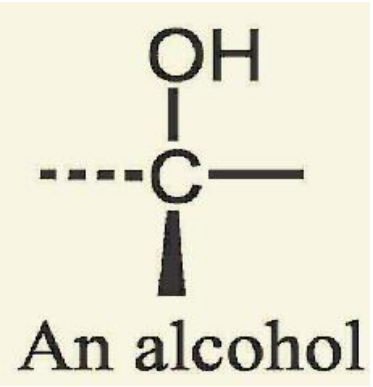
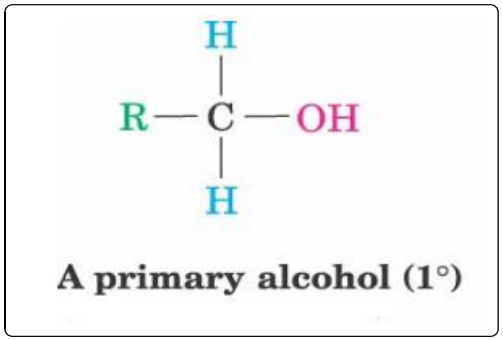
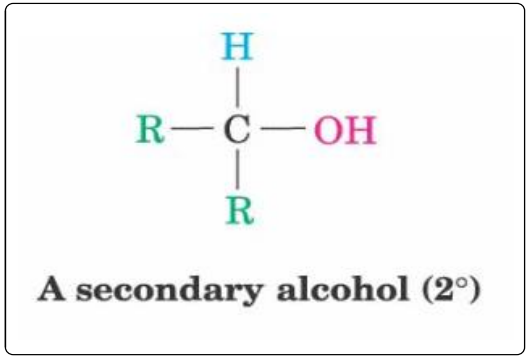
Chapter 6: Alcohols, Phenols and Ether

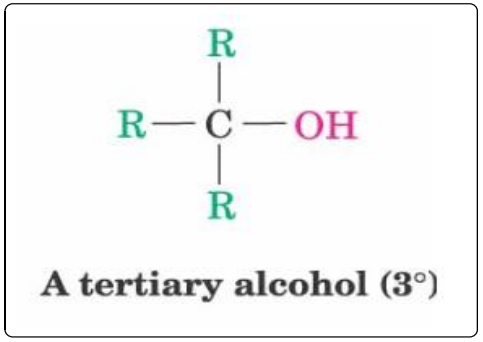
Alcohols contain an OH group connected to a saturated C (sp3)



Classification of alcohols

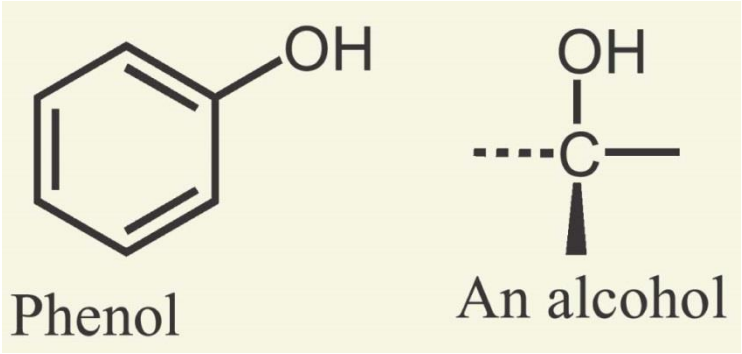






Alcohols and Phenols

- Methanol, CH_3OH, called methyl alcohol, is a common solvent, a fuel additive, produced in large quantities
- Ethanol, CH_3CH_2OH, called ethyl alcohol, is a solvent, fuel, beverage
- Phenol, C_6H_5OH (“phenyl alcohol”) has diverse uses - it gives its name to the general class of compounds



IUPAC Rules for Naming Alcohols

replace (e) in alkane by (ol)

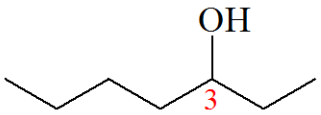
1. Choose the longest continous chain and start near OH.
2. give the substituents less numbers and list them in alphabetical order

Naming Phenols

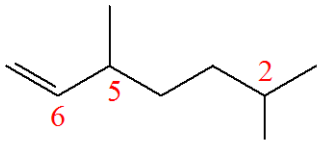
*Use “phen” as the parent hydrocarbon name, not benzene

*Name substituents on aromatic ring by their position from OH

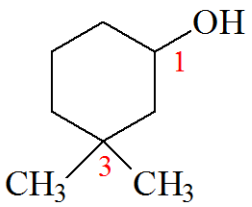
Alcohol Nomenclature



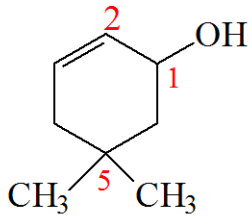
3-heptanol



5-methyl-6-hepten-2-ol

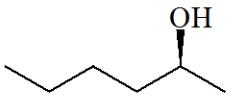


3,3-dimethylcyclohexanol

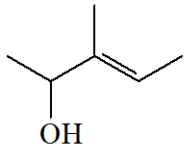


5,5-dimethylcyclohex-2-enol

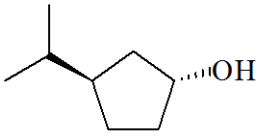
Nomenclature



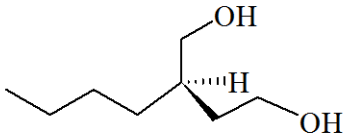
(S) 2-hexanol



(E) 3-methyl-3-penten-2-ol



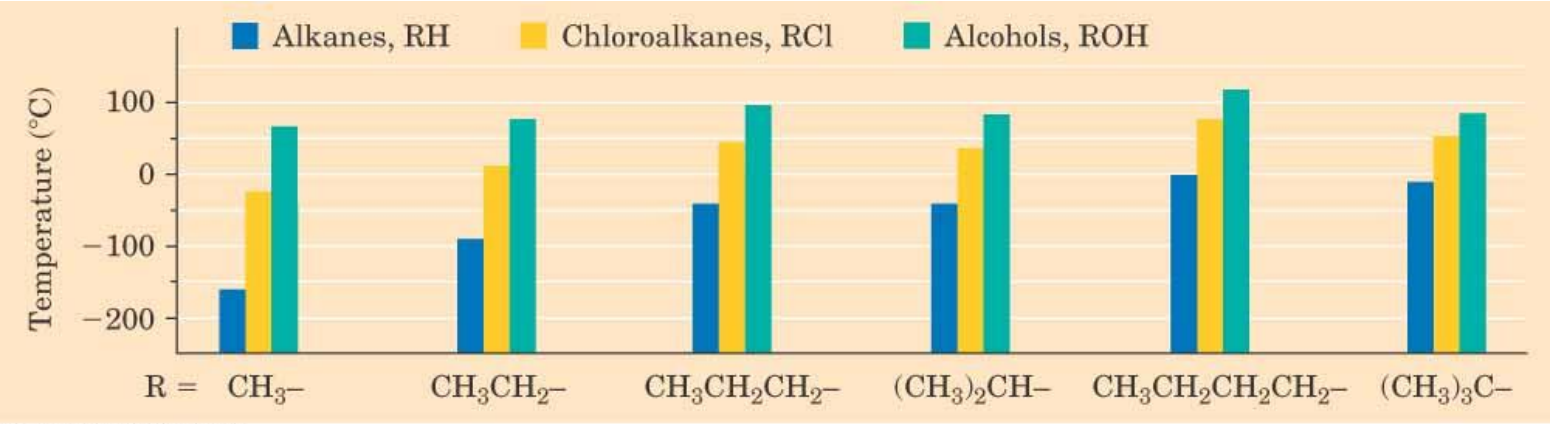
***trans* 3-isopropylcyclopentanol**



(R) 2-butyl-1,4-butanediol
(R) 2-butylbutane-1,4-diol

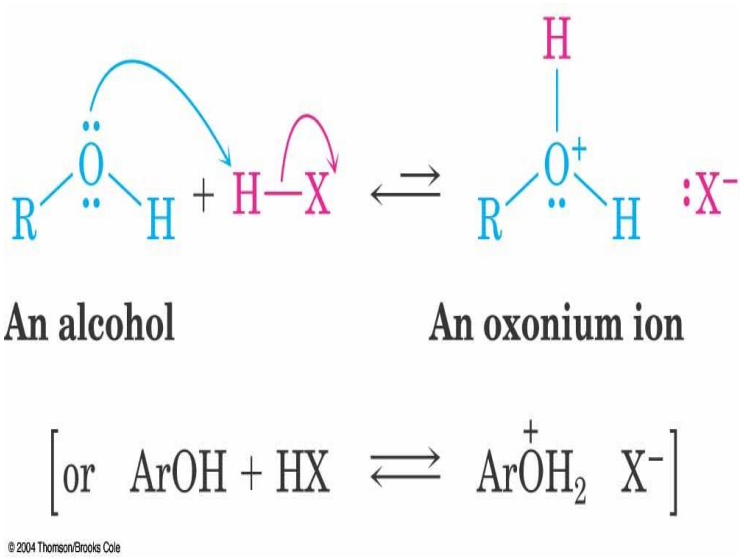
Properties of Alcohols and Phenols: Hydrogen Bonding

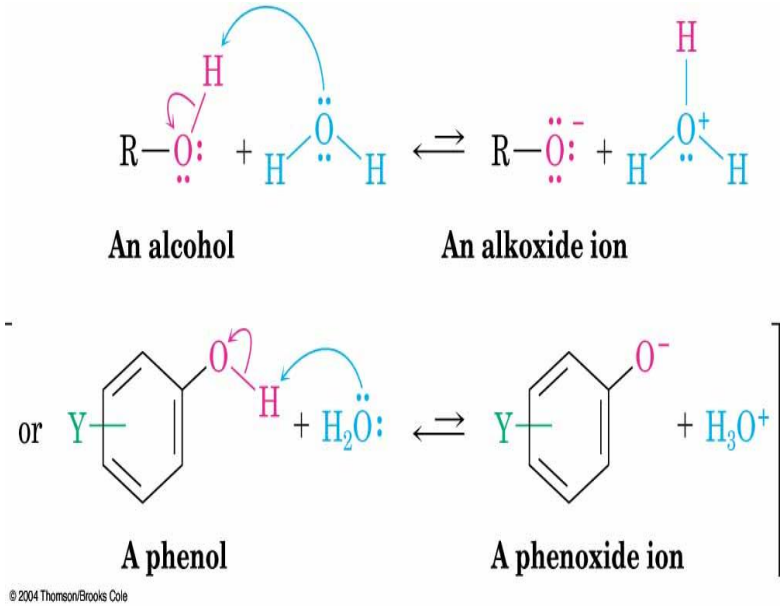
- The structure around O of the alcohol or phenol is similar to that in water, sp^3 hybridized
- Alcohols and phenolshave much higher boiling points than similar alkanes and alkyl halides due to formation of H-bonding (A positively polarized —OH hydrogen atom from one molecule is attracted to a lone pair of electrons on a negatively polarized oxygen atom of another molecule



Acidity and Basicity

- Weakly basic and weakly acidic
- Alcohols are weak Brønsted bases
- Protonated by strong acids to yield oxonium ions, ROH_2^+
- It also Can transfer a proton to water to a very small extent
- Produces H_3O^+ and an **alkoxide ion, RO^-**, or a **phenoxide ion, ArO^-** (act as Bronsted acid)

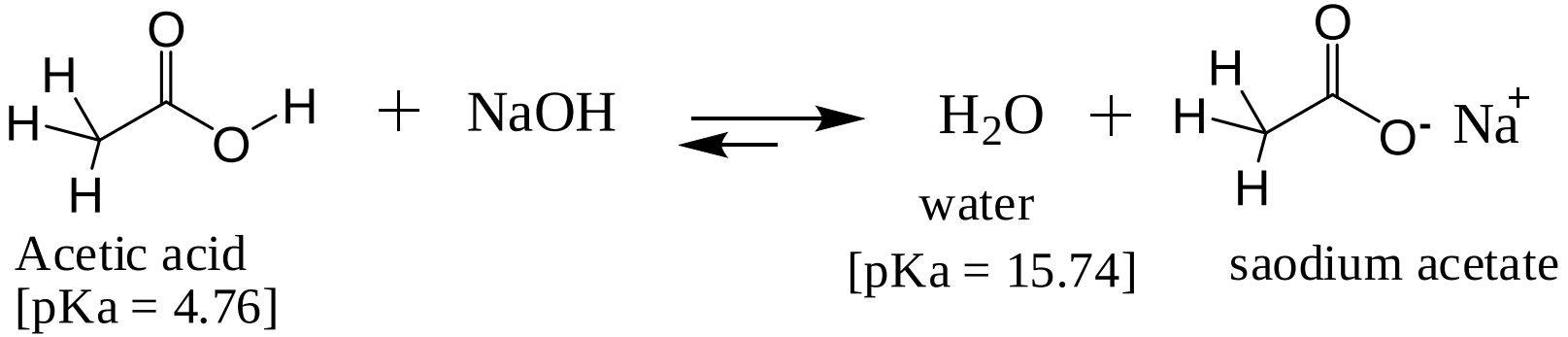




Acid strength is measured by pKa

$$pKa = -\log Ka \qquad \text{Eq.2}$$

strong acid : small pKa



Acetic acid
[pKa = 4.76]

water
[pKa = 15.74]

saodium acetate

- Factors affecting acidity
- Electron-withdrawing groups make an alcohol a stronger acid by stabilizing the conjugate base (alkoxide)
- Electron-donating groups make an alcohol a weaker acid by destabilizing the conjugate base (alkoxide)

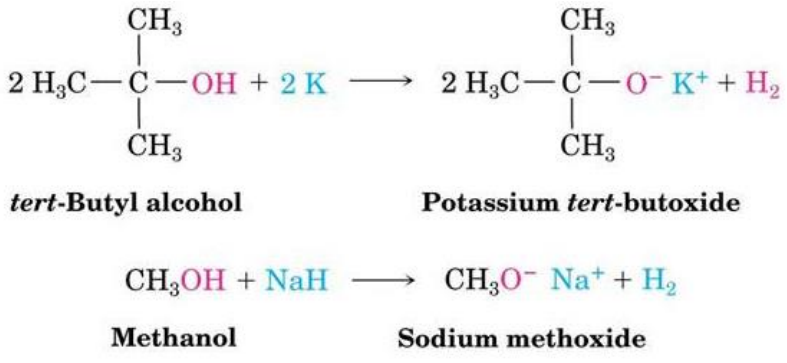
pK_a Values for Typical OH Compounds

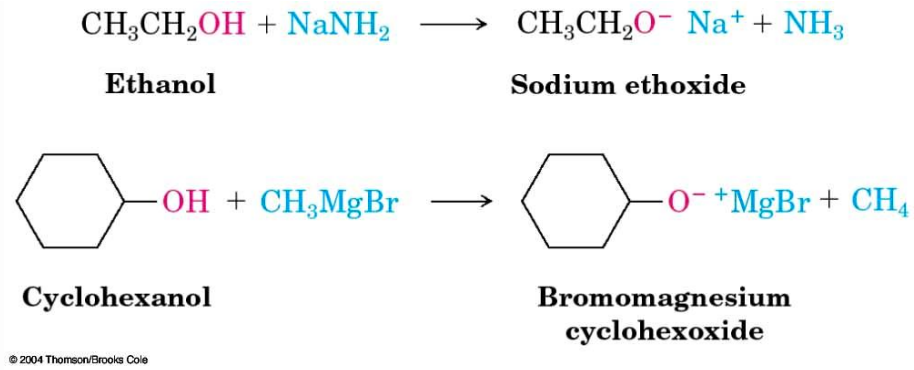
TABLE 17.1 Acidity Constants of Some Alcohols and Phenols

Alcohol or phenol	pK_a	
$(CH_3)_3COH$	18.00	Weaker acid
CH_3CH_2OH	16.00	
HOH (water)	(15.74)	
CH_3OH	15.54	
CF_3CH_2OH	12.43	
p-Aminophenol	10.46	
p-Methoxyphenol	10.21	
p-Methylphenol	10.17	
Phenol	9.89	
p-Chlorophenol	9.38	
p-Bromophenol	9.35	
p-Nitrophenol	7.15	
2,4,6-Trinitrophenol	0.60	Stronger acid

Generating Alkoxides from Alcohols

- Alcohols are weak acids – requires a strong base to form an alkoxide such as NaH, sodium amide $NaNH_2$, and Grignard reagents (RMgX)
- Alkoxides are bases used as reagents in organic chemistry





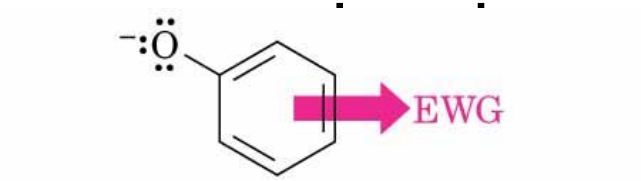
Phenol Acidity

- Phenols (pK_a ~10) are much more acidic than alcohols (pK_a ~ 16) due to resonance stabilization of the phenoxide ion
- Phenols react with NaOH solutions (but alcohols do not), forming soluble salts that are soluble in dilute aqueous
- A phenolic component can be separated from an organic solution by extraction into basic aqueous solution and is isolated after acid is add

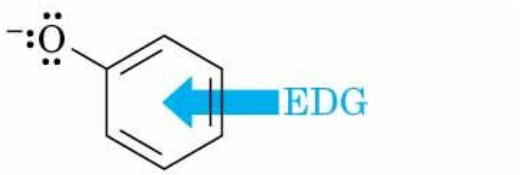
Phenol **Sodium phenoxide**

Substituted Phenols

- Can be more or less acidic than phenol itself
- An electron-withdrawing substituent makes a phenol more acidic by delocalizing the negative charge
- Phenols with an electron-donating substituent are less acidic because these substituents cor



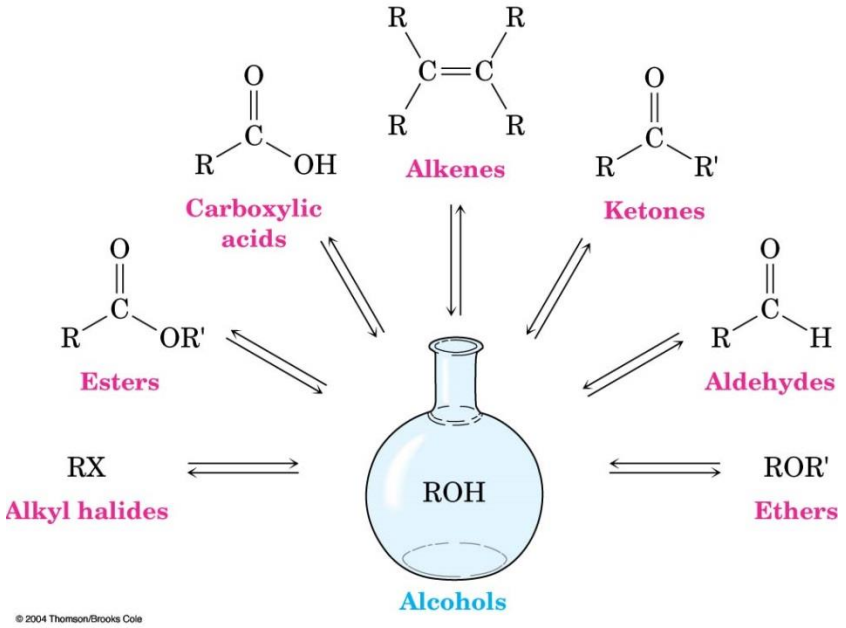
Electron-withdrawing groups (EWG) stabilize phenoxide anion, resulting in increased phenol acidity



Electron-donating groups (EDG) destabilize phenoxide anion, resulting in decreased phenol acidity

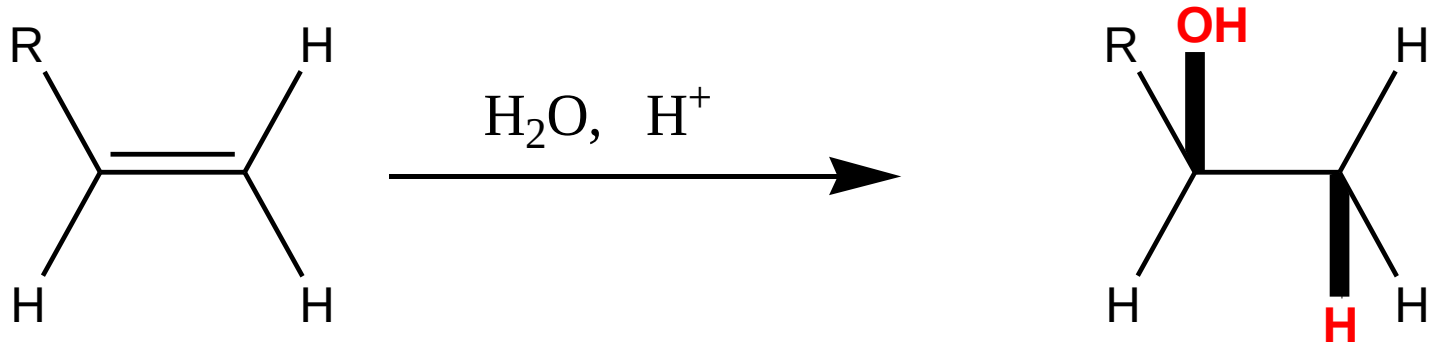
Preparation of Alchols: an Overview

- Alcohols are derived from many types of compounds
- The alcohol hydroxyl can be converted to many other functional groups
- This makes alcohols useful in synthesis



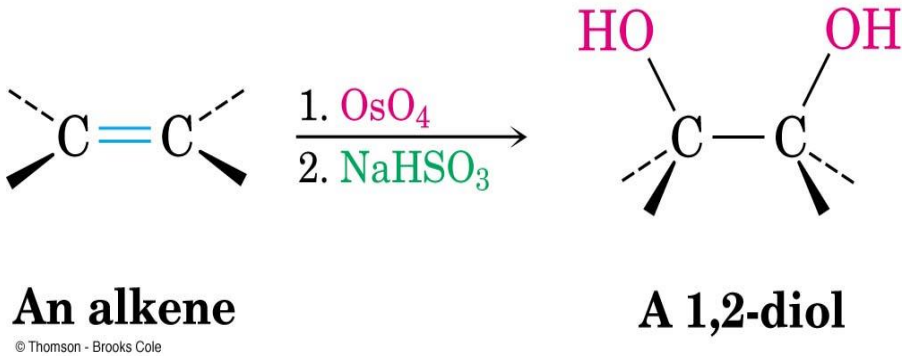
1. Addition of Water to Alkenes: hydration

- Acid catalysts are used in high temperature industrial processes.
- Follow Markonikove rule: H to carbon with more H



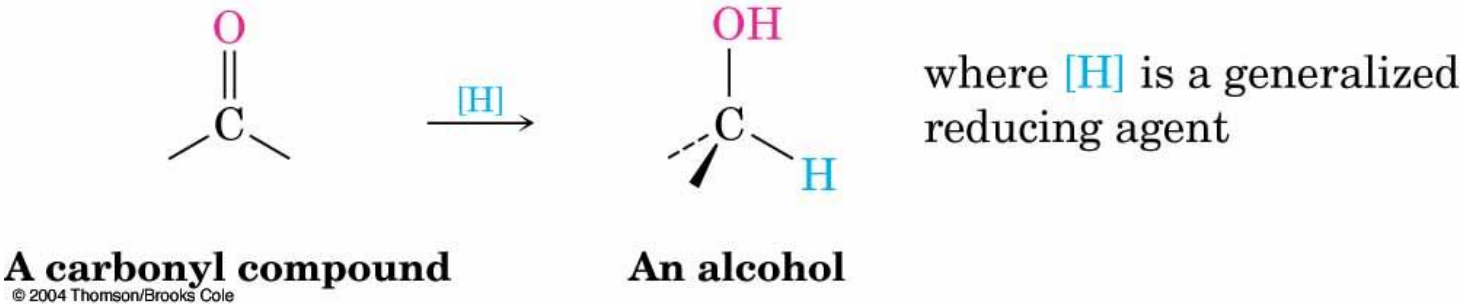
2. Oxidation of Alkenes

- Product is a Cis-1,2-dialcohol or **diol** (also called a **glycol**) Catalyzed by osmium tetroxide

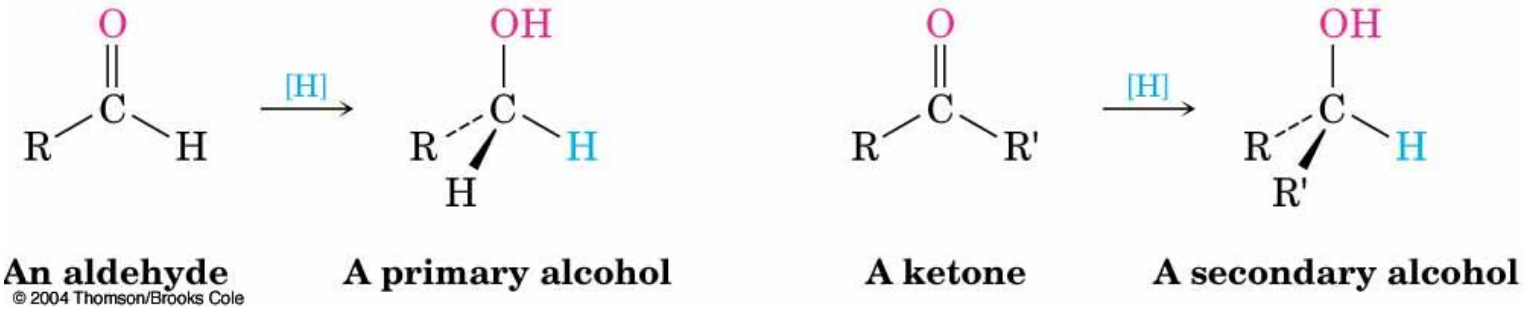


3. Reduction of Carbonyl Compounds

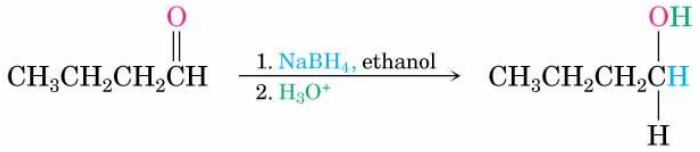
- Reduction of a carbonyl compound in general gives an alcohol
- Note that organic reduction reactions add the equivalent of H_2 to a molecule



- Aldehydes gives primary alcohols
- Ketones gives secondary alcohols

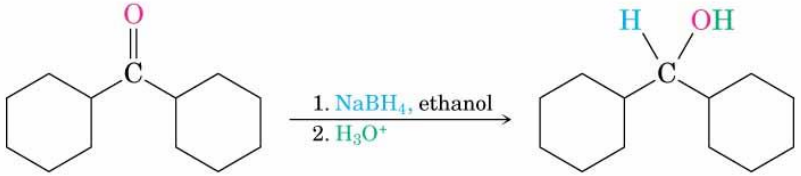


Aldehyde reduction



Butanal — **1-Butanol (85%) (a 1° alcohol)**

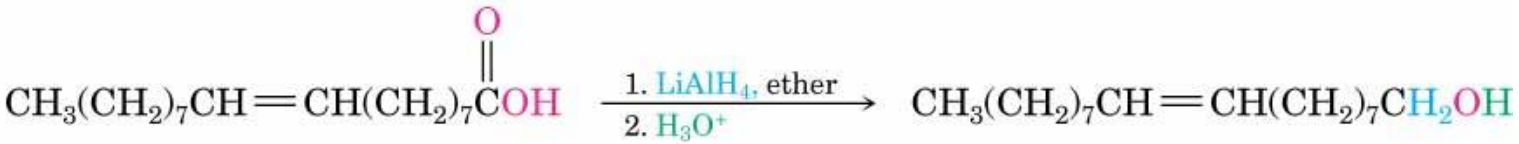
Ketone reduction



Dicyclohexyl ketone — **Dicyclohexylmethanol (88%) (a 2° alcohol)**

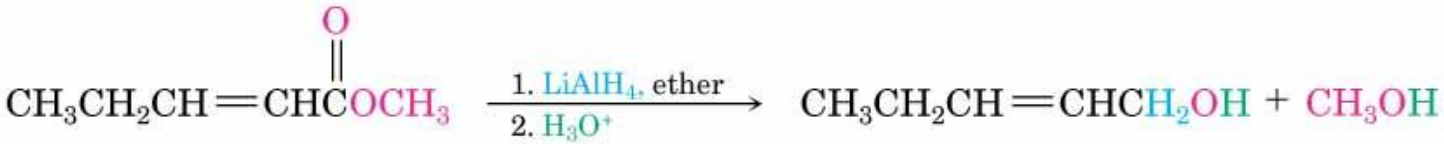
4. Reduction of Carboxylic Acids and Esters

Carboxylic acid reduction



9-Octadecenoic acid (Oleic acid) — **9-Octadecen-1-ol (87%)**

Ester reduction

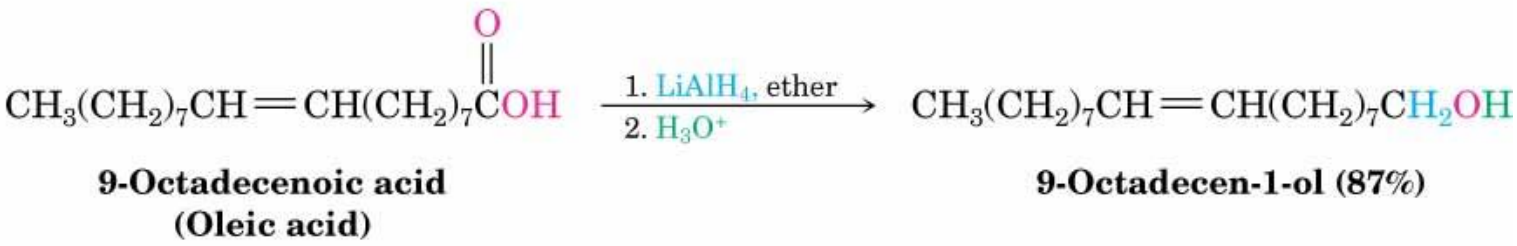


Methyl 2-pentenoate — **2-Penten-1-ol (91%)**

Reduction of Carboxylic Acids and Esters

- Carboxylic acids and esters are reduced to give primary alcohols
- $LiAlH_4$ is used because $NaBH_4$ is not effective

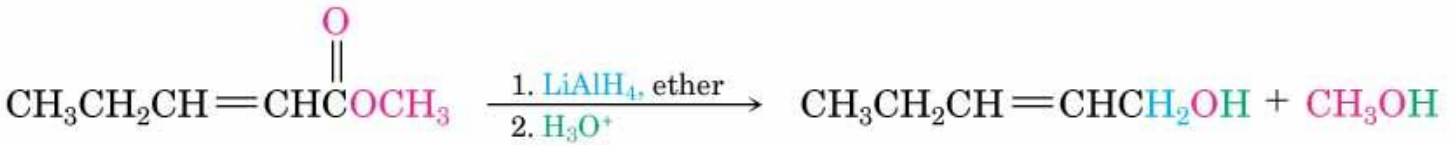
Carboxylic acid reduction



9-Octadecenoic acid (Oleic acid)

9-Octadecen-1-ol (87%)

Ester reduction

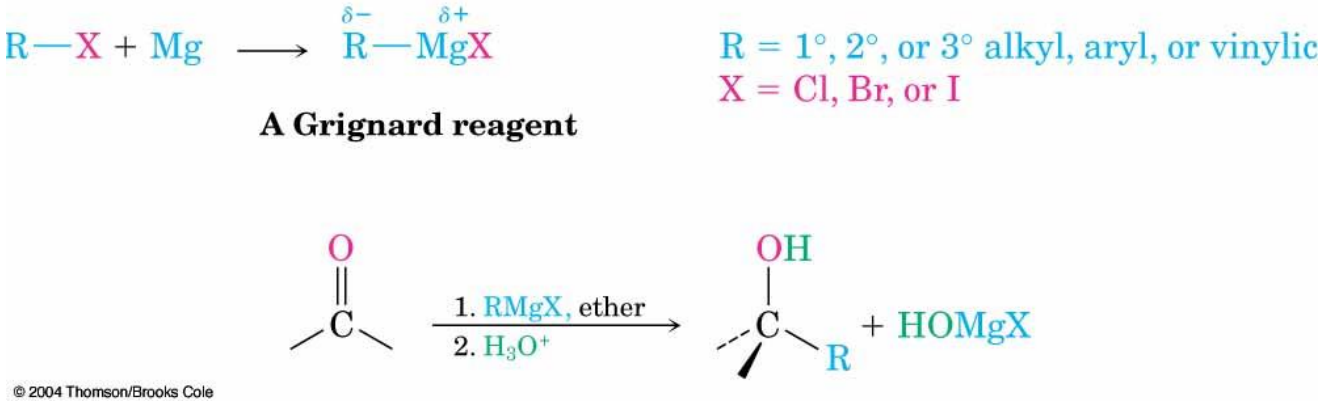


Methyl 2-pentenoate

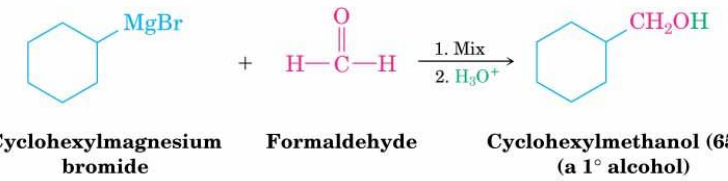
2-Penten-1-ol (91%)

5. Alcohols from Grignard Reagents

Grignard formation

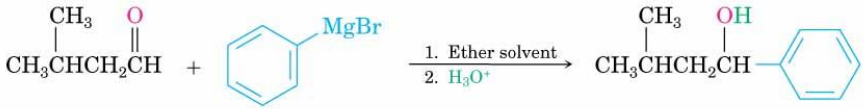


Formaldehyde reaction



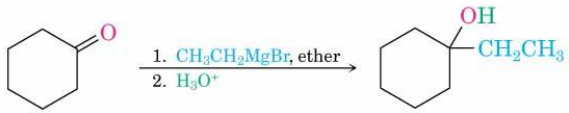
Cyclohexylmagnesium bromide + **Formaldehyde** → **Cyclohexylmethanol (65%) (a 1° alcohol)**

Aldehyde reaction



3-Methylbutanal + **Phenylmagnesium bromide** → **3-Methyl-1-phenyl-1-butanol (73%) (a 2° alcohol)**

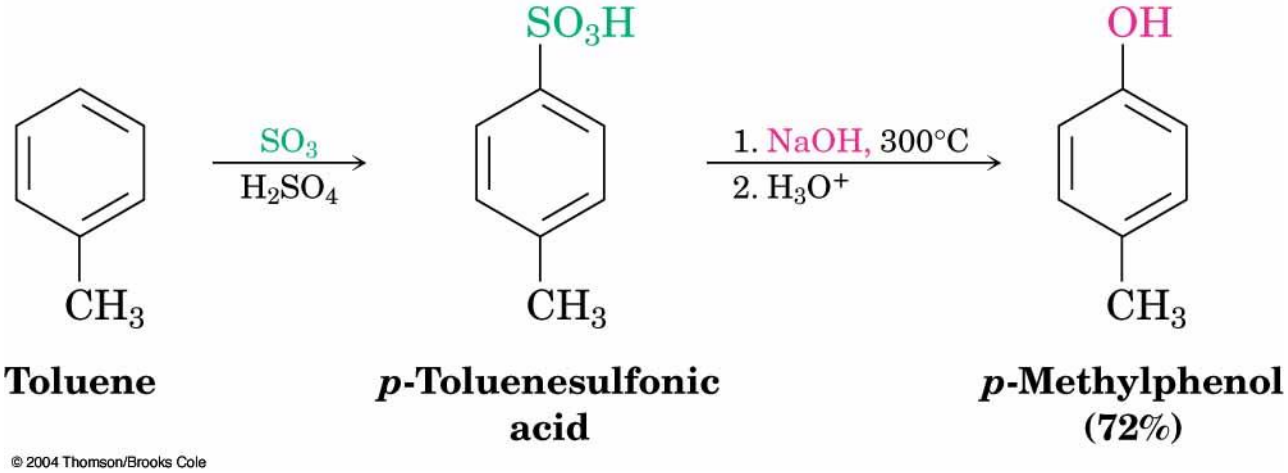
Ketone reaction



Cyclohexanone → **1-Ethylcyclohexanol (89%) (a 3° alcohol)**

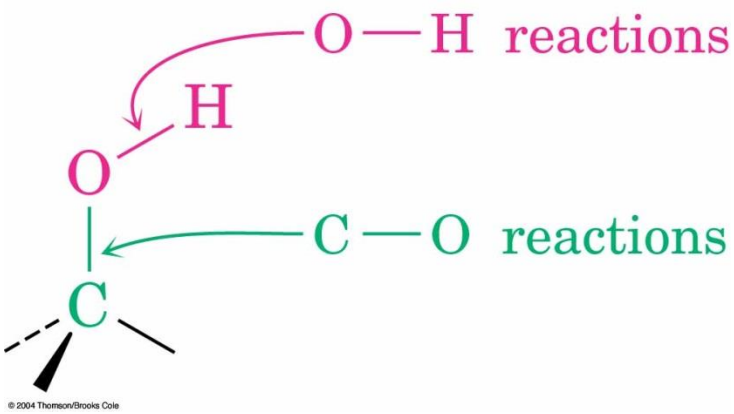
Preparation of Phenols

- From aromatic sulfonic acids by melting with NaOH at high temperature
- Limited to the preparation of alkyl-substituted phenols



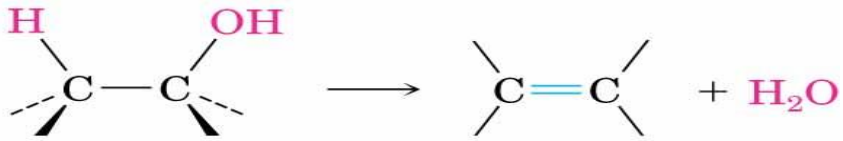
Some Reactions of Alcohols

- Two general classes of reaction
  - At the carbon of the C–O bond
  - At the proton of the O–H bond



1. Dehydration of Alcohols with acid to Yield Alkenes

A dehydration reaction



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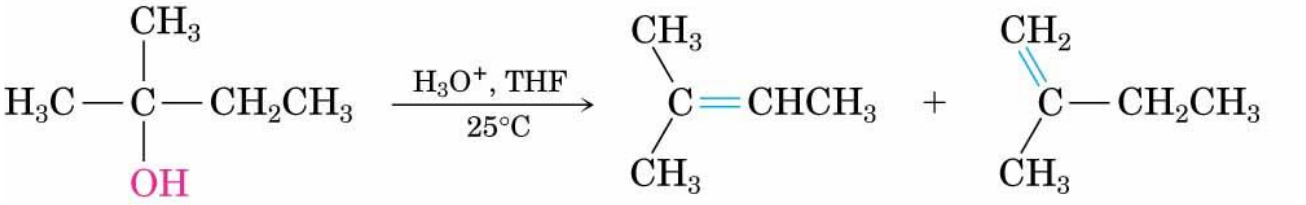

2-Methyl-2-butanol

2-Methyl-2-butene (trisubstituted)

Major product

2-Methyl-1-butene (disubstituted)

Minor product

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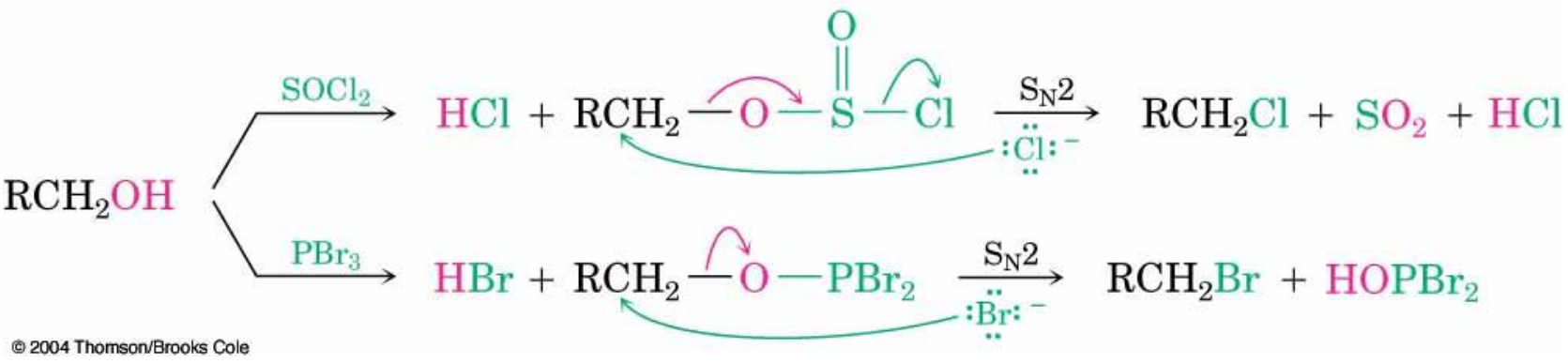
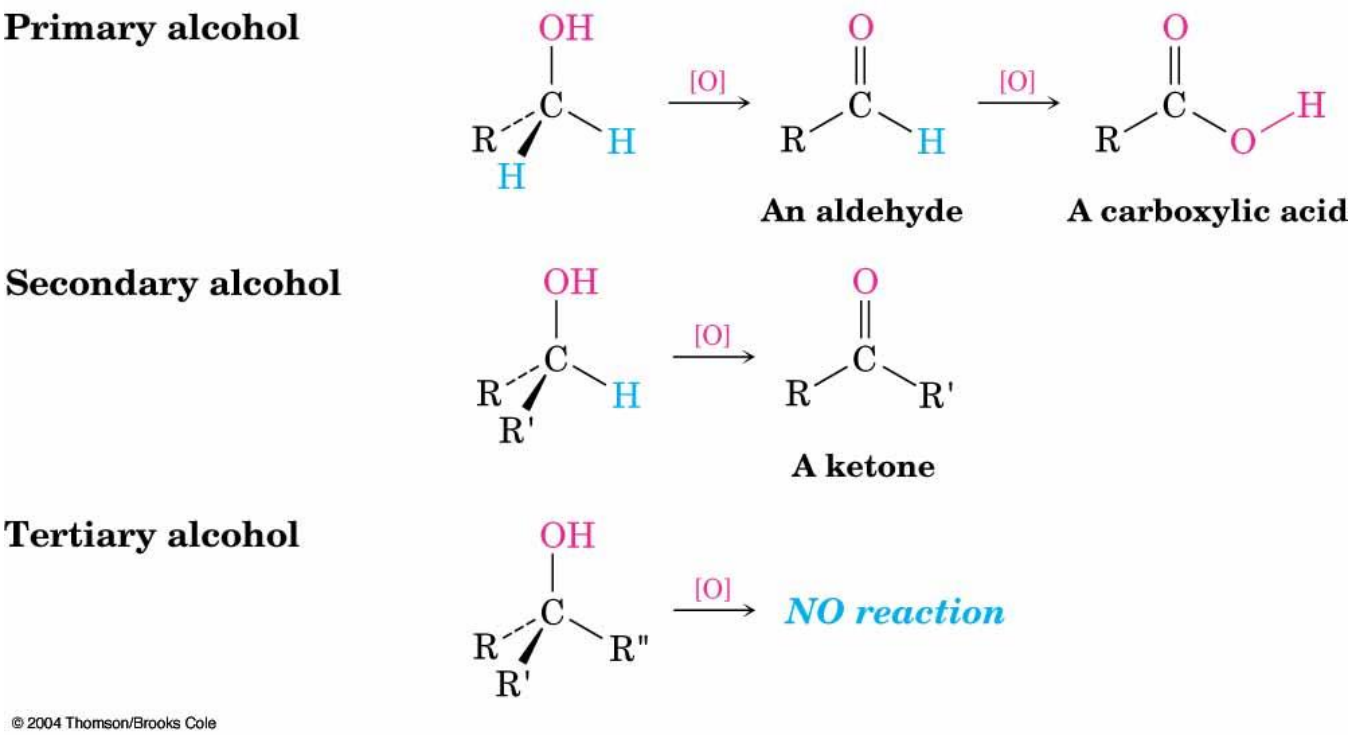
2. Conversion of Alcohols into Alkyl Halides

- 3° alcohols are converted by HCl or HBr at low temperature
- 1° and alcohols are resistant to acid – use $SOCl_2$ or PBr_3 by an S_N2 mechanism



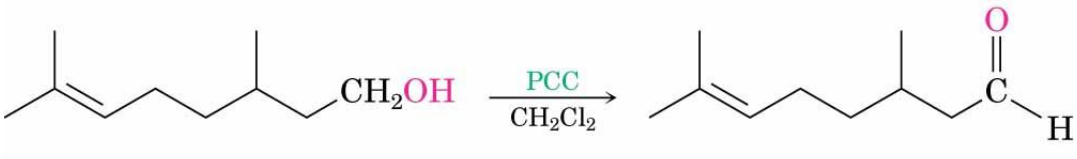
3.Oxidation of Alcohols

- Can be accomplished by inorganic reagents, such as $KMnO_4$, CrO_3, and $Na_2Cr_2O_7$ or by more selective, expensive reagents

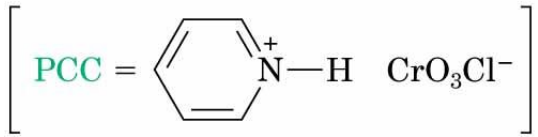


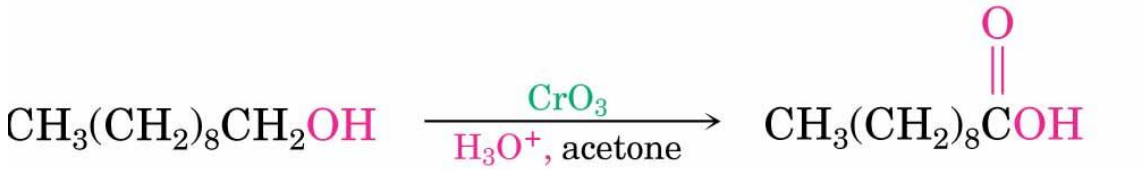
Oxidation of Primary Alcohols

- To aldehyde: pyridinium chlorochromate (PCC, $C_5H_6NCrO_3Cl$) in dichloromethane
- Other reagents produce carboxylic acids



Citronellol (from rose oil) **Citronellal (82%)**

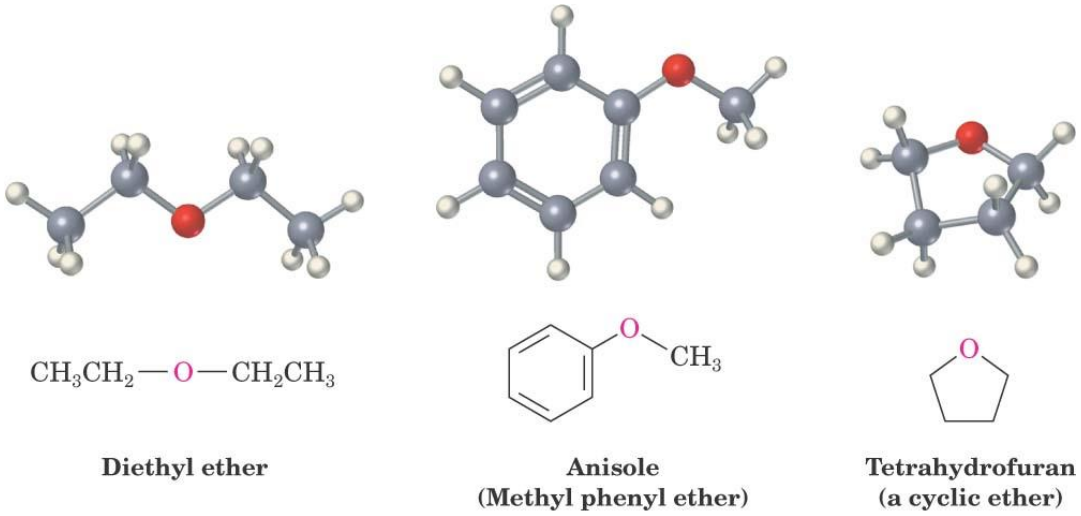




1-Decanol **Decanoic acid (93%)**

Ethers and Their Relatives

- An **ether** has two organic groups (alkyl, aryl, or vinyl) bonded to the same oxygen atom, R–O–R′
- Diethyl ether is used industrially as a solvent
- Tetrahydrofuran (THF) is a solvent that is a cyclic ether
- *Thiols* (R–S–H) and *sulfides* (R–S–R′) are sulfur (for oxygen) analogs of alcohols and ethers



Diethyl ether | **Anisole (Methyl phenyl ether)** | **Tetrahydrofuran (a cyclic ether)**

The Williamson Ether Synthesis

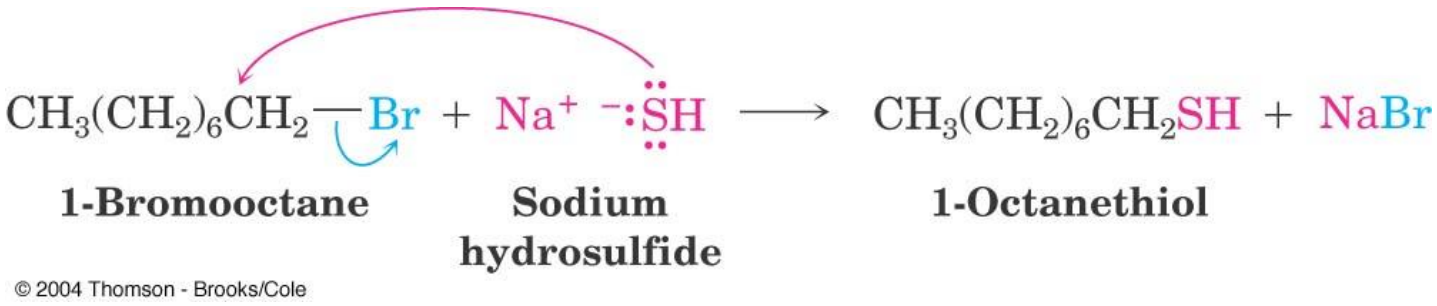
- Reaction of metal alkoxides and primary alkyl halides and tosylates
- Best method for the preparation of ethers
- Alkoxides prepared by reaction of an alcohol with a strong base such as sodium hydride, NaH

Cyclopentoxide ion

Cyclopentyl methyl ether (74%)

Thiol Formation

- From alkyl halides by displacement with a sulfur nucleophile such as –SH
  - The alkylthiol product can undergo further reaction with the alkyl halide to give a symmetrical sulfide, giving a poorer yield of the thiol



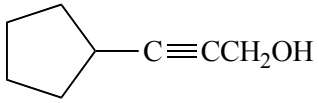
Practice Problems

1. Which of the following is 3-pentyn-1-ol?

a. $CH_3CH_2C{\equiv}CCH_2OH$

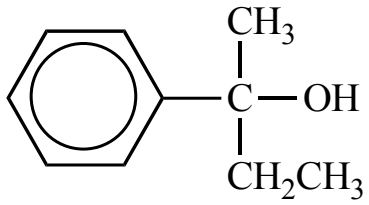
b. $CH_3C{\equiv}CCHCH_3$ (OH)

***c.** $CH_3C{\equiv}CCH_2CH_2OH$

d. 

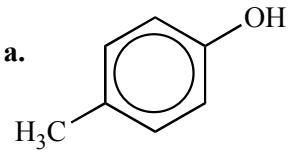
e. $CH_3C{\equiv}CCH_2CH_2CH_2OH$

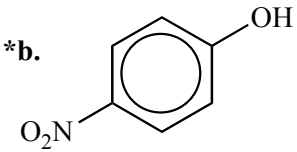
2. What is the name of the following alcohol?

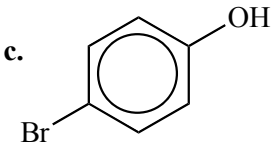


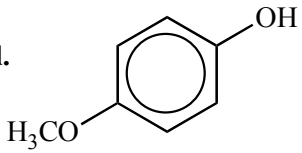
a. 1-ethyl-2-methylbenzyl alcohol **b.** methylphenylpropanol
c. 2-methyl-2-phenyl-1-propanol ***d.** 2-phenyl-2-butanol
e. cumyl alcohol

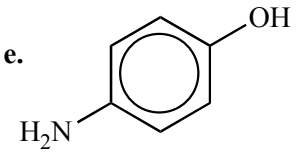
3.Which of the following phenols is the strongest acid?

a. 

***b.** 

c. 

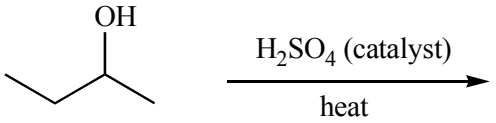
d. 

e. 

4. What type of compound is formed when a secondary (2°) alcohol is treated with $KMnO_4$?

- **a.**an alkene **b.**an alkyne **c.** an aldehyde
- ***d.**a ketone **e.**an acid

5. What is the major product of the following reaction?



a. $CH_3CH_2CH{=}CH_2$ **b.** *cis*-$CH_3CH{=}CHCH_3$
***c.** *trans*-$CH_3CH{=}CHCH_3$ **d.** $(CH_3)_2C{=}CH_2$
e. none of the above

6. Which of the following is a Grignard reagent?

***a.**CH3MgCl **b.**CH3Li **c.**(CH3)2 CuLi
d.CH3Na **e.**(CH3)2 Zn

7. Reduxction of carboxylic acid will give ?

***a.**primary alcohol **b.**secondary alcohol **c.**tert-alcohol
d.ketone **e.**aldehyde