr Wurtz

Final Answer: (a) = 1-bromo-2-methylpropane (isobutyl bromide); (b) = 2-methylprop-1-ene (isobutylene); (c) = 2-bromo-2-methylpropane (t-BuBr); (d) = 2,5-dimethylhexane.

EXPERT'S SOLUTION *: Neha Iyer, M.Sc Chemistry, IIT Kanpur*

Strategic angle. The two clues that nail down (a) are: (1) primary halide, (2) Wurtz product differs from n-octane. Combined, they force (a) = isobutyl bromide.

Logic-puzzle framework. This is a classic "identify the compound from the reactions" puzzle. Whenever an NCERT problem gives you a series of clues, write the candidates that satisfy *each* clue, then take the intersection. Here, "primary C_4H_9Br" has 2 candidates; "Wurtz $\neq$ n-octane" has 1 candidate (since n-BuBr Wurtz = n-octane). The intersection is unique.

Step 1. Filter 1: primary C_4H_9Br: candidates are n-BuBr and isobutyl bromide.

Step 2. Filter 2: Wurtz on (a) gives a C_8H_{18} different from the Wurtz product of n-BuBr (= n-octane). So (a) is isobutyl bromide.

Step 3. Alc. KOH gives the only Saytzeff alkene available: 2-methylprop-1-ene.

Step 4. HBr Markovnikov: H to the less substituted C (=CH_2), Br to the more

substituted C ($C(CH_3)_2$). Product: t-BuBr, an isomer of (a). Tick.

Step 5. Wurtz coupling: two molecules of $(CH_3)_2CHCH_2Br$ couple at the CH_2Br centres to give $(CH_3)_2CHCH_2-CH_2CH(CH_3)_2$ = 2,5-dimethylhexane.

Step 6. **Counter-check (a) by self-consistency.** If (a) were n-BuBr instead, the Wurtz product would be n-octane ($CH_3(CH_2)_6CH_3$) — but the problem explicitly says (d) is *different* from that. So n-BuBr is excluded. The alc. KOH product of n-BuBr is but-1-ene, whose Markovnikov HBr addition gives 2-bromobutane (not an isomer of $(CH_3)_2CHCH_2Br$ in the sense the question intends; it is an isomer of n-BuBr though). Confusing, which is why the Wurtz check is the cleaner filter.

Step 7. **Concept linkage.** This problem packs four named reactions into one identification puzzle: dehydrohalogenation ($E2$ Saytzeff), Markovnikov HX addition, Wurtz coupling. Each clue is itself a one-mark sub-question. CBSE 5-mark questions of this format are routine.

Why this matters. A logic puzzle: each clue removes one candidate. The skill of *intersecting* structural clues (primary, halide, Wurtz product different from a specific isomer) is exactly the analytical thinking that JEE and AIIMS test repeatedly. The same puzzle template applies to any "mystery compound A reacts as follows; identify A" question.

Final Answer: Same (a)–(d) assignments as in main solution.

♥ Wurtz selectivity matters in synthesis

Wurtz coupling has a serious selectivity problem in the lab: $\mathrm{R{-}X + R\prime{-}X + 2\,Na \longrightarrow R{-}R + R{-}R\prime + R\prime{-}R\prime}$ gives *all three* dimers as a mixture if you start with two different alkyl halides. That is why this question uses two molecules of the *same* R–X — to give a single product. For real mixed-coupling, modern chemistry uses transition-metal-catalysed cross-coupling (Suzuki, Negishi) instead.

Q 6.22 What happens when

(i) n-butyl chloride is treated with alcoholic KOH; (ii) bromobenzene is treated with Mg in the presence of dry ether; (iii) chlorobenzene is subjected to hydrolysis; (iv) ethyl chloride is treated with aqueous KOH; (v) methyl bromide is treated with sodium in the presence of dry ether; (vi) methyl chloride is treated with KCN?

SOLUTION

Concept used.

- Alcoholic KOH $\rightarrow$ $E2$ on alkyl halides.
- Mg/dry ether $\rightarrow$ Grignard reagent formation.
- Chlorobenzene hydrolysis requires harsh conditions (high T, high P, NaOH; Dow process).
- Aqueous KOH $\rightarrow$ S_N2 on a primary halide $\rightarrow$ alcohol.
- Na/dry ether $\rightarrow$ Wurtz coupling.
- KCN $\rightarrow$ ambident nucleophile, C-attack $\rightarrow$ nitrile.

Step 1. **(i) n-butyl chloride + alc. KOH** ($E2$, Saytzeff):

$$\mathrm{CH_3CH_2CH_2CH_2Cl + KOH(alc\cdot) \xrightarrow{\Delta} CH_3CH_2CH{=}CH_2 + KCl + H_2O.}$$

Product: **but-1-ene**.

Step 2. **(ii) Bromobenzene + Mg in dry ether** (Grignard):

$$\mathrm{C_6H_5Br + Mg \xrightarrow{dry\,ether} C_6H_5{-}Mg{-}Br} \quad \text{(phenylmagnesium bromide)}.$$

Step 3. **(iii) Chlorobenzene hydrolysis.** No reaction under ordinary aqueous NaOH. Under harsh conditions ($\sim$ 623 K, 300 atm, conc. NaOH):

$$\mathrm{C_6H_5Cl \xrightarrow{NaOH(aq),\,623\ K,\,300\ atm;\,H_3O^+} C_6H_5OH + NaCl} \quad \text{(Dow process)}.$$

Step 4. **(iv) Ethyl chloride + aq. KOH** (S_N2):

$$\mathrm{C_2H_5Cl + KOH(aq\cdot) \longrightarrow C_2H_5OH + KCl.}$$

Product: **ethanol**.

Step 5. **(v) Methyl bromide + Na in dry ether** (Wurtz):

$$\mathrm{2\,CH_3Br + 2\,Na \xrightarrow{dry\,ether} CH_3{-}CH_3 + 2\,NaBr.}$$

Product: **ethane**.

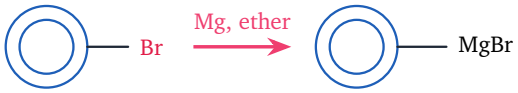
Step 6. **(vi) Methyl chloride + KCN**:

$$\mathrm{CH_3Cl + KCN \longrightarrow CH_3CN + KCl.}$$

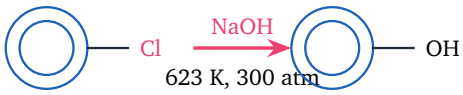
Product: **methyl cyanide / acetonitrile**.

(i) n-BuCl + alc. KOH → but-1-ene

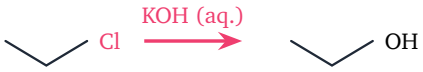
(ii) PhBr + Mg → Grignard



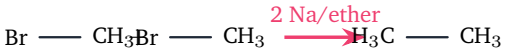
(iii) PhCl Dow process → phenol



(iv) EtCl + aq. KOH → EtOH



(v) MeBr Wurtz → ethane



(vi) MeCl + KCN → MeCN

Final Answer: (i) but-1-ene; (ii) C_6H_5MgBr; (iii) phenol (Dow process, 623 K, 300 atm); (iv) ethanol; (v) ethane (Wurtz); (vi) methyl cyanide.

EXPERT'S SOLUTION *: Ankit Bhat, M.Sc Chemistry, IIT Kanpur*

Quick reading. Six small reactions, one named transformation each. Identify the reagent class, predict the product.

Reagent → named-reaction table. *Alc. KOH* → $E2$ (dehydrohalogenation); *Mg/dry ether* → Grignard; *NaOH at 623 K/300 atm* → Dow process (phenol from chlorobenzene); *Aq. KOH* → S_N (alcohol); *Na/dry ether* → Wurtz coupling; *KCN* → ambident, C-attack, nitrile.

Step 1. (i) Alc. KOH = $E2$ ⇒ alkene. The only Saytzeff product from n-BuCl is but-1-ene.

Step 2. (ii) Mg in dry ether = Grignard formation; C_6H_5MgBr is one of the most useful carbanion equivalents.

Step 3. (iii) Chlorobenzene is essentially inert to ordinary NaOH because the C–Cl bond has partial double-bond character (resonance) and the ring C is sp^2. Industrial Dow process (623 K, 300 atm NaOH) gives phenol.

Step 4. (iv) Aq. KOH = S_N on a primary halide → alcohol. Ethyl chloride gives ethanol.

Step 5. (v) Na in dry ether = Wurtz. Methyl bromide gives CH_3CH_3 (ethane).

Step 6. (vi) CN^- attacks C end; primary halide gives nitrile. Methyl chloride gives acetonitrile.

Step 7. **Why chlorobenzene resists hydrolysis (iii).** Three factors: (a) sp^2 C is more electronegative than sp^3, so the C–Cl bond is shorter and stronger; (b)

lone-pair donation from Cl into the ring gives partial double-bond character to C–Cl; (c) the backside of the sp^2 C is occupied by the π-cloud, so S_N2 backside attack is impossible. The only way around all three is the harsh Dow conditions, which proceed via a benzyne intermediate.

Step 8. **Grignard's silent partner is dry ether.** The ether oxygen lone pairs solvate Mg^{2+}, stabilising the reagent in solution. THF is even better than diethyl ether for unreactive aryl halides; without coordinating solvent, the Grignard would not form.

Step 9. **Concept linkage.** (i) connects to Q 6.20; (ii) to Q 6.12; (iii) to the haloarenes section discussion; (iv) also to Q 6.20; (v) to Q 6.21's Wurtz argument; (vi) to Q 6.8's ambident nucleophile analysis. The six parts of Q 6.22 effectively summarise the entire chapter in capsule form.

Why this matters. Six standard reactions in six lines. Master the reagent $\rightarrow$ outcome mapping. In CBSE board exams, "what happens when X is treated with Y?" is the most frequent 2-mark question format; six such pairs in one question is essentially a comprehensive end-of-chapter test.

Final Answer: Same six products as in main solution.

☞ Why aryl halides resist substitution

The C–Cl bond in chlorobenzene is shorter ($\sim$ 169 pm) and stronger than in cyclohexyl chloride ($\sim$ 177 pm) because of (a) sp^2 hybridisation at C and (b) partial double-bond character from resonance ($+M$ of Cl into the ring). Both make the bond resistant to nucleophilic attack at room temperature.

☞ Exam Tip

For "what happens when" questions, always write *the mechanism name* (Wurtz, $E2$, S_N, Grignard, etc.) *plus the balanced equation plus the product name*. CBSE markers deduct half a mark for missing any of the three components in a 2-mark sub-part.

Key Takeaways

- Haloalkanes have X on sp^3 C; haloarenes have X on sp^2 aromatic C. Reactivity, dipole and hybridisation all differ between the two classes.
- Two limiting substitution mechanisms: S_N2 (one step, backside attack, Walden inversion, rate $\propto$ [RX][Nu], favoured by 1° halides + polar aprotic + strong Nu) and S_N1 (two steps via carbocation, racemisation, rate $\propto$ [RX], favoured by 3° halides + polar protic + weak Nu).
- Two limiting elimination mechanisms: $E2$ (concerted, antiperiplanar) and $E1$ (via carbocation, same intermediate as S_N1). Alcoholic KOH triggers $E2$; bulky bases

(t-BuOK) push toward Hofmann. Saytzeff's rule chooses the most substituted alkene.

- Haloarenes resist nucleophilic substitution because the C–X bond has partial double-bond character (resonance) and the sp^2 C is electron-rich. NCERT specifies the Dow process (NaOH, 623 K, 300 atm) to make phenol.
- Polyhalogen compounds ($CHCl_3$, CCl_4, CHI_3, DDT, freons) have important industrial/medical uses and equally important environmental drawbacks.
- Grignard chemistry (R–MgX) and Wurtz/Wurtz–Fittig couplings extend alkyl chains; both require anhydrous conditions.
- Markovnikov vs anti-Markovnikov (Kharasch peroxide effect) addition of HX to alkenes determines whether an alkene goes to the 2° or 1° halide.

End of Exercise