Alcohols, Phenols & Ethers

Replacement of H atom of a hydrocarbon by the -OH group ~~forms~~ gives an alcohol or phenol. Replacement by -OR / -OAr gives an ether.

R-OH (alc)	Ar-OH (phen)	R-O-R' (ether)

<- 3 <- classes

Classification of Alcohols

(a) By no. of -OH groups :

mono- (1) / di- (2) / tri- (3) / poly-

(b) By C hybridisation bearing -OH :

sp^3 C-OH -> alkyl alcohol (regular)

sp^2 C-OH -> vinylic / phenolic

(c) By C type (sp3 only) :

1° ($-CH_2OH$) / 2° ($>CH-OH$) / 3° ($>C-OH$)

Allylic : -OH on sp3 C next to C=C double bond.

Benzylic : -OH on sp3 C next to benzene ring.

Vinylic : -OH directly on sp2 C of C=C.

Ex. $CH_2=CH-CH_2-OH$ (allyl) ; $Ph-CH_2-OH$ (benzyl)

Phenols : mono-, di- or trihydric (catechol, etc.)

Nomenclature

Alcohols (IUPAC)

Replace 'e' of parent alkane by suffix 'ol'.

Number chain from end nearest to -OH.

Polyhydric : keep ~~the~~ 'e' ; add di / tri.

CH_3OH = methanol C_2H_5OH = ethanol <- common <- names

$HOCH_2-CH_2OH$ -> ethane-1,2-diol (glycol)

Propane-1,2,3-triol -> glycerol.

$(CH_3)_3C-OH$ -> 2-methylpropan-2-ol (t-BuOH)

Phenols

C_6H_5-OH itself is named phenol (also IUPAC).

o-, m-, p- prefixes used for di-substituted.

o-Cresol = 2-methylphenol ; catechol = benzene-1,2-diol ; quinol = benzene-1,4-diol.

Ethers

Common : name the two alkyl groups alphabetically + 'ether'. Same groups -> prefix 'di'.

IUPAC : smaller -OR named as alkoxy substituent ; larger R is the parent hydrocarbon.

Ex. $CH_3OC_2H_5$ = ethylmethyl ether = methoxyethane

$C_6H_5OCH_3$ = anisole = methoxybenzene.

Structure of Functional Group

Alcohol : C-O-H ; C is sp^3, O is sp^3.
C-O-H bond angle = 108.9 deg (< 109.5 deg).
Reason : lone-pair / lone-pair repulsion on O compresses the angle.

Phenol : -OH on sp^2 C of aromatic ring.
C-O bond length = 136 pm (less than methanol)
due to partial double-bond character (resonance).

Ether : R-O-R' bond angle = 111.7° (> 109.5°)
due to steric repulsion between bulky R groups.
C-O length = 141 pm same as in alcohols.

Preparation of Alcohols : From Alkenes

(i) Acid-catalysed hydration (Markovnikov)

$$CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$$

<- dil. H_2SO_4

Mech : (1) H^+ adds -> carbocation
(2) H_2O attacks ; (3) deprotonation

(ii) Hydroboration-Oxidation (anti-Markovnikov)

$RCH{=}CH_2 + (BH_3)_2 \rightarrow RCH_2CH_2BH_2$

then $H_2O_2/OH^- \rightarrow RCH_2CH_2OH$ (1°)

Prep of Alcohols (contd.)

From Aldehydes & Ketones

(i) Catalytic hydrogenation (H_2 / Ni, Pt, Pd)

$R\text{-}CHO + H_2 \rightarrow R\text{-}CH_2\text{-}OH$ (1°)

$R_2C{=}O + H_2 \rightarrow R_2CH\text{-}OH$ (2°)

(ii) By $NaBH_4$ or $LiAlH_4$ (chemo-reduction)

Same product ; $LiAlH_4$ is stronger but expensive ; $NaBH_4$ safe & selective.

From Carboxylic Acids & Esters

$RCOOH \rightarrow RCH_2OH$ [(i) $LiAlH_4$ (ii) H_2O]

Esters reduced commercially by H_2 / catalyst.

From Grignard Reagents

$R\text{-}MgX + R'CHO \rightarrow$ adduct $\rightarrow H_2O \rightarrow$ ~~acid~~ alcohol

$HCHO + RMgX \rightarrow RCH_2OH$ 1deg
<- methanal

$R'CHO + RMgX \rightarrow R'RCH\text{-}OH$ - 2deg
<- aldehyde

$R'R''C{=}O + RMgX \rightarrow R'R''RC\text{-}OH$ - 3deg
<- ketone

Grignard is a versatile C-C bond forming tool ; moisture must be excluded (decomposes RMgX).

Preparation of Phenols

1. From Haloarenes (Dow process)

$PhCl + NaOH \rightarrow PhONa \rightarrow PhOH$ <- 623 K, <- 320 atm

Acidification of sodium phenoxide gives phenol.

2. From Benzene sulphonic acid

$C_6H_6 + H_2SO_4$ (oleum) $\rightarrow C_6H_5SO_3H$

Then $NaOH$ (fused) $\rightarrow PhONa \rightarrow H^+ \rightarrow PhOH$

3. From Diazonium salt

$Ph\text{-}NH_2 + NaNO_2 / HCl$ (273-278 K)

$\rightarrow Ph\text{-}N_2^+Cl^- \rightarrow H_2O$ / warm $\rightarrow PhOH$

(N_2 + HCl evolved)

4. From Cumene (industrial !)

Cumene = isopropylbenzene.

Step 1 : $Ph\text{-}CH(CH_3)_2 + O_2$ (air) $\rightarrow$ cumene hydroperoxide.

Step 2 : + dil. $H^+ \rightarrow PhOH + (CH_3)_2C=O$

Phenol + Acetone (by-product !) <- world <- supply

Most PhOH produced worldwide via this method.

Physical Properties

Boiling Points

B.P. of alcohols & phenols >> hydrocarbons, ethers, haloalkanes of comparable M.W.

Reason : intermolecular ~~vdw~~ H-bonding via -OH.

alkane < ether < alcohol	<- for .<- same M.W.

e.g. C_2H_6 (184) < MeOMe (248) < EtOH (351 K)

Within alcohols : B.P. rises with C count (more vdW). Branching lowers B.P. (less surface).

Order : 1° > 2° > 3° for same C count.

Solubility in Water

Lower alcohols (C1-C3) miscible with water - form H-bonds with H_2O molecules.

Solubility drops as alkyl chain (hydrophobic) grows. Phenol partly soluble (8.3 g / 100 mL).

Ethers

C-O bonds polar, but NO -OH => no H-bond between ether molecules.

B.P. (ether) B.P. (alkane) of similar mass ; << B.P. of alcohol.

Ethers H-bond with water -> miscibility alcohol.

Reactions : O-H Cleavage

1. Acidity (reaction with metals)

$2\ ROH + 2\ Na \rightarrow 2\ RONa + H_2\ (g)$

$2\ PhOH + 2\ Na \rightarrow 2\ PhONa + H_2$

$PhOH + NaOH \rightarrow PhONa + H_2O$ (phenol only !)

Acid strength :

$PhOH > H2O > 1^{\circ} > 2^{\circ} > 3^{\circ}$ <- pKa <- ROH

pK_a : PhOH = 10.0 ; EtOH = 15.9 ; H_2O = 15.7

Why is PhOH million times more acidic ?

(i) -OH on sp2 C => -I effect => O-H polarised

(ii) Phenoxide ion is RESONANCE stabilised :

-ve charge delocalised on o-, p- C of ring.

Alkoxide ion : charge localised on O.

Substituents on phenol :

EW group ($-NO_2$, $-CN$, $-X$) at o-/p- : more acidic

ER group ($-CH_3$, $-OR$) at o-/p- : ~~more~~ less acidic

2. Esterification

$R\text{-}OH + R'COOH \rightarrow R'COO\text{-}R + H_2O$ <- conc. <- H_2SO_4

With acid chloride : use pyridine (neutralise HCl).

Reactions : C-O Cleavage

C-O cleavage => alcohols only (phenol shows this only with Zn dust).

1. With HX (Lucas Test)

$R\text{-}OH + HX \rightarrow R\text{-}X + H_2O$

Reactivity : $3^\circ > 2^\circ > 1^\circ$; $HI > HBr > HCl$

Lucas : conc.HCl + anhyd. $ZnCl_2$ <- test : <- 1/2/3

3° ROH : turbidity at once ; 2° : 5-10 min

1° : no turbidity at room temp (needs heat).

2. Dehydration (-H2O)

$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O$

(conc. H_2SO_4, 443 K ; E1 mechanism)

Ease : $3^\circ > 2^\circ > 1^\circ$ (stability of carbocation).

Mech : $ROH + H^+ \rightarrow R\text{-}OH_2^+ \rightarrow R^+ \rightarrow$ alkene

3. Oxidation

1° ROH $\rightarrow$[PCC] R-CHO (stop here)

1° ROH $\rightarrow$[$KMnO_4$] RCOOH (full !)

2° ROH $\rightarrow$[CrO_3] $R_2C{=}O$ (ketone)

3° ROH : no oxidation under mild conditions.

Strong $KMnO_4$ + heat => C-C bond cleavage.

Reactions of Phenols

-OH is a STRONG o-, p- director and ring activator (+M effect dominates -I).

1. Electrophilic Subst. (EAS)

(a) Nitration

dil. HNO_3 / 298 K : o- + p- nitrophenol

conc. HNO_3 : 2,4,6-tri-NO_2 phenol (picric acid)

(b) Halogenation

Br_2 / CS_2 (low T) : mono- bromo (o-, p-)

Br_2 / H_2O : 2,4,6-tribromophenol (white ppt)

(c) Sulphonation

conc. H_2SO_4 : o- (low T) / p- (high T)

2. Kolbe's Reaction

$PhONa + CO_2 \rightarrow o\text{-}OH\text{-}C_6H_4\text{-}COOH$ <- salicylic <- acid

Phenoxide > phenol => reacts with weak electrophile CO2. (Aspirin made from this ?)

3. Reimer-Tiemann Reaction

$PhOH + CHCl_3/NaOH \rightarrow$ salicylaldehyde <- adds <- -CHO o-

4. Phenol + Zn dust -> benzene (loss of -OH).

5. Oxidation (chromic acid) -> benzoquinone.

Ethers & Important Alcohols

Preparation of Ethers

(i) Dehydration of alcohols

$2\ C_2H_5OH \rightarrow C_2H_5\text{-}O\text{-}C_2H_5 + H_2O$

(conc. H_2SO_4 , 413 K ; SN2 on protonated ROH)

Works for 1° R only ; 2/3° give alkene !

(ii) Williamson Synthesis

$R\text{-}X + R'O^-Na^+ \rightarrow R\text{-}O\text{-}R' + NaX$ SN2 : <- 1deg RX

3° R-X => E2 elimination (only alkene).

Phenoxide + R-X => alkyl aryl ether (anisole).

Cleavage of Ethers (HI / HBr, hot)

$R\text{-}O\text{-}R' + HI \rightarrow R\text{-}I + R'\text{-}OH$ (SN2, smaller R)

$Ph\text{-}O\text{-}R + HI \rightarrow Ph\text{-}OH + R\text{-}I$ (aryl C-O stays)

$(CH_3)_3C\text{-}OR + HI \rightarrow 3°\ R\text{-}I + R'\text{-}OH$ (SN1)

Reactivity : HI > HBr >> HCl.

Commercially Important Alcohols

* Methanol (CH_3OH) : 'wood spirit' ; by $CO + 2H_2$ / $ZnO\text{-}Cr_2O_3$. POISON (blindness).
* Ethanol (C_2H_5OH) : by fermentation of sugar -> zymase / yeast (anaerobic).
  Denatured by $CuSO_4$ + pyridine ; b.p. 351 K.