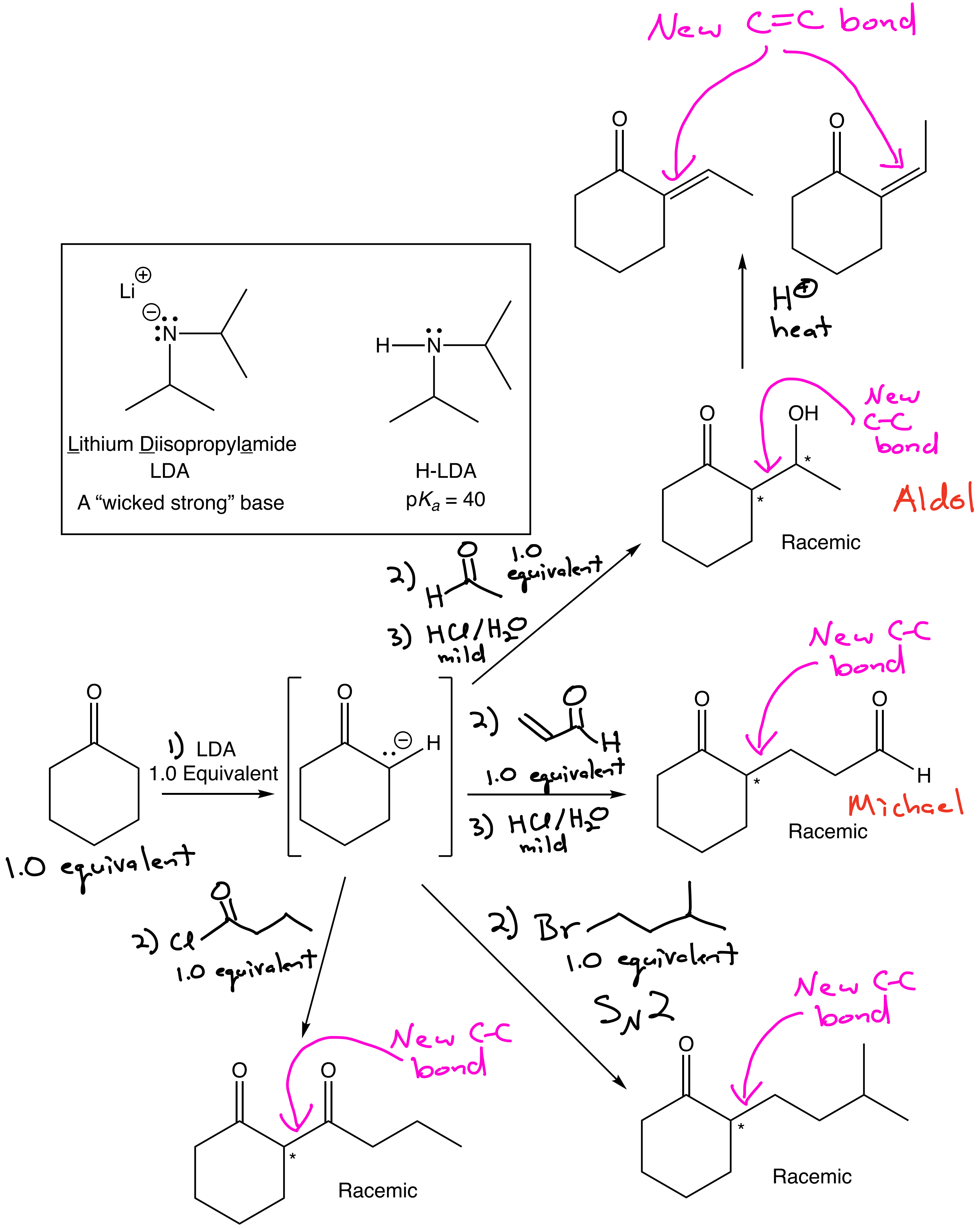
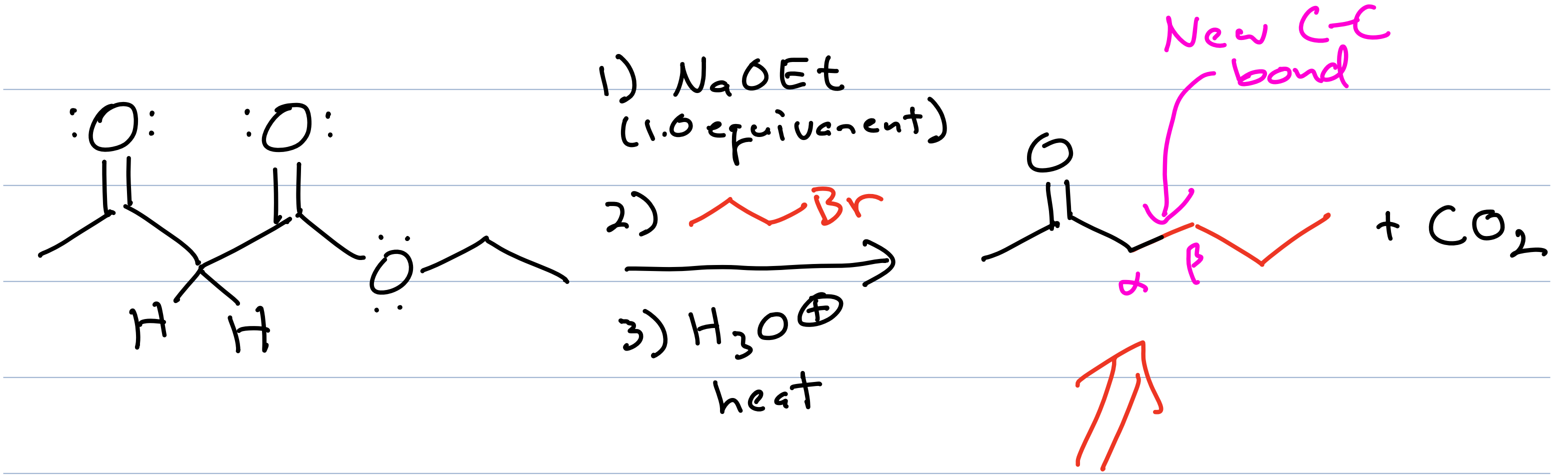
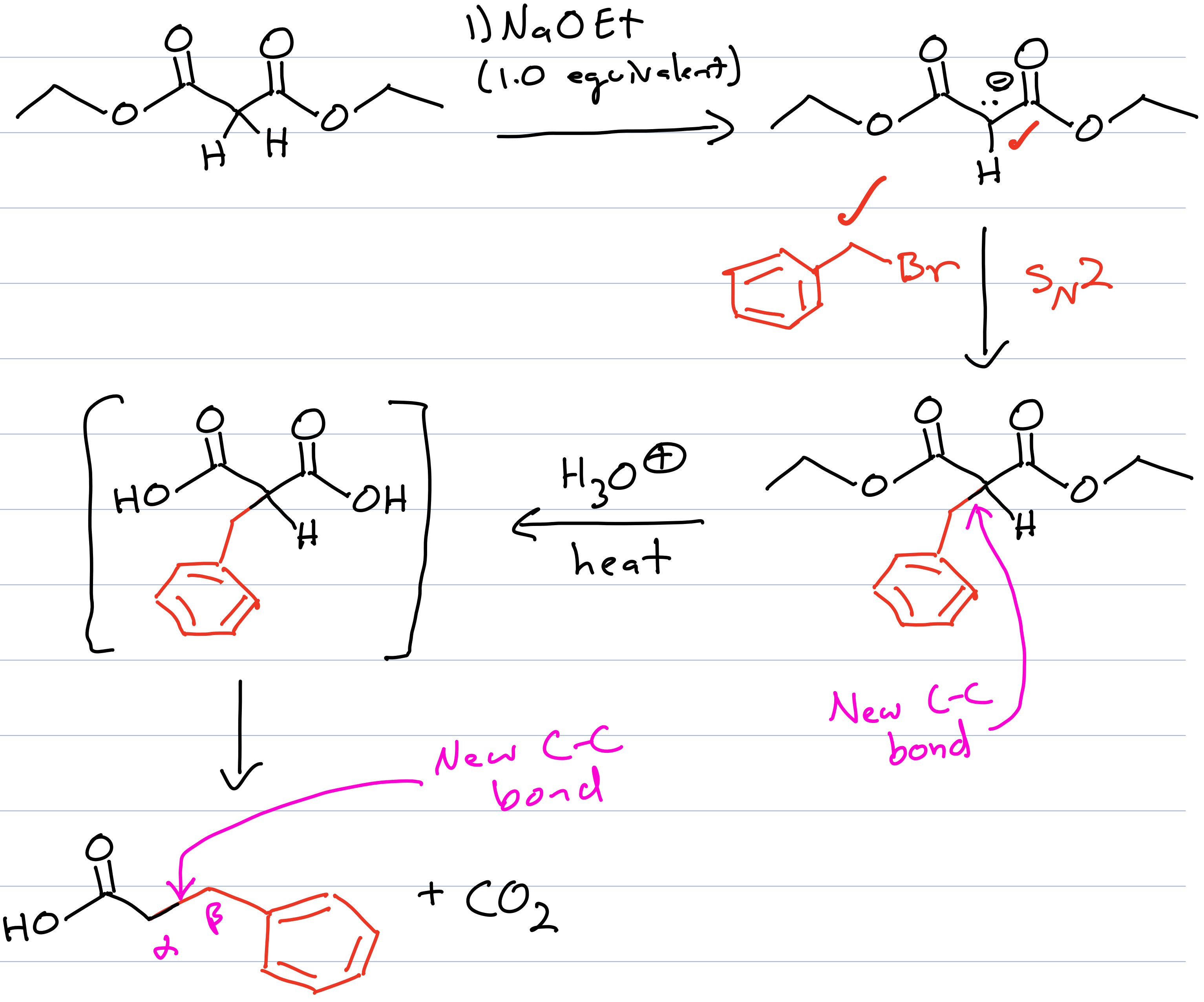

New C=C bond
H⊕
heat
Li⊕
Lithium Diisopropylamide
LDA
A "wicked strong" base
H-LDA
pK_a = 40
OH
New C-C bond
Aldol
Racemic
2) 1.0 equivalent
3) HCl/H$_2$O mild
1) LDA
1.0 Equivalent
1.0 equivalent
2) 1.0 equivalent
3) HCl/H$_2$O mild
New C-C bond
Michael
Racemic
2) Cl 1.0 equivalent
2) Br 1.0 equivalent
S$_N$2
New C-C bond
Racemic
New C-C bond
Racemic

Acetoester Synthesis Summary



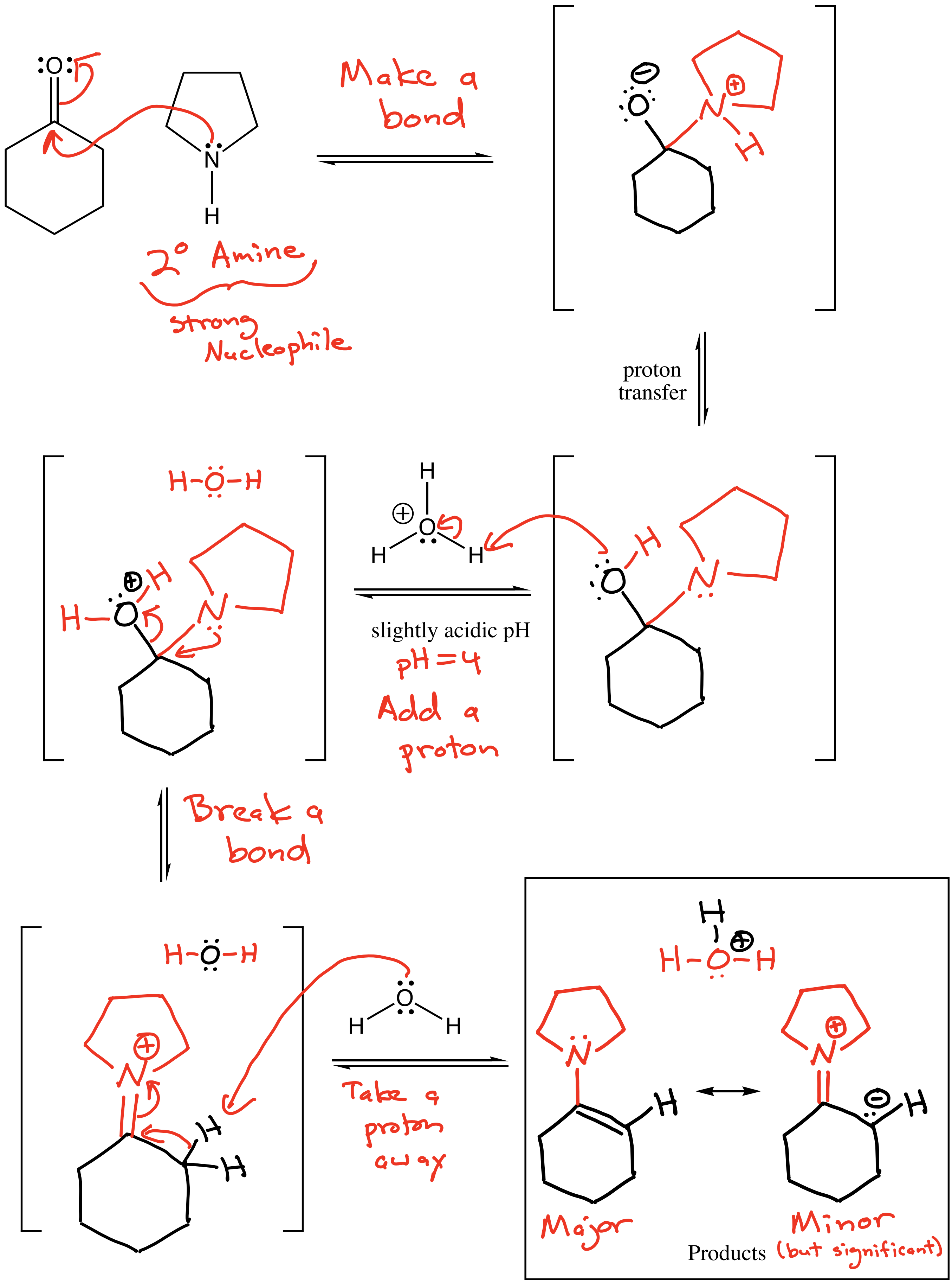
KRE - A methyl ketone with a new C-C bond between the α and β carbon atoms

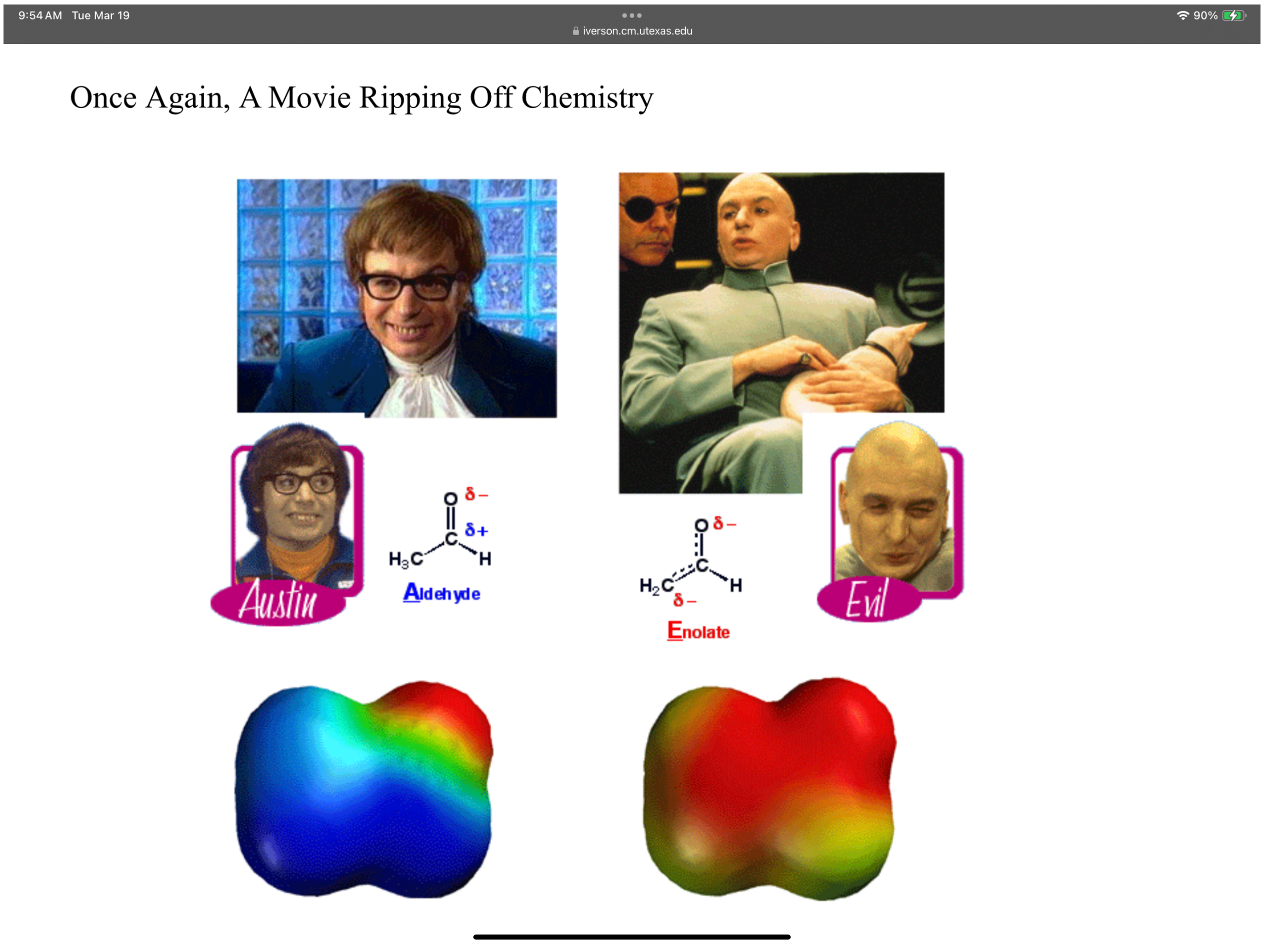
We start with diethyl malonate



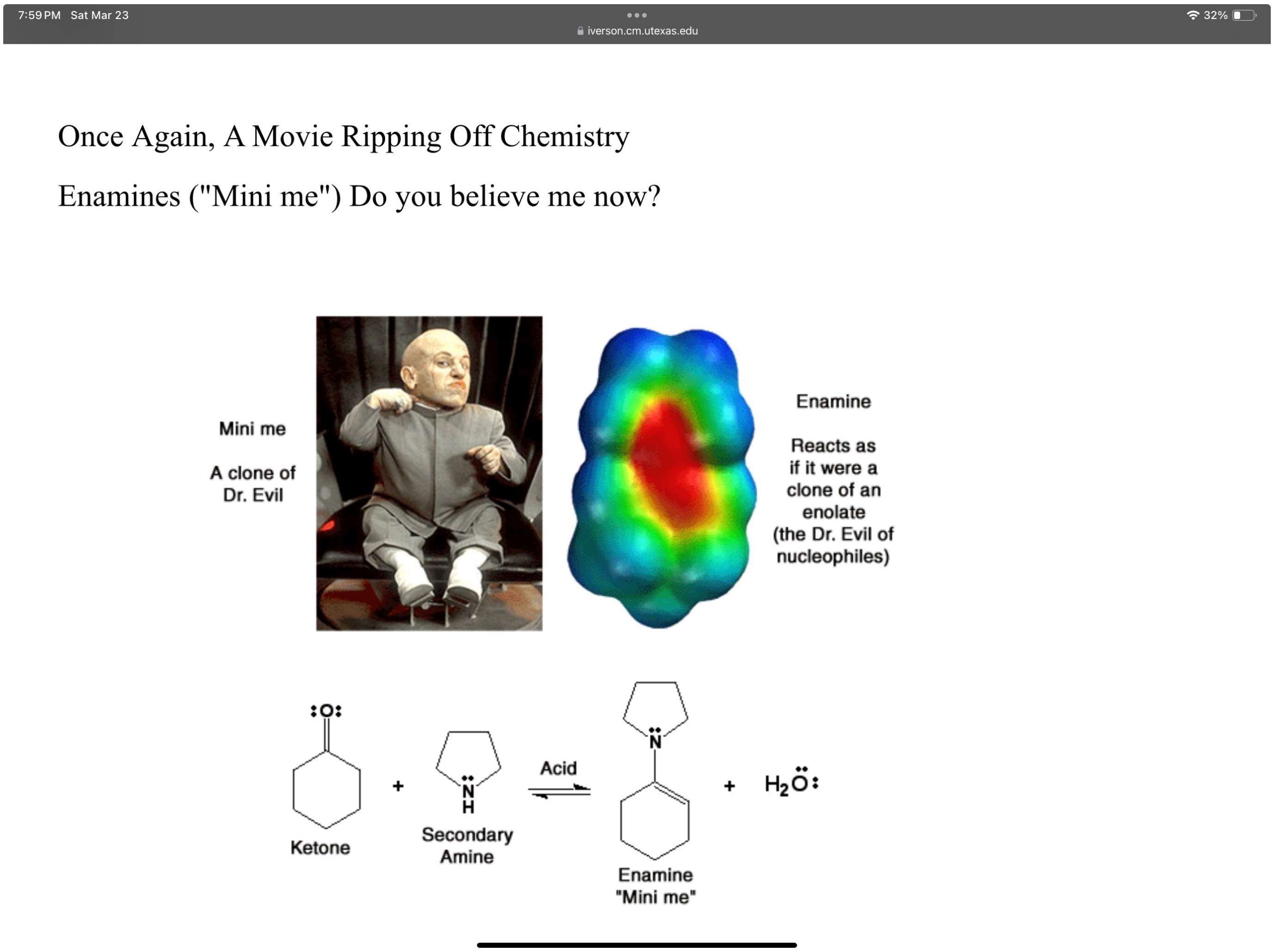
KRE → A carboxylic acid with a new C-C bond between the α and β carbon atoms

Enamine Formation





Once Again, A Movie Ripping Off Chemistry



Once Again, A Movie Ripping Off Chemistry

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

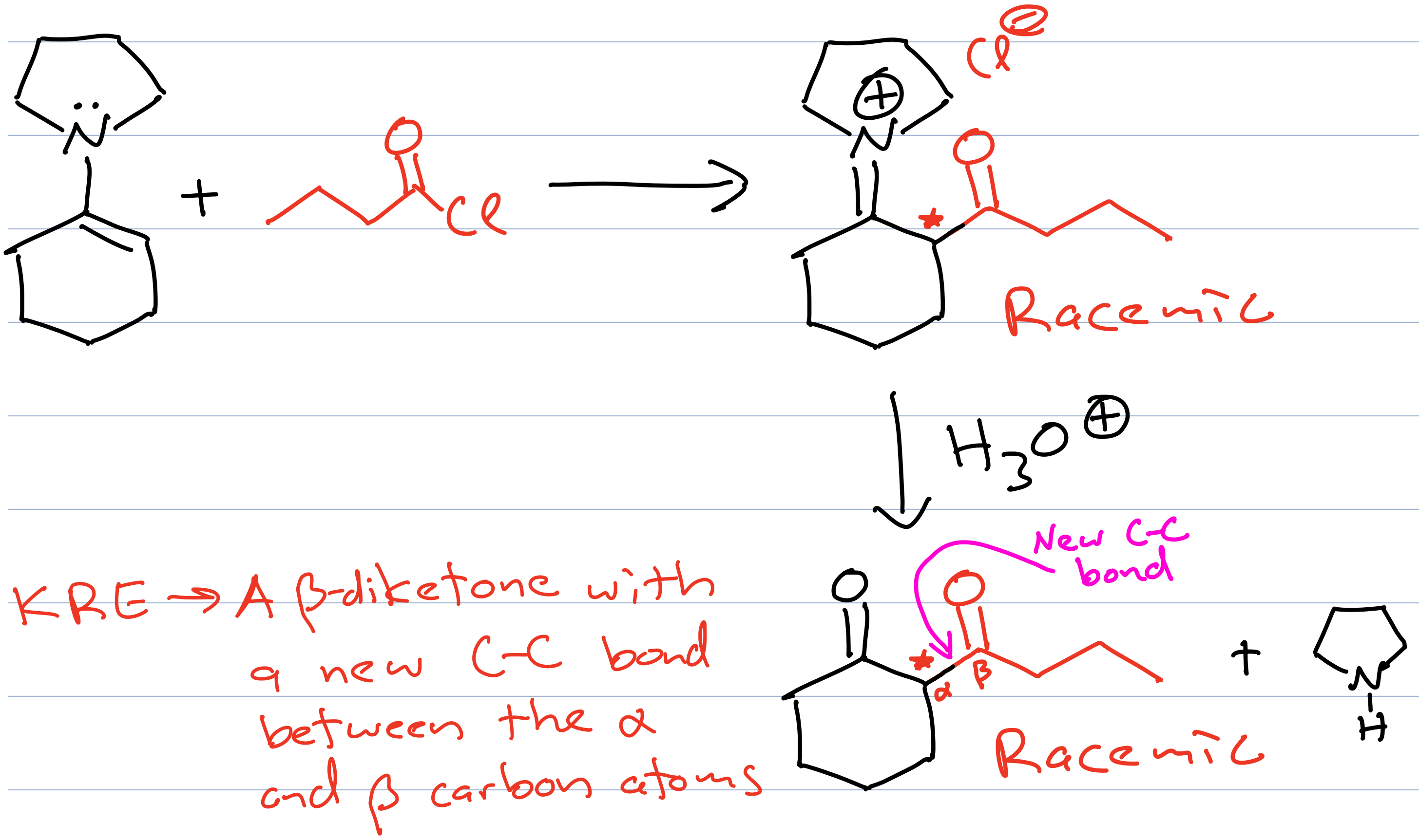
Mini me

A clone of Dr. Evil

Enamine

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

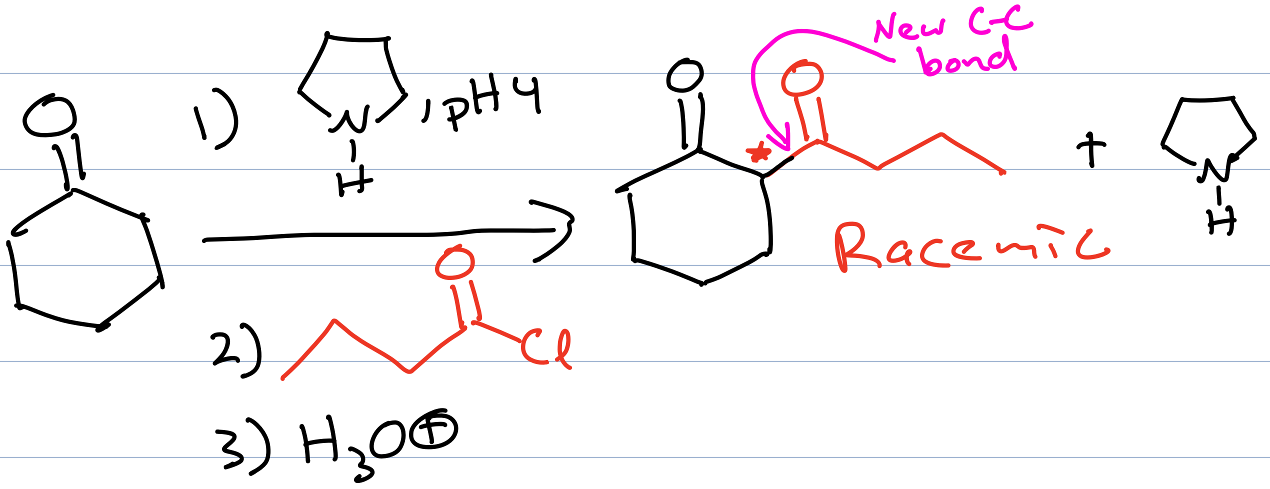
2) Acid chlorides ⇒ β-diketones



KRE → A β-diketone with a new C-C bond between the α and β carbon atoms

β-diketone

Overall Reaction



β-Substituted aldehydes, nitriles, ketones, or esters

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

β-Keto esters

α,β-Unsaturated aldehydes

Acid Chlorides

β-Hydroxy aldehydes

Aldehydes

Ketones

Carboxylic esters

β-Ketoaldehyde

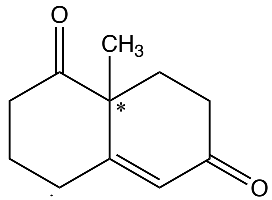
β-Diketone

Carboxylic acids

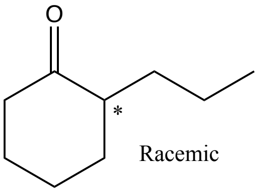
Substituted aldehyde

Substituted ketone

β-Diester



Racemic



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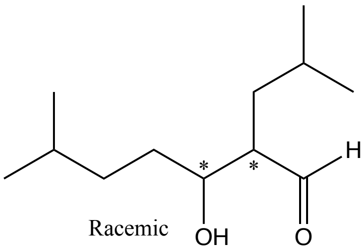

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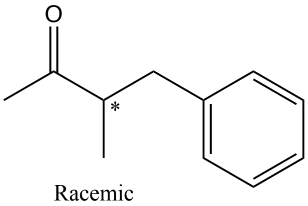
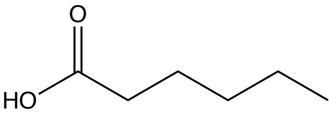
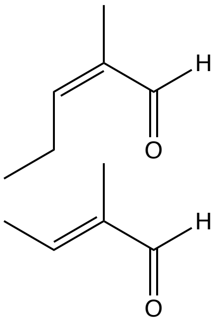
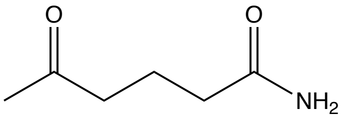
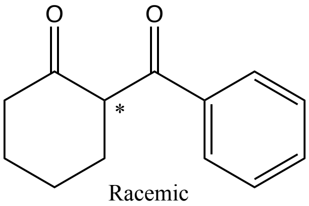


Racemic









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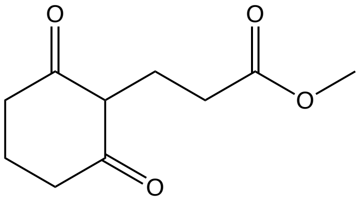

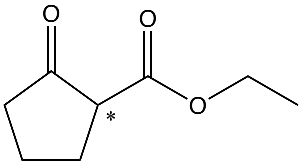

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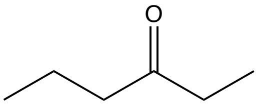

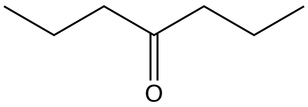

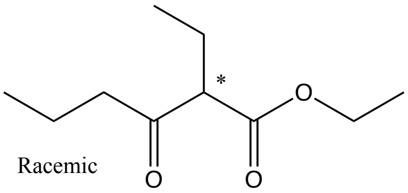

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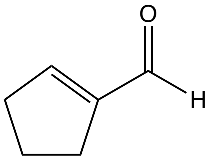
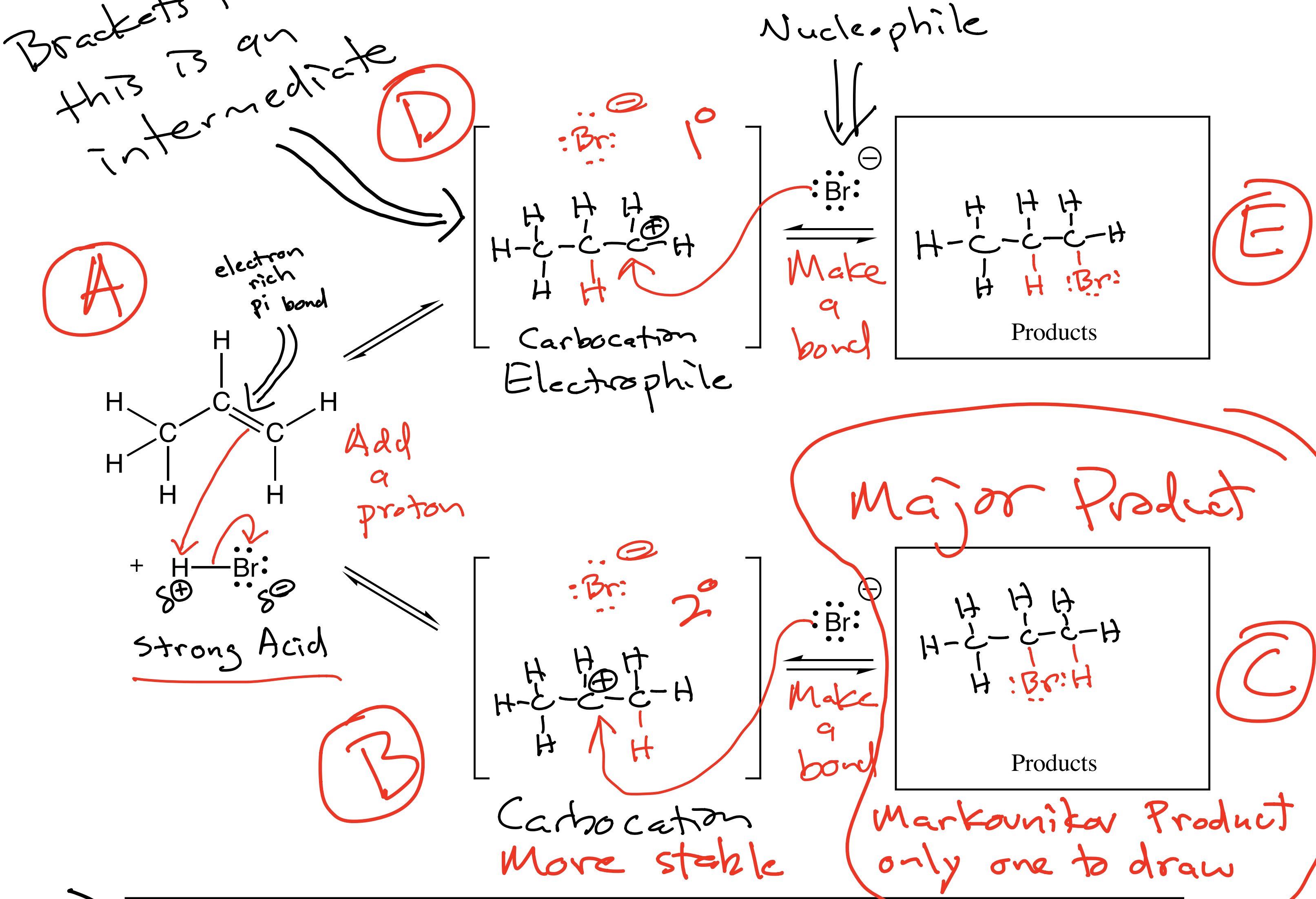



WAYNE'S WORLD

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

Addition of H-X to an Alkene



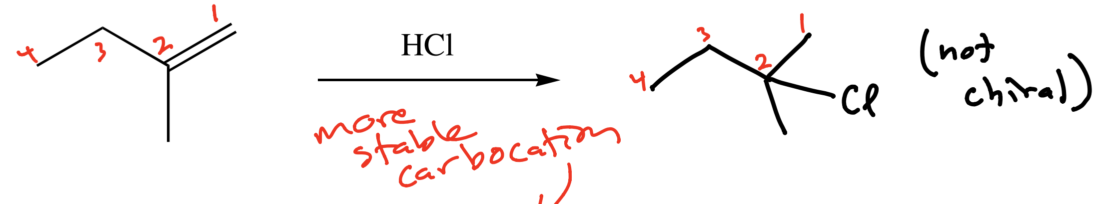
Which constitutional isomer is formed?

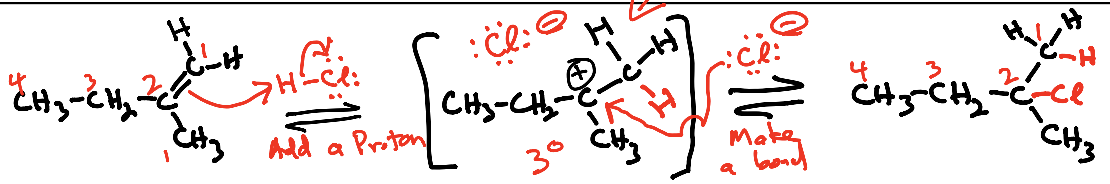
Summary: Alkene pi bond reacts with H-X to add a proton to creat a carbocation intermediate that makes a bond with X⊖ to give the product

Regiochemistry: Markovnikov's Rule

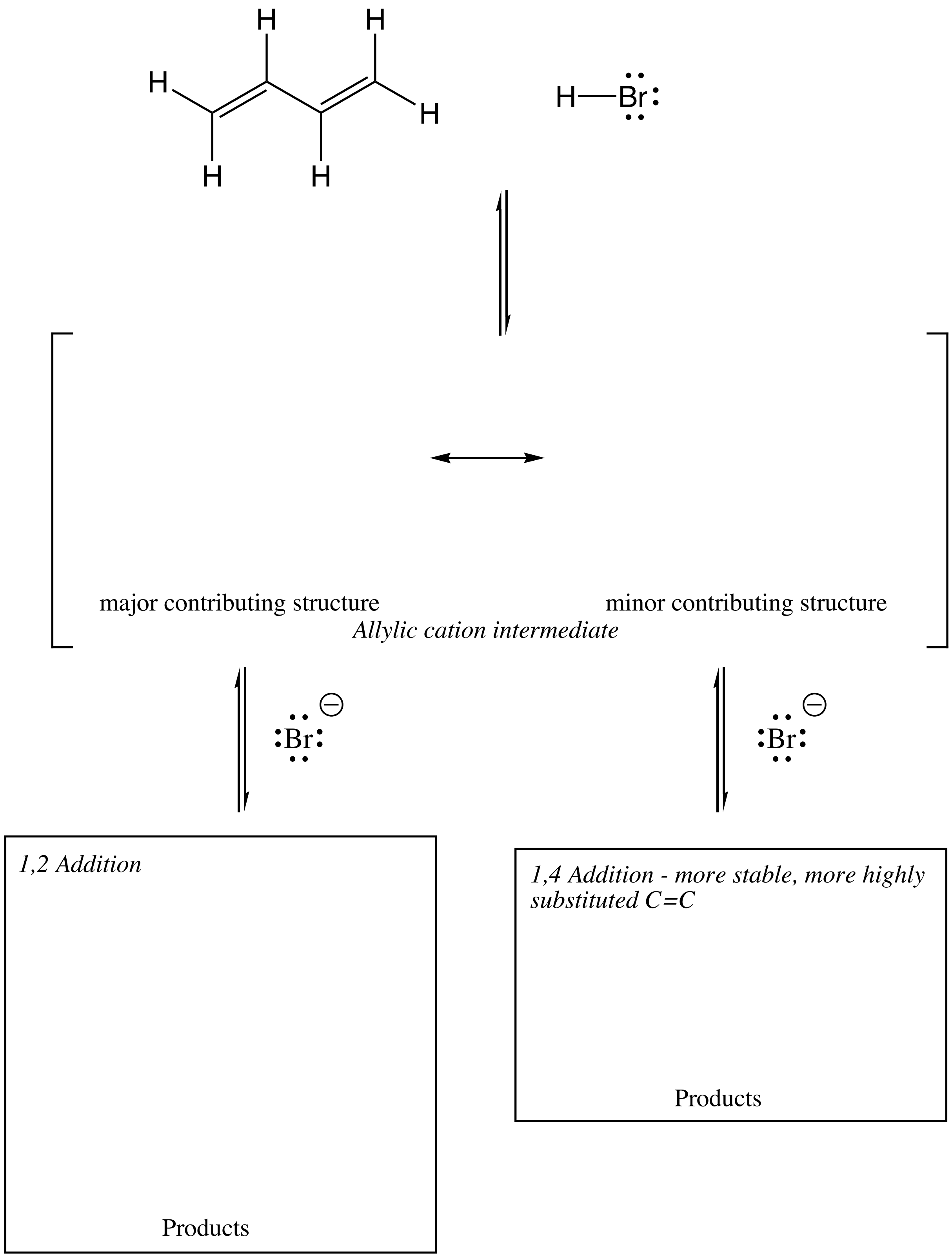
Stereochemistry: Mixed (time capsule) → Racemic Product

Example:





H-X reacting with conjugated dienes



major contributing structure

minor contributing structure

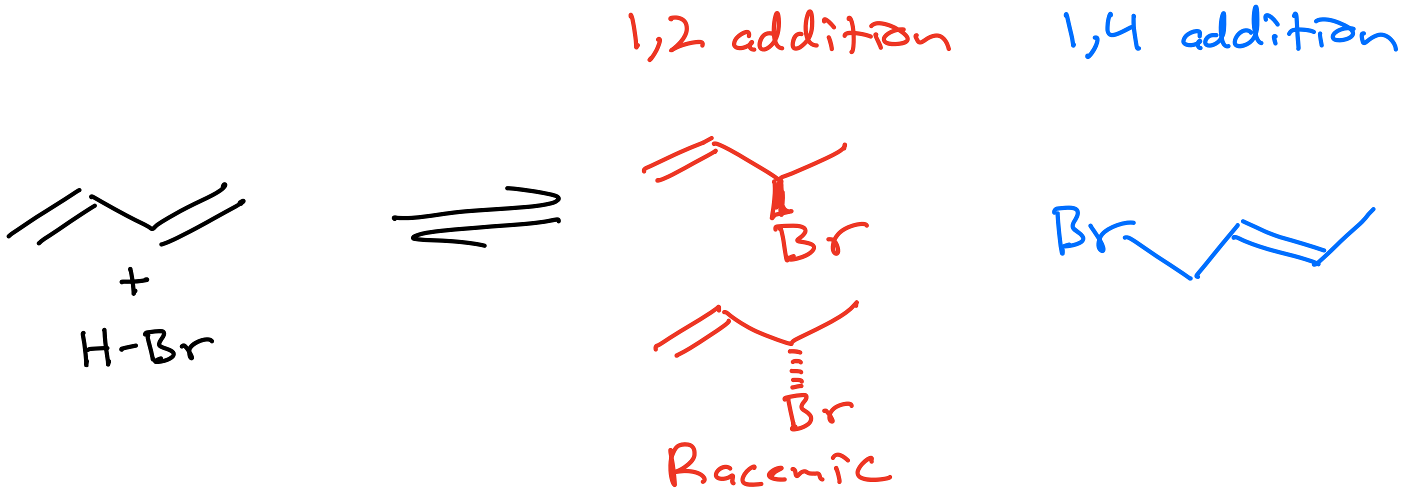
Allylic cation intermediate

1,2 Addition

Products

1,4 Addition - more stable, more highly substituted C=C

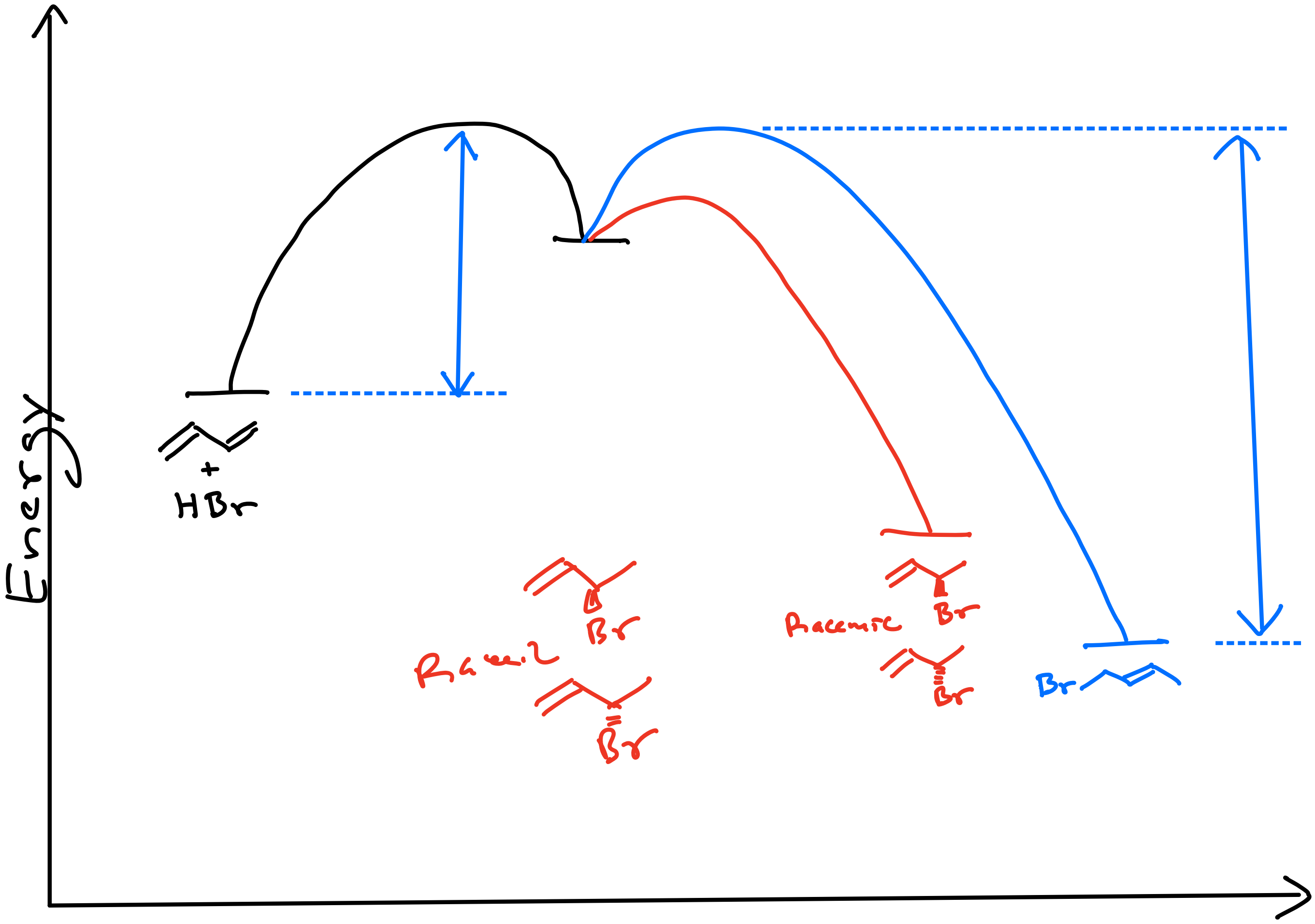
Products



Temperature of Reaction

$-78°$ C

$+40°$ C



Low temperature →

Kinetic
Control

"Fastest" wins

High temperature →

Thermodynamic
Control

Most stable
product wins

Electrons should be thought of as

Orbitals are described by

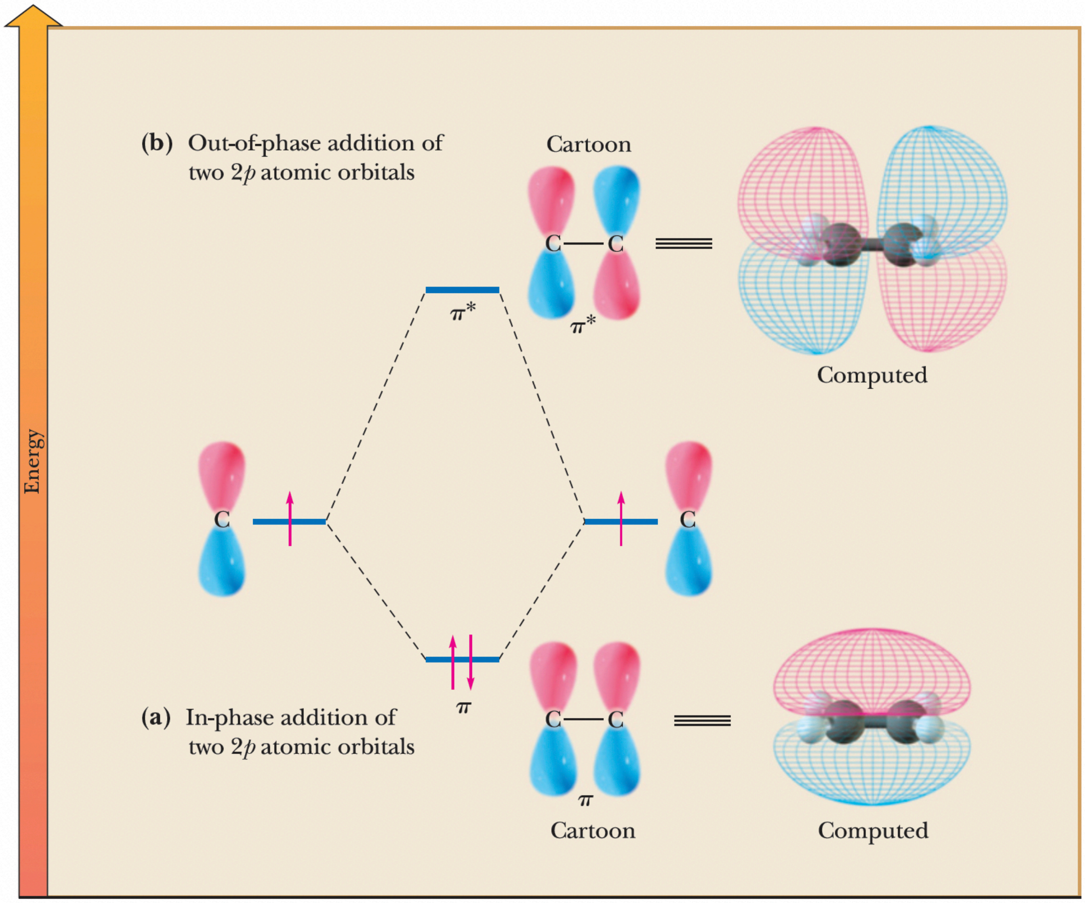
Like waves → orbitals can add
and

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



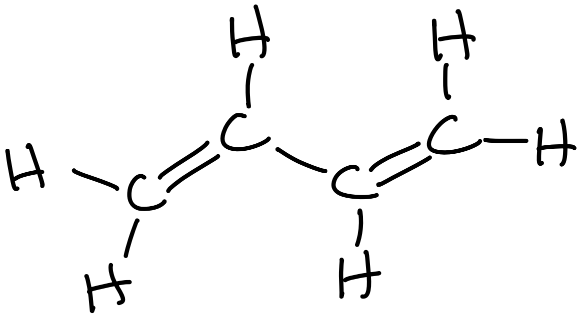
Watch a video explanation

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.

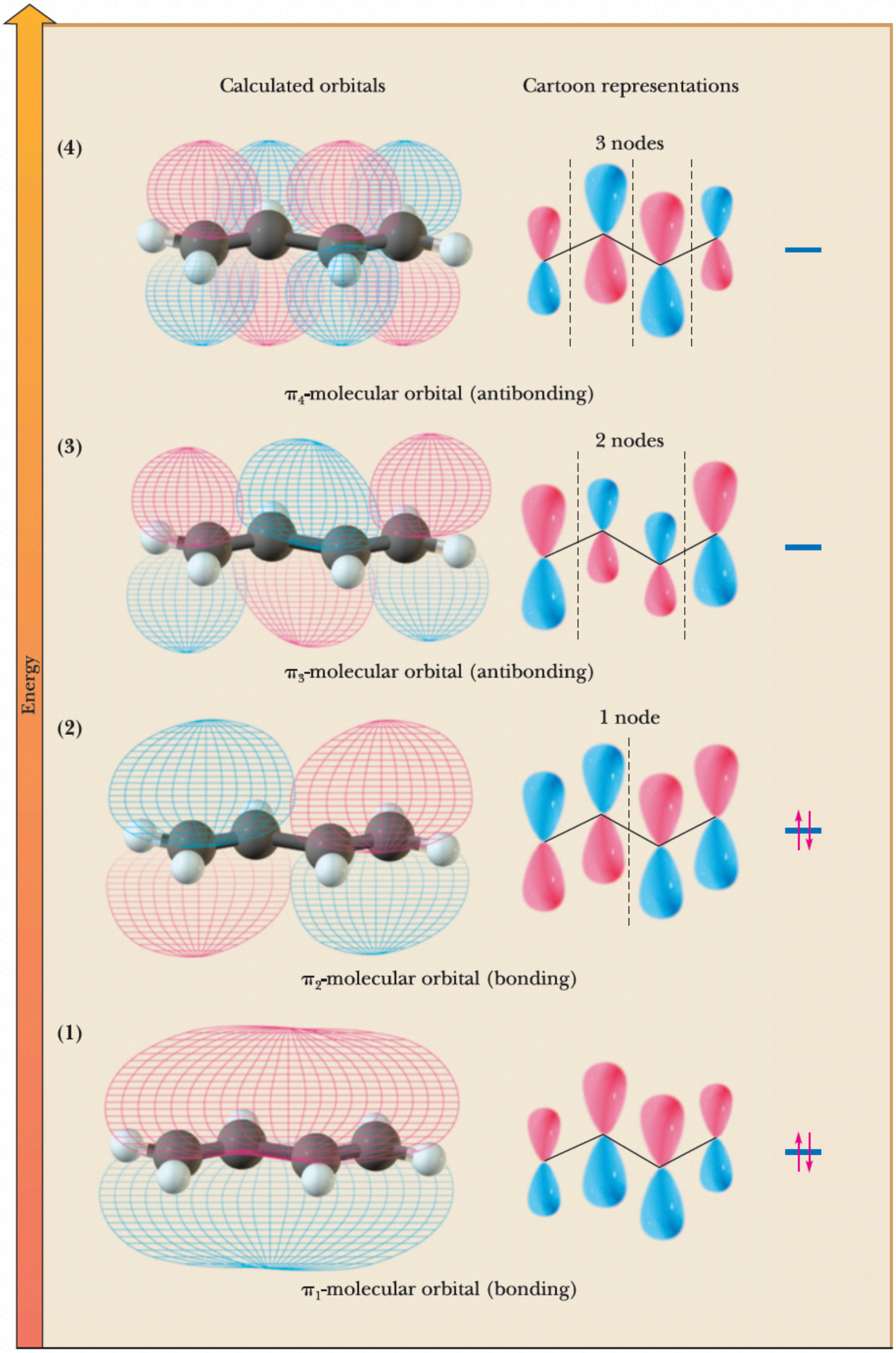
π bonding orbitals look like hot dog buns →

If you drink a lot of this you

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



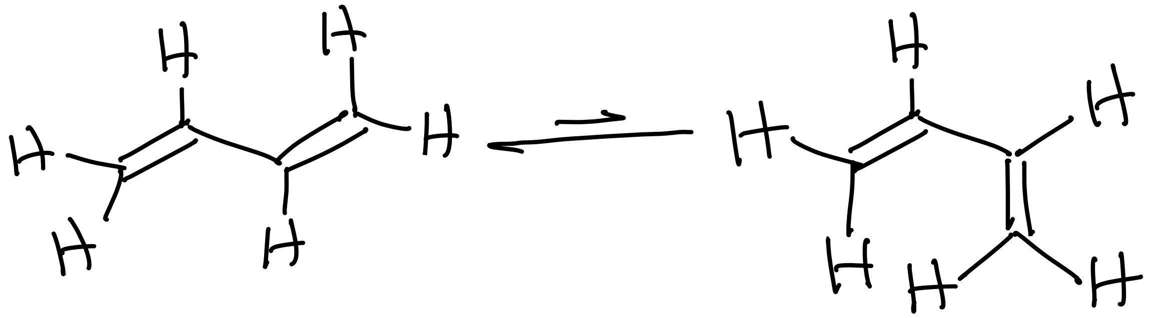
1,3-Butadiene



Watch a video explanation

FIGURE 20.2 Structure of 1,3-butadiene—molecular orbital model. Combination of four parallel 2*p* 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



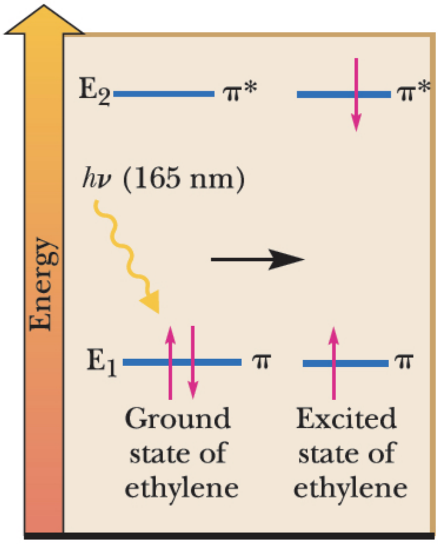


FIGURE 20.6 A $\pi \rightarrow \pi^*$ transition in excitation of ethylene. Absorption of ultraviolet radiation causes a transition of an electron from a π-bonding MO in the ground state to a π-antibonding MO in the excited state. There is no change in electron spin.

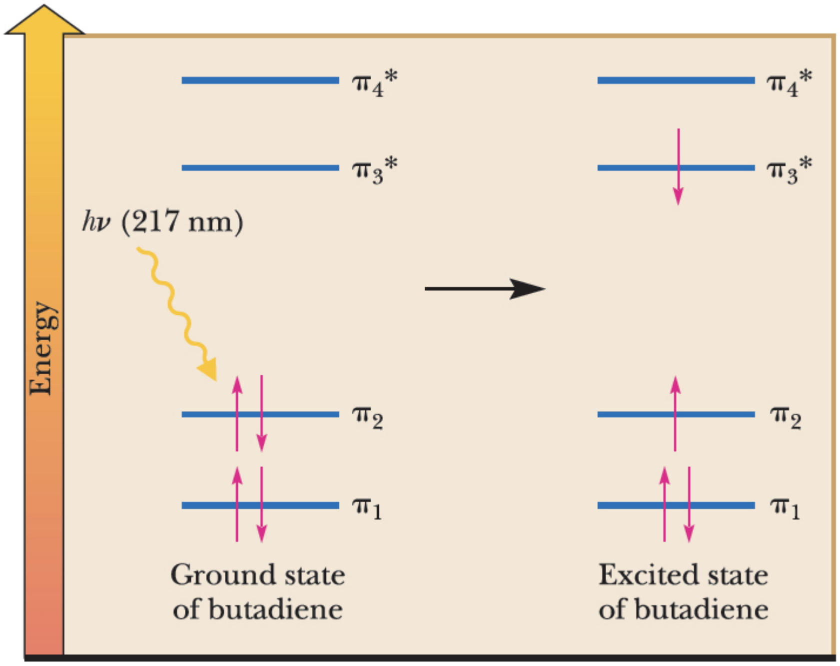


FIGURE 20.7 Electronic excitation of 1,3-butadiene; a $\pi \rightarrow \pi^*$ transition.

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

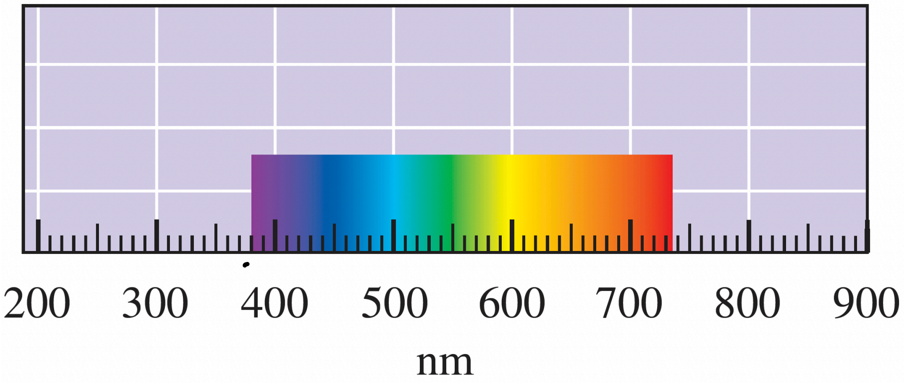
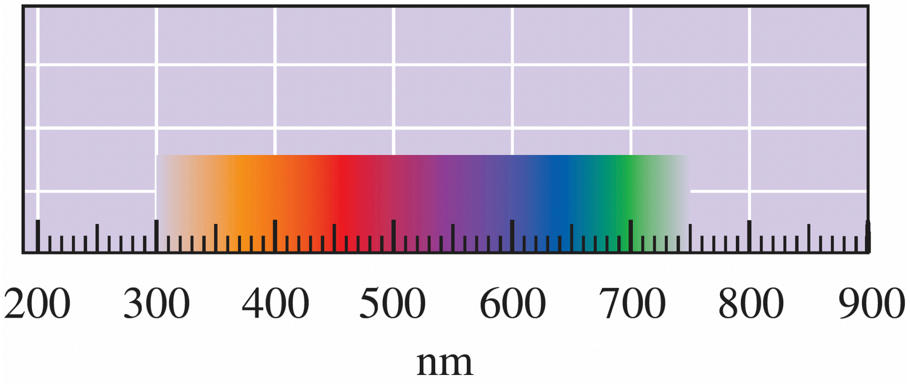
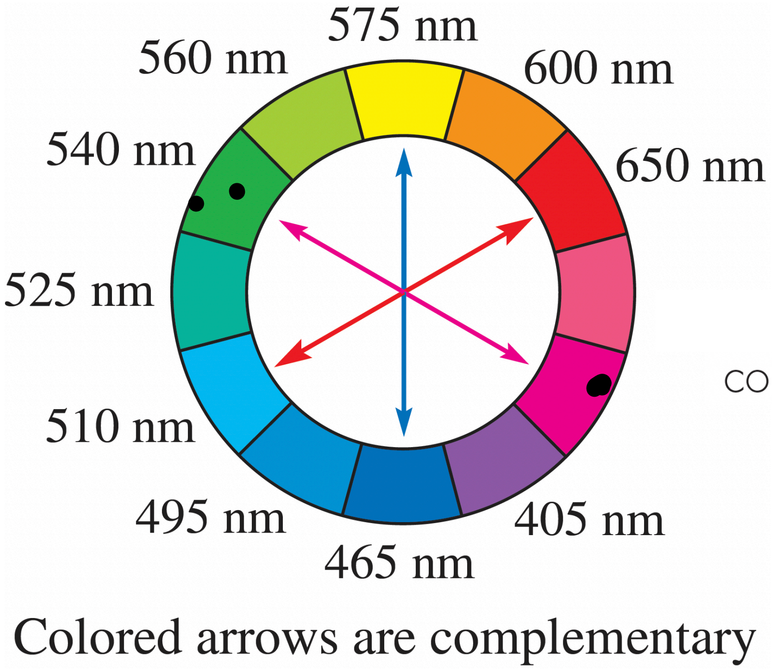


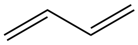
FIGURE 20.5 (a) Visible light color-wavelength correlation.



(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.

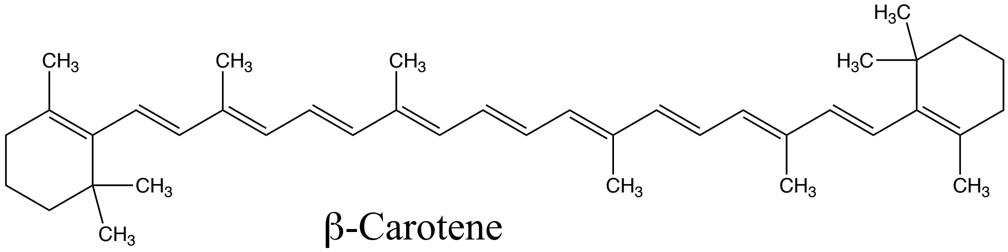


(c) Complementary colors on a color wheel.



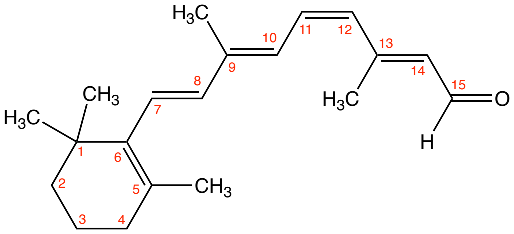
Butadiene

λ_{max} = 217 nm



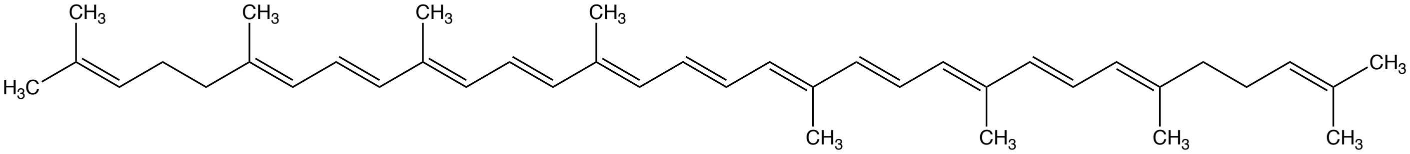
β-Carotene

λ_{max} = 455 nm, 483 nm



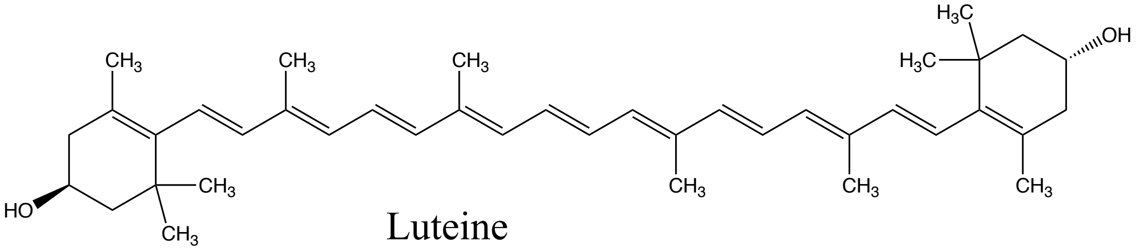
11-*cis*-Retinal

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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HELL WEEK
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