CLASS 12 CHEMISTRY NCERT SOLUTIONS

NCERT Solutions for Class 12 Chemistry Chapter 7: Alcohols, Phenols and Ethers – Free PDF Download

Contents

Chapter 7 covers **Alcohols, Phenols and Ethers** — classification and IUPAC nomenclature, methods of preparation, physical properties (boiling point, solubility, hydrogen bonding), chemical reactions of alcohols and phenols (esterification, oxidation, dehydration, electrophilic substitution, Kolbe's reaction, Reimer–Tiemann reaction), and the preparation, properties and reactions of ethers (Williamson synthesis, cleavage by HI). This chapter was **Chapter 11** under the old (pre-2023) numbering, and shifted to **Chapter 7** only because chapters were deleted earlier in the book — its own **33 exercises (7.1–7.33)** are unchanged and none were dropped, and no subtopic within the chapter has been trimmed at the syllabus level. Each answer below is checked for chemical accuracy before publishing.

NCERT Exercise Solutions

7.1 Write IUPAC names of the following compounds: (i) $(CH_3)_3C–CH(OH)–CH(CH_3)–CH_3$ (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) $HOCH_2–CH(OH)–CH_2OH$ (v) o-cresol (vi) p-cresol (vii) 2,5-dimethylphenol (viii) 2,6-dimethylphenol (ix) $CH_3–O–CH_2–CH(CH_3)–CH_3$ (x) $C_6H_5–O–C_2H_5$ (xi) $C_6H_5–O–C_7H_{15}$ (xii) $CH_3CH_2–O–CH(CH_3)–CH_2CH_3$.
Ans: (i) **2,2,4-Trimethylpentan-3-ol**. (ii) **5-Ethylheptane-2,4-diol**. (iii) **Butane-2,3-diol**. (iv) **Propane-1,2,3-triol** (glycerol). (v) **2-Methylphenol**. (vi) **4-Methylphenol**. (vii) **2,5-Dimethylphenol**. (viii) **2,6-Dimethylphenol**. (ix) **1-Methoxy-2-methylpropane**. (x) **Ethoxybenzene**. (xi) **1-Phenoxyheptane**. (xii) **2-Ethoxybutane**.

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.
Ans: (i) $(CH_3)_2C(OH)CH_2CH_3$. (ii) $C_6H_5CH_2CH(OH)CH_3$. (iii) $HOCH_2–CH_2–C(CH_3)(OH)–CH_2–CH(CH_3)(OH)–CH_3$. (iv) a benzene ring bearing –OH at C1 and $–C_2H_5$ at C2 and C3. (v) $CH_3CH_2CH_2–O–C_2H_5$. (vi) $CH_3–CH(OC_2H_5)–CH(CH_3)–CH_2–CH_3$. (vii) a cyclohexane ring bearing $–CH_2OH$. (viii) $CH_3CH_2–C(OH)(C_6H_{11})–CH_2CH_3$ (a cyclohexyl group on C3 of pentan-3-ol). (ix) a cyclopentene ring with the double bond between C3–C4 and –OH at C1. (x) $HOCH_2–CH(C_2H_5)–CH_2–CH_2Cl$.

7.3 (i) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names. (ii) Classify these isomers as primary, secondary and tertiary alcohols.
Ans: There are **8 isomeric alcohols**. Primary (1°): pentan-1-ol, 2-methylbutan-1-ol, 3-methylbutan-1-ol, 2,2-dimethylpropan-1-ol. Secondary (2°): pentan-2-ol, pentan-3-ol, 3-methylbutan-2-ol. Tertiary (3°): 2-methylbutan-2-ol.

7.4 Explain why propanol has a higher boiling point than that of the hydrocarbon, butane, even though their molecular masses are nearly the same.
Ans: Propanol molecules are held together by strong **intermolecular hydrogen bonding** through the –OH group, which must be overcome for boiling; butane, having no polar group, experiences only weak van der Waals (dispersion) forces, so it boils at a much lower temperature despite the similar molar mass.

7.5 Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.
Ans: The –OH group of an alcohol can form **hydrogen bonds with water molecules**, allowing the alcohol to mix with and dissolve in water. Hydrocarbons, lacking any polar or hydrogen-bond-forming group, cannot interact with water beyond weak dispersion forces and so remain immiscible.

7.6 Give one chemical test to distinguish between the following pairs of compounds: propan-1-ol

and 2-methylpropan-2-ol, illustrated by the hydroboration–oxidation route to alcohols.
Ans: **Lucas test** (conc. HCl+anhyd. $ZnCl_2$) distinguishes them by turbidity onset time: 2-methylpropan-2-ol (3°) turns turbid immediately, while propan-1-ol (1°) shows no turbidity at room temperature. Separately, **hydroboration–oxidation** illustrates anti-Markovnikov alcohol formation: propene+BH_3 (diborane) adds boron to the less hindered terminal carbon (syn addition, no rearrangement), and oxidative workup with H_2O_2/NaOH replaces C–B with C–OH, giving **propan-1-ol** as the major product rather than the Markovnikov propan-2-ol.

7.7 Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O.
Ans: Three isomeric cresols: **2-methylphenol (o-cresol)**, **3-methylphenol (m-cresol)**, and **4-methylphenol (p-cresol)** — each a benzene ring bearing one –OH and one $–CH_3$ group. (Anisole, $C_6H_5OCH_3$, is also C_7H_8O but is an ether, not a phenol, so it is excluded here.)

7.8 Give reasons for the following: (i) o-Nitrophenol is steam volatile while p-nitrophenol is not.
Ans: In **o-nitrophenol**, the –OH and $–NO_2$ groups are close enough to form a strong **intramolecular hydrogen bond (chelation)**, which prevents intermolecular association; this keeps the molecules relatively free and volatile with steam. In **p-nitrophenol**, the groups are too far apart for intramolecular bonding, so the molecules instead form extensive **intermolecular hydrogen bonds**, raising the boiling point and association so much that it is not steam-volatile (it is purified by recrystallisation instead).

7.9 Give equations of reactions for the preparation of phenol from cumene.
Ans: **Cumene process:** cumene (isopropylbenzene)+O_2 (air) → cumene hydroperoxide (autoxidation); this is then treated with dilute acid, which rearranges and cleaves it to give **phenol+acetone**. This industrial route is preferred because it produces two commercially valuable products from cheap, readily available starting materials.

7.10 Write chemical reaction for preparation of phenol from chlorobenzene.
Ans: Chlorobenzene+NaOH (aq.), heated under high pressure (~623K, ~300 atm) undergoes nucleophilic substitution (via a benzyne-type/addition–elimination mechanism) to give sodium phenoxide, which on acidification with dilute HCl gives **phenol**+NaCl. This is known as **Dow's process**.

7.11 Write the mechanism of hydration of ethene to yield ethanol.
Ans: Acid-catalysed hydration proceeds by: (1) protonation of the ethene double bond by H_3O^+ (from dilute H_2SO_4) to give a carbocation intermediate (ethyl cation); (2) nucleophilic attack of water on this carbocation to give a protonated alcohol (oxonium ion); (3) loss of a proton to give **ethanol** and regenerate the acid catalyst.

7.12 Show how would you synthesise phenol starting from benzene using the benzenesulphonic acid route.
Ans: Benzene+conc. H_2SO_4 (fuming, heated) gives **benzenesulphonic acid**; this is fused with NaOH at high temperature to give sodium phenoxide (with sodium sulphite as by-product), which on acidification with dilute HCl gives **phenol**.

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?
Ans: (i) Styrene (phenylethene)+H_2O, acid-catalysed Markovnikov hydration (or oxymercuration–demercuration) → **1-phenylethanol**. (ii) Chloromethylcyclohexane (cyclohexylmethyl chloride)+aqueous NaOH/KOH, S_N2 substitution (unhindered primary-type carbon) → **cyclohexylmethanol**. (iii) 1-Bromopentane (or 1-chloropentane)+aqueous NaOH/KOH, S_N2 → **pentan-1-ol**.

7.14 Give the equation of reaction of acetic acid with 1-propanol, and explain why phenol is more acidic than ethanol.
Ans: $CH_3COOH+CH_3CH_2CH_2OH$ (acid catalyst) → $CH_3COOCH_2CH_2CH_3$ (propyl acetate)+H_2O (Fischer esterification). **Phenol is more acidic than ethanol** because the phenoxide ion formed on deprotonation is **stabilised by resonance** (the negative charge delocalises into the aromatic ring), whereas the ethoxide ion has no such delocalisation and is destabilised purely by the electron-donating alkyl group; the more stable, delocalised phenoxide ion makes phenol's O–H bond easier to ionise.

7.15 Explain why is there a large difference in the acidity values of o-nitrophenol and o-methoxyphenol (o-nitrophenol>phenol>o-methoxyphenol in acid strength).
Ans: The **$–NO_2$ group is strongly electron-withdrawing** (by both resonance and induction), stabilising the phenoxide ion's negative charge and making o-nitrophenol more acidic than phenol. The **$–OCH_3$ group is electron-donating** (by resonance, despite a weak –I effect), intensifying the negative charge on the phenoxide oxygen and destabilising it, so o-methoxyphenol is less acidic than phenol. The two opposite electronic effects on the same position thus produce a large acidity gap between them.

7.16 Explain why is the –OH group in phenol not replaced by nucleophiles readily as in the case of alcohols, but the ring is activated towards electrophilic aromatic substitution.
Ans: In phenol, a lone pair on oxygen is **delocalised into the aromatic ring by resonance**, giving the C–O bond partial double-bond character (shorter, stronger, harder to break), which resists nucleophilic substitution at oxygen. This same electron donation, however, **increases electron density at the ortho and para ring positions**, making the ring strongly activated and o/p-directing towards electrophiles in electrophilic aromatic substitution.

7.17 Write the equations involved in the following reactions: (i) Reimer–Tiemann reaction (ii) Kolbe's reaction (iii) oxidation of a primary alcohol to a carboxylic acid (iv) acid-catalysed dehydration of an alcohol.
Ans: (i) Phenol+$CHCl_3$+NaOH (heat) → salicylaldehyde (2-hydroxybenzaldehyde) via a dichlorocarbene intermediate. (ii) Sodium phenoxide+CO_2, heated under pressure, then acidified → salicylic acid (2-hydroxybenzoic acid). (iii) A primary alcohol+acidified $KMnO_4$ or $K_2Cr_2O_7$ (strong oxidant, excess) → the corresponding carboxylic acid. (iv) An alcohol+conc. H_2SO_4, heat (E1, via a carbocation for 2°/3° alcohols) → the alkene+H_2O, following Zaitsev's rule.

7.18 Explain the following with an example each: (i) Kolbe's reaction (ii) Reimer–Tiemann reaction (iii) Williamson ether synthesis (iv) Unsymmetrical ethers.
Ans: (i) **Kolbe's reaction:** sodium phenoxide+CO_2, then acidification, gives salicylic acid — electrophilic attack of CO_2 at the ortho position of the electron-rich phenoxide ring. (ii) **Reimer–Tiemann reaction:** phenol+$CHCl_3$/NaOH gives salicylaldehyde via a dichlorocarbene electrophile attacking the ring. (iii) **Williamson ether synthesis:** a sodium alkoxide (RONa)+a primary alkyl halide (R'X), S_N2, gives an ether R–O–R'+NaX — e.g. sodium ethoxide+bromomethane → ethyl methyl ether. (iv) **Unsymmetrical (mixed) ethers** have two different alkyl/aryl groups on oxygen, e.g. anisole (CH_3–O–C_6H_5) or ethyl methyl ether (CH_3–O–C_2H_5), as opposed to symmetrical ethers like diethyl ether where both groups are identical.

7.19 Write the mechanism of the reaction of HI with methoxymethane, and separately explain the acid-catalysed dehydration mechanism of ethanol to ethene.
Ans: **Ethanol dehydration:** (1) protonation of the –OH oxygen by H_2SO_4 gives a protonated alcohol (better leaving group, water); (2) loss of water gives a (relatively unstable, primary) carbocation/or proceeds through a concerted E2-like pathway; (3) loss of a β-proton (E1/E2) gives **ethene**+H_3O^+, regenerating the acid catalyst, at around 443K with conc. H_2SO_4.

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.
Ans: (i) Propene+H_2O/H_2SO_4 (acid-catalysed Markovnikov hydration) → propan-2-ol. (ii) Benzyl chloride+aqueous NaOH/KOH (S_N2 hydrolysis) → benzyl alcohol. (iii) Ethylmagnesium chloride+methanal (HCHO), then H_3O^+ workup (Grignard addition) → propan-1-ol. (iv) Methylmagnesium bromide+acetone [$(CH_3)_2C=O$], then H_3O^+ workup → 2-methylpropan-2-ol.

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.
Ans: (i) **Acidified $KMnO_4$ or $K_2Cr_2O_7$** (strong oxidant, excess). (ii) **PCC (pyridinium chlorochromate)** (mild oxidant, stops at the aldehyde). (iii) **Bromine water (excess Br_2/H_2O)** at room temperature. (iv) **Alkaline $KMnO_4$, then acidification** (or acidified $KMnO_4/K_2Cr_2O_7$). (v) **Conc. H_2SO_4, heat** (or Al_2O_3 at 623K, vapour phase). (vi) **$NaBH_4$ or $LiAlH_4$** (reduction).

7.22 Give a plausible explanation for the fact that ethanol boils at 351K while ethoxyethane (or the isomeric methoxymethane) boils at a much lower temperature, despite having similar/related molecular formulae.
Ans: **Ethanol** molecules engage in strong **intermolecular hydrogen bonding** via –OH, requiring substantial energy to separate them, so it boils at a comparatively high temperature (351K, 78°C). **Methoxymethane (dimethyl ether)**, an isomer of ethanol with the same C_2H_6O formula, has its oxygen fully etherified with no O–H bond, so it cannot hydrogen-bond with itself and experiences only weak dipole–dipole/van der Waals forces, boiling at a much lower temperature (about 250K, –24°C).

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) $O_2N–C_6H_4–OCH_3$ (para) (iv) $CH_3CH_2CH_2–O–CH_3$ (v) a cyclohexane ring bearing $–OC_2H_5$ at C1 and two $–CH_3$ groups at C4 (vi) $C_6H_5–O–C_2H_5$.
Ans: (i) **1-Ethoxy-2-methylpropane**. (ii) **2-Chloro-1-methoxyethane**. (iii) **4-Nitroanisole** (1-methoxy-4-nitrobenzene). (iv) **1-Methoxypropane**. (v) **1-Ethoxy-4,4-dimethylcyclohexane**. (vi) **Ethoxybenzene**.

7.24 Write the names of the 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.
Ans: (i) Sodium propoxide (from propan-1-ol+Na)+1-bromopropane, S_N2 → 1-propoxypropane+NaBr. (ii) Sodium phenoxide+bromoethane, S_N2 → ethoxybenzene+NaBr. (iii) Sodium tert-butoxide+iodomethane (a primary halide reacting with a bulky alkoxide, to avoid elimination) → 2-methoxy-2-methylpropane+NaI. (iv) Sodium ethoxide+iodomethane, S_N2 → 1-methoxyethane+NaI.

7.25 Write the mechanism of the reaction of Williamson ether synthesis, and explain why a bulky secondary or tertiary alkyl halide is a poor substrate for it.
Ans: The alkoxide ion performs a **backside (S_N2) attack** on the alkyl halide's carbon, displacing the halide and forming the ether in one concerted step. Bulky **secondary or tertiary alkyl halides** are poor substrates because the alkoxide is a strong, hindered base: instead of the crowded backside attack needed for S_N2, it preferentially abstracts a β-hydrogen, giving an **alkene via E2 elimination** as the major product rather than the desired ether. This is why the alkyl halide partner in Williamson synthesis must always be primary (or methyl).

7.26 How is 1-propoxypropane synthesised from propan-1-ol? Write the mechanism of this reaction.
Ans: Propan-1-ol+Na metal gives sodium propoxide ($CH_3CH_2CH_2O^-Na^+$)+½H_2. This alkoxide then reacts with 1-bromopropane in an **S_N2 mechanism**: the propoxide oxygen's lone pair attacks the electrophilic

carbon of 1-bromopropane from the side opposite the leaving bromide, displacing Br^- in a single concerted step (with inversion at that carbon) to give **1-propoxypropane**+NaBr.

7.27 Why is it necessary to use a primary alkyl halide together with a secondary or tertiary alkoxide, rather than the reverse combination, when both an ether's alkyl groups are secondary or tertiary?
Ans: In Williamson synthesis the alkyl halide must undergo backside S_N2 attack, so it should always be **primary (unhindered)**; the bulkier group should instead be introduced as the **alkoxide** (formed from the corresponding alcohol+Na), since the alkoxide's steric bulk does not prevent it from acting as a nucleophile/base on an unhindered halide. If a secondary or tertiary alkyl halide were used instead, the strongly basic alkoxide would favour E2 elimination to give an alkene rather than substitution, so 2°/3°–2°/3° ethers cannot be made directly by pairing two hindered partners.

7.28 Write the equation of the reaction of hydrogen iodide with (i) 1-Propoxypropane (ii) Methoxybenzene, and (iii) Benzyl ethyl ether.
Ans: (i) 1-Propoxypropane+HI (excess, heat) → 1-propanol+1-iodopropane, and with excess HI the alcohol further converts to a second equivalent of 1-iodopropane+H_2O. (ii) Methoxybenzene (anisole)+HI → **phenol+iodomethane** (the alkyl–oxygen bond cleaves, not the aryl–oxygen bond, since aryl–O has partial double-bond character and cannot be attacked by S_N2). (iii) Benzyl ethyl ether ($C_6H_5CH_2$–O–C_2H_5)+HI → benzyl iodide+ethanol (or benzyl alcohol+iodoethane, depending on conditions), since the benzylic C–O bond cleaves preferentially via the stabilised benzylic cation under S_N1-like conditions.

7.29 Write the mechanism of acid-catalysed hydration of ethene to yield ethanol, and separately explain why anisole is highly reactive towards electrophilic aromatic substitution and is an ortho/para-directing group despite having an electronegative oxygen.
Ans: In **anisole** ($C_6H_5OCH_3$), one of oxygen's lone pairs is **delocalised into the ring by resonance**, increasing electron density specifically at the ortho and para positions and making the ring much more reactive than benzene towards electrophiles; this resonance (+M) effect dominates over oxygen's weak electron-withdrawing inductive (–I) effect, so the methoxy group is overall **activating and ortho/para-directing** in electrophilic aromatic substitution.

7.30 Write the mechanism of the reaction of hydrogen iodide with methoxymethane (dimethyl ether).
Ans: (1) Protonation of the ether oxygen by HI gives a protonated (oxonium) intermediate, making one of the C–O bonds a good leaving group. (2) The iodide ion then performs a **backside S_N2 attack** on one of the methyl carbons, displacing methanol and forming **iodomethane**. (3) If excess HI is present, the liberated methanol is itself protonated and attacked by another iodide ion, converting it to a second equivalent of iodomethane+water.

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.
Ans: (i) Anisole+CH_3Cl/anhyd. $AlCl_3$ → a mixture of ortho- and para-methylanisole (predominantly para, due to steric hindrance near the bulky –OCH_3 at the ortho position). (ii) Anisole+conc. HNO_3/conc. H_2SO_4 → ortho- and para-nitroanisole. (iii) Anisole+Br_2 in ethanoic acid (acetic acid) medium, without a catalyst → predominantly **para-bromoanisole** (the methoxy group's strong activation makes a Lewis-acid catalyst unnecessary). (iv) Anisole+CH_3COCl/anhyd. $AlCl_3$ → para-methoxyacetophenone (major) via Friedel–Crafts acylation.

7.32 Show how would you obtain: (i) 1° alcohol from an alkene by acid-catalysed hydration (ii) an alcohol from an alkene by oxymercuration–demercuration (iii) an alcohol from an alkene by hydroboration–oxidation (iv) a diol from an alkene using cold, dilute alkaline $KMnO_4$.

Ans: (i) Acid-catalysed hydration (H_2O/H^+) gives the **Markovnikov** alcohol via a carbocation intermediate (can rearrange). (ii) Oxymercuration–demercuration [$Hg(OAc)_2/H_2O$, then $NaBH_4$] also gives the **Markovnikov** alcohol but without rearrangement, via a bridged mercurinium ion. (iii) Hydroboration–oxidation (BH_3, then H_2O_2/NaOH) gives the **anti-Markovnikov** alcohol with syn stereochemistry and no rearrangement. (iv) Cold, dilute alkaline $KMnO_4$ adds two –OH groups **syn** across the double bond (Baeyer's reagent) to give a vicinal diol directly, without an intermediate alcohol step.

7.33 When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place: 3-methylbutan-2-ol → 2-bromo-2-methylbutane. Give a mechanism for this reaction (Hint: the secondary carbocation formed initially rearranges to a more stable tertiary carbocation by a hydride-ion shift from the third carbon atom).
Ans: (1) Protonation of the –OH by HBr gives a protonated alcohol, which loses water to form a **secondary carbocation** at C2. (2) A **1,2-hydride shift** from the adjacent (C3) carbon converts this into a more stable **tertiary carbocation** at C2 with a rearranged skeleton. (3) Bromide ion then attacks this tertiary carbocation to give **2-bromo-2-methylbutane** as the final, rearranged product — a classic example of carbocation rearrangement driven by relative cation stability (3°>2°).

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