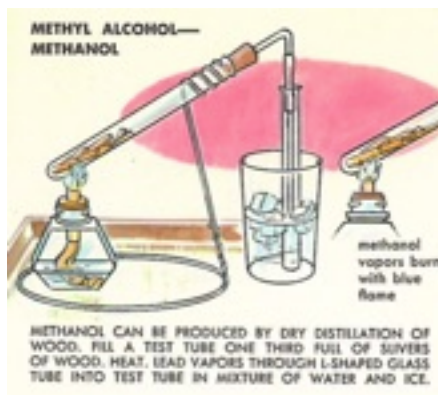
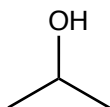
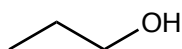
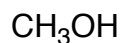


Chapter 13: Alcohols and Phenols

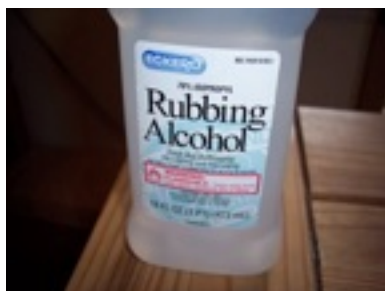
[Chapter 9 Sections: 9.10; Chapter 13 Sections: 13.1-13.3, 13.9-13.10]

Nomenclature of Alcohols

simple alcohols

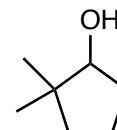
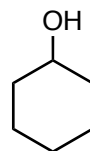
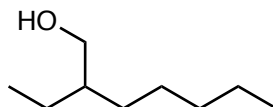
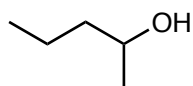


Eddie Sachs
1927-1964

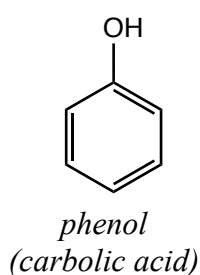
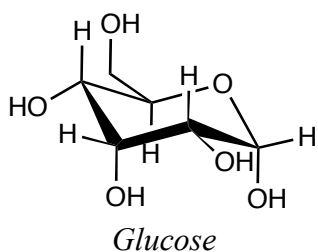


Whisky	40 - 60
Brandy	40 - 60
Vodka	40 - 60
Tequila	35 - 40
Pao-Chu	30 - 60
Saké	14 - 18
Wine	12 - 16
Beer	4 - 15

larger alcohols



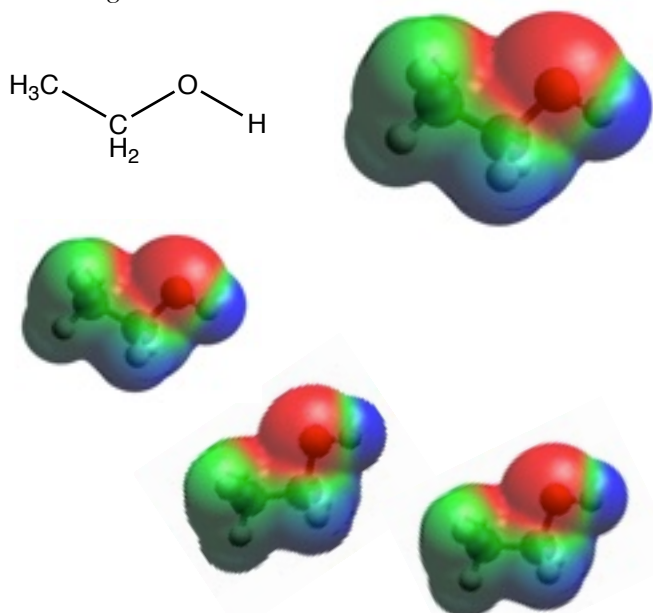
- find the longest continuous carbon chain that contains the OH group (hydroxyl group)
- number the chain to assign the lowest locant value to the OH
- OH takes precedence over C=C and triple bonds
- in cyclic alcohols, the OH group is always at the 1-position
- alcohols are designated as 1°, 2° or 3° based on the type of carbon to which the OH group is attached



Joseph Lister
1827-1912

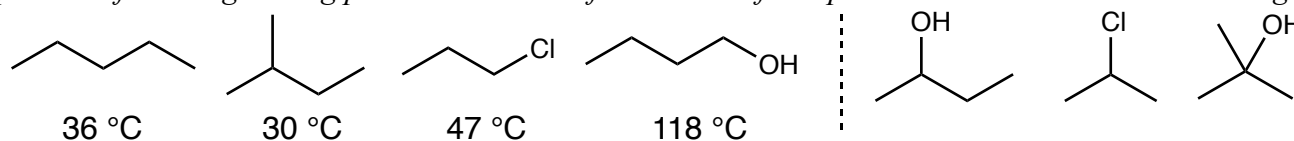
Properties of Alcohols

A. Boiling Points

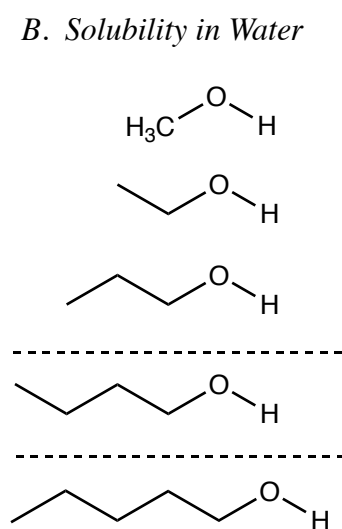


- as with alkyl halides, since oxygen is more electronegative than carbon, carbon takes on a partial positive charge and oxygen a partial negative charge leading to a polar covalent bond
- similarly, the OH bond is polarized strongly towards the oxygen
- the strongly polarized O–H bond results in a very strong dipole-dipole interaction termed a "hydrogen bond"
- alcohols have higher boiling points than similar weight non-hydrogen bonding compounds as a result of this additional intermolecular "hydrogen bonding" interaction
- the term "hydrogen bond" is a misnomer since it is NOT actually a bond, just a strong interaction (~10-20 kJ/mole interaction versus ~300 kJ/mol for actual bonds)

Explain the following boiling point observations for a series of compounds with similar molecular weights



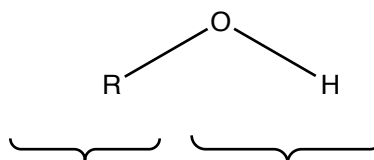
B. Solubility in Water



hexanol
heptanol
etc.



- "like dissolves like"
- alcohols are polar compounds and capable of hydrogen bonding
- low molecular weight alcohols are soluble (i.e., "miscible") in polar solvents and hydrogen bonding solvents (like water)
- higher molecular weight alcohols are more "alkane like" and are rejected by hydrogen bonding solvents (therefore, they are NOT soluble or immiscible)

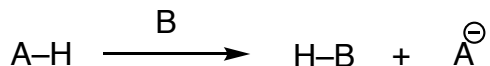


Acidity of Alcohols

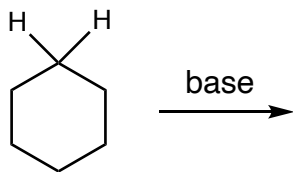
Summary of Factors that Affect Acidity



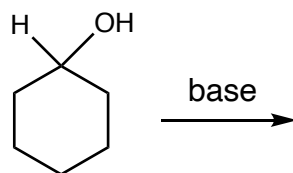
I
M
P
O
R
T
A
N
C
E



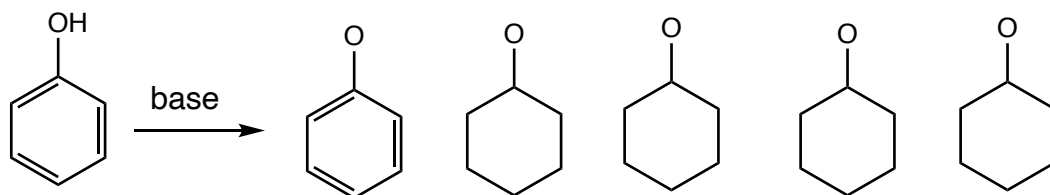
1. **A**tom: what type of atom is the negative charge placed onto when the proton is removed?
2. **R**esonance: is the resulting negative charge of the conjugate base stabilized by resonance?
3. **I**nduction: are there any nearby groups that can inductively stabilize the negative charge of the conjugate base?



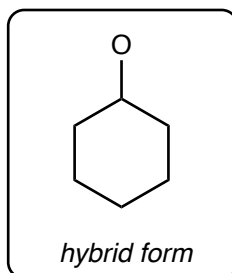
cyclohexane
pKa =



cyclohexanol
pKa =

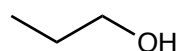


phenol
pKa = 10

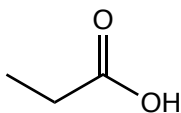


- resonance interactions spread charge over multiple atoms
- since delocalization of charge stabilizes charge, resonance-stabilized anions are always more stable than non-resonance stabilized anions
- phenols are more acidic than typical alcohols

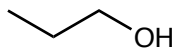
Rationalize the following differences in pKa



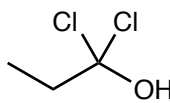
pKa = 16



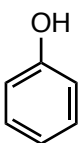
pKa = 5



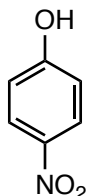
pKa = 16



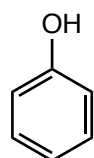
pKa = 12



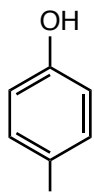
pKa = 10



pKa = 7



pKa = 10

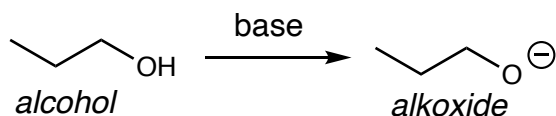


pKa = 11

- electron-withdrawing substituents close to the site of deprotonation serve to stabilize the negative charge and thereby increase acidity
- electron-donating substituents close to the site of deprotonation serve to destabilize the negative charge and thereby decrease acidity

Problems: 6,7

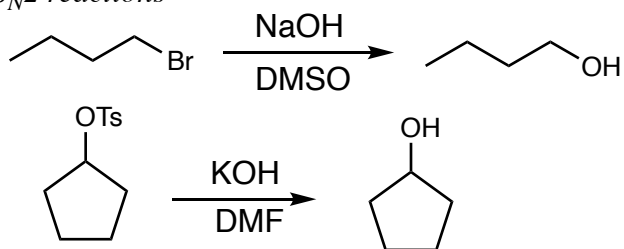
Typical Bases Used



- typical bases for deprotonating alcohols are sodium metal (Na^\ominus), lithium metal (Li^\ominus), sodium hydride (NaH), or sodium amide (NaNH_2)

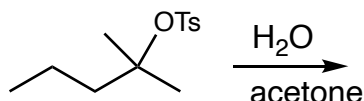
Synthesis of Alcohols

A. $\text{S}_{\text{N}}2$ reactions



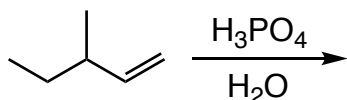
- hydroxide as a nucleophile will react with methyl, 1° and 2° alkyl halides and tosylates to form alcohols
- 3° alkyl halides and tosylates cannot react via the $\text{S}_{\text{N}}2$ reaction ($\text{E}2$ predominates)
- a polar aprotic solvent (DMSO, DMF) are favored for these reactions

B. SN1 reactions

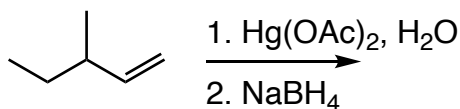


- SN1 reactions require a weaker base than SN2 reactions to prevent competing elimination reactions
- H₂O is the nucleophile
- 2° and 3° alkyl halides and tosylates react via the SN1 reaction (methyl and 1° substrates are unreactive)
- typically water itself is used as solvent (and nucleophile) or a mixture of water and an organic solvent such as acetone

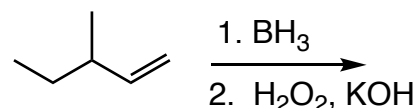
C. Hydration of Alkenes



- acid-catalyzed hydration
- Markovnikov addition
- rearrangements of intermediate carbocation are possible



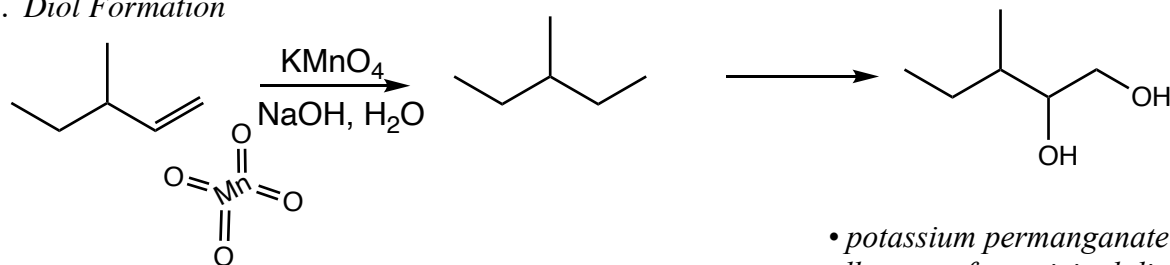
- oxymercuration
- Markovnikov addition
- no rearrangements



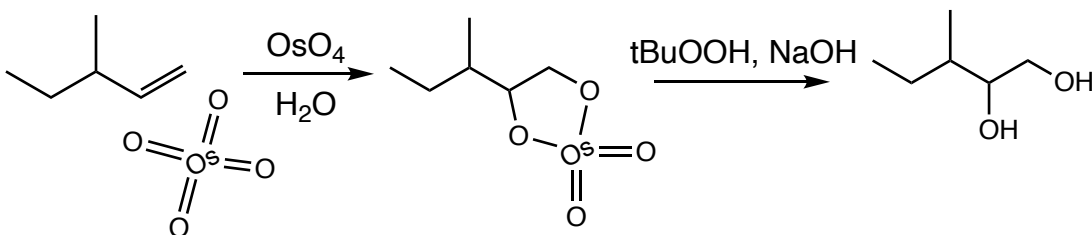
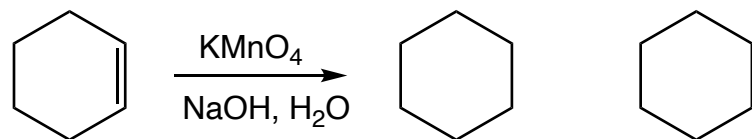
- hydroboration
- anti-Markovnikov addition
- no rearrangements

Problems: 8,9

D. Diol Formation



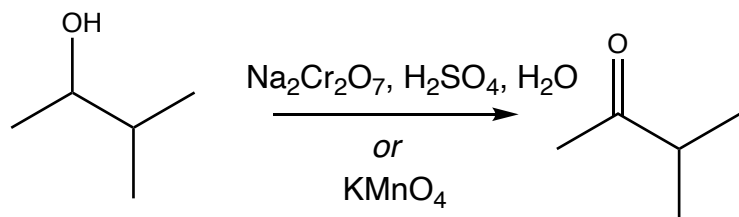
- potassium permanganate reacts with alkenes to form vicinal diols
- the reaction takes place via syn addition



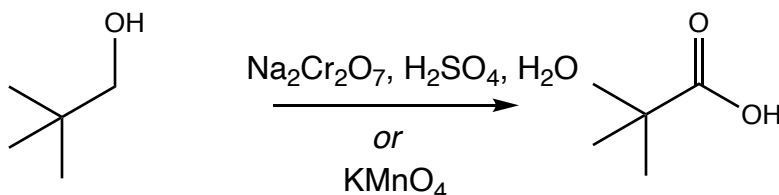
Barry Sharpless
1941-
2001 Nobel Prize

- Osmium tetroxide provides the same product as KMnO₄ with alkenes, but the OsO₄ can be used in catalytic amounts if tBuOOH is present to re-oxidize the OsO₂ byproduct

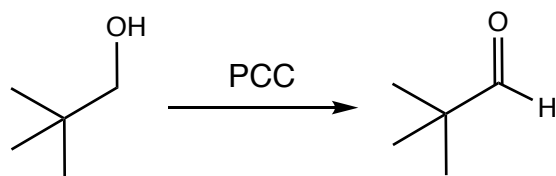
Oxidation of Alcohols



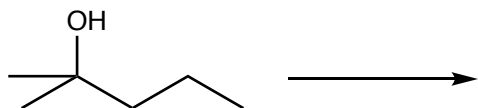
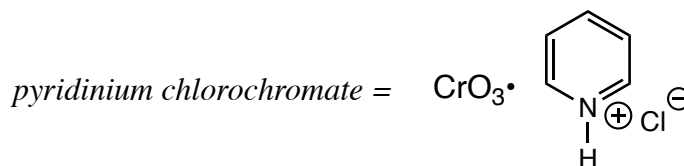
• oxidation of 2° alcohols with strong oxidizing agents results in the formation of ketones



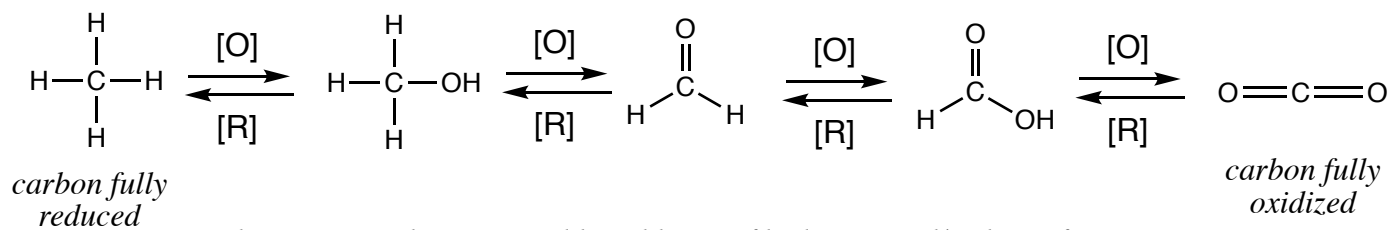
• oxidation of 1° alcohols with strong oxidizing agents results in the formation of carboxylic acids



• oxidation of 1° alcohols with the weaker oxidizing agent PCC results in the formation of aldehydes



• 3° alcohols cannot be oxidized to carbonyl compounds



- reductions are characterized by addition of hydrogen and/or loss of oxygen
 - oxidations are characterized by addition of oxygen and/or loss of hydrogen
-

Chapter 13 *Essential Concepts*

1. Know the names and uses of common alcohols
2. Be able to apply systematic nomenclature to acyclic and cyclic alcohols
3. Know how the presence of the hydroxyl group (OH) affects the properties of alcohols (boiling point, solubility, acidity)
4. Be able to apply the ARI effects of acidity towards evaluating the acidity of organic compounds.
5. Know the reagents commonly used to deprotonate alcohols to form alkoxides
6. Know how to form alcohols via SN1 and SN2 reactions on alkyl halides and tosylates, and the three ways (and nuances involved) to hydrate alkenes.
7. Know the reagents for diol formation from alkenes and the stereochemical implications of the reaction.
8. Know how alcohols are commonly transformed into alkyl halides
9. Understand and know the reagents for oxidation of 1° and 2° alcohols and the lack of reactivity of 3° alcohols.