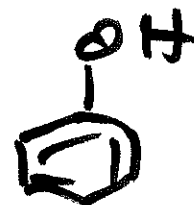


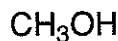
# Chapter 13: Alcohols and Phenols

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



## Nomenclature of Alcohols

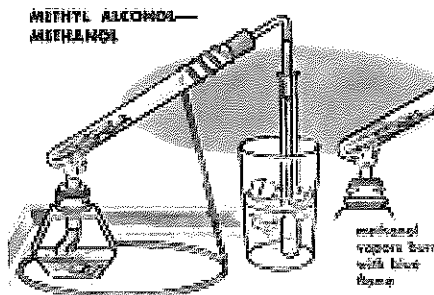
simple alcohols



**METHANOL**



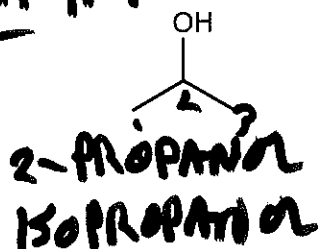
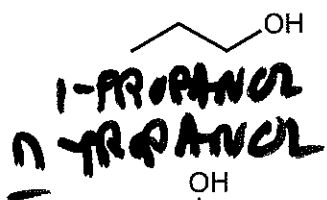
**ETHANOL**  
**ETHYL ALCOHOL**



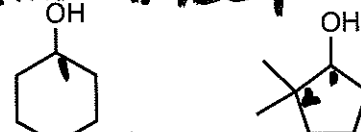
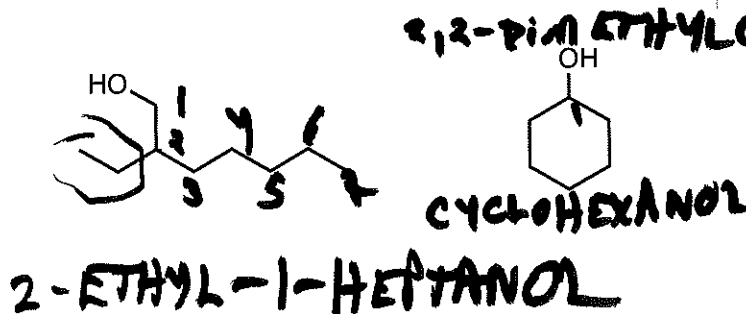
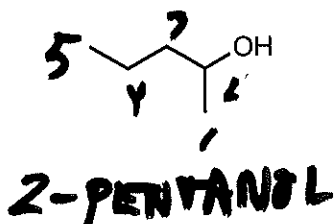
METHANOL CAN BE PRODUCED BY DRY DISTILLATION OF WOODS. FILL A TEST TUBE ONE THIRD UP WITH CHIPS OF WOOD. HEAT. LEAD VAPOR THROUGH L-SHAPED GLASS TUBE INTO TEST TUBE IN Mixture OF WATER AND ICE.



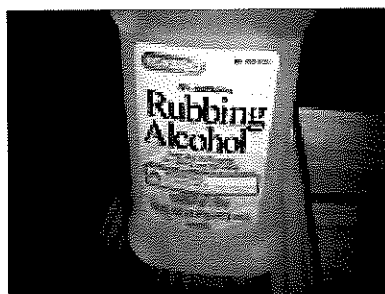
**Eddie Sachs**  
1927-1964



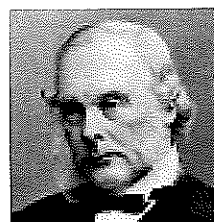
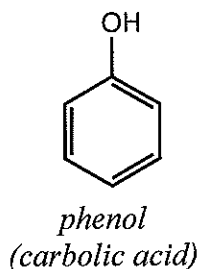
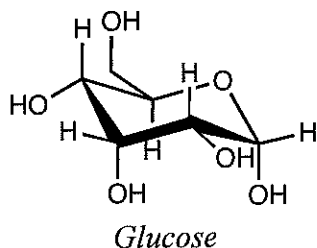
larger alcohols



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



- 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

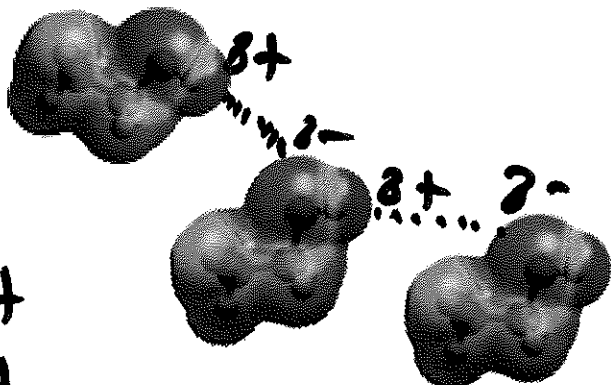
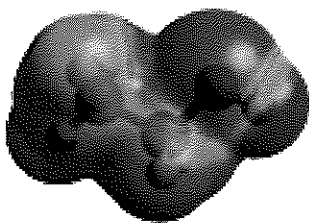
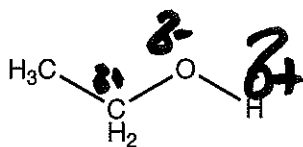


**Joseph Lister**  
1827-1912

# Properties of Alcohols

## A. Boiling Points

LIQ  $\xrightarrow{\Delta}$  GAS  $\cdot$  MW  $\cdot$  INTERMOLEC. FORCES



-OH  
-NH

- 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

<chem>CCCCC</chem> 36 °C	<chem>CC(C)CC</chem> 30 °C	<chem>CCCCl</chem> 47 °C	<chem>CCCCO</chem> 118 °C	<hr/>	<chem>CC(O)CC</chem> 100 °C	<chem>CC(Cl)CC</chem> 75 °C	<chem>CC(C)(C)O</chem> 82 °C
<b>• NONPOLAR</b> <b>• UNBRANCHED</b>	<b>• NONPOLAR</b> <b>• BRANCHED</b>	<b>• POLAR</b>	<b>• POLAR</b> <b>• H-BOND</b> <b>• UNBRANCHED</b>		<b>• POLAR</b> <b>• H-BOND</b> <b>• BRANCHED</b>	<b>• POLAR</b> <b>• BRANCHED</b>	<b>• POLAR</b> <b>• H-BOND</b> <b>• 2 BRANCHED</b>

## B. Solubility in Water

O

CO

CCO

CCCO

---

CCCCO

---

CCCCCO

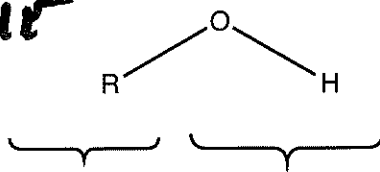
**MISCIBLE**

**PARTIALLY MISCIBLE**

**NOT MISCIBLE**



- "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)



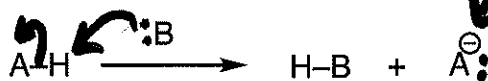
**• HYDROPHOBIC • HYDROPHILIC**

hexanol  
heptanol  
etc.

# Acidity of Alcohols

## Summary of Factors that Affect Acidity

I  
M  
P  
O  
R  
T  
A  
N  
C  
E

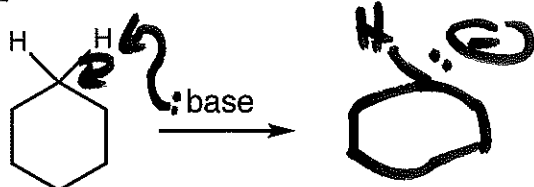


CONJUGATE  
BASE

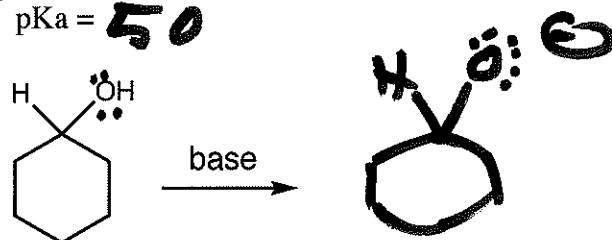


1. Atom: what type of atom is the negative charge placed onto when the proton is removed?
2. Resonance: is the resulting negative charge of the conjugate base stabilized by resonance?
3. Induction: are there any nearby groups that can inductively stabilize the negative charge of the conjugate base?

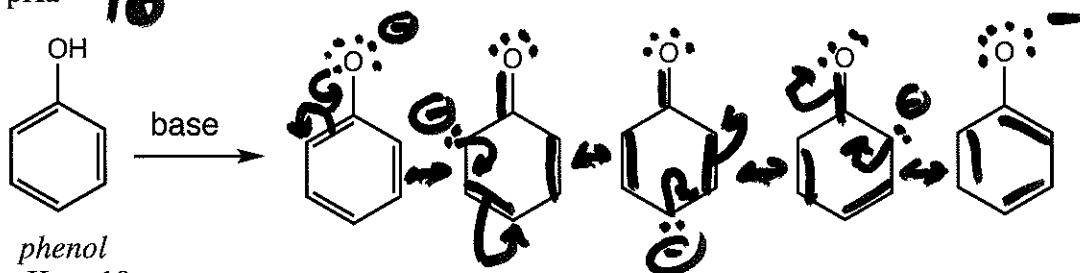
C = NOT PARTICULARLY ELECTRONEGATIVE



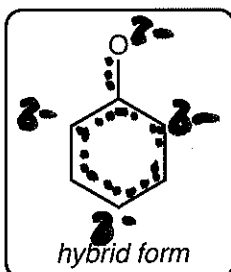
cyclohexane  
pKa = 50



cyclohexanol  
pKa = 16

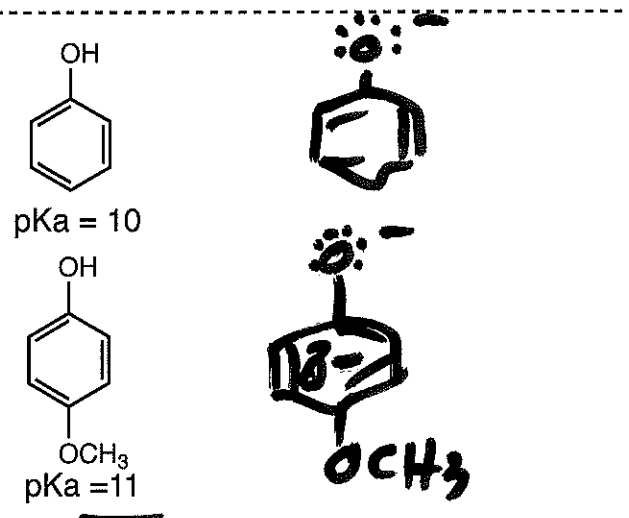
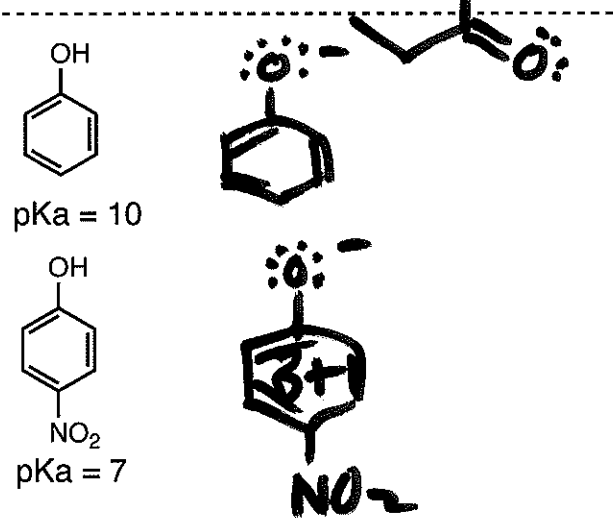
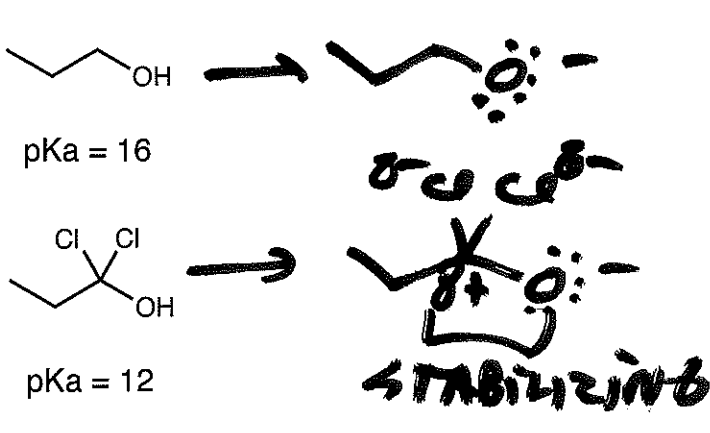
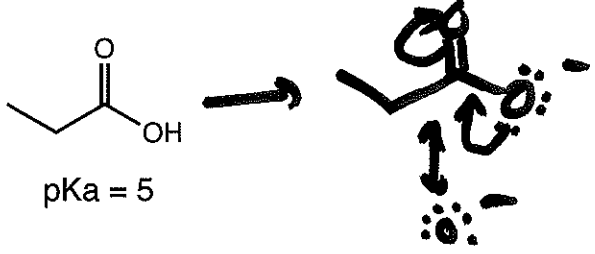
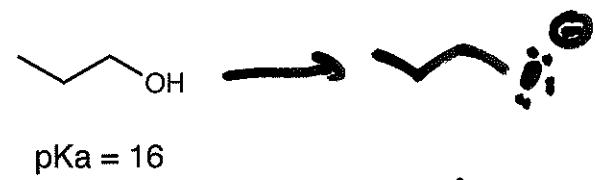


phenol  
pKa = 10

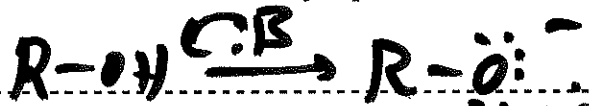


- resonance interactions spread charge over multiple atoms
- since delocalization of charge stabilizes charge, resonance-stabilized anions are always more stable than non-resonance stabilized anions
- phenols are more acidic than typical alcohols

Rationalize the following differences in pKa

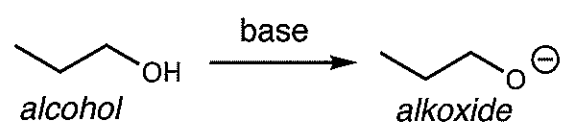


- electron-withdrawing substituents close to the site of deprotonation serve to stabilize the negative charge and thereby increase acidity
- electron-donating substituents close to the site of deprotonation serve to destabilize the negative charge and thereby decrease acidity



Problems: 6,7

Typical Bases Used

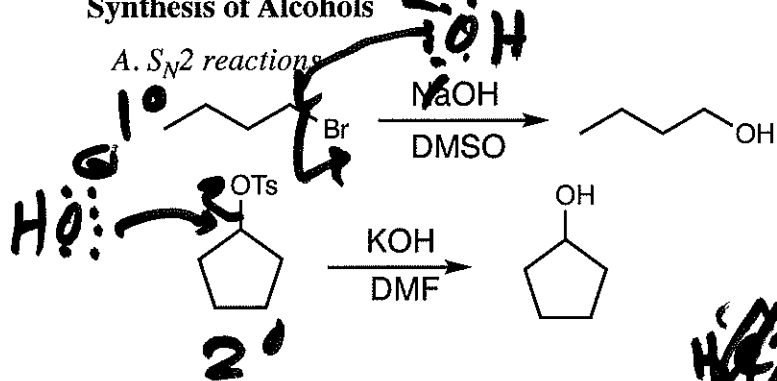


**ALKOXIDE ION**

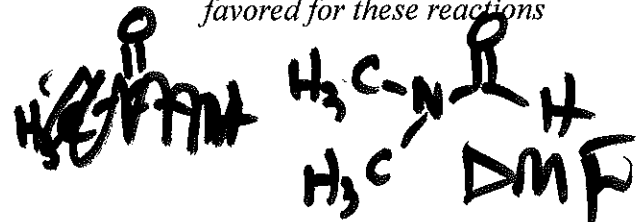
- typical bases for deprotonating alcohols are sodium metal ( $Na^\circ$ ), lithium metal ( $Li^\circ$ ), sodium hydride ( $NaH$ ), or sodium amide ( $NaNH_2$ )

Synthesis of Alcohols

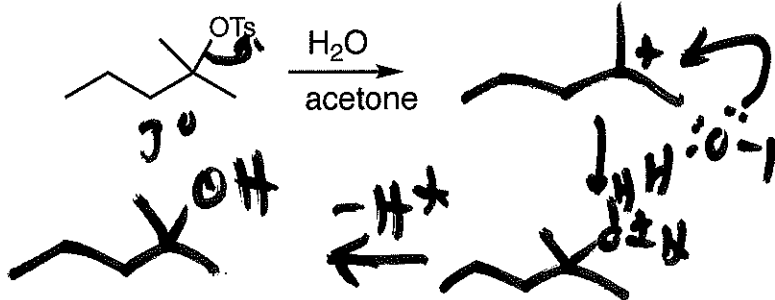
A.  $S_N2$  reactions



- hydroxide as a nucleophile will react with methyl,  $1^\circ$  and  $2^\circ$  alkyl halides and tosylates to form alcohols
- $3^\circ$  alkyl halides and tosylates cannot react via the  $S_N2$  reaction ( $E2$  predominates)
- a polar aprotic solvent (DMSO, DMF) are favored for these reactions

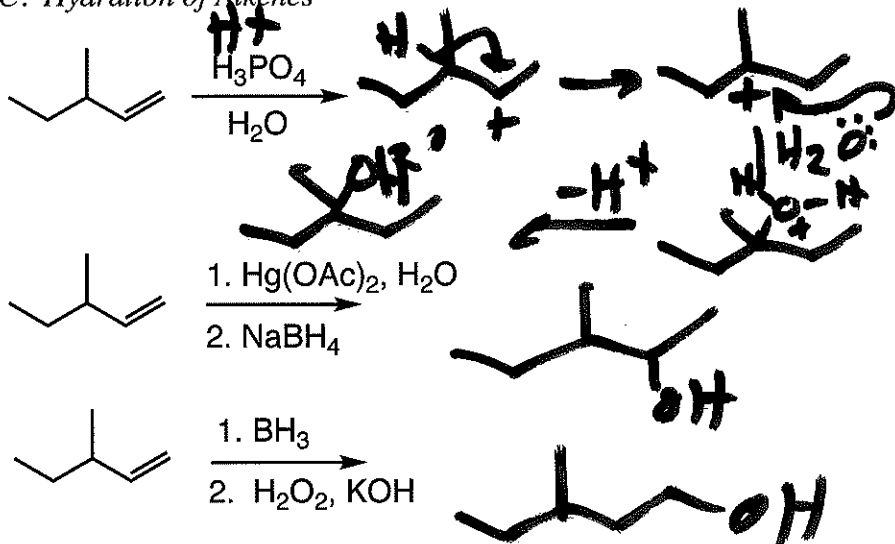


B. SN1 reactions



- SN1 reactions require a weaker base than SN2 reactions to prevent competing elimination reactions
- H<sub>2</sub>O 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

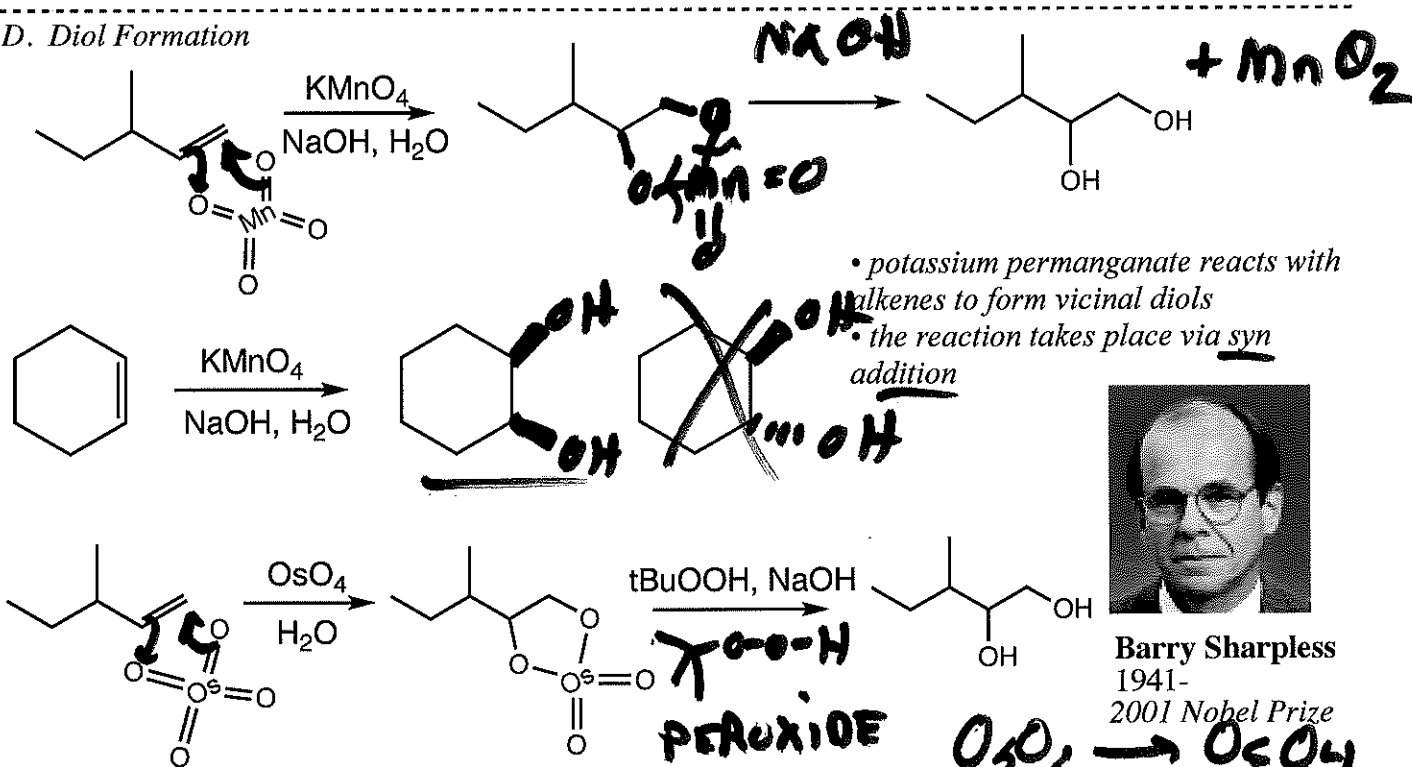
C. Hydration of Alkenes



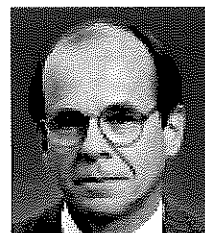
- acid-catalyzed hydration
- Markovnikov addition
- rearrangements of intermediate carbocation are possible
- oxymercuration
- Markovnikov addition
- no rearrangements
- hydroboration
- anti-Markovnikov addition
- no rearrangements

Problems: 8,9

D. Diol Formation



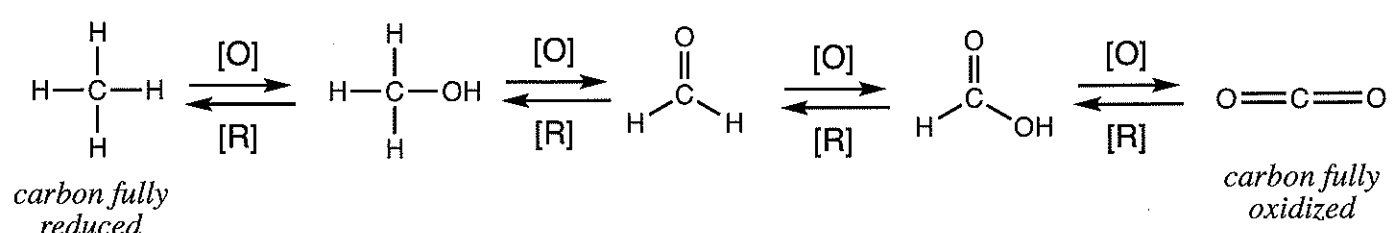
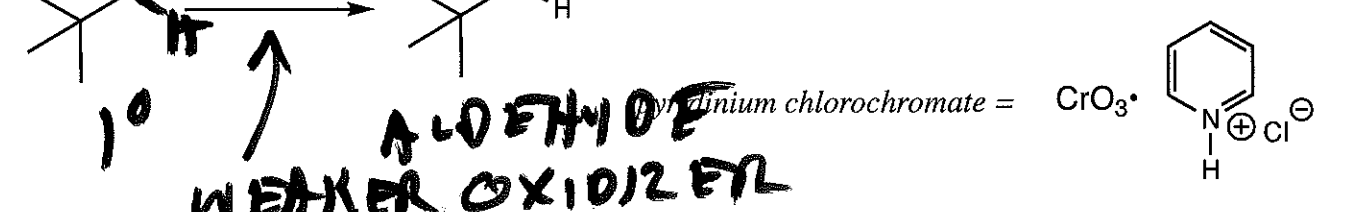
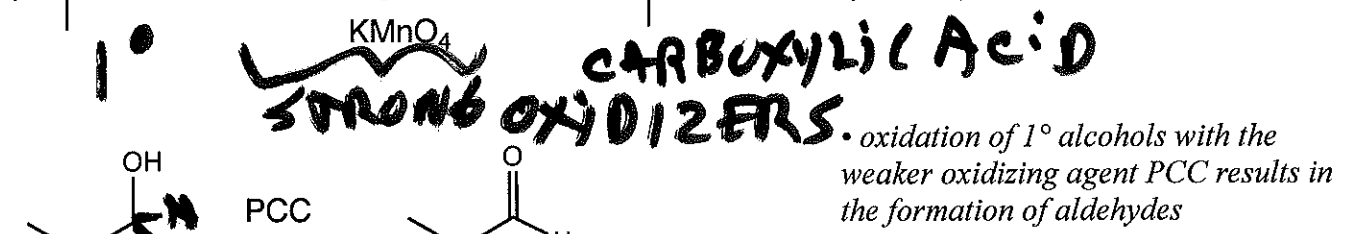
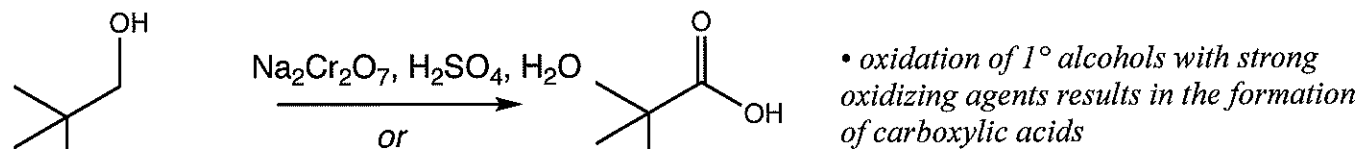
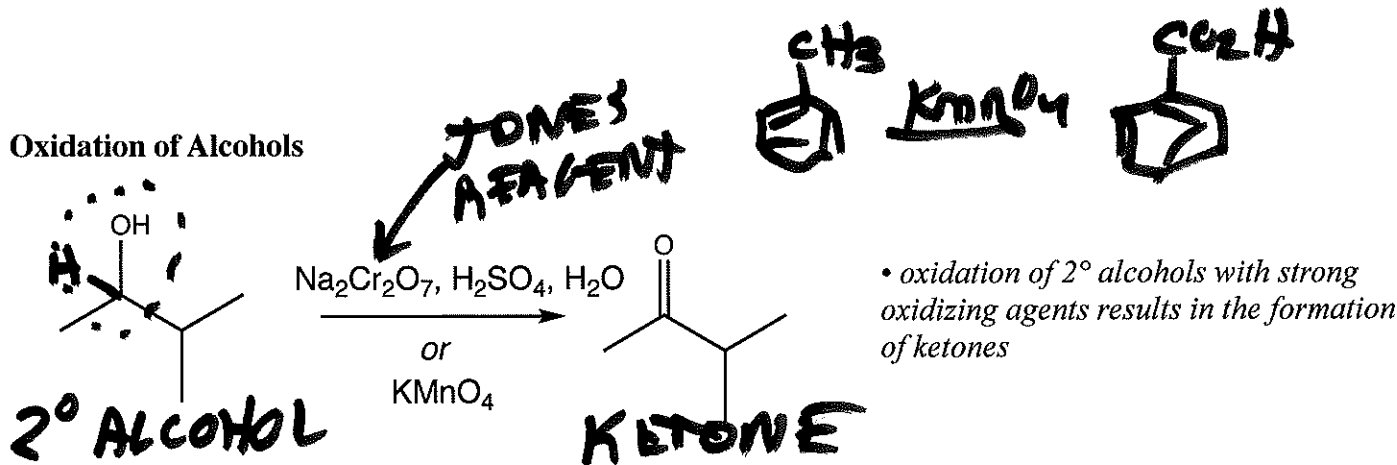
- potassium permanganate reacts with alkenes to form vicinal diols
- the reaction takes place via syn addition



Barry Sharpless  
1941-  
2001 Nobel Prize

- Osmium tetroxide provides the same product as KMnO<sub>4</sub> with alkenes, but the OsO<sub>4</sub> can be used in catalytic amounts if tBuOOH is present to re-oxidize the OsO<sub>2</sub> byproduct

Oxidation of Alcohols



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