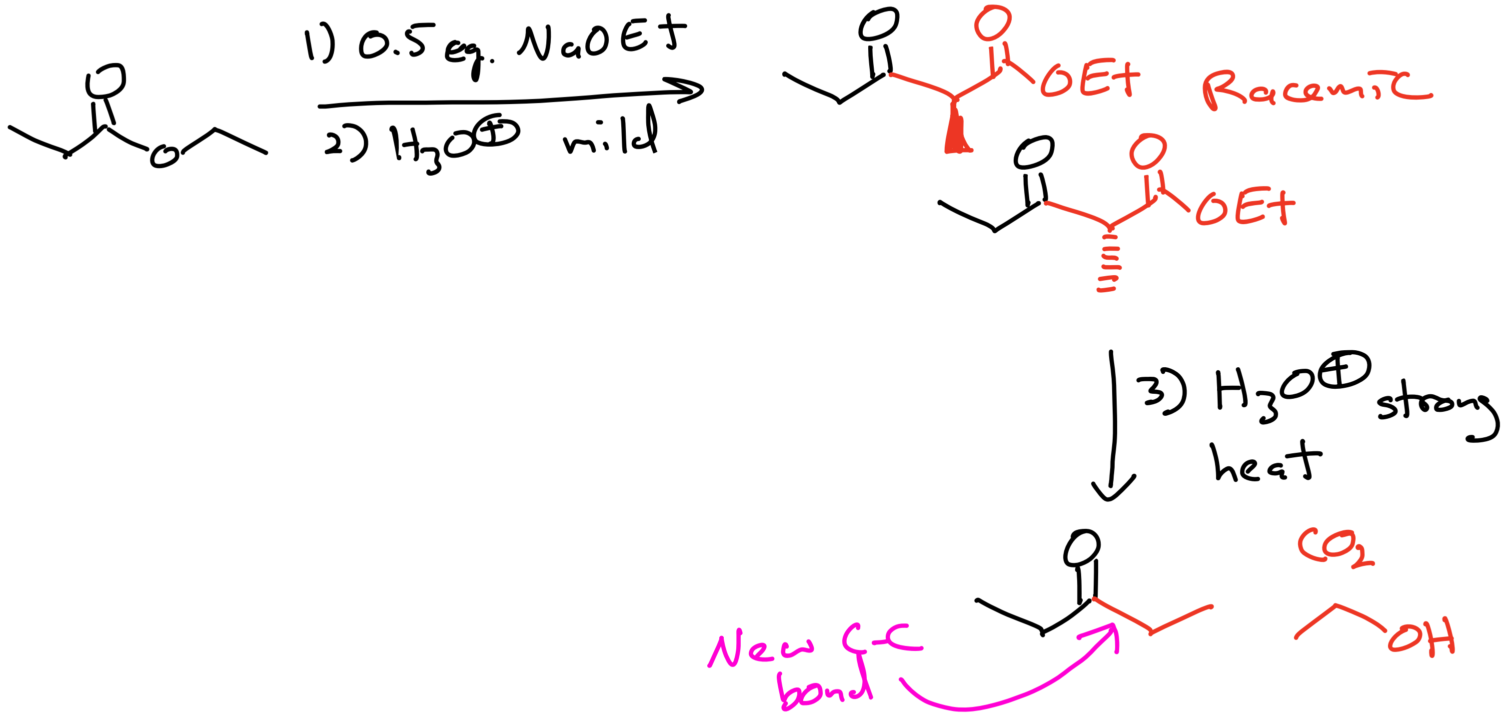
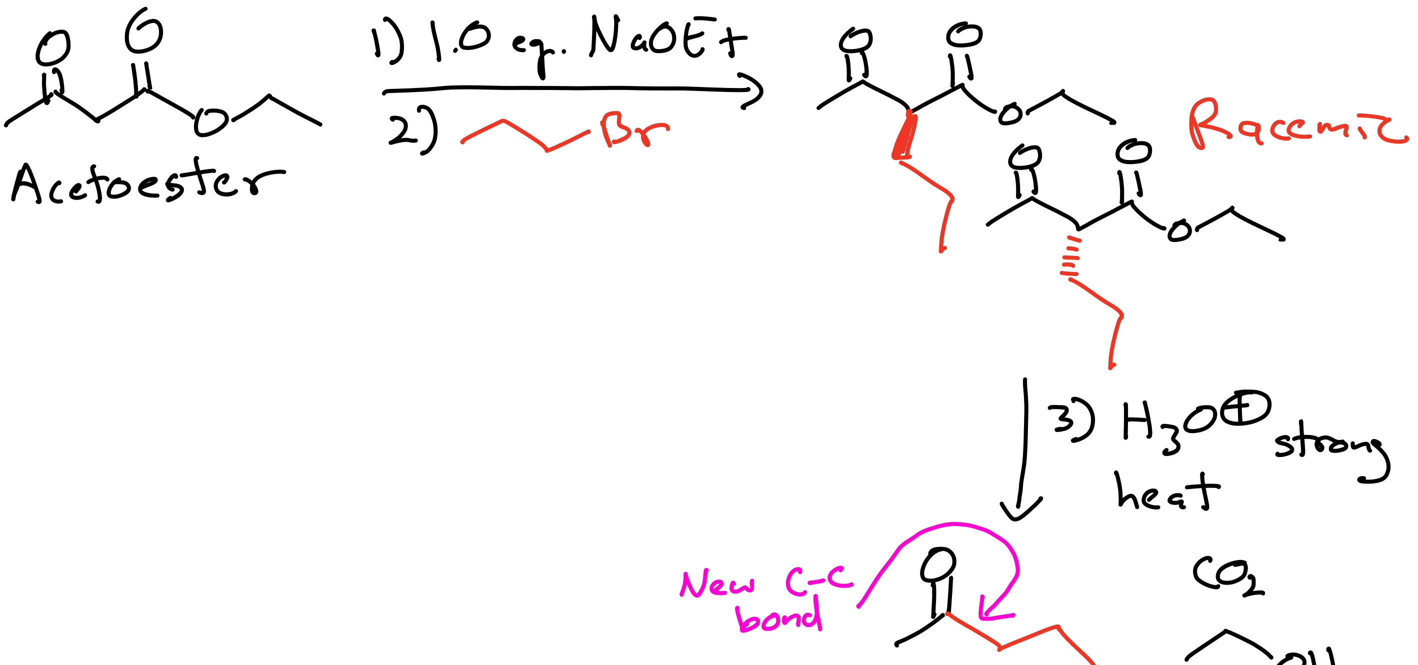
Claisen with Decarboxylation

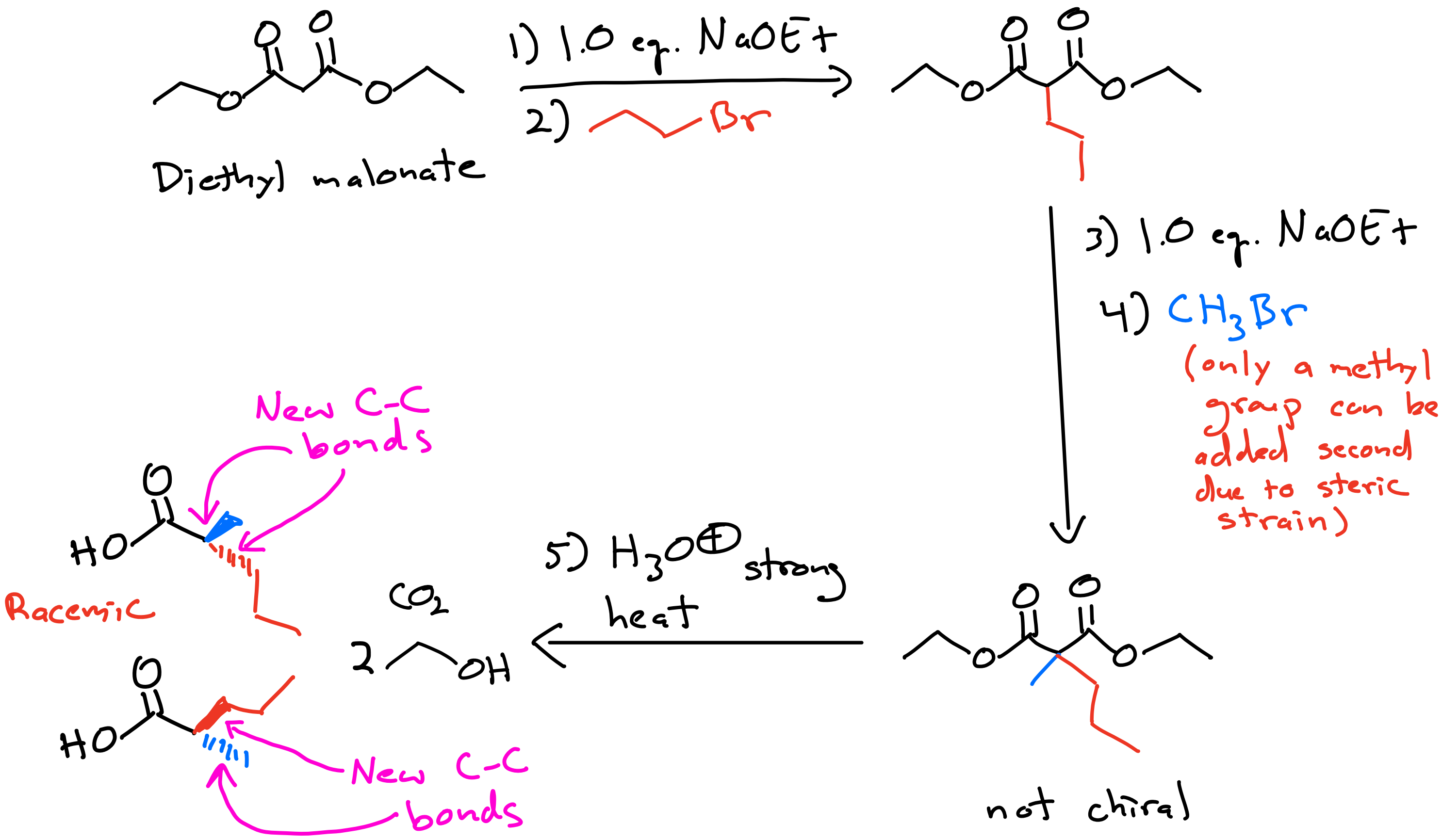


Acetoester Synthesis



KRE → Methyl ketone

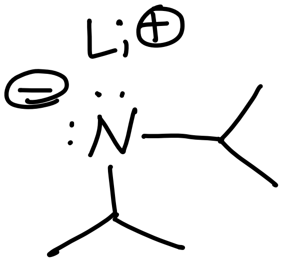
Malonic Ester Synthesis



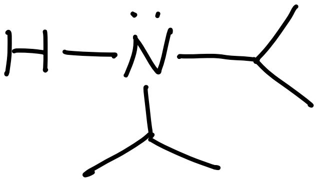
(only a methyl group can be added second due to steric strain)

KRE → Carboxylic acid

The wicked strong base that changes things



NOT a nucleophile



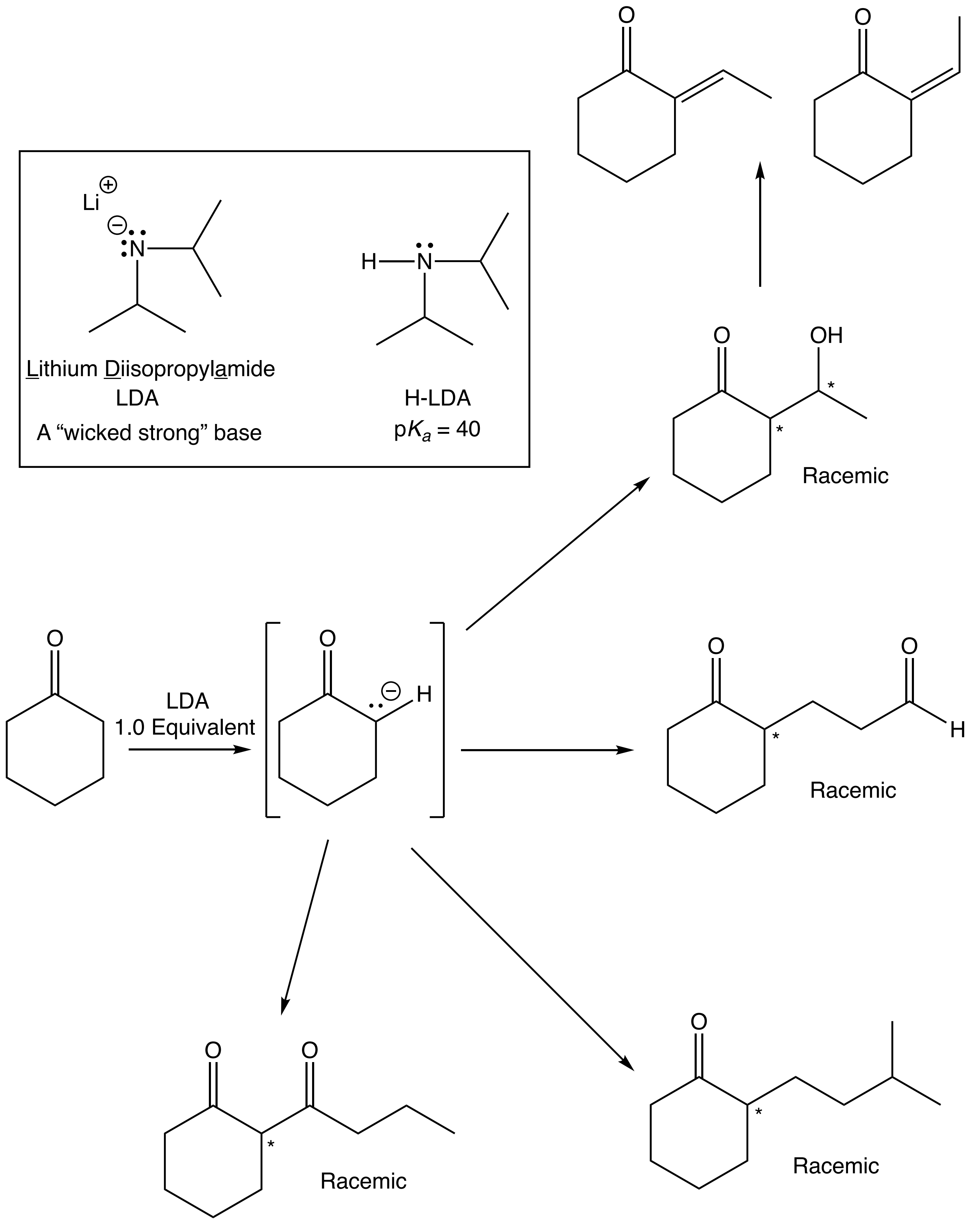
Lithium Diisopropylamide

"LDA"

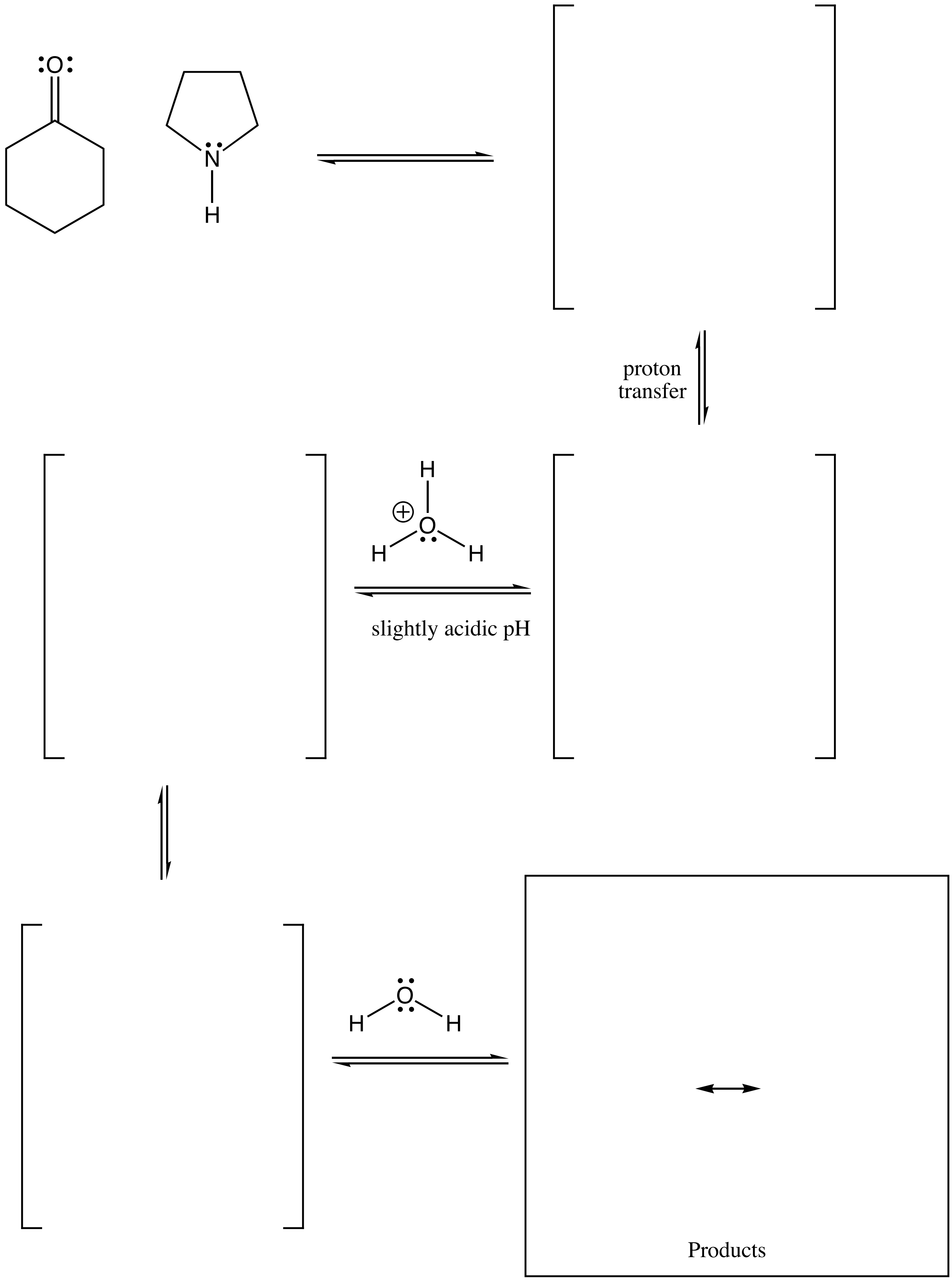
$pK_a \cong 40$

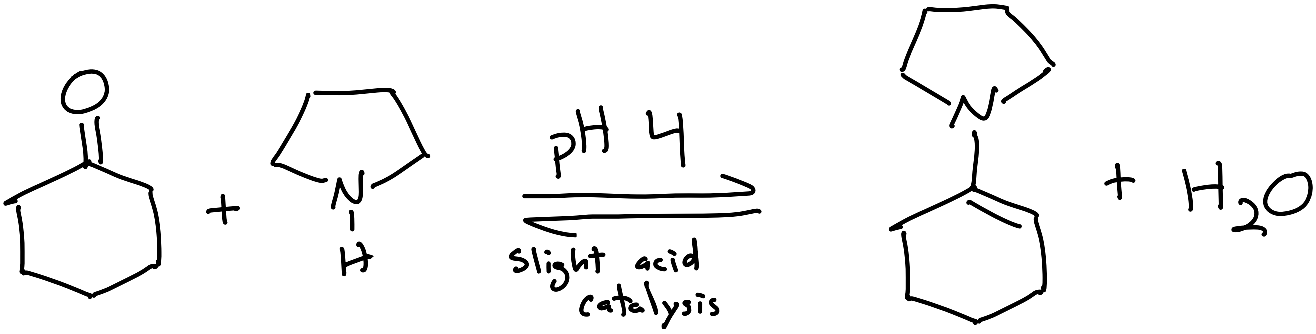
"H-LDA"

LDA will quantitatively deprotonate aldehydes, ketones and esters to make enolates!


Li
N
H
N
Lithium Diisopropylamide
LDA
A “wicked strong” base
H-LDA
pK_a = 40
O
O
OH
*
*
Racemic
O
LDA
1.0 Equivalent
O
H
O
O
H
*
Racemic
O
O
*
Racemic
O
*
Racemic

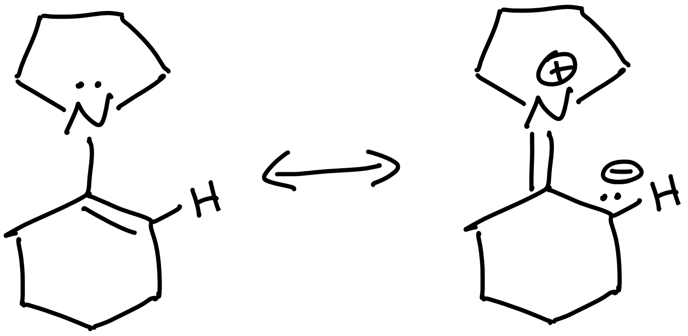
Enamine Formation





Enamine

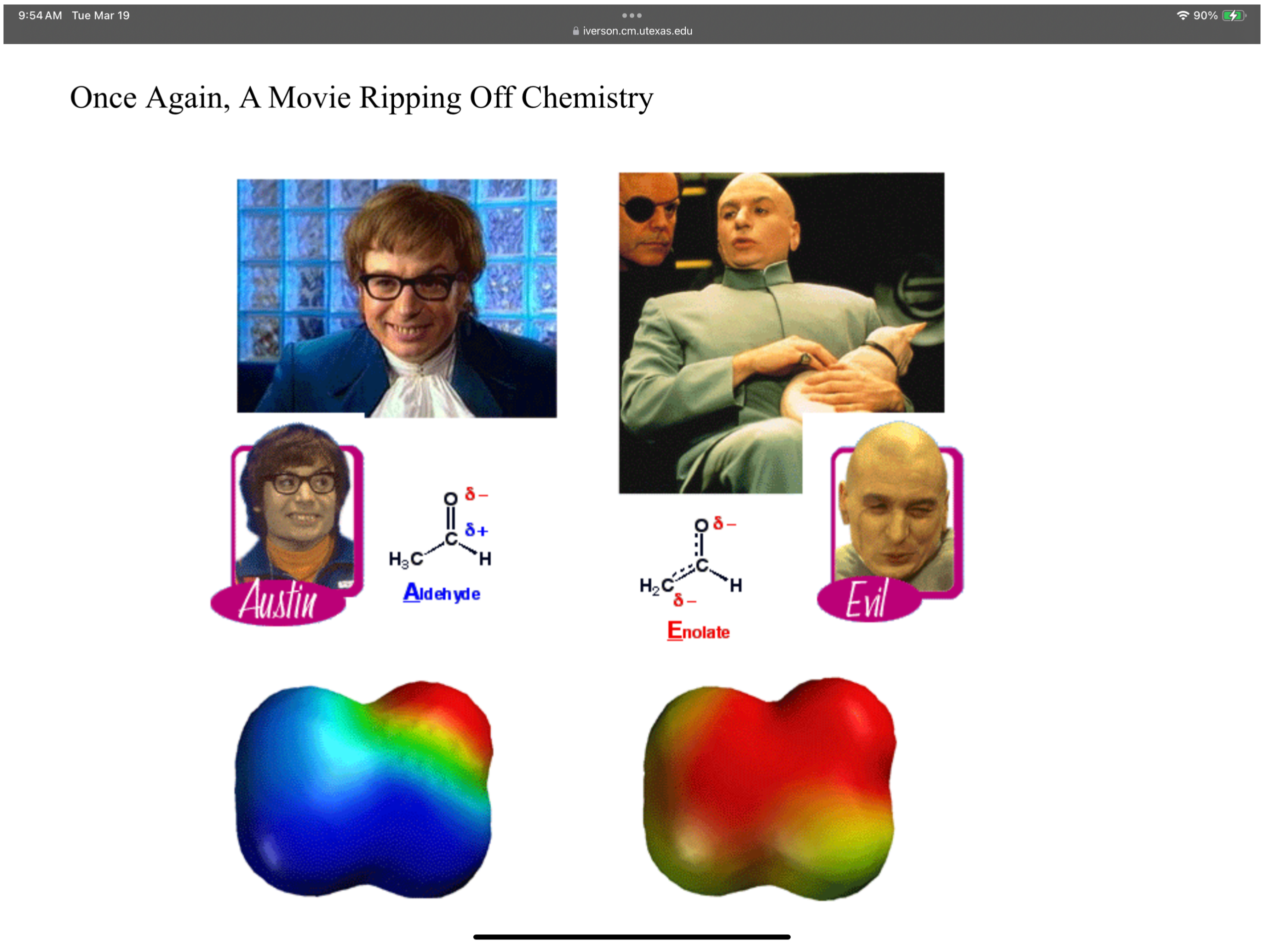
This process is reversible → adding drives it to the left (ketone) and taking away drives it to the right (enamine)



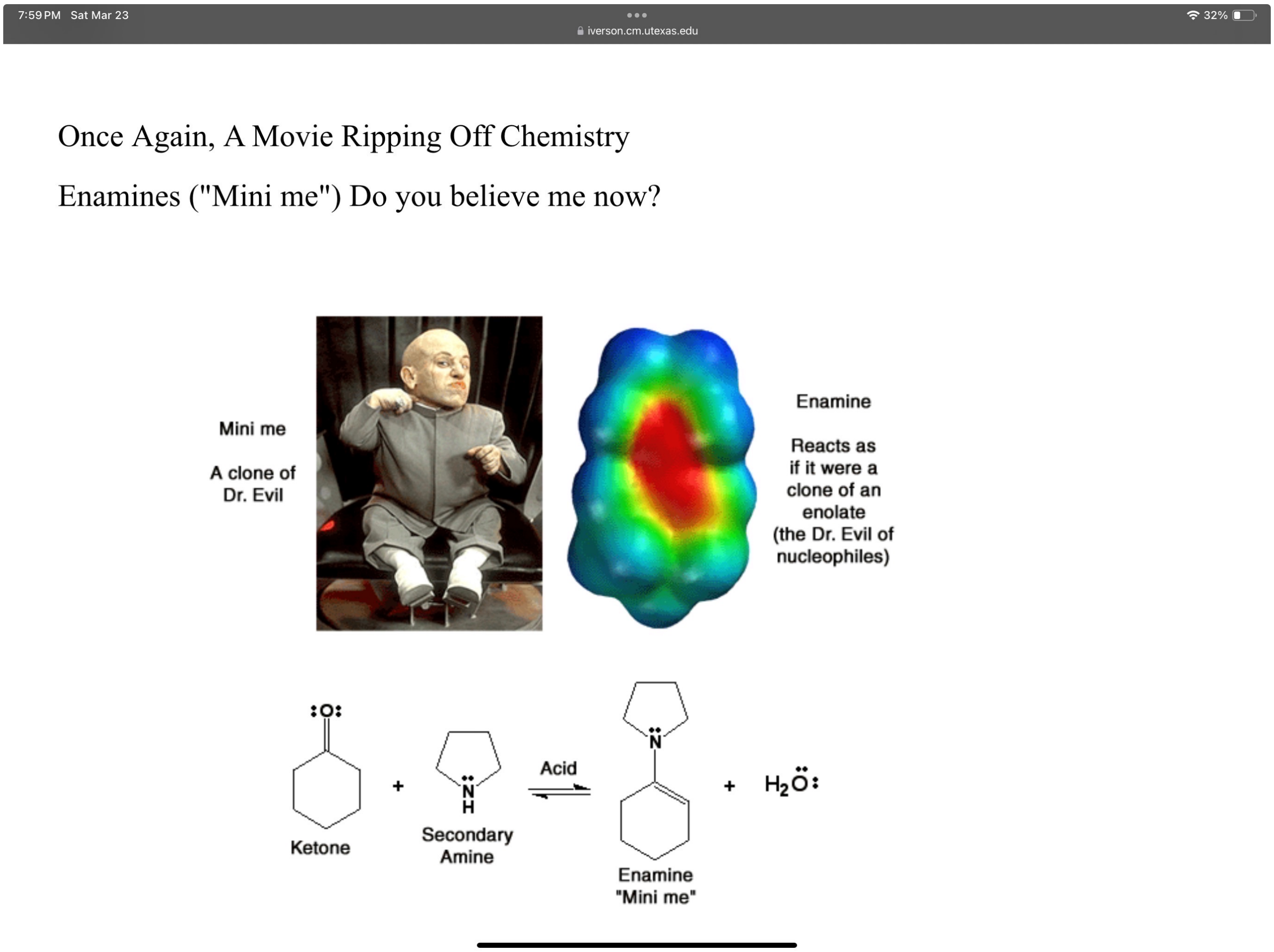
Major Contributor

Minor Contributor (but still significant)

⇒ A "smaller" (i.e. less reactive) version of an enolate ⇒ α C is a nucleophile!!



Once Again, A Movie Ripping Off Chemistry



Once Again, A Movie Ripping Off Chemistry

Enamines ("Mini me") Do you believe me now?

Mini me

A clone of Dr. Evil

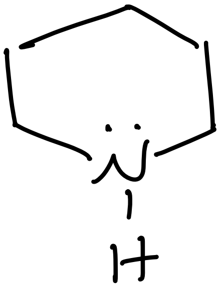
Enamine

Reacts as if it were a clone of an enolate (the Dr. Evil of nucleophiles)

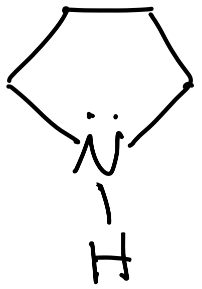
Note the relatively conditions used to make the enamine → pH 4, no harsh acid or base required.

It takes to make an enolate

For this class we will only use the following two secondary amines to make an enamine:

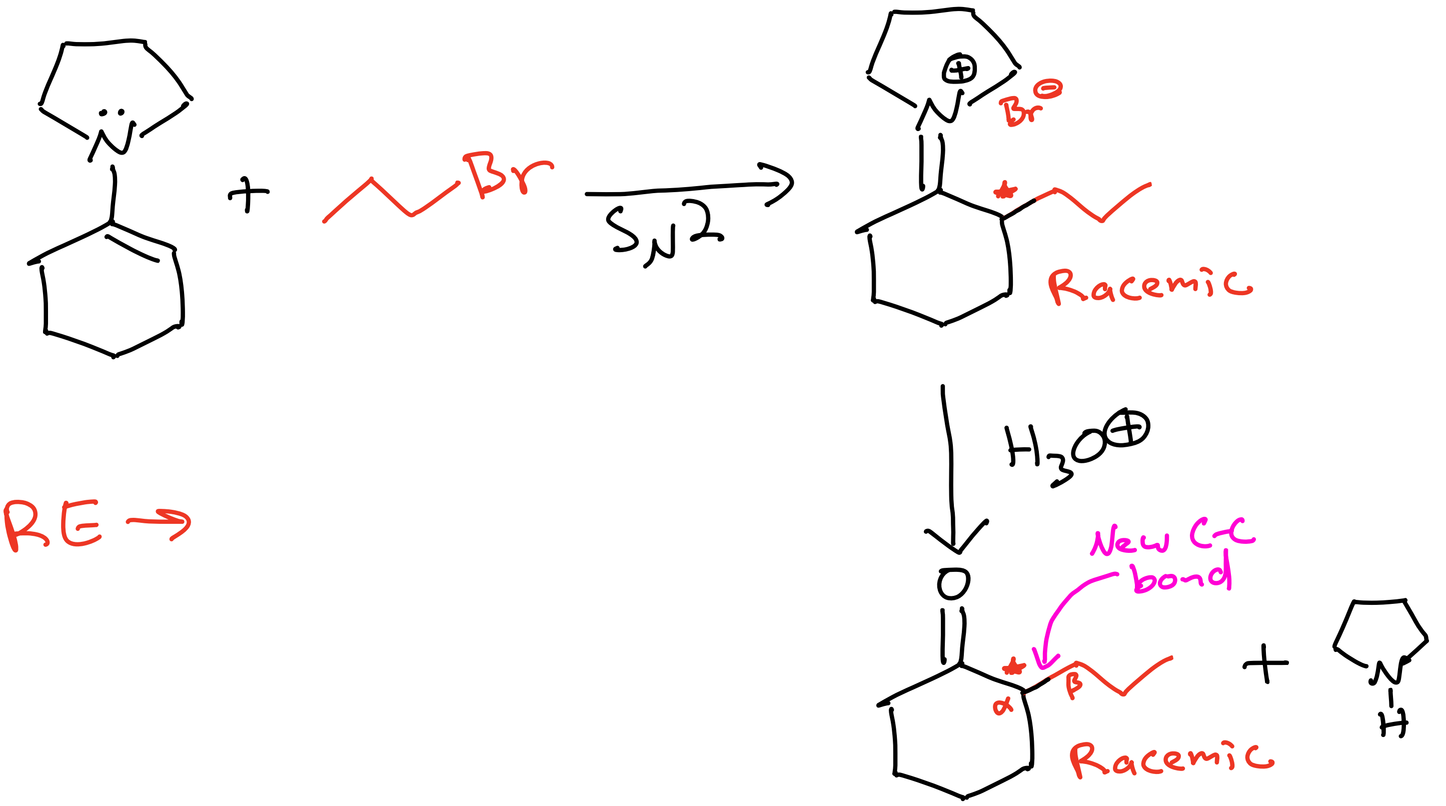


or



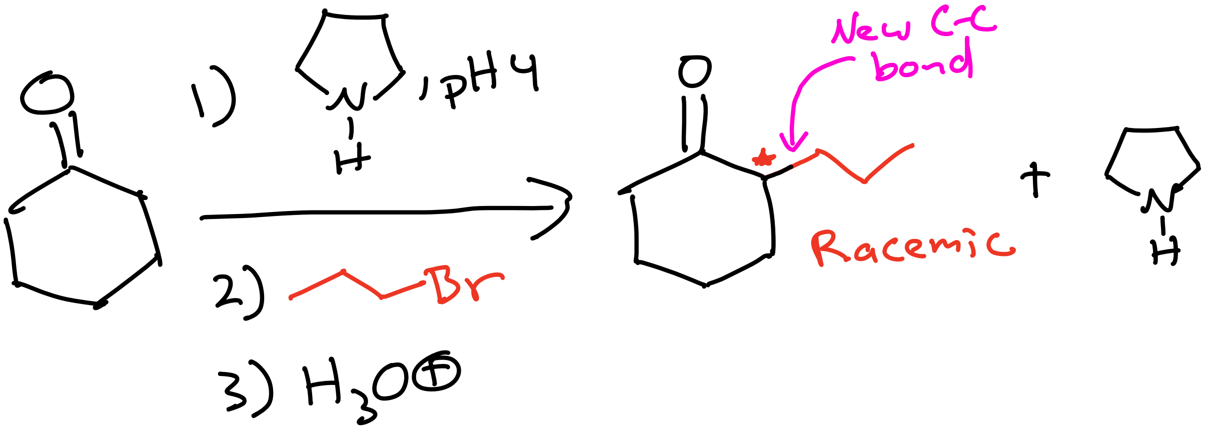
Reactions of enamines

1) Primary haloalkanes (S_N2)

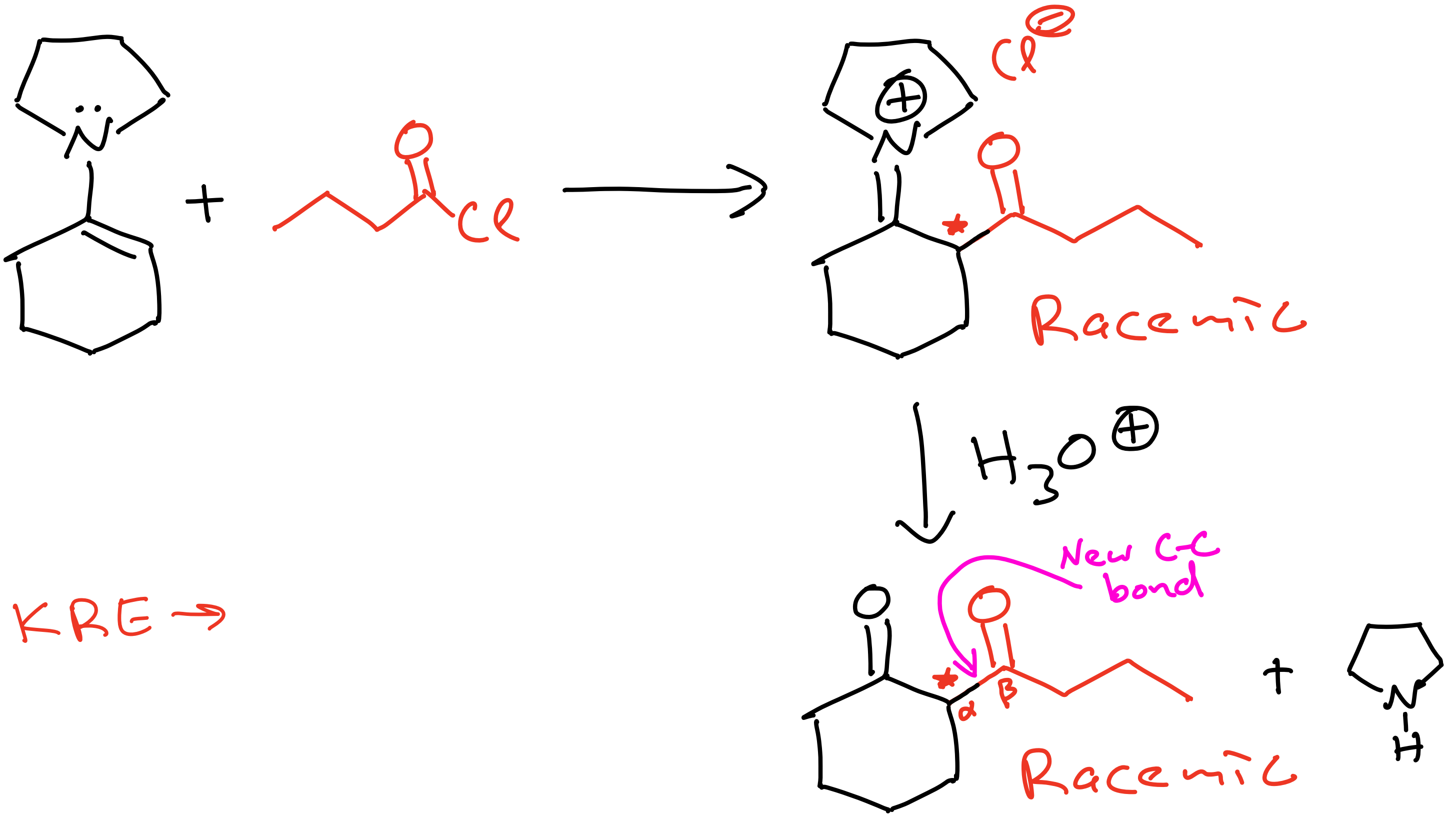


KRE →

Overall Reaction



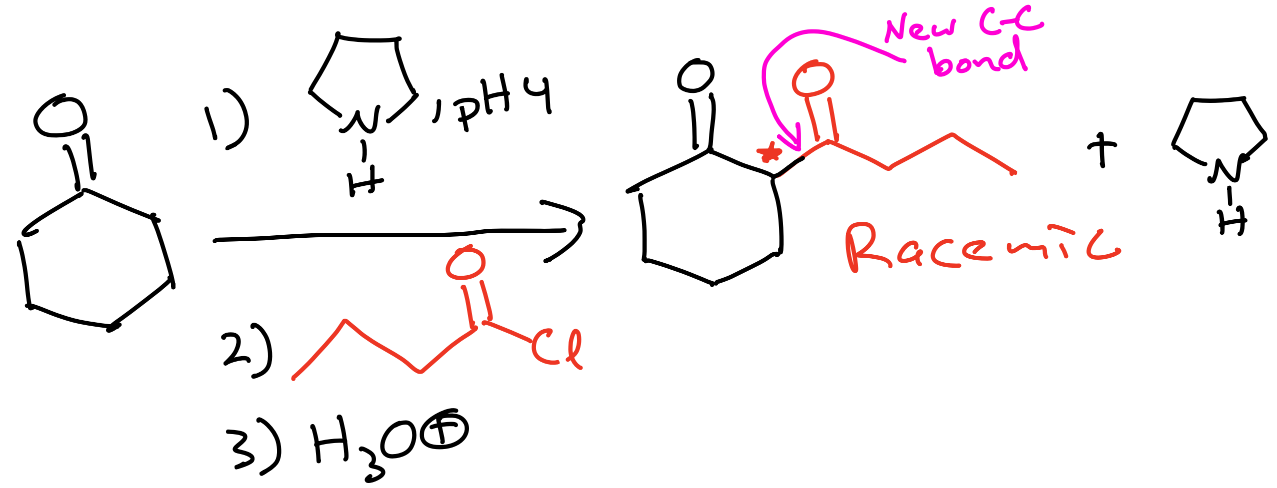
2) Acid chlorides ⇒ β-diketones



KRE →

β-diketone

Overall Reaction



α,β-Unsaturated, nitriles, ketones, or esters

β-Substituted aldehydes, nitriles, ketones, or esters

β-Keto esters

α,β-Unsaturated aldehydes

Acid Chlorides

β-Hydroxy aldehydes

Aldehydes

Ketones

Carboxylic esters

β-Ketoaldehyde

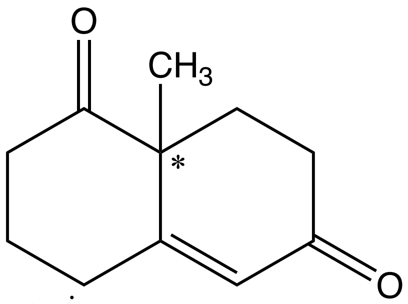
β-Diketone

Carboxylic acids

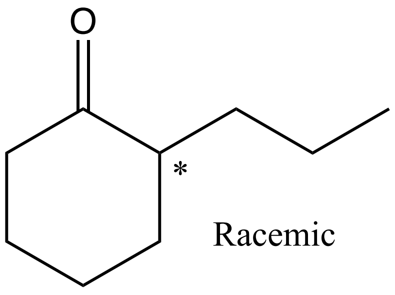
Substituted aldehyde

Substituted ketone

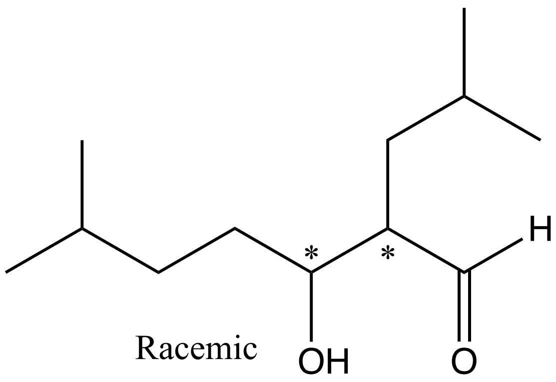
β-Diester



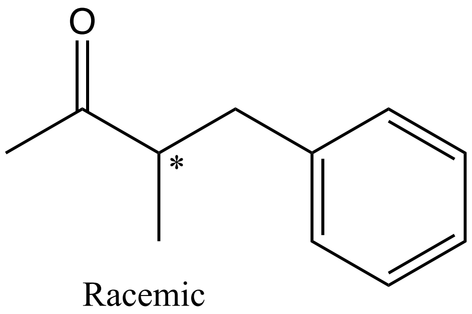
Racemic



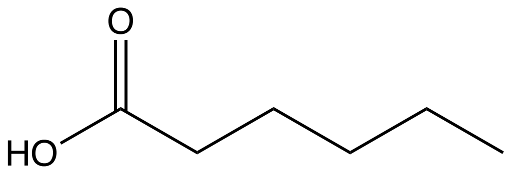
Racemic

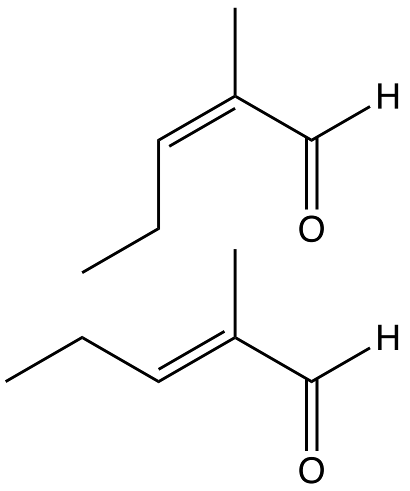


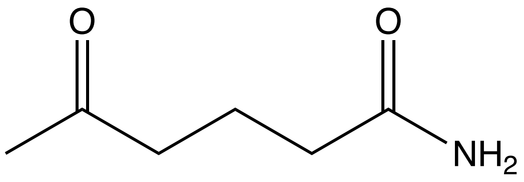
Racemic

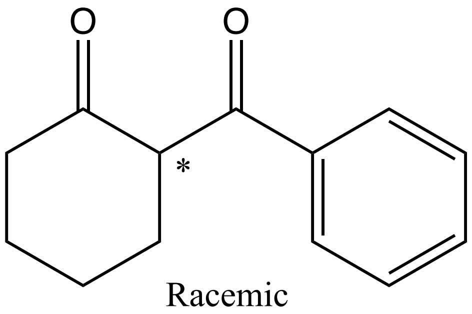


Racemic

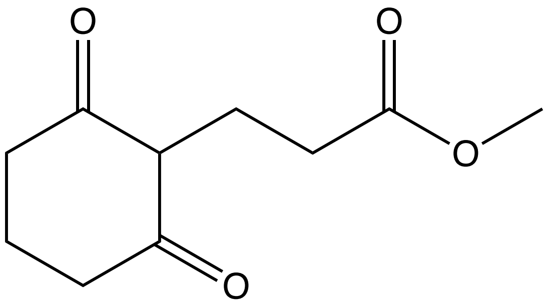


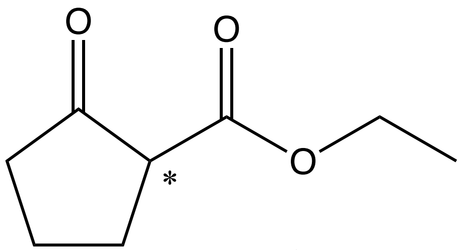






Racemic





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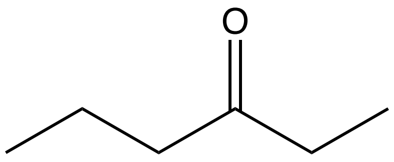
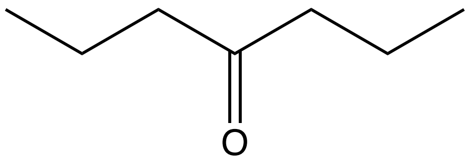
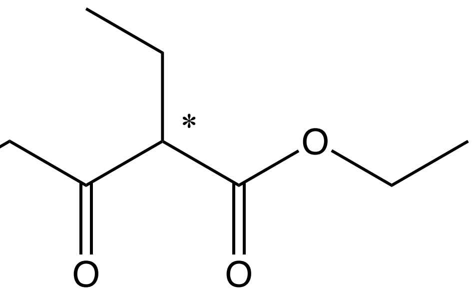
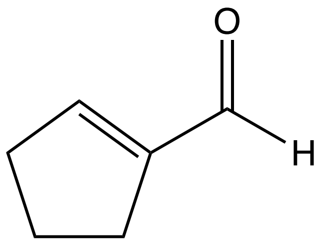




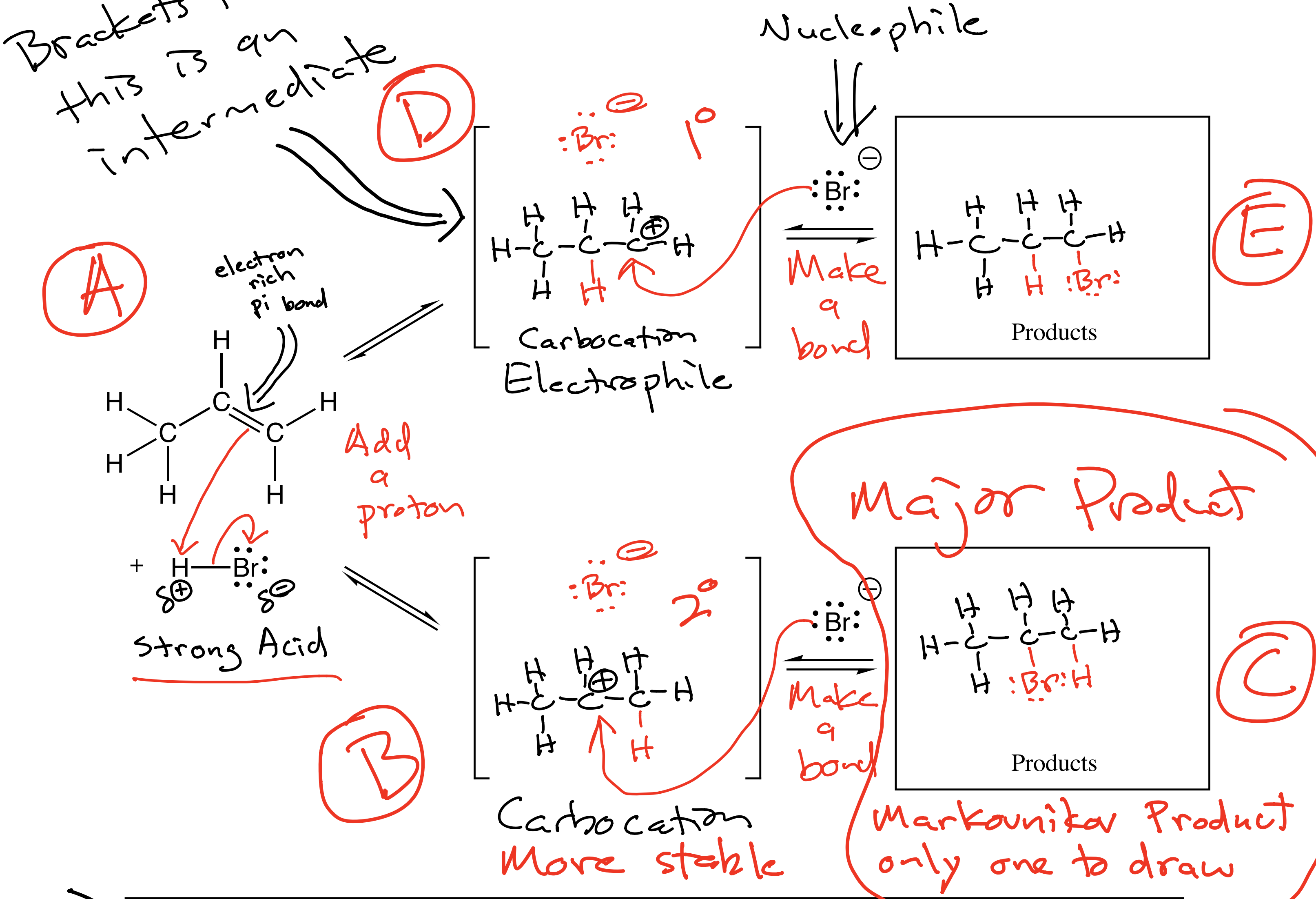


Racemic



"X" can be Cl, Br, I
Not F

Addition of H-X to an Alkene



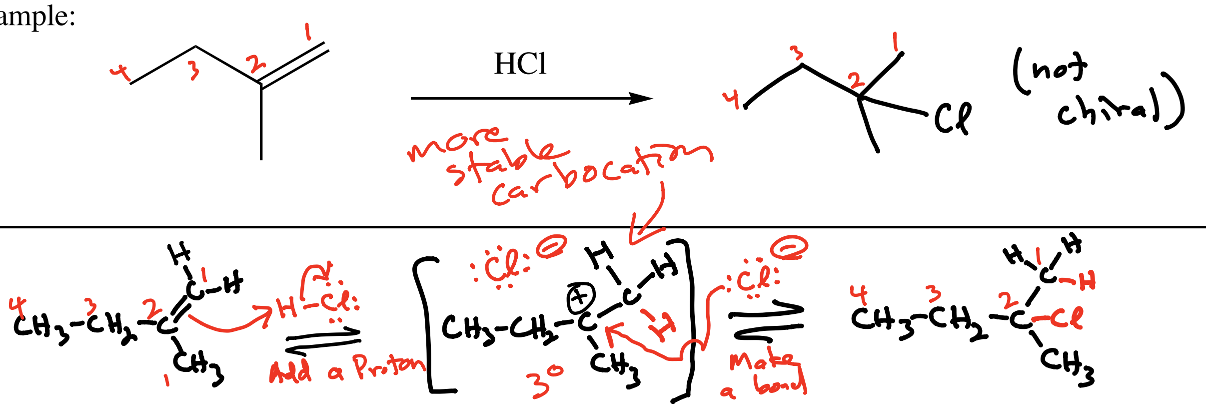
Which constitutional isomer is formed?

Summary: Alkene pi bond reacts with H-X to add a proton to create a carbocation intermediate that makes a bond with X⊖ to give the product

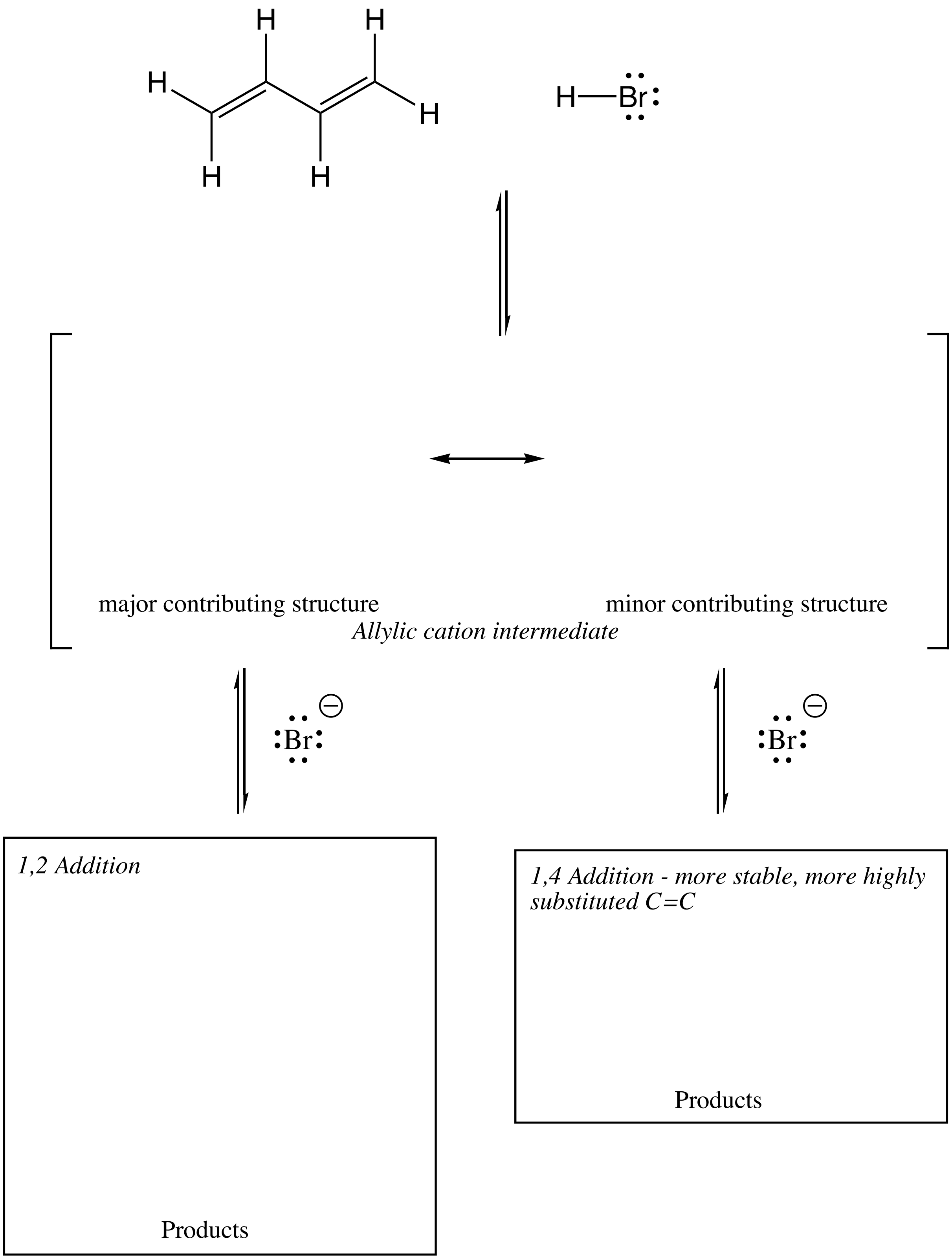
Regiochemistry: Markovnikov's Rule

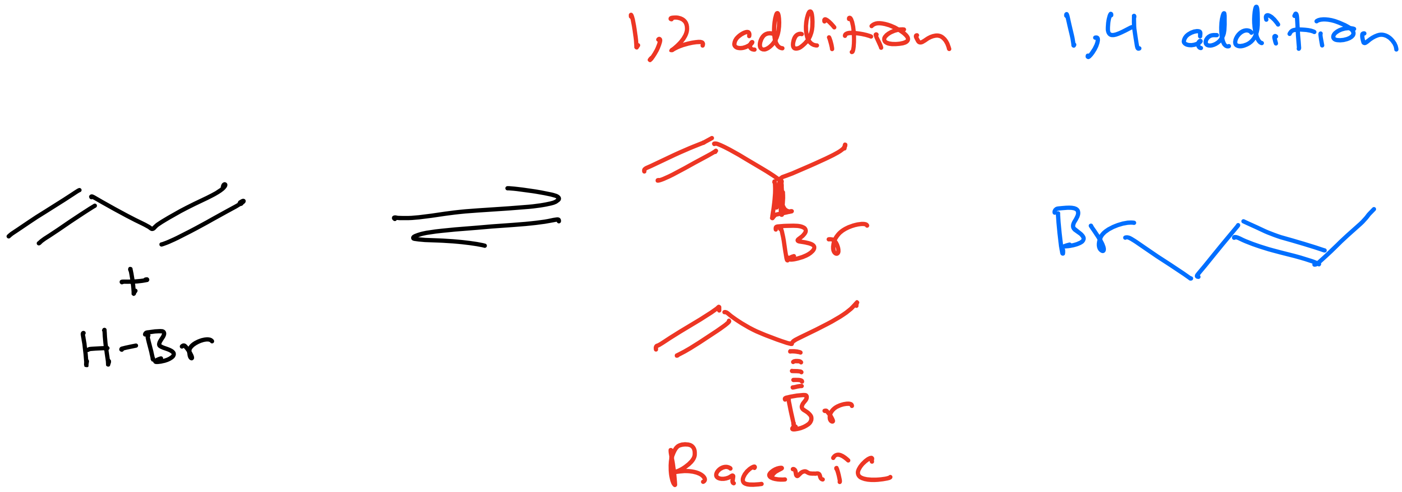
Stereochemistry: Mixed (time capsule) → Racemic Product

Example:



H-X reacting with conjugated dienes

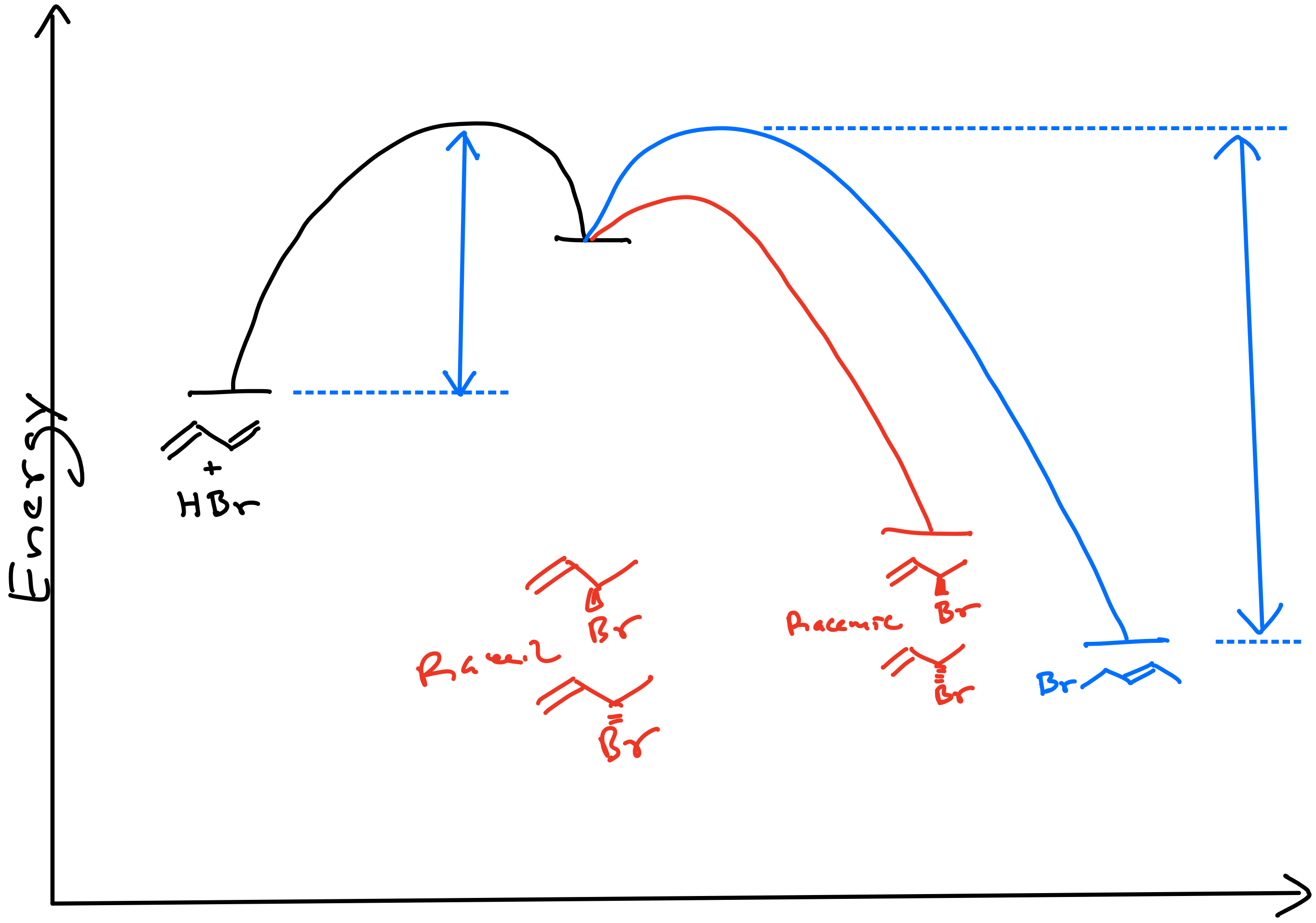




Temperature of Reaction

-78° C

+40° C



Low temperature →

$\underbrace{\text{Kinetic Control}}$

"Fastest" wins

High temperature →

$\underbrace{\text{Thermodynamic Control}}$

Most stable product wins

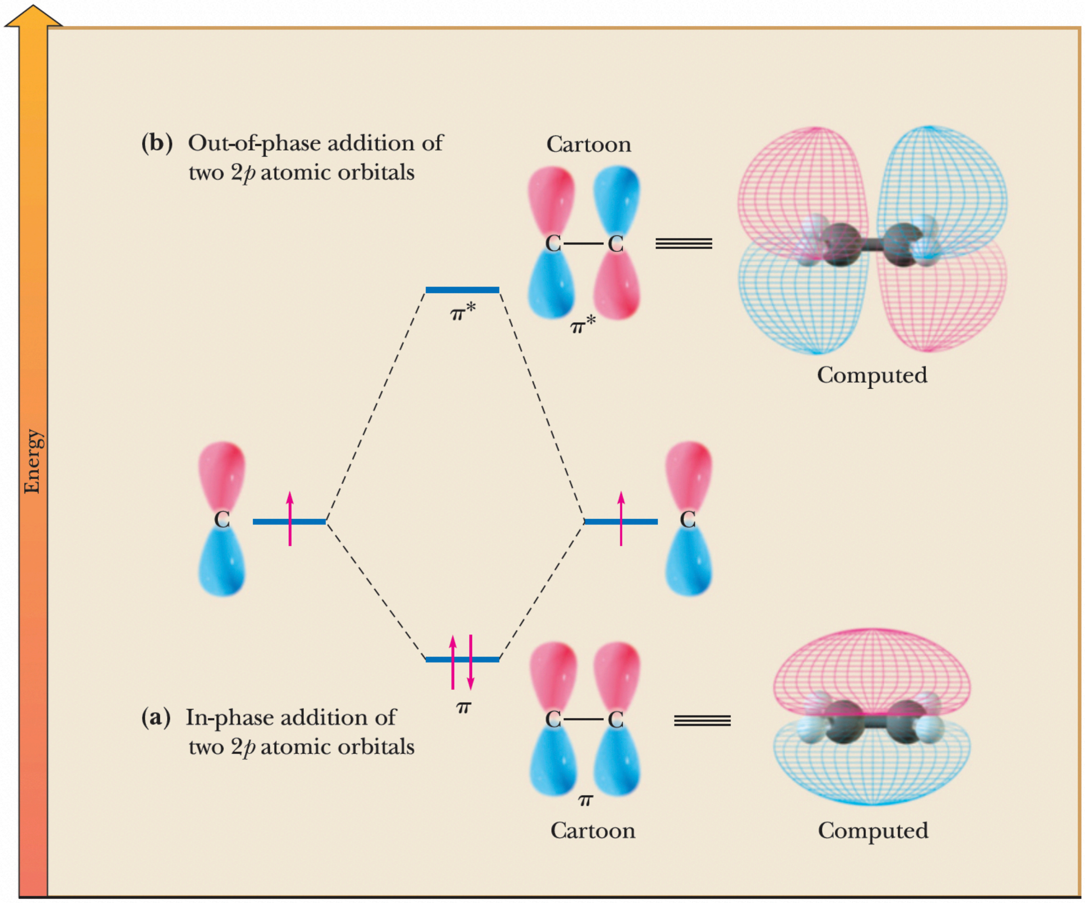
Electrons should be thought of as

Orbitals are described by

Like waves → orbitals can add
and

When adding atomic orbitals, you get as many new molecular orbitals as there are component atomic orbitals

For molecules with adjacent 2p orbitals that overlap the resulting molecular orbitals extend over



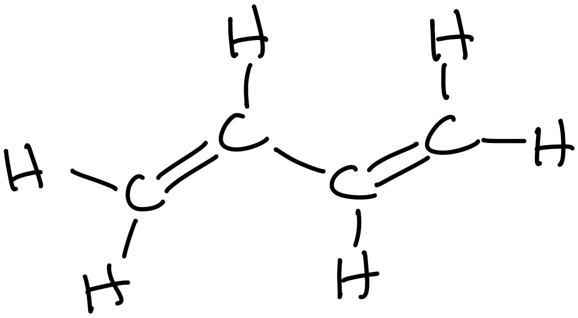
Watch a video explanation

FIGURE 1.21 Molecular orbital mixing diagram for the creation of any C—C π bond. (a) Addition of two p atomic orbitals in phase leads to a π orbital that is lower in energy than the two separate starting orbitals. When populated with two electrons, the π orbital gives a π bond. (b) Addition of the p orbitals in an out-of-phase manner (meaning a reversal of phasing in one of the starting orbitals) leads to a π^* orbital. Population of this orbital with one or two electrons leads to weakening or cleavage of the π bond, respectively.

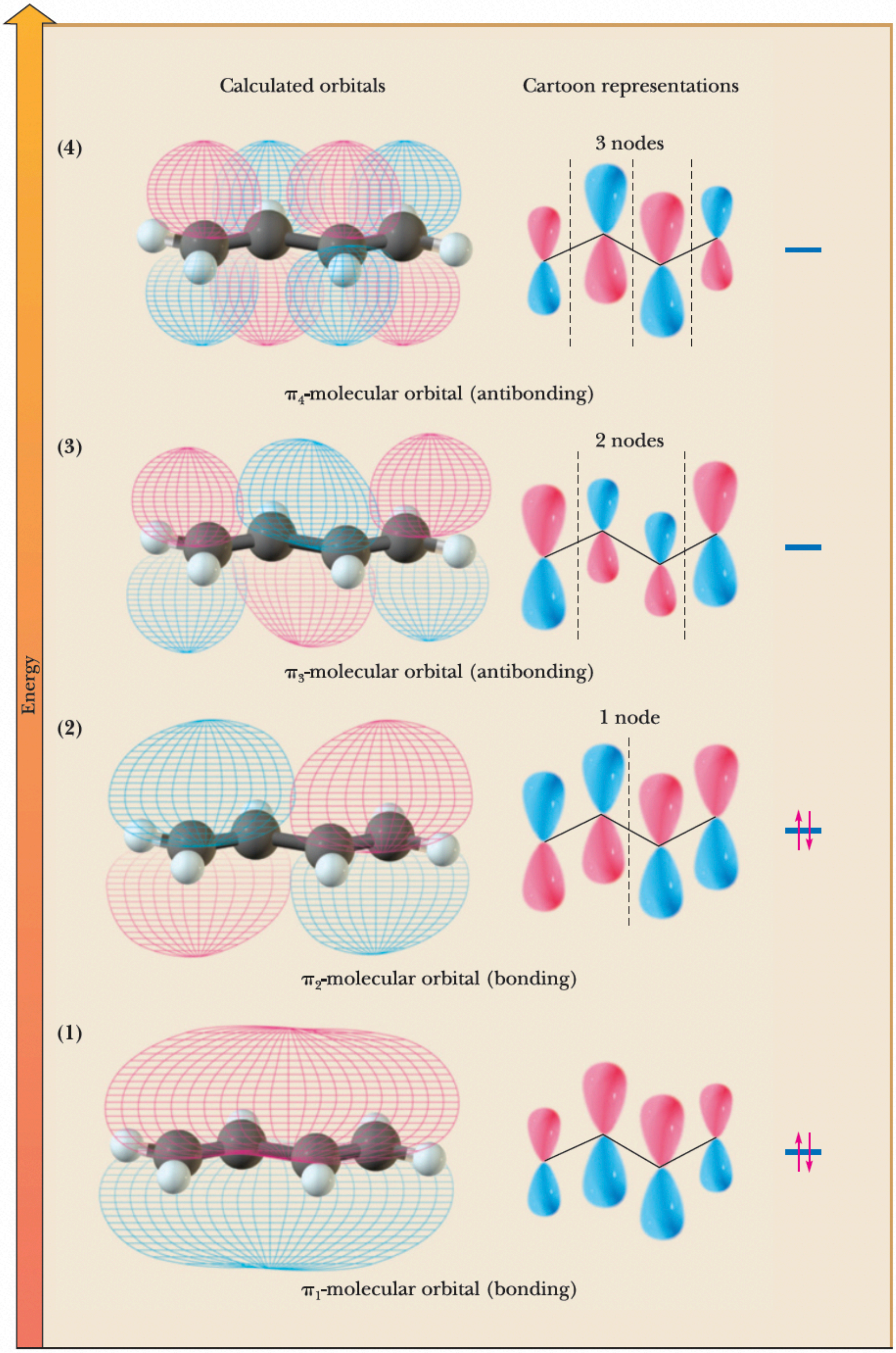
π bonding orbitals look like hot dog buns →

If you drink a lot of this you

The same applies when there are 4 atoms, each with an overlapping 2p orbital:



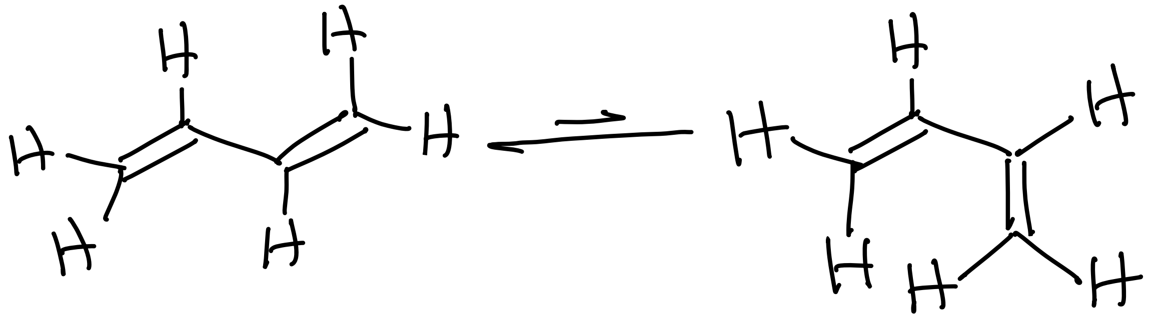
1,3-Butadiene



Watch a video explanation

FIGURE 20.2 Structure of 1,3-butadiene—molecular orbital model. Combination of four parallel $2p$ atomic orbitals gives two π-bonding MOs and two π-antibonding MOs. In the ground state, each π-bonding MO is filled with two spin-paired electrons. The π-antibonding MOs are unoccupied.

Consequence of the "ψ-way" molecular orbital



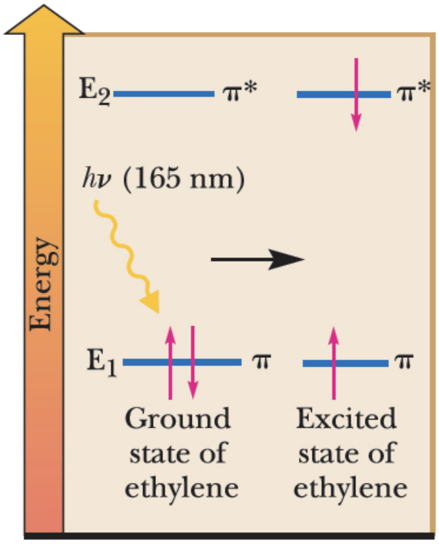


FIGURE 20.6 A $\pi \rightarrow \pi^*$ transition in excitation of ethylene. Absorption of ultraviolet radiation causes a transition of an electron from a π-bonding MO in the ground state to a π-antibonding MO in the excited state. There is no change in electron spin.

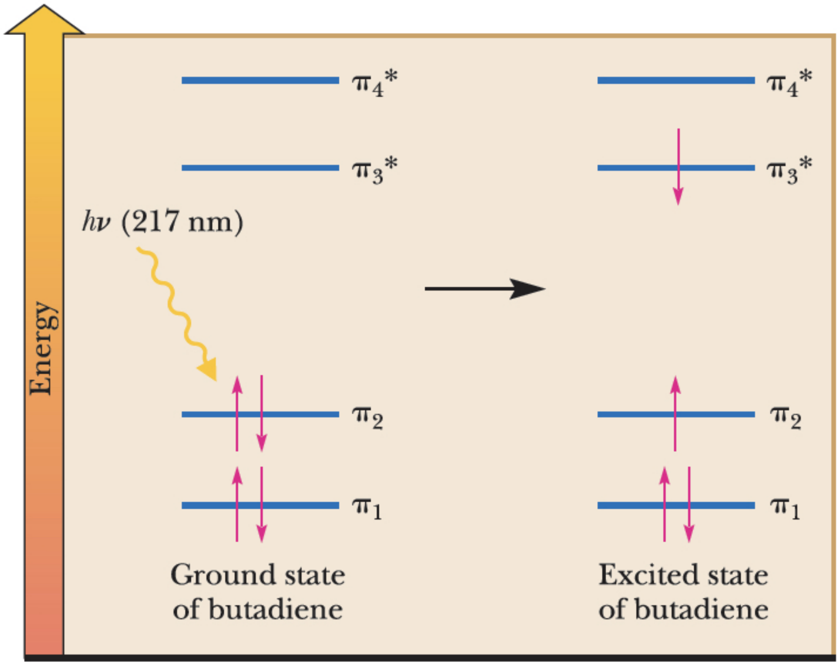


FIGURE 20.7 Electronic excitation of 1,3-butadiene; a $\pi \rightarrow \pi^*$ transition.

As you add 2p orbitals → the energy gap between the highest filled π molecular orbital and the lowest unfilled π molecular orbitals gets smaller

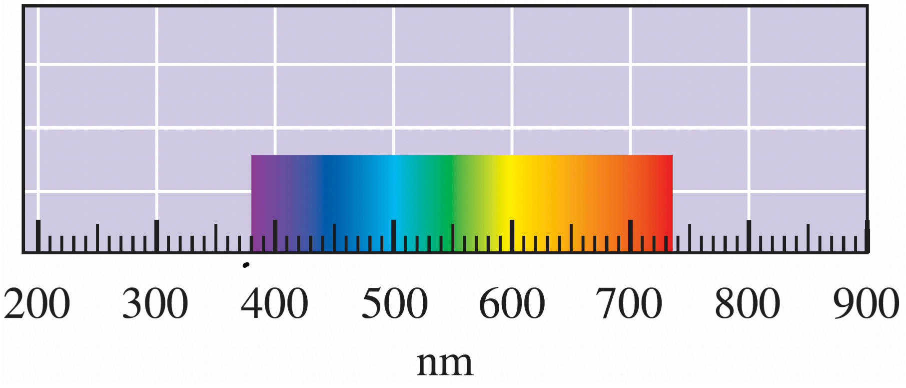
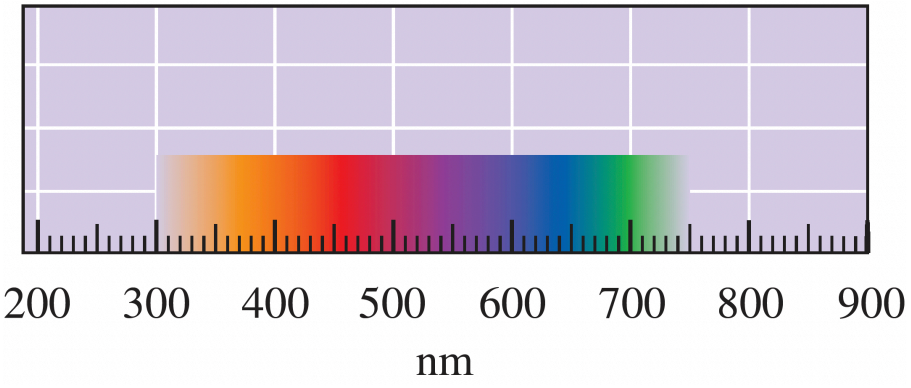
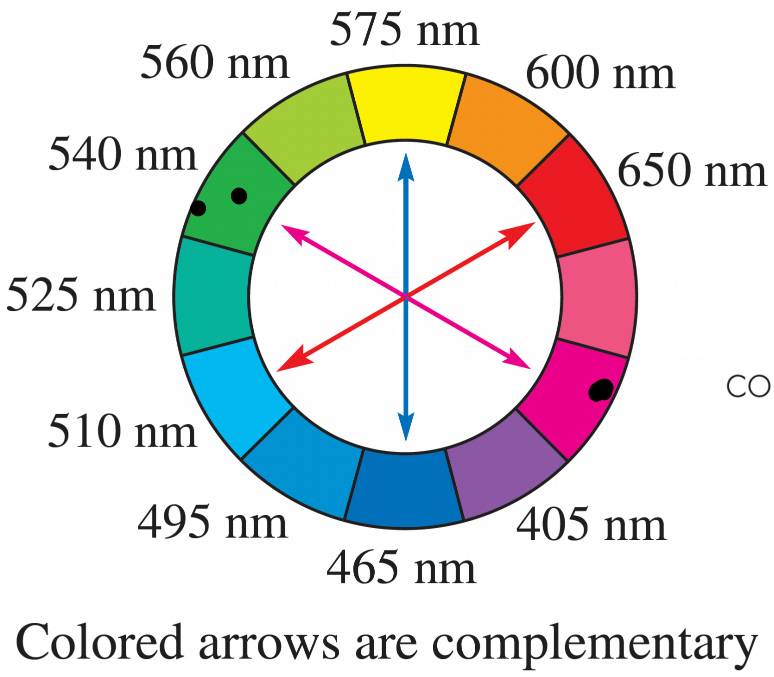


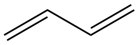
FIGURE 20.5 (a) Visible light color-wavelength correlation.



(b) Approximate color of substance (reflected light) if a single wavelength (i.e., the wavelength listed on the numerical scale of the *x*-axis) is absorbed.

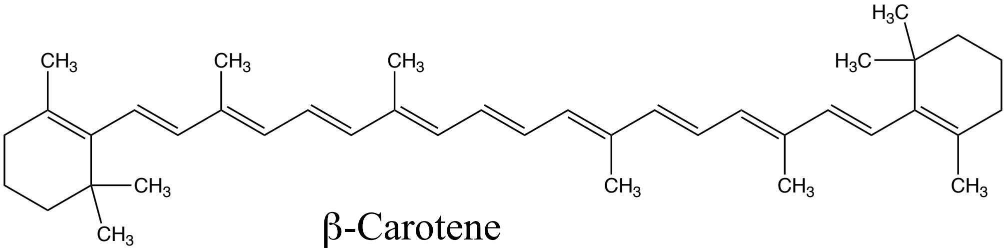


(c) Complementary colors on a color wheel.



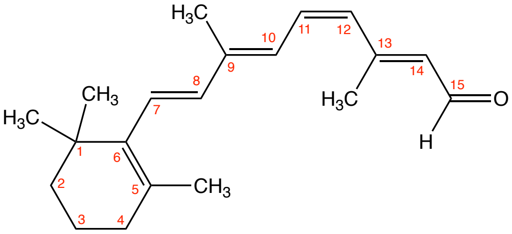
Butadiene

λ_{max} = 217 nm



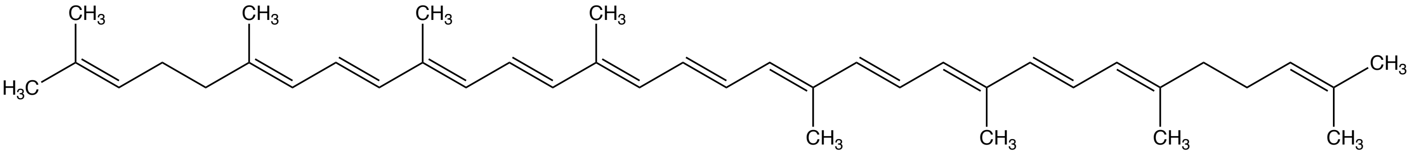
β-Carotene

λ_{max} = 455 nm, 483 nm



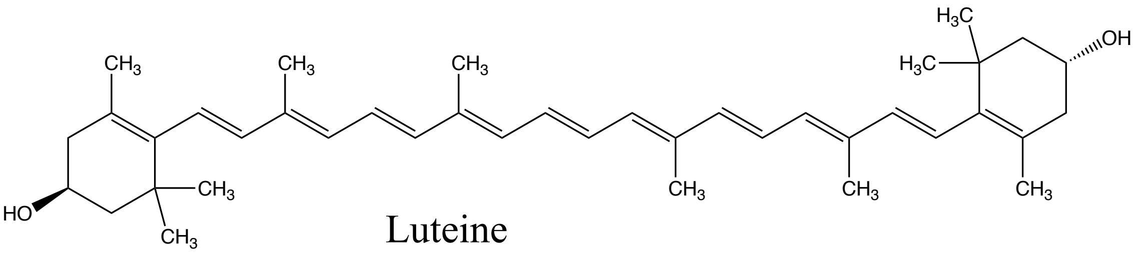
11-*cis*-Retinal

λ_{max} = 380 nm



Lycopene

λ_{max} = 443 nm, 471 nm, 502 nm



Luteine

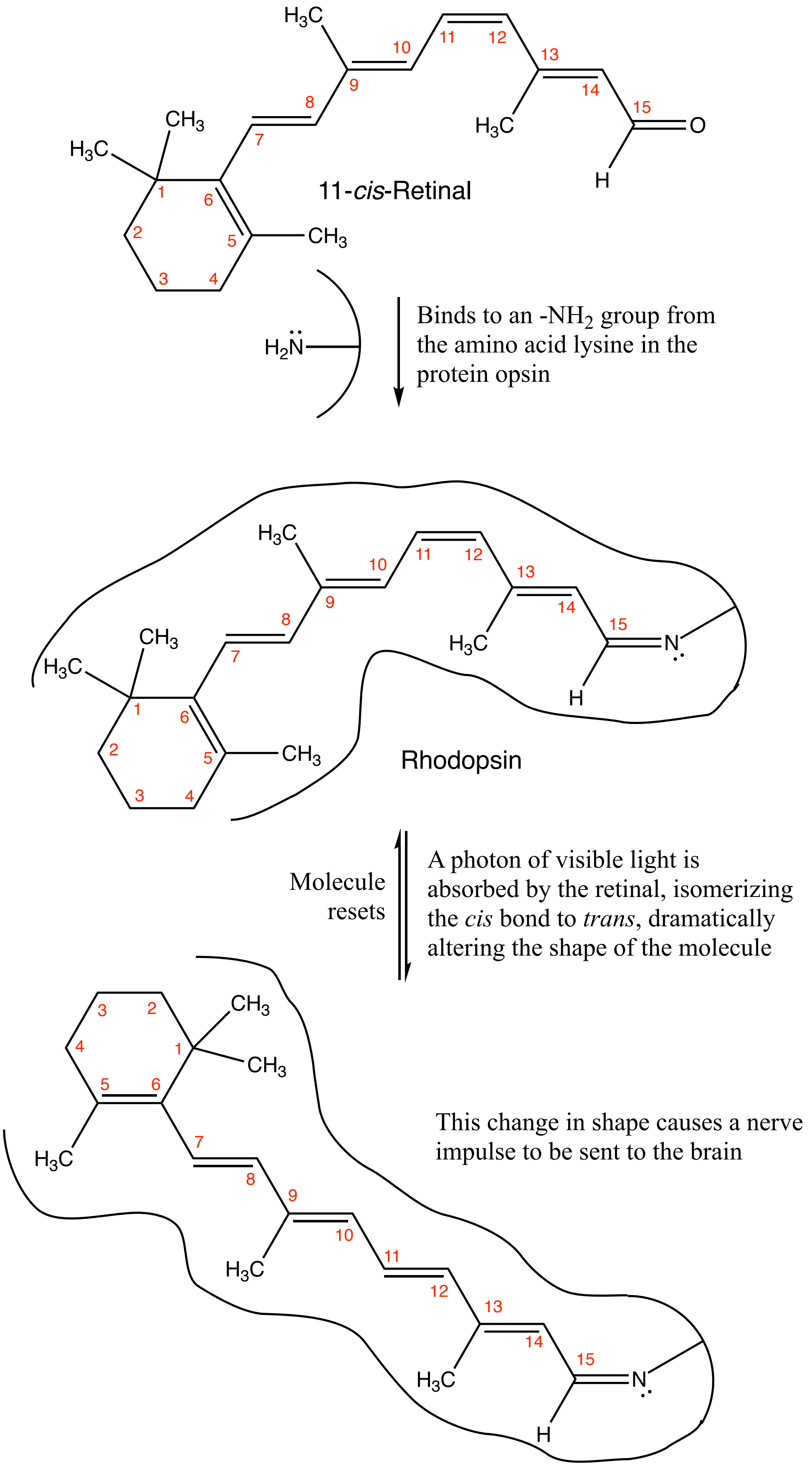
λ_{max} = 445 nm, 474 nm


PATH.
ORANGETHEORY
PATH.
ORANGETHEORY
HELL WEEK
2023
STILL


06 08 36
PATH
ORANGETHEORY
HELL WEEK
2023

How vision works, the final edition!

How vision works



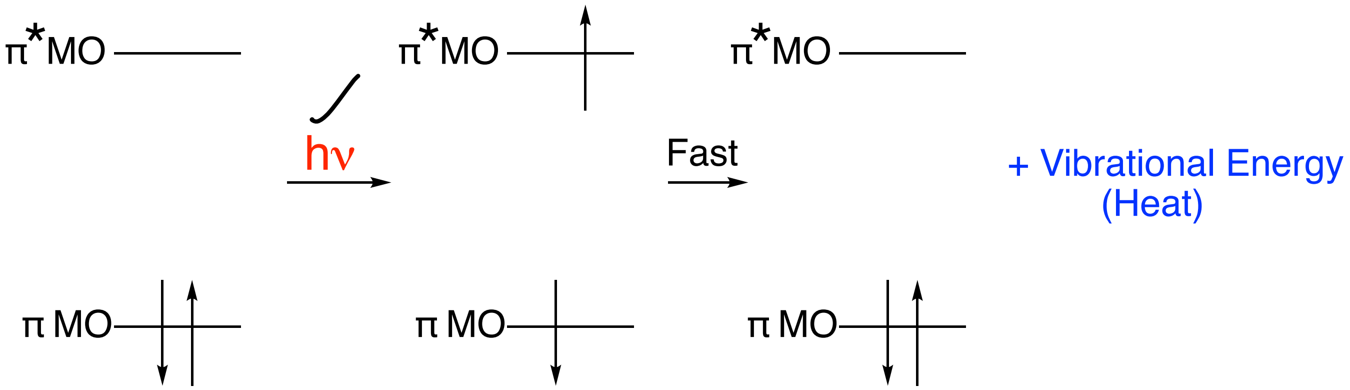
Binds to an -NH_2 group from the amino acid lysine in the protein opsin

Molecule resets

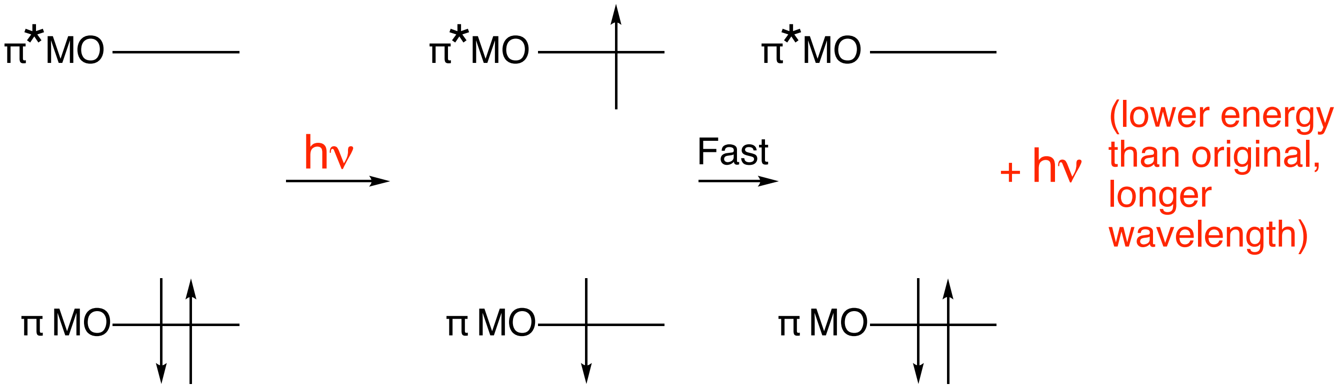
A photon of visible light is absorbed by the retinal, isomerizing the *cis* bond to *trans*, dramatically altering the shape of the molecule

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

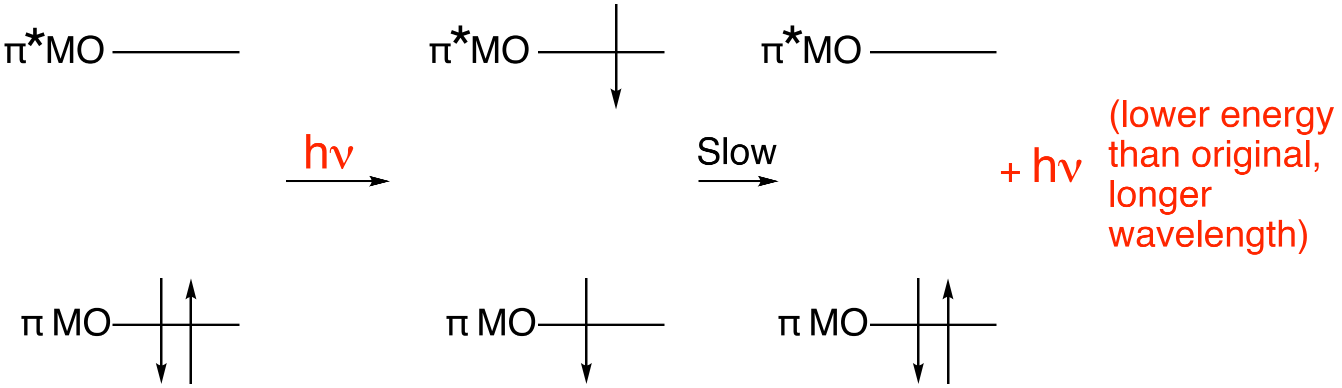
Generation of heat, Most molecules



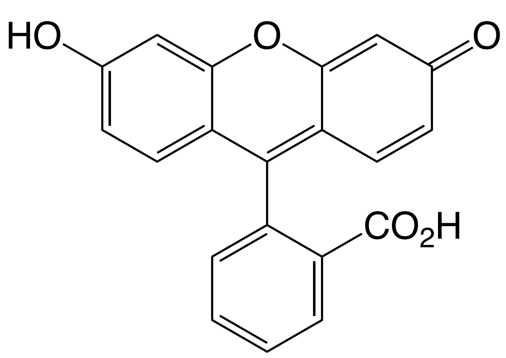
Flourescence - Rigid Molecules, Not uncommon



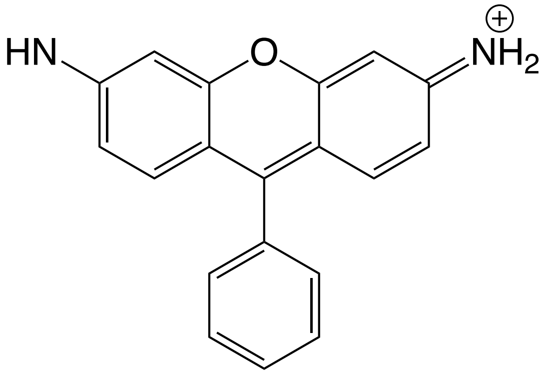
Phosphorescence - “Glow in the Dark”, Rare



Flourescence - Rigid Molecules, Not uncommon

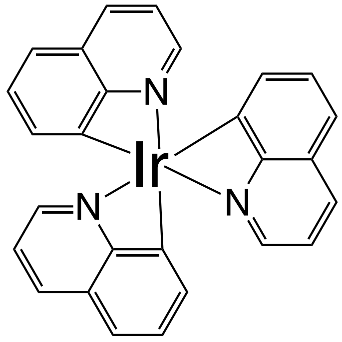


Fluorescein

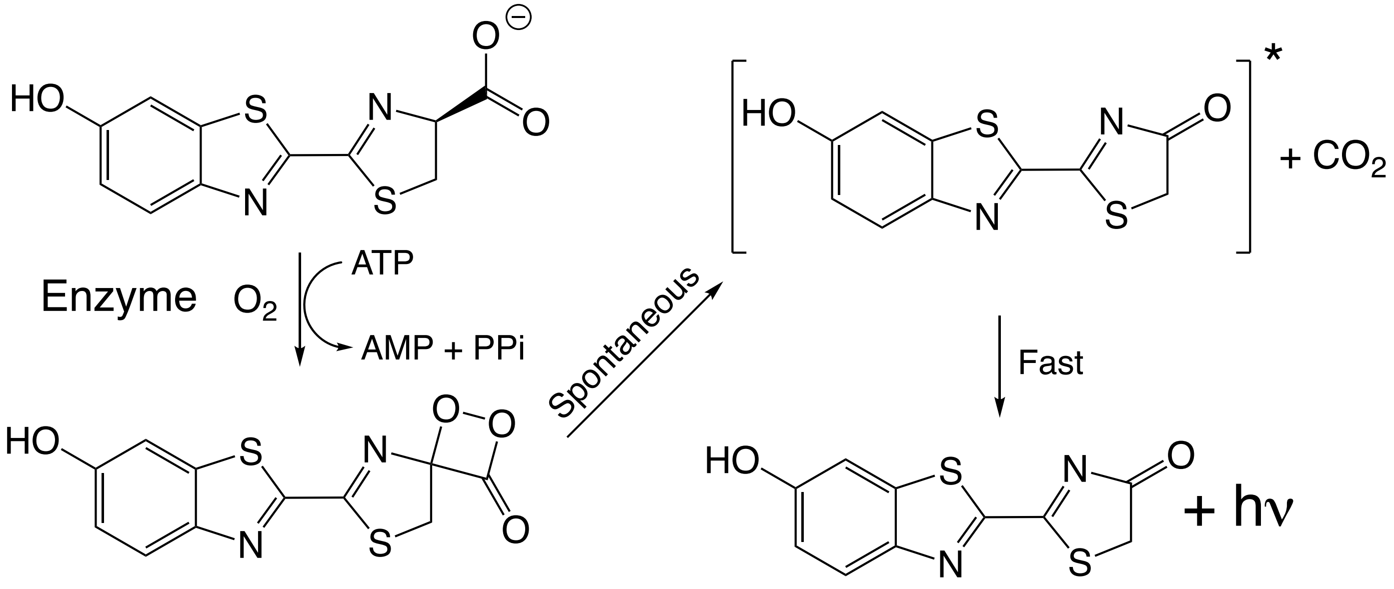


Rhodamine

Phosphorescence - “Glow in the Dark”, Rare



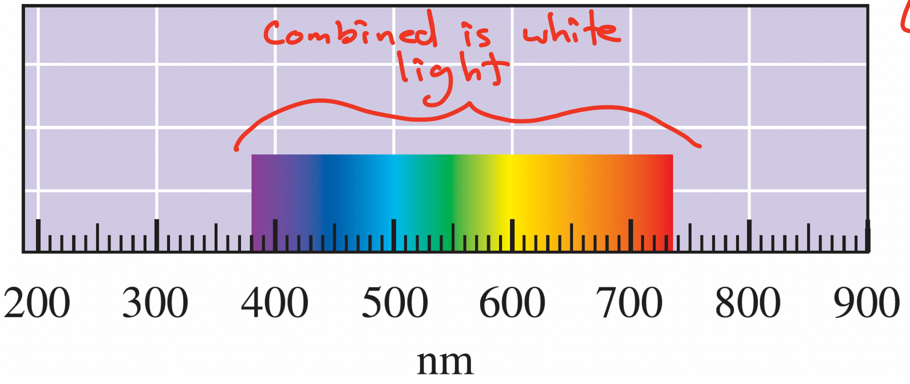
Bioluminescence - Fireflies, Deep Sea Creatures - Chemical Reactions



http://photobiology.info/Branchini2.html

← Energy

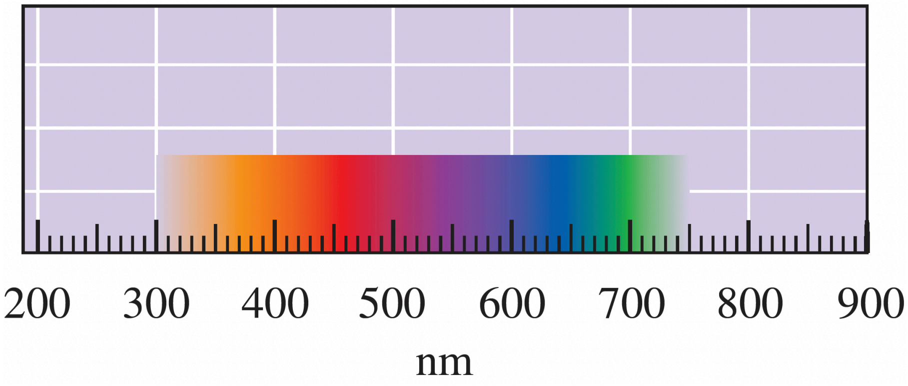
Light source



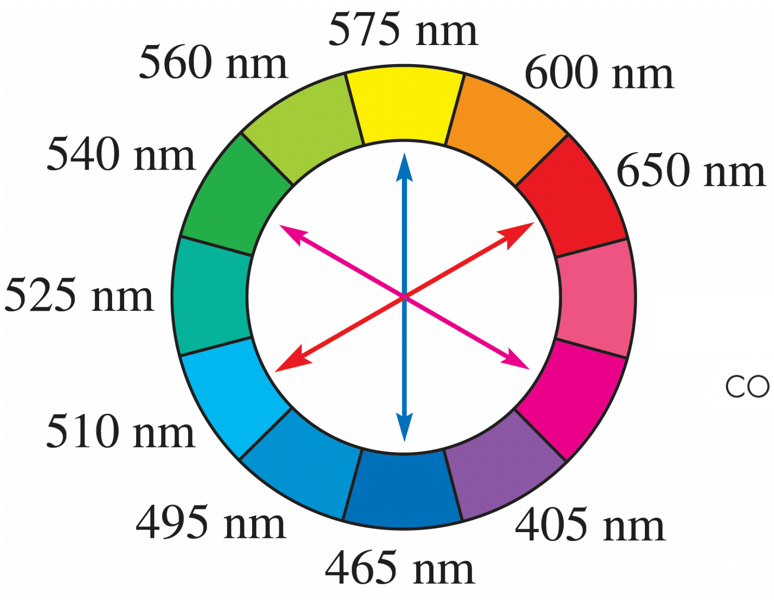
Combined is white light

FIGURE 20.5 (a) Visible light color-wavelength correlation.

*** We "see" the wavelengths reflected minus the wavelengths absorbed ***



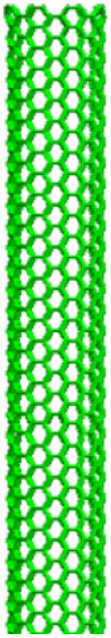
(b) Approximate color of substance (reflected light) if a single wavelength (i.e., the wavelength listed on the numerical scale of the *x*-axis) is absorbed.

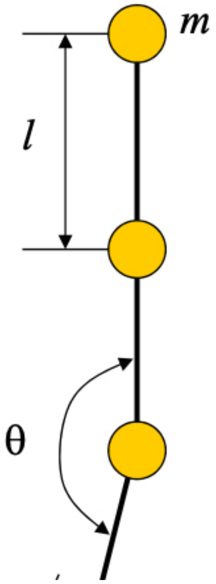


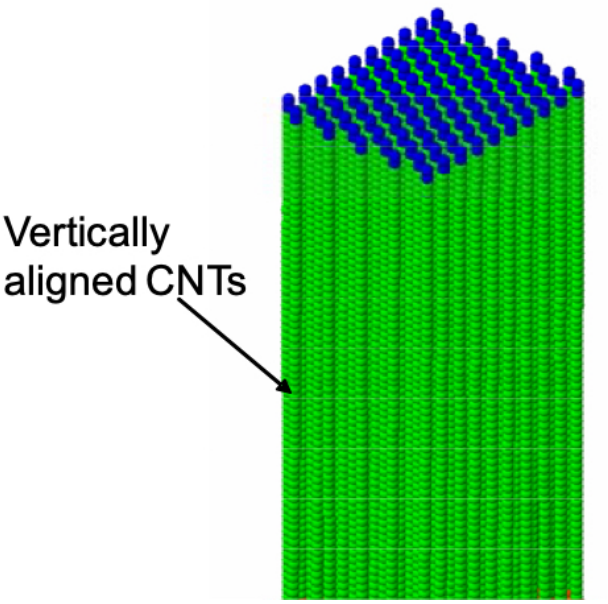
(c) Complementary colors on a color wheel.

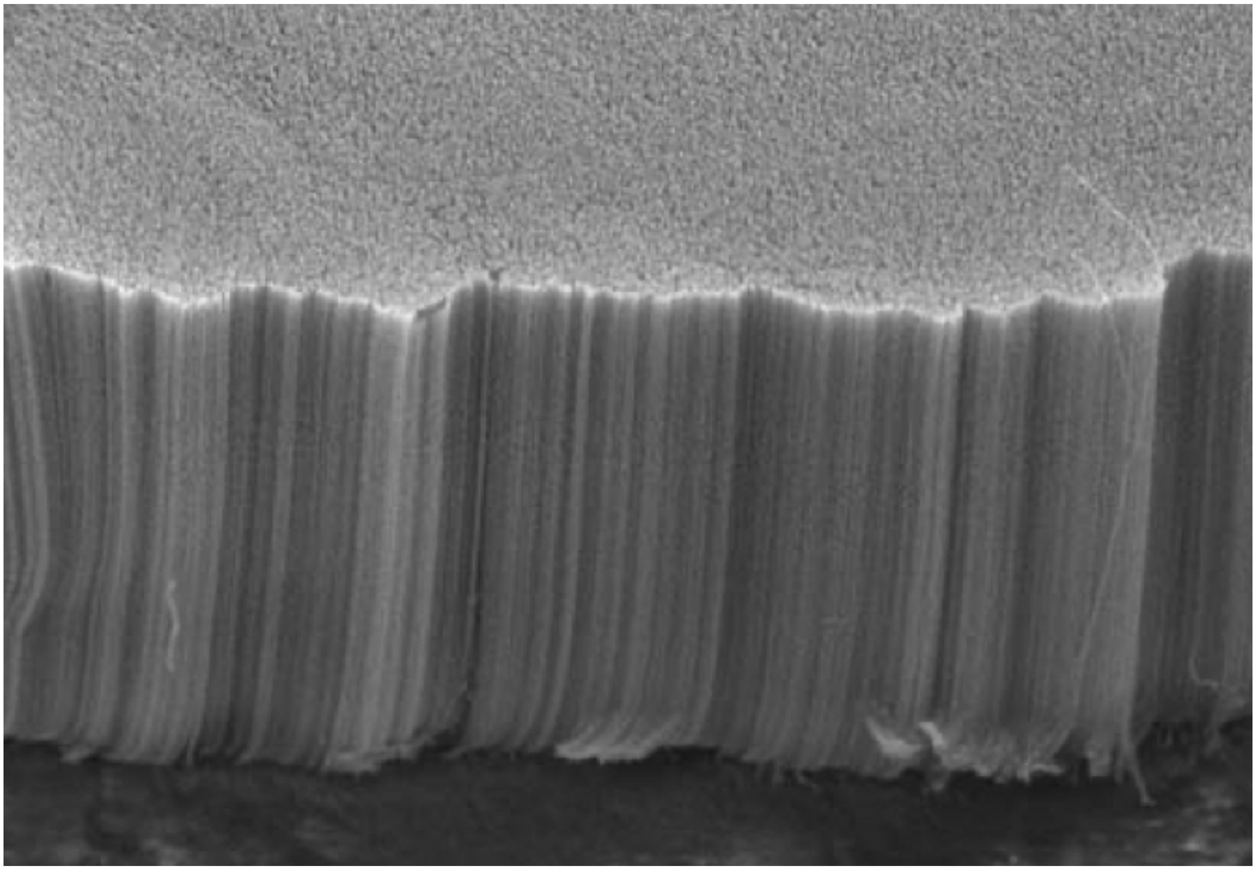
Colored arrows are complementary

Vanta Black → The "blackest" material









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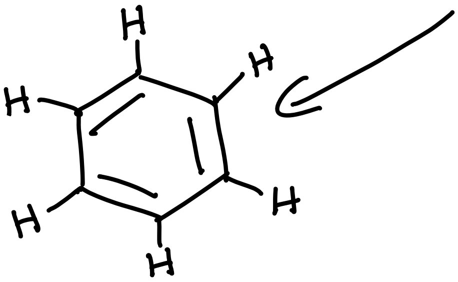
Preview



Extraordinarily Stable!

Benzene

Pericyclic Reactions → π bonds and σ bonds interchange