

ALCOHOLS: Properties & Preparation

General formula: R-OH, where R is alkyl or substituted alkyl.

Ar-OH: phenol - different properties.

Nomenclature

1. Common names: Name of alkyl group, followed by word alcohol.

eg ethyl alcohol, isopropyl alcohol

2. IUPAC:

(a) Parent structure - longest chain containing -OH group: name by replacing -e of alkane by -ol

(b) Position of -OH is indicated by a number, usually the lowest one possible (-OH takes precedence over double and triple bonds if any are present, *ie*, number from the end that gives *the* -OH a lower number).

(c) Substituents on parent chain indicated by name and position number.

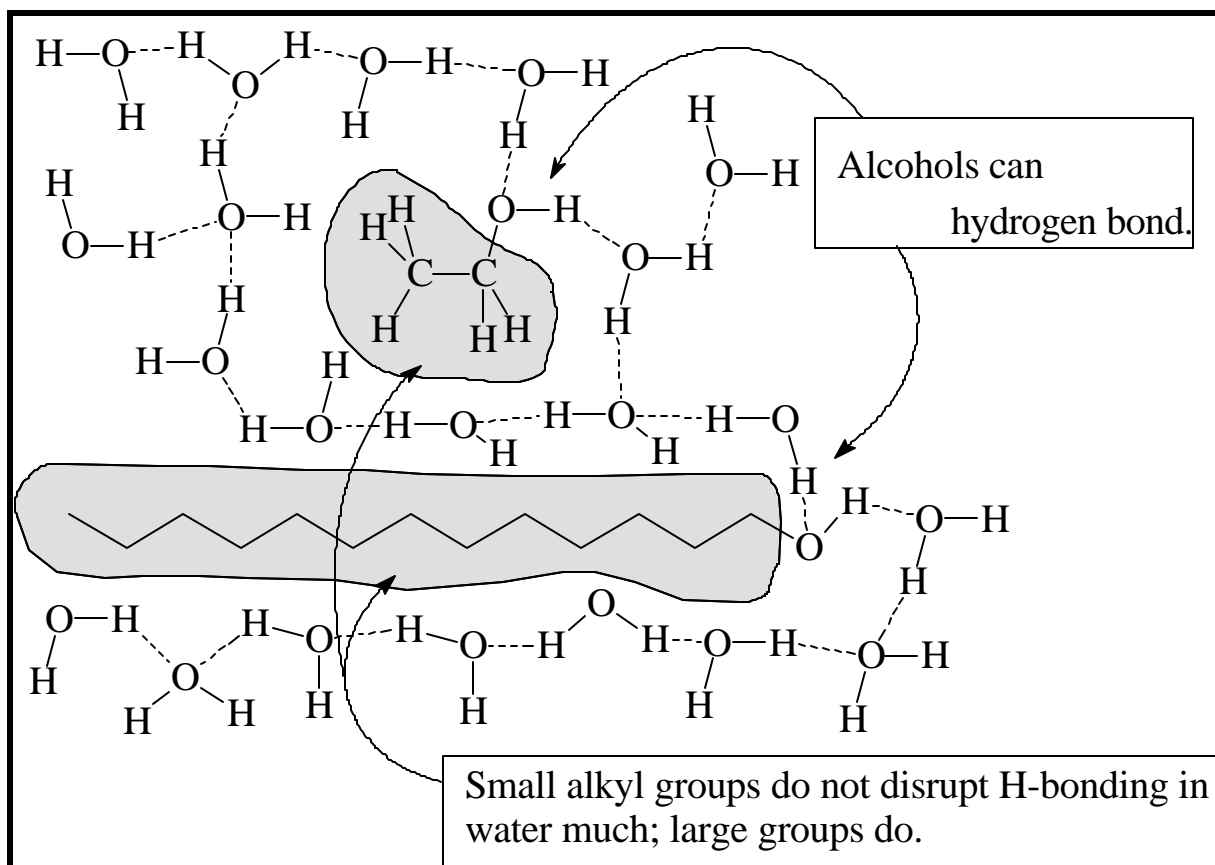
(d) More than one -OH group: -diol, -triol, *etc.*

eg $C_6H_5-CH_2-CHCl-CH(OH)-CH_3$

3-chloro-4-phenyl-2-butanol

Physical Properties

Up to ~6 carbons: soluble in water owing to hydrogen bonding and dipole-dipole interactions with water. The larger the alkyl group, the more alkane-like the alcohol, and the less soluble it is in water.

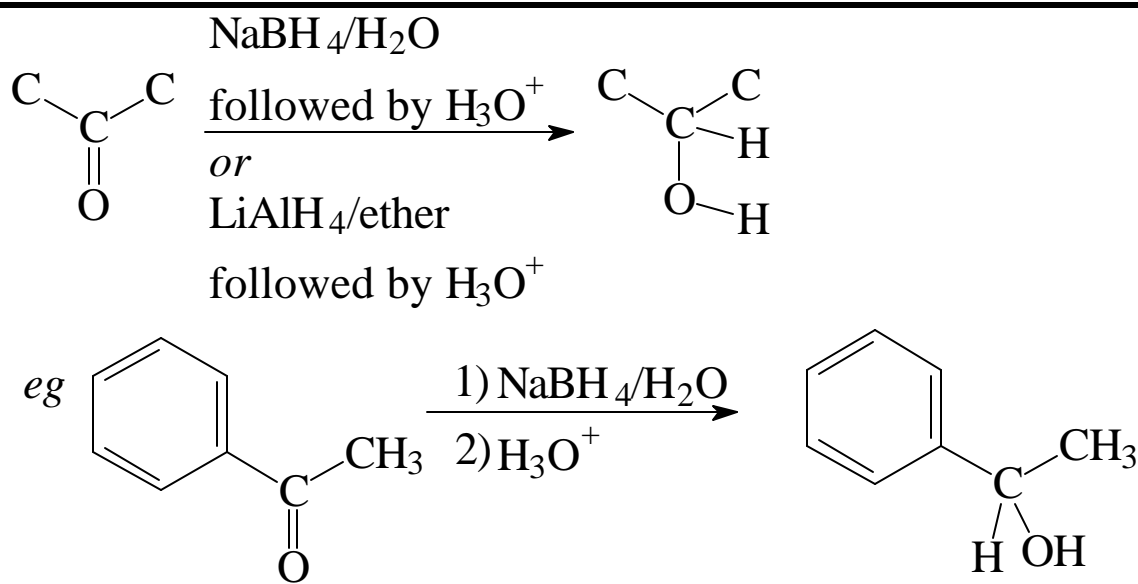


Owing to H-bonding and dipole-dipole interactions, the bps of alcohols are high compared to alkanes of same MW.

Preparation

1) Reduction of Ketones —

Ketones can be reduced to secondary alcohols with lithium aluminum hydride or sodium borohydride.



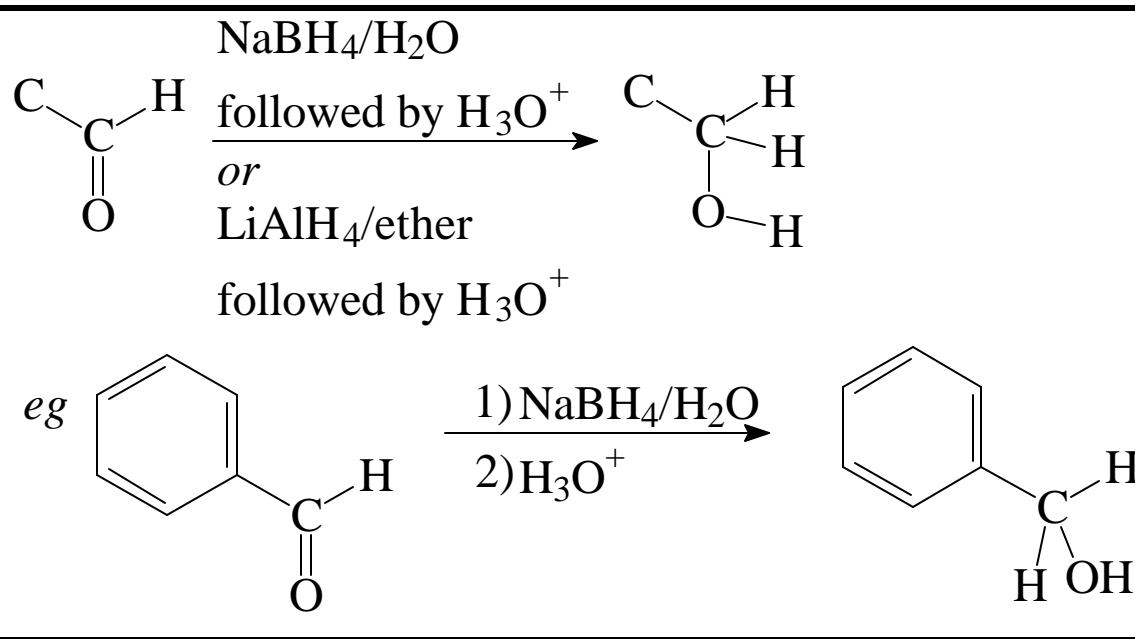
Limitations —

Sodium borohydride may reduce the C-C π bond in conjugated ketones.

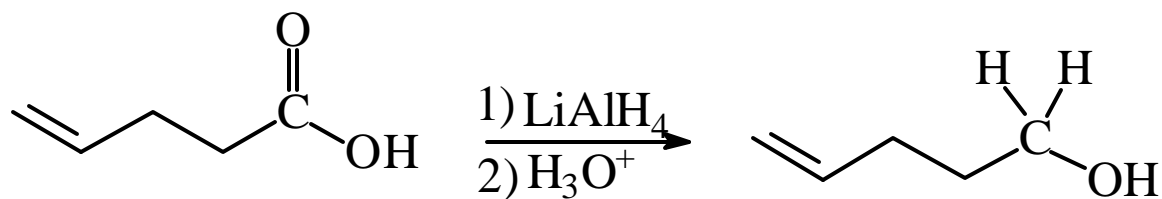
Lithium aluminum hydride is a powerful reducing agent and will reduce carboxylic acids, esters, nitriles, amides and nitro groups; it will replace alkyl halogens with hydrogen (*hydrogenolysis*). It is destroyed by even weakly acidic water and alcohols. It may reduce the C-C π bond in conjugated ketones. It reacts violently with water and, in general, is nasty stuff.

2) Reduction of Aldehydes —

Aldehydes can be reduced to primary alcohols with sodium borohydride or lithium aluminum hydride. This reaction is analogous to (1).

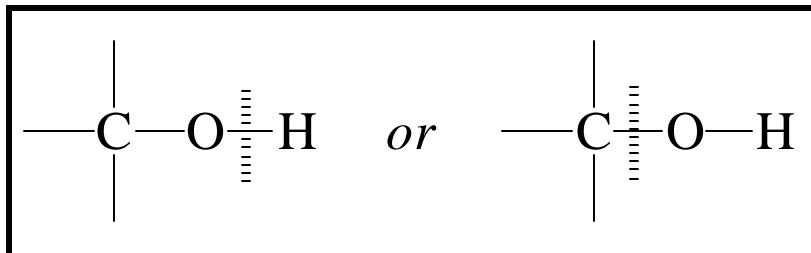


3) Reduction of Carboxylic Acids and Esters —
Both esters and carboxylic acids can be reduced to primary alcohols by lithium aluminum hydride.



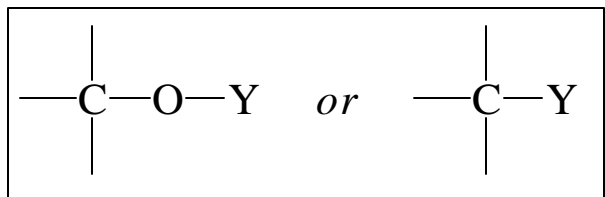
Alcohols: Reactions

The alcohol functional group is -O-H and its reactions involve cleavage of the O-H bond or the C-O bond —

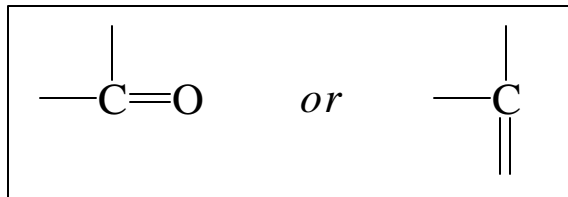


In either case, there can be a subsequent substitution, or an elimination to form a double bond ---

Substitution:

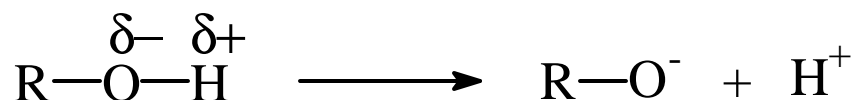


Elimination:

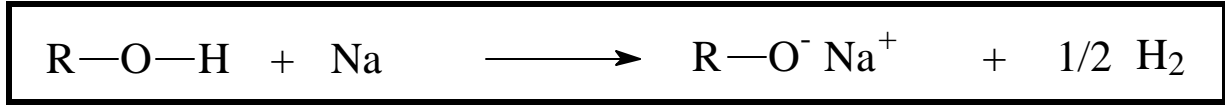


Alcohols As Acids —

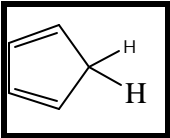
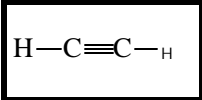

Acidity is the result of the electronegativity of oxygen:



Alcohols react with active metals:



Acidity of Alcohols, Compared to Other Compounds:

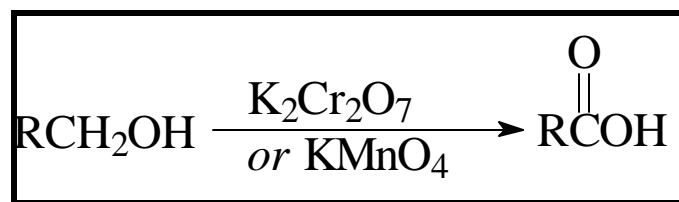
Compound	pK _a	Compound	pK _a
HSO₄H	-10	ArOH	8-11
HCl	-7	HOH	15.74
ArSO₃H	-6.5		16
RCH₂-HOH⁺	-2	RCH₂OH	18
H₂OH⁺	-1.74		25
HNO₃	-1.4	H₂NH	34
HF	3.17	CH₂=HCH	36.5
Ar-H₂NH⁺	3-5	Ph-H	37
RCOOH	4-5	CH₃-H₂CH	42
H₃NH⁺	9		100

Relative Acidities of Alcohols and Water:

Compound	pK _a
HO- H	15.7
CH ₃ O- H	15.5-16
CH ₃ CH ₂ O- H	16-18
(CH ₃) ₂ CHO- H	18
(CH ₃) ₃ CO- H	19

Oxidation of Alcohols —

Primary alcohols can be oxidized to aldehydes (with care) and carboxylic acids.

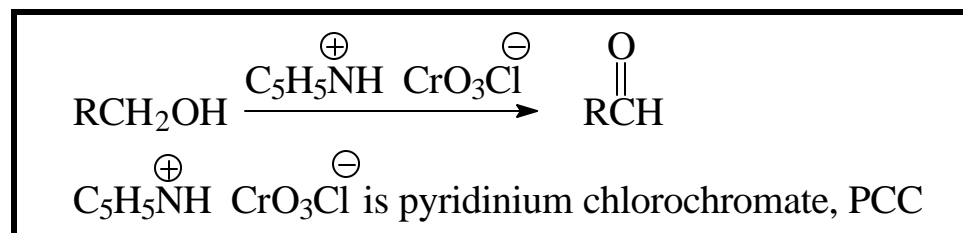


Carboxylic Acids —

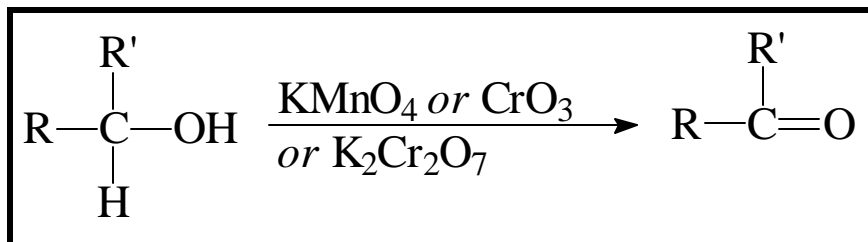
This oxidation occurs in two stages; there is an aldehyde intermediate, but aldehydes are

usually more easily oxidized than alcohols (many aldehydes are oxidized by air) and under the conditions of the reaction the aldehyde is not isolated.

Aldehydes — This reaction is successful under certain carefully controlled conditions.



Secondary alcohols can be oxidized to ketones.



Further oxidation does not take place because it would involve breaking a carbon-carbon bond.

Tertiary alcohols are not oxidized under basic conditions and are converted to alkenes under acidic conditions. [Alkenes may react with oxidizing agents.]

Phenols — Ar-OH

Phenols differ from alcohols in that the -OH is *directly* attached to the aromatic ring. [Ph-CH₂-OH is an alcohol.]

Physical Properties —

Phenol is somewhat soluble in water (hydrogen bonding); other phenols are not very soluble.

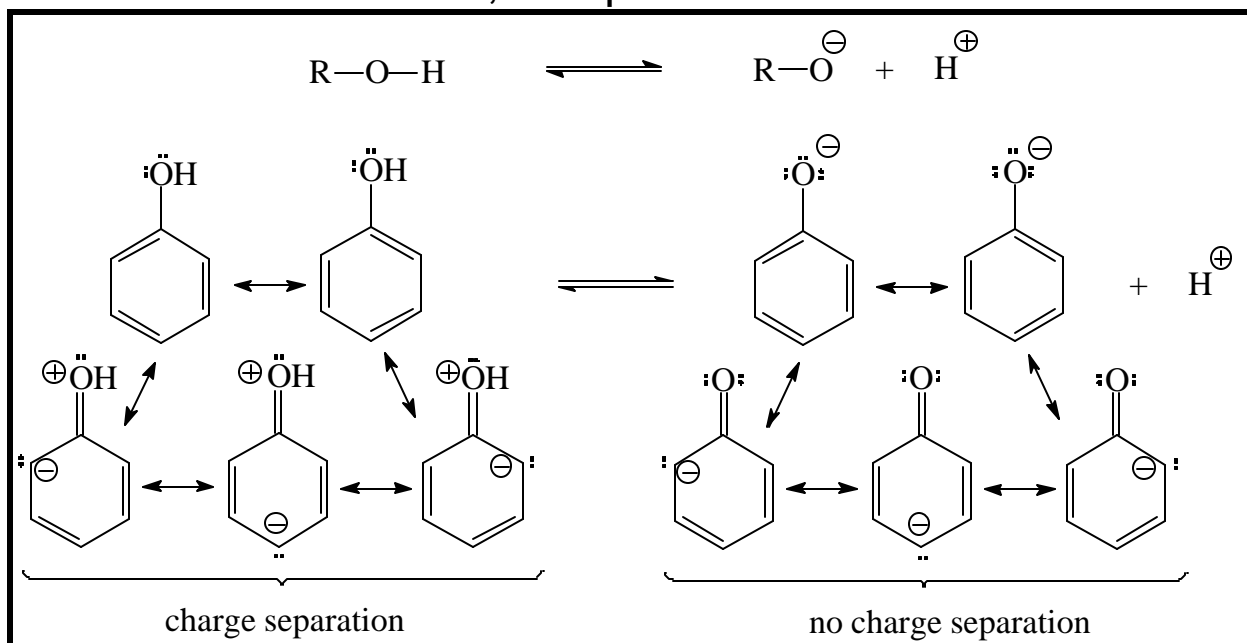
Boiling points are high compared to hydrocarbons owing to hydrogen bonding.

Reactions of Phenols —

Phenols are acidic.

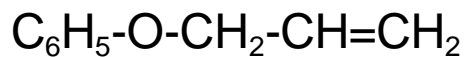
Why are phenols acidic ($K_a \sim 10^{-10}$) compared to alcohols ($K_a \sim 10^{-16}$)?

Compared to a phenol, the phenoxide ion is more stable than an alkoxide ion is, compared to an alcohol —

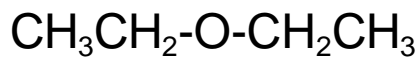


Ethers —

Nomenclature: name both groups, followed by "ether,"
eg

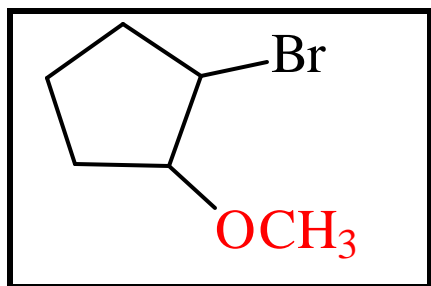


allyl phenyl ether



diethyl ether (ether)

If one group has no simple name, use alkoxy, R-O-,
methoxy, *eg*



1-bromo-2-methoxycyclopentane

Physical properties:

Weakly polar, slightly soluble in water.

