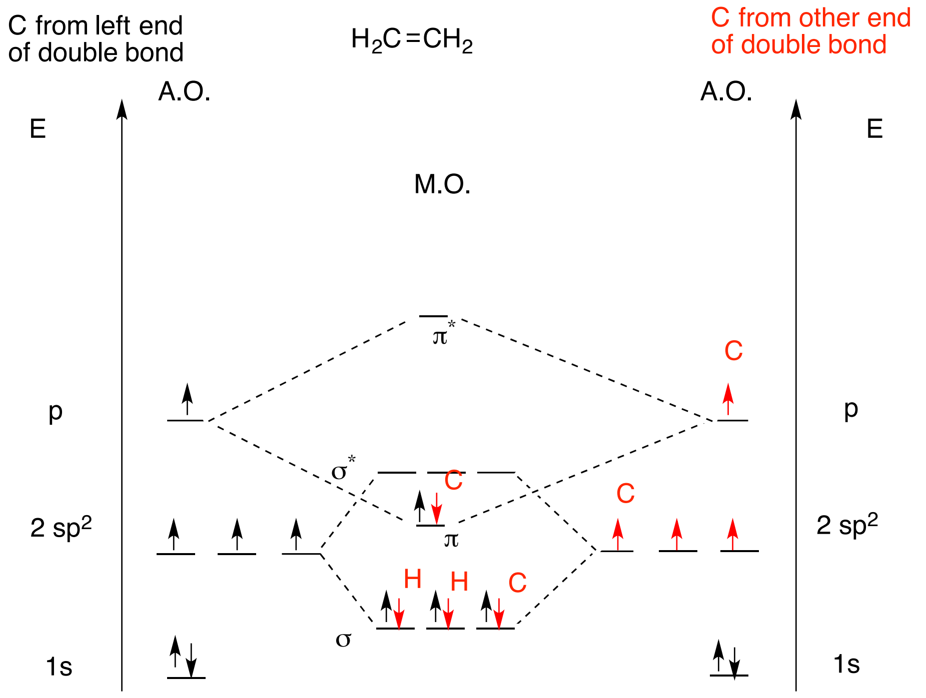
CHEM 261 Nov. 29, 2022

Conjugated Systems

Molecular Orbitals:

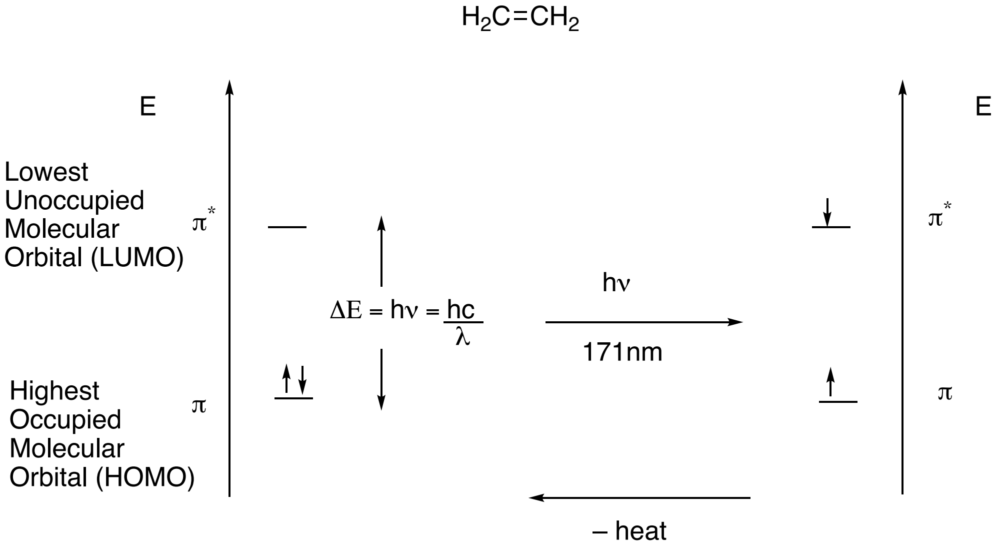
Example 1: Ethylene



Looking at both sigma and pi bonds

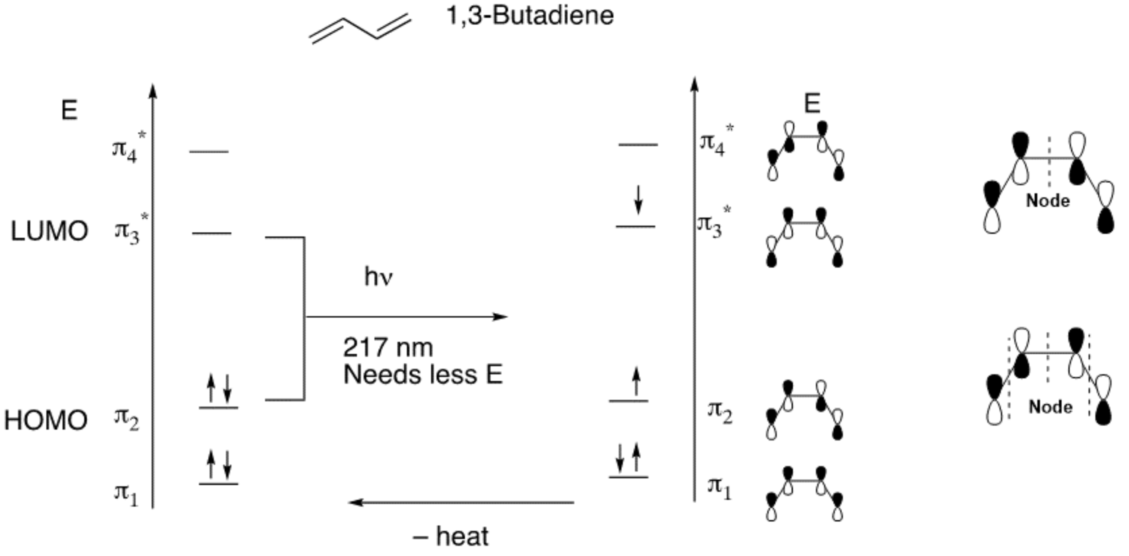
A.O. means atomic orbitals (s, sp^2, p)
M.O. means molecular orbitals (σ , π)

Looking only at the π orbitals:



An electron can be excited from the HOMO to the LUMO using light of a precise wavelength dependent on the energy difference between the two orbitals (since the orbitals are quantized). When the electron is promoted to a higher energy state (excited to a higher energy molecular orbital), it attains a **singlet state**. The electron can go back to it's original orbital and heat (or light) is produced in the process.

Example 2: 1,3-Butadiene

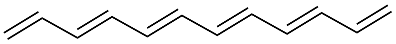


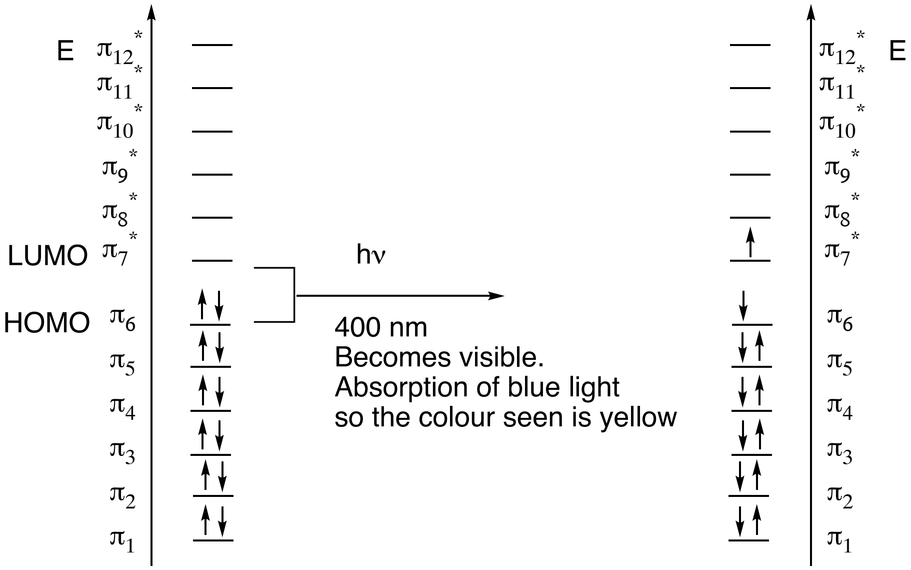
Node: a point or plane of zero electron density in an orbital
HOMO: Highest Occupied Molecular Orbital
LUMO: Lowest Unoccupied Molecular Orbital

- As the # of double bonds in the compound increases, decreasing the HUMO-LUMO gap, the energy of the light needed to excite the compound to its excited state is lower.

- Once the absorption of light leaves the UV range and into the visible range, the transition becomes visible and the colour of the compound can be seen.

Example 3: 1,3,5,7,9,11-dodecahexaene

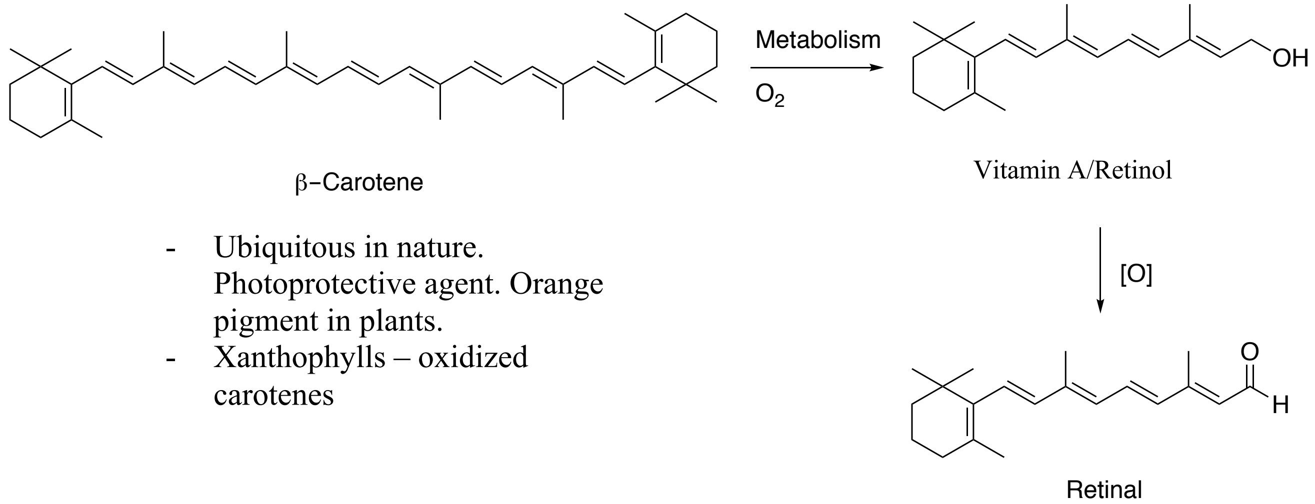




400 nm
Becomes visible.
Absorption of blue light
so the colour seen is yellow

- More energy levels result in decreased ΔE between the HOMO-LUMO gap.
- Any molecule with >6 conjugated double bonds would absorb light in the visible region (400 to 800 nm); hence, these molecules would be colored.

Conjugated molecules in vision:



β−Carotene

Vitamin A/Retinol

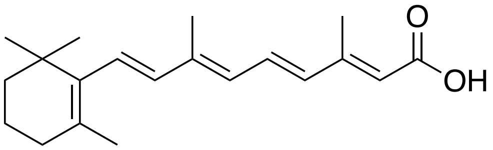
Retinal

- Ubiquitous in nature. Photoprotective agent. Orange pigment in plants.
- Xanthophylls – oxidized carotenes

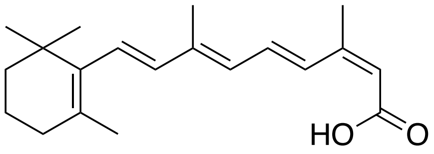
Retinal is combined with the **protein opsin** in the eye to make **rhodopsin**, which is a key protein in the mechanism of sight.

Human vision covers the range of 400 nm (4000 Å) to 800 nm (8000 Å), anything outside of these wavelengths is invisible to the naked eye.

The further oxidized form of retinal is retinoic acid – directing agent during embryogenesis. Changing the double bond bearing the carboxylic acid from trans to cis gives the drug Accutane, used to treat acne. (can cause birth defects = teratogen)



Retinoic acid



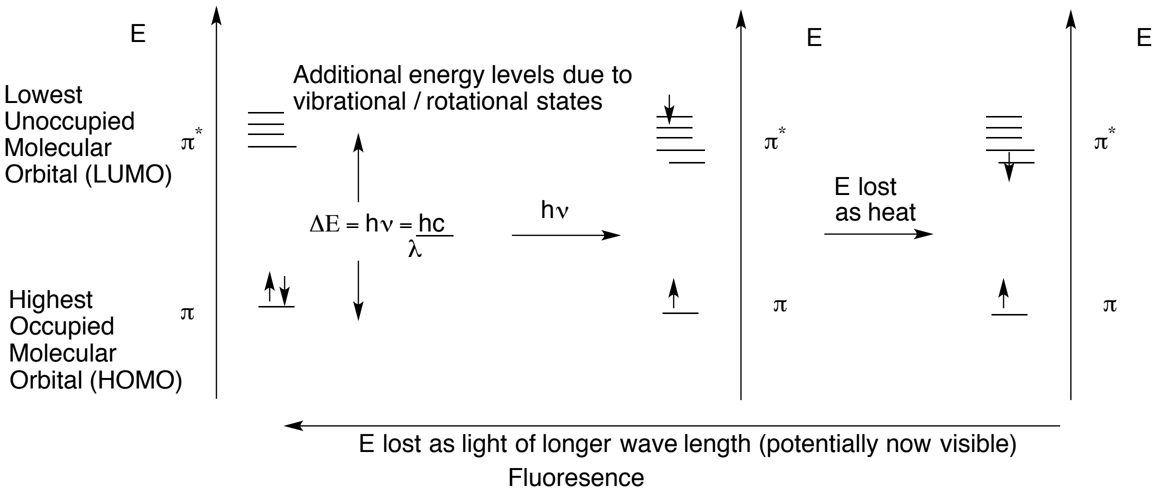
Accutane

Light Emission **Below NOT COVERED IN THIS COURSE for information only**

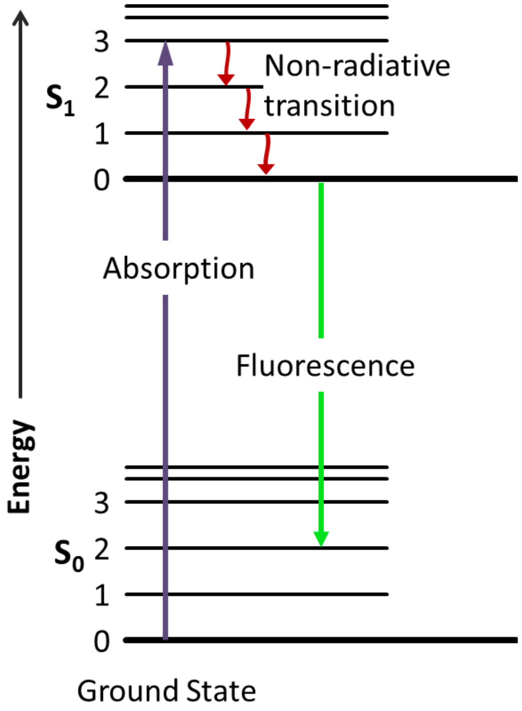
1) Fluorescence
- Absorb UV and emit either UV or Visible
- Short life (singlet state – electrons paired)

2) Phosphorescence
- Absorb UV and emit Visible
- Long life (triplet state – electrons not paired)

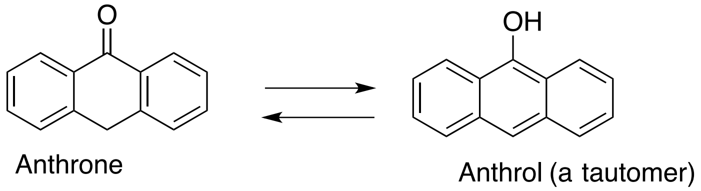
3) Chemiluminescence
- Reactions that produce light



Another diagram (from Wikipedia) depicting the same idea with additional vibrational energy states is shown below

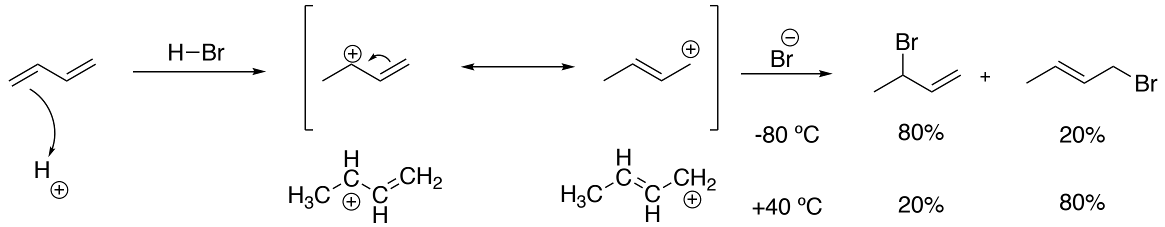


Many commercial clothes detergents contain fluorescent dyes. These absorb in UV and emit in blue, thereby making colours appear brighter and whites appear white. Some are anthrone / anthrol or derivatives. The two compounds are tautomers (rapidly interconverting structural isomers)



Above material on Fluorescence and Phosphorescence not covered in this course

Thermodynamic vs. Kinetic Products: Reaction of Dienes



The two possible products are structural isomers.

The product 3-bromobutene is a **1,2-addition** product, whereas 1-bromo-2-butene is the product of a **1,4-addition** reaction. The numbers (**1,2-** or **1,4-**) indicate the position where the H and Br added to the 1,3-butadiene.

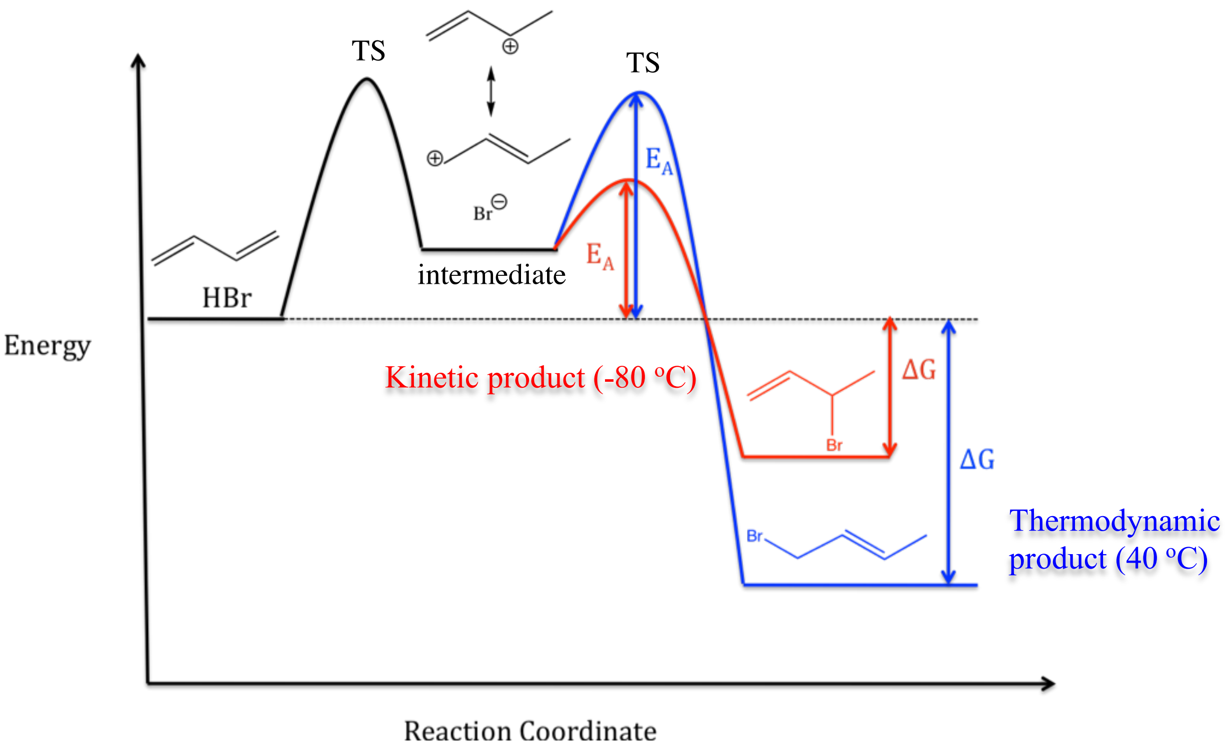
From the 2 resonance forms (connected by the double-headed arrow) of the allylic cation in the above figure, we see that the positive charge is shared between the C2 and C4.

Note: The allylic cation has two electrons delocalized across the three carbons. It was drawn to have two resonance forms, but it is a ***single entity***. Neither resonance form depicts the actual structure, but rather the molecule exists as a combination of the two resonance forms. The 'primary carbocation' is stabilized, as it is allylic.

Why does the temperature affect the ratio obtained?

- 3-bromo-1-butene has a higher yield at the lower temperature because it is formed faster than 1-bromo-2-butene due to it's lower E_a: **kinetic control**
- 3-bromo-1-butene has lower yield than 1-bromo-2-butene at higher temperature due to **thermodynamic control**. The addition of bromine to the allylic cation is reversible at high temperature. 3-Bromo-1-butene can be converted back to the allylic cation, and then form 1-bromo-2-butene which is the thermodynamically more favoured product as it is more stable. The thermodynamic product is determined by the equilibrium result controlled by ΔG.

Now let’s look at the energy diagram of the HBr addition to butadiene reaction



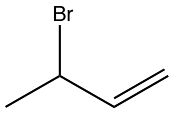
The activation energy barrier to form the 1,2-product, 3-bromo-1-butene is much *smaller* than the 1,4-product, 1-bromo-2-butene (so that it can be formed easier and **faster**. We call this **kinetically favored**).

However, the energy of 1-bromo-2-butene is lower than 3-bromo-1-butene, so that it is more **stable** than 3-bromo-1-butene (it is **thermodynamically favored**).

Kinetic control: governed by the activation energy (Ea)
Thermodynamic control: you get an equilibrium mixture. Governed by ΔG.

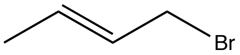
Why is 1-bromo-2-butene more stable?

- The bromine atom is bulky. It likes to stay away from the rest of the molecule to avoid steric clashes.
- Alkene carbons are somewhat electron deficient. More highly substituted alkenes are more stable due to donation of electron density by the substituents (C vs. H)



1,2-addition

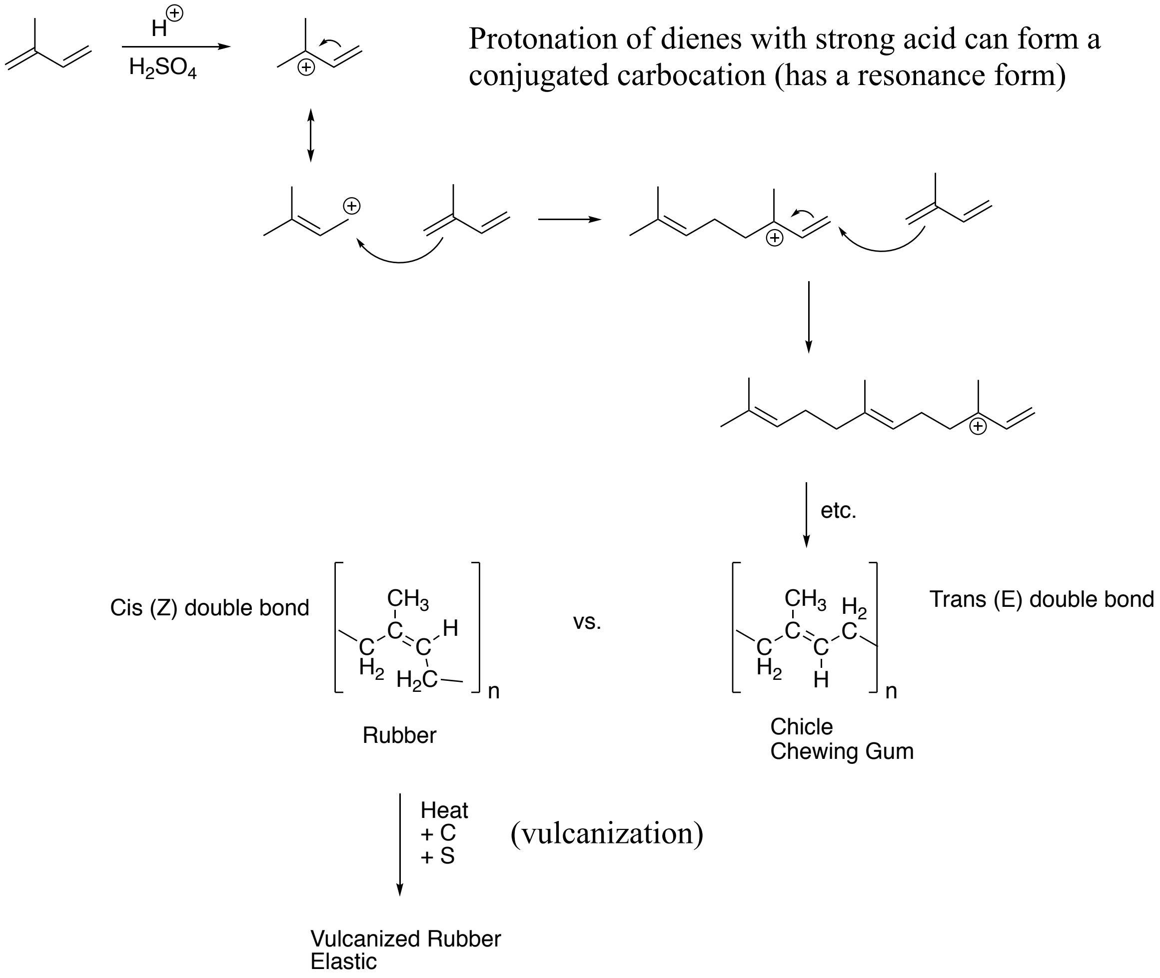
monosubstituted C=C



1,4-addition

disubstituted C=C

Polymerization: If no nucleophile is present in previous addition reaction - e.g. isoprene

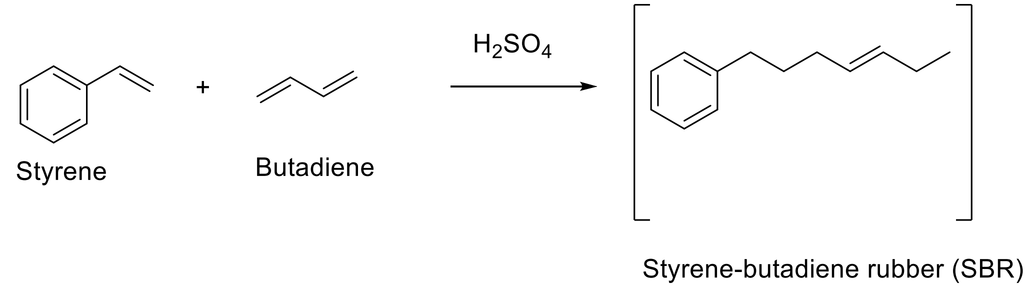


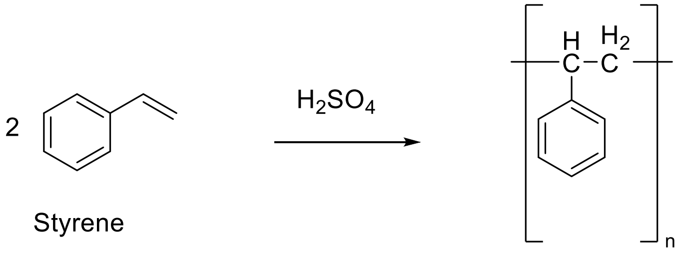
Protonation of dienes with strong acid can form a conjugated carbocation (has a resonance form)

- Rubber tree (*Hivea brasiliensis*) produces approximately 2000 lbs/acre of rubber.

More examples:

Co-polymerization





Polystyrene