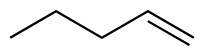
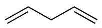
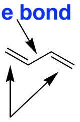
Chapter 14: Conjugated Dienes and Ultraviolet Spectroscopy

Diene: molecule with two double bonds

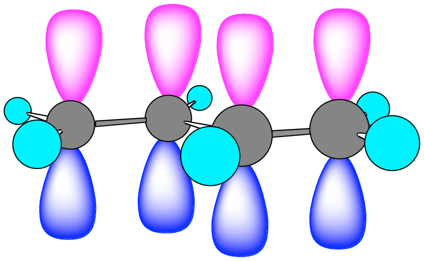
Conjugated diene: alternating double and single bonds


Alkene


Diene



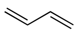
Conjugate Diene

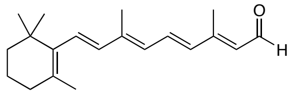


When the carbons of a conjugate diene all lie in the same plane, the □-molecular orbitals overlap.

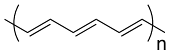
Conjugation: a series of overlapping p-orbitals

alkenes conjugated to alkenes

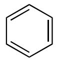

butadiene



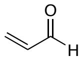
Vitamin A (retinal)



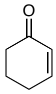
poly-acetylene


Arene

alkenes conjugated to carbonyls

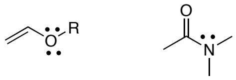


acrolein
(□,□-unsaturated aldehyde, enal)

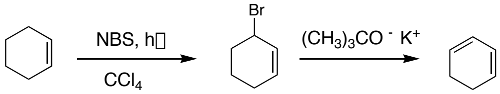


cyclohexenone
(□,□-unsaturated ketone, enone)

alkenes conjugated to non-bonding pairs of electrons

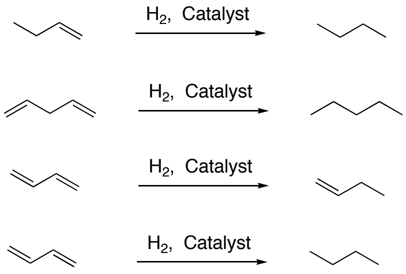


Preparation of conjugated dienes (1,3-dienes) from alkenes: allylic bromination followed by dehydrohalogenation



Stability of conjugated double bonds: the double bonds of conjugated dienes are more stable than isolated double bonds.

Table 14.1 (p. 525) □H° (hydrogenation)



-126 KJ/mol

-253 KJ/mol

(2 x 126 = 252)

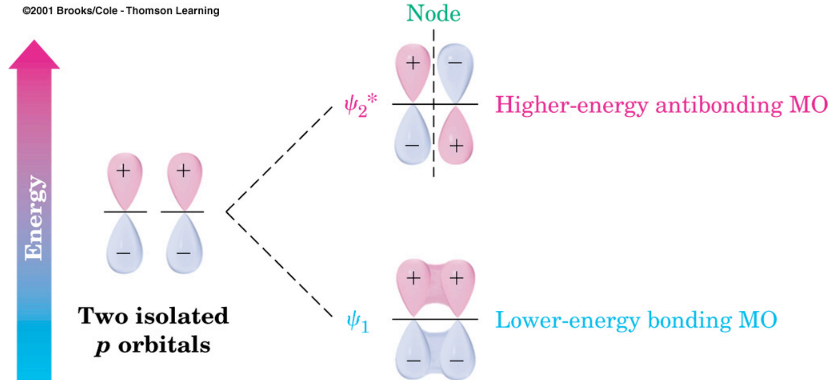
-110 KJ/mol

(126 - 110 = 16)

-236 KJ/mol

(252 - 236 = 16)

□-molecular orbitals of an alkene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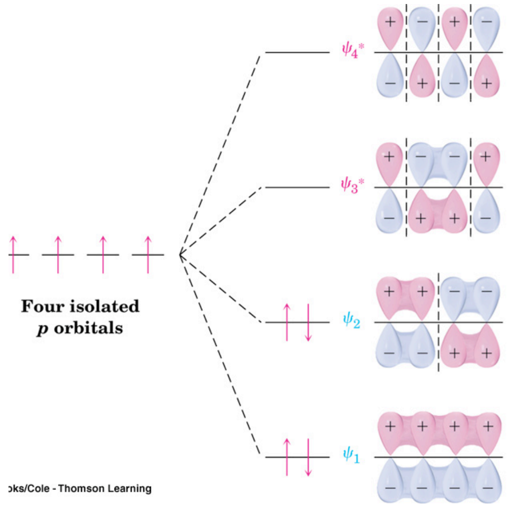
π-molecular orbitals of butadiene



3 Nodes
0 bonding interactions
3 antibonding interactions
ANTIBONDING MO

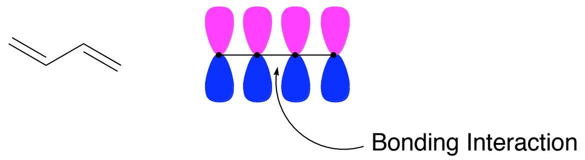
2 Nodes
1 bonding interactions
2 antibonding interactions
ANTIBONDING MO

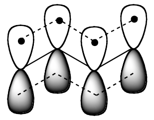
1 Nodes
2 bonding interactions
1 antibonding interactions
BONDING MO

0 Nodes
3 bonding interactions
0 antibonding interactions
BONDING MO

ψ_2 is the Highest Occupied Molecular Orbital (HOMO)
ψ_3 is the Lowest Unoccupied Molecular Orbital (LUMO)

ψ_1 of Butadiene (no nodes, bonding MO)





The four π-electrons in ψ_1 are delocalized over the four p-orbitals

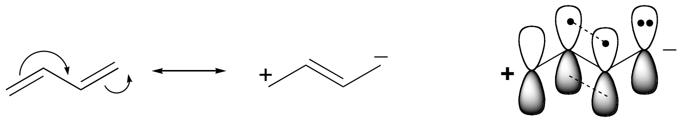
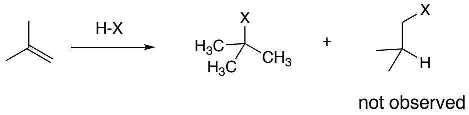


Table 14.2 (p. 528): Bond lengths in pm

H_3C-CH_3	$H_2C=CH_2$	$H_2C=CH-CH_3$	$H_2C=CH-CH=CH_2$	$H_2C=CH-CH=CH_2$
154	133	149	148	134

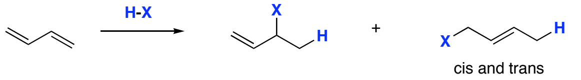
Electrophilic Addition to Conjugated Alkenes:
The addition of HX to butadiene

Recall: Electrophilic addition to alkenes follows Markovnikov's Rule



The observed product is derived from the most stable carbocation intermediate

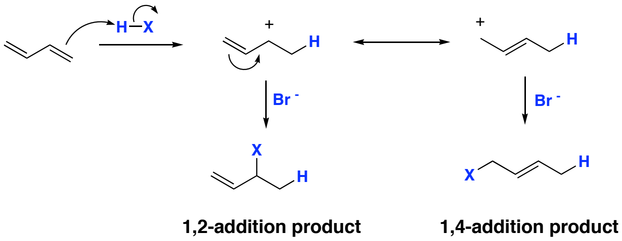
For a conjugated diene:



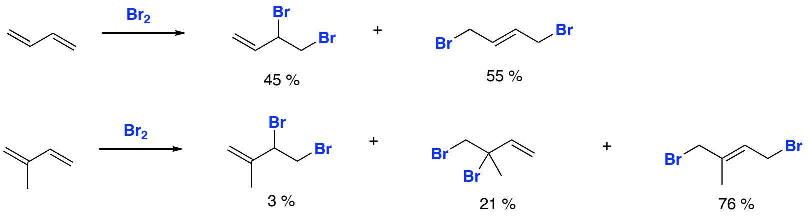
The distribution of products is dependent upon temperature

	1,2-addition product	1,4-addition product
0 °C	71%	29%
40 °C	15%	85%

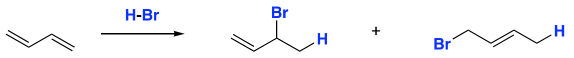
The reaction goes through an allyl carbocation intermediate
allyl carbocation is resonance stablized



Other electrophilc additions give similar results

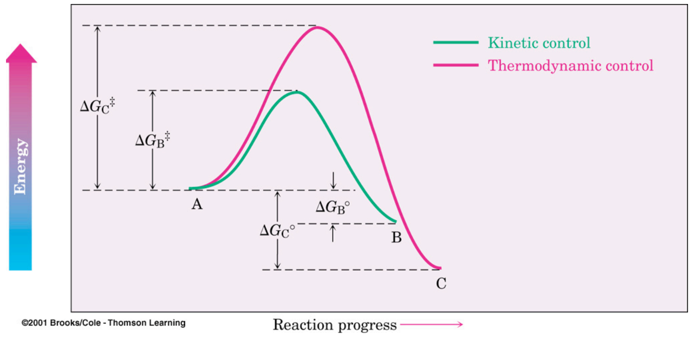


Kinetic vs. Thermodynamic Control of Reacctions



0 °C	71%	29%
40 °C	15%	85%

A ⟶ B + C

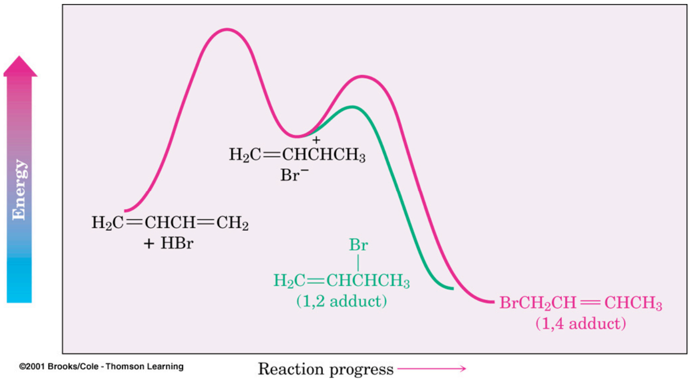


$\Delta G_B^\ddagger > \Delta G_C^\ddagger$ B is formed faster than A. Rate (kinetics) favors B

$\Delta G^\circ_B < \Delta G^\circ_C$ C is more stable than B. Thermodynamics favors C

Thermodynamic Control (ΔG°): At higher temperatures, all reactions are readily reversible. An equilibrium distributions of products is obtained (ΔG° = -RT lnKeq). The product with the lowest ΔG° is favored.

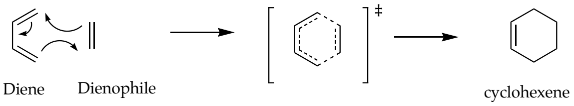
Kinetic Control ($\Delta G^\ddagger$): At lower temperatures, the reactions are *not* readily reversible (irreversible). The product distributions is governed by the rates by which the products form. The product with the lowest $\Delta G^\ddagger$ is favored.



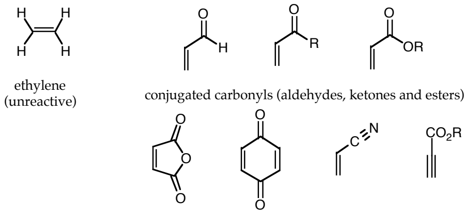
Sect. 14.7 Diene Polymers: Natural and Synthetic Rubbers (read)

14.8 Diels-Alder Cycloaddition Reaction (a very important reaction)

Reaction between a conjugated diene and an alkene (dienophile)
to give a cyclohexene



The Diels-Alder reaction is favored by electron withdrawing groups on the dienophile and electron donating groups on the diene.

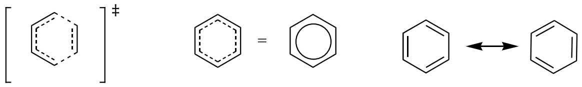


ethylene
(unreactive)

conjugated carbonyls (aldehydes, ketones and esters)

Good dienophiles

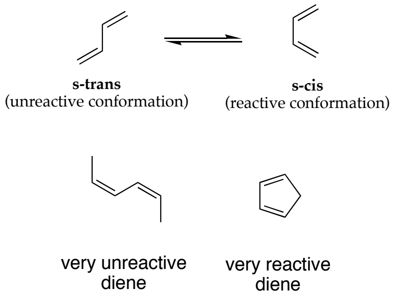
Diels-Adlder Reaction:
Mechanism: Pericyclic Reaction- proceeds in a single step via an "aromatic" transition state (pericyclic reaction).

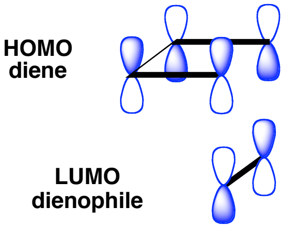


Diels-Alder
Transition State

Benzene

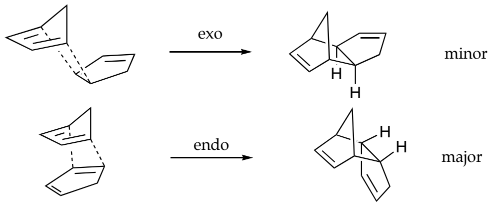
The diene must adopt an <u>s-cis</u> conformation to be reactive:





Endo vs. Exo Transition State:

Generally, the endo transition state is favored.



Stereochemistry: In pericyclic reactions, the stereochemistry of the reactants is preserved in the product. Recall the cyclopropanation of alkenes by carbenes which is also a pericyclic reaction.

R groups are trans in the reactant

R groups are trans in the product

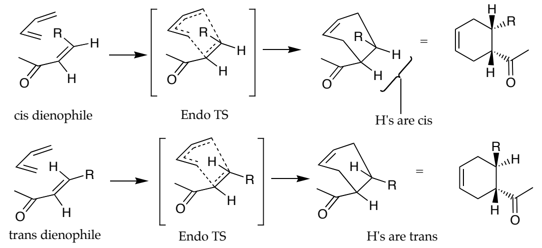
R groups are cis in the reactant

R groups are cis in the product

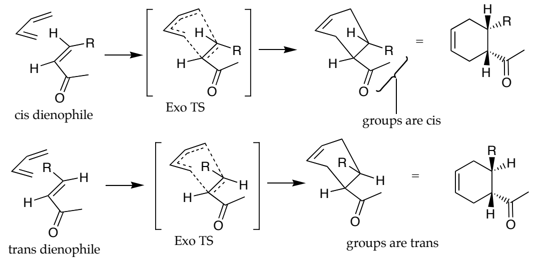
Stereochemistry of the Diels-Alder reaction:

Dienophile: Groups that are cis on the dienophile will be cis in the product; groups that are trans on the dienophile will be trans in the product.

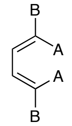
Endo:



Exo:



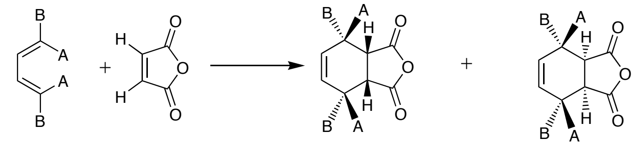
Diene:



In the s-cis conformation:

A= inner rim of diene
B= outer rim of diene

Groups on the inner rim of the diene will be cis in the product and groups on the outer rim of the diene will be cis in the product:



Endo TS

Exo TS

In the product, the groups of the dienophile that are endo in the transition state will be cis to the groups on the outer rim of the diene (in the s-cis conformation) .

Animations of the Diels-Alder Reaction:
http://www.brunel.ac.uk/depts/chem/ch241s/re_view/barry/diels2.htm

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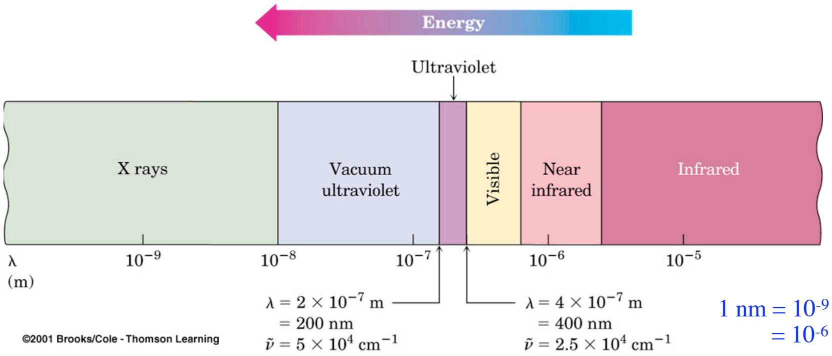
UV-Vis Spectroscopy



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1 nm = 10^{-9} m
= 10^{-6} cm

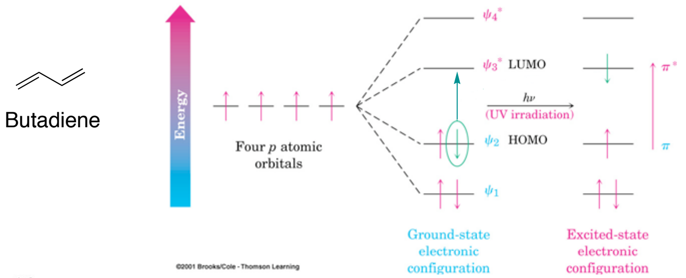
Infrared: molecular vibrations (stretches, bends)
- identify functional groups (Ch. 12)

Radiowaves: nuclear spin an a magnetic field (NMR)
- gives a H and C map of the molecule (Ch. 13)

UV-vis: valance electron transitions (Ch. 14)
- gives information about π-bonds and conjugated systems

UV-Vis light causes electrons in lower energy molecular orbitals to be promoted to higher energy molecular orbitals.

HOMO ⟶ LUMO



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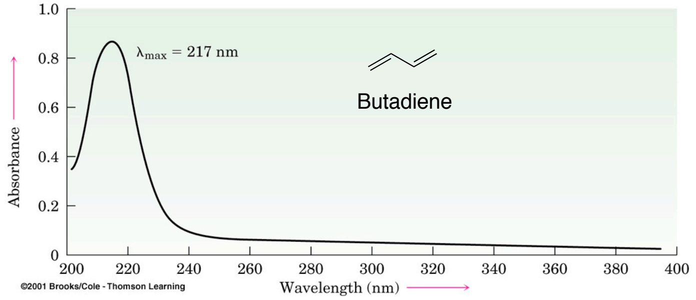

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$E = h\nu$

$\nu = c/\lambda$

$\varepsilon = \frac{h\,c}{\lambda}$

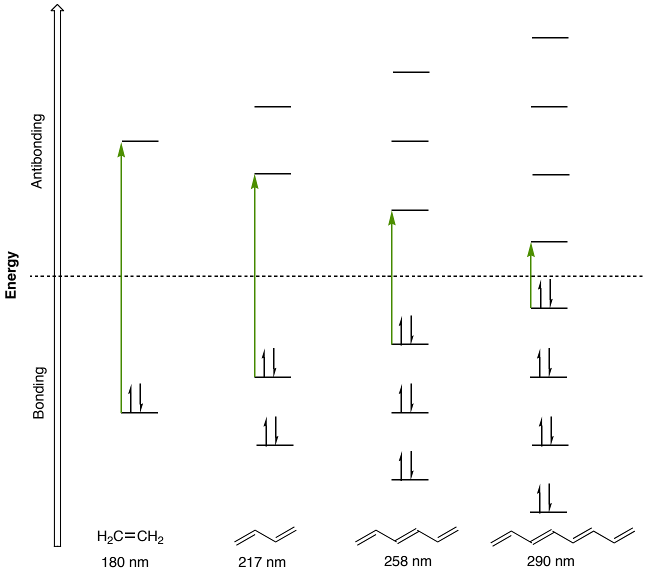
Chromophore: light absorbing portion of a molecule

Beer’s Law: $A = \varepsilon c\, l$

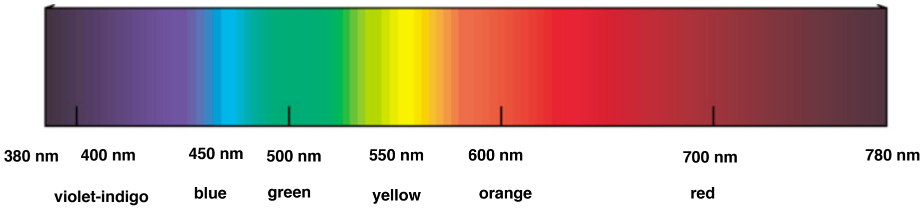
A= absorbance
c = concentration (M, mol/L)
l = sample path length (cm)
e = molar absorbtivity (extinction coefficient) a proportionality constant for a specific absorbance of a substance

Absorbance is directly proportional to concentration

Molecular orbitals of conjugated polyenes

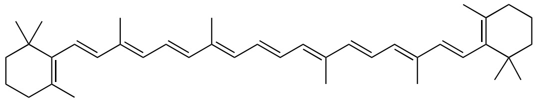


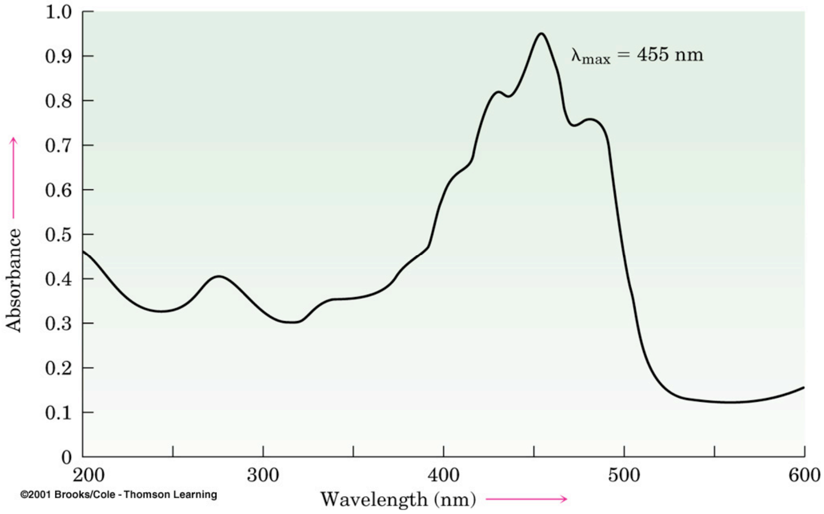
Molecules with extended conjugation move toward the visible region



Color of absorbed light	▯	Color observed
violet	400 nm	yellow
blue	450	orange
blue-green	500	red
yellow-green	530	red-violet
yellow	550	violet
orange	600	blue-green
red	700	green

□-Carotene





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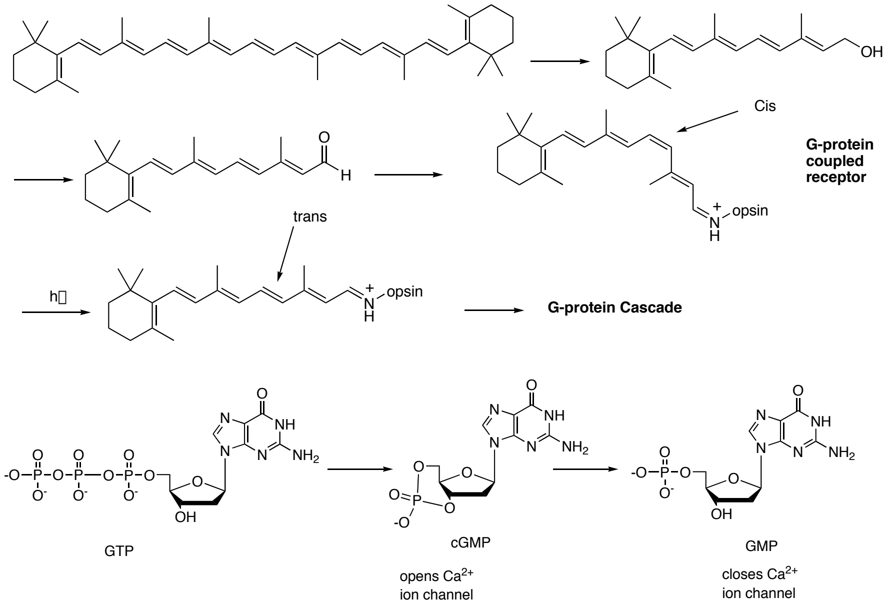
Chemistry of Vision

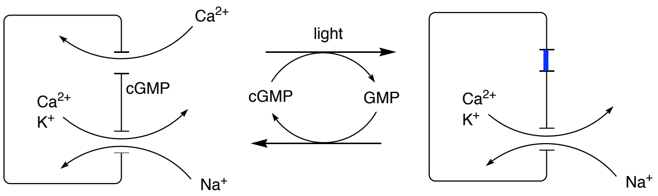


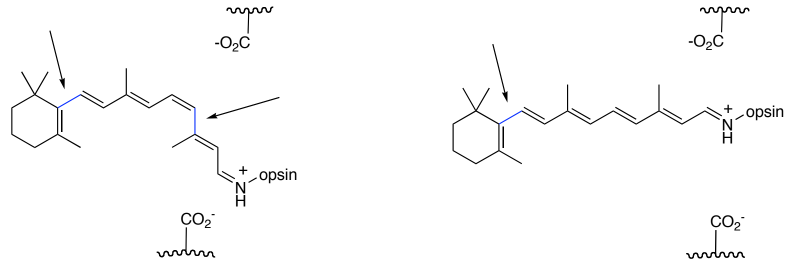
G-protein coupled receptor

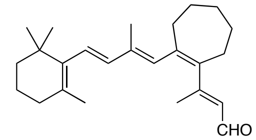
G-protein Cascade

opens Ca^{2+} ion channel

closes Ca^{2+} ion channel







ring locks double bond into the cis geometry