SLE155 Chemistry for the Professional Sciences

Burwood and Geelong

Class 8

Alcohols

Reactions of Alcohols

Phenols

Ethers

References

Blackman A, Bottle S, Schmid G, Mocerino M and Wille U (2019a), *Chemistry*, 4th edn, John Wiley & Sons, Milton, Qld.

Blackman A, Southam D, Lawrie G, Williamson N, Thompson C and Bridgeman A (2019b), *Chemistry: core concepts*, 2nd edn, John Wiley & Sons, Milton, Qld.

Alcohols

Alcohols contain the functional group –OH, called hydroxyl or hydroxy group

- **This hydroxyl group is bonded to an *sp^3* hybridised carbon atom**
- **The oxygen atom is also *sp^3* hybridised**
  - **Two *sp^3* hybrid orbitals overlap to form σ bonds to carbon and hydrogen**
  - **The remaining two *sp^3* hybrid orbitals each contain an unshared pair of electrons**

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Alcohols

- **Contain the hydroxy functional group, -OH.**
- **Alcohols can be classified as primary, secondary or tertiary depending on the type of C atom that the OH group is bonded to.**

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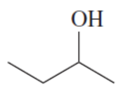
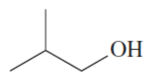
Naming Alcohols

Alcohols are named the same way as alkanes, with some differences

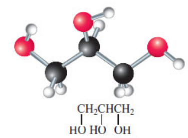
- **The parent alkane is the longest chain of carbon atoms containing the –OH group**
- **Change the suffix of the parent alkane from –e to –ol, and use a number to show the location of the –OH group**
- **Name and number any substituents and list them in alphabetical order**



butan-2-ol
(*sec*-butyl alcohol)



2-methylpropan-1-ol
(isobutyl alcohol)

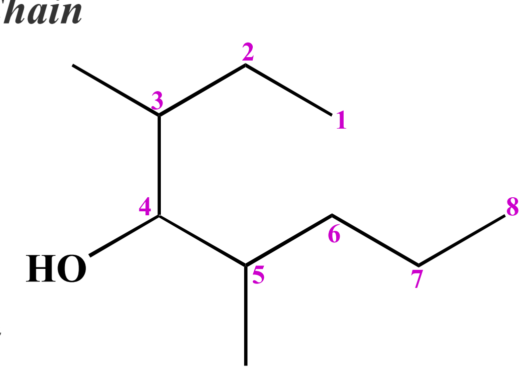


propane-1,2,3-triol
(glycerol, glycerin)

Source: Blackman et al. (2019b:910).

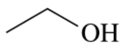
Naming Alcohols

1. *Name the Parent Chain*
   octane
2. *Add the Suffix*
   octanol
3. *Add the Prefix*
   dimethyloctanol
4. *Include the Locant*
   3,5-dimethyloctan-4-ol
   3,5-dimethyl-4-octanol

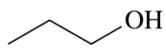


Naming Alcohols

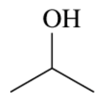
To derive common names for alcohols, we name the alkyl group bonded to the –OH group and add the word alcohol



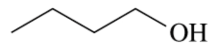
ethanol
(ethyl alcohol)



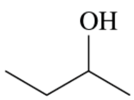
propan-1-ol
(propyl alcohol)



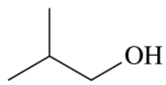
propan-2-ol
(isopropyl alcohol)



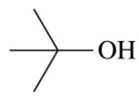
butan-1-ol
(butyl alcohol)



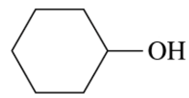
butan-2-ol
(*sec*-butyl alcohol)



2-methylpropan-1-ol
(isobutyl alcohol)



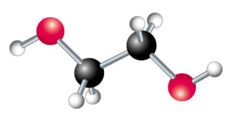
2-methylpropan-2-ol
(*tert*-butyl alcohol)



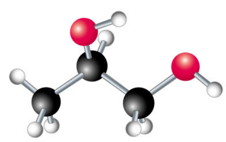
cyclohexanol
(cyclohexyl alcohol)

Naming Alcohols

Compounds with 2 –OH groups are named as diols



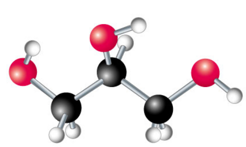
CH_2CH_2
OH OH
ethane-1,2-diol
(ethylene glycol)



CH_3CHCH_2
HO OH
propane-1,2-diol
(propylene glycol)

Source: Blackman et al. (2019b:910).

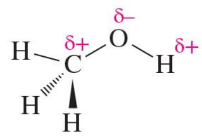
Compounds with 3 –OH groups are named as triols



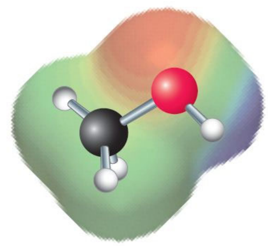
CH_2CHCH_2
HO HO OH
propane-1,2,3-triol
(glycerol, glycerin)

Physical Properties of Alcohols

Both the C-O and O-H bonds of an alcohol are polar covalent, so alcohols are polar molecules. This is demonstrated for methanol below.



Source: Blackman et al. (2019b:913).



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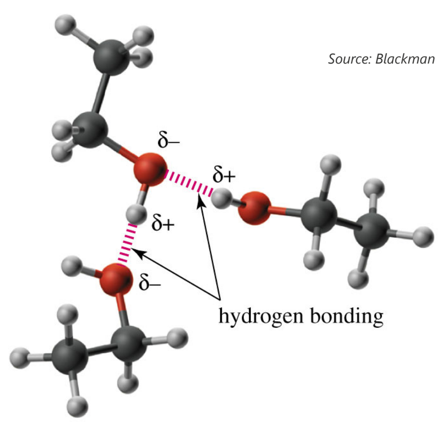
Physical Properties of Alcohols

Alcohols associate in the liquid state by hydrogen bonding

Source: Blackman et al. (2019b:914).



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Physical Properties of Alcohols

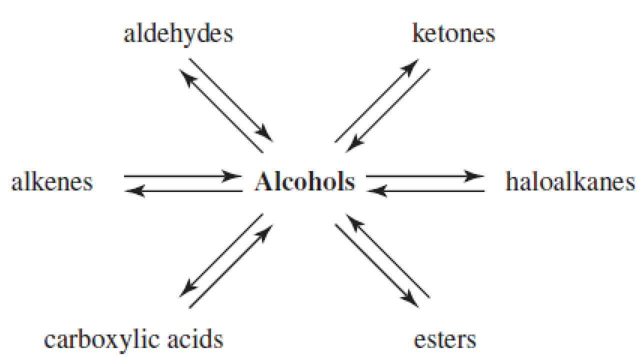
Alcohols have higher boiling points and water solubility than do hydrocarbons of similar molar mass.

Structural formula	Name	Molar mass	Total electrons	Boiling point (°C)	Solubility in water
CH_3OH	methanol	32	18	65	infinite
CH_3CH_3	ethane	30	18	−89	insoluble
CH_3CH_2OH	ethanol	46	26	78	infinite
$CH_3CH_2CH_3$	propane	44	26	−42	insoluble
$CH_3CH_2CH_2OH$	propan-1-ol	60	34	97	infinite
$CH_3CH_2CH_2CH_3$	butane	58	34	0	insoluble
$CH_3CH_2CH_2CH_2OH$	butan-1-ol	74	42	117	8 g/100 g
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	42	36	insoluble
$CH_3CH_2CH_2CH_2CH_2OH$	pentan-1-ol	88	50	138	2.3 g/100 g
$HOCH_2CH_2CH_2CH_2OH$	butane-1,4-diol	90	50	230	infinite
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane	86	50	69	insoluble

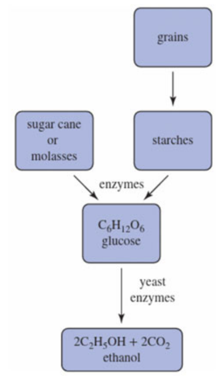
Source: Blackman et al. (2019b:913).

Alcohols

Preparation and reactions of alcohols are closely related.



Fermentation of sugars



Source: Blackman et al. (2019a:1134)

Preparation of Alcohols

From alkenes

Acid catalysed hydration of alkenes

$$H_2C{=}CH_2 + H_2O \xrightarrow[\text{catalyst}]{\text{acid}} CH_3CH_2OH$$

From haloalkanes **Nucleophilic substitution with a hydroxide ion**

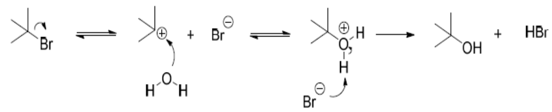
$$\underset{\substack{\text{2-bromo-2-methylpropane}\\(\textit{tert}\text{-butyl bromide})}}{(CH_3)_3C{-}Br} + H_2O \rightleftharpoons \underset{\substack{\text{2-methylpropan-2-ol}\\(\textit{tert}\text{-butyl alcohol})}}{(CH_3)_3C{-}OH} + HBr$$

The reaction is known as an S_N1 reaction:

1.The Br separates from the molecule, taking the bonding electrons to form a Br^- ion, and leaving a tertiary carbocation. (In this example, Br^- is a leaving group – *an atom or group of atoms that is displaced, taking the bonding electrons*. This can happen because the tertiary carbocation left behind is very stable.)

2.The nucleophilic H_2O attacks the carbocation, creating an oxonium ion (oxygen with bonds and a positive charge).

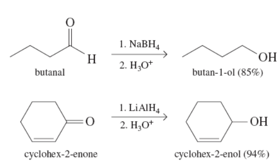
3.The bromide ion attacks the positively charged oxonium ion, causing the removal of a proton. The products of the reaction are a tertiary alcohol and HBr.



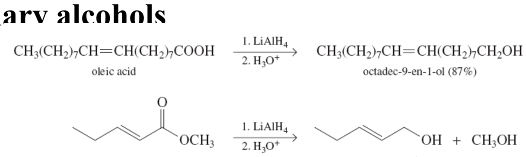
Preparation of Alcohols

Reduction of carbonyl compounds **Aldehydes are reduced to primary alcohols**

Ketones are reduced to secondary alcohols

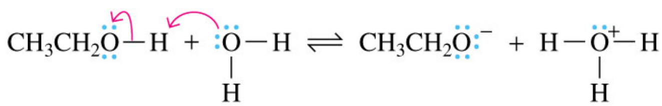


Carboxylic acids and esters can be reduced to form primary alcohols



Reactions of Alcohols

Acidity of alcohols



$$K_a = \frac{[CH_3CH_2O^-][H_3O^+]}{[CH_3CH_2OH]} = 1.3 \times 10^{-16}$$

$$pK_a = 15.9$$

Reactions of Alcohols

Acidity of alcohols

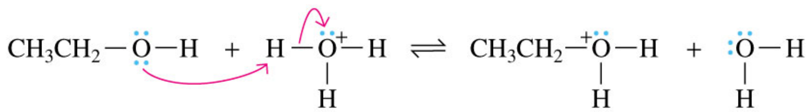
Compound	Structural formula	pK_a	
hydrogen chloride	HCl	–7	stronger acid
acetic acid	CH_3COOH	4.74	↑
methanol	CH_3OH	15.5	
water	H_2O	15.7	
ethanol	CH_3CH_2OH	15.9	
propan-2-ol	$(CH_3)_2CHOH$	17	
2-methylpropan-2-ol	$(CH_3)_3COH$	18	weaker acid

(a) Also given for comparison are pK_a values for water, acetic acid and hydrogen chloride.

Source: Blackman et al. (2019b:918).

Reactions of Alcohols

Basicity of alcohols



ethanol · hydronium ion ($pK_a = -1.7$) · ethyloxonium ion ($pK_a = -2.4$)

Reactions of Alcohols

Reaction with active metals Important!

Alcohols react with Li, Na, K and other active metals to form metal alkoxides.

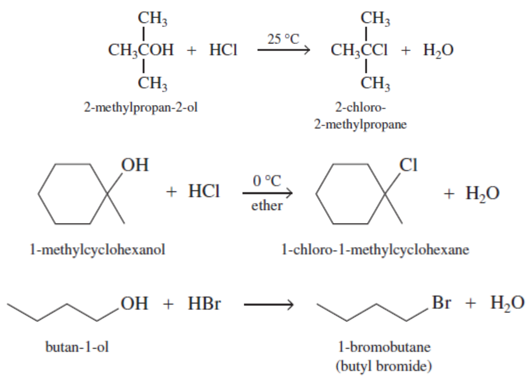
Alkoxide ions are good nucleophiles.

$$2CH_3OH + 2Na \longrightarrow \underset{\text{sodium methoxide}}{2CH_3O^- Na^+} + H_2$$

Source: Blackman et al. (2019b:918).

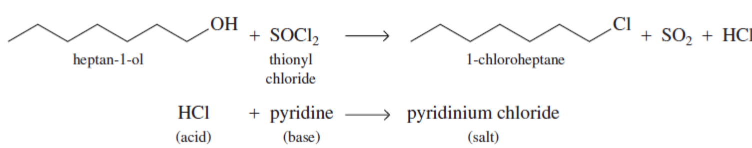
Reactions of Alcohols

Conversion to haloalkanes by reaction with hydrohalic acids (HX, where X is usually Cl or Br)



Reactions of Alcohols

Reaction with thionyl chloride



Reaction with phosphorus halides

Reactions of Alcohols

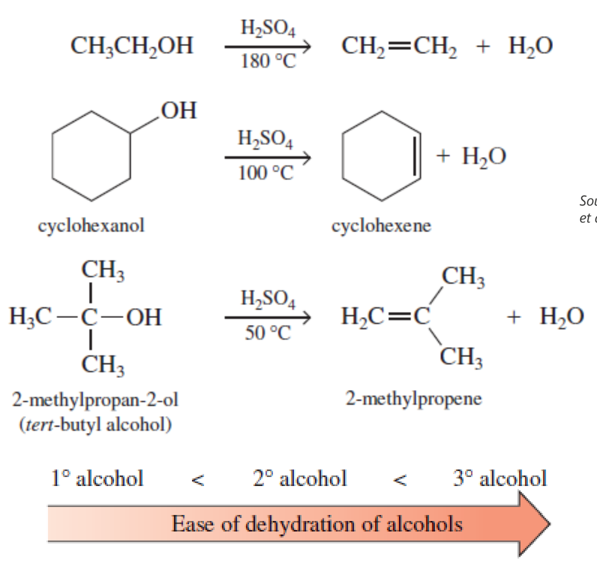
Dehydration of an alcohol occurs when the alcohol is heated with an acid catalyst.

An —H and an —OH are lost from *adjacent* carbon atoms.

Thus dehydration of an alcohol produces an alkene.

Dehydration an alcohol is the opposite of electrophilic addition of water to an alkene.

Reactions of Alcohols



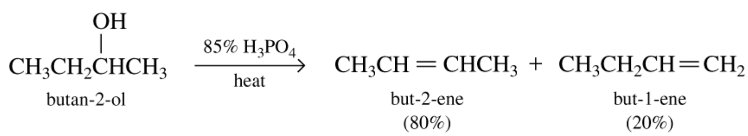
Source: Blackman et al. (2019b:910).

Reactions of Alcohols

When isomeric alkenes are obtained, the more stable alkene is generally the major product

The more stable alkene has the greater number of substituents on the double bond

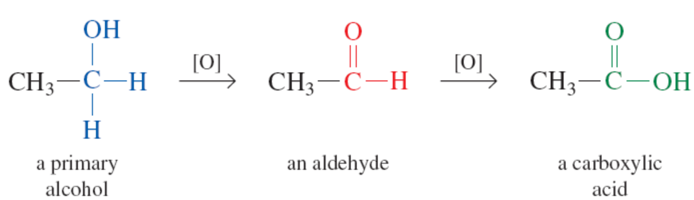
The acid-catalysed dehydration of alcohols follows Zaitsev's rule (check β-elimination in chapter 18)



Reactions of Alcohols

Oxidation of 1° and 2° alcohols

Oxidation of a 1° alcohol gives an aldehyde or carboxylic acid, depending on the experimental conditions.



Source: Blackman et al. (2019b:924).

2° alcohols are oxidised to ketones.

3° alcohols are not easily oxidised.

Reactions of Alcohols

Ester formation

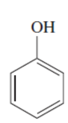
Condensation of alcohols with carboxylic acids, acid chlorides or anhydrides produces esters.

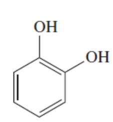
$$\underset{\substack{\text{butanoic acid}\\(\text{bp} = 163\ °\text{C})}}{CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH} + \underset{\substack{\text{ethanol}\\(\text{bp} = 78\ °\text{C})}}{HOCH_2CH_3} \underset{\text{heat}}{\overset{\text{acid catalyst}}{\rightleftharpoons}} \underset{\substack{\text{ethyl butanoate}\\(\text{bp} = 120\ °\text{C})\\(\text{fragrance of pineapple})}}{CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_3} + H_2O$$

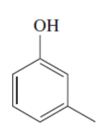
Phenols

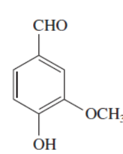
Phenols contain a hydroxyl group bonded directly to a carbon atom of an aromatic ring.

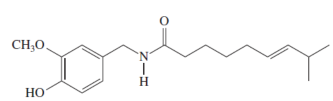
They are solids, with low melting points and are slightly soluble in water.

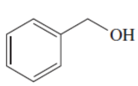

phenol


benzene-1,2-diol (catechol)


3-methylphenol (*m*-cresol)


4-hydroxy-3-methoxy-benzaldehyde (vanillin)


capsaicin

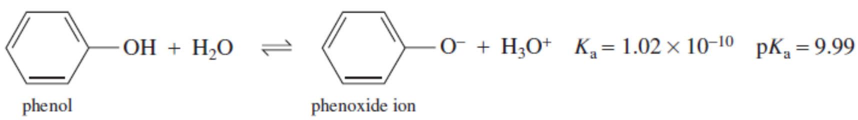

benzyl alcohol

Note that benzyl alcohol is not a phenol!

Phenols

Acidity of phenols

Phenols are much more acidic than alcohols.



$$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+ \quad K_a = 1.3 \times 10^{-16} \quad pK_a = 15.9$$

ethanol — ethoxide ion

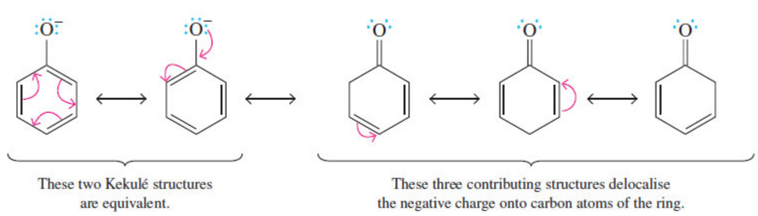
Source: Blackman et al. (2019a:1149).

Phenols

Acidity of phenols

Phenols are much more acidic than alcohols because the phenoxide anion is resonance stabilised.

Source: Blackman et al. (2019a:1149).



Phenols

Acidity of phenols

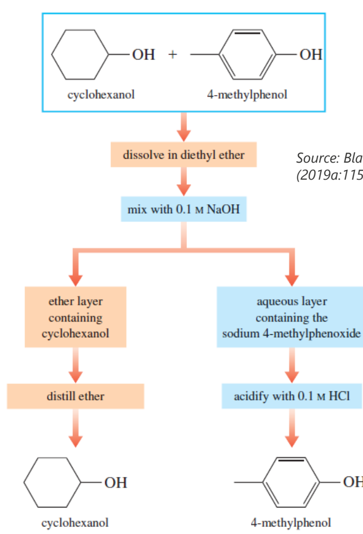
Substituents that withdraw electrons from the aromatic ring increase the acidity.

Name	pK_a
2,4,6-trinitrophenol	0.42
acetic acid	4.76
4-nitrophenol	7.15
4-chlorophenol	9.41
phenol	9.99
4-methoxyphenol	10.21
4-methylphenol	10.26

stronger acid ↑ weaker acid

Phenols as Acids

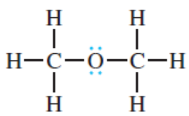
Difference in acidity is used to separate phenols from water-insoluble alcohols



Source: Blackman et al. (2019a:1152).

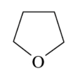
Ethers

Ethers contain an atom of oxygen bonded to 2 carbon atoms.
Oxygen is *sp*^{3} hybridised with bond angles of approximately 109.5°.
The organic groups are usually alkyl or aryl and the oxygen atom may be part of an open chain or a ring.

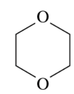


Source: Blackman et al. (2019a:1154).

ethylene oxide



tetrahydrofuran (THF)



1,4-dioxane

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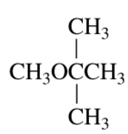
Ethers

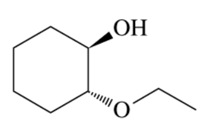
The –OR group bonded to the parent alkane is named as an alkoxy group
Common names are derived by listing the alkyl groups bonded to oxygen in alphabetical order and adding the word ether

$CH_3CH_2OCH_2CH_3$

ethoxyethane
(diethyl ether)



2-methoxy-2-methylpropane
(methyl *tert*-butyl ether, MTBE)



trans-2-ethoxycyclohexanol

Source: Blackman et al. (2019a:1154).

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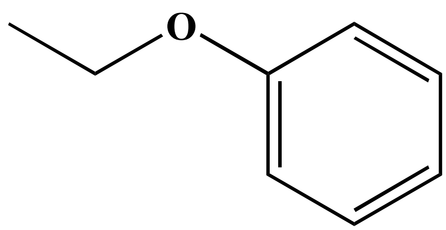
Ethers

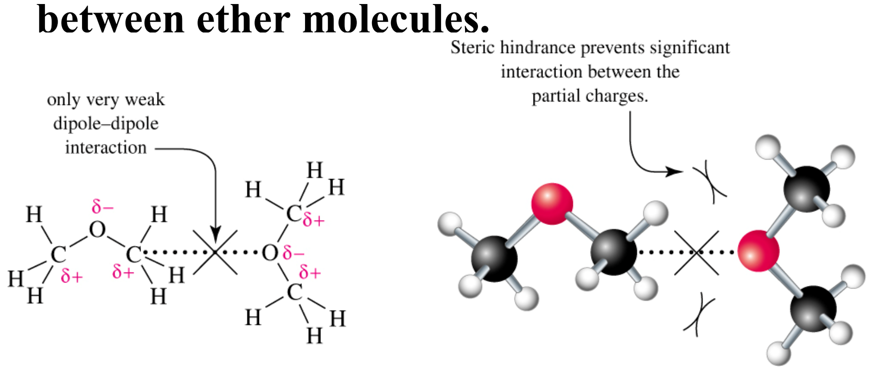
substituents can be listed alphabetically followed by the word ‘ether’



ethyl phenyl ether
ethoxybenzene

Ethers

Ethers are moderately polar compounds. However, only weak forces of attraction exist between ether molecules.

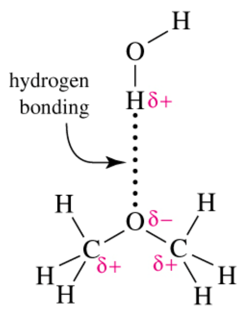


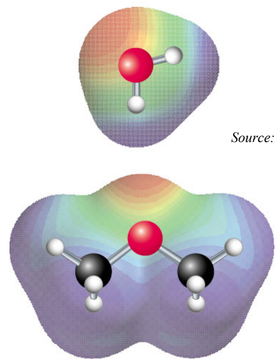
Source: Blackman et al. (2019a:1155).

Ethers

Ethers form hydrogen bonds with water.

They are more soluble in water than hydrocarbons of similar molar mass.





Source: Blackman et al. (2019a:1156).

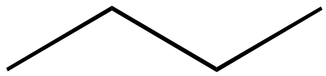
Ethers

Ethers have lower boiling points than alcohols with a similar number of electrons.

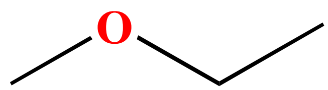
Structural formula	Name	Total electrons	Boiling point (°C)	Solubility in water
CH_3CH_2OH	ethanol	26	78	infinite
CH_3OCH_3	dimethyl ether	26	–24	7.8 g/100 g
$CH_3CH_2CH_2CH_2OH$	butan-1-ol	42	117	7.4 g/100 g
$CH_3CH_2OCH_2CH_3$	diethyl ether	42	35	8 g/100 g
$CH_3CH_2CH_2CH_2CH_2OH$	pentan-1-ol	50	138	2.3 g/100 g
$CH_3CH_2CH_2CH_2OCH_3$	butyl methyl ether	50	71	slight
$CH_3OCH_2CH_2OCH_3$	1,2-dimethoxyethane	50	84	infinite

Source: Blackman et al. (2019a:1156).

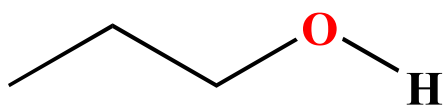
Ethers



butane
molar mass 58 g mol^{-1}
boiling point –0.5 °C



methoxyethane
molar mass 60 g mol^{-1}
boiling point +8 °C



1-propanol
molar mass 60 g mol^{-1}
boiling point +97 °C

Reactions of Ethers

Ethers resemble hydrocarbons in their resistance to chemical reactions.

- **They do not react readily with oxidising agents or reducing agents.**
- **They are not affected by most acids or bases at moderate temperature.**

Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out organic reactions.

Summary

Reactions of alcohols

Alcohols are polar compounds.

Their boiling points are higher than those of hydrocarbons of similar molar mass.

Boiling points of alcohols increase with increasing molar mass.

Alcohols are more soluble in water than hydrocarbons of similar molar mass.

Summary

Phenols

The functional group is an –OH group bonded directly to a C atom of a benzene ring.

Phenol and their derivatives are weak acids.

They have pK_a values of approx. 10.0.

They are considerably stronger acids than alcohols, which have pK_a values of 16-18.