

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 $\rightarrow$ alkyl alcohol (regular)

sp^2 C-OH $\rightarrow$ vinylic / phenolic

(c) By C type (sp^3 only) :

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

Allylic : $-OH$ on sp^3 C next to $C=C$ double bond.

Benzylic : $-OH$ on sp^3 C next to benzene ring.

Vinylic : $-OH$ directly on sp^2 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.

$\text{CH}_3\text{OH} = \text{methanol}$

$\text{C}_2\text{H}_5\text{OH} = \text{ethanol}$

<- common
<- names

$\text{HOCH}_2\text{-CH}_2\text{OH} \rightarrow \text{ethane-1,2-diol (glycol)}$

Propane-1,2,3-triol $\rightarrow$ glycerol.

$(\text{CH}_3)_3\text{C-OH} \rightarrow 2\text{-methylpropan-2-ol (t-BuOH)}$

Phenols

$\text{C}_6\text{H}_5\text{-OH}$ 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 $\rightarrow$ prefix 'di'.

IUPAC : smaller -OR named as alkoxy substituent ;

larger R is the parent hydrocarbon.

Ex. $\text{CH}_3\text{OC}_2\text{H}_5 = \text{ethylmethyl ether} = \text{methoxyethane}$

$\text{C}_6\text{H}_5\text{OCH}_3 = \text{anisole} = \text{methoxybenzene}.$

Structure of Functional Group

Alcohol : $C-O-H$; C is sp^3 , O is sp^3 .

$C-O-H$ bond angle = 108.9° ($< 109.5^\circ$).

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° ($> 109.5^\circ$)

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)

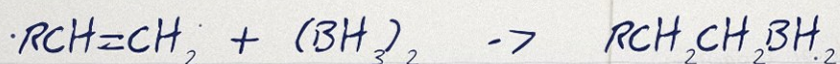


$\leftarrow$ dil.
 $\leftarrow H_2SO_4$

Mech : (1) H^+ adds $\rightarrow$ carbocation

(2) H_2O attacks ; (3) deprotonation

(ii) Hydroboration-Oxidation (anti-Markovnikov)



Prep of Alcohols (contd.)

From Aldehydes & Ketones

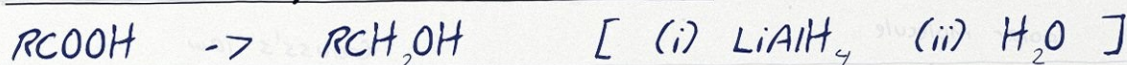
(i) Catalytic hydrogenation (H_2 / Ni, Pt, Pd)



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

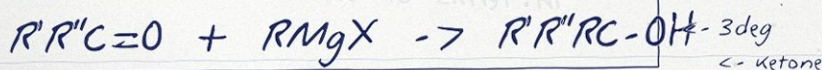
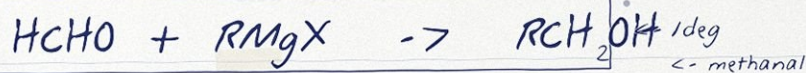
Same product ; $LiAlH_4$ is stronger but expensive ; $NaBH_4$ safe & selective.

From Carboxylic Acids & Esters



Esters reduced commercially by H_2 / catalyst.

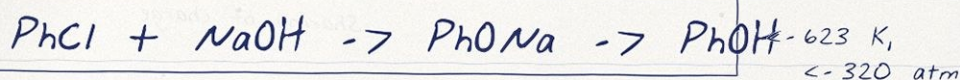
From Grignard Reagents



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

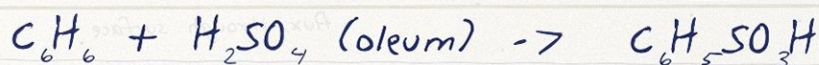
Preparation of Phenols

1. From Haloarenes (Dow process)



Acidification of sodium phenoxide gives phenol.

2. From Benzene sulphonic acid



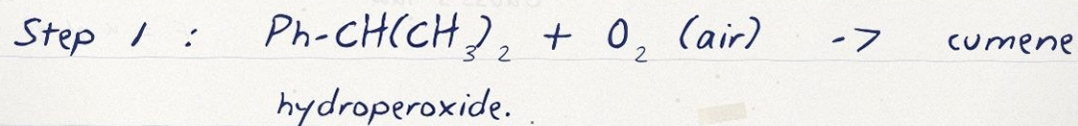
3. From Diazonium salt



($\text{N}_2 + \text{HCl}$ evolved)

4. From Cumene (Industrial ?)

Cumene = isopropylbenzene.



Phenol + Acetone (by-product ?)

<- world
<- supply

Most PhOH produced worldwide via this method.

Physical Properties

Boiling Points

B.P. of alcohols & phenols $\gg$ 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 : $1^\circ > 2^\circ > 3^\circ$ 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 $\Rightarrow$ no H-bond between ether molecules.

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

$\ll$ B.P. of alcohol.

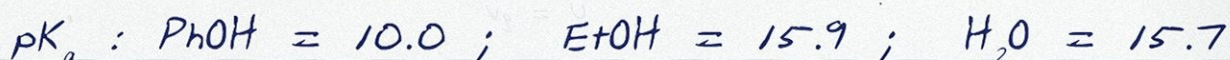
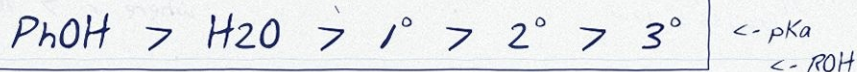
Ethers H-bond with water $\rightarrow$ miscibility alcohol.

Reactions : O-H Cleavage

1. Acidity (reaction with metals)



Acid strength :



Why is PhOH million times more acidic ?

(i) -OH on $\text{sp}^2 \text{C} \Rightarrow -\text{I}$ effect $\Rightarrow$ 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 ($-\text{NO}_2$, $-\text{CN}$, $-\text{X}$) at o-/p- : more acidic

ER group ($-\text{CH}_3$, $-\text{OR}$) at o-/p- : ~~more~~ less acidic

2. Esterification

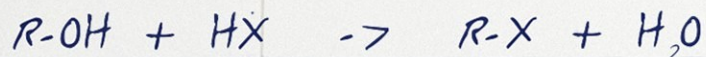


With acid chloride : use pyridine (neutralise HCl).

Reactions : C-O Cleavage

C-O cleavage $\Rightarrow$ alcohols only (phenol shows this only with Zn dust).

1. With HX (Lucas Test)



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

Lucas : conc. HCl + anhyd. $ZnCl_2$

$\leftarrow$ test :
 $\leftarrow$ 1/2/3

3° ROH : turbidity at once ; 2° : 5-10 min
 1° : no turbidity at room temp (needs heat).

2. Dehydration (-H₂O)



(conc. H_2SO_4 , 443 K ; E1 mechanism)

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

Mech : $ROH + H^+ \rightarrow R-OH_2^+ \rightarrow R^+ \rightarrow$ 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 $\Rightarrow$ 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

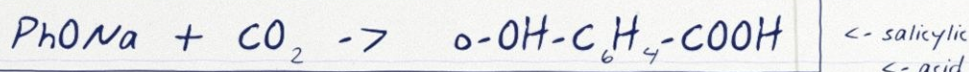
Br_2 / CS_2 (low T) : mono- bromo (o-, p-)

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

(c) Sulphonation

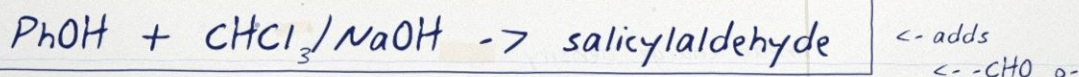
conc. H_2SO_4 : o- (low T) / p- (high T)

2. Kolbe's Reaction



Phenoxide > phenol $\Rightarrow$ reacts with weak electrophile CO_2 . (Aspirin made from this !)

3. Reimer-Tiemann Reaction



4. Phenol + Zn dust $\rightarrow$ benzene (loss of -OH).

5. Oxidation (chromic acid) $\rightarrow$ benzoquinone.

Ethers & Important Alcohols

Preparation of Ethers

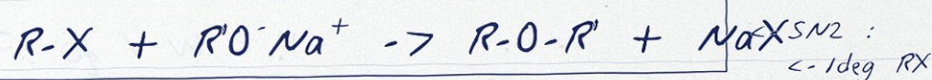
(i) Dehydration of alcohols



(conc. H_2SO_4 , 413 K ; $\text{S}_\text{N}2$ on protonated ROH)

Works for 1° R only ; 2/3 $^\circ$ give alkene !

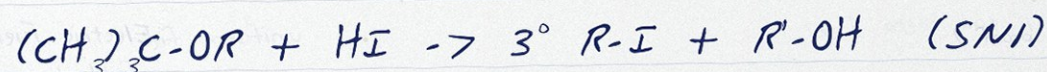
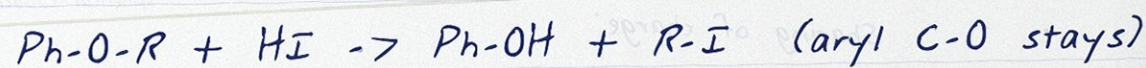
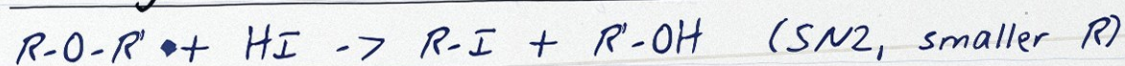
(ii) Williamson Synthesis



$3^\circ \text{ R-X} \Rightarrow \text{E2 elimination (only alkene).}$

Phenoxide + $\text{R-X} \Rightarrow \text{alkyl aryl ether (anisole).}$

Cleavage of Ethers (HI / HBr , hot)



Reactivity : $\text{HI} > \text{HBr} \gg \text{HCl}.$

Commercially Important Alcohols

* Methanol (CH_3OH) : 'wood spirit' ; by $\text{CO} + 2\text{H}_2 / \text{ZnO-Cr}_2\text{O}_3$. POISON (blindness).

* Ethanol ($\text{C}_2\text{H}_5\text{OH}$) : by fermentation of sugar $\rightarrow$ zymase / yeast (anaerobic).

Denatured by CuSO_4 + pyridine ; b.p. 351 K.