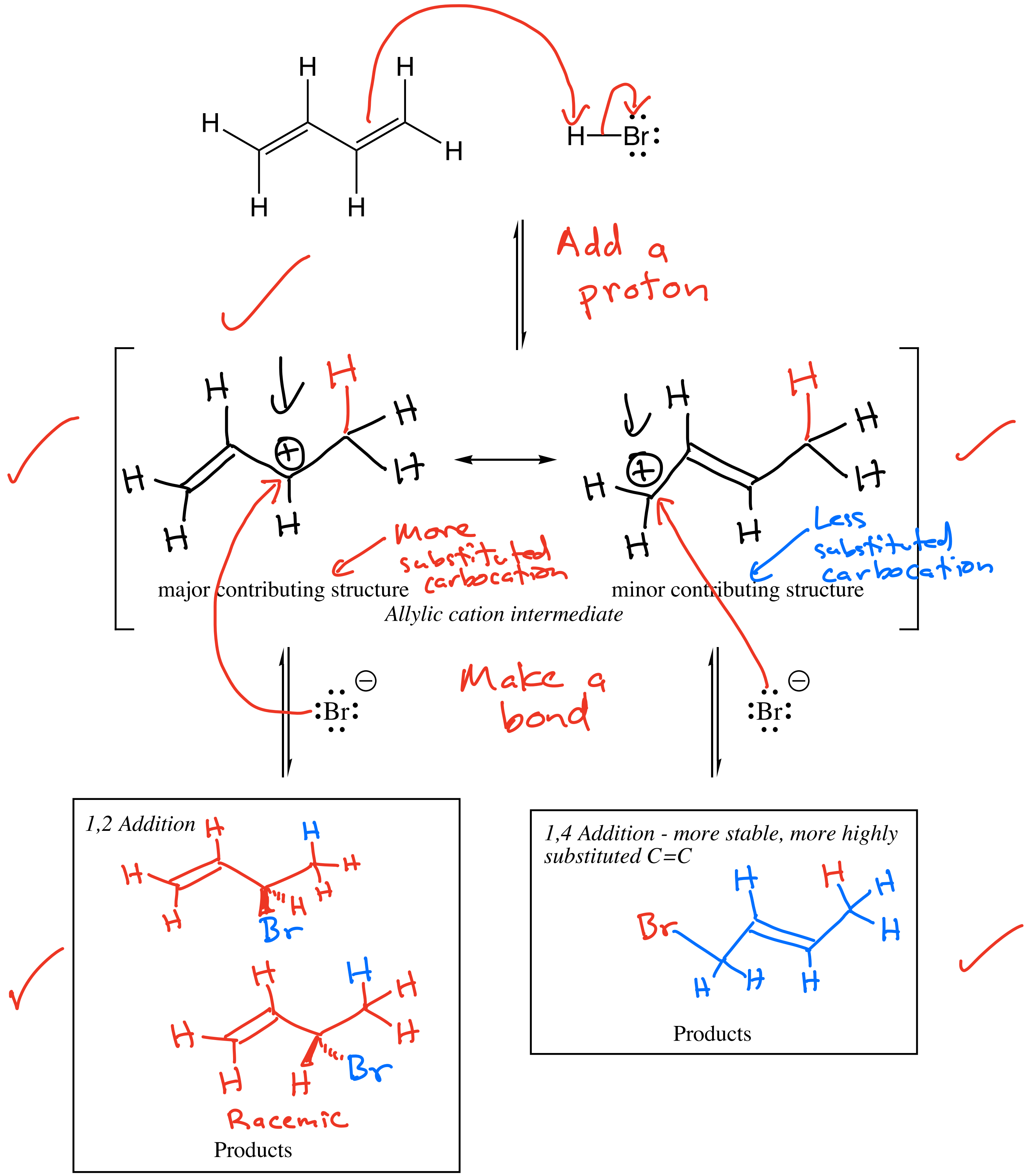
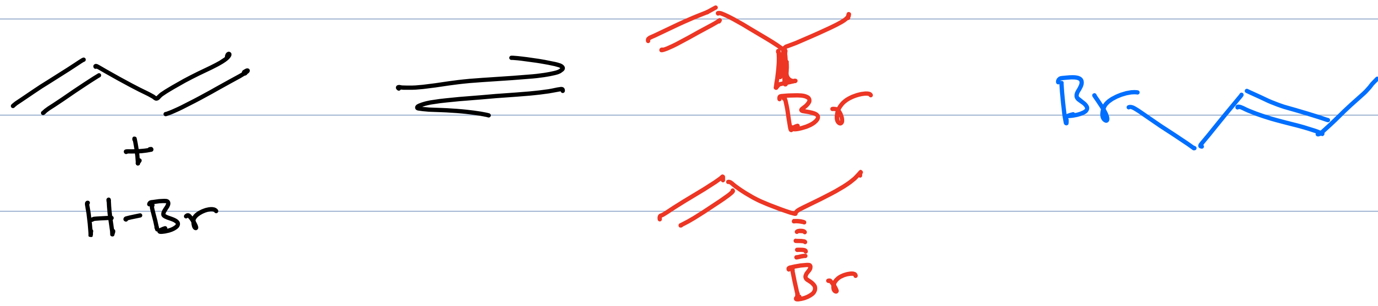
H-X reacting with conjugated dienes

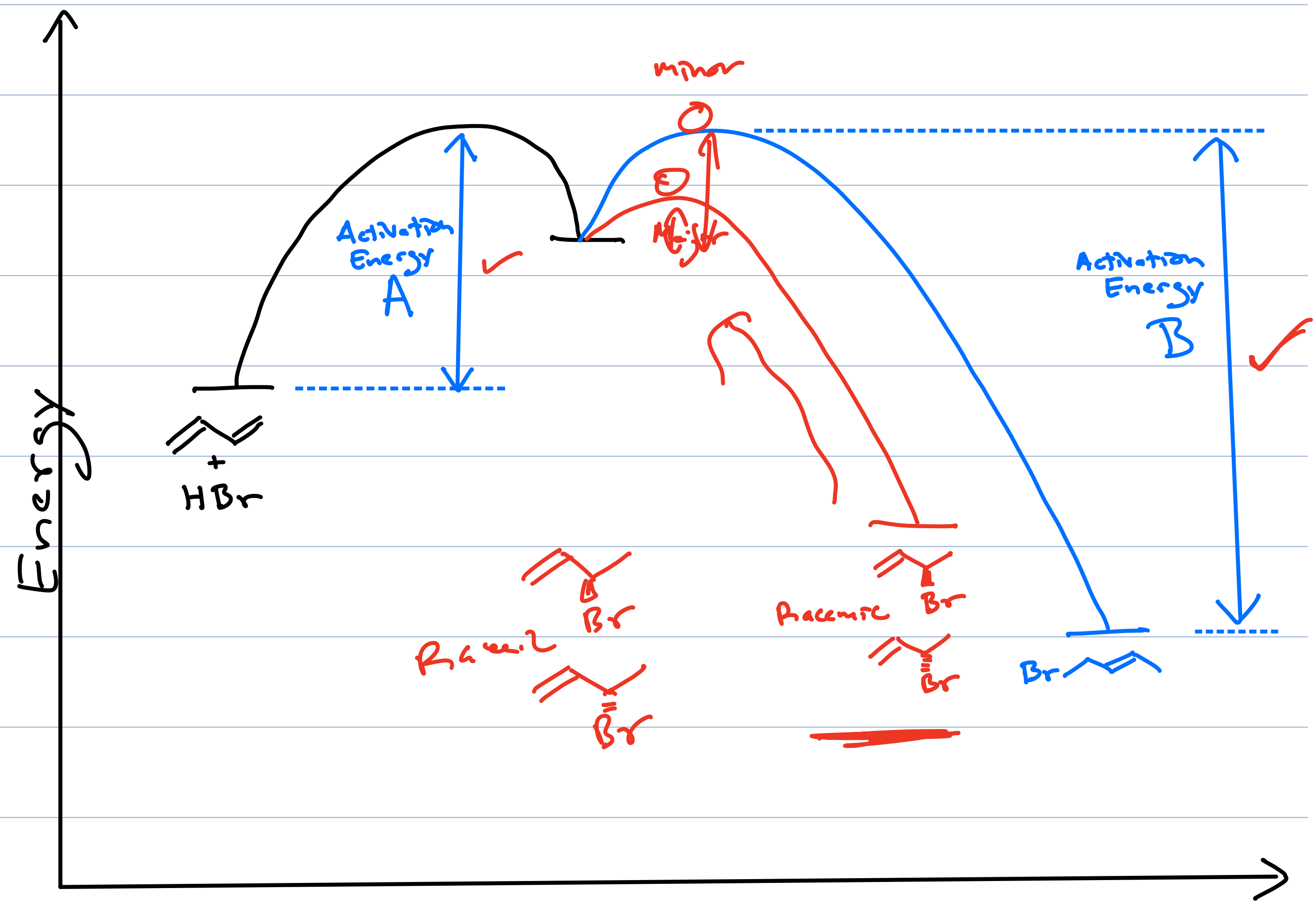


1,2 addition 1,4 addition



Racemic

Temperature of Reaction	1,2 addition	1,4 addition
$-78°C$	✓ 90%	10%
$+40°C$	15%	✓ 85%



Low temperature → Molecules have enough energy to get over activation energy A, but not enough energy to get over activation energy B.

Kinetic Control

"Fastest" wins

High temperature → Molecules have enough energy to get over activation energy A and activation energy B

Thermodynamic Control

Most stable product wins

Electrons should be thought of as waves.

Orbitals are described by wave equations.

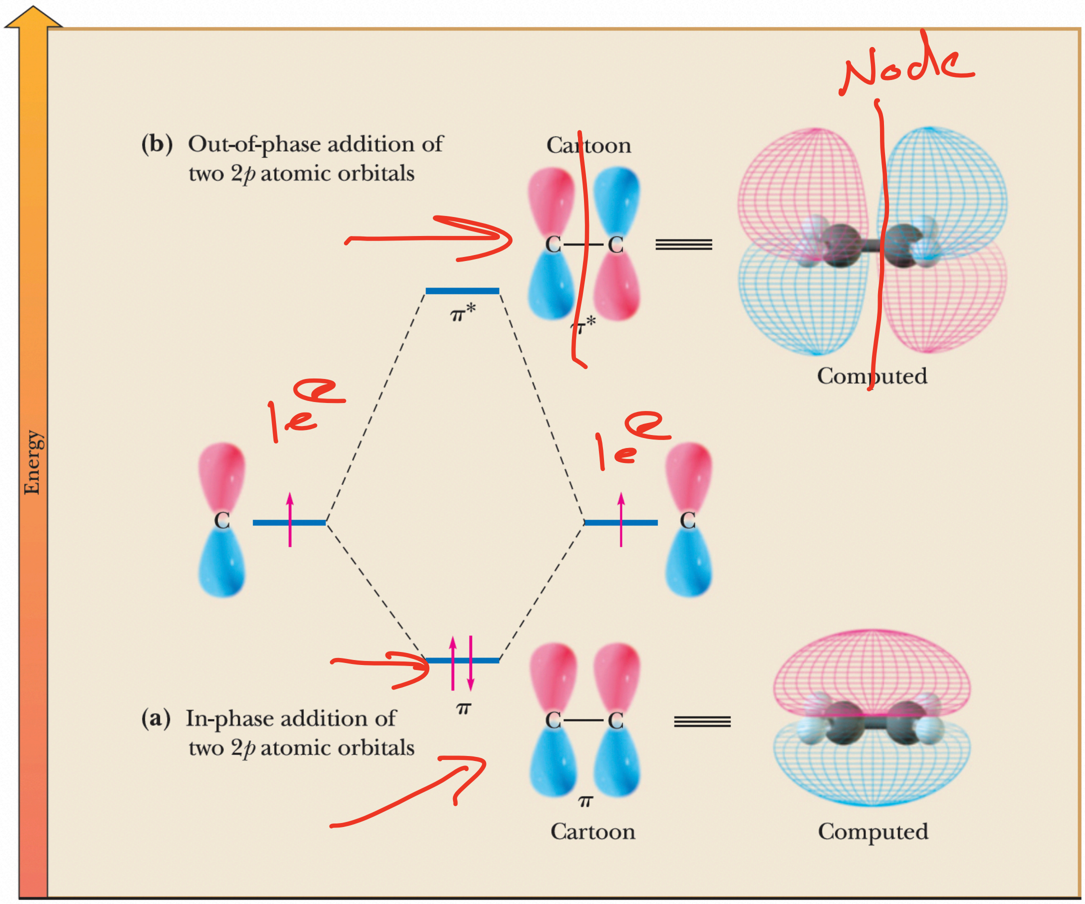
Like waves → orbitals can add constructively and destructively

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

→ Half of these are bonding molecular orbitals

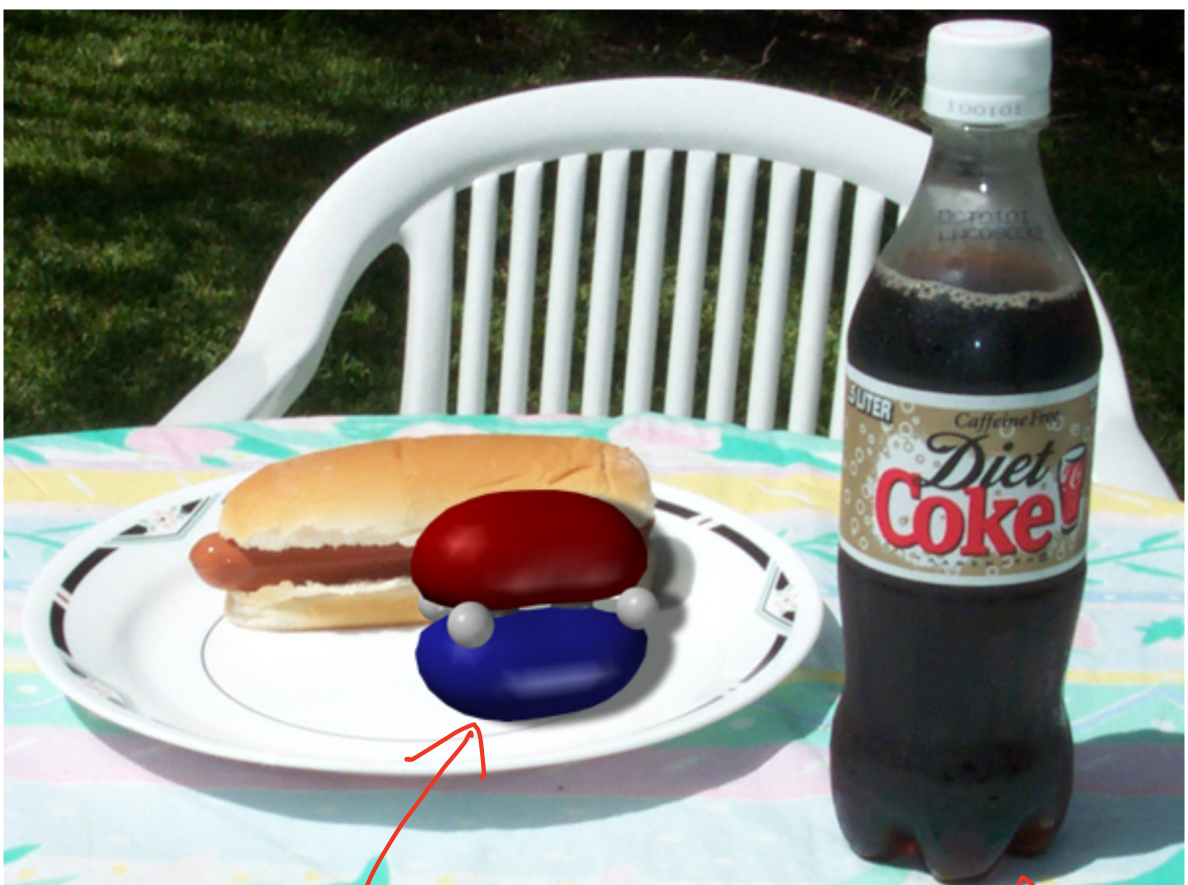
→ Half of these are antibonding molecular orbitals

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



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.



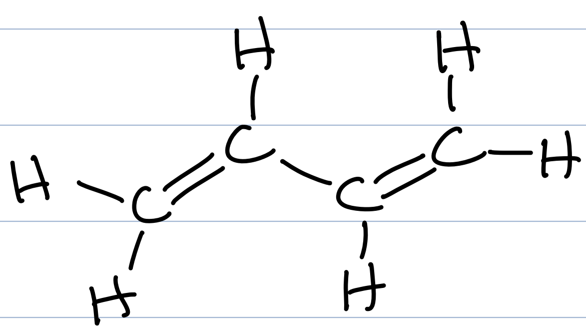
π bonding orbitals look like hot dog buns → formed from overlap of 2p orbitals

⇓

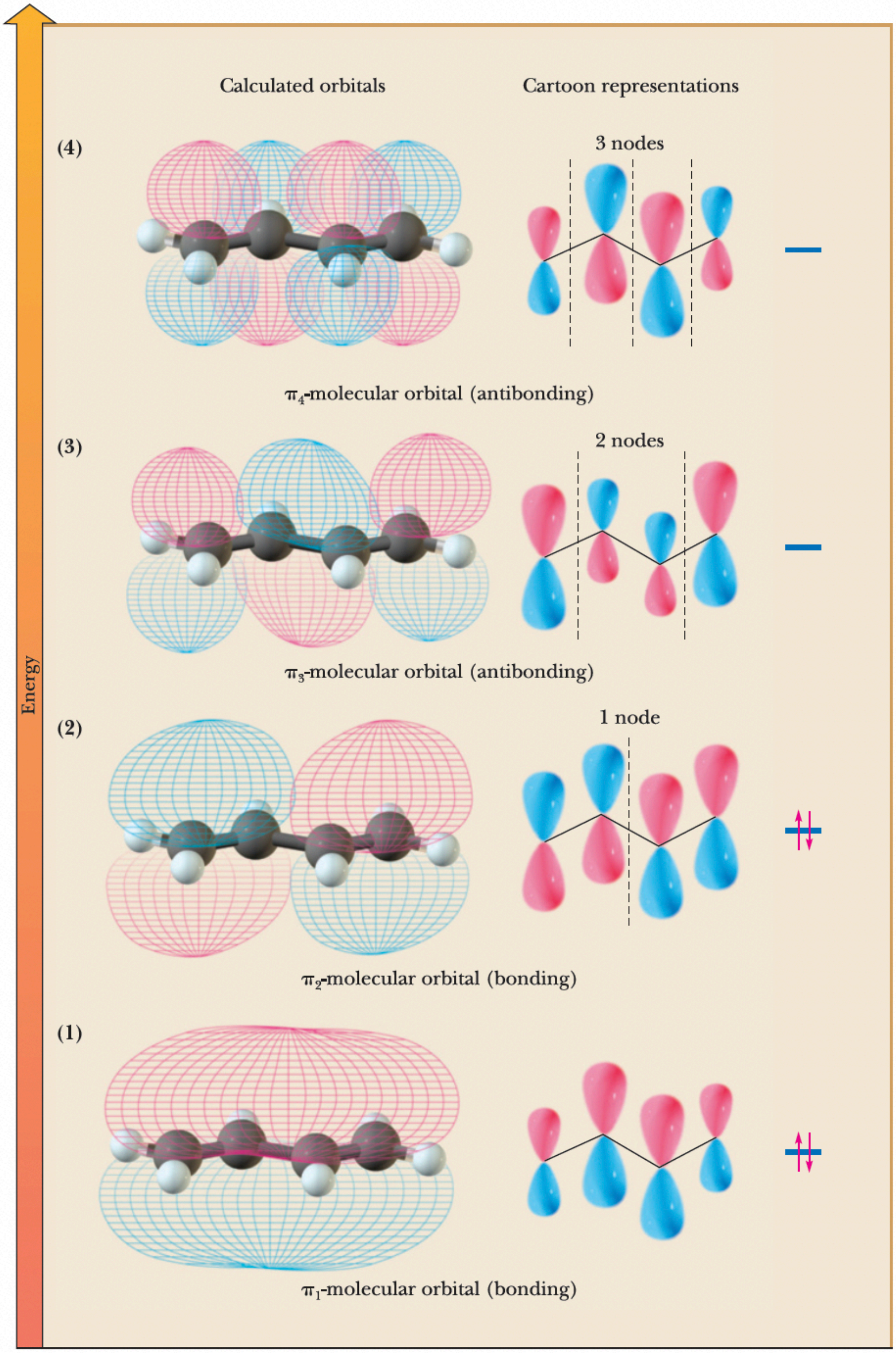
"to pee"

If you drink a lot of this you have 2 p! (to pee)

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



1,3-Butadiene



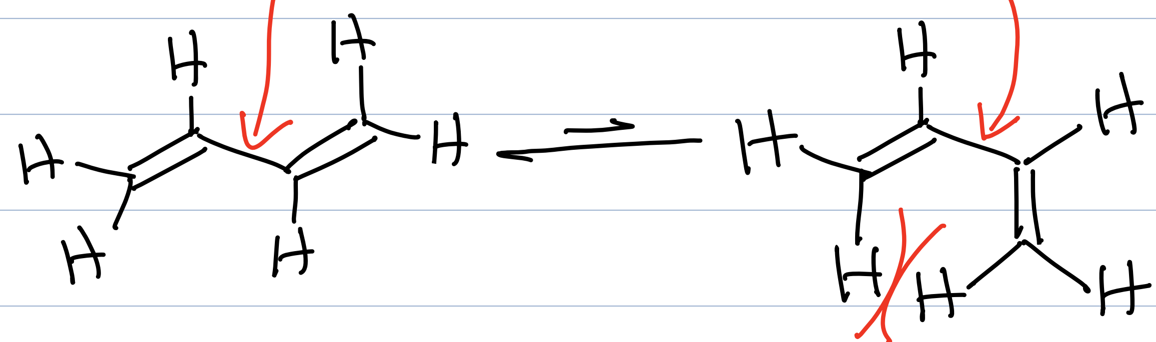
Watch a video explanation

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 "π-way" molecular orbital → The bond between the middle two carbon atoms is not a normal sigma bond

→ Partial π bond

→ Does NOT rotate freely



s-Trans

Steric strain

s-Cis

More stable

Less stable due to some steric strain

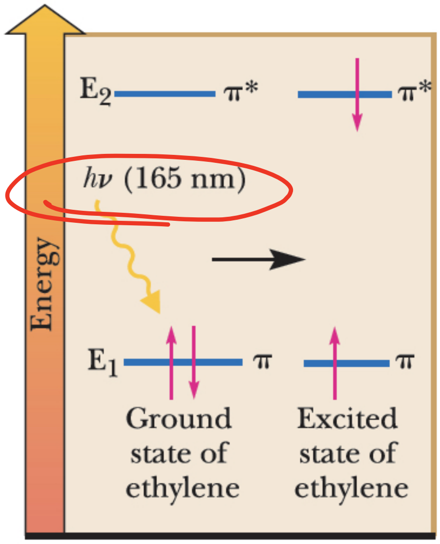
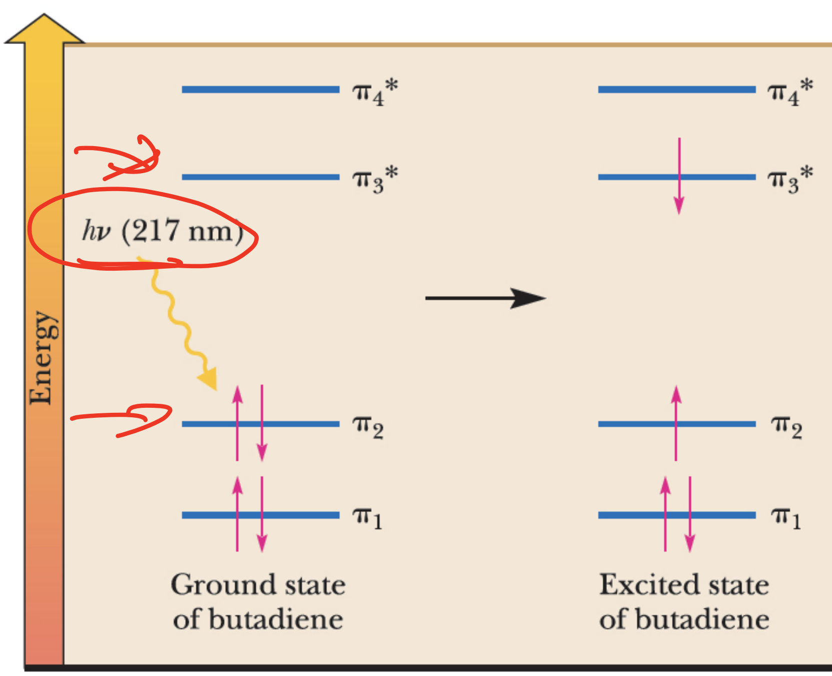


FIGURE 20.6 A $\pi \rightarrow \pi^*$ transition in excitation of ethylene. Absorption of ultraviolet radiation causes a transition of an electron from a π-bonding MO in the ground state to a π-antibonding MO in the excited state. There is no change in electron spin.



π-energy

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

As you add 2p orbitals $\rightarrow$
the energy gap between
the highest filled
π molecular orbital
and the lowest unfilled
π molecular orbitals
gets smaller $\Rightarrow$ leads
to longer wavelength
of light photon of
the correct energy
to be absorbed.

Energy

Light source

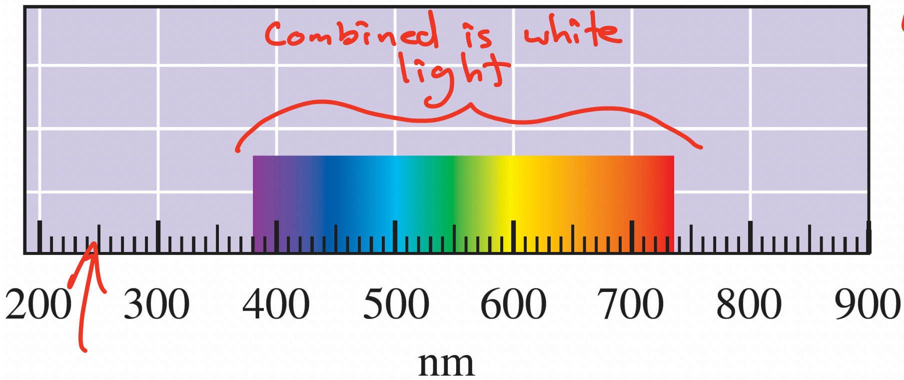
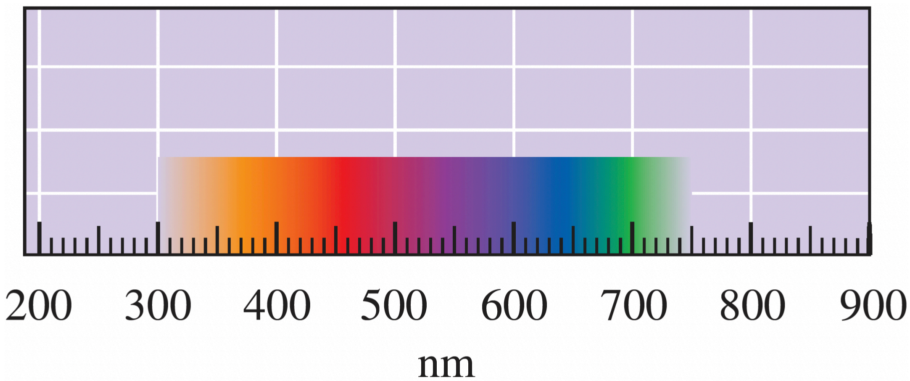
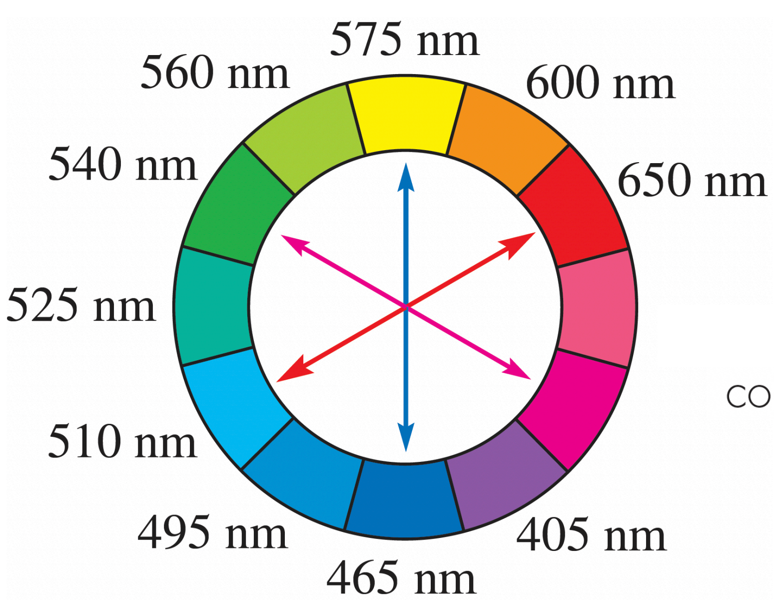


FIGURE 20.5 (a) Visible light color-wavelength correlation.

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

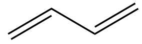


(b) Approximate color of substance (reflected light) if a single wavelength (i.e., the wavelength listed on the numerical scale of the *x*-axis) is absorbed.



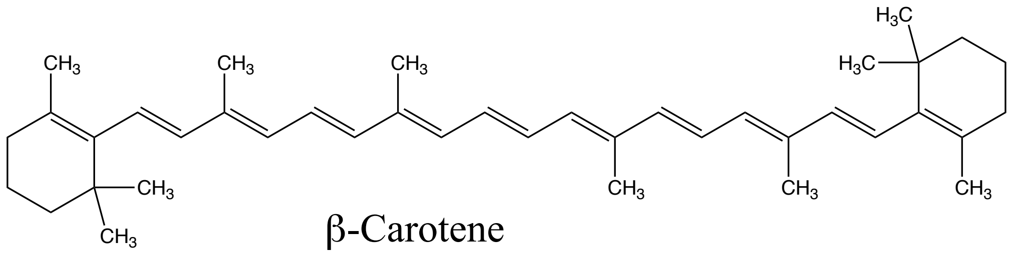
Colored arrows are complementary

(c) Complementary colors on a color wheel.



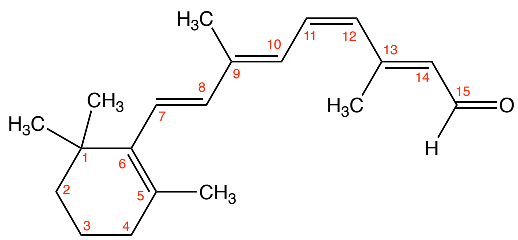
Butadiene

λ_{max} = 217 nm



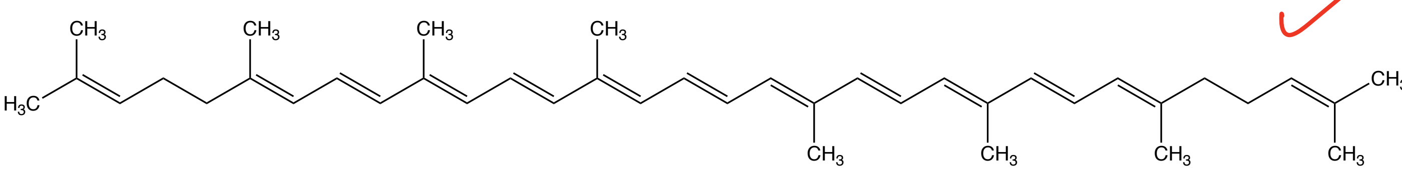
β-Carotene

λ_{max} = 455 nm, 483 nm



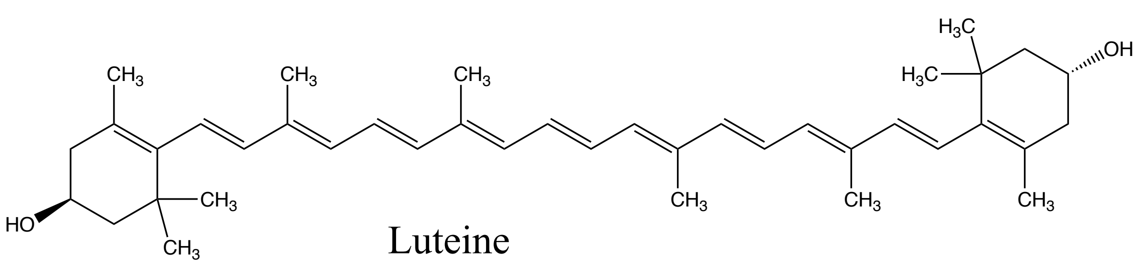
11-*cis*-Retinal

λ_{max} = 380 nm



Lycopene

λ_{max} = 443 nm, 471 nm, 502 nm



Luteine

λ_{max} = 445 nm, 474 nm

White → reflects all wavelengths of visible light
Black → absorbs all wavelengths of visible light

Absorbs all light including orange — it will be black in an orange light.

when illuminated under an orange light — both reflect all of it and look orange

A green laser is entirely absorbed by the <u>red</u> blood (hemoglobin) in your finger because for blood to appear red it must absorb blue and green, while reflecting red.

A red laser is <u>not</u> absorbed by the red blood in your finger — otherwise blood would not be red!!