# Chapter 7: Alcohols, Phenols and Ethers

## Exercises — Exercises

**Q1** Write IUPAC names of the following compounds:
(i) $CH_3$-$CH(CH_3)$-$CH(OH)$-$C(CH_3)_2$-$CH_3$ (ii) $H_3C$-$CH(OH)$-$CH_2$-$CH(OH)$-$CH(C_2H_5)$-$CH_2$-$CH_3$ (iii) $CH_3$-$CH(OH)$-$CH(OH)$-$CH_3$ (iv) HO-$CH_2$-$CH(OH)$-$CH_2$-OH (v) benzene ring: OH at $C_1$, $CH_3$ at $C_2$ (vi) benzene ring: $CH_3$ at $C_1$, OH at $C_4$ (para) (vii) benzene ring: OH at $C_1$, $CH_3$ at $C_2$ and $C_5$ (viii) benzene ring: OH at $C_1$, $CH_3$ at $C_2$ and $C_6$ (ix) $CH_3$-O-$CH_2$-$CH(CH_3)$-$CH_3$ (x) $C_6H_5$-O-$C_2H_5$

### SOLUTION

IUPAC nomenclature is assigned by identifying the longest carbon chain containing the principal functional group (OH for alcohols, OR for ethers), numbering to give the principal group the lowest locant, and using appropriate prefixes/suffixes.

(i) Structure: $CH_3$-$CH(CH_3)$-$CH(OH)$-$C(CH_3)_2$-$CH_3$ — longest chain = 5 C (pentane). Numbering to give OH ($C_3$) lowest locant set: OH at $C_3$, two $CH_3$ at $C_2$, one $CH_3$ at $C_4$.

IUPAC name: 2,2,4-trimethylpentan-3-ol

(ii) Structure: $H_3C$-$CH(OH)$-$CH_2$-$CH(OH)$-$CH(C_2H_5)$-$CH_2$-$CH_3$ — the longest chain containing both OH groups = 7 C (heptane). OH at $C_2$ and $C_4$, ethyl branch at $C_5$.

IUPAC name: 5-ethylheptane-2,4-diol

(iii) Structure: $CH_3$-$CH(OH)$-$CH(OH)$-$CH_3$ — 4 C chain, OH at $C_2$ and $C_3$.

IUPAC name: butane-2,3-diol

(iv) Structure: HO-$CH_2$-$CH(OH)$-$CH_2$-OH — 3 C chain with three OH groups (glycerol).

IUPAC name: propane-1,2,3-triol

(v) Benzene ring with OH at $C_1$ and $CH_3$ at $C_2$ (ortho).

IUPAC name: 2-methylphenol (o-cresol)

(vi) Benzene ring (aromatic) with $CH_3$ at $C_1$ and OH at $C_4$ (para) — this is a phenol, not a cyclohexanol.

IUPAC name: 4-methylphenol (p-cresol)

(vii) Benzene ring with OH at $C_1$ and $CH_3$ groups at $C_2$ and $C_5$.

IUPAC name: 2,5-dimethylphenol

(viii) Benzene ring with OH at $C_1$ and $CH_3$ groups at both ortho positions ($C_2$ and $C_6$).

IUPAC name: 2,6-dimethylphenol

(ix) $CH_3$-O-$CH_2$-$CH(CH_3)$-$CH_3$ — larger group = 2-methylpropane (isobutyl); smaller = methoxy at $C_1$.

IUPAC name: 1-methoxy-2-methylpropane

(x) $C_6H_5$-O-$C_2H_5$ — phenyl ethyl ether (phenetole). Larger group = benzene; substituent = ethoxy.

IUPAC name: ethoxybenzene

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) 2,5-dimethylphenol (viii) 2,6-dimethylphenol (ix) 1-methoxy-2-methylpropane (x) ethoxybenzene

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Q2 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

Each name is decoded by identifying the parent chain, principal group, and substituents.

(i) 2-Methylbutan-2-ol: 4-C chain (butane), OH at $C_2$, $CH_3$ at $C_2$.

Structure: $CH_3$-$C(OH)(CH_3)$-$CH_2$-$CH_3$

(ii) 1-Phenylpropan-2-ol: 3-C chain (propane), OH at $C_2$, $C_6H_5$ at $C_1$.

Structure: $C_6H_5$-$CH_2$-$CH(OH)$-$CH_3$

(iii) 3,5-Dimethylhexane-1,3,5-triol: 6-C chain (hexane), OH at $C_1$, $C_3$, $C_5$; $CH_3$ at $C_3$, $C_5$.

Structure: HO-$CH_2$-$CH_2$-$C(OH)(CH_3)$-$CH_2$-$C(OH)(CH_3)$-$CH_3$

(iv) 2,3-Diethylphenol: benzene ring with OH at $C_1$, $C_2H_5$ at $C_2$, $C_2H_5$ at $C_3$.

Structure: $C_6H_3(OH)(C_2H_5)(C_2H_5)$ — OH at 1, ethyl at 2, ethyl at 3.

(v) 1-Ethoxypropane: 3-C chain (propane), ethoxy (-$OC_2H_5$) at $C_1$.

Structure: $C_2H_5$-O-$CH_2$-$CH_2$-$CH_3$

(vi) 2-Ethoxy-3-methylpentane: 5-C chain (pentane), ethoxy at $C_2$, $CH_3$ at $C_3$.
Structure: $CH_3$-CH($OC_2H_5$)-CH($CH_3$)-$CH_2$-$CH_3$

(vii) Cyclohexylmethanol: cyclohexyl group (-$C_6H_{11}$) attached to methanol ($CH_2OH$).
Structure: $C_6H_{11}$-$CH_2$-OH

(viii) 3-Cyclohexylpentan-3-ol: 5-C chain (pentane), OH at $C_3$, cyclohexyl at $C_3$.
Structure: $CH_3$-$CH_2$-C(OH)($C_6H_{11}$)-$CH_2$-$CH_3$

(ix) Cyclopent-3-en-1-ol: cyclopentane ring with double bond at $C_3$-$C_4$ and OH at $C_1$.
Structure: cyclopentane ring with C=C between $C_3$ and $C_4$, OH at $C_1$.

(x) 4-Chloro-3-ethylbutan-1-ol: 4-C chain (butane), OH at $C_1$, Cl at $C_4$, ethyl at $C_3$.
Structure: HO-$CH_2$-$CH_2$-CH($C_2H_5$)-$CH_2$Cl

Answer: (i) $CH_3C(OH)(CH_3)CH_2CH_3$ (ii) $C_6H_5CH_2CH(OH)CH_3$ (iii) $HOCH_2CH_2C(OH)(CH_3)CH_2C(OH)(CH_3)CH_3$ (iv) 1-OH,2,3-di($C_2H_5$)-$C_6H_3$ (v) $C_2H_5OCH_2CH_2CH_3$ (vi) $CH_3CH(OC_2H_5)CH(CH_3)CH_2CH_3$ (vii) $C_6H_{11}CH_2OH$ (viii) $CH_3CH_2C(OH)(C_6H_{11})CH_2CH_3$ (ix) Cyclopent-3-en-1-ol ring structure (x) $HOCH_2CH_2CH(C_2H_5)CH_2Cl$

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Q3 (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

Molecular formula $C_5H_{12}O$ with one OH group on an aliphatic carbon gives 8 structural isomers.

PRIMARY ALCOHOLS (OH on C bearing 2 H atoms):
1. Pentan-1-ol: $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-OH
2. 2-Methylbutan-1-ol: $CH_3$-$CH_2$-CH($CH_3$)-$CH_2$-OH
3. 3-Methylbutan-1-ol: $(CH_3)_2$CH-$CH_2$-$CH_2$-OH
4. 2,2-Dimethylpropan-1-ol: $(CH_3)_3$C-$CH_2$-OH

SECONDARY ALCOHOLS (OH on C bearing 1 H):
5. Pentan-2-ol: $CH_3$-CH(OH)-$CH_2$-$CH_2$-$CH_3$
6. Pentan-3-ol: $CH_3$-$CH_2$-CH(OH)-$CH_2$-$CH_3$
7. 3-Methylbutan-2-ol: $(CH_3)_2$CH-CH(OH)-$CH_3$

TERTIARY ALCOHOLS (OH on C bearing 0 H):
8. 2-Methylbutan-2-ol: $CH_3$-C(OH)($CH_3$)-$CH_2$-$CH_3$

Answer: 8 isomers: Primary — pentan-1-ol, 2-methylbutan-1-ol, 3-methylbutan-1-ol, 2,2-dimethylpropan-1-ol; Secondary — pentan-2-ol, pentan-3-ol, 3-methylbutan-2-ol; Tertiary — 2-methylbutan-2-ol.

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Q4 Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

SOLUTION

Propanol ($C_3H_7OH$, MW = 60) and butane ($C_4H_{10}$, MW = 58) have comparable molecular masses.

Propanol has a much higher boiling point (370 K) than butane (273 K) because:
- Propanol molecules form strong intermolecular hydrogen bonds through the -OH group (O is highly electronegative; O-H...O hydrogen bonds have energy ~20-40 kJ/mol).
- These hydrogen bonds associate propanol molecules strongly, requiring more energy (higher temperature) to break them during vaporisation.

Butane is a non-polar hydrocarbon. The only intermolecular forces are weak van der Waals (London dispersion) forces. These are much weaker than hydrogen bonds, so butane evaporates at a much lower temperature.

Answer: Propanol has a higher boiling point than butane because propanol molecules are associated by strong intermolecular hydrogen bonds through -OH groups, which are absent in butane (non-polar hydrocarbon with only weak van der Waals forces).

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Q5 Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

SOLUTION

Solubility in water depends on the ability of a solute to interact with water molecules.

Alcohols contain the -OH group, which can form hydrogen bonds with water molecules:

R-OH...O(H)-H and H-O-H...O(H)-R

This hydrogen bonding between alcohol and water makes alcohols soluble in water.

Hydrocarbons are non-polar molecules. They cannot form hydrogen bonds with water and have no significant dipole-dipole interactions. They interact with water only through very weak London dispersion forces. Since 'like dissolves like', non-polar hydrocarbons are sparingly soluble or insoluble in the polar solvent, water.

Hence, lower alcohols (methanol, ethanol, propan-1-ol) are completely miscible with water, while hydrocarbons of comparable molecular mass are essentially insoluble.

Answer: Alcohols form hydrogen bonds with water through their -OH group, making them soluble. Hydrocarbons are non-polar and cannot hydrogen-bond with water, so they are sparingly soluble. The -OH group of alcohols makes them much more water-soluble than hydrocarbons of similar molecular mass.

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Q6 What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

SOLUTION

Hydroboration-oxidation is a two-step method for converting an alkene to an alcohol with anti-Markovnikov regioselectivity.

Step 1 — Hydroboration: Diborane ($B_2H_6$) adds across the double bond. Boron attaches to the less substituted (more H-bearing) carbon, and H attaches to the more substituted carbon. This is a syn addition (both B and H add to the same face).

Step 2 — Oxidation: The organoborane is treated with $H_2O_2$ in the presence of NaOH, replacing the C-B bond with C-OH with retention of configuration.

Net result: The -OH group appears on the carbon that would have received H in Markovnikov addition (the less substituted carbon of the alkene) — anti-Markovnikov product.

Example: Propene -> propan-1-ol

$CH_3\text{-}CH{=}CH_2 + B_2H_6 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}B$ (trialkylborane)

$CH_3\text{-}CH_2\text{-}CH_2\text{-}B + H_2O_2/NaOH \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$ (propan-1-ol) + $B(OH)_3$

Compare: acid-catalysed hydration of propene would give propan-2-ol

(Markovnikov product).

Hydroboration-oxidation gives the anti-Markovnikov alcohol in excellent yield.

Answer: Hydroboration-oxidation converts an alkene to an anti-Markovnikov alcohol: Step 1 — $B_2H_6$ adds (B to less-substituted C); Step 2 — $H_2O_2$/NaOH replaces C-B with C-OH. Example: $CH_3$-CH=$CH_2$ -> $CH_3CH_2CH_2OH$ (propan-1-ol).

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Q7 Give the structures and IUPAC names of monohydric phenols of molecular formula $C_7H_8O$.

SOLUTION

Molecular formula $C_7H_8O$. For a monohydric phenol: benzene ring ($C_6H^{5-}$) with one -OH directly on the ring, plus one extra $CH_2$ unit (since $C_6H_5OH$ = $C_6H_6O$, an extra $CH_2$ makes $C_7H_8O$ -> one methyl group on the ring).

This gives three isomers (ortho, meta, para methylphenols = cresols):

1. 2-Methylphenol (o-cresol): $CH_3$ at $C_2$, OH at $C_1$.
   Structure: 1-OH, 2-$CH_3$ substituted benzene.
2. 3-Methylphenol (m-cresol): $CH_3$ at $C_3$, OH at $C_1$.
   Structure: 1-OH, 3-$CH_3$ substituted benzene.
3. 4-Methylphenol (p-cresol): $CH_3$ at $C_4$, OH at $C_1$.
   Structure: 1-OH, 4-$CH_3$ substituted benzene.

Note: Benzyl alcohol ($C_6H_5$-$CH_2$-OH) also has formula $C_7H_8O$ but is an alcohol (OH not on ring), NOT a phenol.

Answer: Three isomers: (1) 2-methylphenol (o-cresol), (2) 3-methylphenol (m-cresol), (3) 4-methylphenol (p-cresol) — all are methyl-substituted phenols with OH directly on the benzene ring.

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Q8 While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

SOLUTION

Ortho-nitrophenol (2-nitrophenol) is steam volatile.

Reason:

In ortho-nitrophenol, the -OH group and the -$NO_2$ group are at adjacent positions (1 and 2). The -OH hydrogen forms an intramolecular hydrogen bond with the

oxygen of the adjacent -$NO_2$ group:

HO(1)...O=N(2) (intramolecular H-bond, forms a 6-membered ring-like structure)

This intramolecular hydrogen bonding prevents ortho-nitrophenol from forming intermolecular hydrogen bonds with water molecules. As a result, its association with water is weak, making it easily volatile with steam.

In para-nitrophenol, the -OH and -$NO_2$ groups are far apart (positions 1 and 4). Intramolecular H-bonding is not possible. Para-nitrophenol forms strong intermolecular hydrogen bonds with water molecules, causing strong association. This high degree of intermolecular association makes it less volatile and NOT steam-volatile.

Therefore, ortho-nitrophenol distils over with steam while para-nitrophenol remains behind.

Answer: Ortho-nitrophenol is steam volatile, because it forms intramolecular H-bonds (OH...$O_2N$, same molecule) and thus does not associate strongly with water. Para-nitrophenol forms intermolecular H-bonds with water, so it is non-volatile in steam distillation.

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Q9 Give the equations of reactions for the preparation of phenol from cumene.

SOLUTION

Cumene (isopropylbenzene, $C_6H_5$-$CH(CH_3)_2$) is the industrial source of phenol.

Step 1 — Oxidation of cumene with air:

$C_6H_5$-$CH(CH_3)_2$ + $O_2$ -> $C_6H_5$-$C(CH_3)_2$-OOH

(Cumene) (Cumene hydroperoxide)

Conditions: air oxidation (in presence of moisture, ~400 K)

Step 2 — Acid hydrolysis of cumene hydroperoxide:

$C_6H_5$-$C(CH_3)_2$-OOH + $H_2SO_4$(dil) -> $C_6H_5$-OH + $CH_3$-CO-$CH_3$

(Cumene hydroperoxide) (Phenol) (Acetone)

Overall: $C_6H_5$-$CH(CH_3)_2$ -> [$O_2$] -> $C_6H_5$-$C(CH_3)_2$-OOH -> [$H_2SO_4/H_2O$] -> $C_6H_5$-OH + $(CH_3)_2CO$

Acetone ($CH_3COCH_3$) is a valuable by-product of this reaction.

Answer: Step 1: $C_6H_5$-$CH(CH_3)_2$ + $O_2$ -> $C_6H_5$-$C(CH_3)_2$-OOH (cumene hydroperoxide). Step 2: $C_6H_5$-$C(CH_3)_2$-OOH + $H_2SO_4$(dil) -> $C_6H_5$-OH + $CH_3COCH_3$. Phenol and acetone are both obtained.

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Q10 Write chemical reaction for the preparation of phenol from chlorobenzene.

SOLUTION

Chlorobenzene is converted to phenol via the Dow process (fusion with NaOH at high temperature and pressure):

Step 1:

$C_6H_5$-Cl + 2NaOH -> $C_6H_5$-ONa + NaCl + $H_2O$

Conditions: 623 K, 320 atm pressure (Dow process)

Step 2 — Acidification of sodium phenoxide:

$C_6H_5$-ONa + HCl -> $C_6H_5$-OH + NaCl

Or combined:

$C_6H_5$-Cl + 2NaOH (623K, 320 atm) -> $C_6H_5$-ONa + NaCl + $H_2O$

$C_6H_5$-ONa + HCl -> $C_6H_5$-OH + NaCl

The nucleophilic attack occurs at the ipso carbon bearing Cl. The high temperature and pressure overcome the aryl C-Cl bond's resistance to nucleophilic substitution.

Answer: $C_6H_5$-Cl + 2NaOH (623K, 320 atm) -> $C_6H_5$-ONa + NaCl + $H_2O$; then $C_6H_5$-ONa + HCl -> $C_6H_5$-OH + NaCl.

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Q11 Write the mechanism of hydration of ethene to yield ethanol.

SOLUTION

Acid-catalysed hydration of ethene follows an electrophilic addition mechanism in three steps:

Step 1 — Protonation of ethene (electrophilic attack by $H_3O^+$):

$CH_2=CH_2$ + $H_3O^+$ -> $CH_3$-$CH_2$(+) + $H_2O$

(Ethyl carbocation, primary)

Step 2 — Nucleophilic attack of water on the carbocation:

$CH_3$-$CH_2$(+) + $H_2O$ -> $CH_3$-$CH_2$-$OH_2$(+)

(Protonated ethanol / oxonium ion)

Step 3 — Deprotonation (loss of proton to regenerate acid catalyst):

$CH_3\text{-}CH_2\text{-}OH_2(+) \rightarrow CH_3\text{-}CH_2\text{-}OH + H(+)$

$H(+) + H_2O \rightarrow H_3O^+$ (catalyst regenerated)

Overall: $CH_2{=}CH_2 + H_2O$ ($H^+/H_3PO_4$, ~300°C, 70 atm) $\rightarrow CH_3\text{-}CH_2\text{-}OH$

The catalyst ($H_3PO_4$ on diatomite or conc. $H_2SO_4$) provides the proton in step 1.

Answer: Step 1: $CH_2{=}CH_2 + H_3O^+ \rightarrow CH_3CH_2(+) + H_2O$ (protonation, carbocation). Step 2: $CH_3CH_2(+) + H_2O \rightarrow CH_3CH_2OH_2(+)$ (nucleophilic attack). Step 3: $CH_3CH_2OH_2(+) \rightarrow CH_3CH_2OH + H^+$ (deprotonation). Net: $CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$.

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Q12 You are given benzene, conc. $H_2SO_4$ and NaOH. Write the equations for the preparation of phenol using these reagents.

SOLUTION

This route proceeds via benzene sulphonic acid (sulphonation route):

Step 1 — Sulphonation of benzene:

$C_6H_6 + \text{conc. } H_2SO_4 \text{ (oleum)} \rightarrow C_6H_5\text{-}SO_3H + H_2O$

(Benzene) (Benzenesulphonic acid)

Step 2 — Fusion with NaOH (alkali fusion):

$C_6H_5\text{-}SO_3H + 2NaOH \text{ (fused)} \rightarrow C_6H_5\text{-}ONa + Na_2SO_3 + H_2O$

(Benzenesulphonic acid) (Sodium phenoxide)

Conditions: heating with molten NaOH (around 623 K)

Step 3 — Acidification:

$C_6H_5\text{-}ONa + HCl \rightarrow C_6H_5\text{-}OH + NaCl$

[Note: the acid can be $CO_2 + H_2O$ also, but here HCl is implied]

Or: neutralise with a dilute acid

Net: $C_6H_6 \rightarrow C_6H_5SO_3H \rightarrow C_6H_5ONa \rightarrow C_6H_5OH$

Answer: Step 1: $C_6H_6 + H_2SO_4$ (oleum) $\rightarrow C_6H_5SO_3H + H_2O$. Step 2: $C_6H_5SO_3H + 2NaOH$ (fused) $\rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$. Step 3: $C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$.

Q13 Show how will you synthesise:
(i) 1-phenylethanol from a suitable alkene.
(ii) Cyclohexylmethanol using an alkyl halide by an $SN_2$ reaction.
(iii) Pentan-1-ol using a suitable alkyl halide?

SOLUTION

(i) 1-Phenylethanol: $C_6H_5$-CH(OH)-$CH_3$ — secondary alcohol, OH at $C_1$ (benzylic position).
Suitable alkene: styrene ($C_6H_5$-CH=$CH_2$).
Reaction: $C_6H_5$-CH=$CH_2$ + $H_2O$ ($H^+/H_2SO_4$) -> $C_6H_5$-CH(OH)-$CH_3$
(Markovnikov addition: OH on the more substituted/benzylic C, giving 1-phenylethanol)

(ii) Cyclohexylmethanol: $C_6H_{11}$-$CH_2$-OH (primary alcohol).
$SN_2$ requires a primary alkyl halide for best results.
Use: (chloromethyl)cyclohexane [$C_6H_{11}$-$CH_2$-Cl]
Reaction: $C_6H_{11}$-$CH_2$-Cl + NaOH(aq) -> $C_6H_{11}$-$CH_2$-OH + NaCl ($SN_2$)
The primary $C_6H_{11}$-$CH_2$-Cl undergoes $SN_2$ with hydroxide at the unhindered $CH_2$.

(iii) Pentan-1-ol: $CH_3CH_2CH_2CH_2CH_2$-OH (primary alcohol).
Suitable alkyl halide: 1-bromopentane ($CH_3CH_2CH_2CH_2CH_2Br$).
Reaction: $CH_3(CH_2)_3CH_2Br$ + NaOH(aq) -> $CH_3(CH_2)_3CH_2OH$ + NaBr
($SN_2$ substitution at the primary carbon)

Answer: (i) Styrene ($C_6H_5CH=CH_2$) + $H_2O/H^+$ (Markovnikov) -> $C_6H_5CH(OH)CH_3$ (1-phenylethanol). (ii) $C_6H_{11}CH_2Cl$ + NaOH(aq) -> $C_6H_{11}CH_2OH$ + NaCl ($SN_2$). (iii) $CH_3(CH_2)_3CH_2Br$ + NaOH(aq) -> $CH_3(CH_2)_3CH_2OH$ + NaBr.

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Q14 Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

SOLUTION

Acidic nature of phenol is demonstrated by:

Reaction 1 — Reaction with sodium metal:
$2C_6H_5$-OH + 2Na -> $2C_6H_5$-ONa + $H_2$ (gas)
(Phenol reacts with active metals to release $H_2$, showing acidic O-H)

Reaction 2 — Reaction with aqueous NaOH:
$C_6H_5$-OH + NaOH -> $C_6H_5$-ONa + $H_2O$

(Phenol, unlike ethanol, is acidic enough to neutralise NaOH)

Comparison of acidity — Phenol vs Ethanol:

Phenol is much more acidic than ethanol:
- pKa of phenol = 10.0; pKa of ethanol = 15.9
- Phenol is ~$10^6$ (million) times more acidic than ethanol.

Reasons phenol is more acidic:
1. The phenoxide ion ($C_6H_5$-$O^-$) formed on ionisation has the negative charge delocalised over the benzene ring through resonance (5 resonance structures). This stabilises the phenoxide ion.
2. The ethoxide ion ($C_2H_5$-$O^-$) has the negative charge localised on oxygen only — no resonance stabilisation.
3. The $sp^2$-hybridised carbon of benzene (to which -OH is attached) is more electronegative than the $sp^3$-hybridised carbon in ethanol, increasing the polarity of O-H in phenol.

Note: Phenol does NOT dissolve in $NaHCO_3$ (pKa > 6.35 of $H_2CO_3$), whereas carboxylic acids do.

Answer: Two reactions showing acidity: (1) $2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$; (2) $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$. Phenol (pKa 10.0) is ~$10^6$ times more acidic than ethanol (pKa 15.9) due to resonance stabilisation of phenoxide ion and greater electronegativity of $sp^2$-C; ethoxide has no such stabilisation.

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Q15 Explain why is ortho nitrophenol more acidic than ortho methoxyphenol?

SOLUTION

Both compounds are phenols with a substituent at the ortho position. The acidity depends on the stability of the phenoxide ion formed.

Ortho-nitrophenol (2-nitrophenol):
- The -$NO_2$ group is a strong electron-withdrawing group (EWG) by both induction and resonance.
- It withdraws electron density from the ring and from the oxygen of -OH, increasing the polarity of the O-H bond and facilitating proton release.
- The -$NO_2$ group at ortho position also delocalises the negative charge of the phenoxide ion into the ring and onto the nitro group's oxygen atoms (by resonance), stabilising the phenoxide ion further.
- pKa of 2-nitrophenol = 7.2 (more acidic).

Ortho-methoxyphenol (2-methoxyphenol, guaiacol):
- The -$OCH_3$ group is an electron-donating group (EDG) by resonance (+M effect).
- It donates electron density into the ring and increases the electron density on oxygen of -OH, decreasing the polarity of O-H and reducing the tendency to release a proton.
- The -$OCH_3$ group also destabilises the phenoxide ion by adding negative charge on an already negative oxygen.
- pKa of 2-methoxyphenol ≈ 9.9 (less acidic).

Conclusion: The electron-withdrawing -$NO_2$ group stabilises the phenoxide ion (makes phenol more acidic), while the electron-donating -$OCH_3$ group destabilises it (makes phenol less acidic). Hence ortho-nitrophenol is more acidic than ortho-methoxyphenol.

Answer: The -$NO_2$ group (EWG) at ortho position withdraws electrons from the ring, increases O-H polarity, and stabilises the phenoxide ion by delocalising the negative charge — making 2-nitrophenol more acidic (pKa 7.2). The -$OCH_3$ group (EDG) at ortho position donates electrons, decreases O-H polarity, and destabilises the phenoxide ion — making 2-methoxyphenol less acidic (pKa ~9.9).

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Q16 Explain how does the -OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

SOLUTION

The -OH group is an electron-donating group (EDG) that activates the benzene ring towards electrophilic aromatic substitution (EAS) and directs incoming electrophiles to ortho and para positions.

Mechanism of activation:

The oxygen of -OH has lone pairs of electrons in unhybridised p-orbitals. These lone pairs overlap with the pi system of the benzene ring, resulting in resonance delocalisation:

Resonance structures of phenol show increased electron density at ortho ($C_2$, $C_6$) and para ($C_4$) positions relative to -OH:

$C_6H_5$-OH <-> various resonance forms where O(+) carries positive charge and ring carbons at o/p carry negative charge

Specifically, the resonance contributors show:
- Electron density pushed into the ring via the lone pair on O
- Negative charge (high electron density) built up at $C_2$ (ortho), $C_4$ (para), and $C_6$ (ortho)

Due to this increased electron density:
1. The ring is more reactive towards electrophiles (electrophiles are attracted to electron-rich sites).
2. Electrophilic attack is directed to ortho and para positions where electron density is highest.

Net effect: -OH activates the ring by +M (mesomeric/resonance) effect, making EAS faster than in benzene and regioselective for ortho/para substitution.

Answer: The -OH group donates electron density into the benzene ring via resonance (lone pair on O overlaps with ring pi system). This increases electron density at ortho and para positions, activating the ring towards electrophilic substitution and directing incoming electrophiles to ortho/para positions.

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Q17 Give equations of the following reactions:
(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.
(ii) Bromine in $CS_2$ with phenol.
(iii) Dilute $HNO_3$ with phenol.
(iv) Treating phenol with chloroform in presence of aqueous NaOH.

SOLUTION

(i) Oxidation of propan-1-ol with alkaline $KMnO_4$:

Alkaline $KMnO_4$ is a strong oxidising agent that oxidises primary alcohols directly to carboxylic acids.

$CH_3CH_2CH_2OH + [O]$ (alk. $KMnO_4$) -> $CH_3CH_2COOH + H_2O$
(Propan-1-ol) (Propanoic acid)

(ii) Bromine in $CS_2$ with phenol:

$CS_2$ is a low-polarity solvent; at low temperature, monobromination occurs at ortho and para positions.

$C_6H_5$-OH + $Br_2/CS_2$ (low temp.) -> 2-Br-$C_6H_4$-OH + 4-Br-$C_6H_4$-OH + HBr
(Phenol) (o-Bromophenol) (p-Bromophenol)

The -OH group activates the ring without need for a Lewis acid catalyst.

(iii) Dilute $HNO_3$ with phenol (at 298 K):

$C_6H_5$-OH + dilute $HNO_3$ (298 K) -> 2-$NO_2$-$C_6H_4$-OH + 4-$NO_2$-$C_6H_4$-OH + $H_2O$
(Phenol) (o-Nitrophenol) (p-Nitrophenol)
A mixture of ortho (major) and para nitrophenols is formed.

(iv) Phenol + $CHCl_3$ + NaOH (aq) — Reimer-Tiemann reaction:
$C_6H_5$-OH + $CHCl_3$ + NaOH(aq) -> 2-HO-$C_6H_4$-CHO + NaCl + $H_2O$
(Phenol) (2-Hydroxybenzaldehyde / Salicylaldehyde)
Mechanism: $CHCl_3$ + NaOH -> :$CCl_2$ (dichlorocarbene, electrophile) attacks the ring at ortho position; subsequent hydrolysis of the $CHCl_2$ substituent yields -CHO.

Answer: (i) $CH_3CH_2CH_2OH$ + [O](alk. $KMnO_4$) -> $CH_3CH_2COOH$ (propanoic acid). (ii) $C_6H_5OH$ + $Br_2/CS_2$ -> o-bromophenol + p-bromophenol + HBr. (iii) $C_6H_5OH$ + dil. $HNO_3$ (298K) -> 2-nitrophenol + 4-nitrophenol. (iv) $C_6H_5OH$ + $CHCl_3$ + NaOH -> 2-hydroxybenzaldehyde (salicylaldehyde) + NaCl + $H_2O$.

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Q18 Explain the following with an example.
(i) Kolbe's reaction.
(ii) Reimer-Tiemann reaction.
(iii) Williamson ether synthesis.
(iv) Unsymmetrical ether.

SOLUTION

(i) Kolbe's reaction:
Phenol is treated with NaOH to form sodium phenoxide ($C_6H_5$-ONa). Sodium phenoxide is more reactive than phenol towards electrophilic aromatic substitution. When treated with $CO_2$ under pressure, electrophilic substitution occurs at the ortho position to give sodium salicylate, which on acidification yields salicylic acid (2-hydroxybenzoic acid).
$C_6H_5$-ONa + $CO_2$ (300-400 K, 5-7 atm) -> 2-HO-$C_6H_4$-COONa
2-HO-$C_6H_4$-COONa + HCl -> 2-HO-$C_6H_4$-COOH (salicylic acid) + NaCl
Example: Industrial preparation of salicylic acid (used to make aspirin).

(ii) Reimer-Tiemann reaction:
Phenol is treated with chloroform ($CHCl_3$) in the presence of aqueous NaOH. A -CHO group is introduced at the ortho position of the benzene ring.
$C_6H_5$-OH + $CHCl_3$ + NaOH(aq) -> 2-HO-$C_6H_4$-CHO (salicylaldehyde) + 3NaCl + $H_2O$
Mechanism: $CHCl_3$ + $OH^-$ -> :$CCl_2$ (dichlorocarbene electrophile) -> attacks

ortho C of phenoxide -> hydrolysis of $CHCl_2$ -> CHO.

(iii) Williamson ether synthesis:

An alkyl halide (preferably primary) is reacted with a sodium alkoxide (or aryloxide) by $SN_2$ mechanism to form an ether.

R-X + R'-ONa -> R-O-R' + NaX

Example: $CH_3$-Br + $C_2H_5$-ONa -> $CH_3$-O-$C_2H_5$ + NaBr (methoxyethane / methyl ethyl ether)

Limitation: Secondary and tertiary alkyl halides give elimination products instead.

(iv) Unsymmetrical ether:

An ether in which the two alkyl (or aryl) groups attached to the oxygen are DIFFERENT.

Example: $CH_3$-O-$C_2H_5$ (methoxyethane / methyl ethyl ether) — one methyl group and one ethyl group on oxygen.

Compare to symmetrical ether: $C_2H_5$-O-$C_2H_5$ (ethoxyethane) where both groups are identical.

Answer: (i) Kolbe's reaction: $C_6H_5ONa$ + $CO_2$ (300-400K, pressure) -> sodium salicylate -> salicylic acid on acidification. (ii) Reimer-Tiemann: $C_6H_5OH$ + $CHCl_3$ + NaOH -> 2-hydroxybenzaldehyde (via dichlorocarbene intermediate). (iii) Williamson synthesis: R-X + R'ONa -> R-O-R' + NaX ($SN_2$). (iv) Unsymmetrical ether: two different alkyl/aryl groups on O, e.g., $CH_3OC_2H_5$.

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Q19 Write the mechanism of acid dehydration of ethanol to yield ethene.

SOLUTION

Acid-catalysed dehydration of ethanol at 443 K (170°C) with concentrated $H_2SO_4$ yields ethene via an $E_1$-like mechanism in three steps:

Step 1 — Protonation of ethanol (formation of protonated alcohol):

$CH_3CH_2$-OH + H(+) (from $H_2SO_4$) -> $CH_3CH_2$-$OH_2$(+)

(Ethanol) (Protonated ethanol / oxonium ion)

Step 2 — Ionisation to carbocation (slow/rate-determining step):

$CH_3CH_2$-$OH_2$(+) -> $CH_3CH_2$(+) + $H_2O$

(Ethyl carbocation — primary; loss of water is the slow step)

Step 3 — Loss of proton from beta-carbon to give ethene:

$CH_3CH_2$(+) -> $CH_2$=$CH_2$ + H(+)

(Proton removed from adjacent C gives ethene; acid catalyst is regenerated)

Overall: $CH_3CH_2OH$ (conc. $H_2SO_4$, 443 K) -> $CH_2=CH_2 + H_2O$

Ethene is removed as it is formed (low bp = -169°C), driving the equilibrium forward.

At lower temperature (413 K), diethyl ether is the major product instead.

Answer: Step 1: $CH_3CH_2OH + H^+$ -> $CH_3CH_2OH_2^+$ (protonation). Step 2: $CH_3CH_2OH_2^+$ -> $CH_3CH_2(+) + H_2O$ (slow, carbocation). Step 3: $CH_3CH_2(+)$ -> $CH_2=CH_2 + H^+$ (elimination). Net: $CH_3CH_2OH$ (conc.$H_2SO_4$, 443K) -> $CH_2=CH_2 + H_2O$.

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Q20 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

(i) Propene -> Propan-2-ol:

$CH_3$-CH=$CH_2 + H_2O$ ($H_2SO_4$ catalyst) -> $CH_3$-CH(OH)-$CH_3$

(Acid-catalysed hydration; Markovnikov's rule: OH attaches to more substituted $C_2$)

OR: $CH_3CH=CH_2 + H_2SO_4$ -> $CH_3CH(OSO_3H)CH_3$ -> $+H_2O$ / $-H_2SO_4$ -> $CH_3CH(OH)CH_3$

(ii) Benzyl chloride -> Benzyl alcohol:

$C_6H_5$-$CH_2$-Cl + NaOH(aq) -> $C_6H_5$-$CH_2$-OH + NaCl

($SN_2$ substitution; primary benzylic chloride reacts readily with NaOH)

(iii) Ethyl magnesium chloride (EtMgCl) -> Propan-1-ol:

$C_2H_5$-MgCl + HCHO (methanal) -> $C_2H_5$-$CH_2$-OMgCl

$C_2H_5$-$CH_2$-OMgCl + $H_3O(+)$ -> $C_2H_5$-$CH_2$-OH + Mg(OH)Cl

(Grignard addition to formaldehyde gives primary alcohol one C longer than Grignard)

Product: $CH_3CH_2CH_2OH$ (propan-1-ol)

(iv) Methyl magnesium bromide (MeMgBr) -> 2-Methylpropan-2-ol:

$CH_3$-MgBr + $(CH_3)_2C=O$ (propanone/acetone) -> $(CH_3)_3C$-OMgBr

$(CH_3)_3C$-OMgBr + $H_3O(+)$ -> $(CH_3)_3C$-OH + Mg(OH)Br

Product: 2-methylpropan-2-ol [$(CH_3)_3COH$] — tertiary alcohol
(Grignard adds $CH_3$ to the ketone C=O)

Answer: (i) $CH_3CH=CH_2 + H_2O/H^+ \rightarrow CH_3CH(OH)CH_3$ (Markovnikov hydration). (ii) $C_6H_5CH_2Cl + NaOH \rightarrow C_6H_5CH_2OH + NaCl$ ($SN_2$). (iii) $C_2H_5MgCl + HCHO \rightarrow C_2H_5CH_2OMgCl \rightarrow H_3O^+ \rightarrow CH_3CH_2CH_2OH$. (iv) $CH_3MgBr + (CH_3)_2C=O \rightarrow (CH_3)_3COMgBr \rightarrow H_3O^+ \rightarrow (CH_3)_3COH$ (2-methylpropan-2-ol).

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Q21 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

(i) Oxidation of primary alcohol to carboxylic acid:
Reagent: Acidified potassium permanganate ($KMnO_4/H_2SO_4$) or alkaline $KMnO_4$ OR acidified $K_2Cr_2O_7$ (chromic acid).

(ii) Oxidation of primary alcohol to aldehyde (selective, stopping at aldehyde stage):
Reagent: Pyridinium chlorochromate (PCC = $CrO_3 \cdot C_5H_5N \cdot HCl$, in $CH_2Cl_2$)
OR $CrO_3$ in anhydrous medium.
(PCC does not oxidise further to carboxylic acid)

(iii) Bromination of phenol to 2,4,6-tribromophenol:
Reagent: Bromine water ($Br_2/H_2O$)
(Reaction is immediate with $Br_2/H_2O$ giving white precipitate of 2,4,6-tribromophenol)

(iv) Benzyl alcohol to benzoic acid:
Reagent: Acidified $KMnO_4$ (or $K_2Cr_2O_7/H_2SO_4$) — strong oxidising agent.
$C_6H_5\text{-}CH_2\text{-}OH + [O] \rightarrow C_6H_5\text{-}COOH$

(v) Dehydration of propan-2-ol to propene:
Reagent: Concentrated $H_2SO_4$ (or $H_3PO_4$) at 443 K
OR $Al_2O_3$ (alumina) at 623 K.

(vi) Butan-2-one to butan-2-ol (reduction of ketone to secondary alcohol):

Reagent: $NaBH_4$ (sodium borohydride) in ethanol/water
OR $LiAlH_4$ in dry ether (followed by hydrolysis).
OR $H_2$/Ni or $H_2$/Pt (catalytic hydrogenation).

Answer: (i) Acidified $KMnO_4$ (or $K_2Cr_2O_7/H_2SO_4$). (ii) Pyridinium chlorochromate (PCC) or $CrO_3$/anhydrous. (iii) Bromine water ($Br_2/H_2O$). (iv) Acidified $KMnO_4$ (strong oxidising agent). (v) Conc. $H_2SO_4$ at 443 K (or $Al_2O_3$ at 623 K). (vi) $NaBH_4$ or $LiAlH_4$ (or $H_2$/Ni).

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Q22 Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

SOLUTION

Ethanol ($C_2H_5OH$, MW = 46) and methoxymethane ($CH_3OCH_3$, MW = 46) are isomers with the same molecular formula $C_2H_6O$ but very different boiling points:
- Ethanol: bp = 351 K (78°C)
- Methoxymethane: bp = 249 K (-24°C)

Reason for higher bp of ethanol:

Ethanol contains an -OH group. The O-H bond is strongly polar. Ethanol molecules form strong intermolecular hydrogen bonds (O-H...O) with each other:
$CH_3CH_2$-O-H...O-H-$CH_2CH_3$
These hydrogen bonds (bond energy ~20-40 kJ/mol) strongly associate the ethanol molecules, requiring more energy to separate them — hence higher boiling point.

Methoxymethane (dimethyl ether) has no O-H bond. It cannot form intermolecular hydrogen bonds. The only intermolecular forces are weak van der Waals forces and dipole-dipole interactions (from the C-O bond polarity). These are much weaker than H-bonds.

Ether molecules can accept H-bonds from external donors (through the lone pairs on O), but cannot donate H-bonds (no O-H). So no O-H...O H-bonding between ether molecules.

Result: Ethanol has a much higher boiling point than methoxymethane despite identical molecular formula.

Answer: Ethanol (bp 351 K) has a higher bp than methoxymethane (bp 249 K) because ethanol forms strong intermolecular hydrogen bonds (O-H...O) between molecules due to the -OH group. Methoxymethane has no O-H bond and cannot form such H-bonds; it has only weaker van der Waals forces.

Q23 Give IUPAC names of the following ethers (structures from figure):
(i) $C_2H_5$-O-$CH_2$-$CH(CH_3)_2$ (ii) $CH_3$-O-$CH_2$-$CH_2$-Cl (iii) $O_2N$-$C_6H_4$-O-$CH_3$ (para) (iv) $CH_3$-$CH_2$-$CH_2$-O-$CH_3$ (v) cyclohexane ring: gem-dimethyl at $C_1$, $OC_2H_5$ at $C_4$ (vi) benzene ring with -$OC_2H_5$

SOLUTION

IUPAC nomenclature for ethers: the larger alkyl (or ring) group = parent; the smaller alkoxy (-OR) group = substituent.

(i) $C_2H_5$-O-$CH_2$-$CH(CH_3)_2$ — the larger group is 2-methylpropane (isobutyl); ethoxy is the substituent at $C_1$.
IUPAC name: 1-ethoxy-2-methylpropane

(ii) $CH_3$-O-$CH_2$-$CH_2$-Cl — parent is the 2-carbon (ethane) chain bearing Cl; methoxy and Cl are substituents.
IUPAC name: 1-chloro-2-methoxyethane

(iii) $O_2N$-$C_6H_4$-O-$CH_3$ (para) — benzene ring with methoxy at $C_1$ and nitro at $C_4$.
IUPAC name: 1-methoxy-4-nitrobenzene (4-nitroanisole)

(iv) $CH_3$-$CH_2$-$CH_2$-O-$CH_3$ — larger group = propane; methoxy substituent at $C_1$.
IUPAC name: 1-methoxypropane

(v) Cyclohexane ring with two methyl groups on one carbon ($C_1$) and an ethoxy group on the opposite carbon ($C_4$).
Parent: cyclohexane. Substituents: ethoxy at $C_1$, two methyls at $C_4$.
IUPAC name: 1-ethoxy-4,4-dimethylcyclohexane

(vi) Benzene ring with an -$OC_2H_5$ (ethoxy) group.
IUPAC name: ethoxybenzene (phenetole)

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

Q24 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

Williamson's synthesis: R-X + R'-ONa -> R-O-R' + NaX. Use a primary alkyl halide for best yield ($SN_2$).

(i) 1-Propoxypropane (di-n-propyl ether): $CH_3CH_2CH_2$-O-$CH_2CH_2CH_3$
Reagents: Sodium propoxide + 1-bromopropane
Equation: $CH_3CH_2CH_2$-ONa + $CH_3CH_2CH_2$-Br -> $CH_3CH_2CH_2$-O-$CH_2CH_2CH_3$ + NaBr

(ii) Ethoxybenzene (phenetole): $C_6H_5$-O-$C_2H_5$
Reagents: Sodium phenoxide + bromoethane
Equation: $C_6H_5$-ONa + $C_2H_5$-Br -> $C_6H_5$-O-$C_2H_5$ + NaBr

(iii) 2-Methoxy-2-methylpropane (methyl tert-butyl ether, MTBE): $(CH_3)_3$C-O-$CH_3$
To avoid elimination, use sodium tert-butoxide + methyl halide ($CH_3$ is primary):
Reagents: Sodium tert-butoxide + bromomethane
Equation: $(CH_3)_3$C-ONa + $CH_3$-Br -> $(CH_3)_3$C-O-$CH_3$ + NaBr
(Note: Using tert-butyl halide + $CH_3ONa$ would give elimination instead of ether)

(iv) 1-Methoxyethane (methyl ethyl ether): $CH_3$-O-$C_2H_5$
Reagents: Sodium methoxide + bromoethane OR Sodium ethoxide + bromomethane
Equation: $CH_3$-ONa + $C_2H_5$-Br -> $CH_3$-O-$C_2H_5$ + NaBr
OR: $C_2H_5$-ONa + $CH_3$-Br -> $CH_3$-O-$C_2H_5$ + NaBr

Answer: (i) $CH_3CH_2CH_2ONa + CH_3CH_2CH_2Br \rightarrow CH_3CH_2CH_2OCH_2CH_2CH_3 + NaBr$. (ii) $C_6H_5ONa + C_2H_5Br \rightarrow C_6H_5OC_2H_5 + NaBr$. (iii) $(CH_3)_3CONa + CH_3Br \rightarrow (CH_3)_3COCH_3 + NaBr$. (iv) $CH_3ONa + C_2H_5Br \rightarrow CH_3OC_2H_5 + NaBr$.

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Q25 Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

SOLUTION

Williamson synthesis involves $SN_2$ attack of an alkoxide ion on an alkyl halide. It works best with primary alkyl halides. It has the following limitations:

Limitation 1 — Secondary and tertiary alkyl halides undergo elimination:

Alkoxide ions are strong nucleophiles AND strong bases. When they react with secondary or tertiary alkyl halides, the base character dominates and elimination ($E_2$) occurs preferentially over substitution.

Example: $CH_3ONa$ + $(CH_3)_2CH\text{-}Br$ -> $CH_3O^-$ acts as base -> $CH_2{=}CH\text{-}CH_3$ (propene) + $CH_3OH$

(Propene by elimination, NOT methyl isopropyl ether)

Limitation 2 — Tertiary alkyl halides give ONLY alkene:

Example: $CH_3ONa$ + $(CH_3)_3C\text{-}Br$ -> $(CH_3)_2C{=}CH_2$ (2-methylpropene) + $CH_3OH$ + NaBr

No ether is formed. The bulky tertiary carbocation/transition state makes $SN_2$ impossible; $E_2$ is exclusive.

Limitation 3 — Cannot prepare diaryl ethers (Ar-O-Ar):

Aryl halides are unreactive towards $SN_2$ because the C-X bond has partial double bond character ($sp^2$ carbon, resonance with ring). Sodium aroxide cannot displace X from aryl halide.

Example: $C_6H_5\text{-}Cl$ + $C_6H_5\text{-}ONa$ -> does NOT give $C_6H_5\text{-}O\text{-}C_6H_5$ (diphenyl ether)

Limitation 4 — Aryl halides with aryl alkoxides:

Similarly, preparation of aryl alkyl ether by reacting aryl halide with alkoxide fails.

To prepare aryl alkyl ether: use Ar-ONa (aryloxide) + R-X (primary alkyl halide) — this works.

Summary: Williamson synthesis is restricted to primary alkyl halides on one side; secondary/tertiary alkyl halides and aryl halides cannot be used as the halide component.

Answer: Limitations: (1) Secondary/tertiary alkyl halides give elimination (alkene), not ether, because alkoxide is a strong base — e.g., $CH_3ONa$ + $(CH_3)_2CHBr$ -> propene ($E_2$), not ether. (2) Tertiary alkyl halides give only alkene. (3) Aryl halides cannot be used ($SN_2$ on $sp^2$-Ar-C is impossible); diaryl ethers cannot be made by this method.

Q26 How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

SOLUTION

1-Propoxypropane (di-n-propyl ether, $CH_3CH_2CH_2$-O-$CH_2CH_2CH_3$) is synthesised by intermolecular dehydration of propan-1-ol with conc. $H_2SO_4$ at 413 K (bimolecular $SN_2$ mechanism):

Reaction: 2 $CH_3CH_2CH_2$-OH (conc. $H_2SO_4$, 413 K) -> $CH_3CH_2CH_2$-O-$CH_2CH_2CH_3$ + $H_2O$

Mechanism:

Step 1 — Protonation of propan-1-ol by $H^+$ (from $H_2SO_4$):
$CH_3CH_2CH_2$-OH + H(+) -> $CH_3CH_2CH_2$-$OH_2$(+)
(Protonated propan-1-ol / oxonium ion — the -$OH_2$(+) is an excellent leaving group)

Step 2 — $SN_2$ attack by a second propan-1-ol molecule on the protonated alcohol:
$CH_3CH_2CH_2$-OH + $CH_3CH_2CH_2$-$OH_2$(+) -> $CH_3CH_2CH_2$-O(+)(H)-$CH_2CH_2CH_3$ + $H_2O$
(The unprotonated -OH acts as nucleophile; attacks the electrophilic C of oxonium ion from the back; water leaves — $SN_2$)

Step 3 — Deprotonation to give the ether:
$CH_3CH_2CH_2$-O(+)(H)-$CH_2CH_2CH_3$ -> $CH_3CH_2CH_2$-O-$CH_2CH_2CH_3$ + H(+)
($H^+$ is regenerated; acid catalyst is not consumed)

This method is suitable only for primary alcohols. Secondary/tertiary alcohols would form alkenes preferentially at higher temperatures.

Answer: 2 $CH_3CH_2CH_2OH$ (conc.$H_2SO_4$, 413K) -> $CH_3CH_2CH_2OCH_2CH_2CH_3$ + $H_2O$. Mechanism: Step 1: $CH_3CH_2CH_2OH$ + $H^+$ -> $CH_3CH_2CH_2OH_2^+$. Step 2 ($SN_2$): $CH_3CH_2CH_2OH$ + $CH_3CH_2CH_2OH_2^+$ -> $CH_3CH_2CH_2O$+H($CH_2CH_2CH_3$) + $H_2O$. Step 3: $CH_3CH_2CH_2O$+$HCH_2CH_2CH_3$ -> $CH_3CH_2CH_2OCH_2CH_2CH_3$ + $H^+$.

Q27 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

SOLUTION

Acid dehydration of secondary and tertiary alcohols strongly favours the formation of alkenes (elimination) rather than ethers (substitution).

Reasons:

1. Carbocation stability: Secondary and tertiary alcohols form more stable secondary and tertiary carbocations after protonation and loss of water. These stable carbocations preferentially undergo $E_1$ elimination (loss of proton from adjacent C gives alkene) rather than $SN_1$ substitution (attack by another alcohol to give ether).

2. Temperature and substitution: Secondary/tertiary alcohols dehydrate at lower temperatures. At these conditions, alkene formation is kinetically and thermodynamically favoured over ether formation. Ether formation would require $SN_2$ (not feasible for 2° or 3° substrates due to steric hindrance) or $SN_1$ (but $SN_1$ with the bulky intermediate favours the alkene side-product).

3. Steric effects: The bulky groups around the secondary/tertiary carbon hinder the nucleophilic attack of another alcohol molecule (bimolecular dehydration), making $SN_2$ pathway extremely slow.

Example:

$(CH_3)_3C\text{-}OH$ + conc. $H_2SO_4$ -> $(CH_3)_2C{=}CH_2$ (2-methylpropene) [major product]

NOT $(CH_3)_3C\text{-}O\text{-}C(CH_3)_3$ (di-tert-butyl ether) [very minor/negligible]

Therefore, only primary alcohols are suitable for ether synthesis by acid dehydration.

Answer: Secondary/tertiary alcohols form stable carbocations on protonation and water-loss. These carbocations preferentially undergo $E_1$ elimination to give alkenes rather than ether formation, because: (1) steric hindrance prevents $SN_2$ attack of another alcohol; (2) the carbocation preferentially loses a beta-H to give the more stable alkene. Only primary alcohols are suitable for bimolecular acid dehydration to give ethers.

Q28 Write the equation of the reaction of hydrogen iodide with:
(i) 1-propoxypropane (ii) methoxybenzene (iii) benzyl ethyl ether.

SOLUTION

(i) 1-Propoxypropane (di-n-propyl ether) + HI (excess, heat):

Both groups are primary. $SN_2$ attack by $I^-$ on the protonated ether gives propan-1-ol and 1-iodopropane initially.

With excess HI, the propan-1-ol also reacts with HI.

$CH_3CH_2CH_2\text{-}O\text{-}CH_2CH_2CH_3 + 2HI \rightarrow 2\ CH_3CH_2CH_2I + H_2O$

(Di-n-propyl ether -> 2 molecules of 1-iodopropane + water, with excess HI)

(ii) Methoxybenzene (anisole, $C_6H_5\text{-}O\text{-}CH_3$) + HI:

In aryl alkyl ethers, the Ar-O bond is stronger than the Alkyl-O bond (due to resonance / $sp^2$ C of aryl).

Cleavage occurs at the $O\text{-}CH_3$ bond ($SN_2$ by $I^-$ on the methyl):

$C_6H_5\text{-}O\text{-}CH_3 + HI \rightarrow C_6H_5\text{-}OH + CH_3I$

(Phenol + iodomethane — phenol does NOT react further with HI since $sp^2$ Ar-C cannot undergo $SN_2$)

(iii) Benzyl ethyl ether ($C_6H_5\text{-}CH_2\text{-}O\text{-}C_2H_5$) + HI:

The benzylic C-O bond ($C_6H_5\text{-}CH_2\text{-}O$) is more reactive (benzylic carbocation is stabilised).

Cleavage occurs preferentially at the benzylic C-O bond:

$C_6H_5\text{-}CH_2\text{-}O\text{-}C_2H_5 + HI \rightarrow C_6H_5\text{-}CH_2I + C_2H_5OH$

(Benzyl iodide + ethanol)

Answer: (i) $CH_3CH_2CH_2OCH_2CH_2CH_3 + 2HI \rightarrow 2CH_3CH_2CH_2I + H_2O$. (ii) $C_6H_5OCH_3 + HI \rightarrow C_6H_5OH + CH_3I$ (cleavage at alkyl-O bond). (iii) $C_6H_5CH_2OC_2H_5 + HI \rightarrow C_6H_5CH_2I + C_2H_5OH$ (cleavage at benzylic C-O).

Q29 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 benzene ring.

SOLUTION

(i) Activation of the benzene ring by alkoxy group (-OR):

The oxygen of the -OR group has lone pairs of electrons. These lone pairs can overlap with the pi electrons of the benzene ring through resonance:

-O-R <-> -(+O)-R (with negative charge on ring carbons)

This resonance donation of electron density increases the electron density on the benzene ring, making it more reactive (electron-rich) towards electrophilic attack.

Electrophiles are electron-seeking species; they attack more easily at electron-rich aromatic rings.

Hence, anisole (methoxybenzene) is MORE reactive than benzene towards EAS (e.g., bromination occurs without $FeBr_3$ catalyst).

(ii) Ortho/para direction by -OR group:

The resonance structures of aryl alkyl ether (e.g., anisole) show that the electron density donated by -OR is concentrated at ortho ($C_2$, $C_6$) and para ($C_4$) positions relative to the -OR group:

Resonance contributors place negative charge (-) at $C_1$ (ipso), $C_2$ (ortho), $C_4$ (para), and $C_6$ (ortho).

[The carbon at position 3 and 5 do NOT gain extra electron density from the -OR resonance]

Since electrophiles attack the position of highest electron density, attack occurs at ortho and para positions.

The meta positions ($C_3$, $C_5$) are not enriched by the -OR resonance, so meta substitution is disfavoured.

Result: Incoming electrophile is directed to ortho and para positions.

Answer: (i) The -OR group donates electron density into the ring via resonance (lone pairs on O overlap with ring pi system), making the ring electron-rich and more reactive to electrophiles. (ii) Resonance structures show negative charge built up at ortho and para positions, so electrophiles are directed to attack these positions (ortho/para director).

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Q30 Write the mechanism of the reaction of HI with methoxymethane.

SOLUTION

Methoxymethane (dimethyl ether, $CH_3$-O-$CH_3$) reacts with excess HI to give iodomethane ($CH_3I$) and ultimately methanol and iodomethane.

Reaction: $CH_3$-O-$CH_3$ + 2HI -> 2 $CH_3I$ + $H_2O$

Mechanism:

Step 1 — Protonation of ether oxygen (formation of oxonium ion):

$CH_3$-O-$CH_3$ + H(+) -> $CH_3$-O(+)(H)-$CH_3$

(Dimethyl oxonium ion — lone pair on O accepts $H^+$)

Step 2 — $SN_2$ attack by iodide on the less hindered (methyl) carbon:

I^(-) + $CH_3$-O(+)(H)-$CH_3$ -> $CH_3I$ + $CH_3OH$

(Back-side $SN_2$ attack; $I^-$ attacks one $CH_3$, pushing out $CH_3OH$ as leaving group)

Products: iodomethane ($CH_3I$) + methanol ($CH_3OH$)

Step 3 — If HI is in excess:

$CH_3$-OH + HI -> $CH_3I$ + $H_2O$

(Methanol reacts with HI in a further $SN_2$ step)

Overall (excess HI): $CH_3$-O-$CH_3$ + 2HI -> 2$CH_3I$ + $H_2O$

The reactivity order of HX is: HI > HBr > HCl, because $I^-$ is the strongest nucleophile and HI is the strongest acid among these.

Answer: Step 1: $CH_3OCH_3$ + $H^+$ -> $CH_3O^+(H)CH_3$ (protonation). Step 2 ($SN_2$): $I^-$ + $CH_3O^+(H)CH_3$ -> $CH_3I$ + $CH_3OH$. Step 3 (with excess HI): $CH_3OH$ + HI -> $CH_3I$ + $H_2O$. Overall: $CH_3OCH_3$ + 2HI -> 2$CH_3I$ + $H_2O$.

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Q31 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-Crafts acetylation of anisole.

SOLUTION

(i) Friedel-Crafts alkylation of anisole:

Anisole reacts with an alkyl halide in the presence of anhydrous $AlCl_3$ (Lewis acid catalyst).

Example with $CH_3Cl$ (methyl chloride):

$C_6H_5$-$OCH_3$ + $CH_3Cl$ (anhydrous $AlCl_3$) -> 2-$CH_3$-$C_6H_4$-$OCH_3$ + 4-$CH_3$-$C_6H_4$-$OCH_3$ + HCl

(2-Methyl-1-methoxybenzene + 4-methyl-1-methoxybenzene — ortho and para products)

(ii) Nitration of anisole:

$C_6H_5$-$OCH_3$ + conc. $HNO_3$/conc. $H_2SO_4$ (mixed acid) ->

2-$NO_2$-$C_6H_4$-$OCH_3$ (2-nitroanisole, ~31%) + 4-$NO_2$-$C_6H_4$-$OCH_3$ (4-nitroanisole, ~67%)

(ortho-nitroanisole + para-nitroanisole; -$OCH_3$ directs to ortho/para)

(iii) Bromination of anisole in ethanoic acid (acetic acid) medium:

In acetic acid (polar protic, low polarity medium), $Br_2$ does not need a Lewis acid catalyst because the -$OCH_3$ group sufficiently activates the ring.

$C_6H_5$-$OCH_3$ + $Br_2$ (ethanoic acid) -> 4-Br-$C_6H_4$-$OCH_3$ (para-bromoanisole, ~90%) + 2-Br-$C_6H_4$-$OCH_3$ (ortho) + HBr

Para isomer is the major product (less steric hindrance at para position).

(iv) Friedel-Crafts acetylation of anisole:

$C_6H_5$-$OCH_3$ + $CH_3COCl$ (anhydrous $AlCl_3$) -> 2-$CH_3CO$-$C_6H_4$-$OCH_3$ + 4-$CH_3CO$-$C_6H_4$-$OCH_3$ + HCl

(2-Methoxyacetophenone + 4-methoxyacetophenone — ortho and para products)

Para product (4-methoxyacetophenone) is major.

Answer: (i) $C_6H_5OCH_3$ + $CH_3Cl$ ($AlCl_3$) -> o-methylanisole + p-methylanisole + HCl. (ii) $C_6H_5OCH_3$ + $HNO_3/H_2SO_4$ -> o-nitroanisole + p-nitroanisole (major). (iii) $C_6H_5OCH_3$ + $Br_2$ (AcOH) -> p-bromoanisole (90%, major) + o-bromoanisole + HBr. (iv) $C_6H_5OCH_3$ + $CH_3COCl$ ($AlCl_3$) -> o-methoxyacetophenone + p-methoxyacetophenone + HCl.

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Q32 Show how would you synthesise the following alcohols from appropriate alkenes? (Structures from figure: (i) 1-methylcyclohexan-1-ol; (ii) 4-methylheptan-4-ol; (iii) pentan-2-ol; (iv) 2-cyclohexylbutan-2-ol)

SOLUTION

Acid-catalysed hydration adds $H_2O$ across a C=C bond following Markovnikov's rule (OH to the more substituted carbon). Choose the alkene whose double bond is at the carbon that must bear the OH.

(i) 1-Methylcyclohexan-1-ol (tertiary alcohol — OH and $CH_3$ on the same ring carbon):

Alkene: 1-methylcyclohexene (methyl and ring double bond at $C_1$-$C_2$).

Reaction: 1-methylcyclohexene + $H_2O$ (dil. $H_2SO_4$, Markovnikov) -> 1-methylcyclohexan-1-ol.

OH adds to $C_1$ (the more substituted, tertiary carbon).

(ii) 4-Methylheptan-4-ol [$CH_3CH_2CH_2$-$C(OH)(CH_3)$-$CH_2CH_2CH_3$] — tertiary alcohol with OH and $CH_3$ on $C_4$:

Alkene: 4-methylhept-3-ene (or 4-methylhept-4-ene) with the double bond at $C_4$.

Reaction: 4-methylhept-3-ene + $H_2O$ (dil. $H_2SO_4$, Markovnikov) -> 4-methylheptan-4-ol.

OH adds to $C_4$ (the more substituted, tertiary carbon).

(iii) Pentan-2-ol [$CH_3$-CH(OH)-$CH_2$-$CH_2$-$CH_3$] — secondary alcohol:

Alkene: pent-1-ene ($CH_2$=CH-$CH_2CH_2CH_3$).

Reaction: pent-1-ene + $H_2O$ (dil. $H_2SO_4$, Markovnikov) -> $CH_3$-CH(OH)-$CH_2CH_2CH_3$.

OH adds to $C_2$ (the more substituted carbon).

(iv) 2-Cyclohexylbutan-2-ol [$C_6H_{11}$-C(OH)($CH_3$)-$CH_2$-$CH_3$] — tertiary alcohol (cyclohexyl, $CH_3$ and OH on $C_2$ of a butane chain):

Alkene: 2-cyclohexylbut-2-ene (or 2-cyclohexylbut-1-ene) with the double bond at $C_2$.

Reaction: 2-cyclohexylbut-2-ene + $H_2O$ (dil. $H_2SO_4$, Markovnikov) -> 2-cyclohexylbutan-2-ol.

OH adds to $C_2$ (the more substituted, tertiary carbon).

Answer: (i) 1-methylcyclohexene + $H_2O/H^+$ (Markovnikov) -> 1-methylcyclohexan-1-ol. (ii) 4-methylhept-3-ene + $H_2O/H^+$ -> 4-methylheptan-4-ol. (iii) pent-1-ene + $H_2O/H^+$ -> pentan-2-ol. (iv) 2-cyclohexylbut-2-ene + $H_2O/H^+$ -> 2-cyclohexylbutan-2-ol.

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Q33 When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place: Give a mechanism for this reaction. (Hint: The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.)

SOLUTION

Starting material: 3-methylbutan-2-ol — $CH_3$-CH(OH)-CH($CH_3$)-$CH_3$

($C_1$=$CH_3$, $C_2$=CH-OH, $C_3$=CH($CH_3$), $C_4$=$CH_3$)

Product: 2-bromo-2-methylbutane — $CH_3$-$CH_2$-C(Br)($CH_3$)-$CH_3$

Mechanism (carbocation rearrangement via hydride shift):

Step 1 — Protonation of -OH by HBr:

$CH_3$-CH(OH)-CH($CH_3$)-$CH_3$ + H(+) -> $CH_3$-CH($OH_2$(+))-CH($CH_3$)-$CH_3$

(-OH becomes good leaving group -$OH_2^+$)

Step 2 — Loss of water to form a secondary carbocation at $C_2$

(slow/rate-determining step):

$CH_3$-CH($OH_2$(+))-CH($CH_3$)-$CH_3$ -> $CH_3$-CH(+)-CH($CH_3$)-$CH_3$ + $H_2O$

(2° carbocation at $C_2$)

Step 3 — 1,2-Hydride shift from $C_3$ to $C_2$ (carbocation rearrangement):

$CH_3$-CH(+)-CH($CH_3$)-$CH_3$ -> $CH_3$-$CH_2$-C(+)($CH_3$)-$CH_3$

A hydride ($H^-$ with bonding electrons) migrates from $C_3$ to the adjacent $C_2$ carbocation.

This converts the less stable 2° carbocation at $C_2$ into a more stable 3° carbocation at $C_3$.

Step 4 — Attack of $Br^-$ on the tertiary carbocation at $C_3$:

$CH_3$-$CH_2$-C(+)($CH_3$)-$CH_3$ + Br^(-) -> $CH_3$-$CH_2$-C(Br)($CH_3$)-$CH_3$

(2-Bromo-2-methylbutane — tertiary bromide, final product)

Note: The product has Br at $C_3$ of the original numbering ($C_2$ of the product = 2-methylbutane backbone). The rearrangement is driven by the greater stability of the tertiary carbocation.

Answer: Mechanism: Step 1: $CH_3CH(OH)CH(CH_3)CH_3$ + $H^+$ -> $CH_3CH(OH_2^+)CH(CH_3)CH_3$ (protonation). Step 2: Loss of $H_2O$ -> $CH_3CH(+)CH(CH_3)CH_3$ (2° carbocation at $C_2$). Step 3: 1,2-Hydride shift $C_3$->$C_2$ -> $CH_3CH_2C(+)(CH_3)CH_3$ (3° carbocation at $C_3$ — more stable). Step 4: $Br^-$ attacks $C_3$ -> $CH_3CH_2CBr(CH_3)CH_3$ (2-bromo-2-methylbutane).