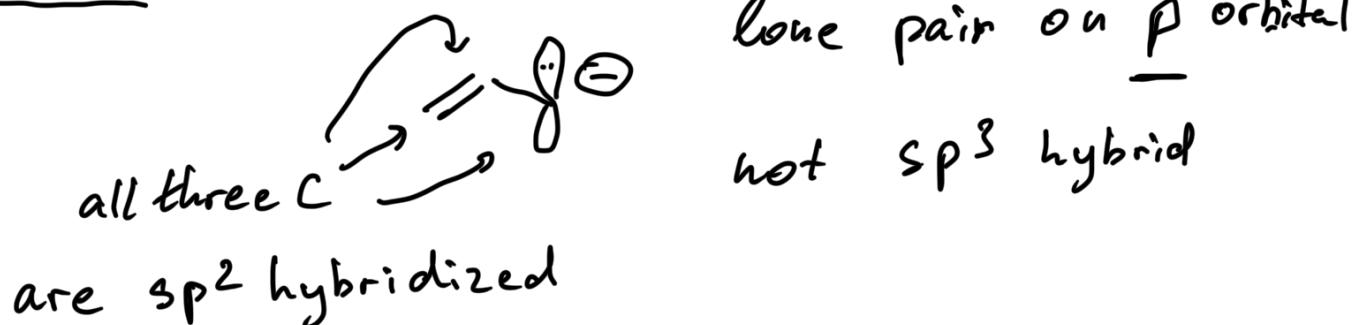
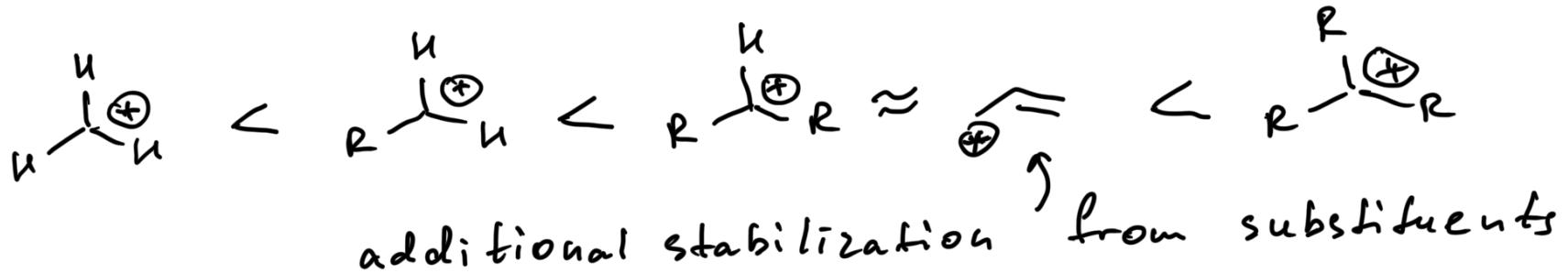


# Resonance: drawing resonance forms

Stability of allylic cations



are  $sp^2$  hybridized

# Resonance: drawing resonance forms

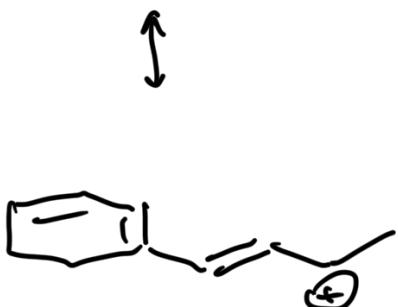
Stability of allylic cations



charge distributed  
between C1 & C3



resonance hybrid



arrow-pushing tells  
you about location of  $\oplus$

# Resonance: examples

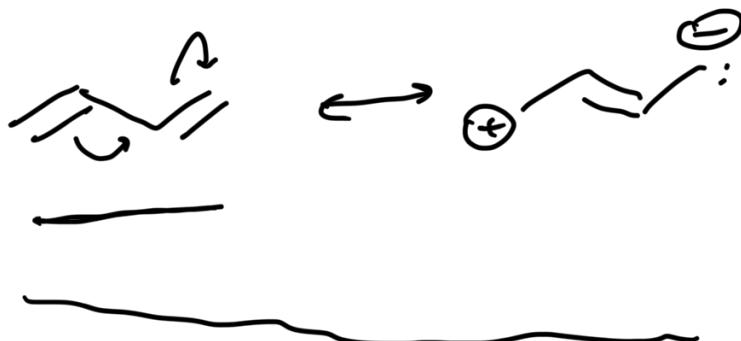
Choosing the most contributing resonance structure

- allyl systems



⊖ charge on more e⁻-negative atom

- conjugated multiple bonds



less charges  
w/ more bonds  
is better

# Resonance: examples

Choosing the most contributing resonance structure

- lone pair next to carbocation

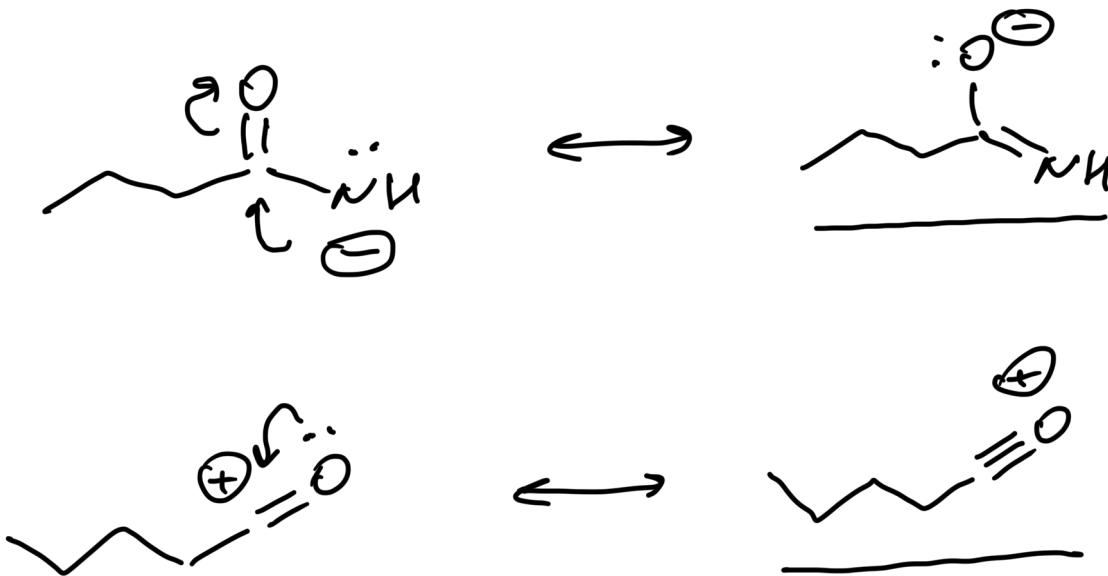


- double bonds w/ atoms of different  $\bar{\epsilon}$ -negativity



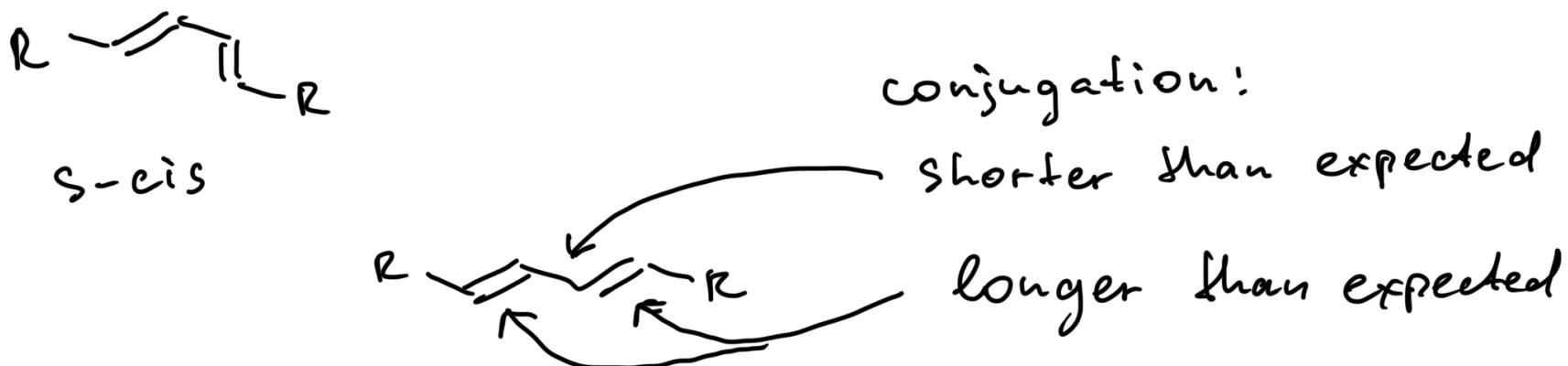
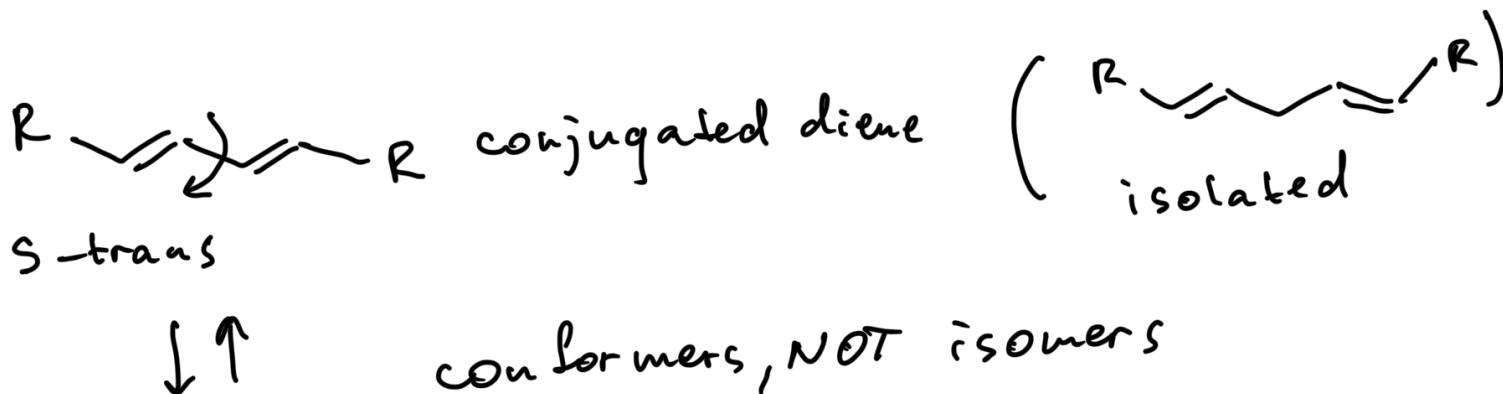
# Resonance: examples

Choosing the most contributing resonance structure



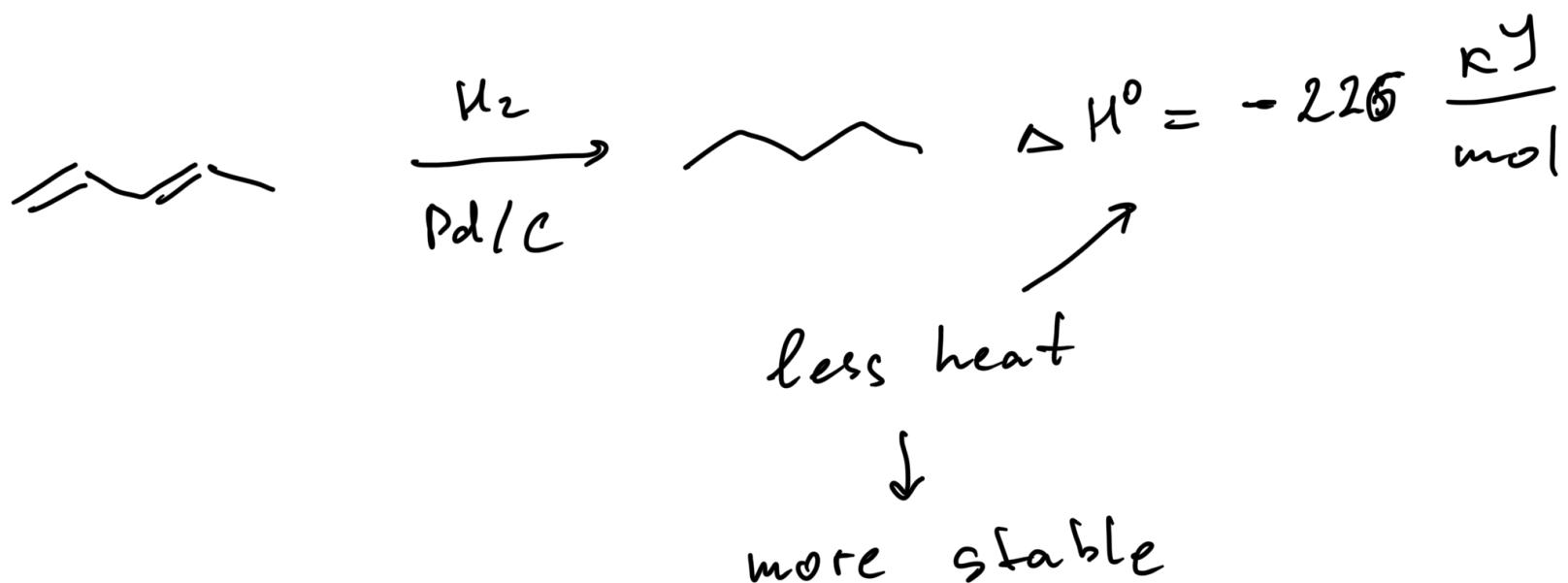
# Conjugated dienes

Structure, conformation, and stability



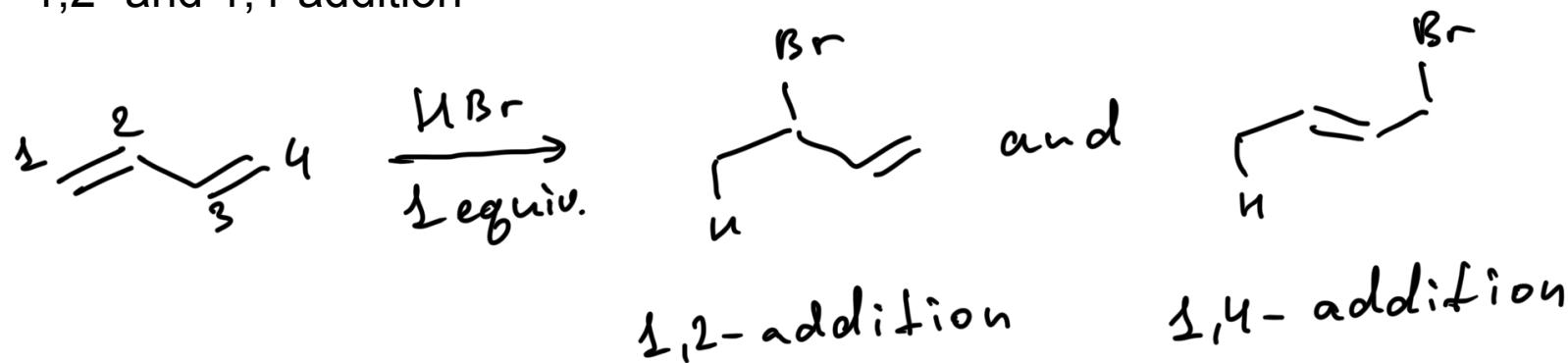
# Conjugated dienes

Structure, conformation, and stability

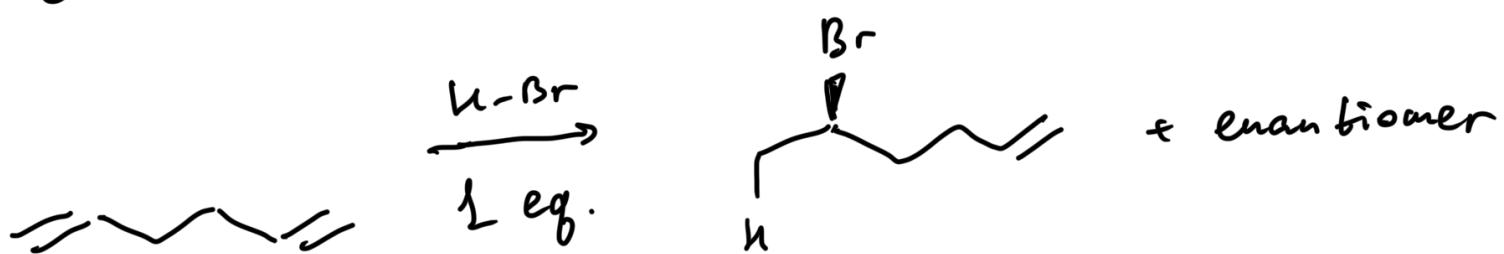


# Conjugated dienes: electrophilic addition

1,2- and 1,4-addition

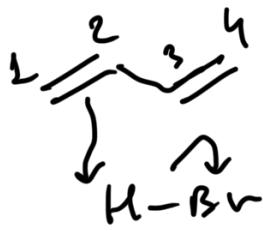


Compare :



# Conjugated dienes: electrophilic addition

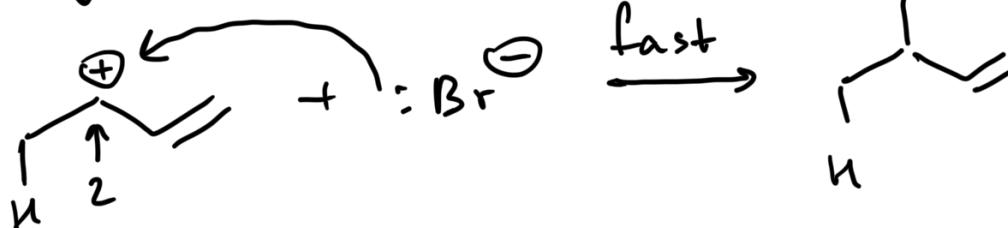
Mechanism. Kinetic and thermodynamic products



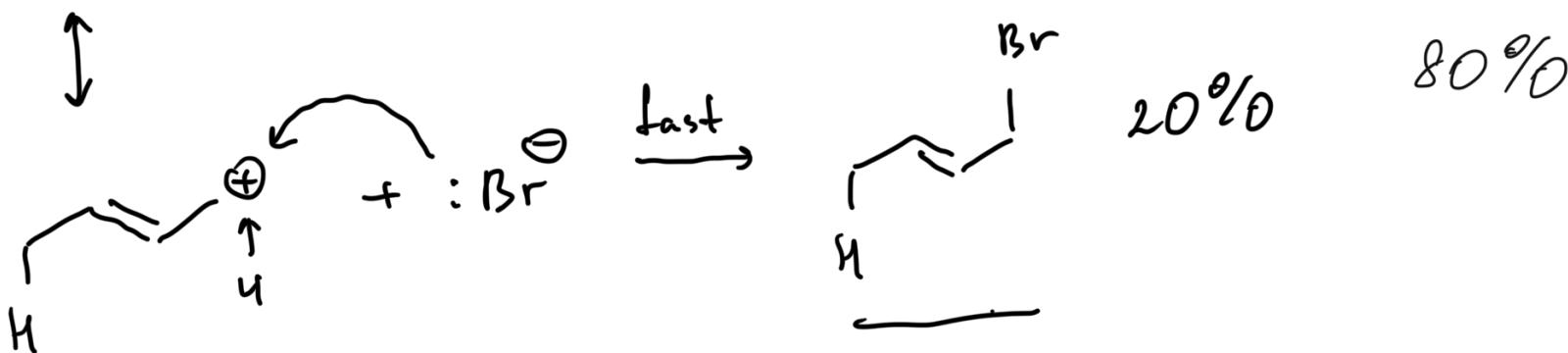
- $\therefore \text{Br}^-$  formed closer to C2  
proximity effect

- 1,4-addition product is more stable

↓ slow



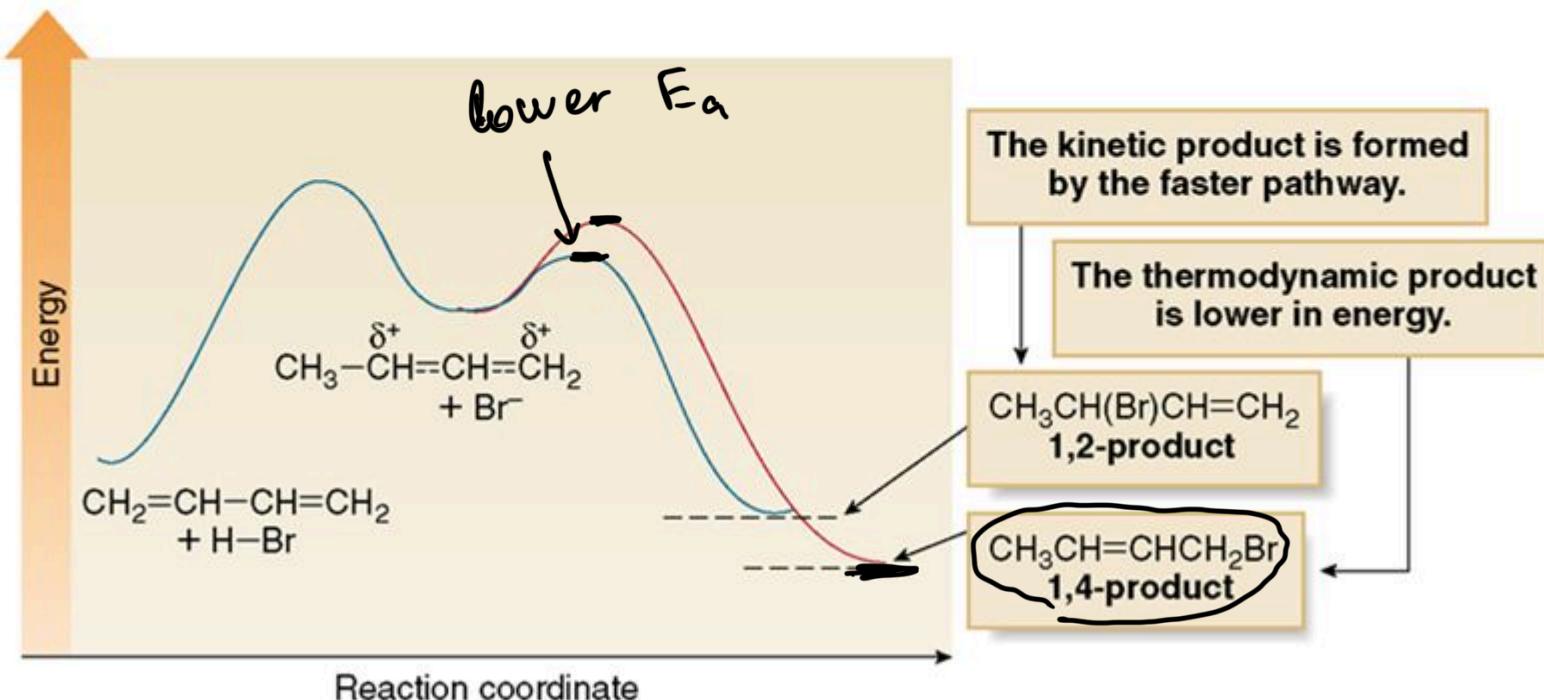
↔



# Conjugated dienes: electrophilic addition

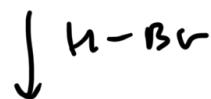
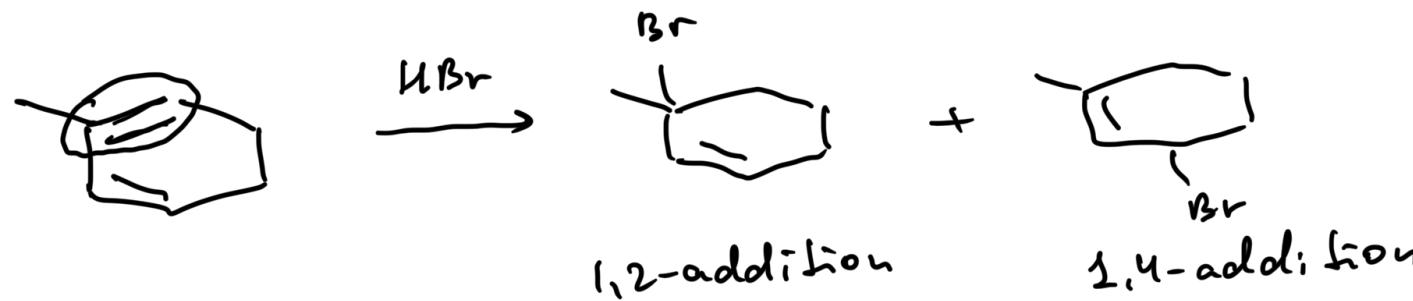
Mechanism. Kinetic and thermodynamic products

lower  $E_a$  for 1,2-addition  $\rightarrow$  kinetic product  
more stable 1,4-addition product  $\rightarrow$  thermodynamic  
equilibrium: 1,2-addition  $\rightleftharpoons$  1,4-addition



# Conjugated dienes: electrophilic addition

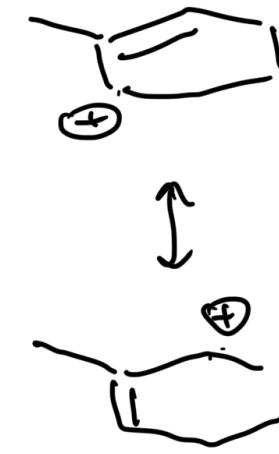
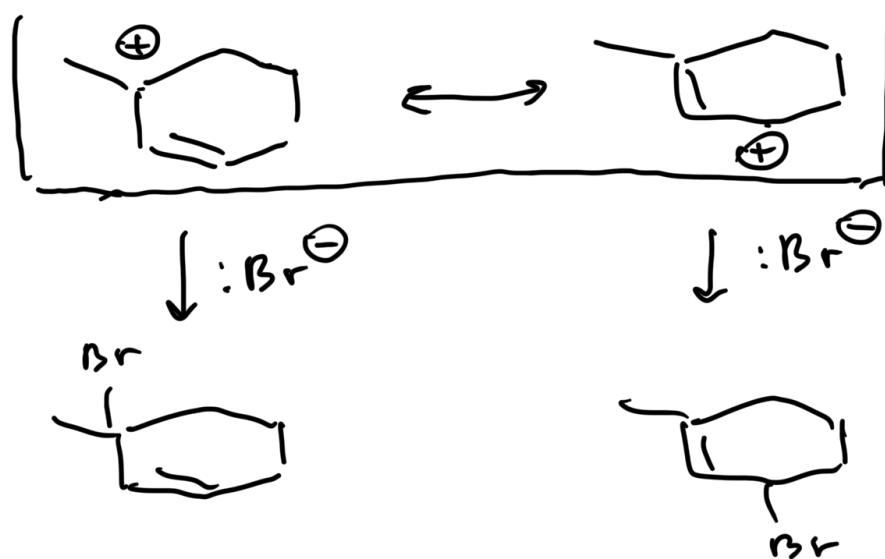
Example of hydrobromination of an unsymmetrical conjugated diene



1,2-addition

1,4-addition

cf. :



# **Conjugated dienes: the Diels-Alder reaction**

Diene and dienophile. Mechanism. Thermodynamics

# **Conjugated dienes: the Diels-Alder reaction**

Stereospecificity

# **Conjugated dienes: the Diels-Alder reaction**

Stereoselectivity. Alder's endo rule