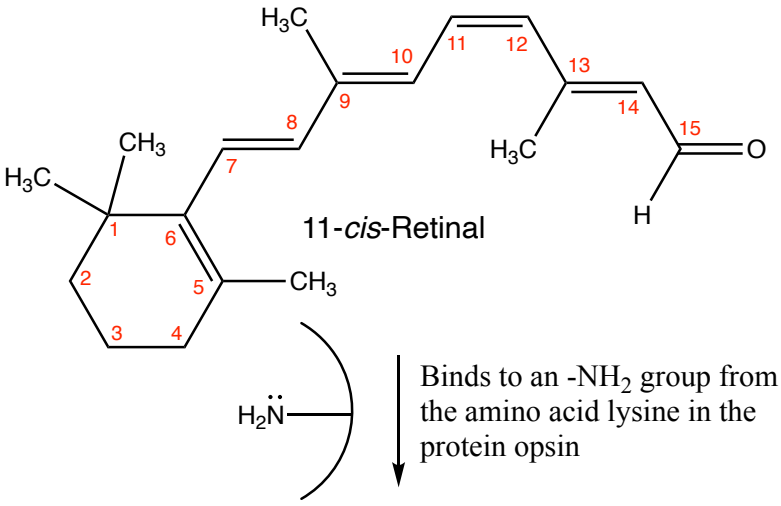
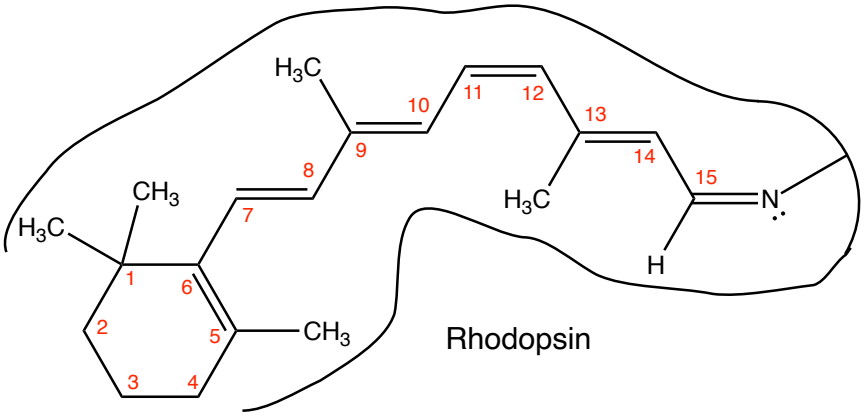
How vision works

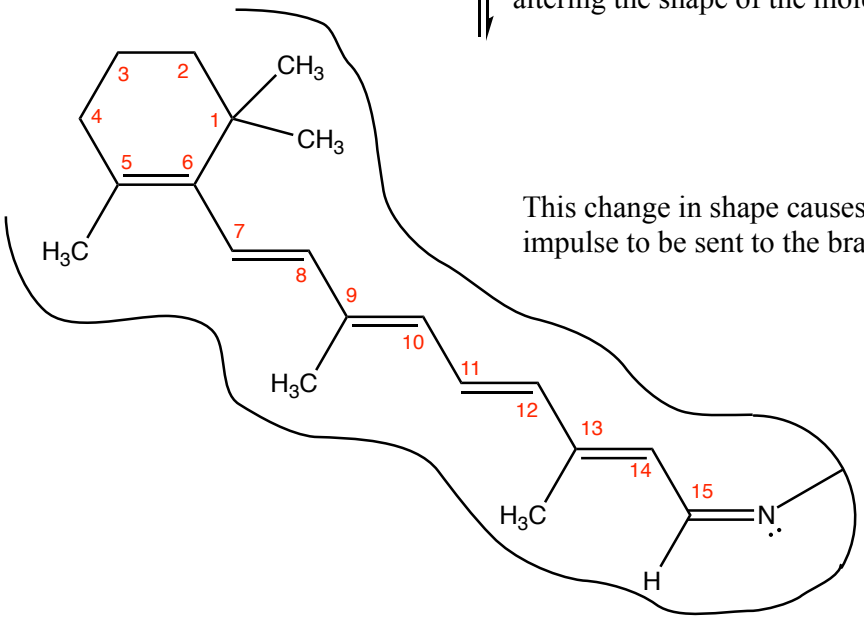


Binds to an -NH_2 group from the amino acid lysine in the protein opsin



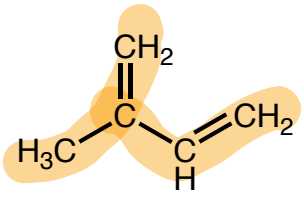
Molecule resets

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

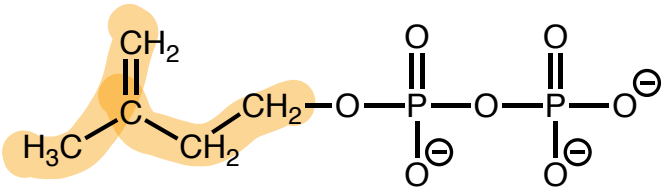


This change in shape causes a nerve impulse to be sent to the brain

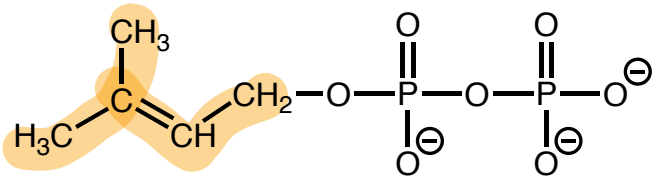
Terpenes



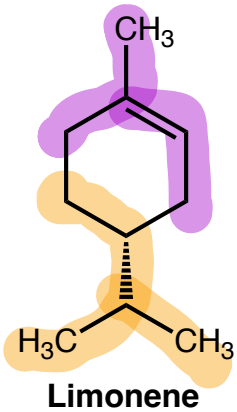
Isoprene



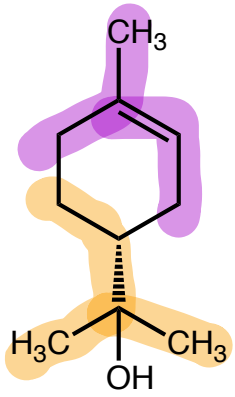
Isopentanyl diphosphate



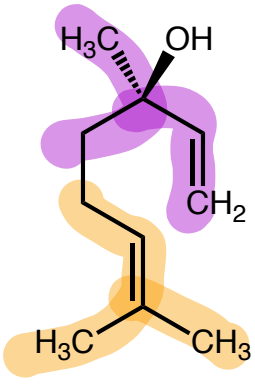
Dimethylallyl diphosphate



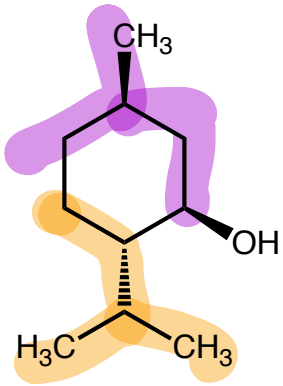
Limonene
(citrus flavor)



α-Terpineol
(from lilacs, used in perfume)

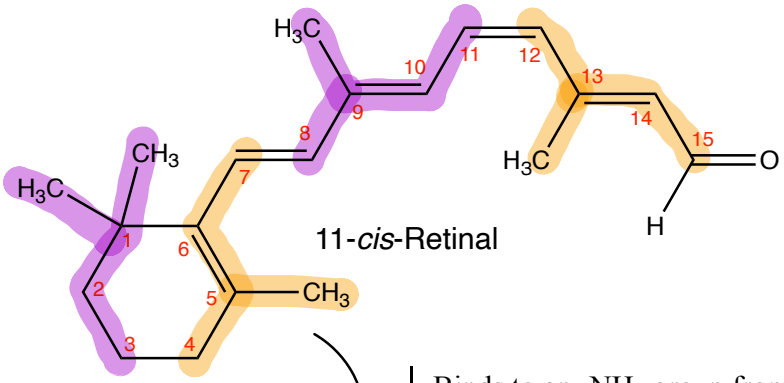


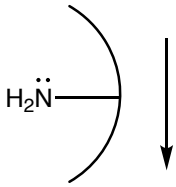
(*R*)-(-)-Linalool
(from lavender, used in perfume)



(-)-Menthol
(common flavoring from peppermint)

How vision works





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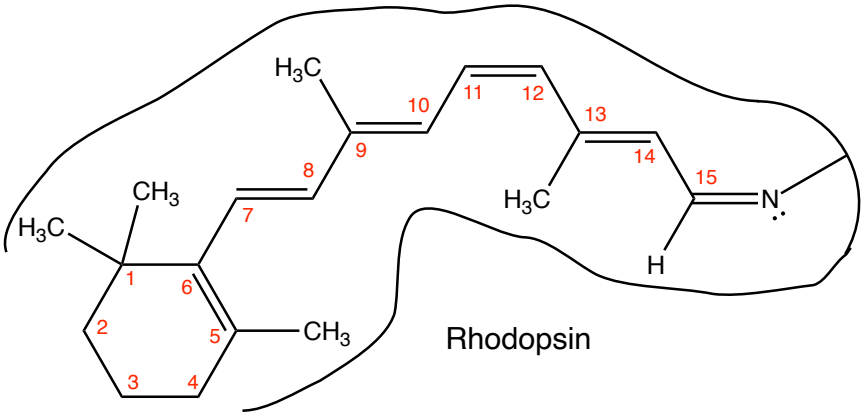

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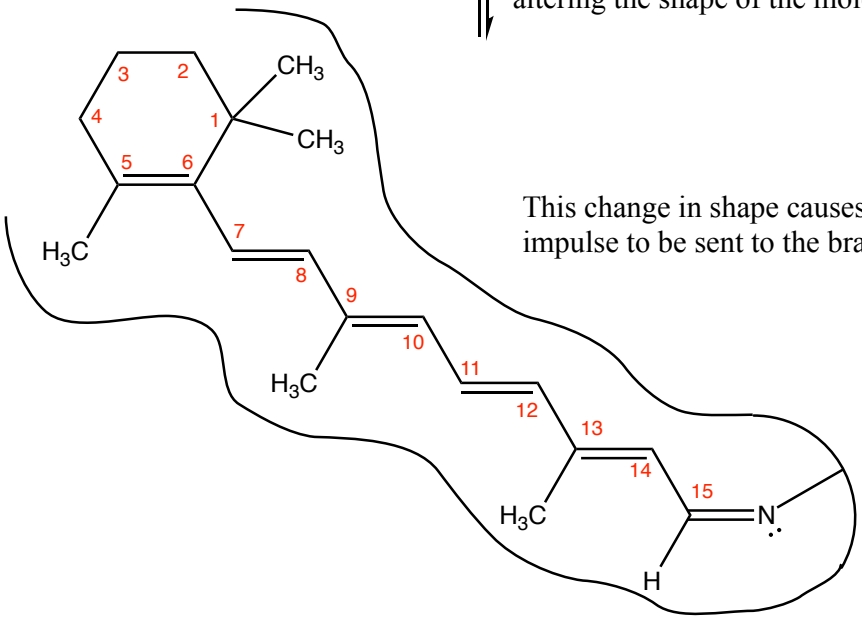

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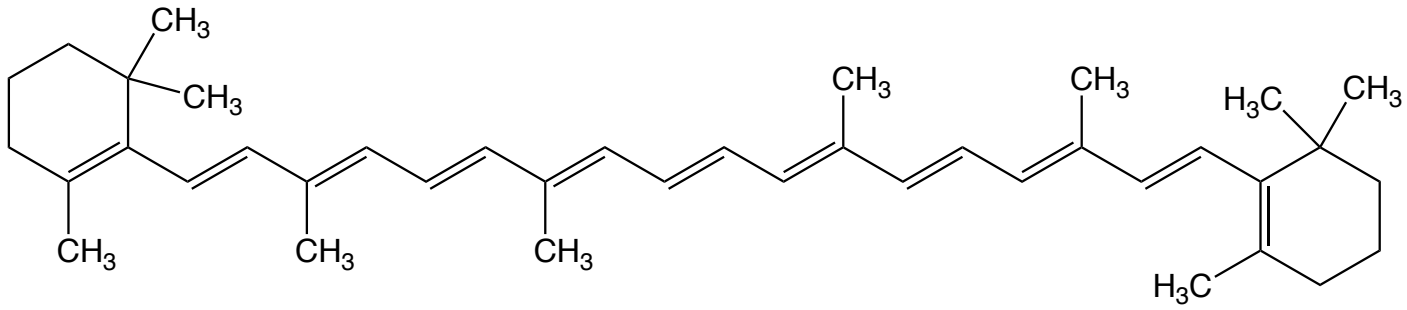
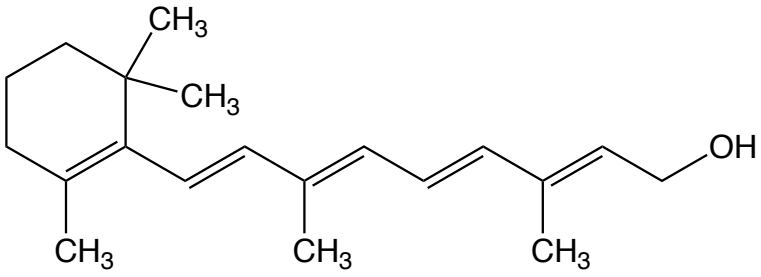
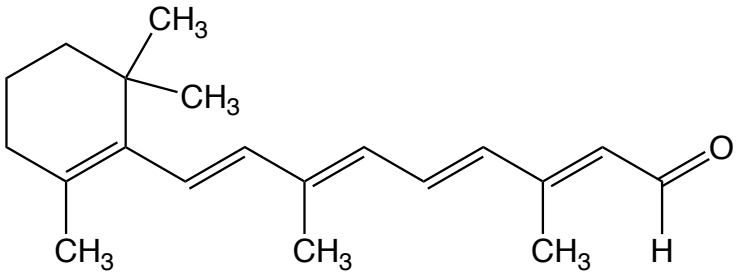


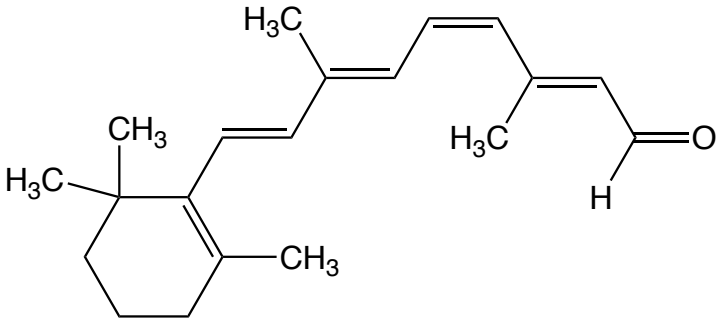
β-Carotene



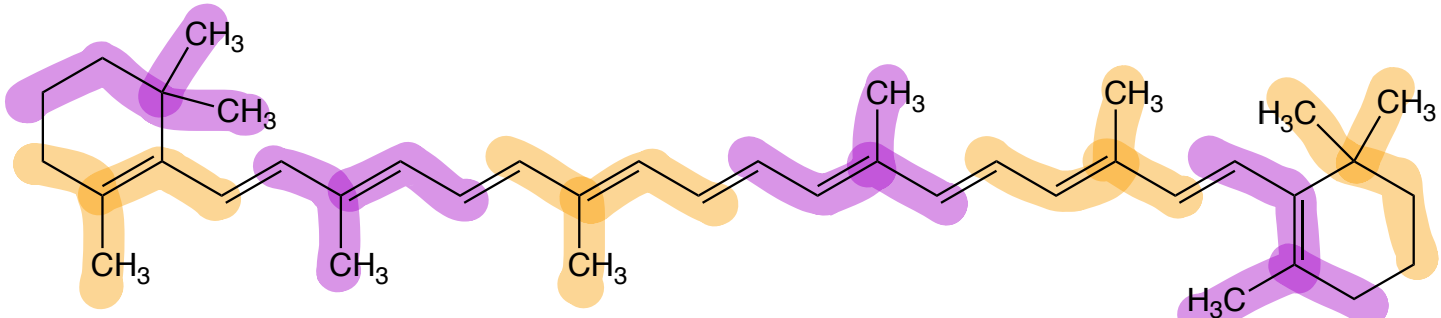
Vitamin A



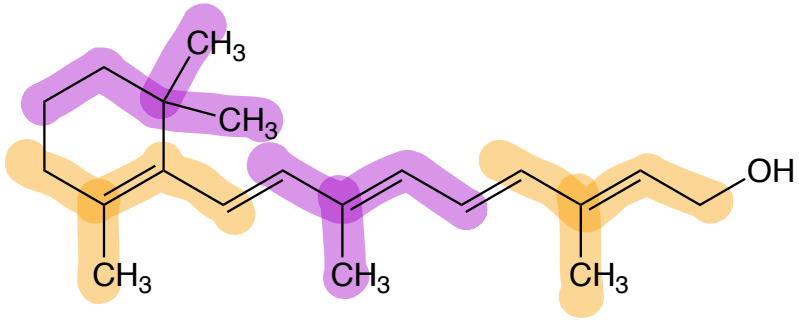
All *trans* Retinal



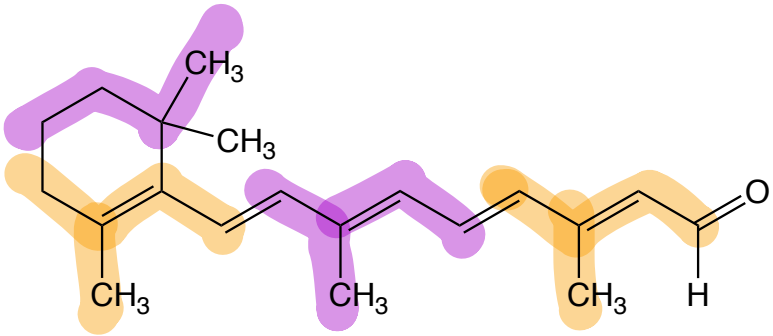
11-*cis*-Retinal



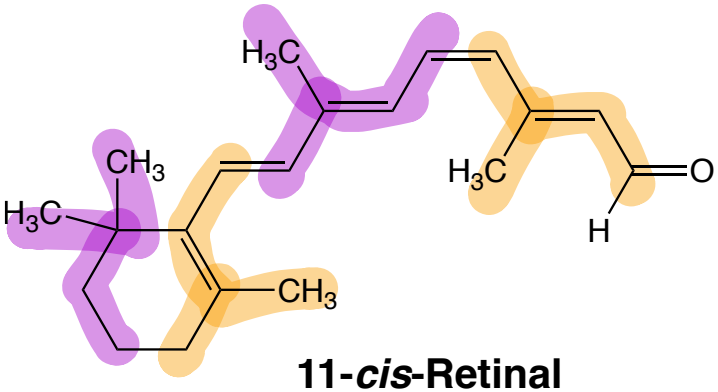
β-Carotene



Vitamin A

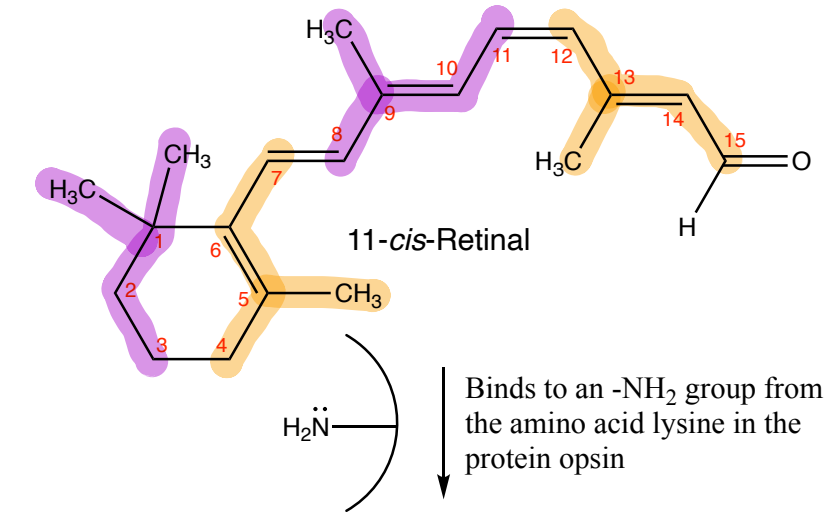


All *trans* Retinal



11-*cis*-Retinal

How vision works



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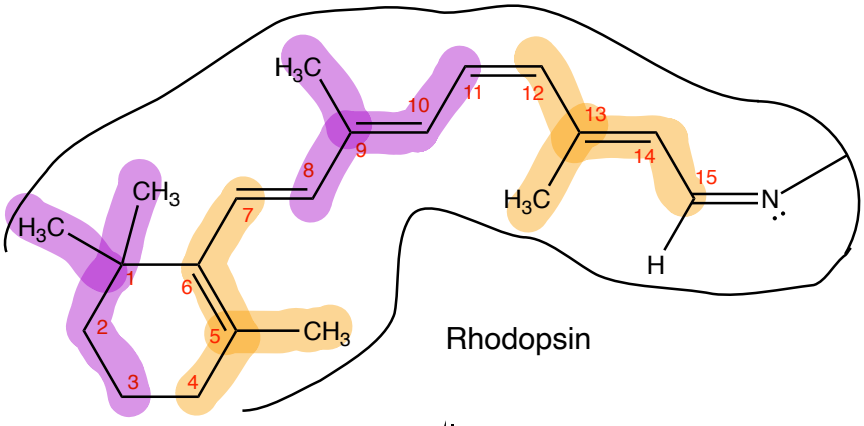

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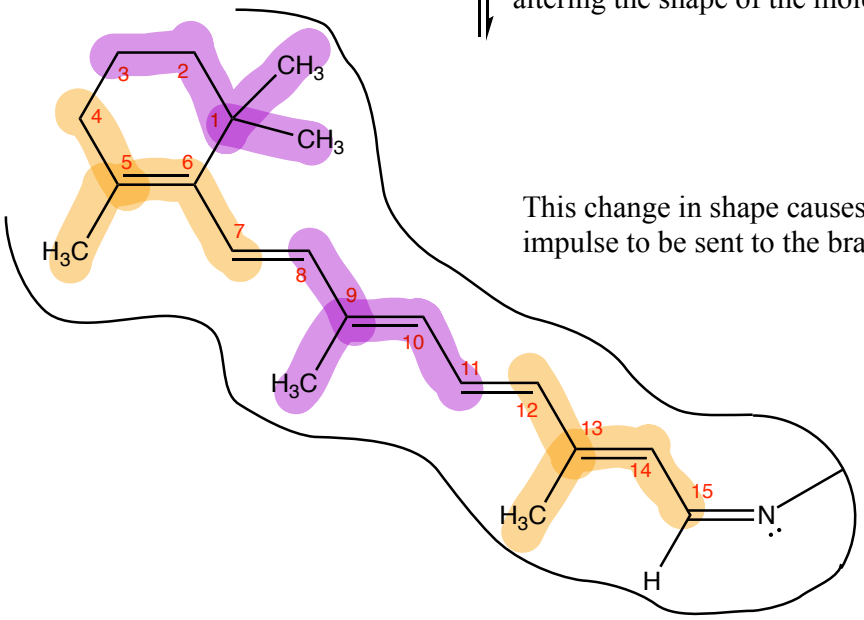
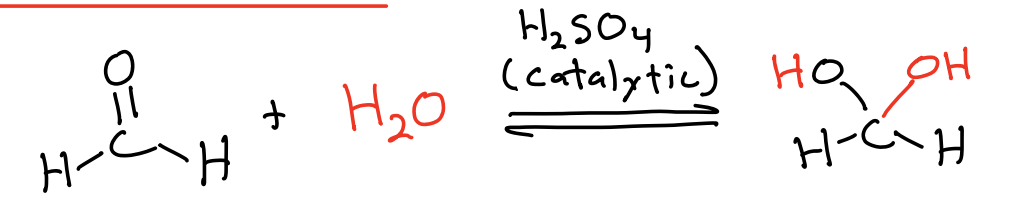


This change in shape causes a nerve impulse to be sent to the brain

Geminal Diols: H_2O instead of ROH

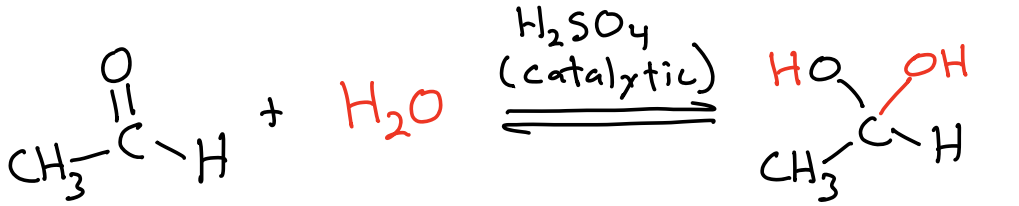
Same mechanism as hemiacetal formation:
Mechanism D



Formaldehyde (gas)

Formalin

Favored at equilibrium



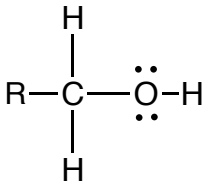
Favored at equilibrium

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

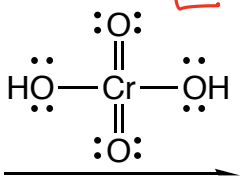
Chromic Acid Oxidation of Alcohols

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

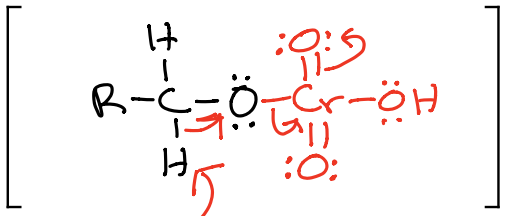
Not responsible for first step

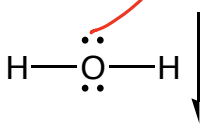


1° Alcohols



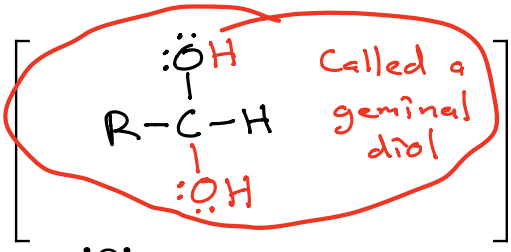
"H_2CrO_4" or "Chromic Acid"



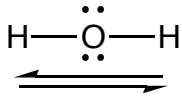


Take a proton away and break a bond

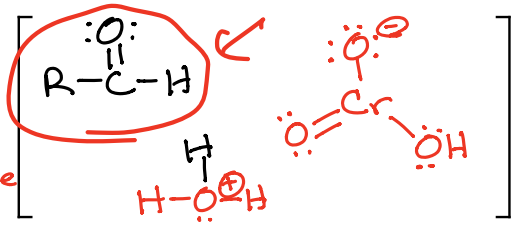
Not responsible for this step

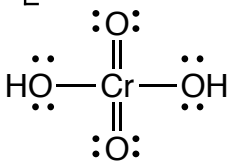


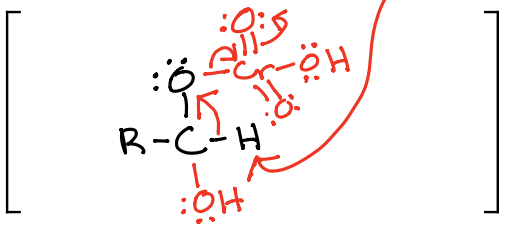
Called a geminal diol

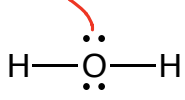


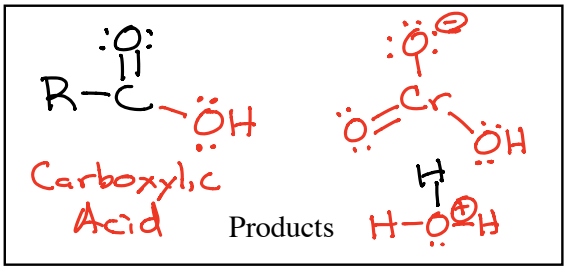
Water reacts with aldehyde – will learn next semester







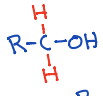




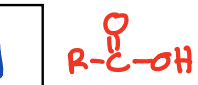
Carboxylic Acid

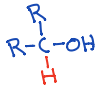
Products

Summary:

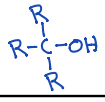


1° alcohols ⇒ Carboxylic Acid





2° alcohols ⇒ Ketone

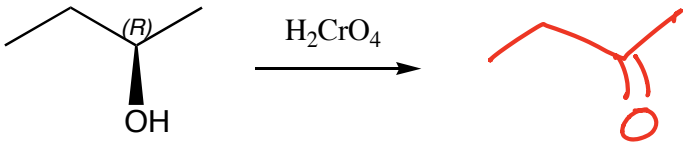


3° alcohols ⇒ NO REACTION

Regiochemistry: N/A

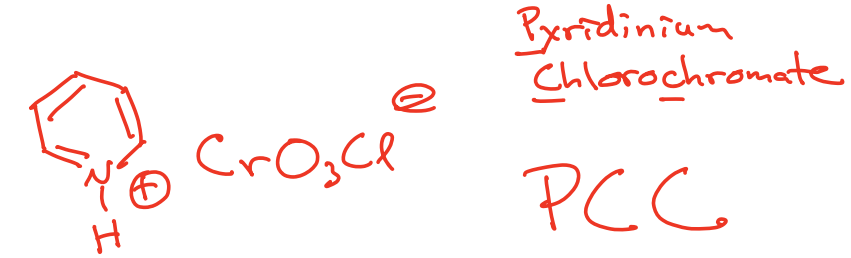
Stereochemistry: N/A

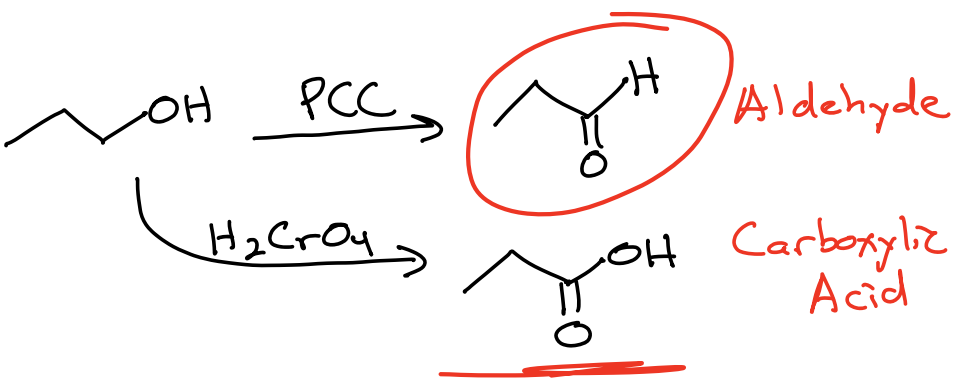
Example:

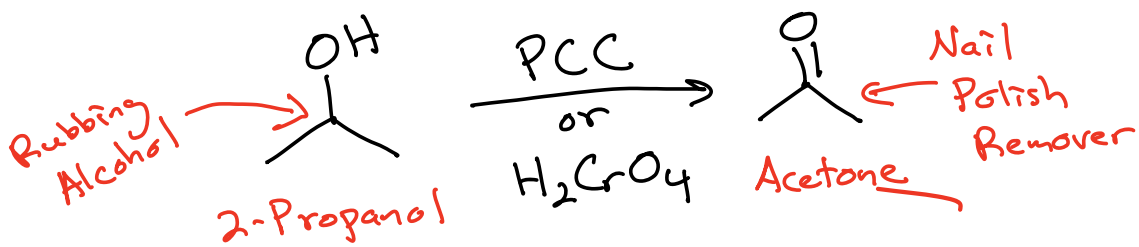


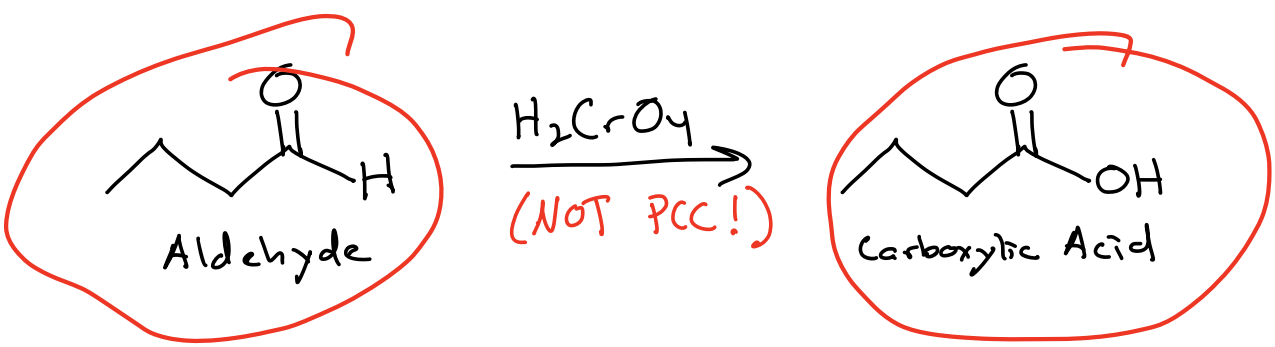
Ketone

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



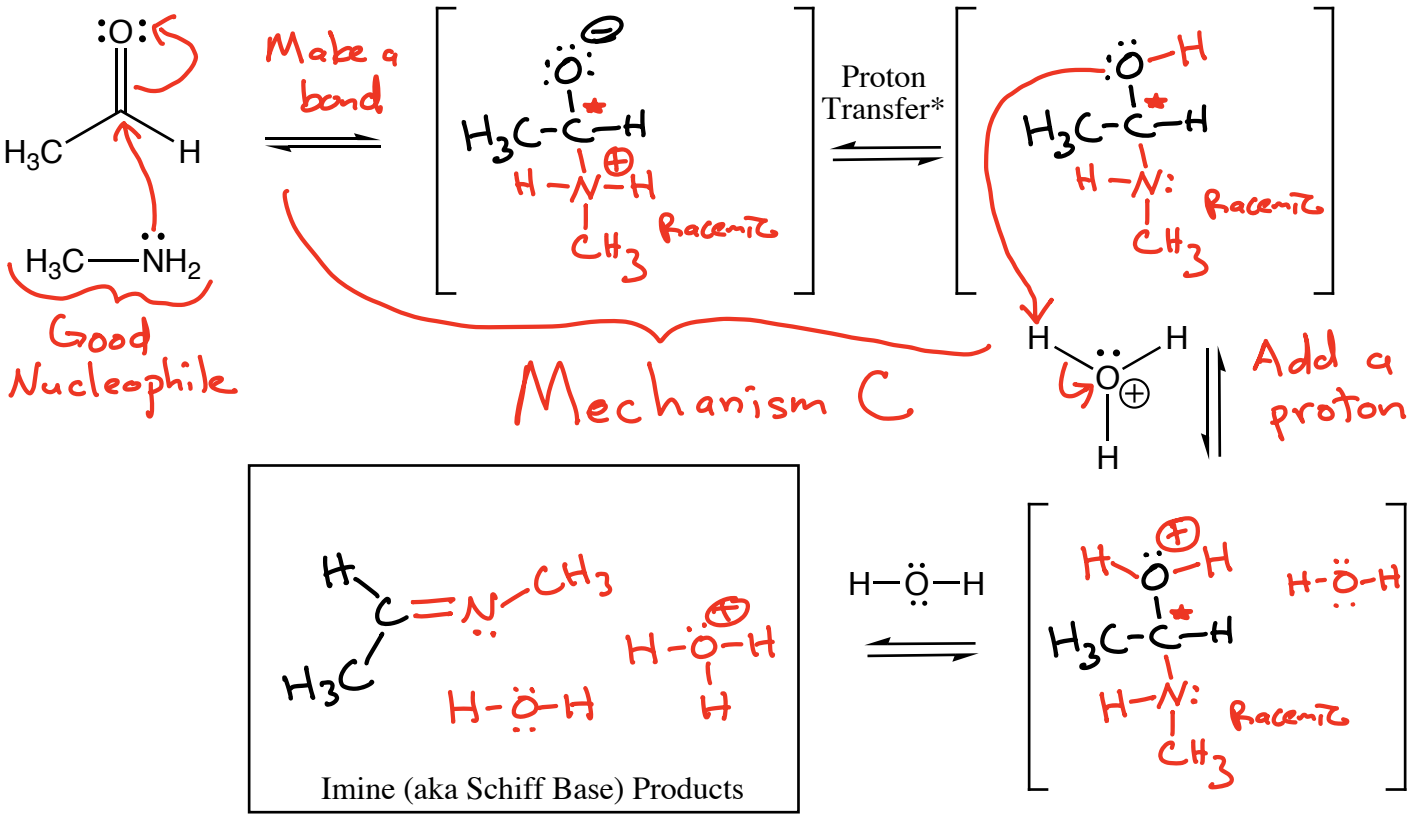






Recall:

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



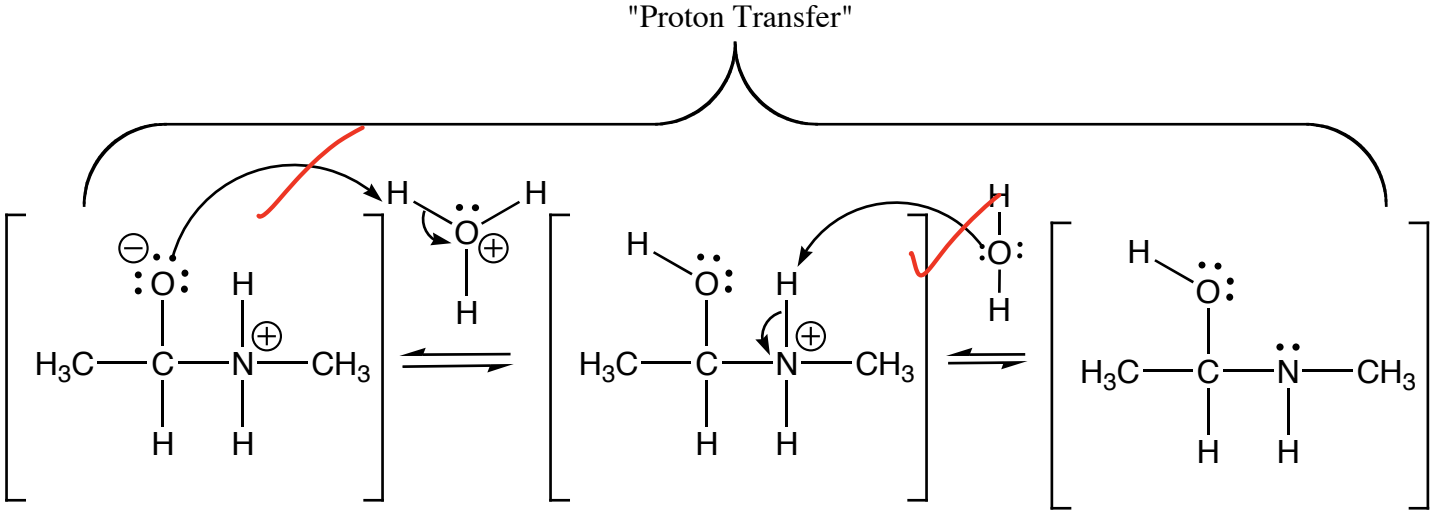
Key Recognition Element (KRE):

The C=O is converted to C=N

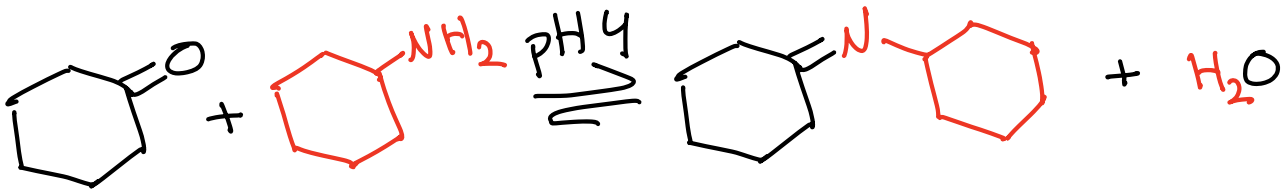
(Note: this last step might actually occur as two steps in some cases.)

---

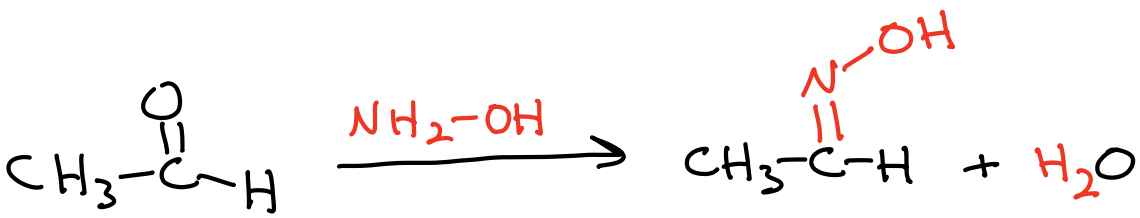
* "Proton Transfer" refers to a situation in which a proton moves from one part of a molecule to another on the SAME MOLECULE. We do not draw arrows for proton transfer steps because that would be deceptive. In some cases, the same proton may move from one part of the molecule to the other directly, 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. Becuase of all the ambiguity, we just write "Proton Transfer" and do not bother with arrows.



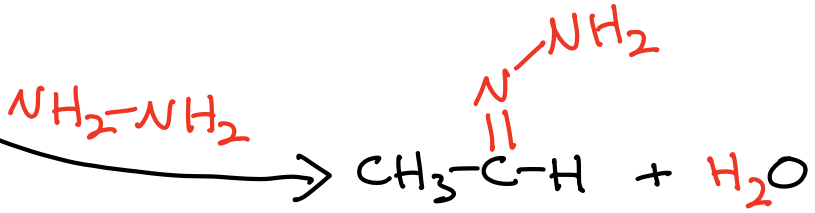
This is reversible:



Other similar reagents react the same way:

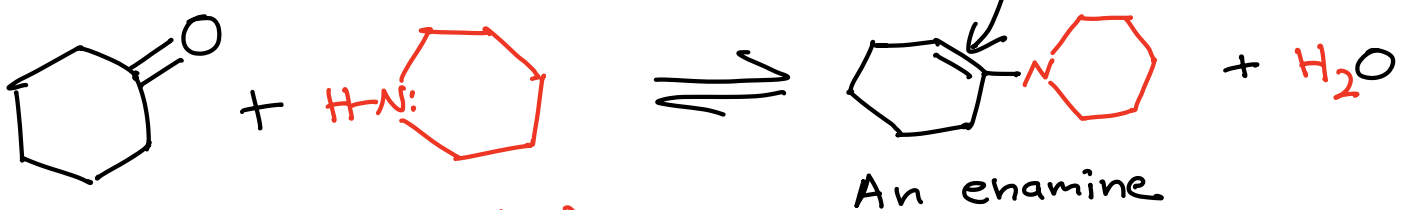


An oxime



A hydrazone

2° Amines



An enamine

2° (secondary) Amine – only one H atom

Time capsule – enamines are great nucleophiles

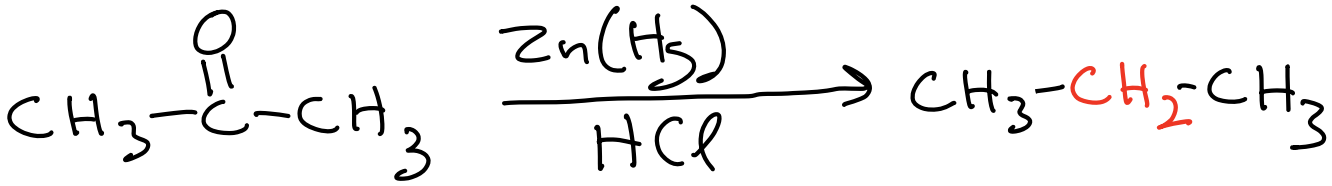
Conversion of ketone and aldehyde C=O groups to $-CH_2-$

In acid

Clemmenson Reduction → you are not responsible for the mechanism

↓

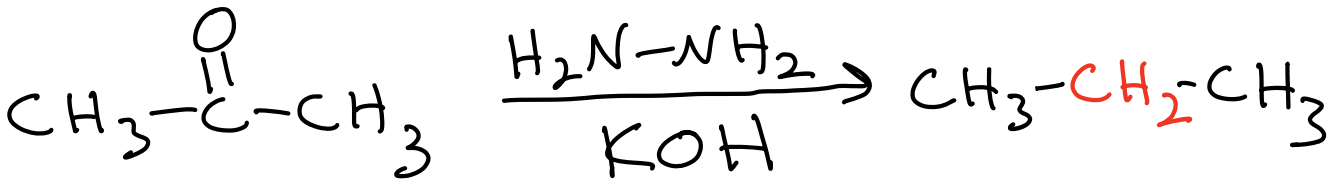
Relatively harsh conditions



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

In base

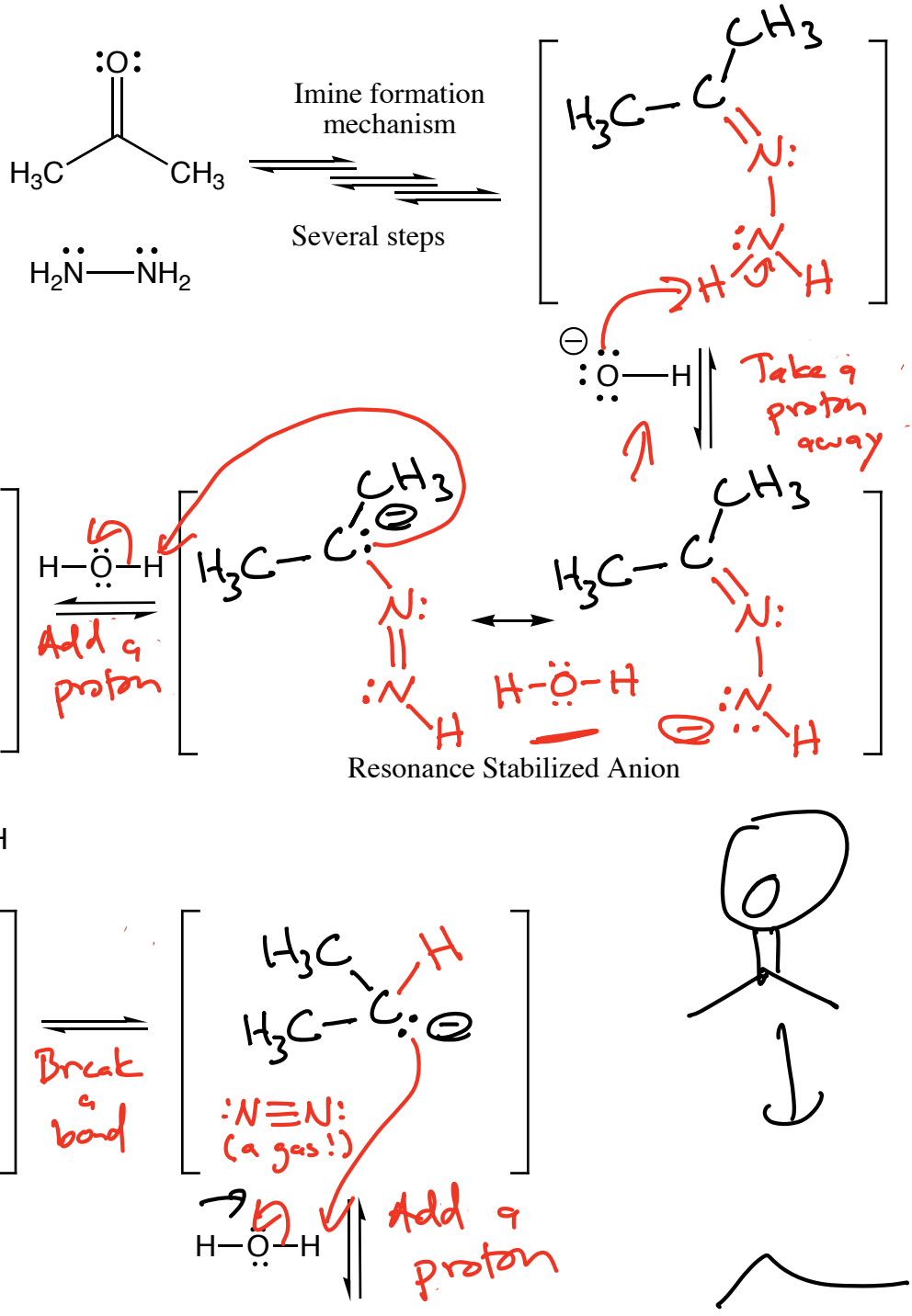
Wolff-Kishner Reduction



Used when there are acid-sensitive groups on a molecule

VERY COOL MECHANISM

Wolff-Kishner Reduction of an Aldehyde or Ketone



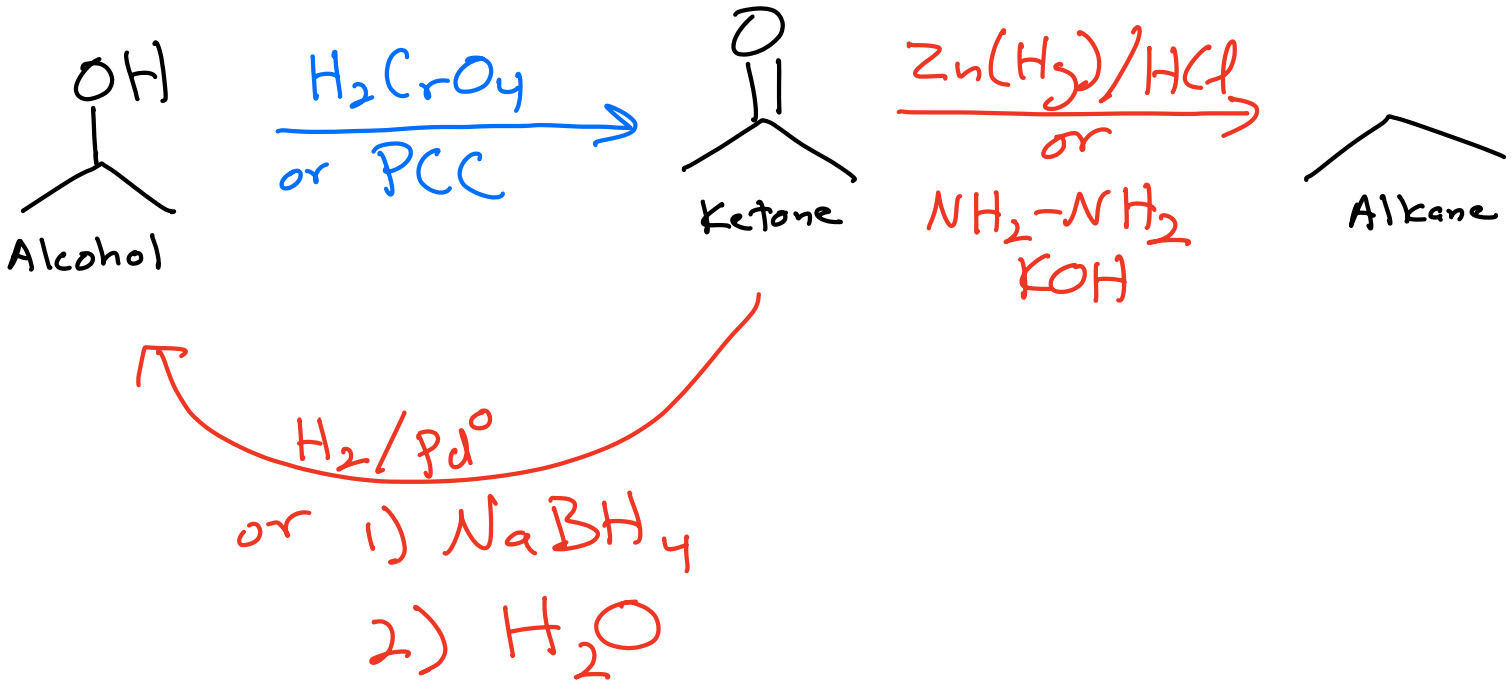
Key Recognition Element (KRE):

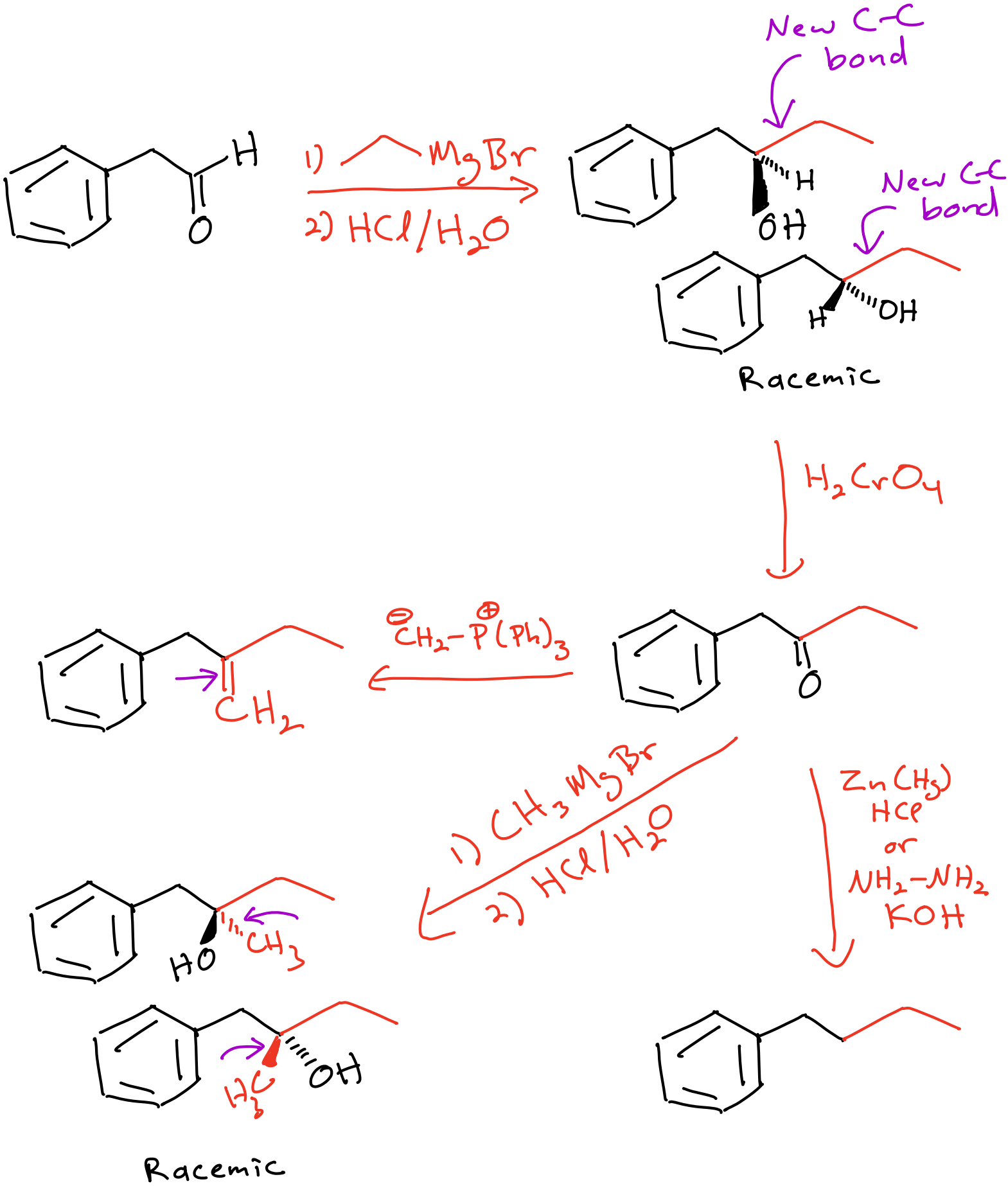
$-CH_2-$ where there was $C=O$

Products

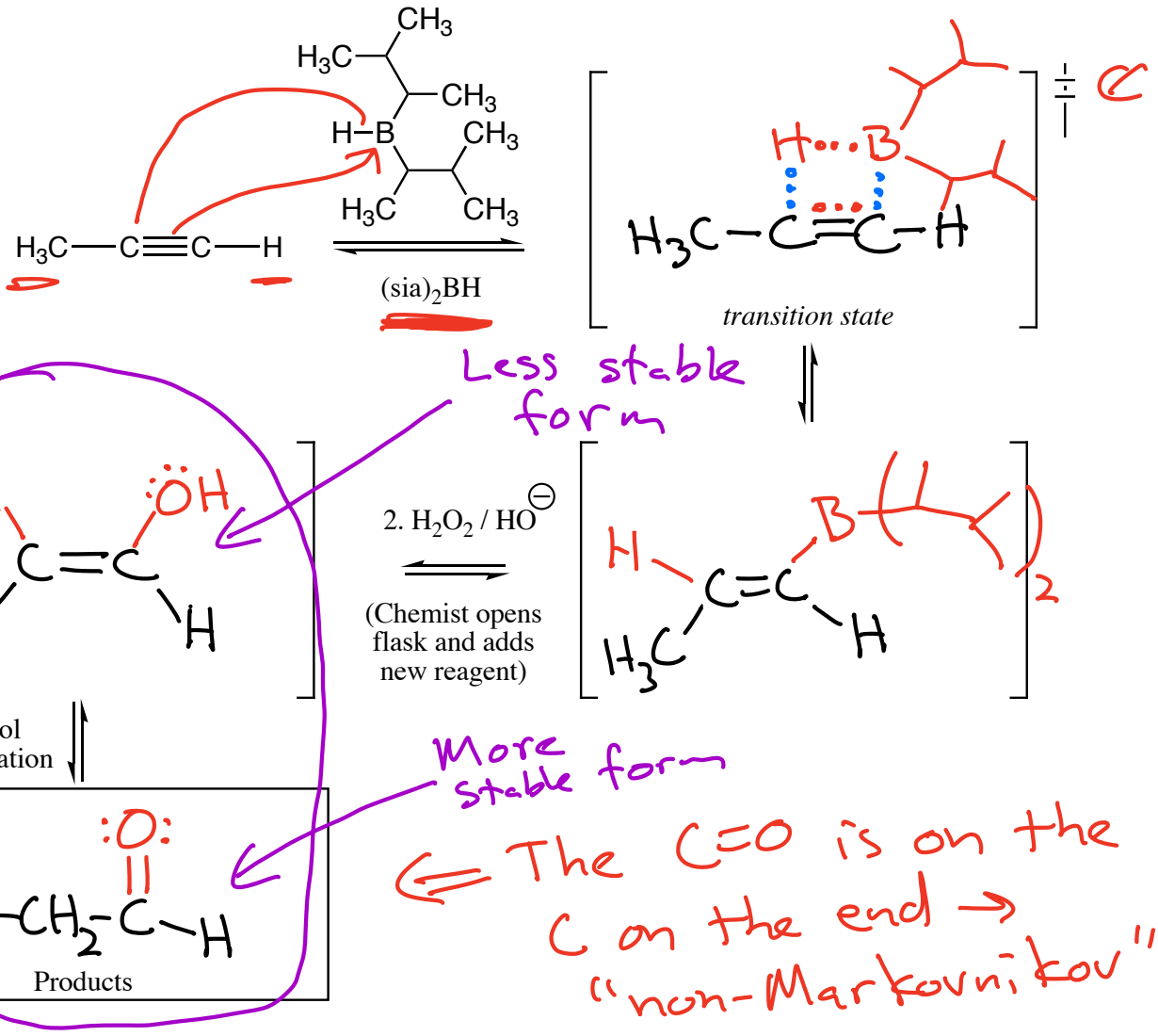

Eek! Don't bite my head off!
O
NH_2-NH_2
KOH

Putting these oxidation and reduction reactions to work in synthesis




New C-C bond
1) MgBr
2) HCl/H2O
H
O
OH
New C-C bond
H
OH
Racemic
H2CrO4
CH2-P(Ph)3
CH2
O
1) CH3MgBr
2) HCl/H2O
Zn(Hg)
HCl
or
NH2-NH2
KOH
HO
CH3
OH
H
Racemic

Terminal Alkyne Hydroboration



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: