Chemistry 304B, Spring 1999 Lecture Notes 14

Lecture 13 was a review session. READING list: Check the Web

Exam I: Regrade policy. Please read the "key" and if you feel you have not been given the proper credit, explain that carefully on a separate sheet of paper, staple it to your exam, and put it in my mailbox in the main chemistry office before Monday noon, 3/8

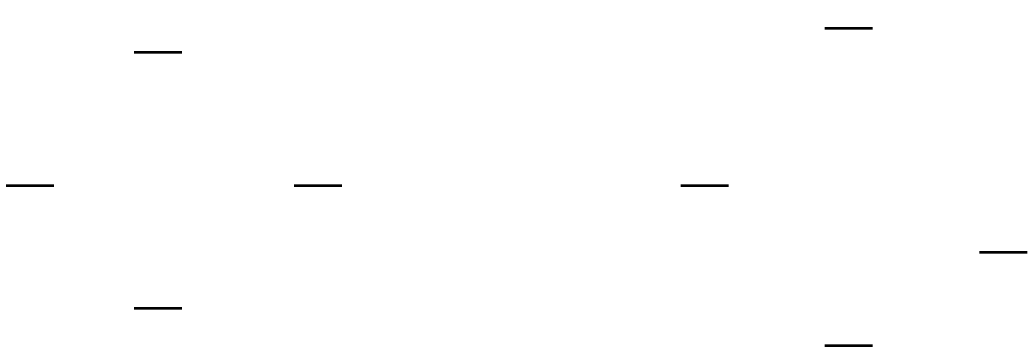
Carbonyl compounds: Key Property: POLARIZED PI BOND

X = halide, SR, OR, OH, NR_2

Nomenclature: pp756-759 Please read it.

Resonance picture:

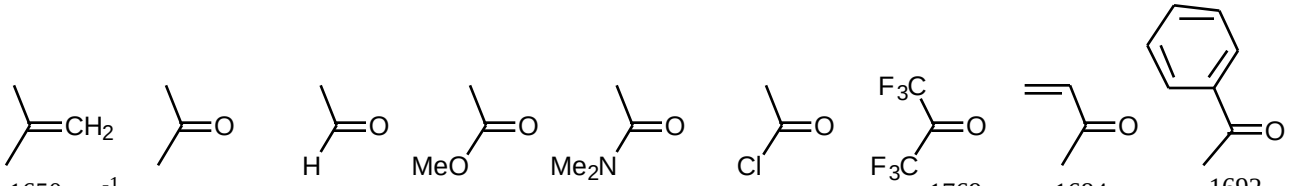
Molecular Orbital picture:



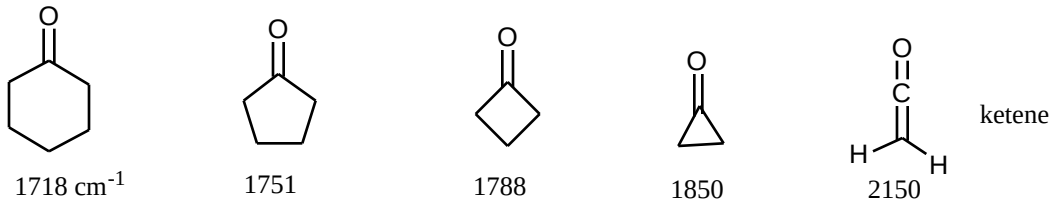
C=C C=O

Infrared Spectroscopy: C=O Good diagnostic for C=O structure: STRETCHING FREQUENCY= BOND STRENGTH

lower wavenumber → λ lower energy, weaker C=O bond.

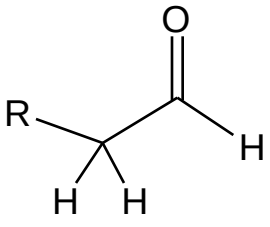


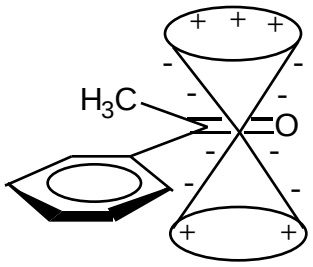
1650 cm^{-1} 1719 1733 1750 1688 1799 1769 1684 1692

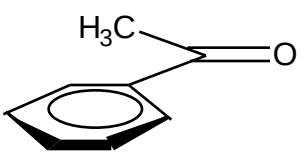


1718 cm^{-1} 1751 1788 1850 2150 ketene

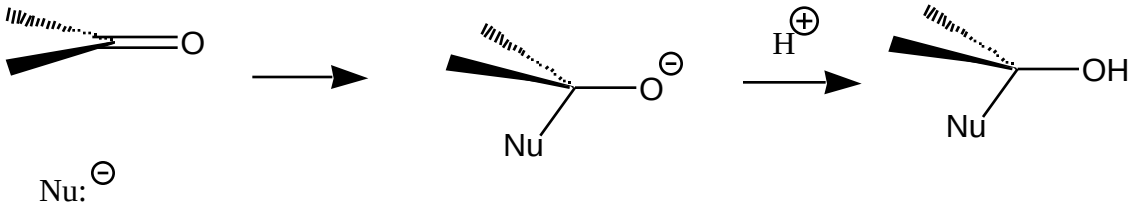
SPECIAL NMR FEATURES:



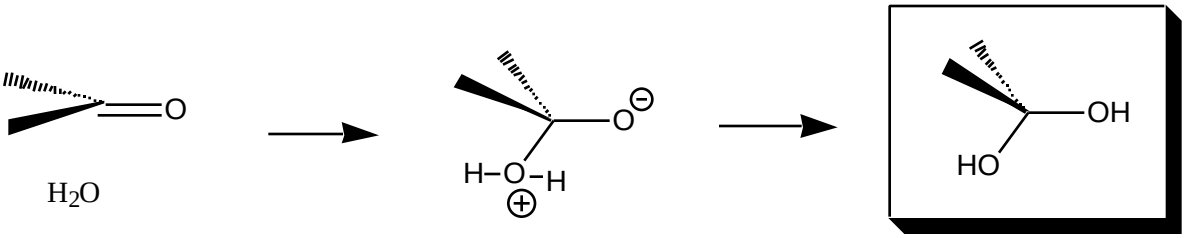




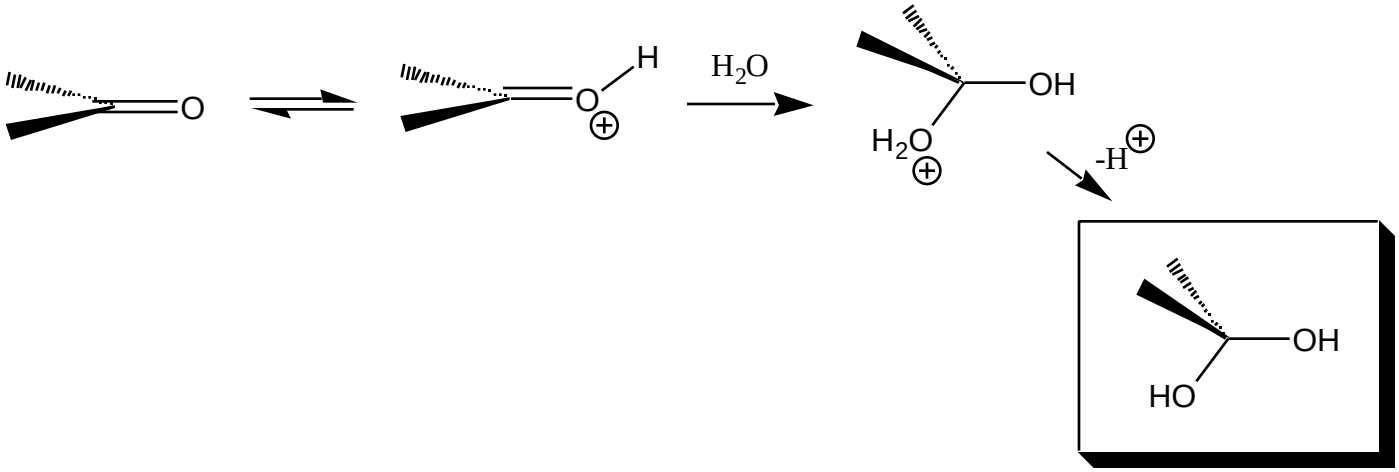
Reactivity of carbonyl groups: ADDITION OF NUCLEOPHILES



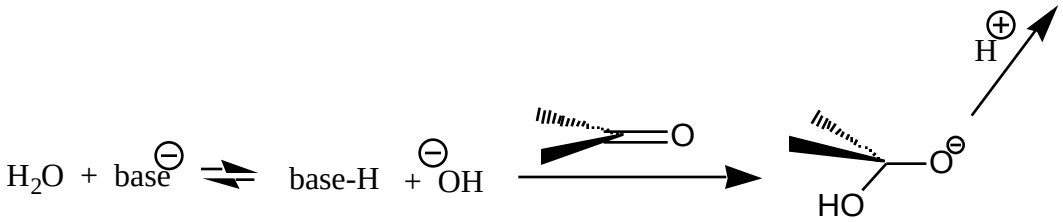
Example: Addition of water (hydration of a ketone or aldehyde)



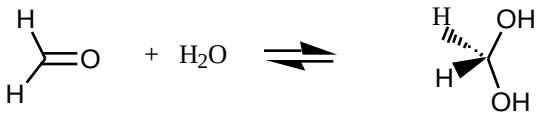
Catalysis by acid:



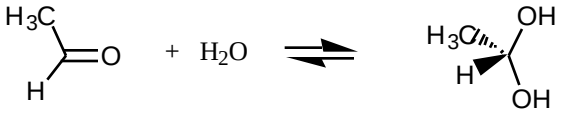
Catalysis by base:



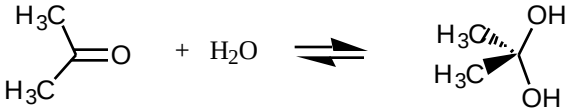
Important feature: Addition of water (and other weak nucleophiles) is easily reversible, low barriers



K_{eq} 2.3 x 10^3

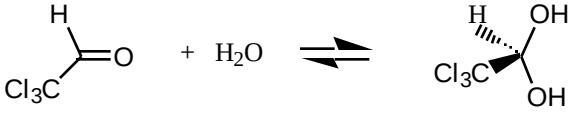


K_{eq} 1.06

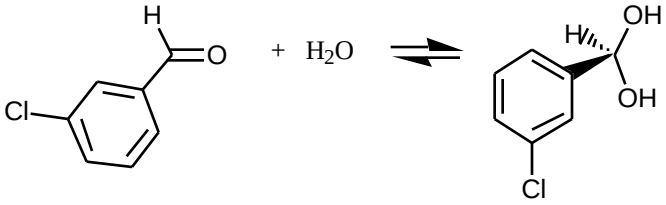


K_{eq} 2 x 10^{-3}

less stable product?
more stable reactant?

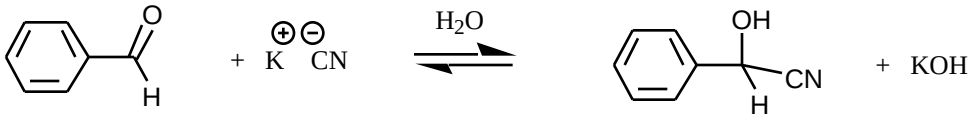


K_{eq} 2.8 x 10^4



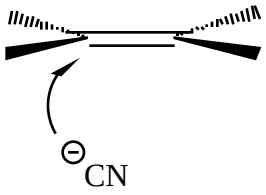
K_{eq} 2.2 x 10^{-2}

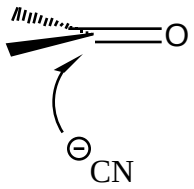
Variations: Cyanide Anion

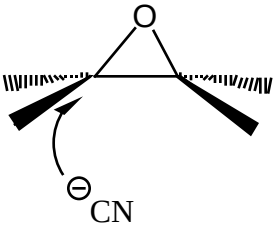


a cyanohydrin

Why does it add this way and not the reverse? why does an alkene not add nucleophiles as well?

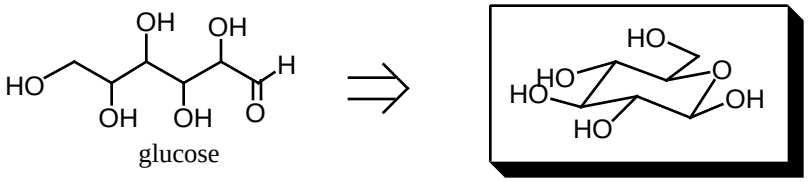




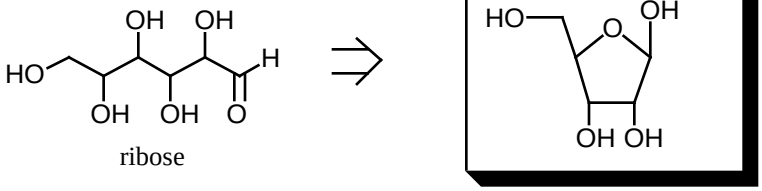


Further reactions after the addition:

A. Acetals and hemiacetals

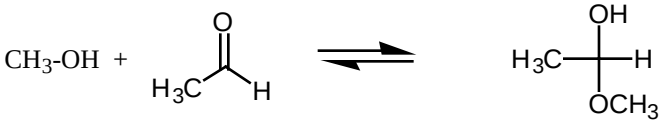


glucose



ribose

General reaction:

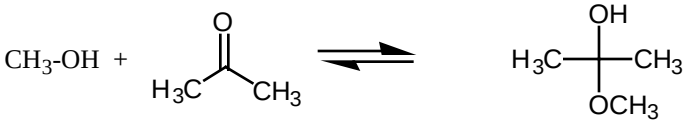


hemiacetal

As for the addition of water, a delicate balance of steric electronic effects

$K_{eq} > 1$

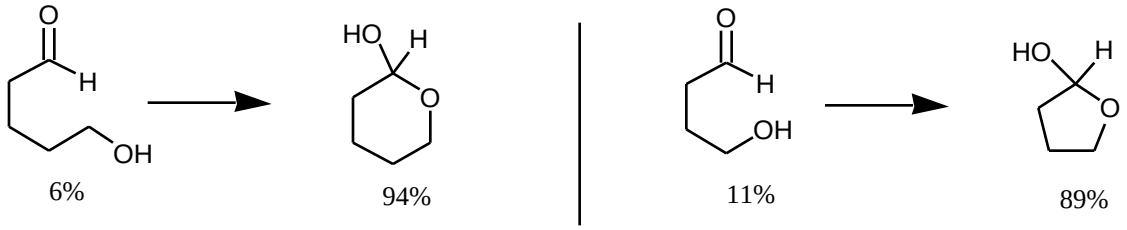
one hydroxy and one alkoxy on a carbon)



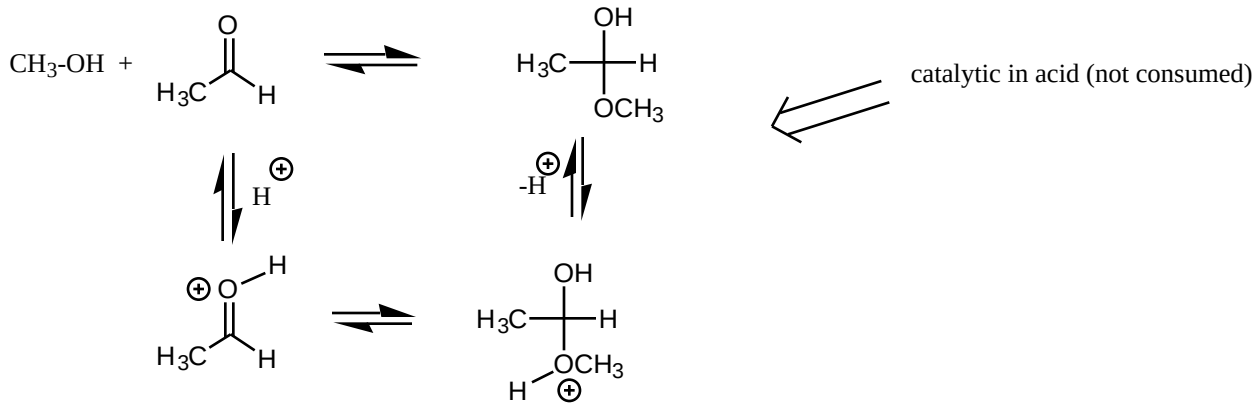
hemiacetal

$K_{eq} < 1$

one hydroxy and one alkoxy on a carbon)



Hemiacetal formation in Acid:



Further reaction in acid: