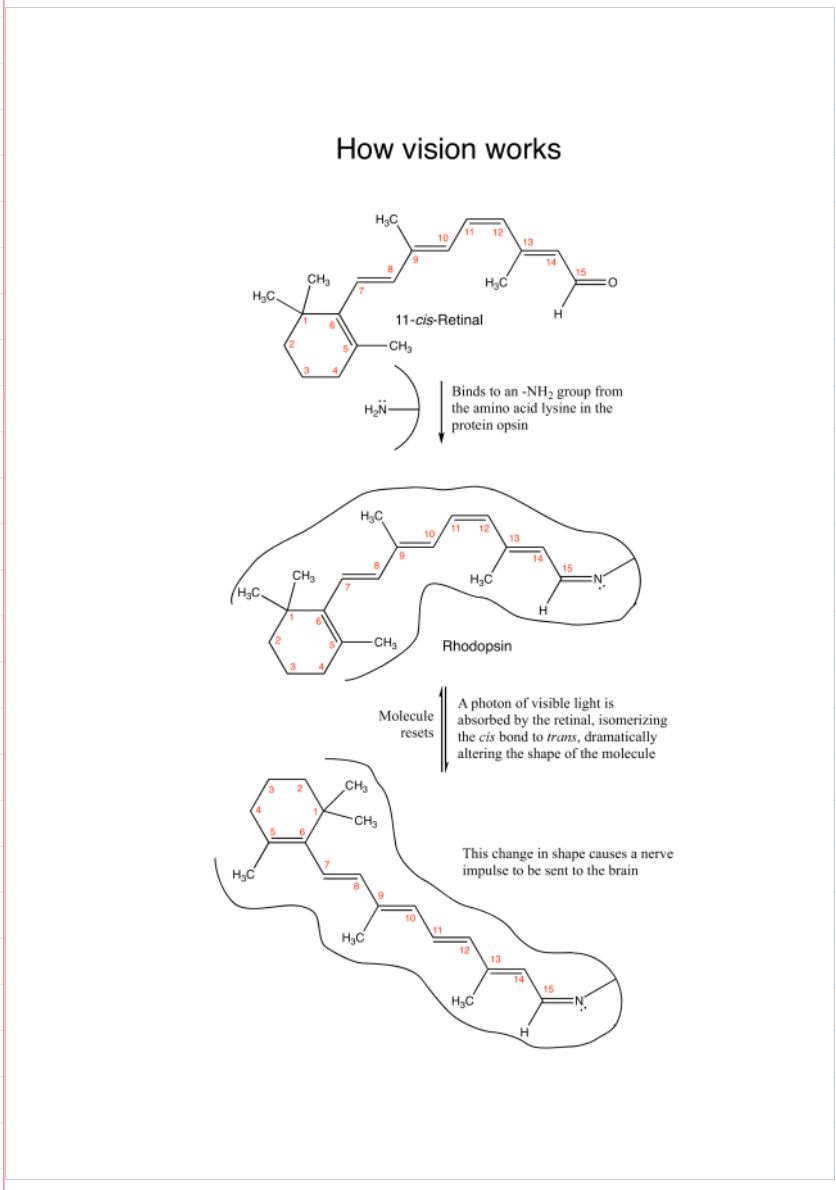
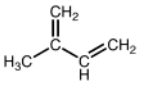
MTW4: 2-6

2023年2月6日 12:32

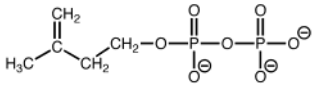
Week 4 Handouts



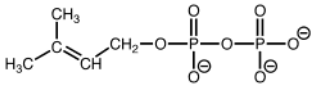
Terpenes



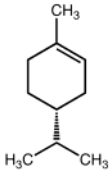
Isoprene



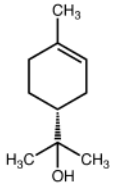
Isopentanyl diphosphate



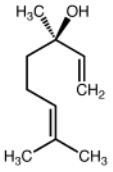
Dimethylallyl diphosphate



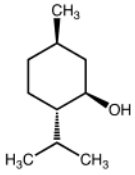
Limonene
(citrus flavor)



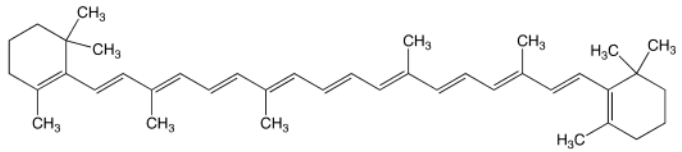
α-Terpineol
(from lilacs, used in perfume)



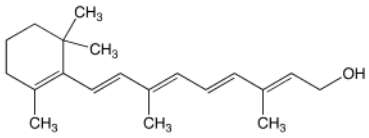
(*R*)-(-)-Linalool
(from lavender, used in perfume)



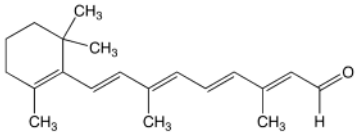
(-)-Menthol
(common flavoring from peppermint)



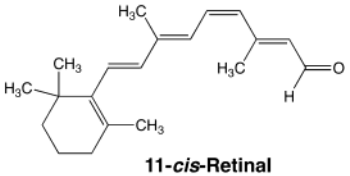
β-Carotene



Vitamin A



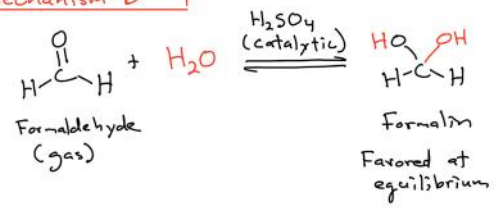
All *trans* Retinal



11-*cis*-Retinal

Geminal Diols: H_2O instead of ROH

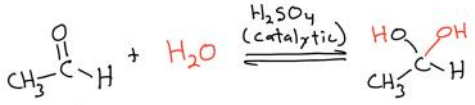
Same mechanism as hemiacetal formation: Mechanism D



Formaldehyde (gas)

Formalin

Favored at equilibrium



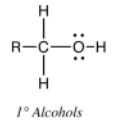
Favored at equilibrium

The geminal diol is in equilibrium with aldehydes and ketones, but it is only favored for the case of formaldehyde/formalin

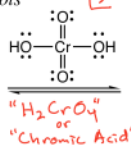
Chromic Acid Oxidation of Alcohols

Called "Jones Reagent" $(CrO_3 + H_2O$ or $K_2CrO_7) + H_2SO_4$

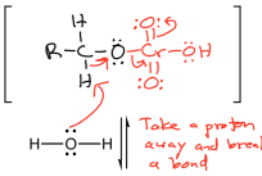
Not responsible for first step



1° Alcohols

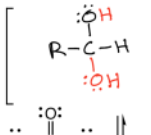


"H_2CrO_4" or "Chromic Acid"

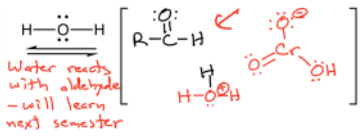


Take a proton away and break a bond

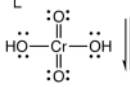
Not responsible for this step

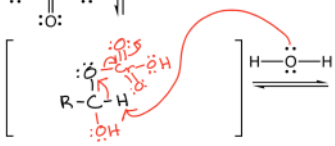


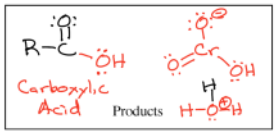
Called a geminal diol



Water reacts with aldehyde – will learn next semester







Carboxylic Acid

Products

Summary:

1° alcohols ⇒ Carboxylic Acid

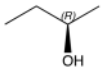
2° alcohols ⇒ Ketone

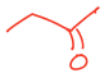
3° alcohols ⇒ NO REACTION

Regiochemistry: N/A

Stereochemistry: N/A

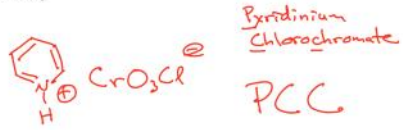
Example:

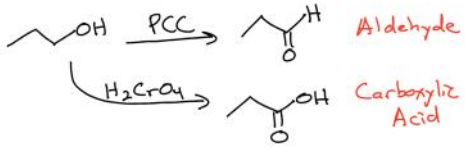


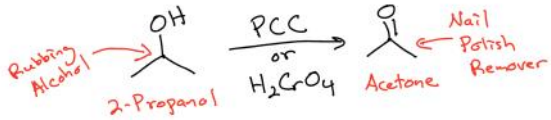


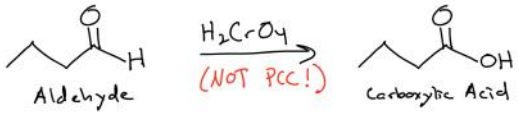
Ketone

A chromic acid-like reagent WITHOUT WATER will stop at the aldehyde when using a primary alcohol as starting material

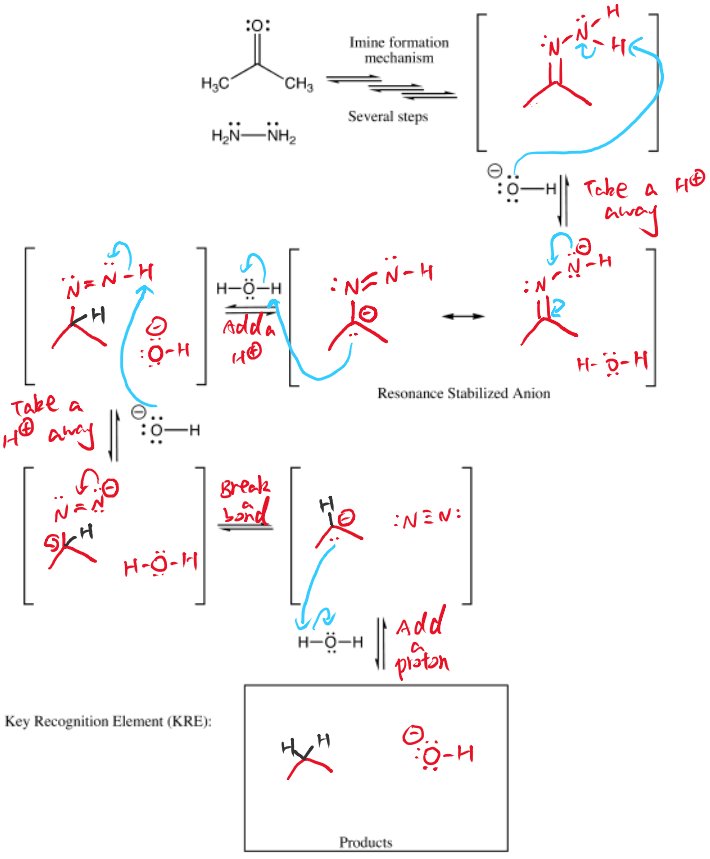






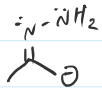


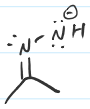
Wolff-Kishner Reduction of an Aldehyde or Ketone



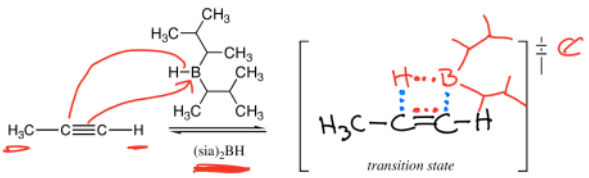
Key Recognition Element (KRE):

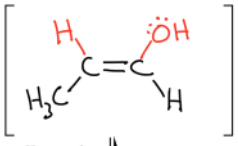
Products





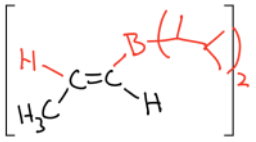
Terminal Alkyne Hydroboration



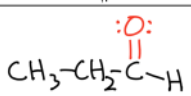


2. H_2O_2 / $HO^{\ominus}$

(Chemist opens flask and adds new reagent)



Keto-enol tautomerization



Products

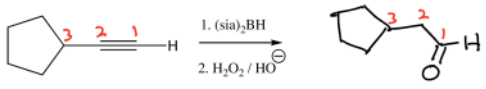
⇐ The C=O is on the C on the end → "non-Markovnikov"

Summary: The $(sia)_2BH$ reacts so the B atom attaches to the C atom on the end. The four-membered ring transition state makes both bonds simultaneously. 2. $H_2O_2/HO^{\ominus}$ → enol → keto

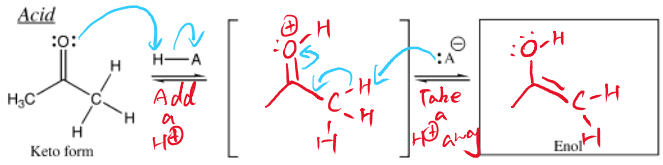
Regiochemistry: non-Markovnikov

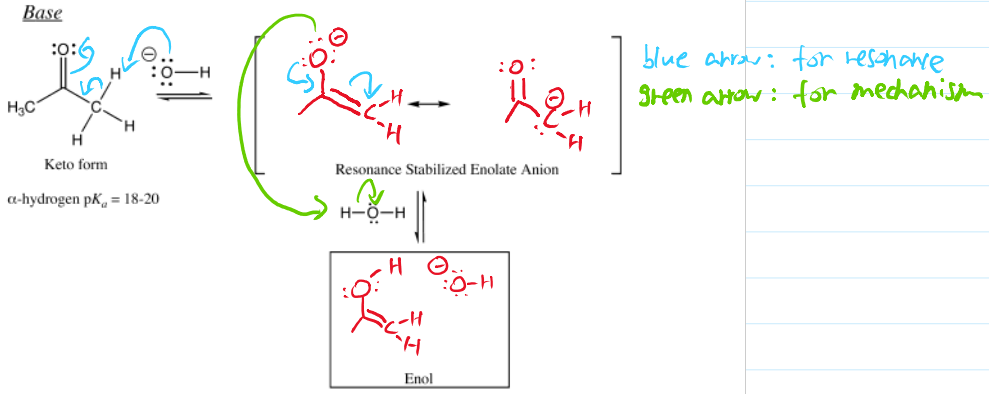
Stereochemistry: N/A

Example:



Keto-Enol Equilibrium Catalyzed by Acid or Base

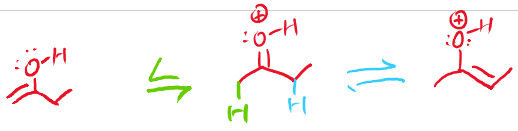




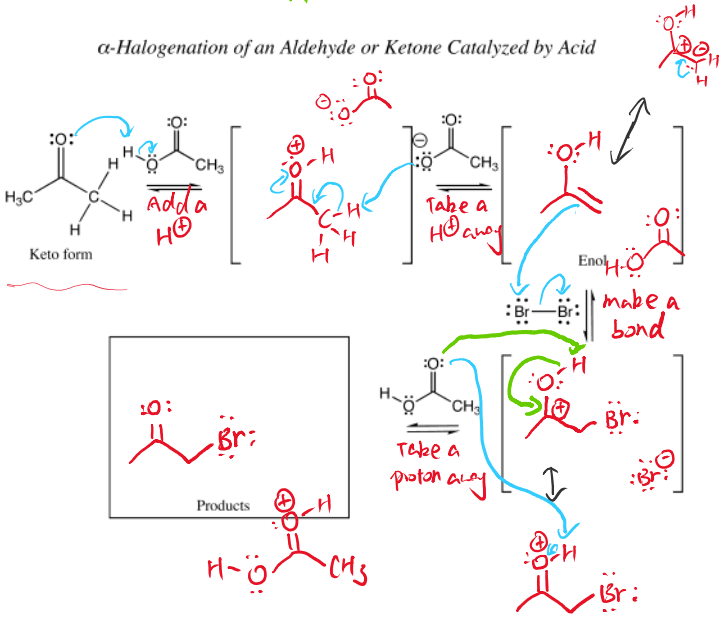
blue arrow: for resonance
green arrow: for mechanism

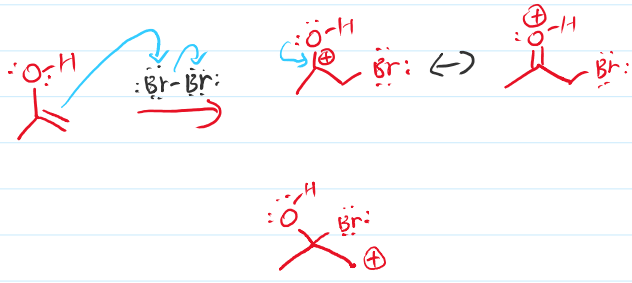
For both aldehydes and ketones, the keto form predominates at equilibrium, because C=O bonds are stronger than C=C bonds.

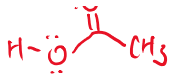
Enols are significant, however, because they react like nucleophiles, not carbonyls, and this is important in certain situations.

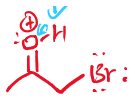


α-Halogenation of an Aldehyde or Ketone Catalyzed by Acid









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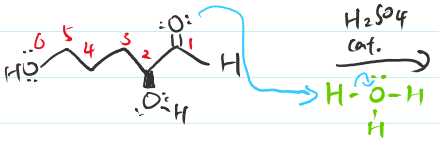
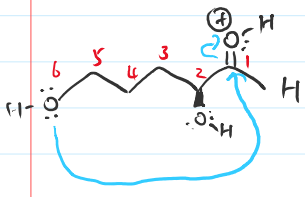
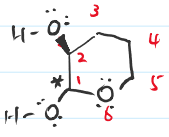
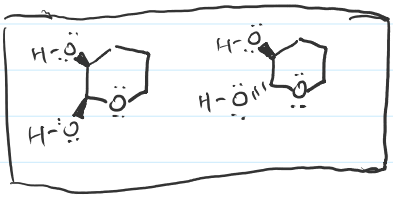


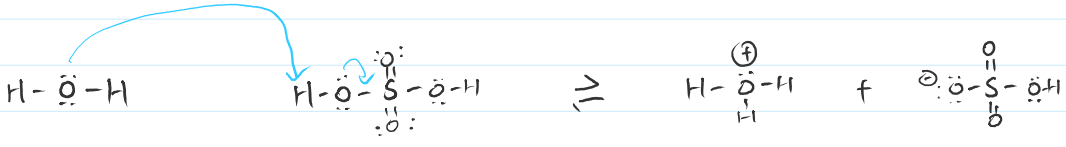
1st Add a $H^{\oplus}$

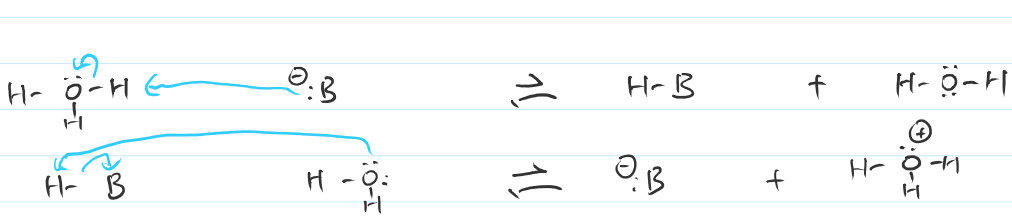


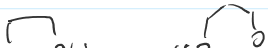
2nd

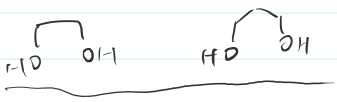


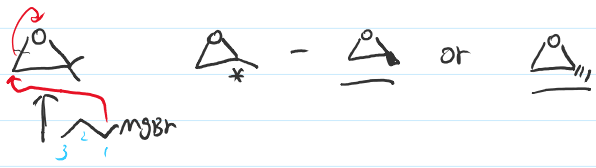


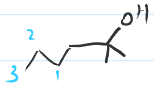


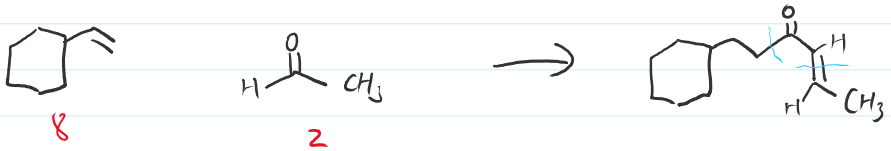


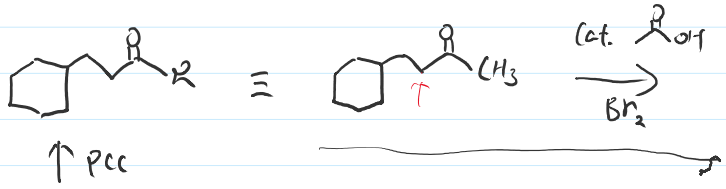





MgBr
3
2
1
or


OH
2
3
1


H
CH3
H
CH3
8
2
12


R
CH3
Cat.
OH
Br2
PCC
OH
R
MgBr
H
CH3