Collegedunia NCERT Solutions

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

Chapter 7: Alcohols, Phenols and Ethers

About this Chapter

This chapter studies three families of oxygen-bearing organic compounds: **alcohols** (R-OH), **phenols** (Ar-OH) and **ethers** (R-O-R′). You will learn how to name them, how they are prepared from alkenes, alkyl halides, carbonyls and Grignard reagents, why phenol is more acidic than an alcohol, how the **Williamson synthesis** builds an ether, and the mechanisms of acid dehydration, ester formation and electrophilic aromatic substitution on phenol and anisole.

Topics covered: Classification of alcohols and phenols • IUPAC nomenclature • Hydration of alkenes • Hydroboration-oxidation • Grignard route to alcohols • Phenol from cumene, chlorobenzene, benzene sulphonate • Acidity of phenol vs ethanol • Kolbe and Reimer-Tiemann reactions • Williamson ether synthesis • Cleavage of ethers by HI • Friedel-Crafts on anisole

Quick Formula Sheet

Acid hydration of alkene (Markovnikov):

$$CH_2{=}CHR + H_2O \xrightarrow{H_2SO_4} CH_3{-}CH(OH){-}R$$

Hydroboration-oxidation (anti-Markovnikov):

$$RCH{=}CH_2 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} RCH_2CH_2OH$$

Williamson ether synthesis:

$$\text{R-ONa} + \text{R}'\text{-X} \rightarrow \text{R-O-R}' + \text{NaX}$$

Acidity (lower pK_a = stronger acid):

Phenol $pK_a \approx 10.0$ vs Ethanol $pK_a \approx 15.9$

Lucas test ($ZnCl_2$/HCl) turbidity time:

3° instant, 2° in 5 min, 1° no reaction.

Exercises (Q 7.1 to Q 7.33)

Q 7.1 **Write IUPAC names of the following compounds:**

(i) $CH_3-CH(CH_3)-CH(OH)-C(CH_3)_2-CH_3$

(ii) $CH_3-CH(OH)-CH_2-CH(OH)-CH(C_2H_5)-CH_2-CH_3$

(iii) $CH_3-CH(OH)-CH(OH)-CH_3$ (iv) $HO-CH_2-CH(OH)-CH_2-OH$
(v) 2-methyl-6-hydroxy substituted benzene
(vi) 4-methylphenol (vii) 3-methylphenol with OH at C-2
(viii) 2,6-dimethylphenol (ix) $CH_3-O-CH_2-CH(CH_3)-CH_2-CH_3$
(x) $C_6H_5-O-C_2H_5$ (xi) $C_6H_5-O-C_7H_{15}$ (n-)
(xii) $CH_3-CH_2-O-CH(CH_3)-CH_2-CH_3$.

SOLUTION

Concept used. IUPAC nomenclature for alcohols and ethers proceeds in three fixed steps. First, find the longest continuous carbon chain that carries the $-OH$ group; this is the parent alkane and the $-OH$ replaces a final "-e" with "-ol". Second, number the chain so that the carbon bearing $-OH$ gets the lowest possible locant ($-OH$ has priority over alkyl branches and halogens for low numbering). Third, list the substituents alphabetically with their locants as prefixes. For ethers we name the smaller $R-O^-$ group as an alkoxy substituent on the longer carbon chain (the parent). For phenols, the benzene ring carrying $-OH$ is named "phenol" and $-OH$ is at C-1 by default.

> ☞ **Priority of suffix groups**
>
> When more than one functional group is present, the principal characteristic group is chosen by the IUPAC priority list. Between $-OH$ (suffix "-ol") and alkyl branches, $-OH$ wins. So locant 1 is assigned to give the lowest number to the carbon bearing $-OH$.

Step 1. **(i)** The skeleton is $CH_3-CH(CH_3)-CH(OH)-C(CH_3)_2-CH_3$. The longest chain containing $-OH$ has 5 carbons (pentane), and the $-OH$ sits on the middle (C-3) carbon. Both numbering directions therefore give the same locant (3) to the principal group. The tie is broken by "lowest locants for substituents at the first point of difference". Numbering from the gem-dimethyl end gives two methyls on C-2 and one methyl on C-4, i.e. locant set $\{2,2,4\}$; numbering from the other end gives $\{2,4,4\}$. Set $\{2,2,4\}$ wins at the second locant ($2 < 4$). Final name: **2,2,4-trimethylpentan-3-ol**.

Step 2. **(ii)** The skeleton $CH_3-CH(OH)-CH_2-CH(OH)-CH(C_2H_5)-CH_2-CH_3$ has the longest $-OH$-containing chain of 7 carbons: number from the left to keep both OH groups low. Locants are C-2 and C-4 (diol set $\{2,4\}$ is lower than $\{4,6\}$ from the right). An ethyl group sits at C-5. Final name: **5-ethylheptane-2,4-diol**.

Step 3. **(iii)** $CH_3-CH(OH)-CH(OH)-CH_3$. Four-carbon chain (butane) with OH at C-2 and C-3. Name: **butane-2,3-diol**.

Step 4. **(iv)** $HO-CH_2-CH(OH)-CH_2-OH$. Three-carbon chain (propane) with three OH groups at C-1, C-2, C-3. Name: **propane-1,2,3-triol** (common name: glycerol).

Step 5. **(v)** A benzene ring with $-OH$ at C-1 and a $-CH_3$ at the adjacent ortho carbon

(C-2). Name: **2-methylphenol** (*o*-cresol).

Step 6. **(vi)** Benzene ring with $-OH$ at C-1 and $-CH_3$ at C-4. Name: **4-methylphenol** (*p*-cresol).

Step 7. **(vii)** Benzene ring with $-OH$ at C-1 and a $-CH_3$ at C-3. Name: **3-methylphenol** (*m*-cresol).

Step 8. **(viii)** Benzene ring with $-OH$ at C-1 and methyls at C-2 and C-6. Name: **2,6-dimethylphenol**.

Step 9. **(ix)** $CH_3-O-CH_2-CH(CH_3)-CH_2-CH_3$. The longer side of the ether oxygen is the butyl chain $(-CH_2-CH(CH_3)-CH_2-CH_3)$; the shorter side is $-OCH_3$ (methoxy). Numbering the parent butane from the end nearer the alkoxy gives OCH_3 at C-1, methyl at C-2. Name: **1-methoxy-2-methylbutane**.

Step 10. **(x)** $C_6H_5-O-C_2H_5$ = ethoxybenzene. Treat the phenyl side as the larger parent (benzene). The smaller ethyl-O side is the alkoxy substituent. Name: **ethoxybenzene** (common: phenetole).

Step 11. **(xi)** $C_6H_5-O-(CH_2)_6-CH_3$ (n-heptyl). Phenoxy substituent on heptane: 1-phenoxyheptane. But IUPAC also accepts naming benzene as the parent when the substituent chain is acyclic. Standard NCERT answer: **1-phenoxyheptane**.

Step 12. **(xii)** $CH_3-CH_2-O-CH(CH_3)-CH_2-CH_3$. The longer side of the oxygen is $-CH(CH_3)-CH_2-CH_3$ (a 3-carbon chain with a methyl branch on C-1 of the parent end); the shorter is $-OC_2H_5$ (ethoxy). The parent (after choosing the longer carbon side) is butane via the chain $CH_3-CH(O\,Et)-CH_2-CH_3$ where the OC_2H_5 is the alkoxy substituent on butane at C-2. Name: **2-ethoxybutane**.

Final Answer: (i) 2,2,4-trimethylpentan-3-ol; (ii) 5-ethylheptane-2,4-diol; (iii) butane-2,3-diol; (iv) propane-1,2,3-triol; (v) 2-methylphenol; (vi) 4-methylphenol; (vii) 3-methylphenol; (viii) 2,6-dimethylphenol; (ix) 1-methoxy-2-methylbutane; (x) ethoxybenzene; (xi) 1-phenoxyheptane; (xii) 2-ethoxybutane.

☞ Numbering trick for diols and triols

For a compound with two or three $-OH$ groups, choose the numbering that minimises the *set* of OH locants, comparing position-by-position. For instance, $\{2, 4\}$ beats $\{4, 6\}$ because $2 < 4$ at the first point of difference.

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

Structural observation. Every name above follows the same template: parent chain length + suffix for the principal group + locants for substituents. The trick is to identify the parent chain correctly when more than one chain length is possible, and to recognise that the priority of the principal characteristic group ($-$OH) overrides the priority of any mere substituent (alkyl, halogen).

Alternative approach: "three-step decoder". For any compound name, (1) circle the suffix and its locant, (2) find the parent chain or ring that bears it, (3) attach all substituents at their locants. The reverse procedure works for naming: tag the principal group, find the longest chain through it, then label substituents.

Step 1. For (i), the parent is pentane (5 C), with the $-$OH on the middle carbon (C-3). Because OH sits at the central carbon, its locant is 3 regardless of numbering direction. The substituent locants decide the tie: numbering from the gem-dimethyl end gives $\{2, 2, 4\}$ for the three methyls, the other way gives $\{2, 4, 4\}$. "Lowest locants at the first point of difference" picks $\{2, 2, 4\}$. Hence **2,2,4-trimethylpentan-3-ol**.

Step 2. For (ii), pick the longest chain that includes *both* OH groups. The continuous chain runs through all seven carbons of the main backbone, giving heptane. Numbering from the methyl end nearer the first OH places OH at C-2 and C-4. An ethyl branch sits at C-5. Final name: **5-ethylheptane-2,4-diol**. The "first point of difference" rule resolves the diol-locant set $\{2, 4\}$ vs $\{4, 6\}$ in favour of the former.

Step 3. For polyols (iii), (iv) the parent name keeps the terminal "-e" before "-diol"/"-triol" to avoid two consecutive vowels colliding: "butane-2,3-diol", not "butan-2,3-diol". The same rule will apply to amines ("-diamine") in the next chapter.

Step 4. For aromatic compounds (v) to (viii) the ring is the parent, $-$OH is at C-1, and the locants are chosen so the methyl substituents get the smallest numbers. The common names $o/m/p$-cresol are still widely accepted in industry but IUPAC nomenclature is required in exams.

Step 5. For ethers (ix) to (xii), apply the substitutive-ether rule: name the smaller side as "R-oxy" ($-$OR) and treat it as a substituent on the larger parent. "Methoxy" = $-OCH_3$, "ethoxy" = $-OC_2H_5$, "phenoxy" = $-OC_6H_5$. For $C_6H_5-O-C_7H_{15}$ (xi) the longer "side" would be the heptane chain (7 C $>$ benzene's effective 6 C in substitutive nomenclature), so heptane is the parent and phenoxy is the substituent.

Concept linkage. The IUPAC priority list places $-$OH (suffix "-ol") below $-$COOH, $-$CHO, $C{=}O$ and a few others, but above amines, ethers, halogens and alkyl branches. So if both $-$OH and $-$COOH sit on the same molecule, the acid takes the suffix and the alcohol becomes "hydroxy" as a prefix. You'll need this hierarchy whenever biomolecules (Ch 14, e.g. carbohydrates with -OH and -CHO) are named.

Exam relevance. JEE Main and CBSE board exams typically allocate one MCQ or one

2-mark question to IUPAC nomenclature of alcohol-ether mixtures; expect at least one such question every year. Common trap: not picking the longest chain that contains $-OH$ (test case is exactly (i) above).

Why this matters. A clean IUPAC name lets a chemist re-draw the structure unambiguously: it is the working language of every later mechanism, spectroscopy or retrosynthesis problem. Spectroscopists also use it as the key to look up reference NMR/IR data.

Final Answer: Names as listed in the main solution.

☞ **IUPAC priority order**

$-COOH > -COOR > -CONH_2 > -CN > -CHO > C{=}O > -OH > -NH_2 > -OR > -X$. The leftmost group present takes the suffix; the others become prefixes.

Q 7.2 **Write structures of the compounds whose IUPAC names are as follows:**
(i) 2-Methylbutan-2-ol (ii) 1-Phenylpropan-2-ol (iii) 3,5-Dimethylhexane-1,3,5-triol (iv) 2,3-Diethylphenol (v) 1-Ethoxypropane (vi) 2-Ethoxy-3-methylpentane (vii) Cyclohexylmethanol (viii) 3-Cyclohexylpentan-3-ol (ix) Cyclopent-3-en-1-ol (x) 4-Chloro-3-ethylbutan-1-ol.

SOLUTION

Concept used. To go from an IUPAC name to a structure, reverse the naming algorithm: identify the parent chain length from the root (but, pent, hex, etc.), place the principal group at its locant, and attach each substituent on its locant carbon.

Step 1. **(i) 2-Methylbutan-2-ol.** Parent: butane (4 C). OH at C-2; methyl at C-2 as well. Structure: $CH_3-C(OH)(CH_3)-CH_2-CH_3$.

Step 2. **(ii) 1-Phenylpropan-2-ol.** Parent: propane. OH at C-2; phenyl at C-1. Structure: $C_6H_5-CH_2-CH(OH)-CH_3$.

Step 3. **(iii) 3,5-Dimethylhexane-1,3,5-triol.** Parent: hexane. OH at C-1, C-3, C-5; methyls at C-3, C-5. Structure: $HO-CH_2-CH_2-C(CH_3)(OH)-CH_2-C(CH_3)(OH)-CH_3$.

Step 4. **(iv) 2,3-Diethylphenol.** Benzene with OH at C-1; ethyl groups at C-2 and C-3: $o\text{-}(C_2H_5)\text{-}m\text{-}(C_2H_5)\text{-}C_6H_3-OH$.

Step 5. **(v) 1-Ethoxypropane.** Parent: propane. Ethoxy $-OC_2H_5$ at C-1. Structure: $CH_3-CH_2-CH_2-O-CH_2-CH_3$.

Step 6. **(vi) 2-Ethoxy-3-methylpentane.** Parent: pentane. Ethoxy at C-2, methyl at

C-3. Structure: $CH_3-CH(OC_2H_5)-CH(CH_3)-CH_2-CH_3$.

Step 7. **(vii) Cyclohexylmethanol.** A $-CH_2OH$ on cyclohexane: $C_6H_{11}-CH_2OH$.

Step 8. **(viii) 3-Cyclohexylpentan-3-ol.** Parent: pentane. OH and a cyclohexyl group both at C-3: $CH_3-CH_2-C(C_6H_{11})(OH)-CH_2-CH_3$.

Step 9. **(ix) Cyclopent-3-en-1-ol.** Cyclopentene with the double bond between C-3 and C-4 and an $-OH$ at C-1. Structure: a 5-membered ring with one C=C two carbons away from the C bearing OH.

Step 10. **(x) 4-Chloro-3-ethylbutan-1-ol.** A 4-carbon parent labelled C-1 to C-4 starting from the $-OH$; ethyl at C-3, Cl at C-4. Structure: $HO-CH_2-CH_2-CH(C_2H_5)-CH_2Cl$. (NCERT names this with $-CH_2Cl$ terminal as "4-chloro-3-ethylbutan-1-ol" even though strict IUPAC would re-number.)

Final Answer: (i)–(x) structures as drawn above.

★ Decoding the name

"*Locant*-substituent-*parent*-*locant*-suffix". Strip off the suffix to get the principal group and its locant first; then drop substituents onto their numbered carbons.

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

Picture-first. The easiest way is to draw the parent skeleton with numbered carbons, then "decorate" it with substituents and the principal group. The opposite of Q 7.1: we go from name to structure, so we read the locant of the "-ol" (or "-en-ol") first, then add substituents.

Alternative approach: build it like LEGO. Start with the parent block (a n-carbon chain or ring numbered 1 to n), snap on the principal group at its locant, then click on each substituent in turn. For polyols, place all OH groups before methyls or ethyls so you do not lose count.

Step 1. For each item, draw the parent: n carbons in a row, labelled C-1, C-2, . . . , C-n left to right (or as a ring for cyclic parents). Use bond-line shorthand if you wish: the ends and corners are carbons, hydrogens are implicit.

Step 2. Attach the suffix group (the "-ol" or "-en-ol") at its locant carbon. Remember that "en" designates a $C=C$ double bond between two specified carbons.

Step 3. Add substituents at their locant carbons. For (iv) the phenol carbon is C-1 (carries OH), then go ortho to it for C-2 and continue around the ring for C-3.

Step 4. For (ix), the double bond "3-en" specifies a $C_3=C_4$ bond, two carbons away from the OH at C-1. That gives the symmetric cyclopent-3-en-1-ol.

Step 5. For (x), 4-chloro-3-ethylbutan-1-ol has an apparent conflict: butan-1-ol's parent has only 4 carbons but "3-ethyl" adds 2 more (making 6 total). The 4-carbon *parent* is chosen because it carries the principal group $-OH$ at C-1; the ethyl branch sits on C-3 and the chloro on C-4.

Concept linkage. Reading a name backwards is the same skill set as drawing organic products from a reaction equation. Both require breaking the name into root, suffix and prefixes, and rebuilding the connectivity on paper.
Exam relevance. Almost every CBSE Class 12 chemistry paper has a 1-mark "draw the structure of X" question somewhere; the trick is to identify the parent length from the root (but, pent, hex) and the principal group from the suffix (-ol, -al, -oic acid, -one).
Numerical sanity check. The molecular formula of each compound should match. For (iii) $3{,}5-\text{dimethylhexane}-1{,}3{,}5-\text{triol}$, count: $C_8H_{18}O_3$ (6 C in hexane + 2 methyl branches = 8 C; 3 OH + the rest is saturated $\rightarrow$ 18 H + 3 O). Cross-check with the drawn structure.
Why this matters. This decode skill is exactly what an exam reverse-name question tests: parse the name into pieces, then re-build the molecule piece by piece. The same skill lets you convert a reaction product like "2-bromo-2-methylbutane" into a drawable structure quickly (Q 7.33).

Final Answer: (i)–(x) structures as drawn above.

☞ Faster reading

Whenever you see "X-Y-parent-Z-suffix" in a name, X-Y is a substituent at locant given just before its name, and Z is the locant of the suffix. Sketch the parent first, place suffix, then substituents.

☞ Watch your locants

For ethers with halogens (like (vi) 2-ethoxy-3-methylpentane extended versions), the "lowest locant" rule applies to the *set* of all named substituents, since there is no suffix-priority group: pick numbering that gives the smallest locant at the first point of difference.

Q 7.3 (i) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.
(ii) Classify the isomers of alcohols in question 7.3 (i) as primary, secondary and tertiary alcohols.

SOLUTION

Concept used. For $C_5H_{12}O$ (a saturated, acyclic formula $C_nH_{2n+2}O$), all isomers with an $-OH$ group on sp^3 carbon are pentanol-type alcohols. An **alcohol** is classified as **primary (1°)** if its $-OH$-bearing carbon is attached to one other C; **secondary (2°)** if to two other C; **tertiary (3°)** if to three. The carbon-skeleton isomers of pentane are three: n-pentane, isopentane (2-methylbutane), neopentane (2,2-dimethylpropane). On each skeleton, the OH can sit at any chemically distinct carbon.

Step 1. **n-pentane skeleton** ($CH_3-CH_2-CH_2-CH_2-CH_3$): OH can go on C-1 (= pentan-1-ol, 1°), C-2 (= pentan-2-ol, 2°), or C-3 (= pentan-3-ol, 2°).

Step 2. **2-methylbutane skeleton** ($CH_3-CH(CH_3)-CH_2-CH_3$): OH can go on C-1 (= 2-methylbutan-1-ol, 1°), C-2 (= 2-methylbutan-2-ol, 3°), C-3 (= 3-methylbutan-2-ol, 2°), or on the terminal of the methyl branch = 3-methylbutan-1-ol, 1°.

Step 3. **2,2-dimethylpropane skeleton**: OH on a CH_3 gives $(CH_3)_3C-CH_2OH$ = 2,2-dimethylpropan-1-ol (neopentyl alcohol), 1°. No other distinct position on this skeleton.

Step 4. **Total: 8 isomeric alcohols** of formula $C_5H_{12}O$.

(ii) Classification.

- **Primary (1°):** pentan-1-ol, 2-methylbutan-1-ol, 3-methylbutan-1-ol, 2,2-dimethylpropan-1-ol. (4 isomers)
- **Secondary (2°):** pentan-2-ol, pentan-3-ol, 3-methylbutan-2-ol. (3 isomers)
- **Tertiary (3°):** 2-methylbutan-2-ol. (1 isomer)

> **Final Answer:** Eight isomers: 4 primary, 3 secondary, 1 tertiary.

☞ Counting check

For $C_5H_{12}O$ alcohols, the standard answer is 8 isomers. If you draw fewer, you missed an OH-position on the 2-methylbutane skeleton; if you draw more, you double-counted a skeleton permutation (e.g. “4-methylbutan-1-ol” is the same as “2-methylbutan-1-ol” reversed).

EXPERT’S SOLUTION *: Karan Mehta, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Walk through the three carbon skeletons of C_5 (pentane, 2-methylbutane, 2,2-dimethylpropane). On each, mark all chemically distinct carbons and place $-OH$ on each in turn. This “skeleton → substitution-site” algorithm is the cleanest way to enumerate structural isomers.

Alternative approach: degree-of-unsaturation check. $C_5H_{12}O$ has DoU =

$(2 \times 5 + 2 - 12)/2 = 0$. So all eight isomers are saturated, acyclic, and have one -OH (no rings, no double bonds). This rules out, e.g. a five-membered ring with an OH (which would have DoU = 1).

Step 1. Pentane has 3 distinct carbons by symmetry (C-1 = C-5, C-2 = C-4, C-3): so 3 OH positions → 3 alcohols. Pentan-1-ol is $1°$; pentan-2-ol and pentan-3-ol are both $2°$.

Step 2. 2-Methylbutane has 4 distinct carbons (the three on the main chain plus the methyl branch): so 4 OH positions → 4 alcohols. 2-Methylbutan-1-ol and 3-methylbutan-1-ol are $1°$; 3-methylbutan-2-ol is $2°$; 2-methylbutan-2-ol is $3°$ (only $3°$ isomer in the set).

Step 3. 2,2-Dimethylpropane (neopentane) has 2 distinct carbons (the central C and the four equivalent methyls): only one OH position gives a valid alcohol (on a methyl); OH on the central C would replace a methyl, which is not a substitution but a different skeleton. So 1 alcohol: 2,2-dimethylpropan-1-ol (neopentyl alcohol), $1°$.

Step 4. Total: $3 + 4 + 1 = 8$ alcohols. Classification: $4\ 1°$ + $3\ 2°$ + $1\ 3°$ = 8 (cross-check).

Concept linkage. The same enumeration trick is used in Q 7.7 (C_7H_8O phenols/alcohols) and in the haloalkanes chapter ($C_5H_{11}Br$, 8 isomers). The pattern "one functional group + all distinct skeletons + all distinct substitution positions" gives every constitutional isomer.

Exam relevance. Counting isomers is a perennial 1- or 2-mark question. The trap is to over-count by treating an already-counted structure as new (e.g., the so-called "4-methylbutan-1-ol" is just 2-methylbutan-1-ol reversed). Use the canonical IUPAC name as a unique key.

Numerical aside. The number of acyclic alcohol isomers of $C_nH_{2n+2}O$ grows quickly: $n = 1 \to 1$, $n = 2 \to 1$, $n = 3 \to 2$, $n = 4 \to 4$, $n = 5 \to 8$, $n = 6 \to 17$.

Why this matters. Counting structural isomers by "skeleton then substitution position" is the cleanest method and generalises to halides, amines and ethers. It is also a prerequisite for spectroscopy: when an NMR shows "six signals, one CHOH at δ 3.7", that already pins one of the eight isomers down.

Final Answer: Eight isomers in total: 4 primary, 3 secondary, 1 tertiary.

♥ Where do these isomers actually appear?

2-Methylbutan-2-ol is a $3°$ alcohol with $pK_a \sim 18$ and is famous for being unreactive toward oxidation (no α-H on the OH-bearing carbon). 3-methylbutan-1-ol (isoamyl alcohol) is the main flavour molecule of banana esters in the food industry.

Q 7.4 Explain why propanol has higher boiling point than that of the hydrocarbon, butane.

SOLUTION

Concept used. Boiling point depends on the strength of **intermolecular forces** that must be broken to take a liquid to the gas phase. For comparable molecular masses, the ranking of these forces is

$$\text{hydrogen bonding} > \text{dipole-dipole} > \text{London dispersion}.$$

Hydrogen bonding (H-bonding) is an unusually strong dipole-dipole attraction between an $-$OH (or $-$NH) on one molecule and a lone pair of an electronegative atom (O, N, F) on a neighbouring molecule.

Step 1. Compare molecular masses. $M(\mathrm{C_3H_7OH}) = 3(12) + 7(1) + 16 + 1 = 60\,\mathrm{g/mol}$; $M(\mathrm{C_4H_{10}}) = 4(12) + 10(1) = 58\,\mathrm{g/mol}$. The two molecules have nearly the same mass and similar size.

Step 2. Identify forces in butane (C_4H_{10}). Butane is non-polar, so its only intermolecular force is weak **London dispersion** (induced dipole-induced dipole). Boiling point: $-0.5\,°\mathrm{C}$.

Step 3. Identify forces in propanol (C_3H_7OH). Propanol has an $-$OH group, which provides a polar O-H bond and a lone pair on oxygen. So propanol molecules form **hydrogen bonds** between an O-H of one molecule and the lone pair of O on another:

$$\mathrm{R{-}O{-}H} \cdots \mathrm{O(H){-}R}.$$

Each H-bond is worth roughly $20\,\mathrm{kJ/mol}$, much stronger than London dispersion ($1\text{–}10\,\mathrm{kJ/mol}$). Boiling point of propan-1-ol: $97\,°\mathrm{C}$.

Step 4. Conclusion. A vapourising propanol molecule must break several hydrogen bonds, while a vapourising butane molecule only needs to break dispersion contacts. So propanol has a much higher boiling point.

Hydrogen-bonded chain in liquid alcohol

Final Answer: Propanol's molecules associate through hydrogen bonding (an extra ~20 kJ/mol attraction per pair) while butane only has weak London forces, so much more energy is needed to vapourise propanol than butane.

♥ Why this matters

The same logic explains why water (H_2O, 18 g/mol) boils at $100\,°\mathrm{C}$ but methane (CH_4, 16 g/mol) at $-161\,°\mathrm{C}$. Strong intermolecular attractions, not mass alone, set the boiling point.

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

Strategic angle. Anchor the comparison in numbers: both molecules weigh about 60 g/mol, yet their boiling points differ by nearly $100\,°\mathrm{C}$. Such a gap can only come from a qualitatively different intermolecular force—hydrogen bonding is the only candidate.

Alternative approach: enthalpy of vaporisation comparison. A clean way to make the case is to look up ΔH_{vap}: $\Delta H_{\text{vap}}(\text{butane}) = 22.4\,\text{kJ/mol}$, $\Delta H_{\text{vap}}(\text{propan-1-ol}) = 47.5\,\text{kJ/mol}$. The gap of $25\,\text{kJ/mol}$ is the energetic cost of breaking roughly one or two hydrogen bonds per molecule on vaporisation—a direct measurement of the H-bond energy.

Step 1. Butane is a non-polar alkane. Its only attractions are London dispersion, which scale with surface area and polarisability. At 58 g/mol they give a b.p. of $-0.5\,°\mathrm{C}$ (about 273 K).

Step 2. Propanol has an $-$OH group. The O-H bond is highly polar ($\Delta\chi = 1.24$ on the Pauling scale), so δ^+ on H and δ^- on O. The H on one molecule attracts the O lone pair on a neighbour: a hydrogen bond. The geometry of the H-bond is almost linear ($\angle$O–H$\cdots$O $\approx 175°$) and the O$\cdots$O distance is about $2.8\,\text{Å}$.

Step 3. Hydrogen-bond strength: about $20\,\text{kJ/mol}$ per O$-$H $\cdots$O contact. Each propanol molecule can act once as donor and twice as acceptor (oxygen has two lone pairs), forming an associated, chain-like cluster in the liquid. In propan-1-ol's solid phase, X-ray data show extended H-bonded helices.

Step 4. To vapourise, the molecule must escape this cluster. That extra cost of breaking H-bonds raises the b.p. to $97\,°\mathrm{C}$ (370 K), almost $100\,°\mathrm{C}$ above butane.

Concept linkage: alcohol vs alkane vs ether. An ether (e.g. methoxymethane, C_2H_6O) has the same skeleton size as propanol but no O-H bond. Its boiling point is $-24\,°\mathrm{C}$, far below propanol's $97\,°\mathrm{C}$. So the lesson generalises: "OH bonded to electronegative atom" is the differentiator, not just "contains O". Q 7.22 explores this with ethanol vs dimethyl ether.

Exam relevance. Boiling-point comparison questions ($\sim$1–2 marks) appear in every CBSE paper. The expected answer must (1) name the intermolecular force in each compound, (2) rank their strengths, and (3) connect to b.p. Stating "hydrogen bonding" alone is half-marks; you must also explain why butane cannot.

Numerical aside. K_b-style intuition: a 25 kJ/mol gap in ΔH_{vap} predicts a b.p. gap by Trouton's rule $T_b \approx \Delta H_{\text{vap}}/85\,\mathrm{J\,K^{-1}\,mol^{-1}} \Rightarrow \Delta T_b \approx (25\,000/85) \approx 290$ K in idealised cases. In practice the gap is smaller ($100\,°\mathrm{C}$) because Trouton's rule overestimates strongly-associated liquids.

Why this matters. Hydrogen bonding is the single biggest reason organic chemistry treats alcohols, amines and water-like solvents very differently from alkanes. The same logic explains why DNA strands hold each other (H-bonds between bases) and why ice floats on water (the H-bond network of solid ice is less dense than liquid water).

> **Final Answer:** Propan-1-ol forms hydrogen bonds; butane does not. Hence propanol has the higher boiling point ($+97$ vs $-0.5\,°\mathrm{C}$).

☞ Three-tier ranking

For Class 12 boiling-point questions, rank intermolecular forces in this order (weakest to strongest): London dispersion $<$ dipole-dipole $<$ hydrogen bonding $<$ ion-dipole. A compound at the higher tier almost always boils higher than one at a lower tier of comparable mass.

☞ H-bond requirements

A hydrogen bond needs (i) an H atom bonded to N, O, or F (the donor) and (ii) a lone pair on N, O, or F on a neighbour (the acceptor). C-H is never a donor in standard cases.

Q 7.5 Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

SOLUTION

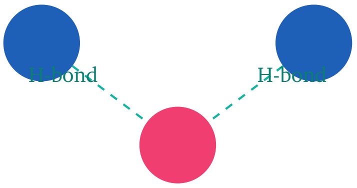
Concept used. A solute dissolves in a solvent when the solute-solvent attractions are comparable to (or stronger than) both the solute-solute and the solvent-solvent attractions that must be broken. For water (H_2O), the solvent-solvent attraction is hydrogen bonding. So a solute that can form hydrogen bonds with water dissolves, while one that cannot is forced out (the “hydrophobic effect”).

Step 1. Identify the H-bonding sites in an alcohol. Each $R{-}OH$ has one O-H (donor) and two lone pairs on O (acceptors). So an alcohol can both *donate* and *accept* hydrogen bonds with water.

Step 2. Identify them in a hydrocarbon. A pure hydrocarbon (e.g. propane, butane) has only C-H bonds. C-H is almost non-polar; H bonded to C cannot serve as an H-bond donor, and there is no lone pair to accept either.

Step 3. Compare solvation energies. Dissolving propan-1-ol in water replaces water-water H-bonds with new $R{-}O{-}H\cdots O(H_2)$ and $R{-}O\cdots H{-}OH$ contacts, which are roughly the same strength. So the process is thermodynamically near-neutral, i.e. propan-1-ol is miscible with water. Butane, on the other hand, can only offer weak dispersion forces to the water network and so it is forced into a separate layer (almost insoluble).

Step 4. Trend with chain length. As the alkyl tail grows, the hydrophobic part dominates over the hydrogen-bonding $-$OH, and solubility falls: methanol and ethanol are fully miscible, but hexan-1-ol is only sparingly soluble.



> **Final Answer:** Alcohols form hydrogen bonds with water (R-O-H acts as donor; lone pair on O acts as acceptor). Hydrocarbons cannot form such bonds, so they are far less soluble than alcohols of comparable molecular mass.

✗ Don't say "polarity alone"

A naive answer is "alcohols are polar, hydrocarbons are non-polar". That is incomplete: dichloromethane is polar but only sparingly soluble in water because it cannot donate hydrogen bonds. The right reason is the hydrogen-bonding capability of the $-$OH group, not polarity in general.

EXPERT'S SOLUTION *: Vivaan Reddy, M.Sc Physical Chemistry, IIT Madras*

Structural observation. Two requirements for a small molecule to dissolve in water are (a) polarity, and (b) the ability to form hydrogen bonds. Alcohols meet both; hydrocarbons meet neither.

Alternative approach: thermodynamic accounting. Dissolution is governed by $\Delta G_{\text{soln}} = \Delta H_{\text{soln}} - T\Delta S_{\text{soln}}$. For alcohols $\Delta H_{\text{soln}} \approx 0$ (water-water H-bonds replaced by water-alcohol H-bonds of similar strength); $\Delta S_{\text{soln}} > 0$ (mixing entropy); so $\Delta G_{\text{soln}} < 0$ and the alcohol dissolves. For hydrocarbons $\Delta H \approx 0$ but $\Delta S_{\text{soln}} < 0$ (the "iceberg" of ordered water around the hydrophobe), so $\Delta G_{\text{soln}} > 0$ and they do not dissolve.

Step 1. In water, every H_2O is surrounded by roughly four H-bonded neighbours (tetrahedral arrangement). To insert a guest molecule, some of these water-water H-bonds must be temporarily broken (cost: $\sim$20 kJ/mol each).

Step 2. An alcohol pays this cost back: it forms new water-alcohol H-bonds of similar strength ($\sim$20 kJ/mol). Net enthalpy of solution is small; entropy of mixing is favourable; so it dissolves. For ethanol, methanol, propan-1-ol, water-miscibility is complete (1:1 in all proportions).

Step 3. A hydrocarbon offers no replacement H-bonds. Water molecules near the hydrocarbon are forced into a more ordered "cage" (lower entropy: ΔS

contribution of -30 to -50 J/(mol K) for small alkanes). Net free energy of solution is positive ($\Delta G \approx +10$ kJ/mol for butane), so the hydrocarbon is excluded: the **hydrophobic effect**.

Step 4. Longer-chain alcohols (hexan-1-ol, heptan-1-ol) increasingly behave like hydrocarbons because the chain length overwhelms the single $-$OH. Standard solubility data: $\mathrm{MeOH, EtOH, PrOH}$: miscible; BuOH: 8.0 g/100 g water; PentOH: 2.2 g/100 g; HexOH: 0.6 g/100 g.

Concept linkage: phenol vs alcohol solubility. Phenol ($pK_a \sim 10$) is moderately soluble in water (8 g/100 g at $20\,^\circ\mathrm{C}$); above $66\,^\circ\mathrm{C}$ it becomes fully miscible. The phenolic OH H-bonds with water, but the aromatic ring is largely hydrophobic. Compare this with octan-1-ol, which is almost insoluble in water despite having an OH. Solubility is always a battle between the H-bonding head and the hydrophobic tail.

Exam relevance. Solubility questions are usually phrased as comparisons. The expected answer always cites (1) intermolecular forces in the pure solute, (2) forces between solute and water, and (3) the net thermodynamic balance.

Numerical hook. The Hildebrand solubility parameter δ provides a quick way to predict miscibility: $\delta(\text{water}) = 47.8\,\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$, $\delta(\text{ethanol}) = 26.5$, $\delta(\text{hexane}) = 14.9$. Compounds with similar δ values are miscible; large gaps mean phase separation. Hexane and water differ by 32 units— they are immiscible.

Why this matters. The "like dissolves like" rule of thumb is really shorthand for matching intermolecular forces. Water dissolves what it can H-bond with; oil dissolves what it can only dispersion-bond with. This is the basis of soap action, membrane biology, and even why colours in your laundry detergent work—each is a balance between hydrophilic and hydrophobic parts of the same molecule.

> **Final Answer:** The $-$OH of an alcohol forms hydrogen bonds with water; a hydrocarbon cannot. Hence alcohols are far more water-soluble than hydrocarbons of comparable mass.

♥ Hydrophobic effect everywhere

The same logic that makes hexane immiscible with water also folds proteins (hydrophobic side chains hide inside), forms soap micelles (oil tails inside, ionic heads outside), and makes cell membranes assemble. Q 7.5 is a tiny window onto a massive biological theme.

Q 7.6 What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

SOLUTION

Concept used. The **hydroboration-oxidation reaction** is a two-step transformation that converts an alkene into a primary alcohol with **anti-Markovnikov** regiochemistry. Step 1 (*hydroboration*): diborane (B_2H_6, equivalent to BH_3) adds across the C=C double bond in a single concerted, syn-addition; boron goes to the less-substituted carbon, hydrogen to the more-substituted carbon. The product is a **trialkylborane**, R_3B. Step 2 (*oxidation*): alkaline hydrogen peroxide (H_2O_2 in aqueous $NaOH$) replaces the C-B bond by a C-OH bond with retention of configuration. The overall result is formal addition of $H{-}OH$ to the alkene with H on the more substituted carbon and OH on the less substituted carbon, the opposite of acid-catalysed hydration (Markovnikov).

Step 1. Step 1, hydroboration. The boron atom in BH_3 has only six valence electrons, so it is electrophilic. The π-electrons of the alkene attack boron; the boron-H bond then breaks, delivering H to the other carbon. Because the B-H adds to one face of the alkene in a single transition state, the addition is *syn*. Three such additions consume one BH_3 to give a trialkylborane R_3B.

$$3\,RCH{=}CH_2 + BH_3 \longrightarrow (RCH_2CH_2)_3B.$$

Step 2. Step 2, oxidation. Treat the trialkylborane with alkaline H_2O_2:

$$(RCH_2CH_2)_3B + 3\,H_2O_2 \xrightarrow{OH^-} 3\,RCH_2CH_2OH + B(OH)_3.$$

The peroxide oxygen displaces the alkyl group from boron, then water delivers the proton to give the alcohol.

Step 3. Example. Start from propene ($CH_3{-}CH{=}CH_2$). Hydroboration places B on C-1 (less substituted) and H on C-2 (more substituted):

$$CH_3{-}CH{=}CH_2 \xrightarrow{\text{(i) } B_2H_6} (CH_3{-}CH_2{-}CH_2)_3B.$$

Oxidation gives propan-1-ol:

$$(CH_3{-}CH_2{-}CH_2)_3B \xrightarrow{\text{(ii) } H_2O_2,\ OH^-} CH_3{-}CH_2{-}CH_2{-}OH + B(OH)_3.$$

Notice that acid-catalysed hydration of the same propene would have given propan-2-ol (Markovnikov), so hydroboration-oxidation gives the *opposite regiochemistry*.

$$\underset{\textbf{(propene)}}{CH_3{-}CH{=}CH_2} \xrightarrow{B_2H_6\ \text{(syn)}} \underset{\textbf{(tri-}n\textbf{-propylborane)}}{(CH_3CH_2CH_2)_3B} \xrightarrow{H_2O_2,\ OH^-} \underset{\textbf{(propan-1-ol)}}{CH_3{-}CH_2{-}CH_2{-}OH}$$

> **Final Answer:** Hydroboration-oxidation = (i) addition of B_2H_6 across an alkene; (ii) oxidation by alkaline H_2O_2 to give an anti-Markovnikov primary alcohol. Example: propene → propan-1-ol.

☞ **Memory hook**

"B_2H_6/H_2O_2 = water adds backwards." Boron delivers H to the more-substituted carbon, so OH ends up on the less-substituted carbon: the opposite of Markovnikov.

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

Strategic angle. Frame the reaction as a two-step "protection-deprotection" of the alkene's two carbons: boron labels the less-substituted carbon, then H_2O_2 swaps the label for OH. The boron is a temporary marker that tells the oxygen where to land. **Alternative approach: Markovnikov vs anti-Markovnikov choice.** For an alkene $RCH{=}CH_2$, you have two main ways to add "water":

- *Acid hydration* (H_2SO_4/H_2O): Markovnikov, OH on the more-substituted carbon (gives a $2°$ alcohol from a terminal alkene).
- *Hydroboration-oxidation* (B_2H_6/H_2O_2, OH^-): anti-Markovnikov, OH on the less-substituted carbon (gives a $1°$ alcohol from a terminal alkene).

Choose based on which alcohol regiochemistry your target demands.

Step 1. In step 1, BH_3 approaches the alkene with the empty p-orbital pointing at the π cloud. Steric bulk forces boron onto the less-substituted end of the double bond—this regiochemistry is set by the transition state, not by any electronic preference (the π-bond is symmetric; the steric clash with the substituent decides).

Step 2. Three equivalents of alkene react with one BH_3 (because BH_3 has three B-H bonds), producing a trialkylborane. The C-B bond is essentially non-polar (electronegativities $\sim$2.0 vs 2.5), so the intermediate is moderately stable and isolable. The addition is syn: H and B end up on the same face of the alkene—useful for stereochemistry.

Step 3. In step 2, the hydroperoxide anion HOO^- (from H_2O_2 in NaOH) adds to boron; an alkyl group migrates from B to O with retention of configuration at carbon; water then hydrolyses the B–O–R bond to give R-OH and boric acid ($B(OH)_3$). The migration is the key step and is one of the rare cases where C-B rearranges to C-O.

Step 4. For propene, the net change is propene $\rightarrow$ propan-1-ol (yield 90–95%). Compare with H_3O^+ hydration, which gives propan-2-ol (Markovnikov, $2°$ alcohol). For 2-methylpropene ($(CH_3)_2C{=}CH_2$), hydroboration gives the $1°$ alcohol $(CH_3)_2CH{-}CH_2{-}OH$ (2-methylpropan-1-ol), while acid hydration would give the $3°$ $(CH_3)_3C{-}OH$.

Concept linkage: protection-deprotection strategy. Hydroboration-oxidation is one of the few additions to alkenes with anti-Markovnikov regiochemistry. Other anti-Markovnikov methods include peroxide-mediated HBr addition (radical mechanism). Knowing both Markovnikov and anti-Markovnikov methods doubles the synthetic toolkit available for any alcohol target.

Exam relevance. "Convert alkene X to alcohol Y" questions test exactly this regiochemistry choice. The dead giveaway is: target is 1° alcohol from terminal alkene $\Rightarrow$ hydroboration-oxidation; target is 2° or 3° alcohol from terminal alkene $\Rightarrow$ acid hydration.

Numerical aside. Stereochemistry yield: in hydroboration of a chiral alkene, both faces are accessible but only one "syn" product forms per face attack, leading to a racemate. The reaction is stereospecific (syn addition) but not enantioselective with achiral BH_3.

Why this matters. This reaction is the standard way to make a *primary* alcohol from a terminal alkene: it is the synthetic complement of acid hydration. H. C. Brown won the 1979 Nobel Prize for developing this and other organoborane reactions. In modern synthesis it remains the cleanest way to install OH at a primary position.

> **Final Answer:** Hydroboration-oxidation = anti-Markovnikov "hydration" of an alkene; propene → propan-1-ol via syn-addition of $B{-}H$ followed by retention-of-configuration oxidation.

✗ Don't forget the alkaline workup

A common mistake is to write only "B_2H_6" as the reagent and skip the oxidation step. The trialkylborane intermediate is not an alcohol! You must add $H_2O_2/NaOH$ to liberate the alcohol. Always write both steps.

☞ Markovnikov in one line

"H goes to the carbon with more H's already". The proton ends up on the less-substituted carbon and the heteroatom on the more-substituted carbon. Hydroboration-oxidation reverses this because boron, not hydrogen, is the bulky labelling group.

Q 7.7 Give the structures and IUPAC names of monohydric phenols of molecular formula C_7H_8O.

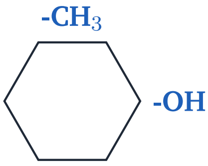
SOLUTION

Concept used. A **monohydric phenol** has one $-OH$ group attached directly to a benzene ring. The formula C_7H_8O contains seven carbons; subtracting the six in the ring leaves one extra carbon, which must be a methyl group on the ring. The methyl group can occupy the *ortho* (C-2), *meta* (C-3) or *para* (C-4) position relative to the $-OH$. We also note that "benzyl alcohol" ($C_6H_5{-}CH_2{-}OH$) has the same molecular formula but is not a phenol because its $-OH$ is on the side-chain carbon, not on the ring.

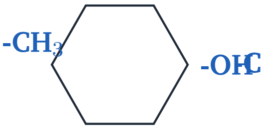
Step 1. **2-methylphenol** (*ortho*-cresol): a benzene ring with $-OH$ at C-1 and $-CH_3$ at C-2.

Step 2. **3-methylphenol** (*meta*-cresol): benzene ring with $-OH$ at C-1 and $-CH_3$ at C-3.

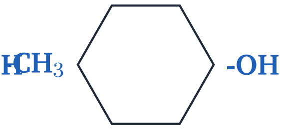
Step 3. **4-methylphenol** (*para*-cresol): benzene ring with $-OH$ at C-1 and $-CH_3$ at C-4.



2-methylphenol



3-methylphenol



4-methylphenol

> **Final Answer:** Three monohydric phenols of formula C_7H_8O: 2-methylphenol, 3-methylphenol and 4-methylphenol.

✗ Don't include benzyl alcohol

$C_6H_5{-}CH_2{-}OH$ (benzyl alcohol) has the same molecular formula C_7H_8O but the $-OH$ is on the methylene, not on the ring. It is an alcohol, not a phenol, so it does not count here.

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

Structural observation. For a monohydric phenol we need one $-OH$ on the benzene ring. With seven carbons in total and six in the ring, exactly one carbon remains as a ring substituent: it has to be $-CH_3$. The only freedom is its ring position.

Alternative approach: degree of unsaturation. For C_7H_8O, $\mathrm{DoU} = (2 \cdot 7 + 2 - 8)/2 = 4$. Four degrees fit one benzene ring (DoU = 4) and nothing else. So every isomer is a benzene derivative; the remaining one carbon must sit as a CH_3 (or be incorporated into the ring as part of a 7-membered ring, but cycloheptatrienol is not stable and is not a monohydric phenol).

Step 1. Fix $-OH$ at C-1. Three distinct positions remain for the methyl: C-2 (ortho), C-3 (meta), C-4 (para). Positions C-5 and C-6 are equivalent by symmetry to C-3 and C-2 respectively, so they are not separate isomers.

Step 2. Each of the three isomers (ortho, meta, para) is a named compound, called o-, m- and p-cresol respectively. They are real-world chemicals found in coal tar and creosote.

Step 3. Confirm that no other phenol-type isomer exists: a seven-carbon phenol must place the seventh carbon as a one-carbon side chain (since two-carbon ones would give $C_8H_{10}O$). So three is the complete count.

Step 4. For completeness, the only non-phenol isomer of C_7H_8O that is also an aromatic alcohol is benzyl alcohol ($C_6H_5-CH_2-OH$), which has the OH on the side chain, not the ring. It is excluded from this question's count.

Concept linkage: alcohol vs phenol distinction. The OH in an alcohol is on a sp^3 carbon; the OH in a phenol is on a sp^2 (aromatic) carbon. This difference shapes everything: acidity ($pK_a \sim 16$ vs ~ 10), reactions with NaOH (no for alcohol, yes for phenol), reactions with $\mathrm{NaHCO_3}$ (no for both, mostly), and reactions with HX (alcohol $\rightarrow$ alkyl halide; phenol does not).

Exam relevance. Counting questions ("how many isomers of formula X are alcohols/phenols/ethers") are standard 1- or 2-mark items in CBSE and JEE. The trap is always benzyl alcohol or other side-chain isomers that the student may mistakenly include in a phenol count.

Spectroscopic distinguisher. ^{1}H NMR of phenols shows the OH proton at δ 4–8 (very variable, depending on solvent and concentration) and a strongly downfield-shifted broad signal. The aromatic protons of cresols cluster around δ 6.8–7.0. Comparing chemical shifts of the three cresols lets us spot ortho/meta/para directly.

Why this matters. Cresols are industrial disinfectants (Lysol is a mixture of these isomers). They also illustrate ortho/meta/para classification, the workhorse of aromatic substitution. *m*-Cresol is used in resin manufacture and is a precursor to vitamin E synthesis.

> **Final Answer:** Three: 2-, 3- and 4-methylphenol (the o-, m-, p-cresols).

☞ Don't miss the side-chain OH

C_7H_8O has *four* total "hydroxy aromatic" isomers: three phenols (Q's answer) + 1 benzyl alcohol. The question specifies "phenols", so the answer is 3. But the general isomer count is 4.

♥ Where do cresols come from?

Coal tar (the residue of coal carbonisation) is the original industrial source of cresols. Modern routes alkylate phenol with methanol over zeolite catalysts. Output: ~200 000 tonnes/year worldwide, mostly going to resin and dye industries.

Q 7.8 **While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.**

SOLUTION

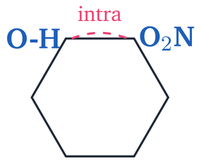
Concept used. A compound is **steam volatile** if it has appreciable vapour pressure at $100\,°\mathrm{C}$ (the temperature of boiling water) and does not associate strongly with water. Strong intermolecular hydrogen bonding between solute molecules lowers vapour pressure and prevents steam volatility. **Intramolecular hydrogen bonding** within a single molecule, in contrast, locks up the $-$OH internally and stops intermolecular association, leaving the molecule free to vapourise. Hence the isomer with *intramolecular* H-bonding is the steam-volatile one.

Step 1. Look at the geometry. In *ortho*-nitrophenol, the $-$OH at C-1 sits right next to the $-NO_2$ at C-2. The O-H hydrogen can swing across to form a hydrogen bond with one of the $-NO_2$ oxygens within the same molecule (a 6-membered chelate ring).

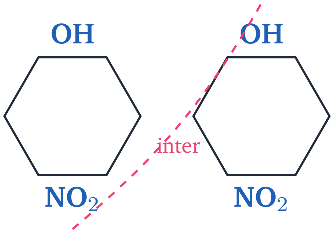
Step 2. In *para*-nitrophenol, the $-$OH (C-1) and the $-NO_2$ (C-4) are diametrically opposite on the ring. Their distance is too large for intramolecular H-bonding. Instead, each $-$OH forms intermolecular H-bonds with neighbouring molecules' $-NO_2$ groups, giving an extended, associated network.

Step 3. Consequence for vapour pressure. *Para*-nitrophenol forms a strongly H-bonded solid (m.p. $114\,°\mathrm{C}$, b.p. $279\,°\mathrm{C}$). *Ortho*-nitrophenol's intramolecular bond replaces some intermolecular ones, so it has weaker overall lattice forces (m.p. $45\,°\mathrm{C}$, b.p. $216\,°\mathrm{C}$).

Step 4. Result. *Ortho*-nitrophenol passes over with the steam; *para*-nitrophenol stays behind. Steam distillation therefore separates them.



o-nitrophenol (intra)



p-nitrophenol (inter)

Final Answer: *Ortho*-nitrophenol is steam-volatile because its $-$OH forms an intramolecular hydrogen bond with the adjacent $-NO_2$, lowering intermolecular association. *Para*-nitrophenol is held in an intermolecular H-bonded network and stays behind.

★ Chelation = intramolecular H-bond ring

A 6-membered ring closed by an O-H$\cdots$O contact is particularly stable. This "chelate" motif explains the extra volatility of *ortho*-nitrophenol and several similar *ortho*-substituted phenols.

EXPERT'S SOLUTION *: Aanya Pillai, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Steam distillation works for a compound whose vapour pressure plus that of water reaches 1 atm at $\leq 100\,°\mathrm{C}$. Anything tied up in a strong intermolecular hydrogen-bonded network has too low a vapour pressure to do this. The decisive factor is whether H-bonding is internal (favours volatility) or external (hinders volatility).
Alternative approach: melting-point comparison. A quick lab proxy for "how associated is this solid" is the melting point: o-nitrophenol melts at $45\,°\mathrm{C}$, m-nitrophenol at $97\,°\mathrm{C}$, p-nitrophenol at $114\,°\mathrm{C}$. The lowest-melting isomer has the weakest lattice forces, exactly what you need for steam volatility.

Step 1. In o-nitrophenol the OH and NO_2 are on adjacent carbons; the O-H bond points toward an $-NO_2$ oxygen across a six-membered ring. The intramolecular hydrogen bond "saturates" the OH so it cannot form many intermolecular contacts. The ring closure for the H-bond involves 6 atoms (O-H$\cdots$O-N-C-C), the most stable ring size for chelation.

Step 2. In p-nitrophenol no such intramolecular contact is geometrically possible (OH at C-1 and NO_2 at C-4 are at opposite ends, separated by $\sim 5.8\,\text{Å}$). Each $-OH$ forms two or more intermolecular bonds: the solid is held together like a 3-D polymer of H-bonded units. Crystal-structure data confirm head-to- tail ribbons in p-nitrophenol crystals.

Step 3. Vapour pressures at $100\,°\mathrm{C}$: o-isomer high enough to co-evaporate with water (about 1 mmHg); p-isomer essentially zero on this scale (< 0.01 mmHg). Steam distillation exploits Dalton's law of partial pressures: total pressure = $p_{\text{water}} + p_{\text{solute}}$. Boiling occurs when total = 1 atm.

Step 4. In the laboratory, the o-isomer condenses in the receiving flask (bright yellow crystals); the p-isomer is recovered from the distillation residue (also yellow but more deeply coloured).

Concept linkage: chelation rings. The same intramolecular H-bond stabilisation appears in salicylaldehyde (2-hydroxybenzaldehyde, where OH and CHO chelate), in 2-nitroaniline (NH_2 and NO_2 chelate), and in β-diketones (enol form chelates). The 6-membered chelate ring is a recurring stabilisation motif throughout organic chemistry.
Exam relevance. The o/p-nitrophenol separation is a standard 2–3 mark question. Always (1) draw both isomers, (2) circle the intramolecular H-bond in the ortho, (3) explain why this lowers intermolecular association, and (4) connect to vapour pressure / b.p. Just saying "ortho has H-bond, para doesn't" is half-marks; the reasoning must connect.
Acidity paradox. The same intramolecular H-bonding also makes o-nitrophenol *less* acidic than the p-isomer in water: the OH proton is partly tied up in the chelate and harder to release. pK_a: o-7.23, p-7.15. A subtle 0.08 unit gap but real.
Why this matters. Steam distillation is a non-trivial separation technique that exploits volatility differences caused by H-bonding. It is used industrially to purify essential oils

(citral, eugenol) and to extract heat-sensitive natural products that would decompose at their true boiling point.

> **Final Answer:** The *ortho* isomer is steam volatile due to its intramolecular H-bond (chelation, 6-membered ring); the *para* isomer is held back by intermolecular H-bonding.

☞ Chelation always wins

For ortho-disubstituted phenols where the second group has a lone pair within H-bond range, intramolecular H-bonding (a "chelate" ring) almost always reduces b.p., m.p., and solubility, and increases volatility relative to the m/p isomers.

✗ Wrong inference: "ortho is always more acidic"

Don't blindly write "ortho > para in acidity". For o-nitrophenol vs p-nitrophenol, the intramolecular H-bond holds onto the proton (slightly), making the ortho isomer *less* acidic in solution. The ranking is $p\text{-} \approx o\text{-} > m\text{-}$ for nitrophenols, but the gap is small.

Q 7.9 **Give the equations of reactions for the preparation of phenol from cumene.**

SOLUTION

Concept used. The **cumene process** (Hock process) is the industrial route to phenol. **Cumene** is isopropylbenzene, $C_6H_5{-}CH(CH_3)_2$. The benzylic C−H of cumene is easily oxidised by atmospheric oxygen to a **hydroperoxide**, which rearranges in acid to give phenol and acetone. The reaction is industrially attractive because both products (phenol and acetone) are valuable.

Step 1. Step 1: prepare cumene by Friedel-Crafts alkylation of benzene with propene over an acid catalyst:

$$C_6H_6 + CH_3{-}CH{=}CH_2 \xrightarrow{H^+} C_6H_5{-}CH(CH_3)_2.$$

Step 2. Step 2: aerial oxidation. Pass air through cumene at $\sim$120 °C in the presence of a small amount of acid; the tertiary benzylic C-H abstracts an oxygen molecule to give cumene hydroperoxide:

$$C_6H_5{-}CH(CH_3)_2 + O_2 \longrightarrow C_6H_5{-}C(CH_3)_2{-}OOH.$$

Step 3. Step 3: acid-catalysed rearrangement (Hock rearrangement). Treat the hydroperoxide with dilute acid; the O-O bond breaks with migration of the phenyl group:

$$C_6H_5{-}C(CH_3)_2{-}OOH \xrightarrow{H_3O^+} C_6H_5{-}OH + CH_3{-}CO{-}CH_3.$$

The two products are phenol and acetone.

Step 4. Cumene is regenerated industrially by alkylating benzene with the acetone-derived propene (after dehydration), making the overall process near-circular.

Final Answer:

$$\text{Cumene} \xrightarrow{O_2} \text{cumene hydroperoxide} \xrightarrow{H_3O^+} \text{phenol} + \text{acetone}.$$

♥ Industrial relevance

About 95% of the world's phenol is made by the cumene process. The co-product acetone is also a major industrial solvent and a feedstock for methyl methacrylate (perspex).

EXPERT'S SOLUTION *: Ishaan Joshi, M.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Track the carbon skeleton: benzene (6 C) plus propene (3 C) gives cumene (9 C); cumene splits back into phenol (6 C) and acetone (3 C). The propene carbons end up in acetone, the benzene carbons in phenol. This atom economy makes the process attractive: every C from the feed ends up in a useful product.

Alternative approach: thermodynamic driving force. The Hock rearrangement is exergonic by about $-90\,\text{kJ/mol}$—driven by formation of two strong $C{=}O$ bonds (in phenol's enol tautomer briefly, and in acetone) at the cost of one O-O bond (a weak $\sim 150\,\text{kJ/mol}$) and one C-C bond. Without this large negative ΔG, the rearrangement would not be spontaneous.

Step 1. The C-H at the benzylic carbon of cumene is weak ($\sim 370\,\text{kJ/mol}$) because the resulting tertiary benzylic radical is stabilised by both hyperconjugation and resonance with the ring. Compare with a typical alkane C-H ($\sim 410\,\text{kJ/mol}$).

Step 2. Air abstracts that hydrogen; the resulting radical traps O_2 to form a peroxy radical, which picks up another H from a fresh cumene molecule (radical chain propagation). Net product: cumene hydroperoxide.

Step 3. In acid, the OH of the peroxide is protonated; water leaves; the phenyl group migrates from C to O (a 1,2-aryl shift). The oxocarbenium intermediate adds water and breaks down to phenol plus a protonated acetone, which tautomerises to acetone. This C-to-O migration is the heart of the Hock rearrangement.

Step 4. Yield of phenol per mole of cumene is essentially quantitative (98–99%); both products are isolated by fractional distillation. Acetone fractions out at $56\,^{\circ}\mathrm{C}$ (atmospheric) and phenol at $182\,^{\circ}\mathrm{C}$.

Concept linkage. The Hock rearrangement is a special case of the broader Bayer-Villiger-like family of "migration to electron-deficient oxygen" reactions. The migrating group tends to be the one that best supports a partial positive charge during migration: aryl $>$ tertiary alkyl $>$ secondary $>$ primary $>$ methyl. In cumene hydroperoxide, phenyl migrates faster than methyl, giving phenol selectively.
Exam relevance. "Preparation of phenol from cumene" is a guaranteed 2–3 mark question. Always (1) write all three reagent/condition equations, (2) name the co-product (acetone), and (3) mention that the process is industrially dominant. Bonus: name the Hock rearrangement.
Yield numerical. If 1 mole of cumene (120 g/mol) gives 1 mole of phenol (94 g/mol) at 95% yield, the mass yield is $94 \times 0.95/120 = 0.74$ g phenol per g cumene. Industrial plants routinely achieve this benchmark.
Why this matters. The Hock rearrangement is one of the few large-scale industrial migrations of an aryl group from carbon to oxygen, exploited because of the value of both products. About 95% of the world's phenol (12 million tonnes/year) and a major share of acetone (6 million tonnes/year) are produced this way.

Final Answer:

$$\text{Cumene} \xrightarrow{\mathrm{O_2}} \text{cumene hydroperoxide} \xrightarrow{\mathrm{H^+}} \text{phenol} + \text{propan-2-one.}$$

☞ Remember the co-product

A standard CBSE marking-scheme bullet says: "$\frac{1}{2}$ mark for naming both products". Always write both phenol *and* acetone (propan-2-one). Do not just write phenol.

☞ Two reagents, three stages

Reagent 1: O_2 (atmospheric oxidation). Reagent 2: dilute H_3O^+ (acid rearrangement). Stage 1: cumene from benzene + propene. Stage 2: hydroperoxide from O_2. Stage 3: phenol + acetone from acid.

Q 7.10 **Write chemical reaction for the preparation of phenol from chlorobenzene.**

SOLUTION

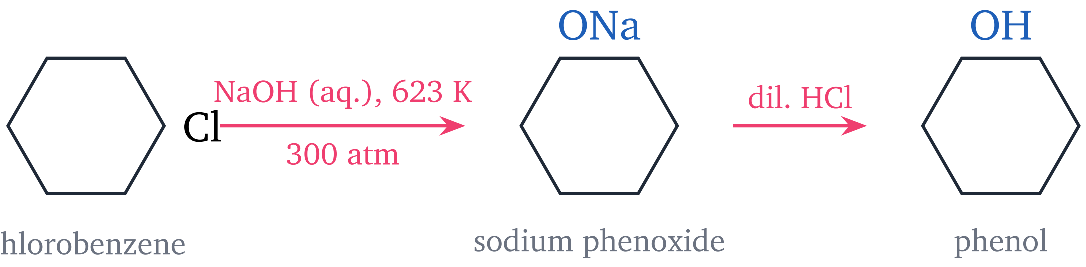
Concept used. **Chlorobenzene** (C_6H_5Cl) is very unreactive in normal nucleophilic substitution because the C-Cl bond has partial double-bond character from π-donation by the chlorine lone pair into the ring. To force the substitution, harsh conditions are needed. The industrial **Dow process** uses $6\,\%$–$8\,\%$ aqueous NaOH at $623\,\mathrm{K}$ ($\sim 350\,°\mathrm{C}$) and high pressure (200–300 atm). The mechanism is the elimination-addition “**benzyne**” pathway.

Step 1. Treat chlorobenzene with fused NaOH (or $8\,\%$ aqueous NaOH at $623\,\mathrm{K}$ and $300\,\mathrm{atm}$) to give sodium phenoxide:

$$\mathrm{C_6H_5Cl} + 2\,\mathrm{NaOH} \xrightarrow{623\,\mathrm{K},\,300\,\mathrm{atm}} \mathrm{C_6H_5ONa} + \mathrm{NaCl} + \mathrm{H_2O}.$$

Step 2. Acidify the resulting phenoxide salt with dilute HCl (or $\mathrm{H_2SO_4}$) to liberate phenol:

$$\mathrm{C_6H_5ONa} + \mathrm{HCl} \longrightarrow \mathrm{C_6H_5OH} + \mathrm{NaCl}.$$



Final Answer:

$$\mathrm{C_6H_5Cl} \xrightarrow{\text{NaOH, 623 K, 300 atm}} \mathrm{C_6H_5ONa} \xrightarrow{\mathrm{H_3O^+}} \mathrm{C_6H_5OH}.$$

★ Why is the temperature so high?

Direct S_NAr of chlorobenzene needs an electron-withdrawing group ortho/para to Cl. With no such activator, the only way is to push hard enough that base deprotonates the ortho hydrogen first, eliminates $\mathrm{Cl^-}$, and goes through a strained “benzyne” intermediate that then adds $\mathrm{OH^-}$.

EXPERT’S SOLUTION : *Krishna Desai, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. The two-step nature of this synthesis is typical of aromatic hydroxylations: first install O–Na on the ring under harsh conditions, then neutralise with acid to free phenol. The same form-salt/acidify motif appears in the benzenesulphonate route (Q 7.12) and in the cumene process indirectly.

Alternative approach: comparing the three industrial routes to phenol.

- *Cumene* (Q 7.9): mild conditions, two valuable products, dominant route today (95% of global phenol).
- *Dow / chlorobenzene* (this question): historical front-runner, harsh conditions (623 K, 300 atm), aryl halide feedstock from electrophilic chlorination of benzene.
- *Benzenesulphonate* (Q 7.12): oldest route (1899), sulphonation then fusion with NaOH.

Knowing all three lets you pick the right answer for any specific exam question.

Step 1. Under industrial conditions ($623\,\mathrm{K}$, 300 atm), the strong base $\mathrm{OH^-}$ deprotonates a ring hydrogen ortho to Cl, then Cl^- leaves to give a benzyne intermediate (a transient sp^2-sp ring with an in-plane π-bond). $\mathrm{OH^-}$ then adds to one of the two triple-bonded carbons, giving phenoxide after proton transfer. This elimination-addition mechanism explains why isotopic labelling at the ortho carbon shows scrambling.

Step 2. The sodium phenoxide is water-soluble (the $\mathrm{C_6H_5O^-}$ ion is moderately stabilised by ring resonance and by Na^+ counter-ion) and is extracted into the aqueous layer; chlorobenzene (unreacted) and benzene byproducts go to the organic layer.

Step 3. Treatment of the phenoxide with HCl protonates the oxygen to release neutral phenol, which is then separated by distillation. The aqueous NaCl byproduct is discarded.

Step 4. Yield of phenol: about 80–85% on industrial scale (historically Dow Chemical's flagship process before the cumene route overtook it). The harsh conditions and equipment cost made it unattractive once the Hock chemistry was perfected.

Concept linkage: nucleophilic aromatic substitution. The Dow process is the *prototype* of an elimination-addition (S_NAr via benzyne) mechanism on an aryl halide. Direct S_NAr (addition- elimination) needs strong $-M$ groups ortho/para to the halide (see ChemDraw of $\mathrm{p\text{-}NO_2{-}C_6H_4{-}Cl + NaOH}$, which goes by addition-elimination at lower temperature). Without such activators, only benzyne works.

Exam relevance. The Dow process is a standard 1–2 mark question. Always (1) write the equation with $623\,\mathrm{K}$, 300 atm conditions, (2) note that you need a strong base, and (3) include the acidification step. Optional bonus: mention benzyne mechanism.

Why this matters. The Dow process illustrates how "unreactive" aryl halides become reactive under forcing basic conditions via benzyne. It also shows the typical two-step "form-the-salt, then-acidify" protocol of phenol synthesis. The benzyne intermediate, demonstrated by Wittig and Roberts in the 1950s, was a watershed in mechanistic organic chemistry.

Final Answer: $C_6H_5Cl + NaOH \xrightarrow{623\,K,\,300\,atm} C_6H_5ONa$; then $C_6H_5ONa + HCl \longrightarrow C_6H_5OH$.

☞ **State all conditions**

For the Dow synthesis answer, the marking key usually wants **NaOH (fused or 6–8% aqueous)**, $623\,K$, $300\,atm$. Missing any of these costs marks.

♥ **Why chlorobenzene is so unreactive**

The C-Cl bond in chlorobenzene has partial double-bond character because the Cl lone pair donates into the ring ($+M$). C-Cl bond length in $C_6H_5{-}Cl$: $1.70\,Å$ vs. $1.79\,Å$ in $CH_3{-}Cl$. Shorter → stronger → less reactive. That is why standard S_N2 doesn't work, and we need the brute-force benzyne route.

Q 7.11 Write the mechanism of hydration of ethene to yield ethanol.

SOLUTION

Concept used. Acid-catalysed hydration of an alkene is an electrophilic addition. The proton from H_3O^+ (generated by H_2SO_4 in water) attacks the π-bond first, giving a carbocation. Water then attacks the carbocation as a nucleophile, and finally a base (water itself) removes the extra proton from the oxocarbenium to give the neutral alcohol. The reaction is reversible: low water-content favours dehydration, high water-content favours hydration.

Step 1. Step 1: protonation of the alkene. A water molecule carrying a proton (H_3O^+ from H_2SO_4 in water) attacks the π-electrons of ethene. The proton adds to one carbon, leaving a primary carbocation on the other:

$$CH_2{=}CH_2 + H_3O^+ \rightleftharpoons CH_3{-}CH_2{}^+ + H_2O.$$

This is the slow, rate-determining step.

Step 2. Step 2: nucleophilic attack of water on the carbocation. A second water molecule uses one of its oxygen lone pairs to attack the empty p-orbital of the cation:

$$CH_3{-}CH_2{}^+ + H_2O \rightleftharpoons CH_3{-}CH_2{-}OH_2{}^+.$$

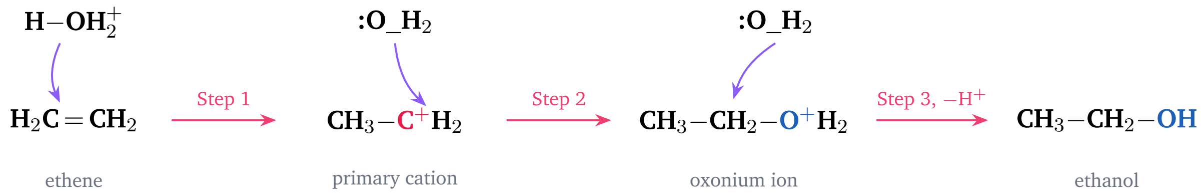
This gives a protonated alcohol (an oxocarbenium ion).

Step 3. Step 3: deprotonation. A third water molecule removes the extra proton from the oxocarbenium, regenerating H_3O^+ and giving neutral ethanol:

$$CH_3{-}CH_2{-}OH_2{}^+ + H_2O \rightleftharpoons CH_3{-}CH_2{-}OH + H_3O^+.$$

Step 4. The catalyst H_3O^+ is regenerated at the end, as expected. Overall:

$$CH_2{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3{-}CH_2{-}OH.$$



Violet curly arrows show electron-pair flow: π pair grabs H^+ from H_3O^+; an O lone pair of water then attacks C^+; finally a water base lifts H^+ off the oxonium ion to deliver ethanol.

> **Final Answer:** Three-step mechanism: protonation → carbocation → nucleophilic attack of water → deprotonation → ethanol.

☞ All steps are reversible

Each step in the hydration mechanism is reversible ($\rightleftharpoons$). The same arrows in reverse give the *dehydration* of ethanol to ethene. So Q 7.19's mechanism of dehydration is just this mechanism, read right-to-left.

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

Structural observation. The intermediate is an ethyl cation, $CH_3{-}CH_2{}^+$, which is primary. The reaction is slower than the corresponding hydration of propene (which goes through the more stable secondary cation $CH_3{-}CH^+{-}CH_3$). For this reason, ethene needs higher temperature and pressure than propene.

Alternative approach: Markovnikov framing. Although ethene's two carbons are identical (by symmetry, no regiochemistry question), the general acid-hydration mechanism is the textbook Markovnikov example. For propene, the cation lands on C-2 (more substituted) and OH ends up there too—this is the mnemonic "rich gets richer". For ethene, the symmetry makes the issue trivial.

Step 1. In a typical industrial setup, ethene is mixed with $98\,\%$ H_2SO_4 at $300\,°C$ and 70 atm. The first step is protonation of the alkene to form $CH_3{-}CH_2{}^+$. The acid donor in concentrated H_2SO_4 is actually $H_3SO_4{}^+$ (protonated sulphuric acid) or the equivalent H_3O^+ in dilute conditions.

Step 2. The proton donor under these conditions is actually H_3O^+ or H_2SO_4 itself; both work the same way mechanistically. The slow step is this protonation (activation energy $120\,kJ/mol$ for ethene; only $90\,kJ/mol$ for propene—hence the rate gap).

Step 3. Once the carbocation is formed, water (the bulk solvent) traps it rapidly: the lone pair on O attacks the empty p-orbital of C^+. This is barrierless within the diffusion limit for primary carbocations.

Step 4. The protonated alcohol is then deprotonated by another water molecule to give ethanol and regenerate H_3O^+. Le Chatelier's principle: an excess of water pushes the equilibrium toward ethanol; an excess of H_2SO_4 at higher T reverses it to ethene (Q 7.19).

Concept linkage: hydration vs hydroboration-oxidation. Acid hydration: Markovnikov; cation mechanism; works best for non-terminal or branched alkenes (stable 2° or 3° cation). Hydroboration-oxidation (Q 7.6): anti-Markovnikov; concerted; works best for terminal alkenes when a 1° alcohol is desired. Both deliver the same atoms but to opposite carbons.

Exam relevance. The mechanism of ethene hydration is a 3–4 mark CBSE question. The complete answer must show (1) protonation, (2) cation formation, (3) water attack, and (4) deprotonation, with curly arrows for each step. Skipping the third water (the proton remover) is a common deduction.

Numerical context. Industrial conversion per pass: about 5%. The unreacted ethene is recycled. Worldwide production of "synthetic" ethanol (from ethene rather than sugar fermentation): about 5 million tonnes/year. Total ethanol (sugar + synthetic) production is over 100 million tonnes/year.

Why this matters. This is one of the workhorse industrial routes to ethanol; understanding the mechanism is the foundation for the broader topic of electrophilic addition to alkenes (HX, X_2, hypohalous acids), all of which follow the same protonation-cation-trap-deprotonation logic.

> **Final Answer:** Mechanism: protonation $\rightarrow$ ethyl cation $\rightarrow$ water attack $\rightarrow$ deprotonation $\rightarrow$ ethanol.

☞ Three steps, three water molecules

Mnemonic: "protonate, attack, deprotonate"—each step uses a water (or its conjugate acid). The first water donates an H^+; the second water donates a lone pair; the third water accepts an H^+. All three steps are reversible.

✗ Don't write E1 here

This is electrophilic ADDITION to an alkene, not E1 elimination of an alcohol. The intermediate is an open carbocation, but the electron flow goes alkene→proton (not alcohol→cation →alkene). Reserve E1 for Q 7.19.

Q 7.12 **You are given benzene, conc. H_2SO_4 and $NaOH$. Write the equations for the**

preparation of phenol using these reagents.

SOLUTION

Concept used. This is the **benzenesulphonate fusion route** to phenol. Sulphonate the benzene ring with conc. H_2SO_4 to install $-SO_3H$; neutralise to the sodium sulphonate; then fuse with solid NaOH at high temperature so that the $-SO_3^-$ group is displaced by $-O^-$, giving sodium phenoxide. Acidify to free phenol.

Step 1. Sulphonation. Heat benzene with concentrated H_2SO_4. The electrophile SO_3 (or the protonated form) substitutes a ring H:

$$C_6H_6 + H_2SO_4 \xrightarrow{\Delta} C_6H_5{-}SO_3H + H_2O.$$

The product is benzenesulphonic acid.

Step 2. Neutralisation. Treat the sulphonic acid with NaOH to make the salt:

$$C_6H_5{-}SO_3H + NaOH \longrightarrow C_6H_5{-}SO_3Na + H_2O.$$

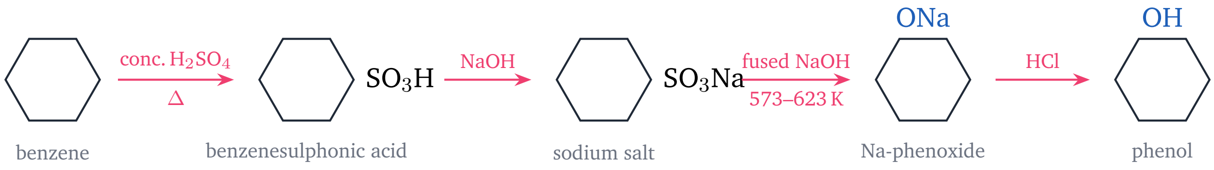
Step 3. Alkali fusion. Heat solid sodium benzenesulphonate with solid NaOH at $\sim$573 K–623 K:

$$C_6H_5{-}SO_3Na + 2\,NaOH \xrightarrow{\Delta} C_6H_5{-}ONa + Na_2SO_3 + H_2O.$$

The strong base displaces the sulphonate (a nucleophilic aromatic substitution under forcing conditions).

Step 4. Acidification. Dissolve the sodium phenoxide in water and acidify with dilute HCl (the conjugate acid of H_2O, or even CO_2/water in industry):

$$C_6H_5{-}ONa + HCl \longrightarrow C_6H_5{-}OH + NaCl.$$



Final Answer:

$$\text{Benzene} \xrightarrow{H_2SO_4} \text{benzenesulphonic acid} \xrightarrow{NaOH} \text{Na-benzenesulphonate} \xrightarrow{\text{fused NaOH, }\Delta} \text{Na-phenoxide} \xrightarrow{HCl} \text{phenol.}$$

♥ Historical importance

This was the first industrial route to phenol (BASF, 1899) before the cumene process took over. It is still useful in the laboratory where you do not have Cl_2 or $AlCl_3$.

EXPERT'S SOLUTION *: Pranav Nair, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. The plan is electrophilic substitution (to install $-SO_3H$) followed by harsh nucleophilic substitution (to swap $-SO_3Na$ for $-ONa$). Both SO_3^- and Cl^- can be "forced off" an aromatic ring at high temperature with strong base, but SO_3^- is the better leaving group of the two—hence why this route uses milder conditions than the Dow process (Q 7.10).

Alternative approach: comparing leaving groups on benzene. The classic "hard-to-displace" aromatic leaving groups are arranged in increasing order of how easily they leave when fused with NaOH: $-H < -NH_3^+ < -Cl < -Br < -SO_3^- < -N_2^+$. So sulphonate *is* a useful leaving group at moderately high T, while $-H$ never leaves directly.

Step 1. Conc. H_2SO_4 at $40\,°C–60\,°C$ sulphonates benzene; the active electrophile is SO_3 (or its protonated form HSO_3^+). This is reversible (heating with dilute acid would reverse it), which is actually exploited in the "ipso protection" strategy for selective EAS on complex aromatics.

Step 2. The free acid is converted to its sodium salt by neutralisation with aqueous $NaOH$. The sodium sulphonate is highly water-soluble and is easily isolated by evaporation.

Step 3. Alkali fusion is done in solid state at high temperature $(573–623\,K)$ because aqueous OH^- alone is not strong enough for S_NAr without an activator on the ring. The molten $NaOH$ generates an aggressive "naked" O^{2-} equivalent, which attacks the aromatic carbon, expelling sulphite. The byproduct Na_2SO_3 goes into the aqueous wash.

Step 4. Final acidification with dilute HCl liberates phenol; it is extracted into an organic solvent (typically ether or chloroform) and purified by distillation (b.p. $182\,°C$).

Concept linkage: three routes for phenol.

1. *Sulphonation route* (this question): historical, still viable for small-scale lab synthesis with the reagents at hand (benzene, H_2SO_4, NaOH).
2. *Dow route* (Q 7.10): chlorobenzene + NaOH; harsh but uses only one harsh step (no sulphonation).
3. *Cumene route* (Q 7.9): industrial dominant; mild conditions, two products.

Exam relevance. The exact question prompt names the three reagents: benzene, conc. H_2SO_4, and $NaOH$. You must use *all three*. Forgetting the final acidification step (which actually requires a fourth reagent, HCl) costs marks; some marking schemes accept CO_2/water or even no extra reagent (the phenoxide is acidic enough to be displaced by carbonic acid).

Why this matters. The route demonstrates that even "unreactive" aromatic positions can be functionalised if you choose the right leaving group and apply enough heat. The BASF (Germany) process used this route from 1899 until the 1950s—it was the workhorse of European phenol production before the cumene era.

> **Final Answer:** Four steps: sulphonation, salt formation, alkali fusion, acidification; net $C_6H_6 \longrightarrow C_6H_5OH$.

☞ Use all the given reagents

The question gives three reagents (benzene, conc. H_2SO_4, NaOH). Your answer must logically use all three. If you find yourself needing additional reagents (HCl, CO_2/H_2O for the final acidification), mention it but note that the question restricts you to the three named ones.

☞ Reversal of sulphonation

Sulphonation is one of the few EAS reactions that is reversible. Heating $C_6H_5{-}SO_3H$ with hot dilute H_2SO_4 (or just steam) regenerates benzene + H_2SO_4. Synthetic chemists exploit this to use $-SO_3H$ as a temporary "blocking" group on aromatic rings.

Q 7.13 **Show how will you synthesise:**

(i) 1-phenylethanol from a suitable alkene.

(ii) cyclohexylmethanol using an alkyl halide by an S_N2 reaction.

(iii) pentan-1-ol using a suitable alkyl halide.

SOLUTION

Concept used. Three different alcohol syntheses: acid-catalysed Markovnikov hydration of an alkene (i), nucleophilic substitution of an alkyl halide by $-OH^-$ via S_N2 (ii), and an indirect route through a Grignard reagent or through dilution of an aldehyde via reduction (iii). Pick the simplest disconnection for each.

Step 1. **(i) 1-Phenylethanol from an alkene.** 1-Phenylethanol is $C_6H_5{-}CH(OH){-}CH_3$. The Markovnikov hydration of styrene ($C_6H_5{-}CH{=}CH_2$) places the OH on the more substituted carbon (the benzylic one), giving exactly this alcohol:

$$C_6H_5{-}CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} C_6H_5{-}CH(OH){-}CH_3.$$

Step 2. **(ii) Cyclohexylmethanol by S_N2.** Cyclohexylmethanol is $C_6H_{11}{-}CH_2{-}OH$. Start from cyclohexylmethyl bromide (the primary halide $C_6H_{11}{-}CH_2{-}Br$) and treat it with aqueous NaOH:

$$\mathrm{C_6H_{11}{-}CH_2{-}Br + OH^-} \xrightarrow{S_N2} \mathrm{C_6H_{11}{-}CH_2{-}OH + Br^-}.$$

The primary halide undergoes a clean back-side S_N2 displacement.

Step 3. **(iii) Pentan-1-ol from an alkyl halide.** Pentan-1-ol is $\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}OH}$. Use 1-bromopentane and aqueous NaOH:

$$\mathrm{CH_3{-}(CH_2)_3{-}CH_2{-}Br + OH^-} \xrightarrow{S_N2} \mathrm{CH_3{-}(CH_2)_3{-}CH_2{-}OH + Br^-}.$$

Primary 1° halides give the cleanest S_N2 reactions (least competition from $E2/S_N1$).

> **Final Answer:** (i) Hydrate styrene with dilute $\mathrm{H_2SO_4}$; (ii) treat $\mathrm{C_6H_{11}{-}CH_2{-}Br}$ with aq. NaOH; (iii) treat $\mathrm{C_5H_{11}{-}Br}$ with aq. NaOH.

☞ Choose the right disconnection

For a benzylic alcohol like 1-phenylethanol, alkene hydration is preferred (Markovnikov gives the right regiochemistry because the benzylic cation is extra-stable). For straight-chain primary alcohols, an S_N2 hydrolysis of the corresponding primary halide is simplest.

EXPERT'S SOLUTION *: Siddharth Gupta, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Three syntheses, each illustrating a different disconnection: (i) C-O bond from a π-bond, (ii) C-O bond from a C-X bond, (iii) same idea as (ii) on a longer chain. Pick the reagent that gives the target with no isomerisation or rearrangement.

Alternative approach: retrosynthetic disconnection. For any alcohol $\mathrm{R{-}OH}$, disconnect at the C-O bond:

- *Disconnection A*: $\mathrm{R^+}$ + $\mathrm{OH^-}$. Source of $\mathrm{R^+}$: cation from alkene + $\mathrm{H^+}$ (Markovnikov path).
- *Disconnection B*: $\mathrm{R^-}$ + electrophilic O (rare in practice).
- *Disconnection C*: $\mathrm{R{-}X}$ + $\mathrm{OH^-}$. Source of $\mathrm{R{-}X}$: existing alkyl halide.
- *Disconnection D*: $\mathrm{R^-}$ + carbonyl. Source of $\mathrm{R^-}$: Grignard reagent + aldehyde / ketone / epoxide.

(i) uses A; (ii) and (iii) use C.

Step 1. For (i), styrene's hydration is Markovnikov because the benzylic cation $\mathrm{C_6H_5{-}CH^+(CH_3)}$ is resonance-stabilised by the ring (3 resonance forms delocalise charge over o/p carbons). So the OH lands on the carbon bonded to the ring, exactly as required. The 1-phenylethanol product has $pK_a \sim 15$, slightly more acidic than a simple alcohol due to the benzylic anion's resonance.

Step 2. For (ii), the back-side attack of OH^- on the primary carbon of $C_6H_{11}-CH_2-Br$ is a textbook S_N2; the cyclohexyl ring is bulky enough to slow down any S_N1 alternative (the secondary cyclohexyl cation is much less stable than the primary cyclohexylmethyl), leaving S_N2 dominant. The S_N2 rate is about 10^3 times faster than for comparable secondary halides.

Step 3. For (iii), 1-bromopentane is a primary halide; aq. $NaOH$ at moderate temperature gives the alcohol cleanly. Tertiary halides would not work here (they would lose HBr to give an alkene instead via E2). Yield of pentan-1-ol: typically 80–90%.

Step 4. In all three cases, the byproducts ($NaBr$, excess water, or starting alkene) are easily removed by aqueous workup followed by simple distillation.

Concept linkage: when to use Grignard. For (iii) pentan-1-ol, an alternative Grignard route is $CH_3(CH_2)_3-MgBr + HCHO$. This is sometimes preferred when 1-bromopentane is more expensive than 1-bromobutane. For (i) 1-phenylethanol, the Grignard alternative is $CH_3MgBr + C_6H_5-CHO$. Both routes give the same product; choose by reagent cost and chain-length compatibility.

Exam relevance. "Synthesise X from Y" is a standard multi-mark question. Always (1) state the reagent + conditions, (2) write the equation with the correct S_N2 / Markovnikov notation, (3) name the mechanism explicitly.

Why this matters. The three reactions cover the two big strategies for installing a C-O bond: oxymetalation/ hydration of an alkene, and nucleophilic substitution on a halide. Together with Grignard addition (Q 7.20), these are the entire alcohol-synthesis toolkit at NCERT level.

> **Final Answer:** (i) Markovnikov hydration of styrene; (ii) S_N2 hydrolysis of $C_6H_{11}-CH_2-Br$; (iii) S_N2 hydrolysis of $CH_3(CH_2)_4Br$.

☞ S_N2 essentials

S_N2 = single-step, concerted, back-side attack of nucleophile on sp^3 C bearing leaving group. Rate = $k[\text{halide}][\text{nucleophile}]$. Inversion of configuration. Works only with primary or methyl halides; fails for tertiary and aryl.

♥ Three workhorses for any -OH target

Together, alkene hydration, halide hydrolysis, and Grignard addition cover almost every alcohol you will be asked to make in a Class 12 or JEE paper. Master these three and you can attack any synthesis question with confidence.

Q 7.14 Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

SOLUTION

Concept used. Phenol behaves as a weak acid because its O-H proton can be removed by a base, leaving a **phenoxide** anion in which the negative charge is delocalised over the ring carbons (resonance). The corresponding conjugate base of ethanol, the **ethoxide** ion, has the negative charge localised on oxygen (with destabilising inductive donation from the ethyl group). So phenoxide is more stable than ethoxide, which means phenol ($pK_a \approx 10.0$) is much more acidic than ethanol ($pK_a \approx 15.9$).

Step 1. Reaction 1, with aqueous NaOH. Phenol dissolves in dilute NaOH giving a soluble sodium phenoxide:

$$\mathrm{C_6H_5{-}OH + NaOH \longrightarrow C_6H_5{-}ONa + H_2O}.$$

Ethanol does not react with cold dilute NaOH, because ethanol's pK_a (≈ 15.9) is comparable to water's (≈ 15.7); the equilibrium does not favour the ethoxide.

Step 2. Reaction 2, with metallic sodium. Phenol releases $\mathrm{H_2}$ on treatment with sodium metal:

$$\mathrm{2\,C_6H_5{-}OH + 2\,Na \longrightarrow 2\,C_6H_5{-}ONa + H_2\uparrow}.$$

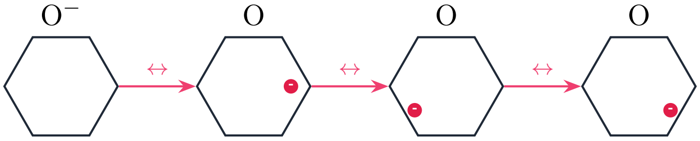
Ethanol also gives this reaction, but more slowly:

$$\mathrm{2\,CH_3{-}CH_2{-}OH + 2\,Na \longrightarrow 2\,CH_3{-}CH_2{-}ONa + H_2\uparrow}.$$

Phenol fizzes vigorously; ethanol reacts steadily.

Step 3. Comparison: in phenoxide, four resonance structures place the negative charge on oxygen and on three ring carbons (ortho, ortho, para). This delocalisation lowers the energy of the phenoxide by tens of kJ/mol relative to a localised charge. In ethoxide $\mathrm{CH_3CH_2O^-}$, no such delocalisation is possible; in fact the C_2H_5-group's inductive +I effect *destabilises* the charge by pushing electron density onto an already-negative oxygen.

Step 4. So $K_a(\text{phenol})/K_a(\text{ethanol}) \approx 10^{(15.9-10.0)} = 10^{5.9} \approx 8 \times 10^5$: phenol is about a million times more acidic than ethanol.



Resonance delocalisation of −charge in phenoxide

Final Answer: Phenol reacts with NaOH and with Na metal, releasing $\mathrm{H_2}$. Phenol ($pK_a \approx 10$) is about 10^5 times more acidic than ethanol ($pK_a \approx 16$) because the phenoxide ion is resonance-stabilised whereas ethoxide is not.

★ Inductive vs. resonance effects

The +I effect of the ethyl group destabilises ethoxide; the ring's π-system stabilises phenoxide by resonance. The two effects work in opposite directions, and resonance wins.

EXPERT'S SOLUTION *: Diya Chatterjee, M.Sc Physical Chemistry, IIT Madras*

Picture-first. Imagine the conjugate base in each case and ask: where does the negative charge live? The answer to this single question explains all the acidity behaviour.

Alternative approach: acidity ranking via inductive and resonance effects. For any X-O-H system, the conjugate base XO^- is stabilised (and the acid X-OH made stronger) by groups that withdraw electrons by $-I$ or $-M$, and destabilised by groups that donate by $+I$ or $+M$. So:

- Ethanol ($C_2H_5{-}OH$): ethyl group donates by $+I$, destabilising ethoxide. Weak acid ($pK_a \sim 16$).
- Water ($H{-}OH$): no substituent. Reference ($pK_a = 15.7$).
- Phenol ($C_6H_5{-}OH$): aryl ring withdraws by $-M$, stabilising phenoxide via resonance. Moderate acid ($pK_a \sim 10$).
- Acetic acid ($CH_3{-}COOH$): C=O withdraws by $-I$ and $-M$, gives full resonance stabilisation. Stronger acid ($pK_a \sim 4.8$).

Step 1. In $C_2H_5O^-$ the charge sits on a single oxygen atom with no neighbours that can share it. The σ-only ethyl group cannot delocalise charge; it actually destabilises the anion through its $+I$ effect (pushing more electron density onto the already-negative O).

Step 2. In $C_6H_5O^-$ the lone pair on oxygen overlaps with the ring π-system; resonance moves the negative charge onto carbons C-2, C-4, C-6 of the ring (ortho, ortho, para positions). Four equivalent resonance structures contribute: one with charge on O, and three with charge on the ring carbons.

Step 3. Spreading a charge over several atoms lowers its free energy. So phenoxide is more stable than ethoxide; equivalently, phenol holds onto its proton less tightly than ethanol does. The free-energy difference is about $34\,\mathrm{kJ/mol}$ (from $\Delta pK_a \cdot RT\ln 10$).

Step 4. Quantitatively, $pK_a(\text{phenol}) = 10.0$, $pK_a(\text{ethanol}) = 15.9$. So $\Delta pK_a = 5.9$; phenol is roughly $10^{5.9} \approx 8 \times 10^5$ times more acidic. Reactions: phenol + NaOH goes to completion ($K_{\text{eq}} = 10^{15.7-10.0} = 10^{5.7}$); ethanol + NaOH is essentially unreactive ($K_{\text{eq}} = 10^{-0.2}$).

Concept linkage: phenol vs alcohol vs ether. The three oxygen-containing classes have very different oxygen-pK_a:

Compound	Class	pK_a (on O)
Methanol CH_3OH	alcohol	15.5
Water H_2O	solvent	15.7
Ethanol C_2H_5OH	alcohol	15.9
Phenol C_6H_5OH	phenol	10.0
p-Nitrophenol	phenol+EWG	7.2
Picric acid (2,4,6-trinitrophenol)	phenol+3EWG	0.4

Ethers cannot ionise (no O-H bond) and are essentially non-acidic.

Exam relevance. "Why is phenol more acidic than ethanol?" is a classic 3-mark CBSE question. Full marks require (1) draw both conjugate bases, (2) name the resonance structures and inductive effects, (3) cite numerical pK_a values, and (4) explicitly compare with NaOH reactivity.

Numerical sanity check. The K_a of phenol is $10^{-10.0} = 1.0 \times 10^{-10}$ mol/L. In a 0.1 M phenol solution, $[\mathrm{H}^+] = \sqrt{K_a C_0} = \sqrt{10^{-10} \cdot 0.1} = 10^{-5.5}$ M, giving pH ≈ 5.5. Compare with ethanol: same concentration gives pH ≈ 8.4 (essentially neutral).

Why this matters. The same logic explains why p-nitrophenol ($pK_a \approx 7.2$) is more acidic than phenol: the $-NO_2$ group provides an additional resonance sink for the negative charge. And why p-cresol ($pK_a \approx 10.3$) is slightly less acidic: the methyl group donates by $+I/+H$, destabilising the phenoxide a little.

> **Final Answer:** Phenol is acidic enough to react with NaOH; ethanol is not. Resonance stabilisation of phenoxide (4 forms) is the reason; phenol is $\sim 10^6$ times more acidic.

☞ Acidity ranking trick

For any X-OH compound, the pK_a ranks roughly as: **carboxylic acid** (4–5) $<$ **phenol with EWG** (0–8) $<$ **phenol** (10) $<$ **alcohol** (15–18) $<$ **methane** ($\sim$50, not acidic). EWGs always lower pK_a; EDGs always raise it.

♥ Acidity at NEET/JEE level

Ranking the acidity of phenols substituted with various groups (nitro, halo, methyl, methoxy) is one of the highest-frequency JEE Main MCQ types. The decoder is: $-I$ and $-M$ groups increase acidity at o/p; $+I$ and $+M$ decrease acidity.

Q 7.15 Explain why is *ortho*-nitrophenol more acidic than *ortho*-methoxyphenol?

SOLUTION

Concept used. The acidity of a substituted phenol depends on how the substituent stabilises (or destabilises) the resulting phenoxide. Two electronic effects matter: **inductive (-I)** (electron withdrawal through σ-bonds, stabilises the anion) and **mesomeric** ($-M$ resonance withdrawal or $+M$ resonance donation through π-bonds). The $-NO_2$ group is strongly $-I$ and $-M$ (both withdrawing), while $-OCH_3$ is weakly $-I$ but strongly $+M$ (donates π-density through the oxygen lone pair).

Step 1. Look at the phenoxide of *o*-nitrophenol. The adjacent $-NO_2$ pulls electron density toward itself through both σ and π pathways, dispersing the negative charge of the phenoxide ion over the $-NO_2$ oxygens as well. The conjugate base is significantly stabilised. So *o*-nitrophenol gives up its proton easily: $pK_a \approx 7.2$.

Step 2. Look at the phenoxide of *o*-methoxyphenol. The $-OCH_3$ group's oxygen has lone pairs which can donate π-density into the ring ($+M$), *adding* to the negative charge on the phenoxide oxygen. This is destabilising. The $-I$ effect of $-OCH_3$ is weak. Net effect: destabilisation. So *o*-methoxyphenol is *less* acidic than phenol itself: $pK_a \approx 9.8$.

Step 3. Compare. Lower pK_a = stronger acid. Since $pK_a(o-\mathrm{NO_2}) = 7.2 < pK_a(o-\mathrm{OCH_3}) = 9.8$, *o*-nitrophenol is the stronger acid by a factor of $10^{2.6} \approx 400$.

Step 4. Reason in one line: $-NO_2$ withdraws electrons and stabilises the negative phenoxide; $-OCH_3$ donates electrons and destabilises it.

> **Final Answer:** *o*-Nitrophenol is more acidic because the $-NO_2$ group is an electron-withdrawing group ($-I$, $-M$) that stabilises the phenoxide anion; whereas $-OCH_3$ is electron-donating ($+M$) and destabilises the anion.

☞ Acidity decoder

Electron-withdrawing groups ($-NO_2$, $-CN$, $-CHO$, $-CF_3$) at ortho or para positions *increase* the acidity of a phenol. Electron-donating groups ($-OMe$, $-OH$, $-NMe_2$, $-CH_3$) *decrease* it. Meta substituents only act inductively (no resonance into the phenoxide oxygen).

EXPERT'S SOLUTION *: Meera Joshi, Ph.D Organic Chemistry, IISc Bangalore*

Structural observation. The key is to draw the phenoxide ion in each case and ask whether the substituent helps to spread the negative charge or works against it.

Alternative approach: substituent-effect calculator. Use the Hammett σ-parameter table to estimate pK_a shifts:

Substituent	σ_p
$-NO_2$	+0.78 (strong EWG)
$-CN$	+0.66
$-Cl$	+0.23
$-H$	0
$-CH_3$	-0.17
$-OMe$	-0.27 (resonance donor)
$-NH_2$	-0.66

For phenols, $pK_a = 10.0 - 2.2\,\sigma_p$. So $pK_a(p\text{-NO}_2\text{-phenol}) \approx 10.0 - 2.2(0.78) \approx 8.3$ (lit: 7.2; close enough). For p-OMe-phenol: $10.0 - 2.2(-0.27) \approx 10.6$ (lit: 10.2). The ortho data are trickier because of steric and chelation effects, but the direction is correctly predicted.

Step 1. In o-nitrophenoxide, an extra resonance form places the negative charge on an oxygen of the NO_2 group. That extra delocalisation (5 resonance forms total, vs 4 for plain phenoxide) makes the conjugate base much more stable. The $-I$ effect of the NO_2 group adds further σ-withdrawal.

Step 2. In o-methoxyphenoxide, no such resonance form is available. The OMe oxygen instead pumps lone-pair density into the ring (the $+M$ effect), increasing electron density at the phenoxide oxygen, which is already negative. Two negative charges on neighbouring atoms repel; the conjugate base is destabilised.

Step 3. Quantitatively, pK_a values are 7.2 for o-nitrophenol and 9.8 for o-methoxyphenol; both compared to phenol's 10.0. So o-nitrophenol is $10^{2.6} \approx 400$ times more acidic than o-methoxyphenol.

Step 4. Bigger picture: substituent effects on phenol acidity sit on a sliding scale of $-M/+M$ and $-I/+I$. $-NO_2$ is the strongest $-M$ group in NCERT, $-OMe$ is a moderate $+M$ donor. The trend is general: EWGs lower pK_a, EDGs raise it.

Concept linkage: o vs m vs p. For the same substituent, the order of acidity-modifying effect depends on position:

- p position: full $-M/+M$ resonance through the ring (4 resonance structures involve the substituent).
- o position: full $-M/+M$ plus an inductive boost from the proximity. Often the most acidifying (or basifying) but sometimes complicated by chelation (Q 7.8).
- m position: only $-I/+I$ matters; resonance does not reach (no resonance form puts charge on the meta carbon).

For $-NO_2$: p-nitrophenol pK_a 7.2; m-nitrophenol 8.4; o-nitrophenol 7.2 (the o and p are similar, m is less acidic because no resonance).

Exam relevance. Comparison-of-acidity MCQs are a JEE staple. The decoder: bigger $-M/-I$ at o/p → more acidic. NCERT tends to ask 4-option MCQs ranking substituted phenols.

Why this matters. Predicting which phenol is more acidic is a classic exam question that uses exactly this substituent-effect logic; the same reasoning applies to carboxylic acids and aromatic amines. The Hammett equation quantifies the trend and is the basis of much of physical-organic chemistry.

> **Final Answer:** $-NO_2$ stabilises the phenoxide anion ($-I$, $-M$); $-OCH_3$ destabilises it ($+M$). Hence *o*-nitrophenol is the stronger acid (pK_a 7.2 vs 9.8).

☞ Position matters too

For a fixed substituent like $-NO_2$, acidity ranking is typically $o \approx p \gg m$ for phenols (resonance reaches o/p; only inductive at m). For $-OH$, $-OMe$, $-NH_2$ (donor groups), the same logic predicts $o \approx p < m$ (donors hurt acidity more at o/p).

☞ σ_p as a one-number summary

The Hammett σ_p parameter combines $-I$ and $-M$ effects into a single number for each substituent. Phenol $pK_a \approx 10 - 2.2\sigma_p$. Memorise: $\sigma_p(\mathrm{NO_2}) = +0.8$, $\sigma_p(\mathrm{Cl}) = +0.2$, $\sigma_p(\mathrm{Me}) = -0.2$, $\sigma_p(\mathrm{OMe}) = -0.3$.

Q 7.16 Explain how does the $-OH$ group attached to a carbon of benzene ring activate it towards electrophilic substitution?

SOLUTION

Concept used. An **electrophilic aromatic substitution** (EAS) proceeds by an electrophile E^+ attacking the ring's π-cloud to form a positively charged **arenium ion** (sigma complex), which then loses a proton. The rate of EAS depends on how electron-rich the ring is and how stable the arenium intermediate is. The $-OH$ group strongly activates the ring because its oxygen lone pair donates π-density into the ring ($+M$, mesomeric donation), making the ring more nucleophilic and the arenium intermediate extra-stable.

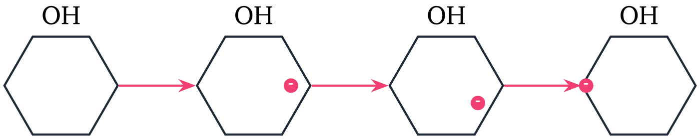
Step 1. Look at the ground-state ring. Lone pair of the OH oxygen overlaps with the π-orbital of the ring, pumping electron density to the ortho and para carbons. The resonance structures place a δ^- on C-2, C-4 and C-6.

Step 2. Look at the transition state. When an electrophile E^+ attacks at the ortho or para position, the resulting arenium ion has a resonance form in which the positive charge sits on the *carbon bearing OH*; the lone pair on O then stabilises that positive charge by forming an oxocarbenium-like resonance structure

$(\text{HO}{-}\text{C}^+ \rightleftharpoons \text{HO}^+{=}\text{C})$.

Step 3. Because the OH lone pair shares the burden of positive charge, the arenium ion is much more stable than that of unsubstituted benzene. Lower activation energy means a faster reaction.

Step 4. Regiochemistry. The same resonance argument shows that only ortho and para attack benefit from this stabilisation: meta attack puts the + charge on carbons not bonded to OH, so the oxygen lone pair cannot help. Hence –OH is an **ortho/para director** and a strong activator.



Resonance: OH lone pair pushes density to o,p positions

> **Final Answer:** The –OH oxygen's lone pair donates π-electron density into the ring $(+M)$, raising the HOMO of the ring and stabilising the arenium intermediate at o/p positions. Hence phenol is far more reactive than benzene toward EAS, especially at o/p.

♥ Phenol vs. benzene reactivity

Phenol nitrates with dilute HNO_3 at room temperature, while benzene needs a hot mixture of conc. HNO_3 and conc. H_2SO_4. The single OH group makes the ring at least 10^6 times more reactive.

EXPERT'S SOLUTION *: Ananya Rao, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Activation = lowering the activation energy of EAS. The OH group lowers it both in the starting material (raises HOMO) and especially in the arenium ion (directly donates to the cationic centre). The bigger stabilisation in the transition state translates to a faster reaction by the Hammond postulate.

Alternative approach: resonance structure count. For unsubstituted benzene, the arenium ion from electrophilic attack has 3 resonance forms. For phenol, attack at o/p gives 4 resonance forms including an oxocarbenium-like form with O donating its lone pair. Attack at m gives only 3 forms (no extra stabilisation). The 4-vs-3 ratio explains both the activation (faster reaction) and the directing effect (o/p preferred over m).

Step 1. In phenol's resonance structures the OH oxygen has a formal + charge and the ring carbon next to it has a − charge: the ring is electron-rich at o/p. There are three such "charge-separated" resonance forms contributing to the ground-state stabilisation.

Step 2. In the arenium ion formed by ortho or para attack, the OH oxygen can donate its lone pair into the positively charged ring system, forming an "oxocarbenium" resonance form that has all atoms with full octets. This is the key stabilising form. Activation energy of EAS at o/p is lowered by ~30 kJ/mol compared to benzene.

Step 3. Meta attack does not benefit from this donation because the positive charge lands on carbons not adjacent to the OH-bearing carbon. So m-EAS on phenol is only marginally faster than on benzene, while o/p-EAS is 10^5–10^6 times faster.

Step 4. Result: phenol nitrates at room temperature with dilute $\mathrm{HNO_3}$ to give o/p-nitrophenols (Q 7.17 iii); it brominates with $\mathrm{Br_2}$ in water to give 2,4,6-tribromophenol straight away (all three available o/p positions get attacked). Compare benzene, which requires conc. HNO_3/H_2SO_4 at 60°C for mononitration.

Concept linkage: $+M$ **donors in EAS.** The same activation logic applies to $-$OR, $-NH_2$, $-NR_2$ substituents. All are strong $+M$ donors and all are powerful ortho/para directors. Rate enhancement vs benzene:

Substituent	Relative rate of nitration
$-NH_2$ (aniline)	$\sim 10^9$
$-$OH (phenol)	$\sim 10^3 - 10^5$
$-$OMe (anisole)	$\sim 10^4$
$-CH_3$ (toluene)	~ 25
$-$H (benzene)	1 (reference)
$-NO_2$ (nitrobenzene)	$\sim 10^{-7}$

Exam relevance. "Explain why phenol activates the ring" is a 3-mark CBSE question. Show (1) ground-state resonance with charge-separated forms, (2) arenium-ion resonance with oxocarbenium form, (3) explicit mention of o/p (not m) and why, (4) experimental comparison with benzene.

Why this matters. The same activation logic applies to many synthetic problems. Knowing that phenol is far more reactive than benzene also explains why protecting OH as OMe (anisole) is sometimes needed (Q 7.31): plain phenol can *over-react* (tri-bromo product instead of mono).

> **Final Answer:** Lone pair on OH donates π-density into the ring; arenium ion at o/p is extra-stabilised by an oxocarbenium resonance form; phenol is therefore 10^5–10^6 times more reactive than benzene in EAS.

♥ Aspirin synthesis depends on this

The first step of the aspirin synthesis (salicylic acid + acetic anhydride) and the salicylic acid synthesis itself (Kolbe carboxylation of phenoxide) both exploit phenol's o/p activation.

Without it, none of these reactions would proceed at practical rates.

☞ **Reciting the activator list**

Strong activators (and o/p directors): $-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-OR$, $-O^-$ (very strong). Moderate: $-NHCOR$, $-OCOR$. Weak (o/p too): $-R$ (alkyl). All deactivators (and m directors except halogens): $-NO_2$, $-CN$, $-COOH$, $-CHO$, $-COR$, $-SO_3H$.

Q 7.17 **Give equations of the following reactions:**

(i) Oxidation of propan-1-ol with alkaline $\mathrm{KMnO_4}$ solution.

(ii) Bromine in $\mathrm{CS_2}$ with phenol.

(iii) Dilute $\mathrm{HNO_3}$ with phenol.

(iv) Treating phenol with chloroform in the presence of aqueous NaOH.

SOLUTION

Concept used. Four different reactions of $-OH$ compounds: (i) alkaline $\mathrm{KMnO_4}$ is a strong oxidant that takes a primary alcohol all the way to a carboxylic acid; (ii) $\mathrm{Br_2}$ in $\mathrm{CS_2}$ at low temperature is a mild brominating reagent for phenol, giving mainly para monobromination; (iii) dilute $\mathrm{HNO_3}$ nitrates phenol at room temperature, giving a mixture of *o*- and *p*-nitrophenol; (iv) chloroform + aqueous NaOH on phenol is the **Reimer-Tiemann reaction**, which installs a $-CHO$ group ortho to the OH.

Step 1. **(i)** Alkaline $\mathrm{KMnO_4}$ on propan-1-ol gives propanoic acid (passing through propanal as an intermediate):

$$\mathrm{CH_3{-}CH_2{-}CH_2{-}OH \xrightarrow{KMnO_4,\,OH^-} CH_3{-}CH_2{-}COOH.}$$

Step 2. **(ii)** Phenol + $\mathrm{Br_2}$ in $\mathrm{CS_2}$ at low temperature $(273\,\mathrm{K})$ gives mainly **4-bromophenol** (*p*-bromophenol). The non-polar solvent $(\mathrm{CS_2})$ and low temperature suppress polybromination:

$$\mathrm{C_6H_5{-}OH + Br_2 \xrightarrow{CS_2,\,273\,K} p\text{-}HO\text{-}C_6H_4\text{-}Br + HBr.}$$

Step 3. **(iii)** Dilute $\mathrm{HNO_3}$ with phenol at room temperature gives a mixture of o- and p-nitrophenols:

$$\mathrm{C_6H_5{-}OH + HNO_3(dil\cdot) \longrightarrow o\text{-}NO_2\text{-}C_6H_4\text{-}OH + p\text{-}NO_2\text{-}C_6H_4\text{-}OH + H_2O.}$$

Step 4. **(iv) Reimer-Tiemann.** Phenol with $\mathrm{CHCl_3}$ and aqueous NaOH at $340\,\mathrm{K}$, followed by acidic workup, gives salicylaldehyde (**2-hydroxybenzaldehyde**). The reactive electrophile is dichlorocarbene $:\mathrm{CCl_2}$, generated from

$CHCl_3 + OH^-$:

$$CHCl_3 + OH^- \to :CCl_2 + Cl^- + H_2O,$$
$$C_6H_5{-}O^- + :CCl_2 \to o\text{-}HOC_6H_4{-}CHO \text{ (after hydrolysis).}$$

Final Answer: (i) $CH_3CH_2CH_2OH \xrightarrow{KMnO_4/OH^-} CH_3CH_2COOH$; (ii) $C_6H_5OH + Br_2 \xrightarrow{CS_2}$ p-$BrC_6H_4OH + HBr$; (iii) $C_6H_5OH + \text{dil} \cdot HNO_3 \longrightarrow$ o-+p-$NO_2C_6H_4OH$; (iv) Reimer-Tiemann: $C_6H_5OH + CHCl_3 + NaOH \longrightarrow 2$-$HOC_6H_4CHO$.

☞ **Why CS_2 for (ii)**

The non-polar solvent CS_2 depresses the ionisation of phenol, so the ring is less activated. That stops the reaction at monobromination. In water (a polar solvent that supports the more reactive phenoxide), Br_2 gives 2,4,6-tribromophenol immediately.

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

Strategic angle. Group the four reactions by type: oxidation (i), electrophilic aromatic substitution (ii)+(iii), and carbene insertion (iv).

Step 1. (i) The C–H on the –OH-bearing carbon is successively oxidised: $-CH_2OH \to -CHO \to -COOH$. With alkaline $KMnO_4$, the reaction does not stop at the aldehyde because the aldehyde is itself easily oxidised. Acidic workup gives the free carboxylic acid.

Step 2. (ii) Br_2/CS_2 at $273\,K$ is the textbook condition for monobromination of phenol; para is the major isomer due to less steric clash with the OH.

Step 3. (iii) Dilute HNO_3 has just enough NO_2^+ to nitrate phenol once; both o- and p-isomers form and are separated by steam distillation (Q 7.8).

Step 4. (iv) The Reimer-Tiemann reaction proceeds by attack of dichlorocarbene at the ortho carbon of the phenoxide. After alkaline hydrolysis of the $-CHCl_2$ group, you get the –CHO substituent.

Why this matters. These four reactions are the "greatest hits" of phenol chemistry: oxidation, ring substitution and –CHO installation are all standard JEE questions.

Final Answer: Equations as written in the main solution.

Q 7.18 **Explain the following with an example.**

(i) Kolbe's reaction.

(ii) Reimer-Tiemann reaction.
(iii) Williamson ether synthesis.
(iv) Unsymmetrical ether.

SOLUTION

Concept used. Four named transformations or terms: (i) the carboxylation of phenoxide by CO_2 to give salicylic acid; (ii) the formylation of phenol via dichlorocarbene; (iii) the alkoxide + alkyl halide synthesis of an ether; (iv) the definition of an ether with two different R groups on oxygen.

Step 1. **(i) Kolbe's reaction.** Treat sodium phenoxide with CO_2 at $400\,K$ and 4–7 atm; acidify. The phenoxide attacks CO_2 at the ortho carbon, giving sodium salicylate, which on acidification gives **salicylic acid** (2-hydroxybenzoic acid):

$$C_6H_5{-}ONa + CO_2 \xrightarrow{\text{400 K, 4–7 atm}} 2\text{-}NaOOC\text{-}C_6H_4\text{-}OH \xrightarrow{H_3O^+} 2\text{-}HOOC\text{-}C_6H_4\text{-}OH.$$

Salicylic acid is the precursor of aspirin.

Step 2. **(ii) Reimer-Tiemann reaction.** Phenol + $CHCl_3$ + aqueous $NaOH$ at $340\,K$, followed by acidic workup, gives **salicylaldehyde** (2-hydroxybenzaldehyde). The electrophile is dichlorocarbene ($:CCl_2$), made in situ from $CHCl_3 + OH^-$. The carbene attacks the ortho carbon of the phenoxide; the resulting $-CHCl_2$ group is hydrolysed to $-CHO$ by the alkaline medium:

$$C_6H_5{-}OH \xrightarrow{CHCl_3,\text{NaOH, 340 K}} \xrightarrow{H_3O^+} \text{o-}HOC_6H_4\text{-}CHO.$$

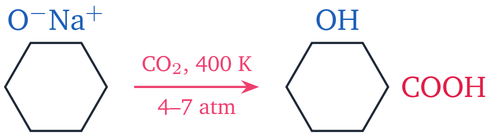
Step 3. **(iii) Williamson ether synthesis.** React an alkoxide ($R{-}O^-Na^+$) with a primary alkyl halide (R′-X with X = Cl, Br, I). The alkoxide acts as a nucleophile in an S_N2 attack on the alkyl halide:

$$R\text{-}O^-Na^+ + R'\text{-}X \to R\text{-}O\text{-}R' + NaX.$$

Example: $CH_3{-}ONa + CH_3{-}CH_2{-}Br \longrightarrow CH_3{-}O{-}CH_2{-}CH_3 + NaBr$ gives methoxyethane (methyl ethyl ether). The alkyl halide must be primary or methyl; tertiary halides give alkene by $E2$ instead.

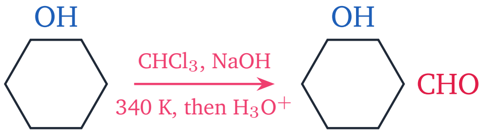
Step 4. **(iv) Unsymmetrical (mixed) ether.** An ether $R\text{-}O\text{-}R'$ in which $R \neq R'$. Example: **ethyl methyl ether**, $CH_3{-}O{-}C_2H_5$. Versus a symmetrical ether like $CH_3{-}O{-}CH_3$ (dimethyl ether).

(i) Kolbe:



salicylic acid

(ii) R-T:



salicylaldehyde

(iii) Williamson: $\mathbf{CH_3{-}O^- \; Na^+ \; + CH_3CH_2{-}Br \xrightarrow{S_N2} CH_3{-}O{-}CH_2CH_3}$

methoxyethane (ethyl methyl ether)

Final Answer: (i) Kolbe: $\mathrm{PhO^-Na^+ + CO_2 \longrightarrow}$ salicylate; (ii) Reimer-Tiemann: $\mathrm{PhOH + CHCl_3/NaOH \longrightarrow}$ salicylaldehyde; (iii) Williamson: $\mathrm{R\text{-}ONa + R'\text{-}X \rightarrow R\text{-}O\text{-}R'}$; (iv) Unsymmetrical ether: $\mathrm{R\text{-}O\text{-}R'}$ with $\mathrm{R \neq R'}$.

★ Mechanism summary

Kolbe: nucleophilic addition of $\mathrm{O^-}$-activated ring carbon on $\mathrm{CO_2}$. Reimer-Tiemann: dichlorocarbene insertion at ortho. Williamson: S_N2 on a primary halide.

EXPERT'S SOLUTION *: Riya Patel, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Three of these (i, ii, iii) are named reactions on the JEE syllabus, each with a known mechanism. The fourth (iv) is just a definition.

Step 1. Kolbe's reaction works because the phenoxide ion is electron-rich at ortho/para; it attacks the electrophilic carbon of $\mathrm{CO_2}$ to form a new C-C bond. The ortho carboxylate is thermodynamically favoured under the reaction conditions.

Step 2. Reimer-Tiemann uses the same activated phenoxide ring as the nucleophile. The carbene $\mathrm{:CCl_2}$ inserts at the ortho position, and aqueous NaOH hydrolyses the dichloromethyl group to an aldehyde.

Step 3. Williamson's S_N2 step proceeds with inversion at carbon. The alkoxide must be unhindered; $\mathrm{(CH_3)_3CO^-}$ does *not* attack primary alkyl halides well because of steric crowding.

Step 4. Unsymmetrical ethers (R-O-R′) are more useful synthetic intermediates than symmetrical ones because their two halves can be derived from two different building blocks.

Why this matters. Together, Kolbe and Reimer-Tiemann explain how Nature (and pharma) extracted aspirin and methyl salicylate from phenol in the 19th century; Williamson is the universal ether disconnection in modern synthesis.

> **Final Answer:** Definitions and examples as written in the main solution.

Q 7.19 Write the mechanism of acid dehydration of ethanol to yield ethene.

SOLUTION

Concept used. **Acid-catalysed dehydration** is the reverse of acid-catalysed hydration (Q 7.11). It is an $E1$ elimination passing through the same ethyl cation intermediate. Concentrated H_2SO_4 at $443\,K$ ($\sim 170\,°C$) gives the elimination product (ethene); milder conditions ($413\,K$) give the substitution product (diethyl ether), and even milder ($373\,K$) give the ester ethyl hydrogen sulphate.

Step 1. Step 1: protonation. Conc. H_2SO_4 protonates the OH of ethanol to make a good leaving group (H_2O):

$$CH_3{-}CH_2{-}OH + H_2SO_4 \rightleftharpoons CH_3{-}CH_2{-}OH_2{}^+ + HSO_4{}^-.$$

Step 2. Step 2: ionisation. Water leaves, forming the ethyl cation:

$$CH_3{-}CH_2{-}OH_2{}^+ \rightleftharpoons CH_3{-}CH_2{}^+ + H_2O.$$

This is the slow, rate-determining step.

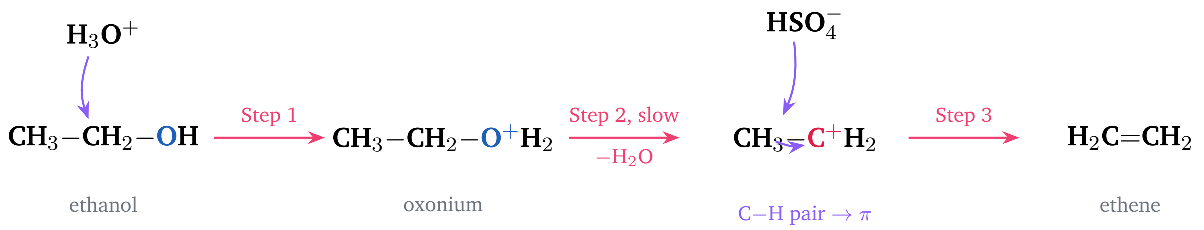
Step 3. Step 3: deprotonation ($E1$). A base ($HSO_4{}^-$ or another water) abstracts a proton from the carbon *next to* the cation, and the two electrons of the C-H bond drop into the empty p-orbital to form the new π-bond:

$$CH_3{-}CH_2{}^+ + HSO_4{}^- \rightleftharpoons CH_2{=}CH_2 + H_2SO_4.$$

H_2SO_4 is regenerated, confirming its catalytic role.

Step 4. Overall:

$$CH_3{-}CH_2{-}OH \xrightarrow{\text{conc. } H_2SO_4\text{, 443 K}} CH_2{=}CH_2 + H_2O.$$



$E1$ mechanism: (1) O lone pair grabs H^+; (2) water leaves slowly to give the primary ethyl cation; (3) HSO_4^- (acting as a weak base) takes a β-proton while its C–H bonding pair (violet) drops into the empty p-orbital to form the new π bond of ethene.

> **Final Answer:** Three-step $E1$ mechanism: protonation of OH → loss of H_2O to form $CH_3{-}CH_2{}^+$ → loss of proton from the adjacent carbon to give $CH_2{=}CH_2$.

☞ Hydration vs dehydration

The same set of three steps explains both directions: high water content drives hydration to the right (Q 7.11), low water content (conc. H_2SO_4) drives dehydration to the left.

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

Strategic angle. The reaction is Le Chatelier in action: remove water (conc. H_2SO_4 is a desiccant) and the equilibrium shifts to the alkene. Add water and the alkene re-hydrates.

Step 1. The first step is reversible protonation of the alcohol. Sulphuric acid donates a proton to one of the lone pairs on oxygen, converting -OH into the much better leaving group -OH_2^+.

Step 2. The second step is unimolecular ionisation: the oxocarbenium loses water to give the ethyl cation. This is rate-determining and accounts for the "unimolecular" label E1.

Step 3. The third step is deprotonation of a β-carbon by any base in solution (the $HSO_4{}^-$ counter-ion, water itself, or even another ethanol molecule). The freed electron pair forms the π bond.

Step 4. Higher temperatures favour the elimination because $\Delta S^\ddagger > 0$ for E1 (two molecules of product from one of reactant): elimination is entropically favoured.

Why this matters. This is a textbook example of an **E1** mechanism: a carbocation intermediate, β-H abstraction, no stereospecificity at β. Use it as the template for all acid-catalysed alcohol dehydrations.

Final Answer: Mechanism: protonation → loss of water (slow, gives $CH_3CH_2{}^+$) → loss of β-H to give ethene.

Q 7.20 **How are the following conversions carried out?**
(i) Propene → Propan-2-ol.
(ii) Benzyl chloride → Benzyl alcohol.
(iii) Ethyl magnesium chloride → Propan-1-ol.
(iv) Methyl magnesium bromide → 2-Methylpropan-2-ol.

SOLUTION

Concept used. Standard reagent-conversion problems. (i) Markovnikov hydration of an alkene; (ii) hydrolysis of a benzyl halide by aqueous NaOH (S_N2); (iii) the **Grignard reagent** adding to an aldehyde or a primary epoxide to give a 1° alcohol; (iv) the same Grignard reagent adding to a *ketone* to give a tertiary alcohol.

Step 1. **(i) Propene → Propan-2-ol.** Treat propene with dilute H_2SO_4 (or use oxymercuration-demercuration for cleaner conditions); Markovnikov adds OH to C-2:

$$CH_3{-}CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3{-}CH(OH){-}CH_3.$$

Step 2. **(ii) Benzyl chloride → Benzyl alcohol.** Reflux $C_6H_5{-}CH_2{-}Cl$ with aqueous NaOH or aqueous Na_2CO_3:

$$C_6H_5{-}CH_2{-}Cl + OH^- \xrightarrow{S_N2} C_6H_5{-}CH_2{-}OH + Cl^-.$$

The benzyl cation is stabilised by the ring; both S_N1 and S_N2 pathways are accessible, but the primary halide makes S_N2 dominant.

Step 3. **(iii)** C_2H_5MgCl → **Propan-1-ol.** Add the Grignard to formaldehyde (HCHO); the ethyl carbanion attacks the carbonyl carbon, then aqueous workup gives the primary alcohol:

$$C_2H_5MgCl + HCHO \longrightarrow C_2H_5{-}CH_2{-}OMgCl,$$
$$C_2H_5{-}CH_2{-}OMgCl + H_3O^+ \longrightarrow C_2H_5{-}CH_2{-}OH + Mg(OH)Cl.$$

Result: propan-1-ol $CH_3{-}CH_2{-}CH_2{-}OH$.

Step 4. **(iv)** CH_3MgBr → **2-Methylpropan-2-ol.** 2-Methylpropan-2-ol is $(CH_3)_3C{-}OH$. Add the Grignard to *acetone* (propan-2-one, $CH_3{-}CO{-}CH_3$); the methyl carbanion adds to the ketone carbon, giving the tertiary alcohol after workup:

$$CH_3MgBr + CH_3{-}CO{-}CH_3 \longrightarrow (CH_3)_3C{-}OMgBr,$$
$$(CH_3)_3C{-}OMgBr + H_3O^+ \longrightarrow (CH_3)_3C{-}OH + Mg(OH)Br.$$

Final Answer: (i) Dil. $H_2SO_4 + H_2O$; (ii) aq. NaOH; (iii) HCHO then H_3O^+; (iv) CH_3COCH_3 then H_3O^+.

★ Grignard menu

RMgX + HCHO → 1° alcohol; **RMgX + R'CHO** → 2° alcohol; **RMgX + R'COR"** → 3° alcohol. Always end with aqueous acid workup.

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

Strategic angle. Each conversion is one of four classic "install –OH" strategies: hydration of an alkene; hydrolysis of a halide; Grignard addition to an aldehyde or to a ketone. Pick the right one for each starting material.

Step 1. (i) Markovnikov hydration. The 2° carbocation $CH_3{-}CH^+{-}CH_3$ is more stable than the primary $CH_3{-}CH_2{-}CH_2{}^+$, so water adds to give propan-2-ol (the 2° product).

Step 2. (ii) Hydrolysis of benzyl chloride is rapid because the benzyl carbon is electrophilic and primary (S_N2). Even mild base like Na_2CO_3 works.

Step 3. (iii) Match the Grignard chain length with the aldehyde so that the sum equals the chain length of the target alcohol. C_2H_5MgCl (2 carbons) + HCHO (1 carbon) = propan-1-ol (3 carbons).

Step 4. (iv) For a 3° alcohol you need a ketone. Methyl magnesium bromide (1 C) + acetone (3 C, two methyls and a carbonyl) gives the tertiary $(CH_3)_3C{-}OH$ after workup.

Why this matters. These four conversions cover the three big families of starting materials (alkenes, halides, carbonyls) for making any saturated alcohol on a JEE/NEET question paper.

Final Answer: (i) dil H_2SO_4/H_2O; (ii) aq NaOH; (iii) HCHO, then H_3O^+; (iv) CH_3COCH_3, then H_3O^+.

Q 7.21 Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2,4,6-tribromophenol.

(iv) Benzyl alcohol to benzoic acid.

(v) Dehydration of propan-2-ol to propene.

(vi) Butan-2-one to butan-2-ol.

SOLUTION

Concept used. Each conversion tests recall of a standard reagent. Strong oxidants take a 1° alcohol all the way to a carboxylic acid; mild, selective oxidants stop at the aldehyde. Brominating Br_2 in water gives full tri-bromination of phenol. Dehydration of a 2° alcohol needs strong acid and heat. Reduction of a ketone to a 2° alcohol is done with $NaBH_4$ or $LiAlH_4$.

Step 1. **(i) 1° alcohol → acid.** Reagents: acidified $KMnO_4$ (or alkaline $KMnO_4$ followed by H_3O^+); also acidified $K_2Cr_2O_7$, or chromic acid (CrO_3 in H_2SO_4).

Step 2. **(ii) 1° alcohol → aldehyde.** Reagent: pyridinium chlorochromate (PCC) in CH_2Cl_2. PCC is mild enough to stop at the aldehyde without over-oxidising to acid.

Step 3. **(iii) Phenol → 2,4,6-tribromophenol.** Reagent: bromine water (Br_2 in H_2O). The polar aqueous solvent supports the phenoxide form; bromination proceeds three times consecutively at each ortho/para position to give a white precipitate of 2,4,6-tribromophenol.

Step 4. **(iv) Benzyl alcohol → benzoic acid.** Reagents: acidified $KMnO_4$ (or $K_2Cr_2O_7/H_2SO_4$), or alkaline $KMnO_4$ followed by acid workup.

Step 5. **(v) Propan-2-ol → propene.** Reagent: concentrated H_2SO_4 at $440\,K$ (alcohol dehydration, $E1$ mechanism, see Q 7.19). Alternative: H_3PO_4 or anhydrous Al_2O_3 at higher temperature.

Step 6. **(vi) Butan-2-one → butan-2-ol.** Reagent: $NaBH_4$ (sodium borohydride) in ethanol, or $LiAlH_4$ in dry ether. Both deliver a hydride to the carbonyl carbon; aqueous workup gives the 2° alcohol.

> **Final Answer:** (i) acidified $KMnO_4$; (ii) PCC in CH_2Cl_2; (iii) Br_2 in water; (iv) acidified $KMnO_4$; (v) conc. H_2SO_4, $440\,K$; (vi) $NaBH_4$ (or $LiAlH_4$).

☞ Mild vs strong oxidants

"Mild and selective" = PCC, $Cu/_{573}\,K$, Collins' reagent. "Strong" = $KMnO_4$, $K_2Cr_2O_7/H_2SO_4$, CrO_3/H_2SO_4 (Jones reagent). Mild oxidants give the aldehyde; strong ones go to the acid.

EXPERT'S SOLUTION *: Kavya Verma, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Six different reagents, each tied to a specific functional-group change. Memorise the matchings rather than just the names.

Step 1. (i) and (iv) both go from –CH_2OH (or –CHO) to –COOH; any strong oxidant works. Acidified $KMnO_4$ is the canonical choice.

Step 2. (ii) needs to stop one oxidation level short. PCC is the textbook reagent because it does not contain any water (so it cannot hydrolyse the aldehyde further to a hydrate then to an acid).

Step 3. (iii) In water, the bromination goes all the way to the 2,4,6-tribromide because each successive bromination is still fast on the highly activated ring; once the three positions are filled, the substitution stops on its own.

Step 4. (v) Concentrated H_2SO_4 at $440\,K$ is the standard $E1$ dehydration condition; lower temperature $(413\,K)$ would have given diisopropyl ether instead.

Step 5. (vi) Carbonyl reduction. $NaBH_4$ is selective for ketones and aldehydes; it does not touch esters or acids. $LiAlH_4$ is a more aggressive hydride and will reduce esters too.

Why this matters. Mastering the reagent-product matching is the single most rewarding investment for the chemistry portion of any entrance exam.

> **Final Answer:** Reagent list as in the main solution.

Q 7.22 **Give reason for the higher boiling point of ethanol in comparison to methoxymethane.**

SOLUTION

Concept used. Ethanol $CH_3{-}CH_2{-}OH$ and methoxymethane (dimethyl ether) $CH_3{-}O{-}CH_3$ have the same molecular formula C_2H_6O and the same molecular mass (46 g/mol), but very different boiling points: ethanol $78.4\,°C$, dimethyl ether $-24.8\,°C$. The gap of $\sim 100\,°C$ is due to hydrogen bonding.

Step 1. Ethanol has an –OH hydrogen: the H is bonded to a highly electronegative O. So ethanol acts as a hydrogen-bond *donor* in $R{-}O{-}H \cdots O(H){-}R$.

Step 2. Methoxymethane does *not* have any –OH hydrogen. Its only hydrogens are on carbon, and C-H is too non-polar to donate a hydrogen bond. The oxygen has lone pairs (it can be an acceptor) but there is no partner that can donate.

Step 3. So ethanol forms intermolecular H-bonds; dimethyl ether does not. To vapourise ethanol you must break these bonds (each $\sim 20\,kJ/mol$); to vapourise dimethyl ether you only fight dipole-dipole and dispersion forces.

Step 4. Numerical comparison. Heat of vaporisation: $\Delta H_{vap}(\text{ethanol}) \approx 38.6\,kJ/mol$;

$\Delta H_{\text{vap}}(\text{Me2O}) \approx 21.5\,\text{kJ/mol}$. The $\sim$17 kJ/mol gap is exactly the order of magnitude of one or two hydrogen bonds per molecule.

> **Final Answer:** Ethanol's $-$OH forms intermolecular hydrogen bonds; dimethyl ether cannot (no H bonded to O). So ethanol boils about $100\,^\circ\text{C}$ above dimethyl ether despite having the same molecular mass.

♥ Same formula, different forces

C_2H_6O has two constitutional isomers (ethanol and dimethyl ether). Their boiling points differ by a factor of nearly two on the Kelvin scale: a beautiful demonstration that *intermolecular forces* matter more than molecular mass.

EXPERT'S SOLUTION : *Sneha Reddy, M.Sc Chemistry, IIT Kanpur*

Picture-first. Draw both molecules and look at where the polar bonds are.

Step 1. Ethanol's polar bond is O-H ($\Delta\chi = 1.24$). The H is positive enough ($\delta^+ \approx +0.4e$) to attract another molecule's O lone pair. Result: chains of H-bonded ethanol molecules in the liquid.

Step 2. Methoxymethane's most polar bond is C-O ($\Delta\chi = 0.89$). The C-H bonds are nearly non-polar, so the molecule has only weak dipole-dipole and London dispersion interactions.

Step 3. The energetic cost of vapourisation is therefore much higher for ethanol: $38.6\,\text{kJ/mol}$ vs $21.5\,\text{kJ/mol}$.

Step 4. By the Trouton's rule estimate, b.p. $\propto \Delta H_{\text{vap}}$: a 17 kJ/mol gap gives roughly a $100\,^\circ\text{C}$ boiling-point gap.

Why this matters. The same logic explains why water ($H{-}O{-}H$) boils much higher than hydrogen sulfide ($H{-}S{-}H$) despite H_2S being heavier: only water forms H-bonds.

> **Final Answer:** Hydrogen bonding makes ethanol's b.p. $78\,^\circ\text{C}$ vs methoxymethane's $-25\,^\circ\text{C}$.

Q 7.23 Give IUPAC names of the following ethers:

(i) $C_2H_5{-}O{-}CH_2{-}CH(CH_3){-}CH_3$ **(ii)** $CH_3{-}O{-}CH_2{-}CH_2{-}Cl$

(iii) $p\text{-}O_2N{-}C_6H_4{-}O{-}CH_3$ **(iv)** $CH_3{-}CH_2{-}CH_2{-}O{-}CH_3$

(v) cyclohexane bearing gem-dimethyl groups at one ring carbon and $-OC_2H_5$ at the opposite (1,4) ring carbon

(vi) $C_6H_5-O-C_2H_5$.

SOLUTION

Concept used. Same rules as in Q 7.1 for ethers. Name the smaller $R-O^-$ side as an **alkoxy** substituent ("methoxy", "ethoxy") and treat it as a prefix on the longer parent. For aromatic ethers, benzene (or a longer parent) is the ring; the alkoxy group sits on it. Numbering chooses the lowest locant for the alkoxy group when other choices are tied.

Step 1. **(i)** $C_2H_5-O-CH_2-CH(CH_3)-CH_3$: longer side is the 3-carbon chain $-CH_2-CH(CH_3)-CH_3$ (isobutyl). Numbering from the O-end places the $-OC_2H_5$ (ethoxy) at C-1, the methyl branch at C-2. Name: **1-ethoxy-2-methylpropane**.

Step 2. **(ii)** $CH_3-O-CH_2-CH_2-Cl$: parent is 2-chloroethane ($Cl-CH_2-CH_2^-$); methoxy is the substituent at C-1, Cl at C-2. Both locants tie; use alphabetical order to break the tie. Name: **1-chloro-2-methoxyethane**.

Step 3. **(iii)** p-$O_2N-C_6H_4-O-CH_3$: parent is benzene; substituents are methoxy at C-1 and nitro at C-4. Name: **1-methoxy-4-nitrobenzene** (or *p*-nitroanisole).

Step 4. **(iv)** $CH_3-CH_2-CH_2-O-CH_3$: parent is propane; methoxy at C-1. Name: **1-methoxypropane**.

Step 5. **(v)** A cyclohexane ring with two methyls at one carbon (the gem-dimethyl carbon) and an $-OC_2H_5$ at the opposite (1,4) carbon. No suffix-priority group is present, so numbering is chosen to give the lowest locant set across all substituents. Placing the two methyls at C-1 (gem) and the ethoxy at C-4 gives the locant set $\{1, 1, 4\}$; the reverse choice (ethoxy at C-1, methyls at C-4) gives $\{1, 4, 4\}$. Set $\{1, 1, 4\}$ wins at the second locant ($1 < 4$). Name: **4-ethoxy-1,1-dimethylcyclohexane**.

Step 6. **(vi)** $C_6H_5-O-C_2H_5$: parent is benzene with $-OC_2H_5$ as the substituent. Name: **ethoxybenzene** (common: phenetole).

> **Final Answer:** (i) 1-ethoxy-2-methylpropane; (ii) 1-chloro-2-methoxyethane; (iii) 1-methoxy-4-nitrobenzene; (iv) 1-methoxypropane; (v) 4-ethoxy-1,1-dimethylcyclohexane; (vi) ethoxybenzene.

☞ Alphabetical tie-break

When two substituents would get the same locant set, list them alphabetically; the one earlier in the alphabet gets the lower number. Chloro < methoxy, so chloro gets C-1 in (ii) by *first point of difference*: actually the rule is "lowest locants at first point of difference" for the set; in (ii) both substituents are at adjacent carbons so the set $\{1, 2\}$ is forced.

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

Structural observation. Every ether name is "*alkyl*-oxy-*parent*" or "*aryl*-oxy *-parent*". Identify the longer chain or ring first.

Step 1. For acyclic ethers (i, ii, iv) the longer C-chain attached to O is the parent; the shorter is the $-$OR substituent.

Step 2. For aromatic ethers (iii, vi) the benzene ring is the parent (because it is a 6-carbon ring, longer than any $-$OR). The substituent on the ring is the alkoxy.

Step 3. For cyclic ether (v) the cyclohexane ring is the parent; the substituents are two methyls (gem) at C-1 and an ethoxy at C-4 (chosen to give the lower locant set $\{1, 1, 4\}$).

Step 4. Numbering rules: principal group gets the lowest locant; if ties exist, alphabetical order of substituents breaks the tie.

Why this matters. You will rely on the same "alkoxy-on-parent" template throughout the chapter for products of Williamson synthesis.

> **Final Answer:** Names as listed in the main solution.

Q 7.24 **Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:**

(i) 1-Propoxypropane (ii) Ethoxybenzene

(iii) 2-Methoxy-2-methylpropane (iv) 1-Methoxyethane.

SOLUTION

Concept used. Williamson synthesis: alkoxide $\mathrm{R{-}O^-Na^+}$ + primary alkyl halide → ether + NaX. The S_N2 step requires that the alkyl halide be primary or methyl. For ethers with a 3° alkyl group, the alkoxide must come from the 3° alcohol and the halide must be primary, never the other way around.

Step 1. **(i) 1-Propoxypropane** $\mathrm{CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3}$ (di-n-propyl ether). Both halves are n-propyl, so use sodium n-propoxide and n-propyl bromide:

$$\mathrm{CH_3CH_2CH_2{-}ONa{+}Br{-}CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3{+}NaBr.}$$

Step 2. **(ii) Ethoxybenzene** $\mathrm{C_6H_5{-}O{-}C_2H_5}$. The alkoxide must come from phenol (sodium phenoxide), and the alkyl halide must be primary ethyl iodide or bromide:

$$\mathrm{C_6H_5{-}ONa + C_2H_5{-}Br \longrightarrow C_6H_5{-}O{-}C_2H_5 + NaBr.}$$

Reverse choice ($\mathrm{C_2H_5{-}ONa + C_6H_5{-}X}$) fails because $\mathrm{C_6H_5{-}X}$ does not undergo S_N2.

Step 3. **(iii) 2-Methoxy-2-methylpropane** $(CH_3)_3C{-}O{-}CH_3$. The 3° butyl group is on the alkoxide side (from *tert*-butanol); the methyl side is the halide:

$$(CH_3)_3C{-}ONa + CH_3{-}I \longrightarrow (CH_3)_3C{-}O{-}CH_3 + NaI.$$

Reverse choice (CH_3ONa + $(CH_3)3C{-}Br$) would mostly give isobutylene by $E2$, not the ether.

Step 4. **(iv) 1-Methoxyethane** $CH_3{-}O{-}C_2H_5$. Symmetric mix-and-match: either sodium methoxide + ethyl iodide, or sodium ethoxide + methyl iodide:

$$CH_3{-}ONa + C_2H_5{-}I \longrightarrow CH_3{-}O{-}C_2H_5 + NaI.$$

> **Final Answer:** (i) $C_3H_7ONa + C_3H_7Br$; (ii) $C_6H_5ONa + C_2H_5Br$; (iii) $(CH_3)_3CONa + CH_3I$; (iv) $CH_3ONa + C_2H_5I$.

✗ Don't swap alkoxide and halide

For **(ii)** and **(iii)**, the bulky/aryl group *must* be on the alkoxide. If you try $C_2H_5ONa +$ C_6H_5Br in (ii), nothing happens (no S_N2 on sp^2 C). If you try $CH_3ONa + (CH_3)_3CBr$ in (iii), you get isobutylene (E2) rather than the desired ether.

EXPERT'S SOLUTION *: Dev Sharma, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. The retrosynthetic question for any Williamson is: "which side becomes the alkoxide, and which side becomes the halide?" Answer: the alkoxide is the sp^3-O- with a phenyl, vinyl, 3° alkyl, or other group that cannot undergo S_N2; the halide is the primary or methyl side that *can* undergo S_N2.

Step 1. For (i), both sides are n-propyl, so any assignment works. The classical choice is sodium propoxide + propyl bromide; the byproduct is NaBr.

Step 2. For (ii), benzene cannot undergo S_N2 (sp^2 carbon, partial π-bond C-X). So phenol must be on the alkoxide side; ethyl bromide is the alkyl halide.

Step 3. For (iii), the *tert*-butyl group is on the alkoxide side. Reagents: dry *tert*-butanol + Na to give sodium *tert*-butoxide, then CH_3I.

Step 4. For (iv), the two ways are symmetric; pick whichever starting materials are cheaper.

Why this matters. Williamson synthesis is by far the most common ether-making reaction. Knowing which side becomes the alkoxide saves you from the most common student mistake.

Final Answer: See main solution for the four equations.

Q 7.25 **Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.**

SOLUTION

Concept used. The Williamson S_N2 step has the usual S_N2 requirements: the alkyl halide must be primary (or methyl); secondary halides give some S_N2 and some $E2$; tertiary halides give exclusively $E2$ (alkene). Vinyl and aryl halides do not react at all by S_N2. So Williamson synthesis cannot make any ether whose halide side would be $2°$, $3°$, vinyl or aryl.

Step 1. **Limitation 1:** $3°$ **alkyl halides.** If you try to make *tert*-butyl methyl ether by reacting $\mathrm{CH_3{-}ONa}$ with $\mathrm{(CH_3)_3C{-}Br}$, the $3°$ halide gives isobutylene by $E2$ instead of the ether:

$$\mathrm{(CH_3)_3C{-}Br + CH_3O^-Na^+ \longrightarrow (CH_3)_2C{=}CH_2 + CH_3OH + NaBr.}$$

Fix: invert the roles. Use $\mathrm{(CH_3)_3C{-}O^-Na^+}$ and $\mathrm{CH_3{-}I}$ instead.

Step 2. **Limitation 2: aryl (or vinyl) halides.** Aryl halides such as $\mathrm{C_6H_5{-}Br}$ cannot undergo S_N2 (the sp^2 carbon and the partial π-overlap of C-Br with the ring block back-side attack). So you cannot make $\mathrm{C_6H_5{-}O{-}R}$ by reacting $\mathrm{R{-}O^-Na^+}$ with $\mathrm{C_6H_5{-}X}$. Instead, you must use sodium phenoxide $\mathrm{C_6H_5{-}O^-Na^+}$ and the primary alkyl halide $\mathrm{R{-}X}$.

Step 3. **Limitation 3: secondary halides give mixtures.** With a $2°$ halide, $E2$ competes substantially. For instance, isopropyl bromide + sodium ethoxide gives a mixture of ethyl isopropyl ether and propene:

$$\mathrm{(CH_3)_2CH{-}Br{+}C_2H_5O^-Na^+ \longrightarrow (CH_3)_2CH{-}O{-}C_2H_5{+}CH_3{-}CH{=}CH_2{+}NaBr.}$$

Yield of the desired ether is modest.

Step 4. **Limitation 4: bulky alkoxides.** A very hindered alkoxide such as *tert*-butoxide $\mathrm{(CH_3)_3C{-}O^-}$ attacks even primary halides poorly because the alkoxide cannot reach the back side. Williamson synthesis is best with small, primary alkoxides.

Final Answer: Williamson works cleanly only when the alkyl halide side is primary (or methyl). It fails (or gives the wrong product) for $3°$, vinyl, and aryl halides, and gives mixtures for $2°$ halides.

☞ Always pick the primary halide side

For *any* unsymmetrical ether R-O-R′, ask: which of R or R′ is primary or methyl? Put the OTHER group on the alkoxide and the primary one on the halide.

EXPERT'S SOLUTION *: Ankit Joshi, M.Tech Chemical Engineering, IIT Delhi*

Structural observation. The S_N2 transition state needs the nucleophile to approach the carbon from the side opposite the leaving group. Anything that blocks that approach breaks the reaction.

Step 1. A tertiary carbon has three alkyl groups around it plus the leaving group; the back side is fully shielded. The molecule sheds the leaving group unimolecularly (S_N1) or, in the presence of a base, loses a proton from a β-carbon ($E2$) instead.

Step 2. An aryl (or vinyl) carbon is sp^2. Its σ^* orbital is rotated by 90° relative to the back-side direction, so an incoming nucleophile cannot align with it.

Step 3. Secondary carbons are intermediate: S_N2 works but $E2$ competes. The strong base $\mathrm{R{-}O^-}$ pulls a β-proton at almost the same rate it displaces the halide.

Step 4. Bulky alkoxides are themselves blocked from approach. Even a primary halide reacts only slowly with *tert*-butoxide, and instead acts as a strong base to deprotonate any acidic site.

Why this matters. These limits explain why Williamson synthesis is best taught as "always use the primary side for the halide". They also motivate alternative ether syntheses such as acid dehydration of alcohols, alkoxymercuration of alkenes, or Mitsunobu reactions in modern labs.

> **Final Answer:** Limitations: no Williamson with tertiary, vinyl, or aryl halides; mixtures with secondary halides; sluggish with bulky alkoxides.

Q 7.26 How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

SOLUTION

Concept used. **Acid-catalysed dehydration of a primary alcohol** at *moderate* temperature ($413\,\mathrm{K}$, $\sim 140\,°\mathrm{C}$) and excess alcohol gives the symmetric ether (here 1-propoxypropane, $\mathrm{CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3}$). The mechanism is **$S_N2$ with the alcohol as nucleophile** on a protonated second molecule of alcohol. Higher temperature would give the alkene (propene) by $E1$; lower temperature stops at the alkyl hydrogen sulphate. So the temperature window for ether formation is narrow.

Step 1. Step 1: protonate one molecule of propan-1-ol. Conc. H_2SO_4 protonates the OH to a much better leaving group:

$$CH_3CH_2CH_2{-}OH + H^+ \rightleftharpoons CH_3CH_2CH_2{-}OH_2{}^+.$$

Step 2. Step 2: a second molecule of propan-1-ol attacks the protonated first molecule by S_N2 from the back side of the leaving water:

$$CH_3CH_2CH_2{-}OH_2{}^+ + HO{-}CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2{-}OH^+(CH_2CH_2CH_3) + H_2O.$$

(Mid-product: protonated 1-propoxypropane.)

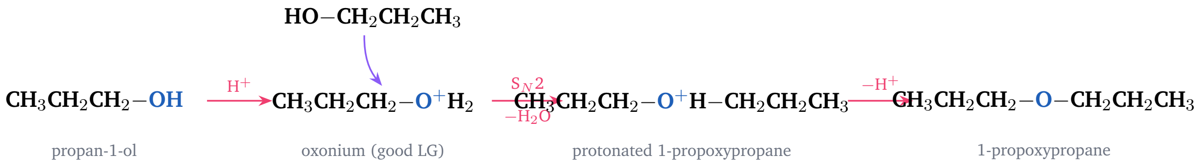
Step 3. Step 3: a third base (the conjugate base $HSO_4{}^-$, water, or another alcohol) removes the extra proton:

$$CH_3CH_2CH_2{-}OH^+(CH_2CH_2CH_3) \rightleftharpoons CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3 + H^+.$$

The catalyst H^+ is regenerated.

Step 4. Net reaction:

$$2\,CH_3CH_2CH_2{-}OH \xrightarrow{H_2SO_4,\ 413\text{ K}} CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3 + H_2O.$$



Two propan-1-ol molecules: one is protonated on O to make $-OH_2^+$ *a leaving group; the second alcohol's O lone pair (violet curly arrow) attacks the protonated* α*-C by* S_N2*, expelling water. Loss of* H^+ *gives the neutral ether.*

> **Final Answer:** Dehydrate two molecules of propan-1-ol with conc. H_2SO_4 at $\sim 413\,K$. Mechanism: protonation → S_N2 by a second alcohol on the protonated first → deprotonation → ether.

★ Temperature controls the product

- Below $373\,K$: ester (ethyl/propyl hydrogen sulphate).
- $413\,K$: ether (this reaction).
- $443\,K$ and above: alkene (propene).

Same reagents, different products: a beautiful example of kinetic vs thermodynamic control.

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

Picture-first. Think of one molecule as "nucleophile" (the un-protonated alcohol) and the other as "electrophile" (the protonated alcohol with -OH_2^+ as the leaving group). The carbon between them is primary, so the back-side displacement is easy.

Step 1. At $413\,\text{K}$, the equilibrium favours S_N2 of alcohol on protonated alcohol over $E1$ elimination. Primary cations are unstable, so the unimolecular E1 pathway is suppressed.

Step 2. The S_N2 step happens twice in succession (each end of the new C-O bond comes from a different alcohol molecule), but is effectively one back-side attack with H_2O as leaving group.

Step 3. The reaction is limited to symmetrical ethers between primary alcohols. Trying to make $(CH_3)_3C{-}O{-}CH_3$ by this method would not work (E1 elimination of *tert*-butyl alcohol would dominate).

Step 4. For unsymmetrical ethers, use Williamson synthesis (Q 7.24).

Why this matters. This is the cheapest industrial route to symmetric ethers like diethyl ether (anaesthetic) and dipropyl ether (solvent).

Final Answer:

$$2\,CH_3CH_2CH_2OH \xrightarrow{\text{conc. } H_2SO_4\text{, 413 K}} CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3 + H_2O.$$

Mechanism: S_N2 of alcohol on protonated alcohol.

Q 7.27 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

SOLUTION

Concept used. Whether acid dehydration of an alcohol gives an ether (via S_N2) or an alkene (via $E1$) depends on how stable the carbocation intermediate is. Primary alcohols have unstable 1° cations, so S_N2 dominates (= ether). 2° and 3° alcohols have much more stable cations, so $E1$ elimination dominates (= alkene). At the temperatures needed for any ether-forming step, the elimination has already taken over.

Step 1. Recall the two competing pathways from a protonated alcohol $R{-}OH_2{}^+$: S_N2 with a second alcohol gives an ether; $E1$ (loss of β-H from the carbocation) gives an alkene.

Step 2. Carbocation stability: $3^\circ > 2^\circ > 1^\circ$. For a 3° alcohol, the cation R_3C^+ forms easily; β-H abstraction (E1) is fast; alkene is the major product. For a 2° alcohol, $E1$ is again dominant though somewhat slower.

Step 3. Steric factor. The S_N2 ether-forming step requires another alcohol molecule to attack the carbon bearing the leaving group. A 3° carbon is too crowded for S_N2 by any nucleophile; a 2° carbon is modestly hindered. Both factors push the reaction toward elimination.

Step 4. Worked example. *tert*-butanol with conc. H_2SO_4 at $413\,K$ gives *isobutylene* ($(CH_3)_2C{=}CH_2$), not *tert*-butyl ether. The ether route fails.

Step 5. Conclusion. Use acid dehydration only for primary alcohols (or for symmetric secondary ethers under controlled conditions). For 3° or unsymmetrical ethers, use Williamson synthesis instead.

> **Final Answer:** For 2° or 3° alcohols the protonated intermediate undergoes $E1$ (loss of β-H from a stable carbocation) much faster than S_N2 by another alcohol, so the alkene is the major product and very little ether forms.

☞ Use the right method for the right substrate

Primary alcohols: acid dehydration at moderate T (ether) or high T (alkene). Tertiary alcohols: only alkene by acid dehydration. Unsymmetrical ethers and tertiary ethers: Williamson synthesis is the only reliable route.

EXPERT'S SOLUTION *: Arjun Kapoor, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Think of S_N2 vs $E1$ as a race between two pathways out of the same intermediate. Whichever is faster wins; for 2° and 3° alcohols, $E1$ wins by a wide margin.

Step 1. Once a 3° alcohol is protonated, the leaving water departs spontaneously to give a stable 3° cation. The cation is too short-lived (and the approach to its sp^2 carbon too crowded for any second alcohol to make a back-side attack.

Step 2. Instead, a nearby base (water, $HSO_4{}^-$, even another alcohol acting as a base) plucks a β-proton; the C-H electrons drop into the empty p-orbital and the alkene is formed.

Step 3. For a 2° alcohol, the same logic applies but less extreme: $\sim$80% alkene, $\sim$20% ether at best.

Step 4. The "no good" verdict in NCERT therefore means 2° alcohols give a mixture (with the alkene dominating) and 3° alcohols give essentially 100% alkene. Use

Williamson instead.

Why this matters. This is one of those important "don't make this product this way" lessons. Knowing why a method fails is as useful as knowing why one succeeds.

> **Final Answer:** Acid dehydration of 2° or 3° alcohols gives mainly the alkene via $E1$, not the ether. Use Williamson instead.

Q 7.28 **Write the equation of the reaction of hydrogen iodide with: (i) 1-propoxypropane (ii) methoxybenzene (iii) benzyl ethyl ether.**

SOLUTION

Concept used. Cleavage of ethers by HI proceeds in two main ways: (a) with an alkyl-alkyl ether, the smaller alkyl group goes to iodine and the larger one retains the OH (via S_N2); (b) with an alkyl-aryl ether, the aryl-O bond is unbreakable, so the alkyl group goes to iodine and the aryl group retains the OH (giving phenol). With excess HI, both halves of an alkyl-alkyl ether become alkyl iodides. The reaction is S_N2 in cold HI for primary alkyl groups and S_N1 in hot HI for tertiary alkyl groups.

Step 1. **(i) 1-Propoxypropane + HI.** Both alkyl groups are n-propyl. Mechanism: protonate the ether O, then I^- attacks one of the C atoms by S_N2, breaking the C-O bond. With one equivalent of HI:

$$CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3 + HI \longrightarrow CH_3CH_2CH_2{-}I + CH_3CH_2CH_2{-}OH.$$

With excess HI, the alcohol product reacts further:
$CH_3CH_2CH_2{-}OH + HI \longrightarrow CH_3CH_2CH_2{-}I + H_2O.$

Step 2. **(ii) Methoxybenzene (anisole) + HI.** Anisole is $C_6H_5{-}O{-}CH_3$. The aryl-O bond is too strong (and aryl carbon does not undergo S_N2). So I^- attacks the methyl carbon, giving methyl iodide and phenol:

$$C_6H_5{-}O{-}CH_3 + HI \longrightarrow C_6H_5{-}OH + CH_3{-}I.$$

Note that the phenol does *not* react further with HI to give an aryl iodide (aryl C-O is stable).

Step 3. **(iii) Benzyl ethyl ether + HI.** $C_6H_5{-}CH_2{-}O{-}C_2H_5$. The benzyl carbon is special: it forms a very stable benzyl cation. Under acidic conditions, the cleavage goes by S_N1 at the benzyl side. Iodide attacks the benzyl cation, giving benzyl iodide and ethanol:

$$C_6H_5{-}CH_2{-}O{-}C_2H_5 + HI \longrightarrow C_6H_5{-}CH_2{-}I + C_2H_5{-}OH.$$

Final Answer: (i) $C_3H_7-O-C_3H_7 + HI \longrightarrow C_3H_7-I + C_3H_7-OH$; (ii) $C_6H_5-O-CH_3 + HI \longrightarrow C_6H_5-OH + CH_3-I$; (iii) $C_6H_5-CH_2-O-C_2H_5 + HI \longrightarrow C_6H_5-CH_2-I + C_2H_5-OH$.

★ Which side keeps the OH?

Alkyl-alkyl ether: smaller alkyl → R-I, larger → R-OH (via S_N2 on the less hindered side).
Alkyl-aryl ether: aryl side keeps the OH; alkyl becomes R-I (aryl-O is unbreakable by HI).
Benzyl-alkyl ether: benzyl becomes R-I (benzyl cation forms easily), alkyl keeps OH.

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

Strategic angle. For every ether cleavage by HI, identify the weakest C-O bond (the one that breaks) and follow it: the carbon on *that* side picks up the iodide, and the carbon on the other side keeps the oxygen (as OH).

Step 1. In (i), both carbons are primary alkyl; either C-O breaks with equal probability. By stoichiometry, one mole of HI cleaves only one C-O bond, giving 1 mole of propyl iodide and 1 mole of propan-1-ol.

Step 2. In (ii), the aryl-O bond is too strong to cleave (π-conjugation locks it in place). HI must attack the methyl carbon by S_N2, displacing $C_6H_5-O^-$ which then picks up a proton.

Step 3. In (iii), the benzyl carbon stabilises a positive charge through resonance with the ring. So under the acidic conditions HI provides, an S_N1 cleavage is possible at the benzyl C. Iodide traps the cation. The ethyl group keeps the O (as ethanol).

Step 4. All three reactions are exothermic and quantitative in laboratory practice.

Why this matters. The cleavage rule "aryl side keeps the OH; benzyl side becomes the iodide" is a high-yield JEE question and a useful synthetic tool for hydrolysing methyl protective groups on phenols.

Final Answer: (i) n-Pr-I + n-Pr-OH; (ii) PhOH + MeI; (iii) $PhCH_2$-I + EtOH.

Q 7.29 Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in the benzene ring.

SOLUTION

Concept used. Same logic as Q 7.16. The **alkoxy group $-\mathrm{OR}$** has a lone pair on oxygen that can donate π-density into the ring ($+M$, mesomeric donation). The ring becomes electron-rich (activation), and the donation pushes excess density to the ortho and para positions (directing).

Step 1. **Activation: lone pair pushes density into the ring.** Draw resonance structures for the aryl alkyl ether $\mathrm{Ar{-}O{-}R}$. The lone pair on O donates into the ring, putting δ^- on the ortho and para carbons: $\mathrm{Ar{-}O^+R} \rightleftharpoons {}^-\mathrm{Ar{=}O^+R}$ (with the negative charge on the ring's o/p carbons). So the ring is more nucleophilic than benzene itself; an electrophile attacks faster.

Step 2. **Directing to o/p: stable arenium intermediate at o/p.** When E^+ attacks the ortho or para carbon, the resulting arenium ion has a resonance structure with the positive charge directly on the carbon bonded to OR. The OR oxygen's lone pair donates into that empty orbital, forming an *oxocarbenium*-like resonance structure with all atoms having full octets. This contributes a large stabilisation.

Step 3. For meta attack, the positive charge lands on carbons not bonded to OR, so the oxygen lone pair cannot help. The meta intermediate is therefore much less stable than the o/p intermediates.

Step 4. Experimental confirmation: anisole reacts with $\mathrm{Br_2}$ in glacial acetic acid at room temperature to give about 90% p-bromoanisole and 10% o-bromoanisole, with no meta isomer at all.

> **Final Answer:** (i) Activation: $-\mathrm{OR}$ donates π-density into the ring through O's lone pair ($+M$), raising the ring's HOMO and stabilising every transition state of EAS. (ii) o/p directing: the arenium intermediate at o/p has an oxocarbenium resonance structure (full-octet), absent for meta. So o/p attack is much more favourable.

♥ Same logic as -OH on phenol

The $-\mathrm{OR}$ of an alkyl aryl ether behaves almost identically to $-\mathrm{OH}$ on phenol: both are strong $+M$ donors that activate the ring and direct to o/p. The difference is mostly in the basicity of the oxygen (ether more basic than phenol).

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

Strategic angle. Two questions reduce to one observation: the lone pair on O delocalises into the ring, both in the ground state (activation) and in the EAS transition state at o/p (directing).

Step 1. Sketch the ground state. In $C_6H_5{-}OR$, oxygen has two lone pairs; one is in a p-orbital aligned with the ring's π-system. That lone pair overlaps and donates π-density.

Step 2. Sketch the arenium intermediate for o-attack: the $+$ charge sits on C-2 (alongside the OR oxygen). Oxygen pushes its lone pair into the cation, forming a Friedel-Crafts-like “oxocarbenium” resonance form.

Step 3. Same drawing for p-attack: the positive charge again ends up on the OR-bearing C-1; oxygen's lone pair stabilises it the same way.

Step 4. For m-attack, the $+$ charge sits on C-3 or C-5; the OR oxygen at C-1 cannot reach them with its lone pair. So the meta arenium ion is much less stabilised.

Why this matters. Predicting o/p vs m directing is the bread-and-butter of EAS problems. The same logic applies to $-OH$, $-OR$, $-NH_2$, $-NR_2$.

> **Final Answer:** The -OR lone pair pushes π-density into the ring (activation) and stabilises only the o and p arenium intermediates (o/p directing).

Q 7.30 Write the mechanism of the reaction of HI with methoxymethane.

SOLUTION

Concept used. Methoxymethane (dimethyl ether), $CH_3{-}O{-}CH_3$, reacts with HI by an S_N2 mechanism. Step 1 protonates the ether oxygen, turning it into a leaving group; step 2 sees I^- attack one of the methyl carbons from the back side, displacing methanol; step 3 (if excess HI is present) protonates and substitutes the methanol to give a second molecule of methyl iodide.

Step 1. Step 1: protonation. The ether oxygen is mildly basic; in HI, one of its lone pairs picks up a proton:

$$CH_3{-}O{-}CH_3 + HI \rightleftharpoons CH_3{-}O(^+)(H){-}CH_3 + I^-.$$

The protonated ether (an oxonium ion) now has a much better leaving group: CH_3OH.

Step 2. Step 2: S_N2 by iodide. The iodide ion attacks one methyl carbon from the back side of the leaving $O(H)CH_3$ group; the C-O bond breaks as the new C-I bond forms:

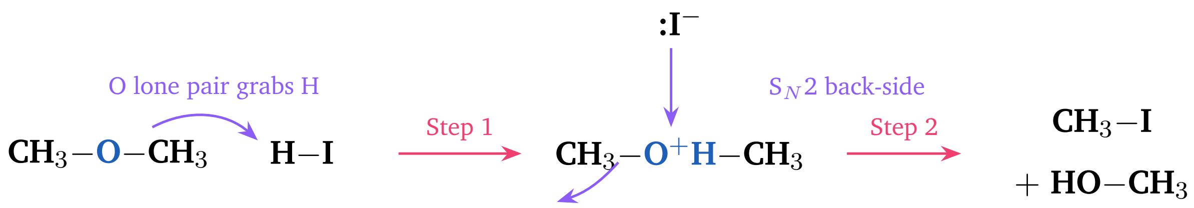
$$I^- + CH_3{-}O(^+)(H){-}CH_3 \longrightarrow CH_3{-}I + HO{-}CH_3.$$

The first methyl carbon is now in $CH_3{-}I$; the other methyl carbon stays in $CH_3{-}OH$ (methanol).

Step 3. Step 3: with excess HI, the methanol also reacts. It is first protonated to $CH_3{-}OH_2{}^+$, then iodide displaces water by S_N2:

$$CH_3OH + HI \longrightarrow CH_3{-}I + H_2O.$$

Net product with excess HI: 2 equiv of CH_3I and 1 equiv of H_2O.



Curly arrows: (1) ether O lone pair grabs H^+ of HI; (2) I^- attacks one CH_3 from the back side (S_N2), breaking the C–O bond and expelling CH_3OH.

Final Answer: Mechanism: (1) HI protonates the ether oxygen to give an oxonium ion; (2) I^- attacks a methyl carbon by S_N2, displacing CH_3OH; (3) excess HI converts the methanol to a second equivalent of methyl iodide.

☞ The leaving group is alcohol, not oxide

The first thing HI does is protonate the ether to give an oxonium ion. Without this protonation, CH_3O^- would be a hopelessly bad leaving group. After protonation, CH_3OH leaves cleanly.

EXPERT'S SOLUTION *: Aanya Sharma, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. The S_N2 step is the rate-determining step. The reaction is fastest with the most nucleophilic halide ion among HF, HCl, HBr, HI. Iodide is the largest, softest, and most nucleophilic anion in the series; that is why HI works so well for ether cleavage.

Step 1. Both methyl carbons are equivalent in dimethyl ether, so iodide can attack either: the rate is twice that of attack on a single methyl.

Step 2. The S_N2 transition state has trigonal-bipyramidal geometry around the attacked carbon, with I^- and the leaving methanol on opposite sides.

Step 3. In water-free conditions, the released methanol is protonated again by HI and converted to CH_3I, so the final yield is 2 mol CH_3I per mol of ether (with 1 mol of water as the only other product).

Step 4. The reaction works for any methyl-methyl, methyl-primary, or primary-primary ether by the same mechanism. For *tert*-alkyl ethers, S_N1 takes over.

Why this matters. The reaction is the "demethylation" workhorse: protecting an OH as an OMe ether and then removing the methyl with HI lets a chemist work on the rest of the molecule unhindered.

> **Final Answer:** Mechanism: protonation → S_N2 by I^- at the methyl carbon → $CH_3I + CH_3OH$ (and with excess HI, a second equivalent of CH_3I from the methanol).

Q 7.31 **Write equations of the following reactions:**
(i) Friedel-Crafts reaction – alkylation of anisole.
(ii) Nitration of anisole.
(iii) Bromination of anisole in ethanoic acid medium.
(iv) Friedel-Craft's acetylation of anisole.

SOLUTION

Concept used. Anisole is $C_6H_5{-}OCH_3$ (methoxybenzene). The $-OCH_3$ group is a strong $+M$ ring activator and an ortho/para director (Q 7.29). So every electrophilic aromatic substitution on anisole goes mainly para (and some ortho), with para usually the major isomer due to lower steric clash with $-OCH_3$.

Step 1. **(i) Friedel-Crafts alkylation.** React anisole with an alkyl halide $R{-}Cl$ in the presence of anhydrous $AlCl_3$. The Lewis acid ionises the alkyl halide to a carbocation R^+, which attacks the activated ring. With CH_3Cl:

$$C_6H_5{-}OCH_3 + CH_3{-}Cl \xrightarrow{AlCl_3} \text{p-}CH_3O\text{-}C_6H_4\text{-}CH_3 + HCl$$

(major) plus some *o*-methylanisole.

Step 2. **(ii) Nitration of anisole.** Mix anisole with a 1:1 mixture of conc. HNO_3 and conc. H_2SO_4 at $20\,^\circ C$; mostly the *para*-nitro product forms (with some *ortho*):

$$C_6H_5{-}OCH_3 + HNO_3 \xrightarrow{H_2SO_4} \text{p-}CH_3O\text{-}C_6H_4\text{-}NO_2 + H_2O$$

(major) plus some *o*-nitroanisole.

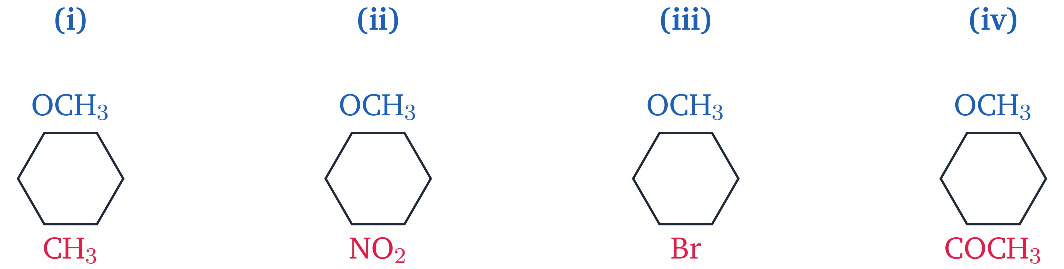
Step 3. **(iii) Bromination in ethanoic acid.** Anisole + Br_2 in glacial CH_3COOH at $0\,^\circ C$ gives mainly *p*-bromoanisole (yield about 90%) and a small amount of *o*-bromoanisole:

$$C_6H_5{-}OCH_3 + Br_2 \xrightarrow{CH_3COOH} \text{p-}CH_3O\text{-}C_6H_4\text{-}Br + HBr.$$

Step 4. **(iv) Friedel-Crafts acetylation.** React anisole with acetyl chloride CH_3COCl in the presence of anhydrous $AlCl_3$ in CS_2:

$$C_6H_5{-}OCH_3 + CH_3{-}CO{-}Cl \xrightarrow{AlCl_3} p\text{-}CH_3O\text{-}C_6H_4\text{-}CO\text{-}CH_3 + HCl.$$

The major product is *para*-methoxy acetophenone.



p-methylanisole *p*-nitroanisole *p*-bromoanisole *p*-methoxyacetophenone

The $-OCH_3$ group is at C-1; the electrophile (CH_3, NO_2, Br, $COCH_3$) lands predominantly at the para (C-4) position. A small amount of the corresponding ortho isomer also forms.

> **Final Answer:** All four reactions give predominantly the *para* isomer because the $-OCH_3$ group is a strong o/p director and the para position is sterically preferred over ortho.

★ Why no Friedel-Crafts on phenol

Friedel-Crafts acylation/alkylation works well on anisole ($-OR$) but is troublesome on phenol ($-OH$). The acidic phenolic OH coordinates strongly to $AlCl_3$, deactivating the catalyst and the ring at once. Protecting the OH as an OMe (anisole) lets the reaction proceed.

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

Strategic angle. Anisole is the textbook activated arene for Friedel-Crafts and nitration/bromination. Predict the product by drawing the o/p resonance stabilisation of the arenium ion.

Step 1. In each of the four reactions, generate the electrophile first: alkylation (R^+ from $R{-}Cl/AlCl_3$), nitration (NO_2^+ from HNO_3/H_2SO_4), bromination (Br^+ from Br_2 in CH_3COOH), acetylation (CH_3CO^+ from $CH_3COCl/AlCl_3$).

Step 2. Each electrophile attacks the ring at the o or p position; para is sterically preferred.

Step 3. The leaving group from the arenium ion is H^+, which gets sucked up by Cl^- (or HSO_4^-, etc.) to give HCl (or H_2SO_4).

Step 4. In aqueous-free conditions (e.g., for the Friedel-Crafts), the catalyst $AlCl_3$ is regenerated and continues to ionise more electrophile.

Why this matters. The reactivity of an activated arene like anisole is the basis of dye chemistry, pharmaceutical synthesis, and the production of vanillin and eugenol.

> **Final Answer:** Equations as written; in each case the major product is the para isomer.

Q 7.32 **Show how would you synthesise the following alcohols from appropriate alkenes?**
(i) 1-methylcyclohexan-1-ol (ii) 4-methylheptan-4-ol
(iii) pentan-2-ol (iv) 2-cyclohexylbutan-2-ol.

SOLUTION

Concept used. To make a tertiary or secondary alcohol from an alkene we use **Markovnikov hydration** (acid + water, or oxymercuration/demercuration), placing OH on the more substituted carbon. For each target alcohol, identify the carbon that carries OH and work backwards to the alkene formed by removing OH and a β-H.

Step 1. **(i) 1-methylcyclohexan-1-ol** (3° alcohol on a cyclohexane ring with a methyl at the same carbon). Start from 1-methylcyclohex-1-ene:

$$1\text{-methylcyclohex-}_1\text{-ene} + H_2O \xrightarrow{H_2SO_4} 1\text{-methylcyclohexan-}_1\text{-ol.}$$

Markovnikov adds OH to the more substituted (and 3°) carbon.

Step 2. **(ii) 4-methylheptan-4-ol** (a 3° alcohol with a methyl, an n-propyl and an n-propyl group all on the OH-bearing C-4 of heptane). Start from 4-methylhept-3-ene. Markovnikov hydration puts OH on the more substituted carbon (the C bearing the methyl), giving the 3° alcohol directly:

$$4\text{-methylhept-}_3\text{-ene} + H_2O \xrightarrow{H_2SO_4} 4\text{-methylheptan-}_4\text{-ol.}$$

Step 3. **(iii) Pentan-2-ol** (a 2° alcohol, $CH_3{-}CH(OH){-}CH_2{-}CH_2{-}CH_3$). Hydrate pent-1-ene ($CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$) under Markovnikov conditions; OH lands on the more substituted internal carbon (C-2):

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3 + H_2O \xrightarrow{H_2SO_4} CH_3{-}CH(OH){-}CH_2{-}CH_2{-}CH_3.$$

Step 4. **(iv) 2-cyclohexylbutan-2-ol.** Structure: $C_6H_{11}{-}C(OH)(CH_3){-}CH_2{-}CH_3$. Hydrate 2-cyclohexylbut-2-ene ($C_6H_{11}{-}C(CH_3){=}CH{-}CH_3$); OH lands on the more substituted (cyclohexyl-bearing) carbon, giving the 3° alcohol:

$$C_6H_{11}{-}C(CH_3){=}CH{-}CH_3 + H_2O \xrightarrow{H_2SO_4} C_6H_{11}{-}C(OH)(CH_3){-}CH_2{-}CH_3.$$

> **Final Answer:** Each alcohol is made by Markovnikov hydration of the alkene that results from removing OH + a β-H from the target. Reagent in each case: dil. H_2SO_4 + H_2O (or oxymercuration-demercuration).

☞ Markovnikov retrosynthesis

For any 3° or 2° alcohol target, ask: "what alkene gives this alcohol with H and OH adding across the C=C"? OH must go on the more substituted carbon. So the double bond was between the OH-bearing carbon and a neighbouring less-substituted carbon.

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

Strategic angle. Mark the OH-bearing carbon and a neighbouring carbon with one fewer H atoms; that bond is the double bond of the precursor alkene. Markovnikov regiochemistry guarantees the same regio outcome on hydration.

Step 1. For (i), the 3° OH is on C-1 of cyclohexane, with a methyl also at C-1. Removing OH from C-1 and a H from C-2 gives the disubstituted endocyclic alkene 1-methylcyclohex-1-ene. Markovnikov adds H-OH back: OH lands at C-1 again, as required.

Step 2. For (ii), the 3° OH at C-4 of heptane bears a methyl branch; removing OH and a β-H from C-3 gives 4-methylhept-3-ene. Markovnikov hydration replaces the OH cleanly on the more substituted (methyl-bearing) carbon.

Step 3. For (iii), pentan-2-ol is made from pent-1-ene by Markovnikov hydration; OH lands on the more substituted internal C-2.

Step 4. For (iv), the alkene is 2-cyclohexylbut-2-ene; Markovnikov adds OH to the more substituted (cyclohexyl-and-methyl-bearing) carbon, giving the 3° alcohol 2-cyclohexylbutan-2-ol.

Why this matters. Retrosynthetic disconnection of an alcohol to an alkene is a standard exam exercise; the same two carbons that flank the original C=C bond now flank the new C-O bond.

> **Final Answer:** Reagents: dil H_2SO_4 + H_2O in each case; alkene precursors as listed in the main solution.

Q 7.33 **When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:**

$CH_3{-}CH(CH_3){-}CH(OH){-}CH_3 + HBr \longrightarrow CH_3{-}CBr(CH_3){-}CH_2{-}CH_3$.

Give a mechanism for this reaction.
(Hint: the 2° carbocation formed in step II rearranges to a more stable 3° carbocation by a hydride ion shift from the 3rd carbon atom.)

SOLUTION

Concept used. Acid-catalysed conversion of an alcohol to an alkyl halide via S_N1: protonation of OH, loss of water to give a carbocation, and capture of the cation by the halide. If the initially formed cation can rearrange by a hydride shift or methyl shift to a more stable cation, it does so before being captured. Here the secondary cation rearranges to a tertiary cation.

Step 1. **Step 1: protonation.** HBr donates a proton to the OH of 3-methylbutan-2-ol:

$$\mathrm{CH_3{-}CH(CH_3){-}CH(OH){-}CH_3 + HBr \rightleftharpoons CH_3{-}CH(CH_3){-}CH(OH_2{}^{+}){-}CH_3 + Br^-}.$$

The OH is now an excellent leaving group (H_2O).

Step 2. **Step 2: loss of water (slow, R-D step).** The protonated alcohol loses water unimolecularly to give a *secondary* carbocation at C-2:

$$\mathrm{CH_3{-}CH(CH_3){-}CH(OH_2{}^{+}){-}CH_3 \longrightarrow CH_3{-}CH(CH_3){-}CH({}^{+}){-}CH_3 + H_2O}.$$

Call this cation **A** (the 2° cation at C-2).

Step 3. **Step 3: 1,2-hydride shift.** The hydrogen on C-3 (the carbon adjacent to the cation, which bears a methyl group) migrates with its bonding electron pair to C-2. The positive charge moves from C-2 to C-3, where it sits on a now-tertiary carbon:

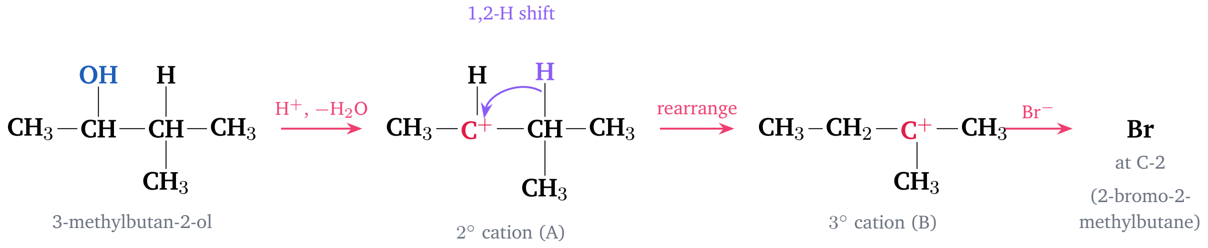
$$\mathrm{CH_3{-}CH(CH_3){-}CH({}^{+}){-}CH_3 \longrightarrow CH_3{-}C({}^{+})(CH_3){-}CH_2{-}CH_3}.$$

Call this cation **B** (the more stable 3° cation at C-3). The shift is essentially barrierless because it gives a much more stable cation.

Step 4. **Step 4: capture by bromide.** The bromide ion attacks the 3° cation from either face, giving the product:

$$\mathrm{CH_3{-}C({}^{+})(CH_3){-}CH_2{-}CH_3 + Br^- \longrightarrow CH_3{-}CBr(CH_3){-}CH_2{-}CH_3}.$$

Final product: **2-bromo-2-methylbutane**.



The violet curly arrow shows the C—H bonding pair migrating from C-3 to C-2 (a 1,2-hydride shift), promoting the 2° cation to a 3° cation before Br$^-$ traps it.

> **Final Answer:** Mechanism: protonation of OH → loss of water to give a 2° cation → 1,2-hydride shift from C-3 to C-2, producing a 3° cation → capture by Br^- to give 2-bromo-2-methylbutane.

♥ Why does the hydride shift happen?

A 3° carbocation is more stable than a 2° one by about $30\,\mathrm{kJ/mol}$ (more σ C-H/C-C hyperconjugation donors and stronger inductive donation from three alkyl groups). The hydride shift is essentially barrierless when the more stable cation lies >20 kJ/mol below the less stable one. The NCERT hint points to exactly this rearrangement.

EXPERT'S SOLUTION *: Aarav Mehta, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Whenever the obvious carbocation intermediate has a neighbouring carbon that would, on a 1,2 shift, give a more substituted cation, the rearrangement happens. Here the obvious cation is 2° at C-2; the C-3 carbon already carries a methyl branch, so a hydride shift from C-3 promotes the cation to 3°.

Step 1. Protonation of the OH is the standard first step in any acid-catalysed alcohol substitution. The protonated form has a very weak C-$\mathrm{OH_2^+}$ bond.

Step 2. The C-$\mathrm{OH_2^+}$ bond breaks heterolytically, releasing water and leaving a 2° cation at C-2. This is the slow step.

Step 3. Within nanoseconds, the cation undergoes a 1,2-H shift from C-3. The migrating hydride brings its bonding electrons with it; the positive charge moves to C-3, which now has three C substituents.

Step 4. The tertiary cation is trapped by bromide, giving 2-bromo-2-methylbutane. Note that no Br is on C-2 (the original OH carbon); rearrangement has moved the substitution one carbon over.

Why this matters. Carbocation rearrangements are a classic "why doesn't the obvious product form" question. Always check for a neighbouring carbon that, after a 1,2 shift, gives a more stable cation.

> **Final Answer:** Mechanism: protonation → loss of $\mathrm{H_2O}$ to 2° cation → 1,2-hydride shift to 3° cation → trap by Br^-. Product: 2-bromo-2-methylbutane.

Key Takeaways

- **Classification:** alcohols can be $1°$, $2°$ or $3°$ depending on how many C atoms are attached to the $-\mathrm{OH}$-bearing carbon; phenols have $-\mathrm{OH}$ on an aromatic ring; ethers have an oxygen between two carbon groups, symmetric ($\mathrm{R{-}O{-}R}$) or unsymmetrical ($\mathrm{R{-}O{-}R'}$).
- **IUPAC naming:** alcohols use "-ol"; phenols use "phenol" (with $-\mathrm{OH}$ at C-1 by default); ethers use the smaller side as "alkoxy" prefix on the larger parent.
- **Preparation of alcohols:** (1) Markovnikov hydration of alkenes; (2) hydroboration-oxidation (anti-Markovnikov); (3) hydrolysis of primary alkyl halides; (4) Grignard addition to aldehydes ($\rightarrow 2°$ alcohol) or ketones ($\rightarrow 3°$ alcohol); (5) reduction of carbonyls by $\mathrm{NaBH_4}$ or $\mathrm{LiAlH_4}$.
- **Preparation of phenol:** (a) cumene process (industrial); (b) chlorobenzene + fused NaOH (Dow); (c) benzene → benzenesulphonate → phenol.
- **Acidity:** phenol ($pK_a \approx 10$) $\gg$ ethanol ($pK_a \approx 16$) because the phenoxide is resonance-stabilised. $-\mathrm{NO_2}$ and other EWG substituents raise phenol acidity; $-\mathrm{OMe}$ and $-\mathrm{NH_2}$ lower it.
- **Hydrogen bonding** explains alcohol's high boiling point vs hydrocarbons of similar mass and vs ethers of the same formula; it also explains why o-nitrophenol is steam-volatile (intramolecular H-bond) but p-nitrophenol is not (intermolecular H-bond).
- **Reactions of alcohols:** substitution (S_N1 or S_N2 by HX), dehydration (E1 with conc. $\mathrm{H_2SO_4}$), oxidation (PCC to aldehyde, $\mathrm{KMnO_4}$ to acid), esterification with carboxylic acids.
- **Reactions of phenol:** react with NaOH ($\rightarrow$ phenoxide), with Na metal ($\rightarrow \mathrm{H_2}$), with $\mathrm{Br_2}$ (in water → tribromo; in $\mathrm{CS_2}$ → monobromo), with conc. $\mathrm{HNO_3}$ (→ picric acid), with $\mathrm{CO_2}$ (Kolbe → salicylic acid), with $\mathrm{CHCl_3/NaOH}$ (Reimer-Tiemann → salicylaldehyde).
- **Williamson ether synthesis:** $\mathrm{R{-}ONa} + \mathrm{R'{-}X} \rightarrow \mathrm{R{-}O{-}R'} + \mathrm{NaX}$. The halide side must be primary; failed for $3°$, vinyl, aryl halides.
- **Cleavage of ethers by HI:** smaller alkyl becomes alkyl iodide; larger keeps the OH. For alkyl-aryl ethers, the aryl side keeps the OH; for benzyl-alkyl ethers, the benzyl side becomes the iodide.
- **Anisole's reactions:** the $-\mathrm{OCH_3}$ group is a strong $+M$ activator and o/p director. Anisole nitrates, brominates, and undergoes Friedel-Crafts alkylation/acetylation cleanly to give mostly the para product.
- **Carbocation rearrangements:** during any S_N1 / E1 reaction, if the obvious carbocation can rearrange (1,2-H shift or 1,2-methyl shift) to a more stable one, it does (Q 7.33).

End of Exercises (Q 7.1 to Q 7.33)