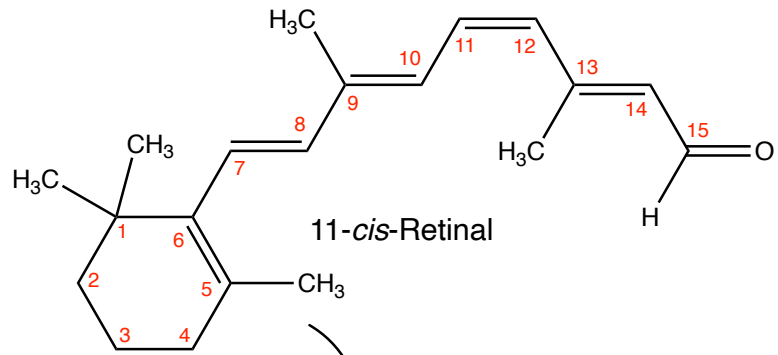
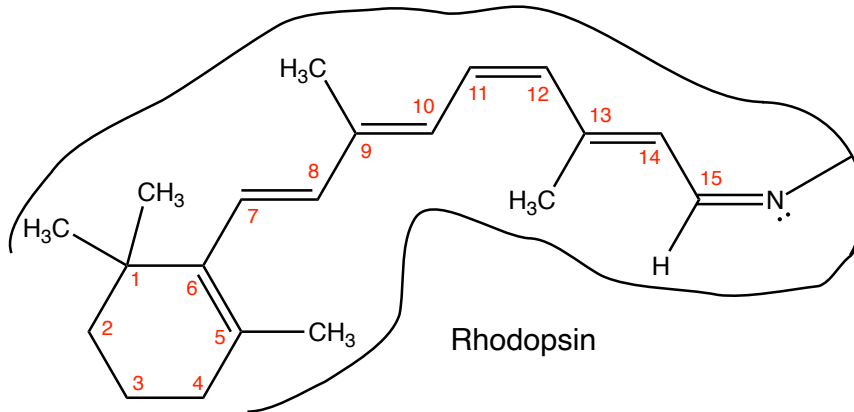




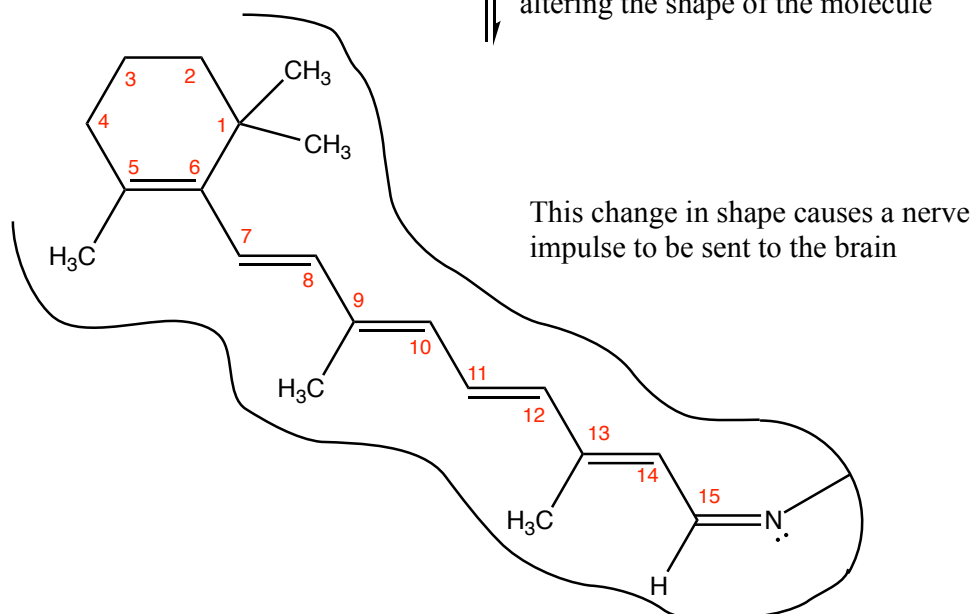
# How vision works



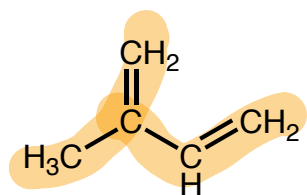
$\text{H}_2\ddot{\text{N}}\text{---}$   $\downarrow$  Binds to an  $\text{-NH}_2$  group from the amino acid lysine in the protein opsin



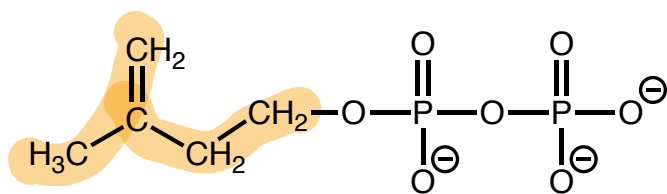
Molecule resets  $\updownarrow$  A photon of visible light is absorbed by the retinal, isomerizing the *cis* bond to *trans*, dramatically altering the shape of the molecule



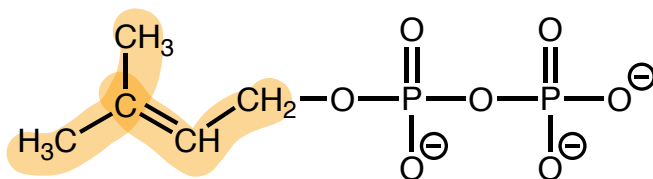
# Terpenes



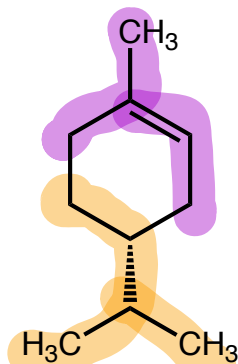
**Isoprene**



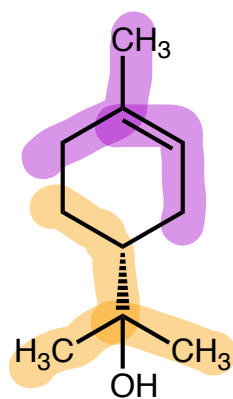
**Isopentanyl diphosphate**



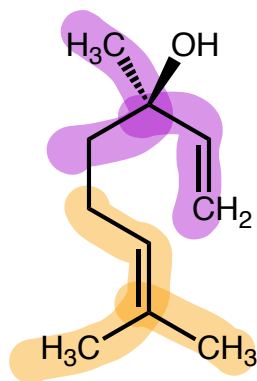
**Dimethylallyl diphosphate**



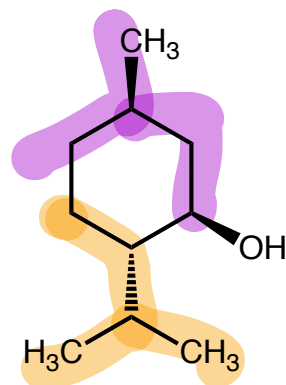
**Limonene**  
(citrus flavor)



**$\alpha$ -Terpineol**  
(from lilacs, used in perfume)

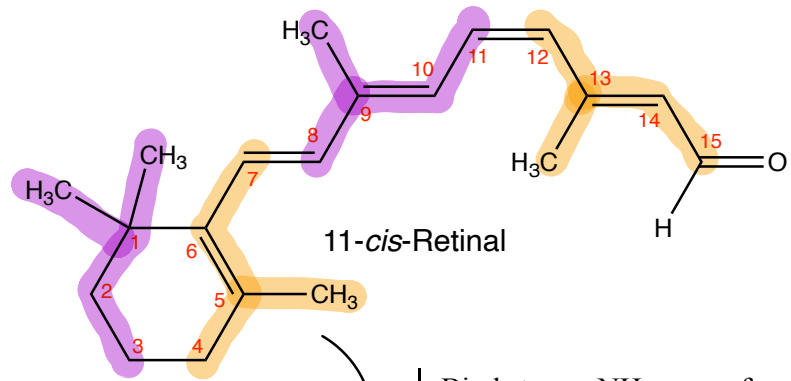


**(*R*)-(-)-Linalool**  
(from lavender, used in perfume)

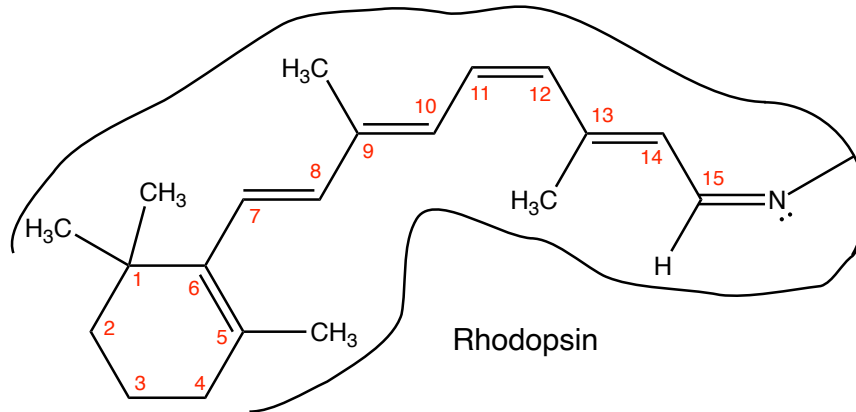


**(-)-Menthol**  
(common flavoring from peppermint)

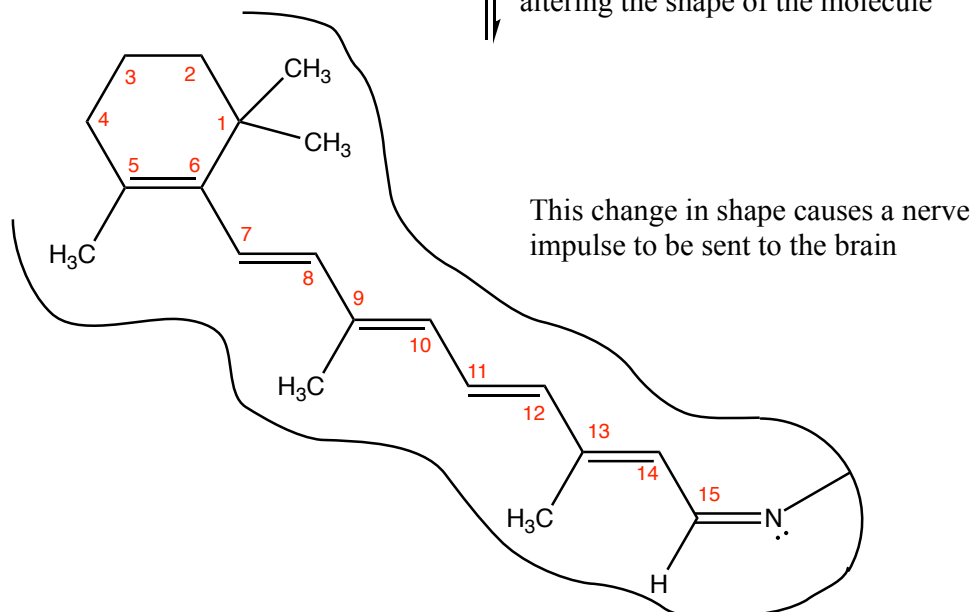
# How vision works

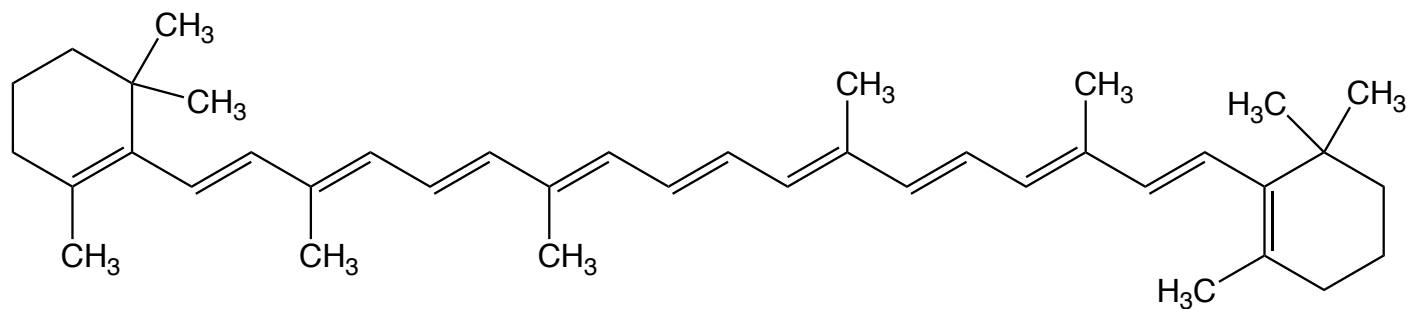


$\text{H}_2\ddot{\text{N}}\text{---}$  )  
↓  
Binds to an  $\text{-NH}_2$  group from the amino acid lysine in the protein opsin

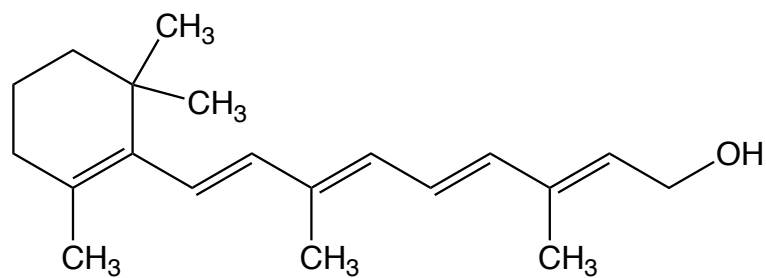


Molecule  
resets  
↕  
A photon of visible light is absorbed by the retinal, isomerizing the *cis* bond to *trans*, dramatically altering the shape of the molecule

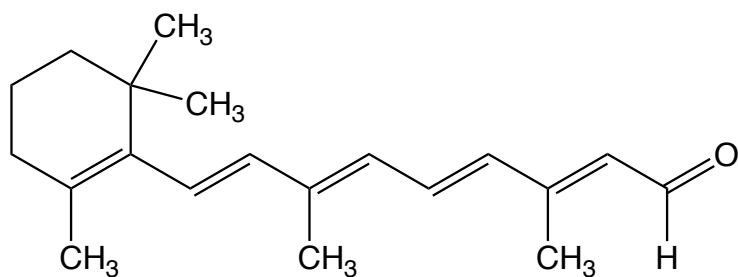




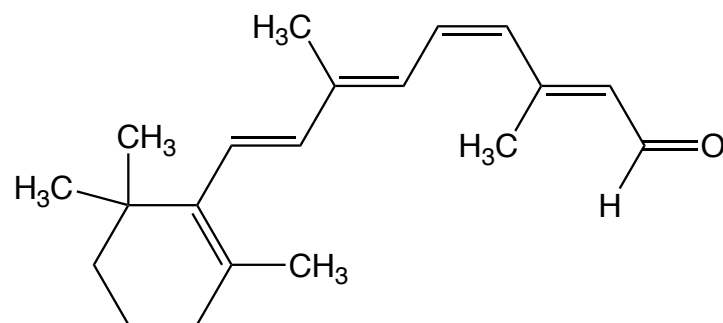
**β-Carotene**



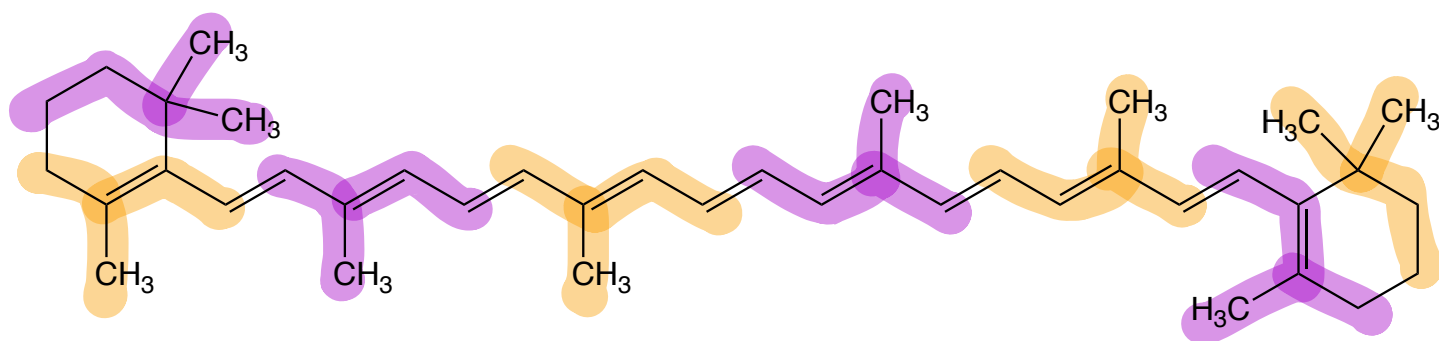
**Vitamin A**



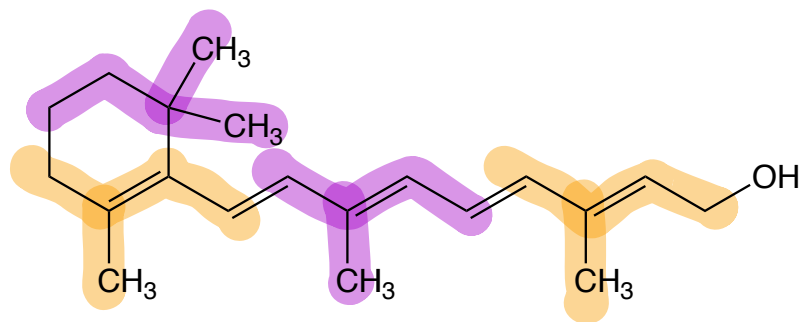
**All *trans* Retinal**



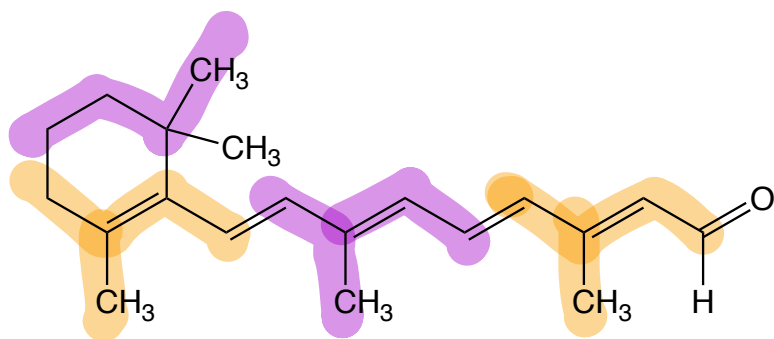
**11-*cis*-Retinal**



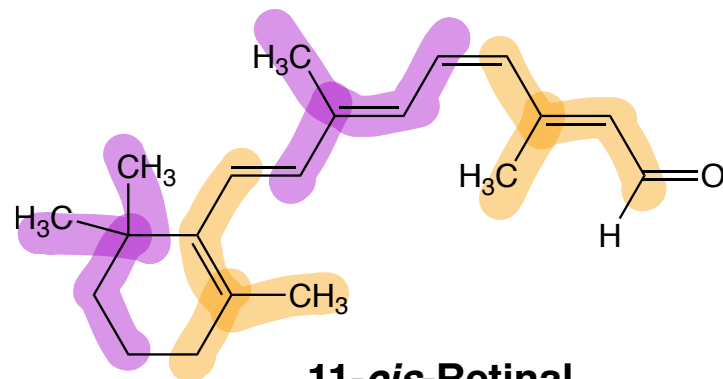
**$\beta$ -Carotene**



**Vitamin A**



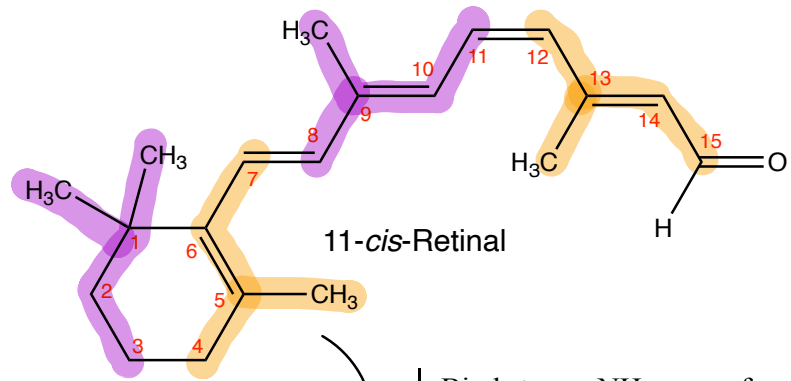
**All *trans* Retinal**



**11-*cis*-Retinal**



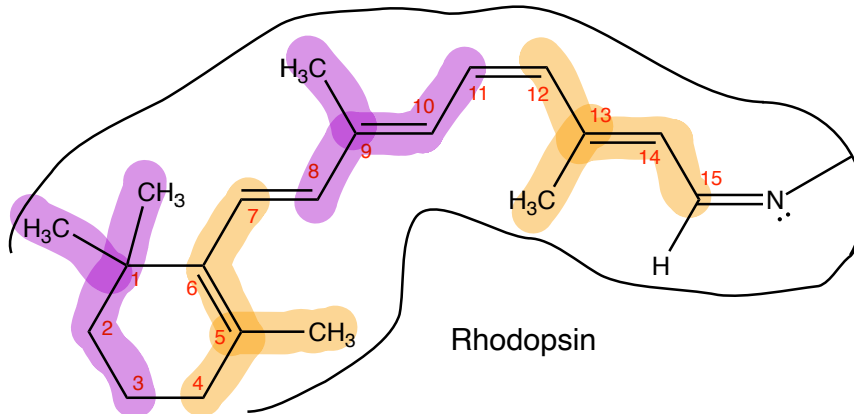
# How vision works



$\text{H}_2\ddot{\text{N}}$  )

↓

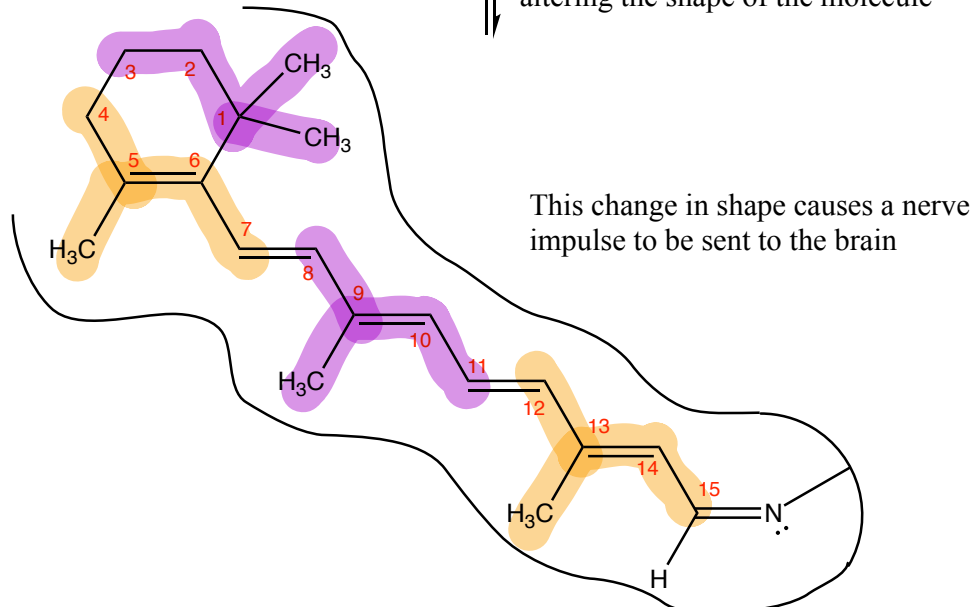
Binds to an  $-\text{NH}_2$  group from the amino acid lysine in the protein opsin



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

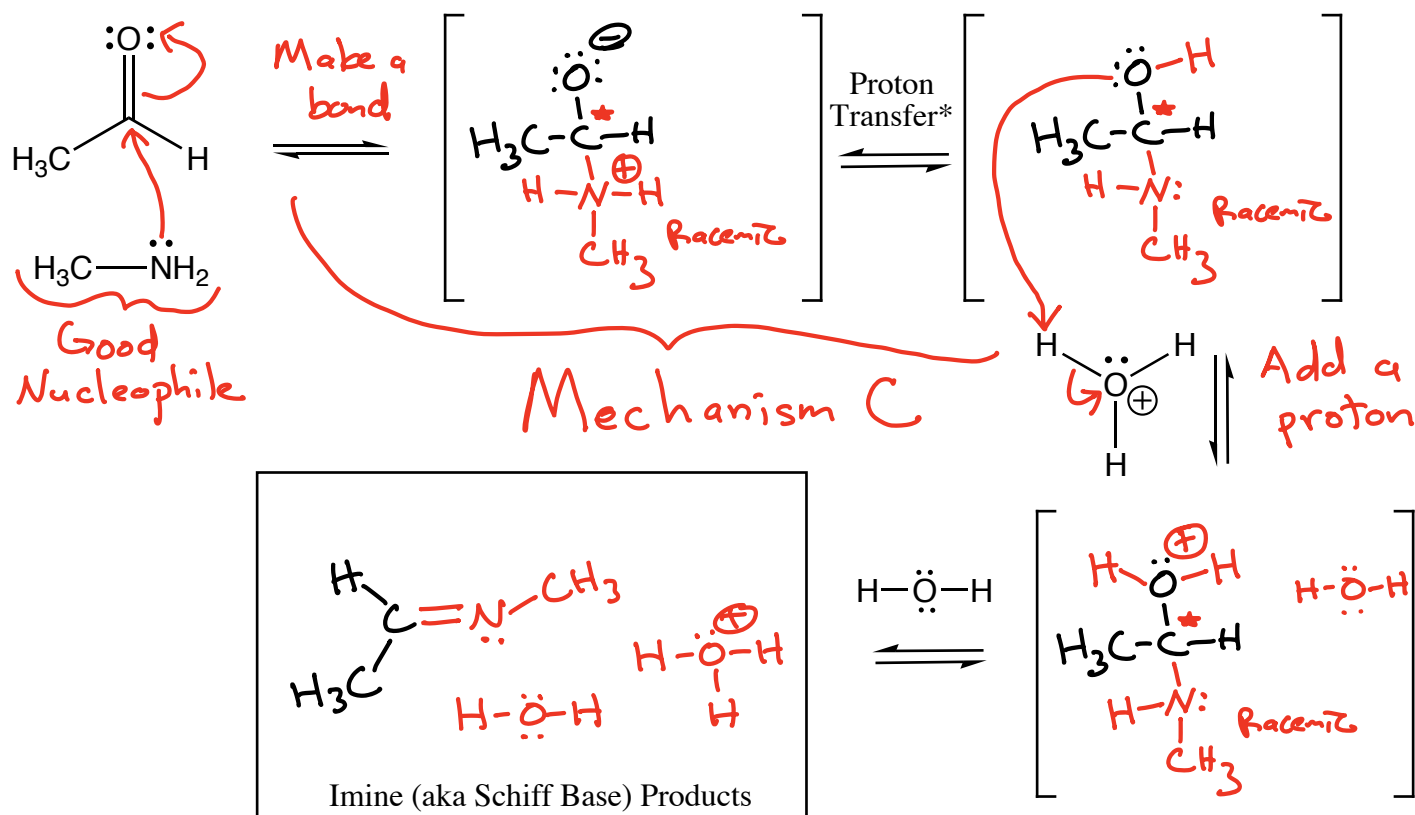




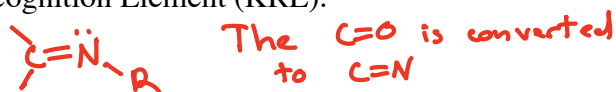


# Recall:

## Formation of an Imine (Schiff Base) From an Aldehyde or Ketone Reacting with an Amine



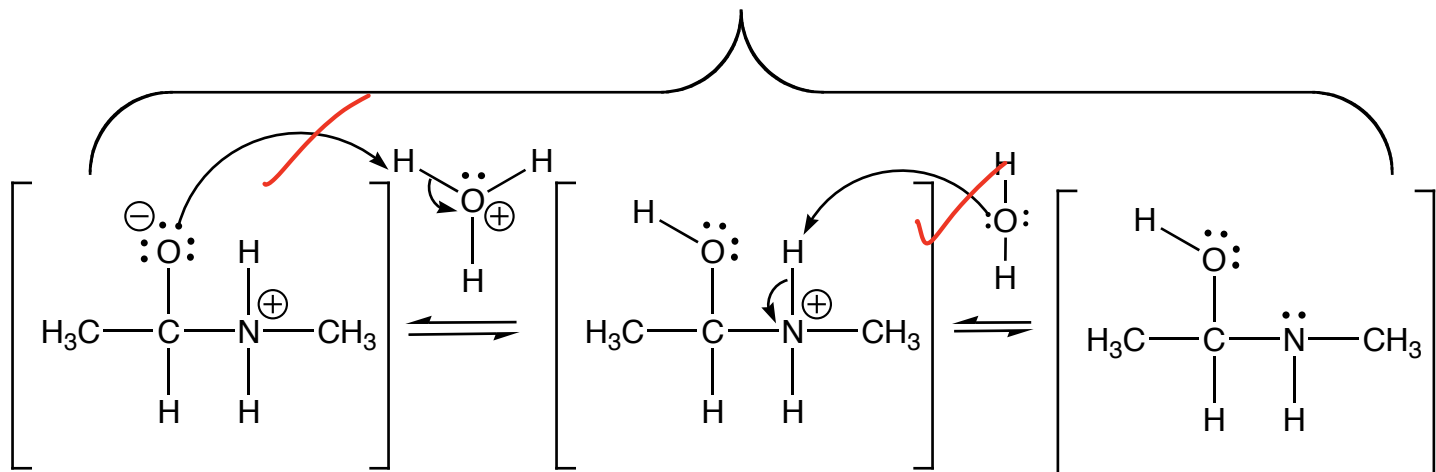
Key Recognition Element (KRE):



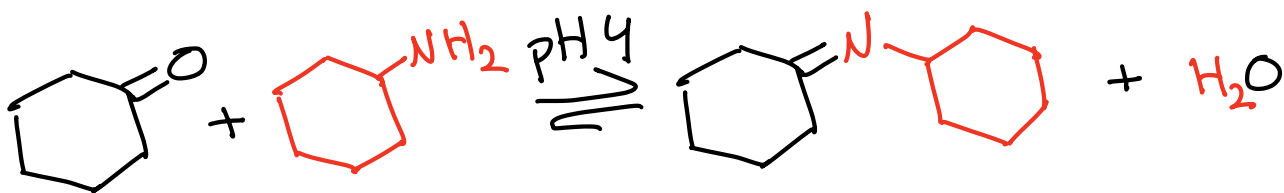
(Note: this last step might actually occur as two steps in some cases.)

\* "Proton Transfer" refers to a situation in which a proton moves from one part of a molecule to another on the SAME MOLECULE. We do not draw arrows for proton transfer steps because that would be deceptive. In some cases, the same proton may move from one part of the molecule to the other directly, but in other cases, solvent molecules may be involved as indicated in the following scheme. To make things even more interesting, the following two steps might even be reversed in some cases. Because of all the ambiguity, we just write "Proton Transfer" and do not bother with arrows.

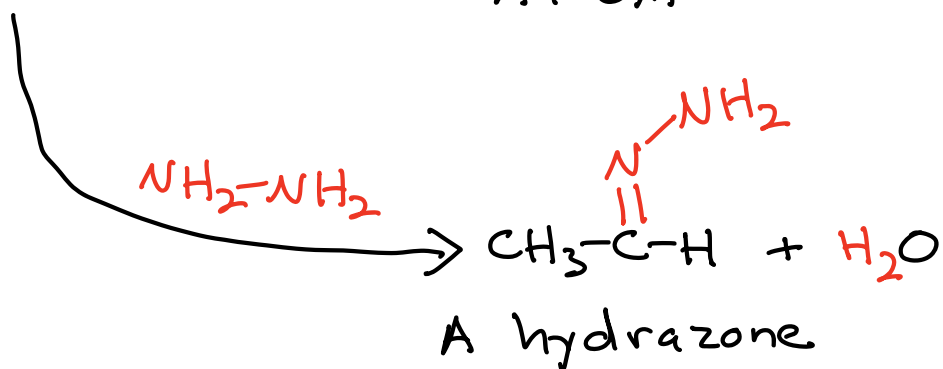
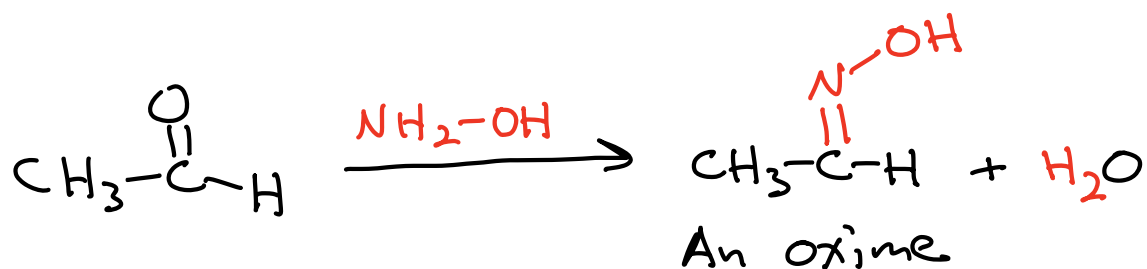
"Proton Transfer"



This is reversible:



Other similar reagents react the same way:



## 2° Amines



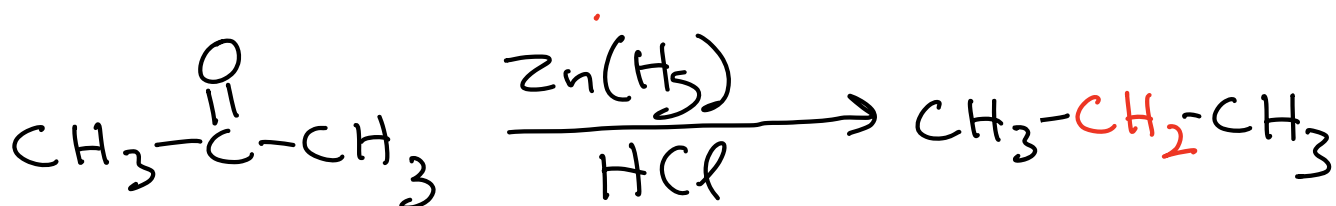
2° (secondary)  
Amine -  
only one  
H atom

Time capsule -  
enamines are  
great nucleophiles

Conversion of ketone and aldehyde C=O groups to -CH<sub>2</sub>-

In acid

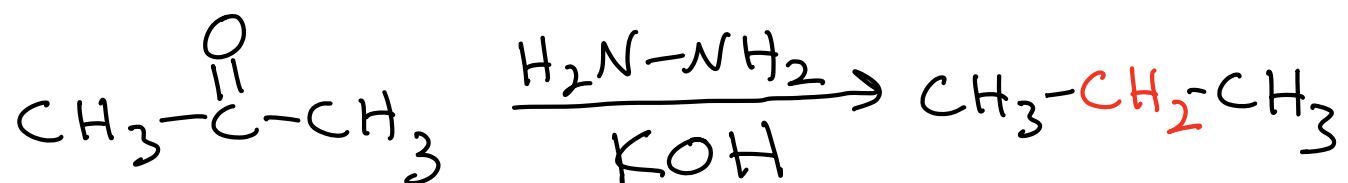
Clemmenson Reduction → you are not responsible for the mechanism  
⇓  
Relatively harsh conditions



↳ Strong acid - cannot be used with acid-sensitive groups like 3° alcohols (they dehydrate to give alkenes)

In base

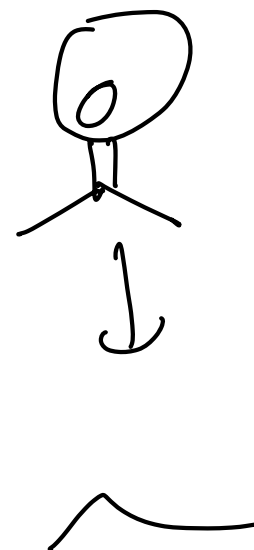
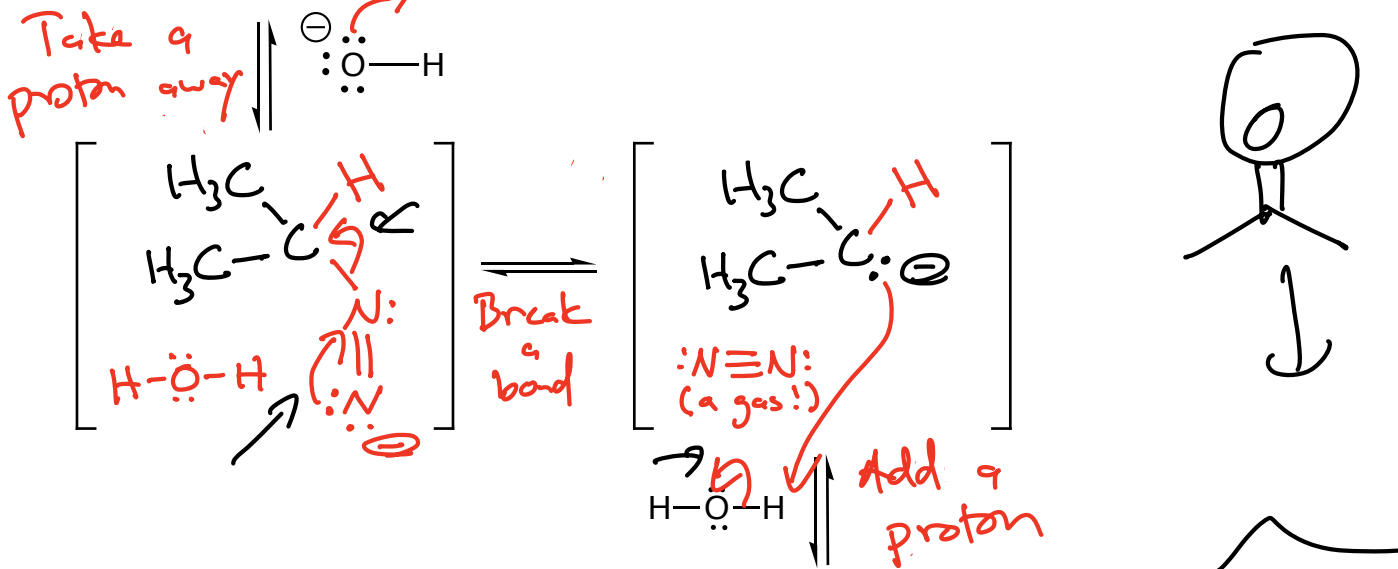
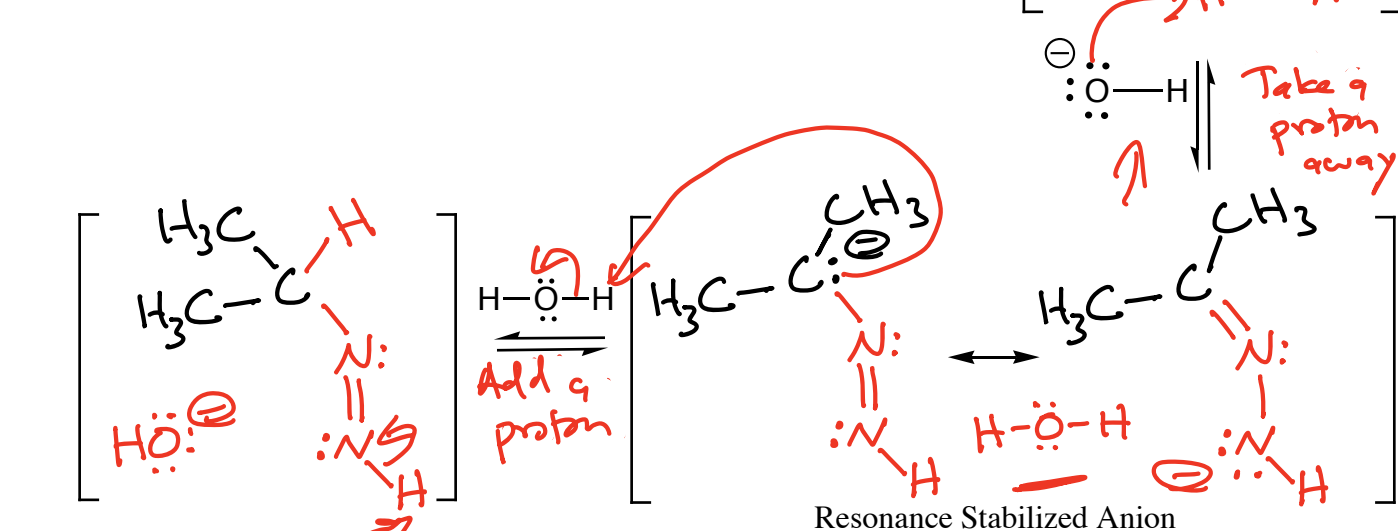
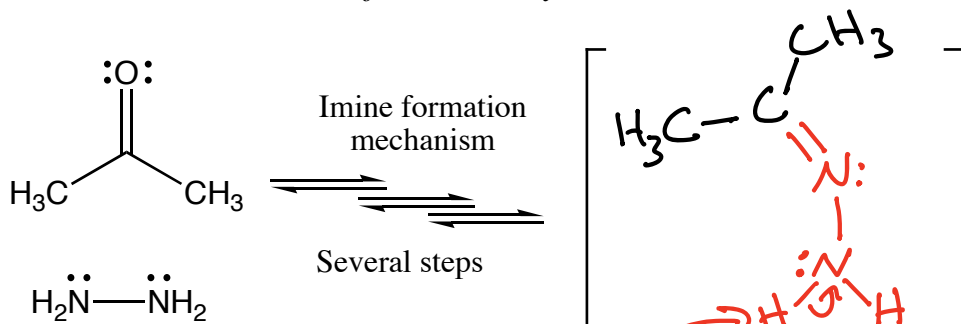
Wolff-Kishner Reduction



Used when there are acid-sensitive groups on a molecule

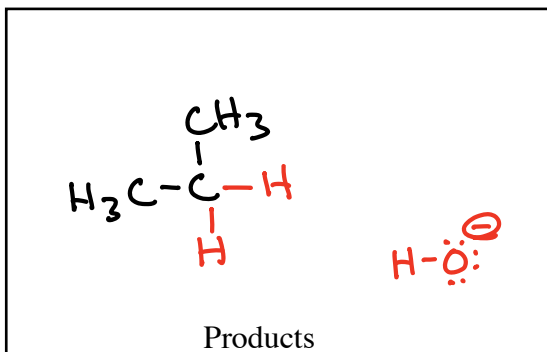
VERY COOL MECHANISM

# Wolff-Kishner Reduction of an Aldehyde or Ketone



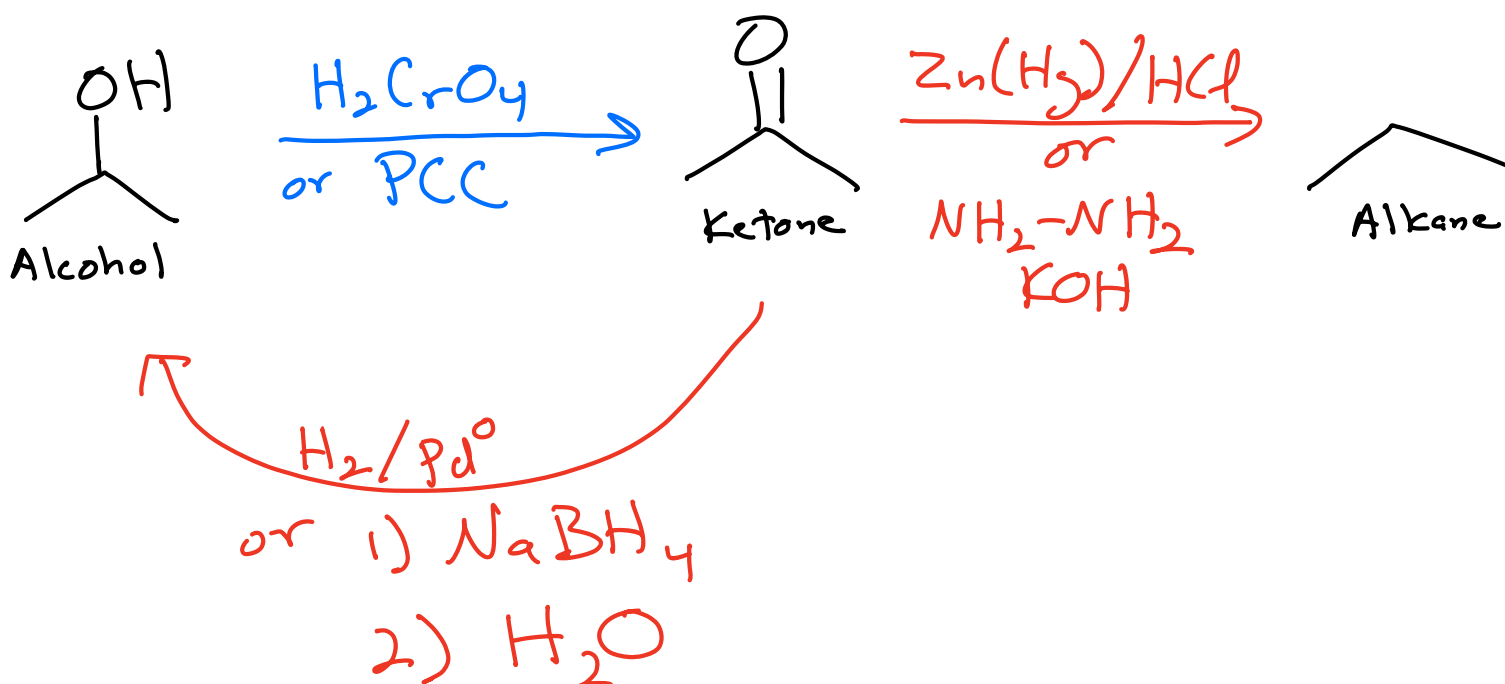
Key Recognition Element (KRE):

-CH<sub>2</sub>- where there was C=O

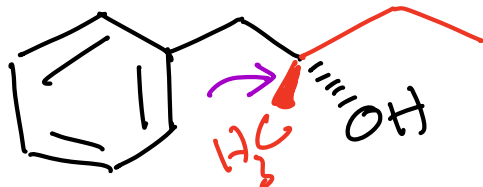
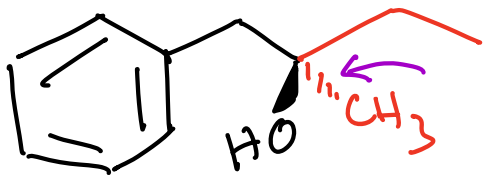
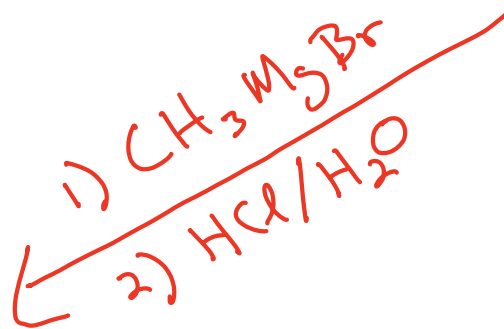
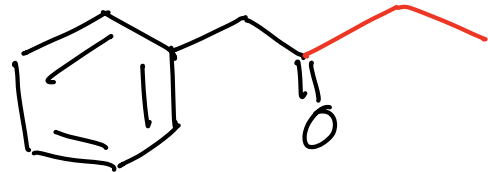
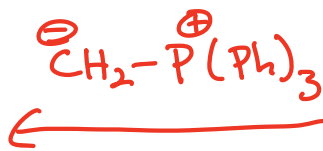
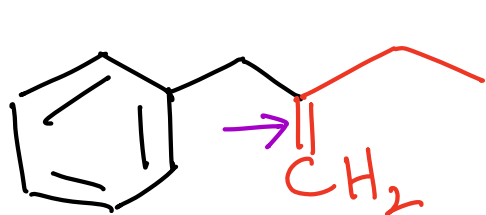
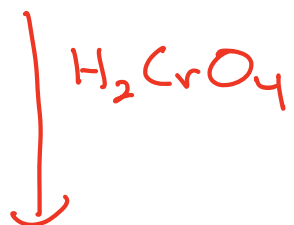
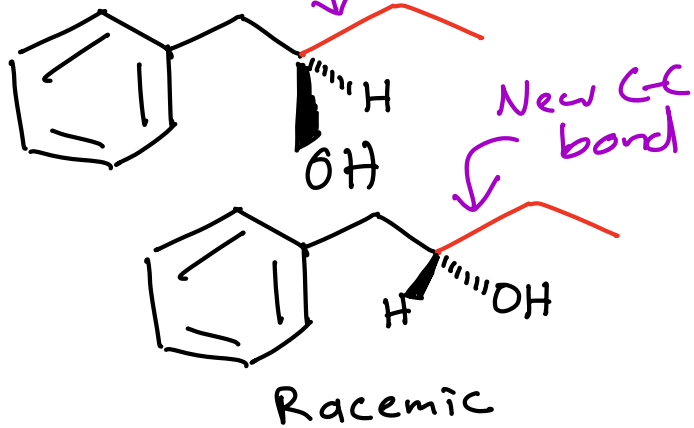
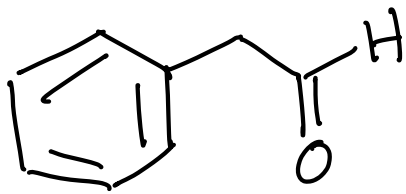




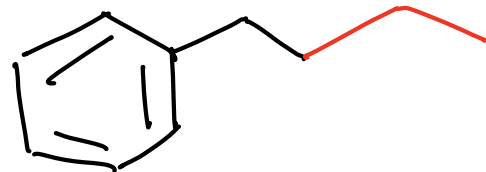
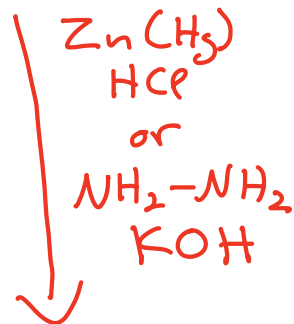
Putting these **oxidation** and **reduction** reactions to work  
in synthesis

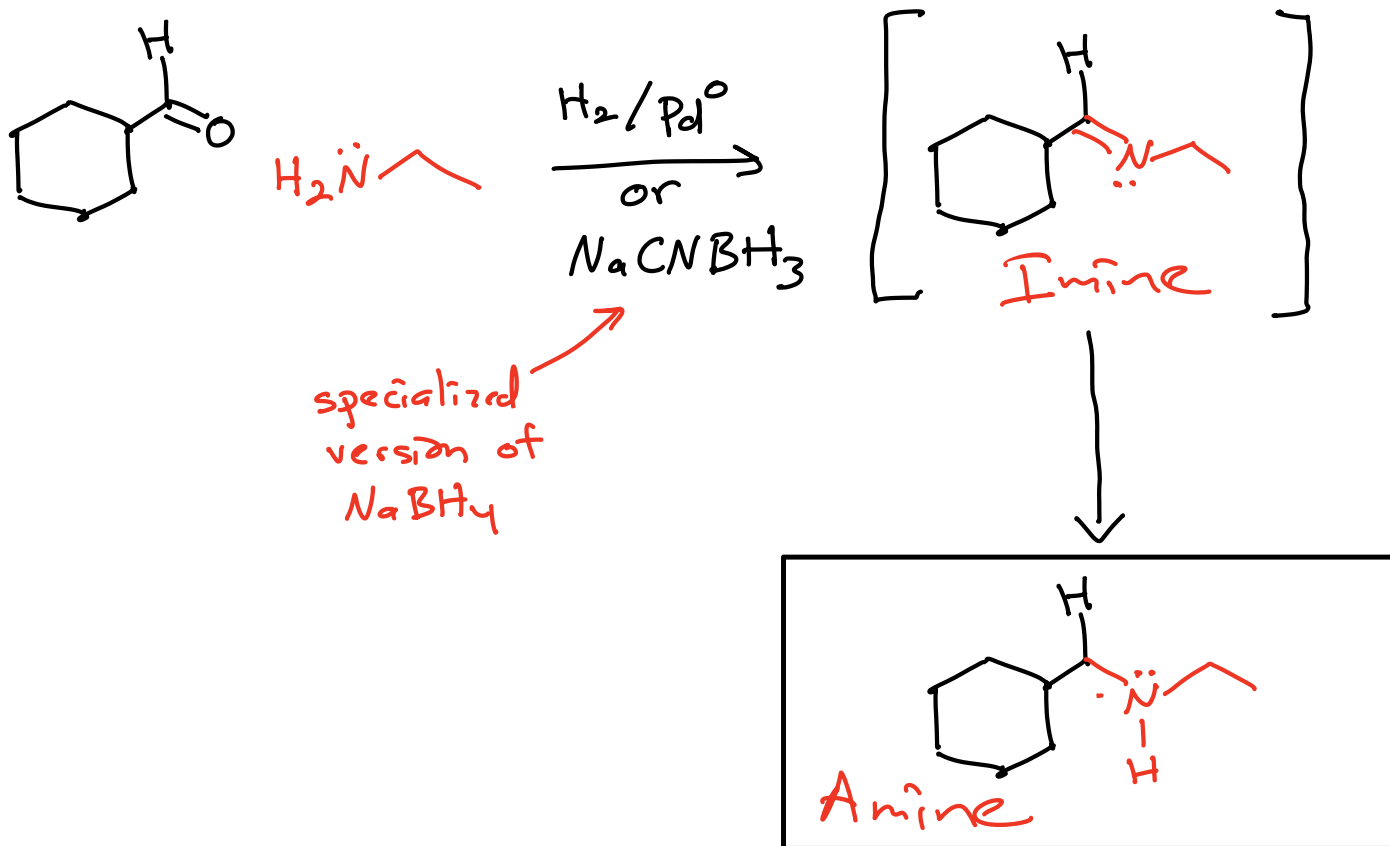






Racemic

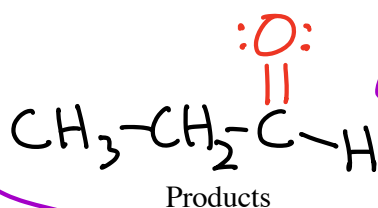
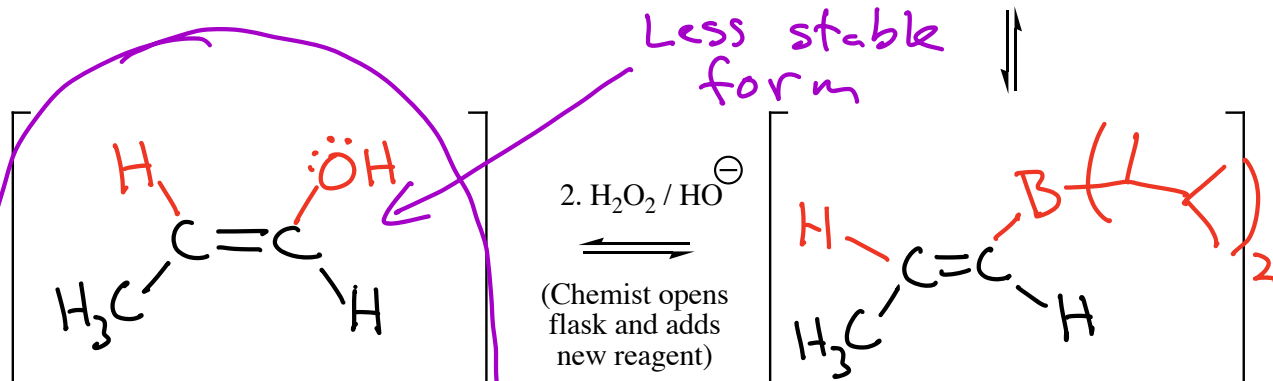
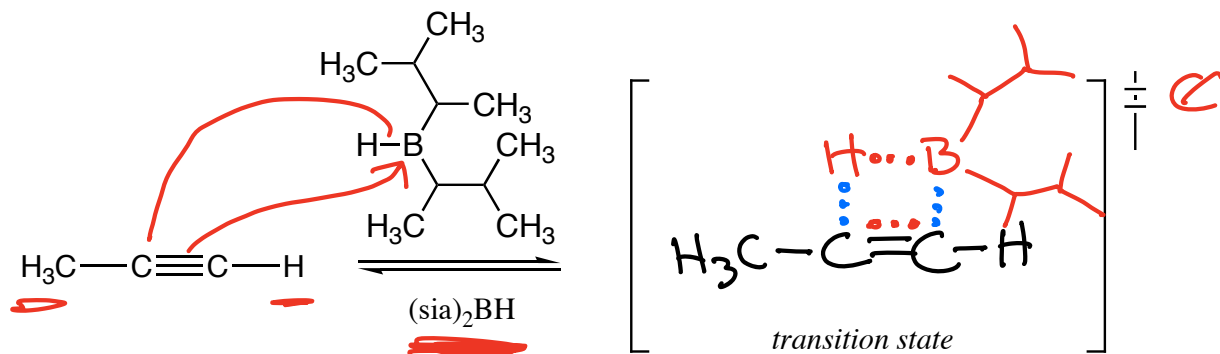




Reductive amination  $\rightarrow$  reducing the  $\text{C}=\text{N}$  of an imine as it forms in the reaction.



## Terminal Alkyne Hydroboration



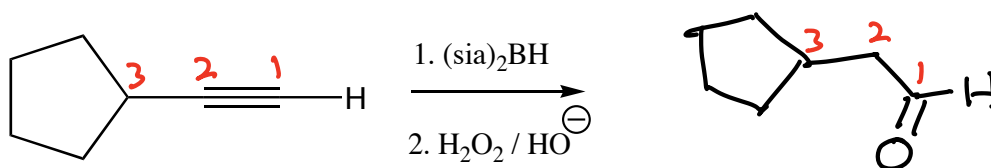
$\Leftarrow$  The C=O is on the C on the end  $\rightarrow$  "non-Markovnikov"

Summary: The  $(\text{sia})_2\text{BH}$  reacts so the B atom attaches to the C atom on the end. The four-membered ring transition state makes both bonds simultaneously.  $2. \text{H}_2\text{O}_2 / \text{HO}^\ominus \rightarrow \text{enol} \rightarrow \text{keto}$

Regiochemistry: non-Markovnikov

Stereochemistry: N/A

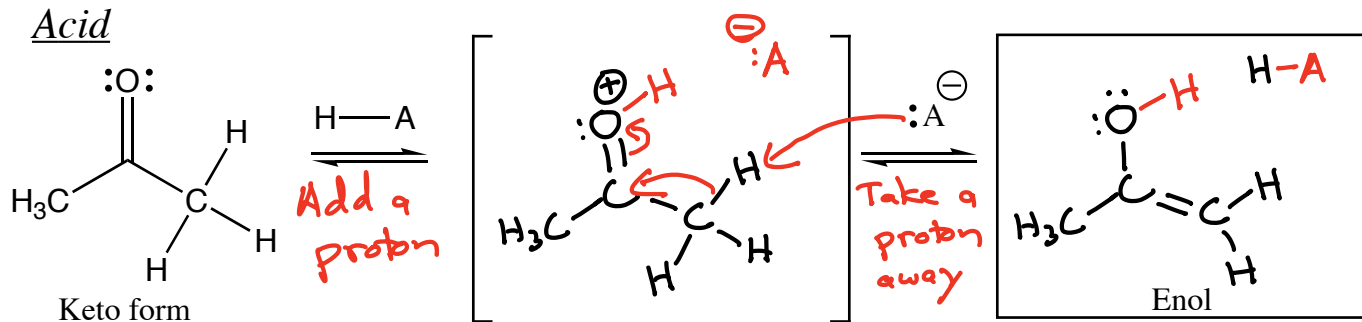
Example:



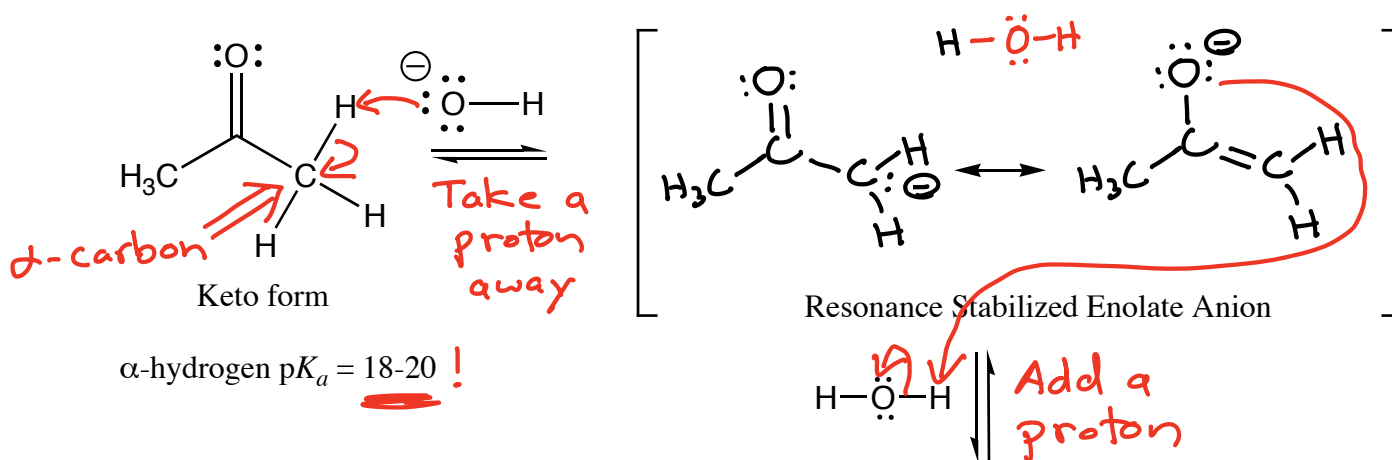
The process of interconverting the keto and enol forms is called "tautomerization"

Keto-Enol Equilibrium Catalyzed by Acid or Base

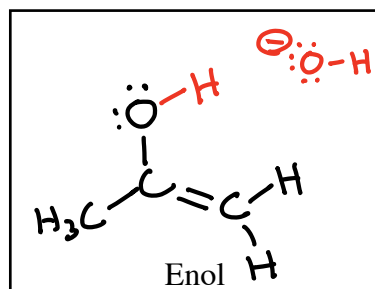
Acid



Base



keto and enol forms are called "tautomers"

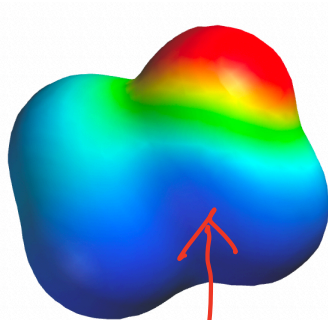
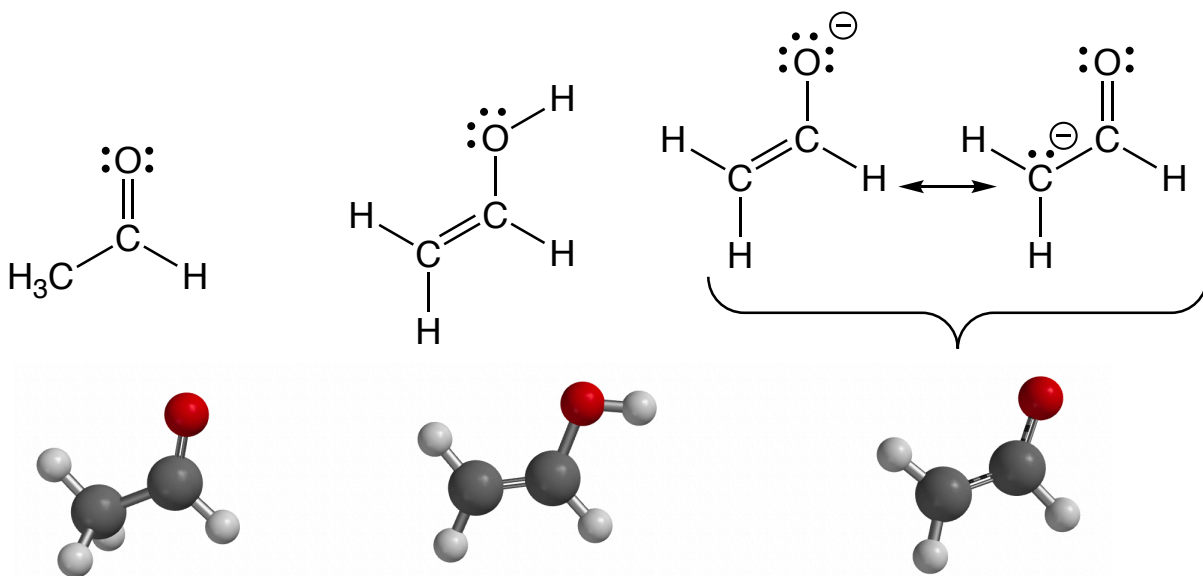


For both aldehydes and ketones, the keto form predominates at equilibrium, because C=O bonds are stronger than C=C bonds.

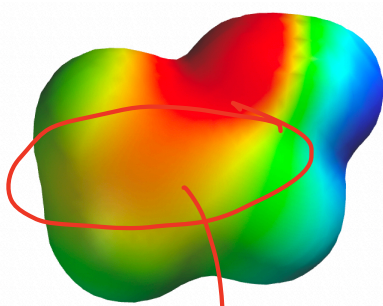
Enols are significant, however, because they react like nucleophile, not carbonyls, and this is important in certain situations.

# Changing Personality:

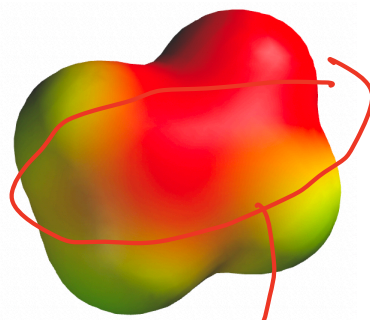
An aldehyde or ketone is a weak **electrophile**.  
An enol of that same aldehyde or ketone has a  $\pi$  bond that is a weak **nucleophile!**



nucleophiles attack here



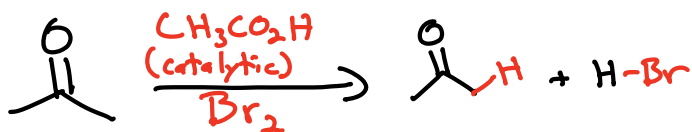
$\pi$  bond is weakly nucleophilic



Strong Nucleophile!

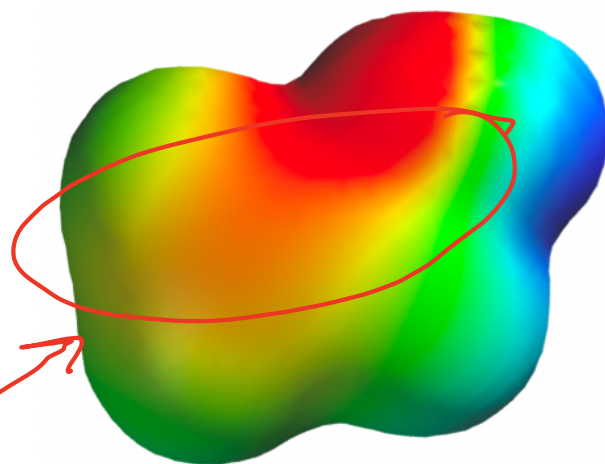
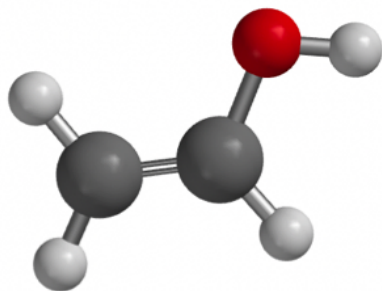
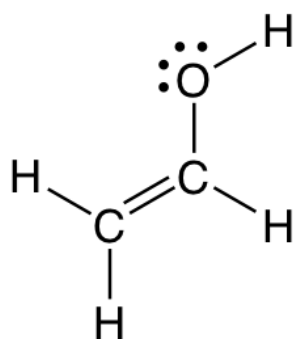
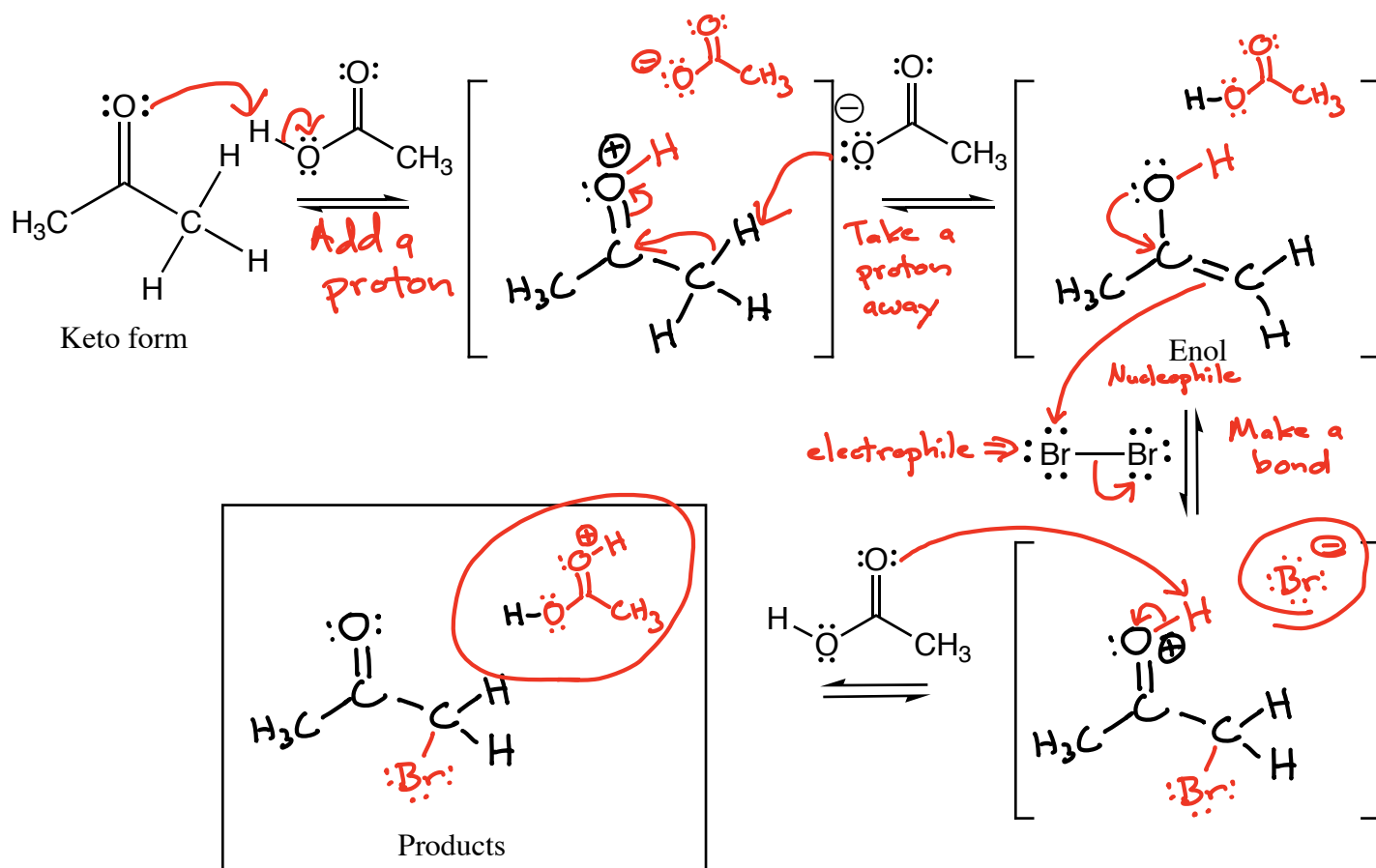
$\alpha$ -Halogenation of Aldehyde or Ketone in Acid

Overall Reaction



ves

## $\alpha$ -Halogenation of an Aldehyde or Ketone Catalyzed by Acid



Nucleophile