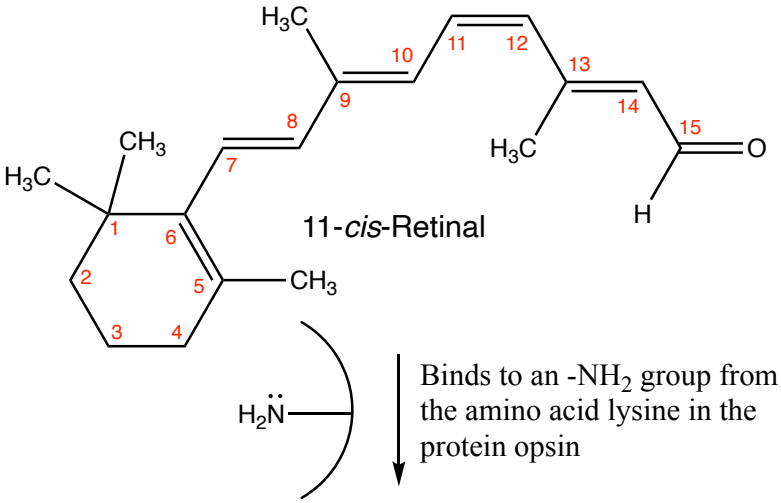
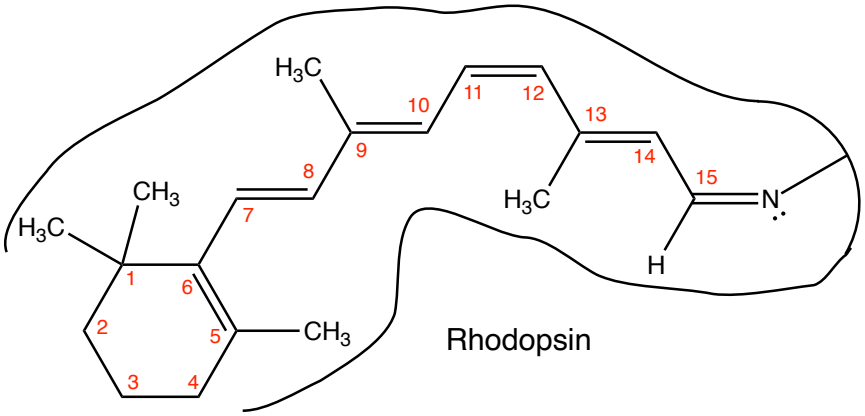
How vision works

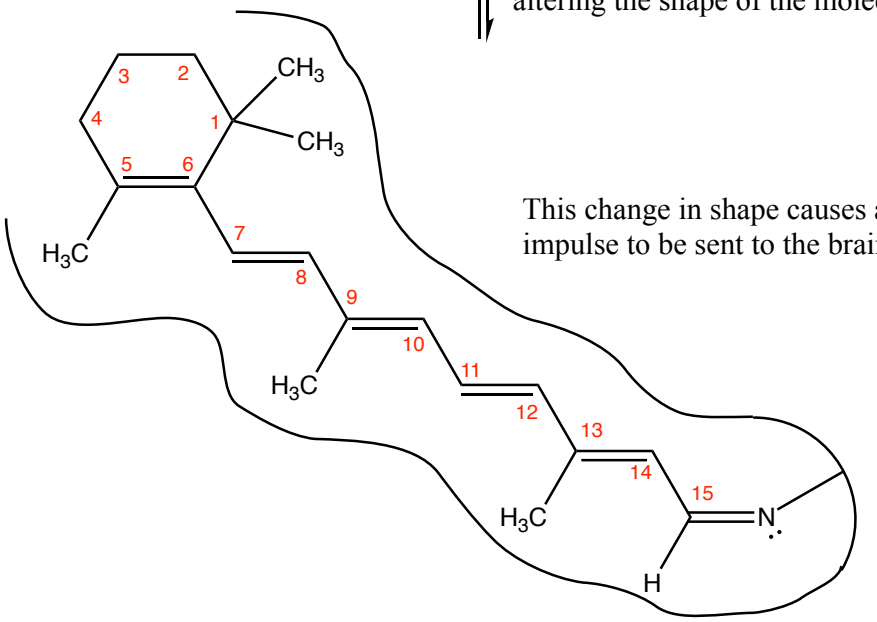


Binds to an -NH_2 group from the amino acid lysine in the protein opsin



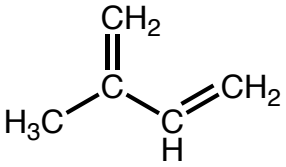
Molecule resets

A photon of visible light is absorbed by the retinal, isomerizing the *cis* bond to *trans*, dramatically altering the shape of the molecule

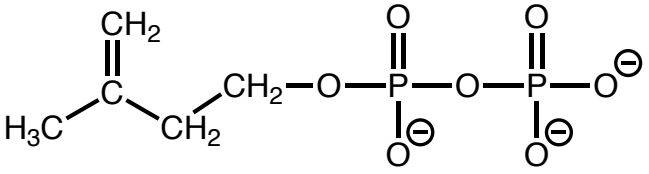


This change in shape causes a nerve impulse to be sent to the brain

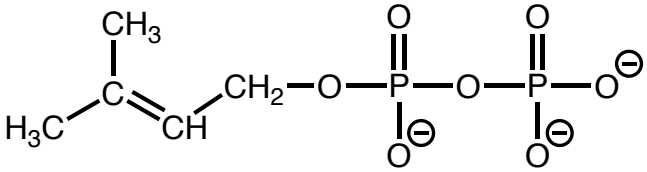
Terpenes



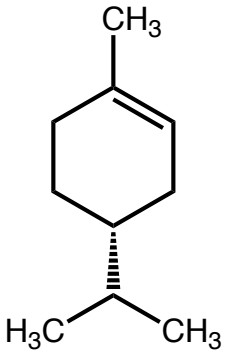
Isoprene



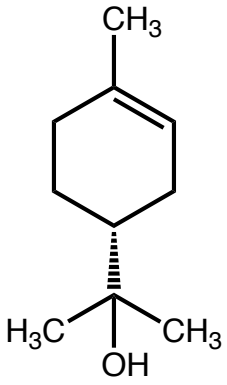
Isopentanyl diphosphate



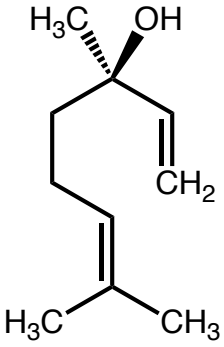
Dimethylallyl diphosphate



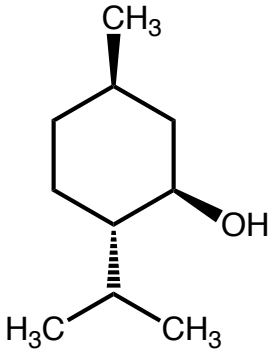
Limonene
(citrus flavor)



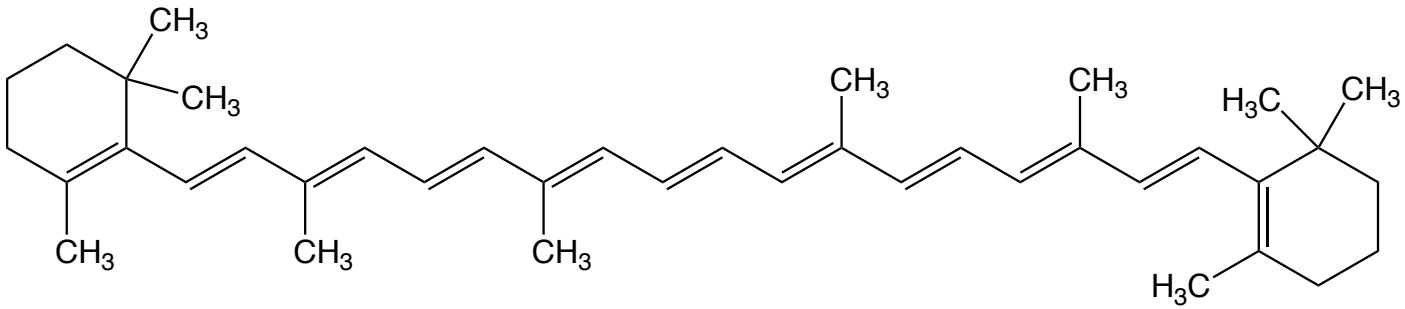
α-Terpineol
(from lilacs, used in perfume)



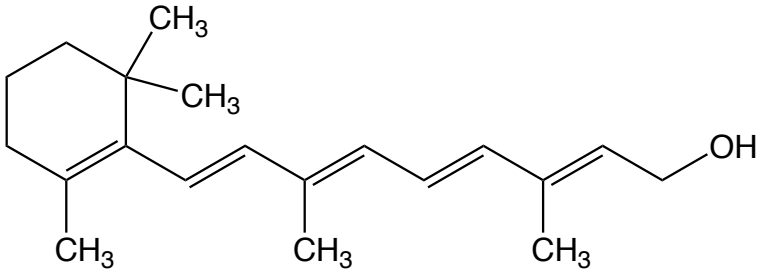
(*R*)-(-)-Linalool
(from lavender, used in perfume)



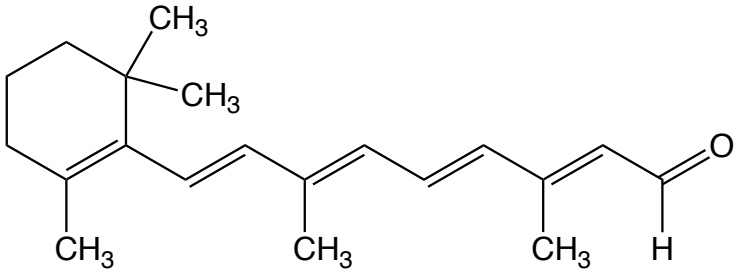
(-)-Menthol
(common flavoring from peppermint)



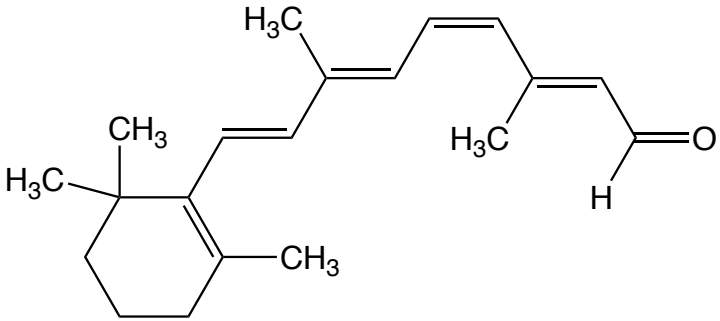
β-Carotene



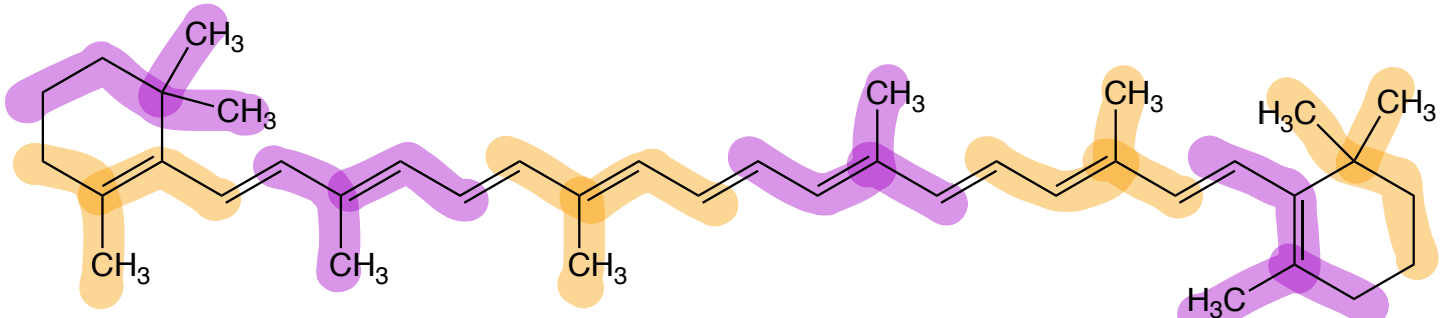
Vitamin A



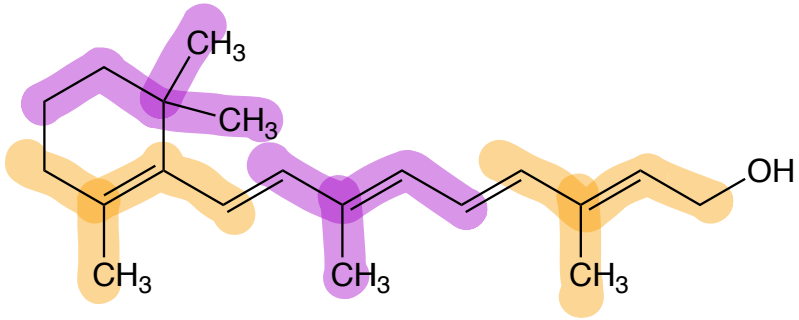
All *trans* Retinal



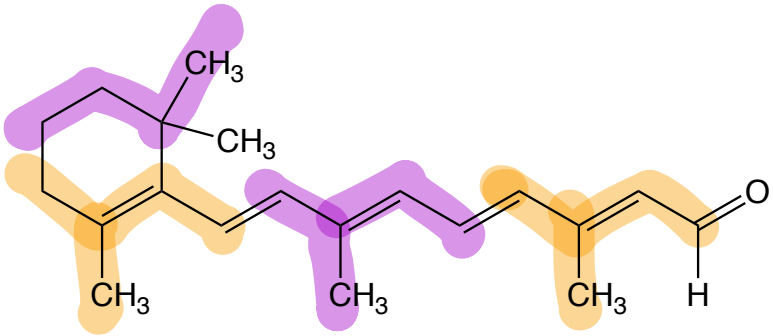
11-*cis*-Retinal



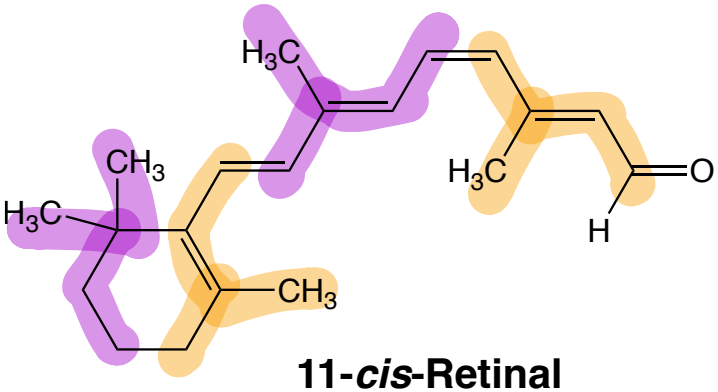
β-Carotene



Vitamin A



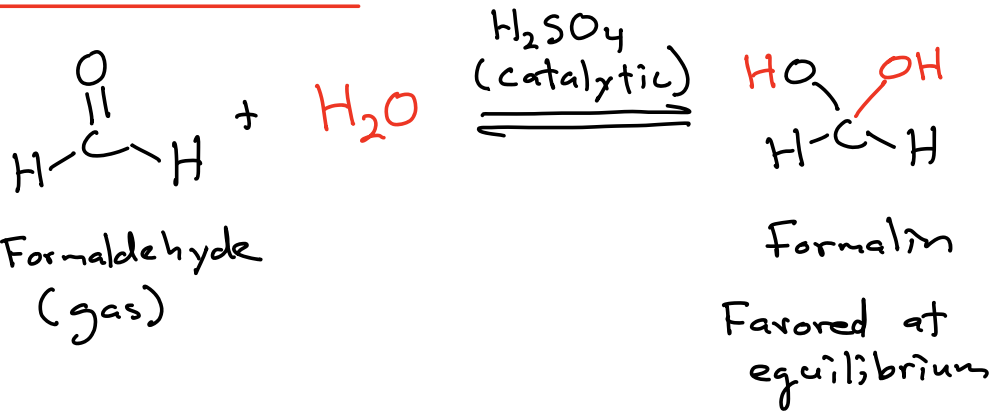
All *trans* Retinal



11-*cis*-Retinal

Geminal Diols: H_2O instead of ROH

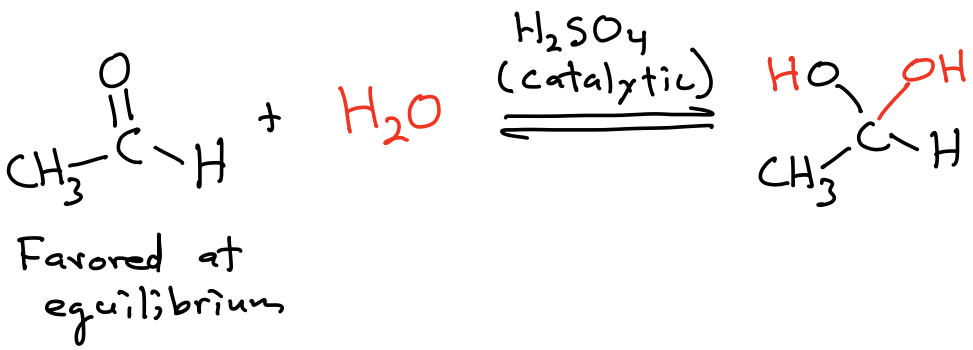
Same mechanism as hemiacetal formation:
Mechanism D



Formaldehyde (gas)

Formalin

Favored at equilibrium



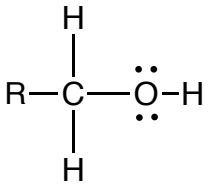
Favored at equilibrium

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

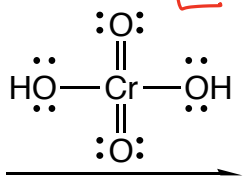
Chromic Acid Oxidation of Alcohols

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

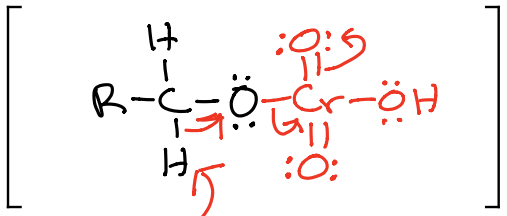
Not responsible for first step

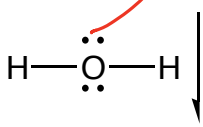


1° Alcohols



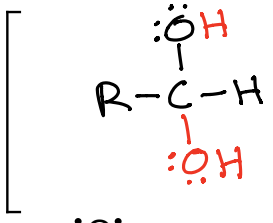
"H_2CrO_4" or "Chromic Acid"



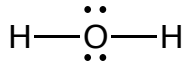


Take a proton away and break a bond

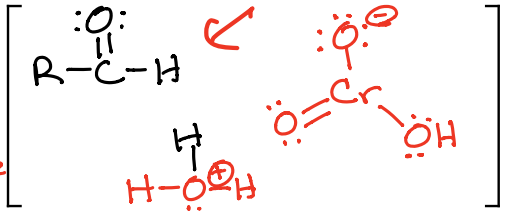
Not responsible for this step

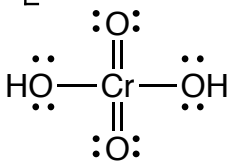


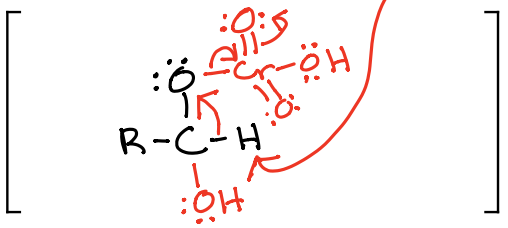
Called a geminal diol

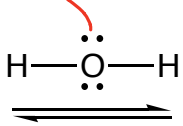


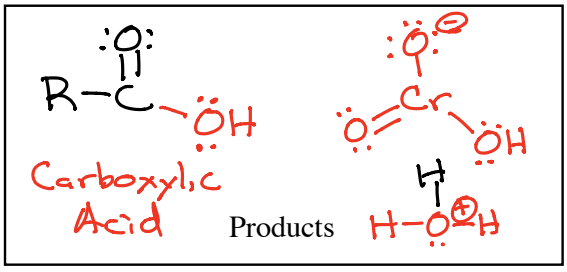
Water reacts with aldehyde – will learn next semester







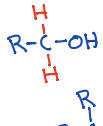




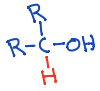
Carboxylic Acid

Products

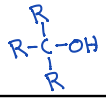
Summary:



1° alcohols ⇒ Carboxylic Acid



2° alcohols ⇒ Ketone

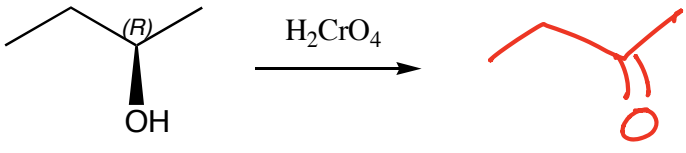


3° alcohols ⇒ NO REACTION

Regiochemistry: N/A

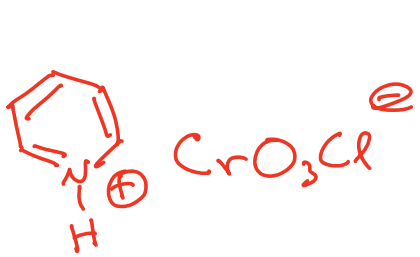
Stereochemistry: N/A

Example:



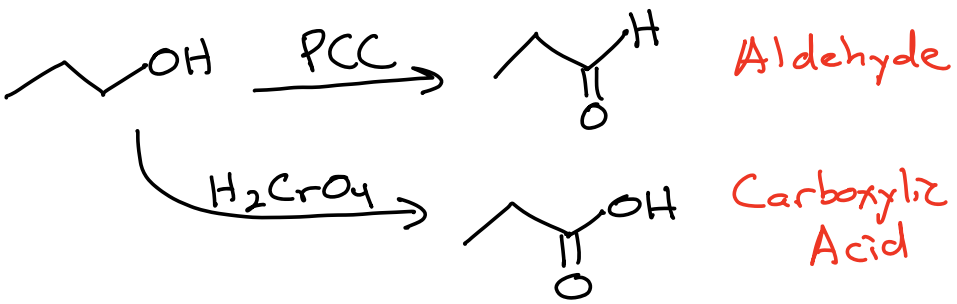
Ketone

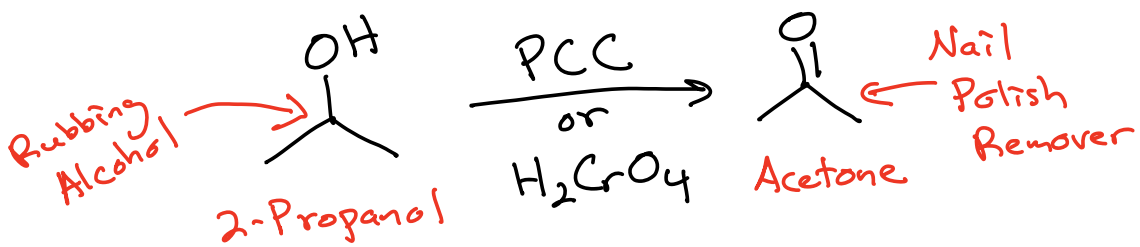
A chromic acid-like reagent WITHOUT WATER will stop at the aldehyde when using a primary alcohol as starting material

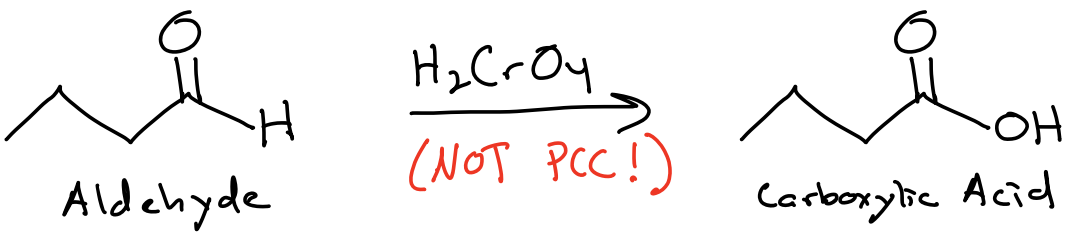


Pyridinium Chlorochromate

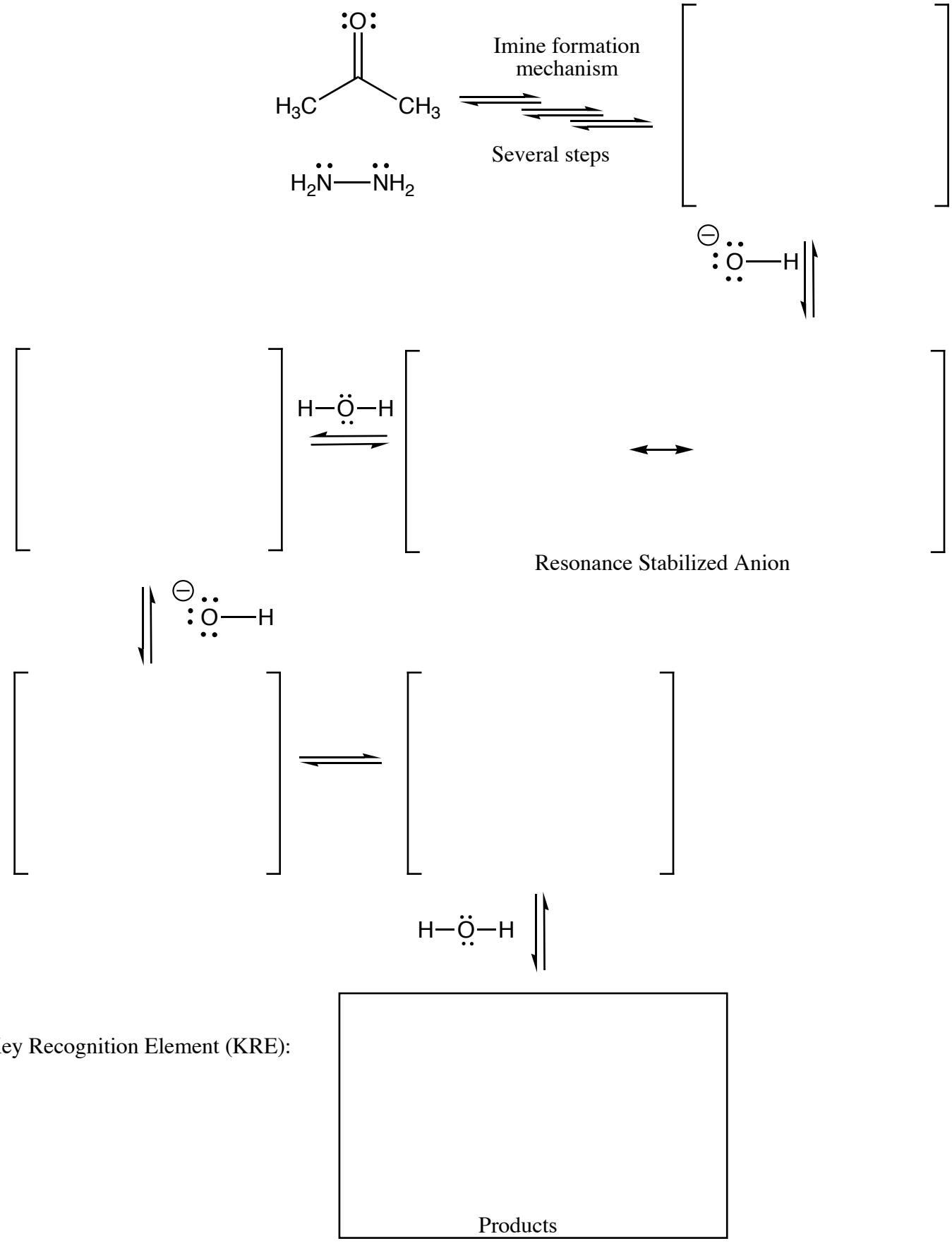
PCC







Wolff-Kishner Reduction of an Aldehyde or Ketone

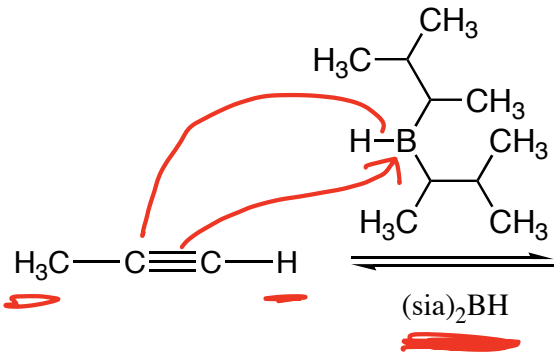


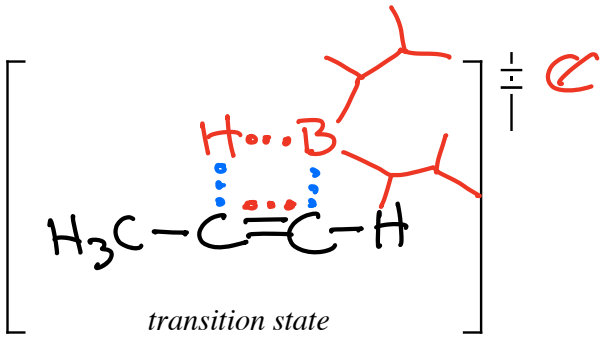
Key Recognition Element (KRE):

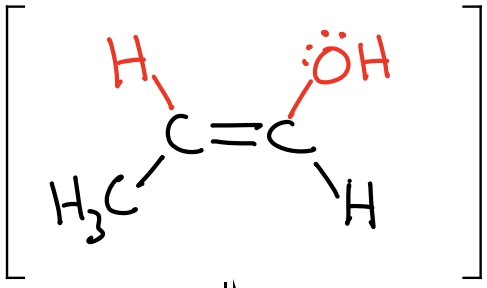
Products


Eek! Don’t bite my head off!
O
NH_2-NH_2
KOH

Terminal Alkyne Hydroboration

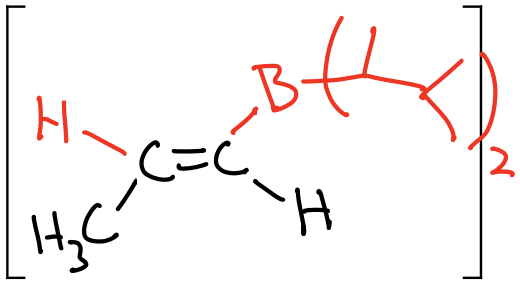




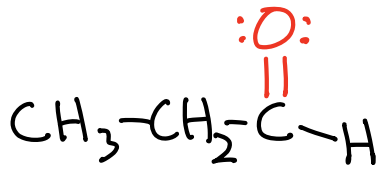


2. H_2O_2 / $HO^{\ominus}$

(Chemist opens flask and adds new reagent)



Keto-enol tautomerization



Products

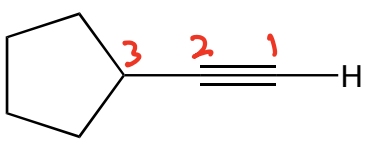
⇐ The C=O is on the C on the end → "non-Markovnikov"

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

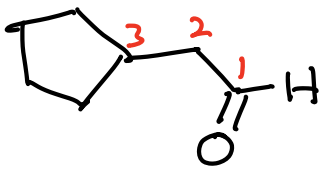
Stereochemistry: N/A

Example:



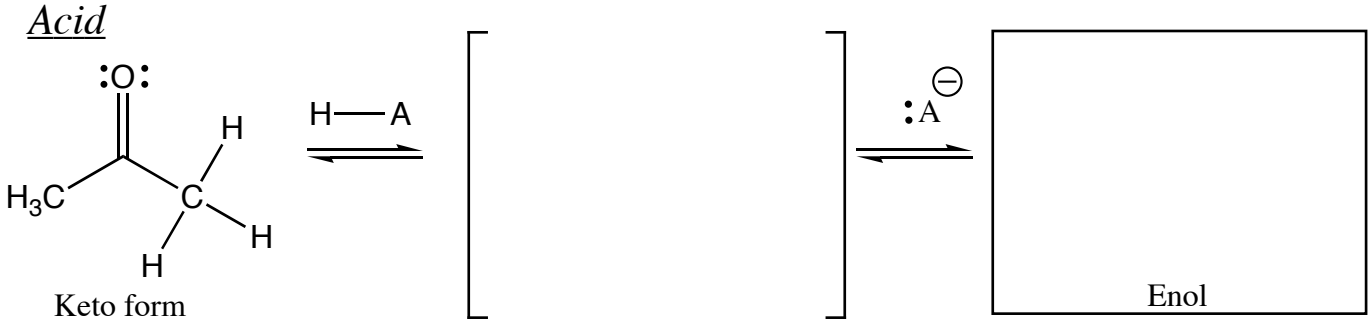
1. $(sia)_2BH$

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



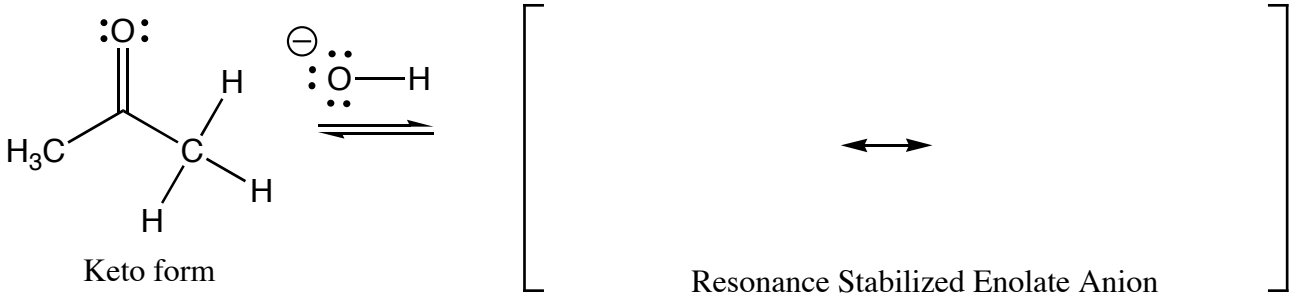
Keto-Enol Equilibrium Catalyzed by Acid or Base

Acid



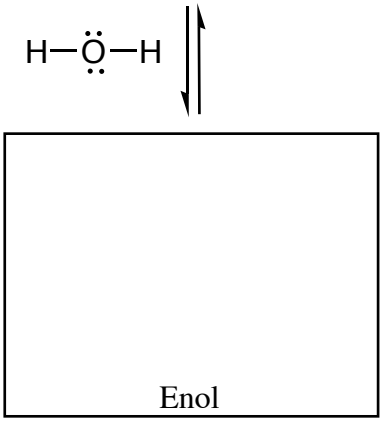
Keto form

Base



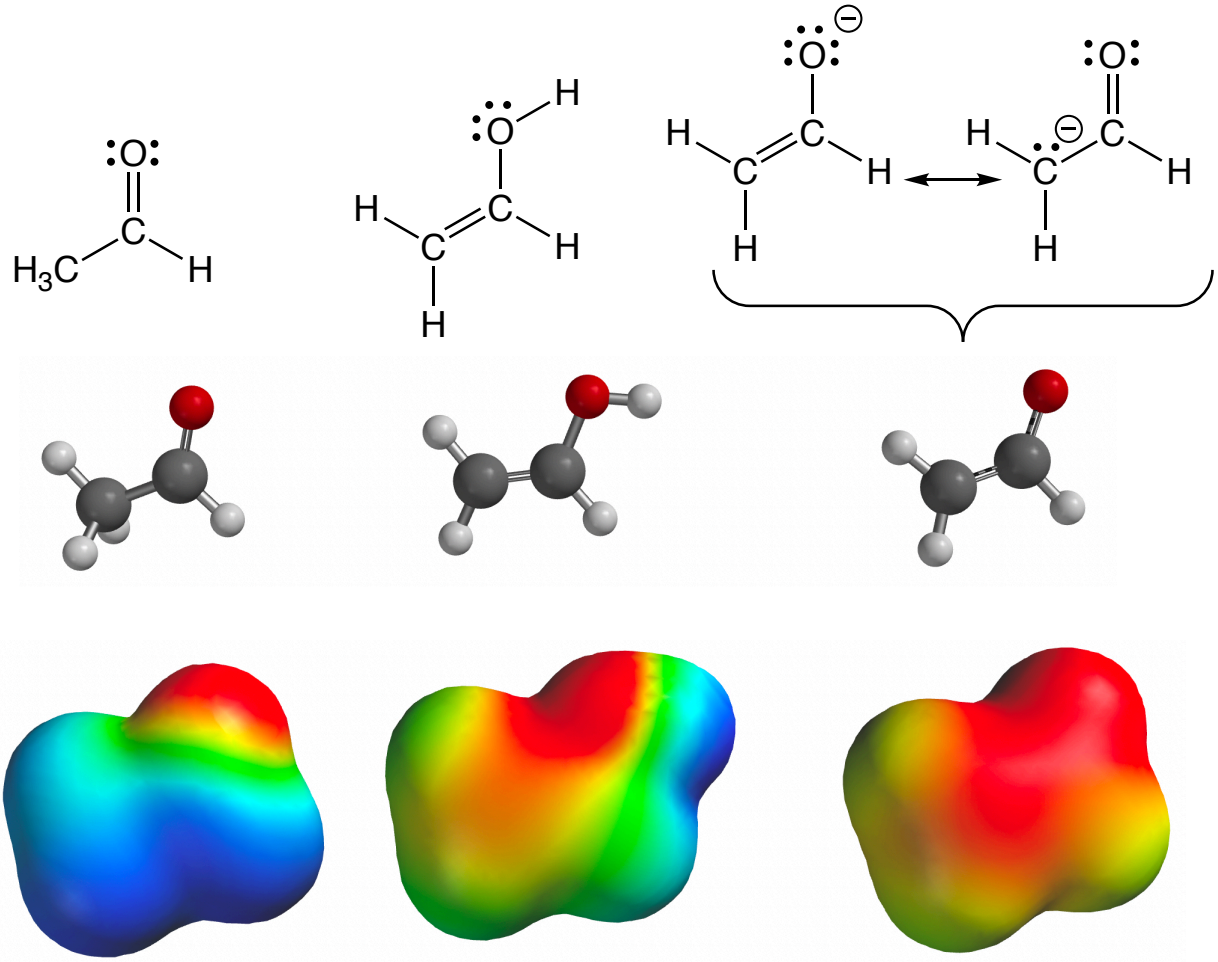
Keto form

α-hydrogen pK_a = 18-20

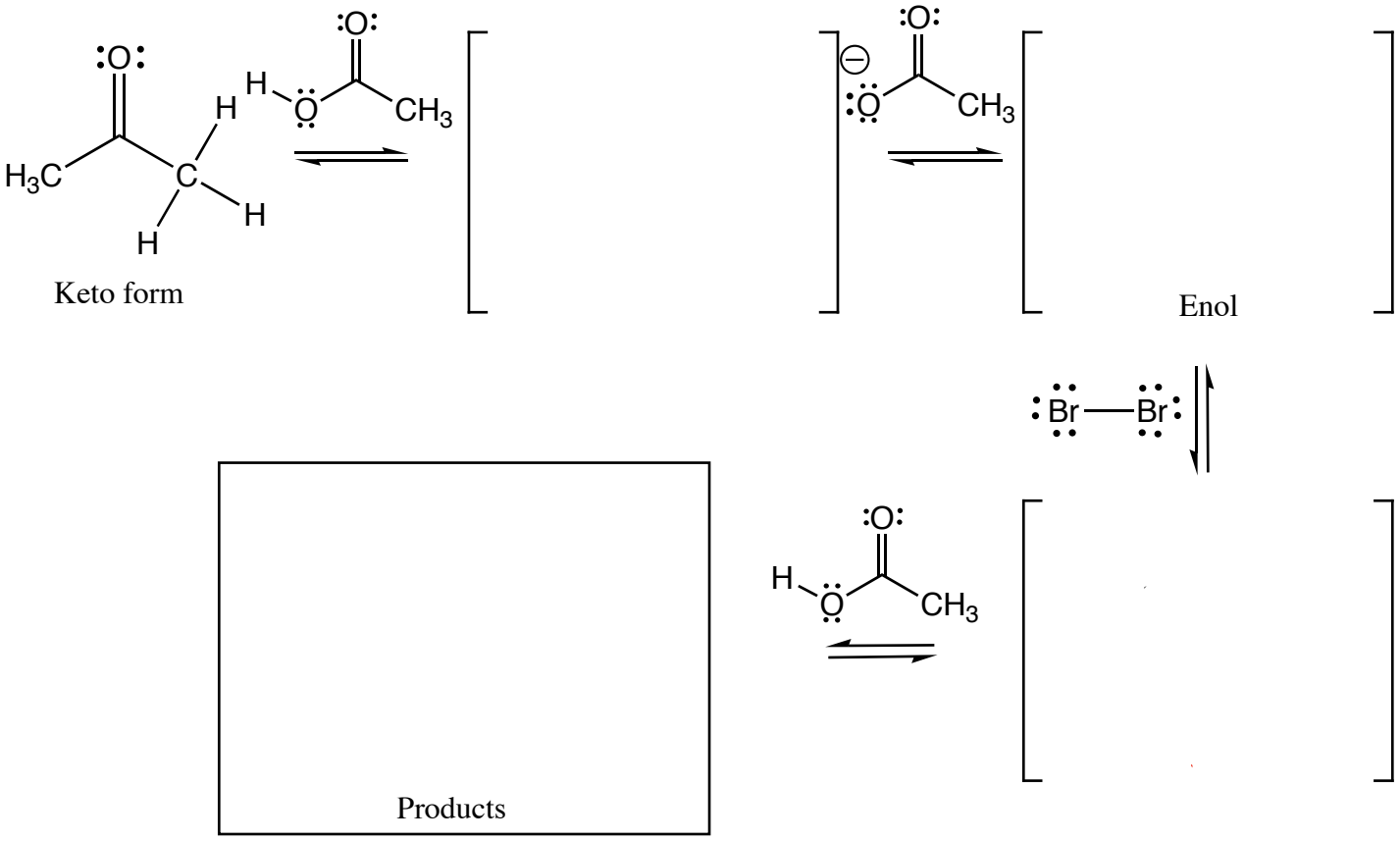


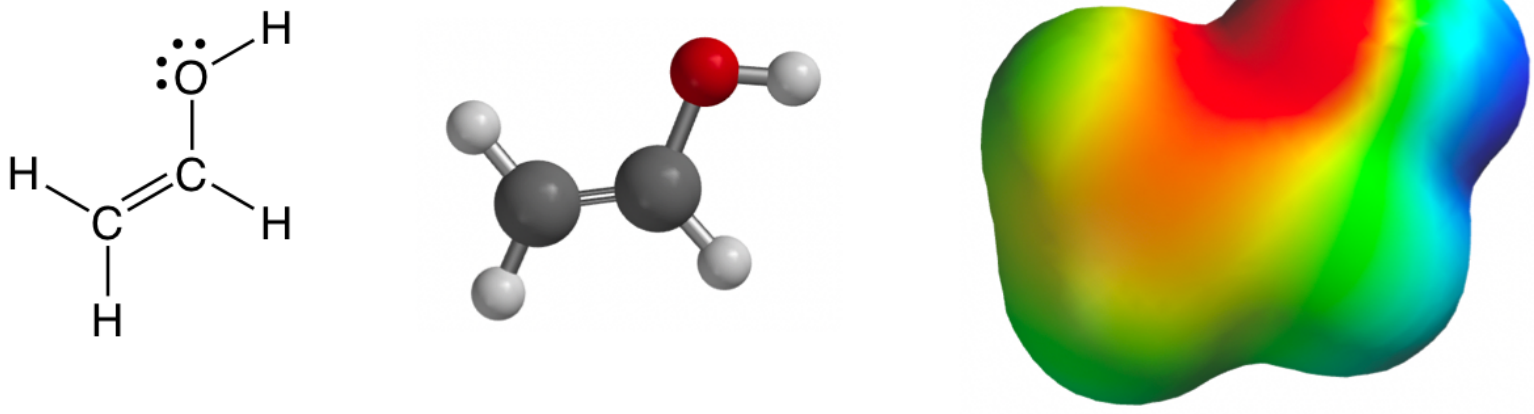
For both aldehydes and ketones, the keto form predominates at equilibrium, because _____ bonds are stronger than _____ bonds.

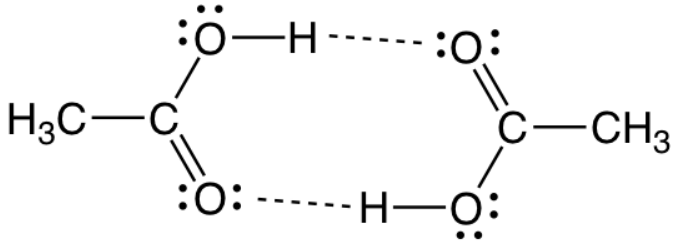
Enols are significant, however, because they react like _____, not carbonyls, and this is important in certain situations.

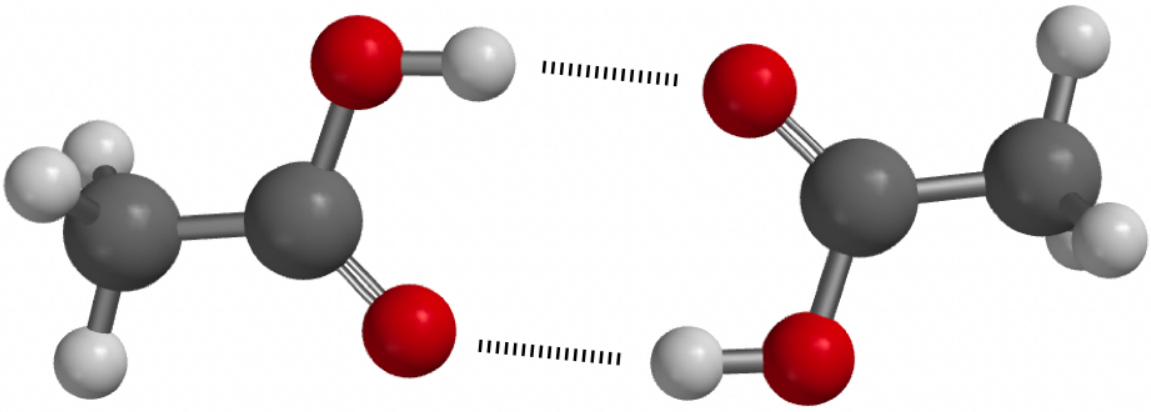

O
C
H3C
H
O
H
C
H
C
H
H
O
H
C
C
H
H
H
O
C
H
H
C
H
O
C
H
H

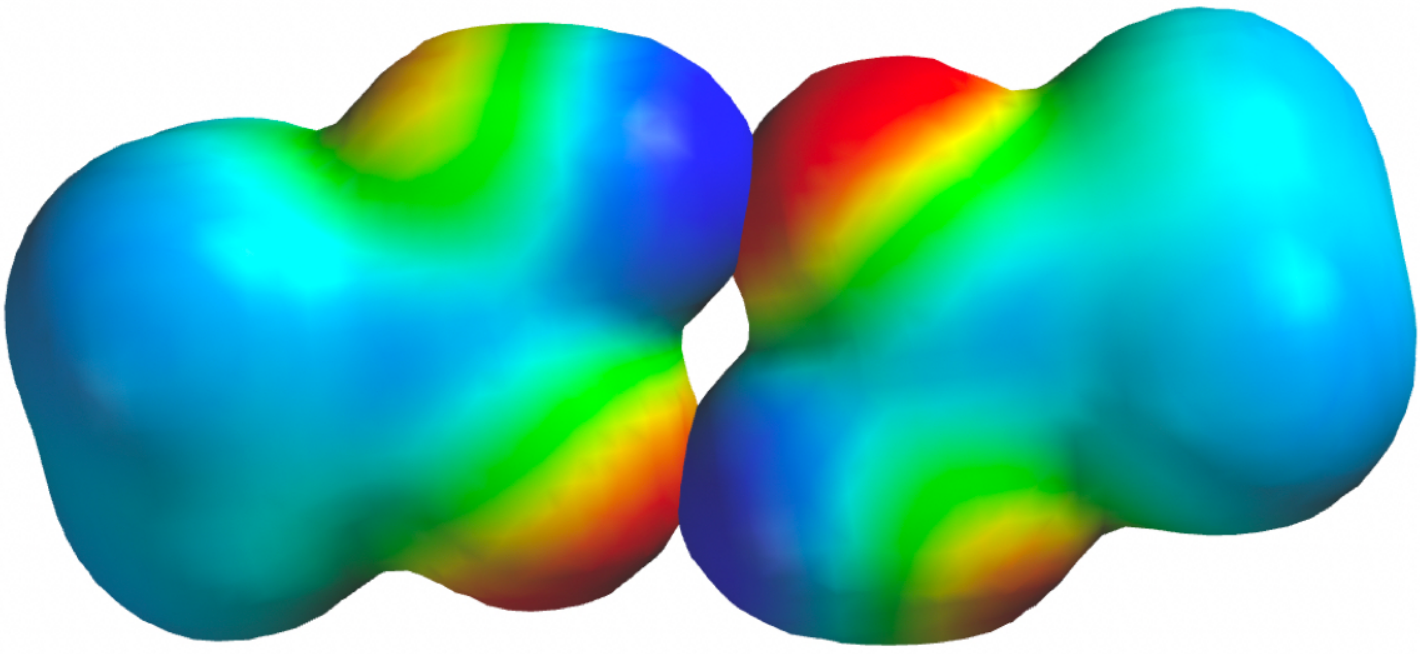
α-Halogenation of an Aldehyde or Ketone Catalyzed by Acid






O
H
O
H3C
C
C
CH3
O
H
O



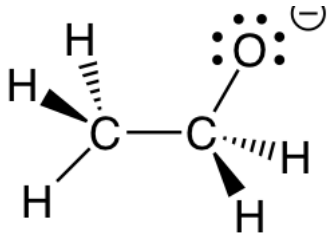


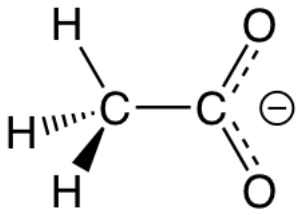
Acidity Revisited

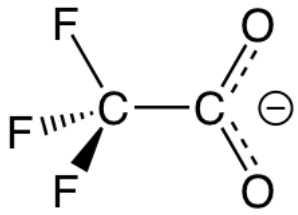
$$H\text{-}A \rightleftharpoons H^{\oplus} + :A^{\ominus}$$

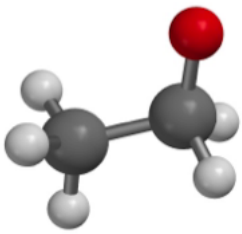
$$K_a = \frac{[A:^{\ominus}][H^{\oplus}]}{[HA]}$$

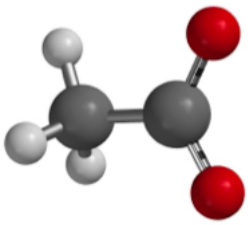
$$pK_a = -\log_{10} K_a$$

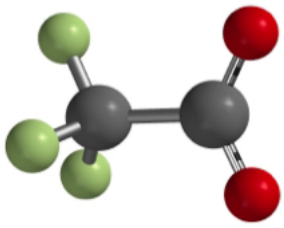

H
H
O
C
C
H
H
H

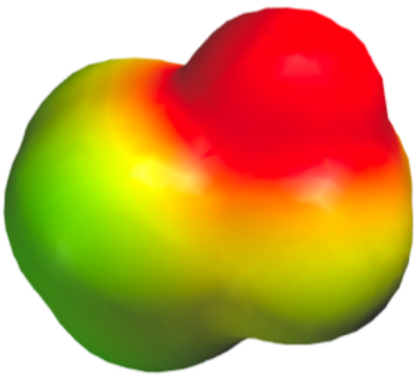

H
H
C
C
O
O

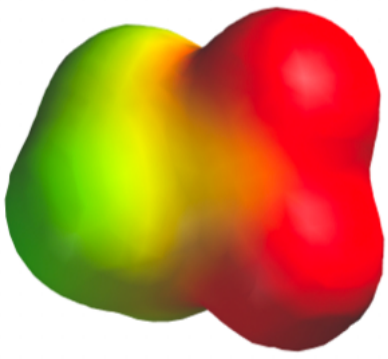

F
F
C
C
O
O

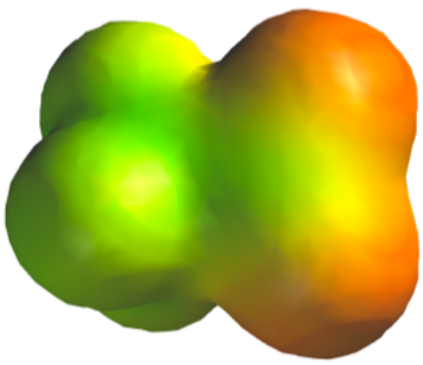












For an acid H-A

$$K_a = \frac{[A^{\ominus}][H^{\oplus}]}{[HA]}$$

$$pK_a = -\log_{10} K_a$$

$$pH = -\log_{10} [H^{\oplus}]$$

$$\frac{K_a}{[H^{\oplus}]} = \frac{[A^{\ominus}]}{[HA]} = 10^{(pH - pK_a)}$$

If $pH = 7$ and $pK_a = 3$

$$\frac{[A^{\ominus}]}{[HA]} = 10^{(pH - pK_a)} = 10^{(7-3)} = 10^4$$