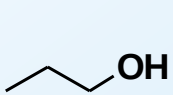
Alcohols Nomenclature, Properties and Applications

Dr. Sapna Gupta

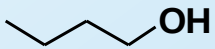
Nomenclature

- IUPAC names
  - The OH group gets priority over alkenes, alkynes, alkyl groups and halides.
  - Find the parent chain to give the OH group the lowest possible number.
  - Change the suffix -e to -ol. (e.g. methane to methanol)
- Common names: first two are methanol (methyl alcohol) and ethanol (ethyl alcohol)
  - Name the alkyl group bonded to oxygen followed by the word alcohol.

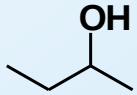


1-Propanol
(Propyl alcohol)

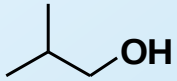
2-Propanol
(Isopropyl alcohol)



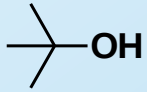
1-Butanol
(Butyl alcohol)



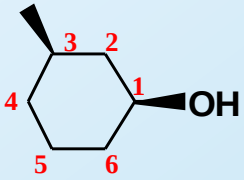
2-Butanol
(*sec*-Butyl alcohol)



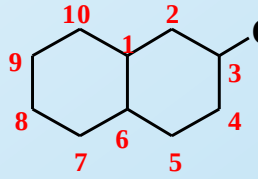
2-Methyl-1-propanol
(Isobutyl alcohol)



2-Methyl-2-propanol
(*tert*-Butyl alcohol)



***cis*-3-Methylcyclohexanol**

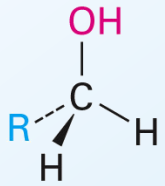


Bicyclo[4.4.0]decan-3-ol

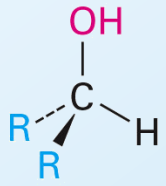
Numbering of the bicyclic ring takes precedence over the location of -OH

Nomenclature, contd..

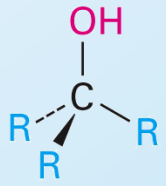
- General classifications of alcohols based on substitution on C to which OH is attached
- Methyl (C has 3 H's), Primary (1^o) (C has two H's, one R), secondary (2^o) (C has one H, two R's), tertiary (3^o) (C has no H, 3 R's)



A primary (1°) alcohol



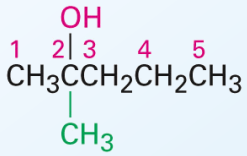
A secondary (2°) alcohol



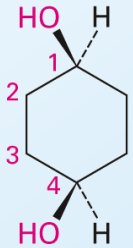
A tertiary (3°) alcohol

Nomenclature – contd..

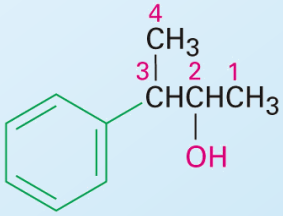
- For benzene with alcohol group, use “phenol” as the parent hydrocarbon name, not benzene
- Name substituents on aromatic ring by their position from OH
- Compounds with more than one OH group are named diols, triols, etc.
- Unsaturated alcohols
  - Show the double bond by changing the infix from -an- to -en-.
  - Number the chain to give OH the lower number



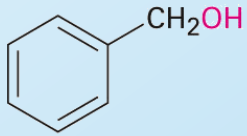
2-Methyl-2-pentanol
(New: 2-Methylpentan-2-ol)



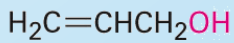
***cis*-1,4-Cyclohexanediol**
(New: *cis*-Cyclohexane-1,4-diol)



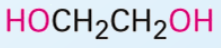
3-Phenyl-2-butanol
(New: 3-Phenylbutan-2-ol)



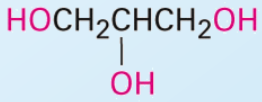
Benzyl alcohol
(phenylmethanol)



Allyl alcohol
(2-propen-1-ol)



Ethylene glycol
(1,2-ethanediol)



Glycerol
(1,2,3-propanetriol)

Physical Properties

- Unusually high boiling points due to hydrogen bonding between molecules.
- Small alcohols are miscible in water, but solubility decreases as the size of the alkyl group increases.
- Odor – most alcohols have a sweet smell.

TABLE 10-3 Solubility of Alcohols in Water (at 25°C)

Alcohol	Solubility in Water
methyl	miscible
ethyl	miscible
n-propyl	miscible
t-butyl	miscible
isobutyl	10.0%
n-butyl	9.1%
n-pentyl	2.7%
cyclohexyl	3.6%
n-hexyl	0.6%
phenol	9.3%
hexane-1,6-diol	miscible

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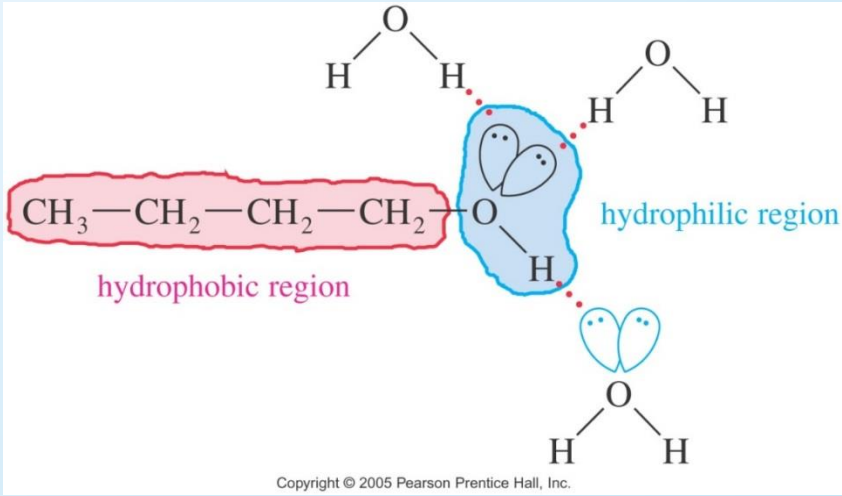

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Solubility decreases as the size of the alkyl group increases.

Physical Properties – contd.

- Ethanol and dimethyl ether are constitutional isomers.
- Their boiling points are dramatically different
  - Ethanol forms intermolecular hydrogen bonds resulting in a higher boiling point whereas ether has only dipole-dipole interactions.

CH_3CH_2OH	CH_3OCH_3
Ethanol	**Dimethyl ether**
bp 78° C	**bp -24°C**

- In relation to alkanes of comparable size and molecular weight, alcohols
  - have higher boiling points.
  - are more soluble in water.
- The presence of additional -OH groups in a molecule further increases solubility in water and boiling point.

Acidity of Alcohols

- pK_a range: 15.5-18.0 (water: 15.7)
- Acidity decreases as alkyl group increases.
- Halogens increase the acidity.
- Phenol is 100 million times more acidic than cyclohexanol!

TABLE 10-4 Acid-Dissociation Constants of Representative Alcohols

Alcohol	Structure	K_a	pK_a
methanol	$CH_3—OH$	3.2×10^{-16}	15.5
ethanol	$CH_3CH_2—OH$	1.3×10^{-16}	15.9
2-chloroethanol	$Cl—CH_2CH_2—OH$	5.0×10^{-15}	14.3
2,2,2-trichloroethanol	$Cl_3C—CH_2—OH$	6.3×10^{-13}	12.2
isopropyl alcohol	$(CH_3)_2CH—OH$	3.2×10^{-17}	16.5
t-butyl alcohol	$(CH_3)_3C—OH$	1.0×10^{-18}	18.0
cyclohexanol	$C_6H_{11}—OH$	1.0×10^{-18}	18.0
phenol	$C_6H_5—OH$	1.0×10^{-10}	10.0
	Comparison with Other Acids		
water	H_2O	1.8×10^{-16}	15.7
acetic acid	CH_3COOH	1.6×10^{-5}	4.8
hydrochloric acid	HCl	$1.6 \times 10^{+2}$	−2.2

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Formation of Alkoxide Ions

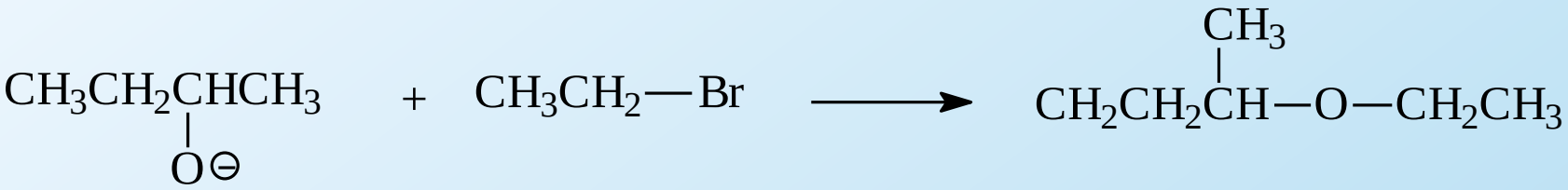
ROH + Na (or NaH) yields sodium alkoxide

React methanol and ethanol with sodium metal (redox reaction).

$$CH_3OH + Na \longrightarrow CH_3O^-Na^+$$

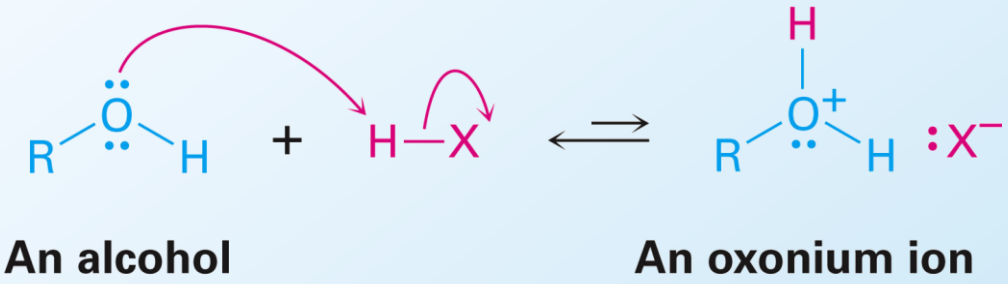
React less acidic alcohols with more reactive potassium. Some other bases (other than alkali metals), can be NaH, $NaNH_2$.

RO^- + 1° alkyl halide yields ether
(Williamson ether synthesis) (*next chapter*)



Basicity of Alcohols

- Weakly basic
- Alcohols are weak Brønsted bases
- Protonated by strong acids to yield oxonium ions, ROH_2^+



Methanol

- Also called “Wood alcohol”
- Common industrial solvent
- Fuel at Indianapolis 500
- Toxic: consumption leads to blindness.

Ethanol

- Formed by fermentation of sugar and starches in grains
- Distillation produces “hard” liquors
- Azeotrope: 95% ethanol, constant boiling
- Denatured alcohol used as solvent
- Gasahol: 10% ethanol in gasoline

Other Alcohols of Interest

- Isopropyl alcohol – disinfectant
- Ethylene Glycol – antifreeze
- Glycerol – used as medication
- Sugar – all carbohydrates have alcohol groups.

Key Concepts

- Nomenclature
- Primary, secondary and tertiary alcohols
- Physical properties
- Acidity of alcohols
- Alkoxides