Chapter 16 Kline – Conjugated Systems
- Conjugate addition
- Diels-Alder
- Pericyclic Reactions

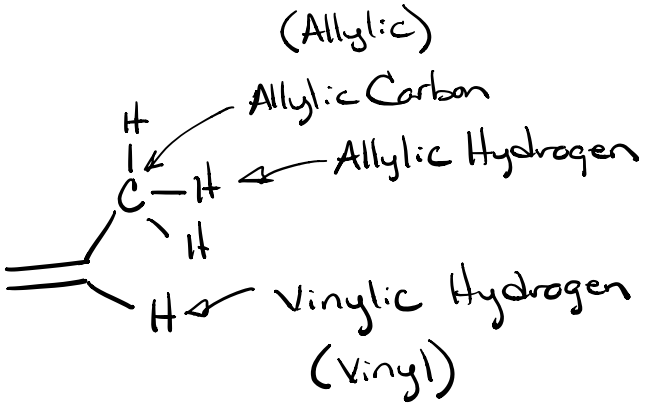
Covered

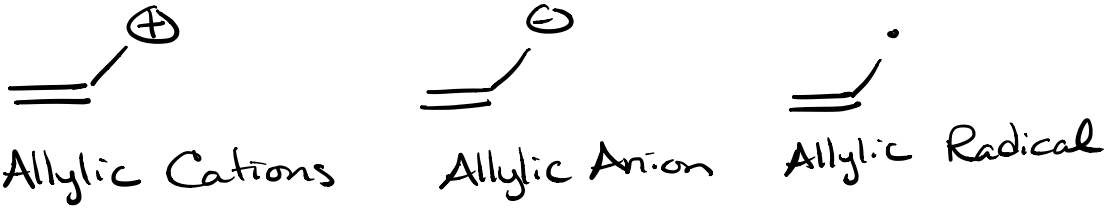
Chapter 17 – Aromaticity

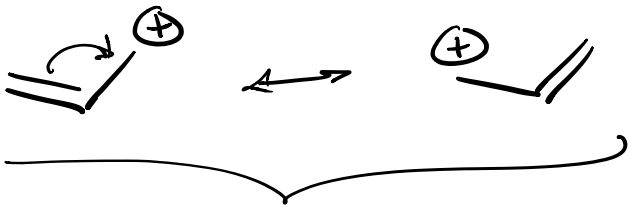
Chapter 18 – Electrophilic & ~~Nucleophilic~~ Skip
Aromatic Substitution

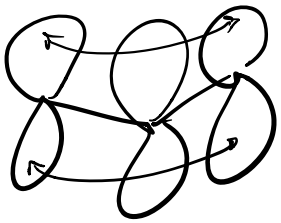
Chapter 19 – Aldehydes & Ketones

Conjugated Systems

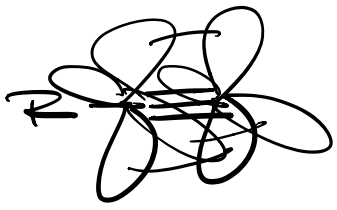


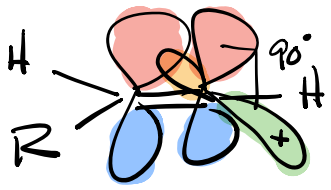


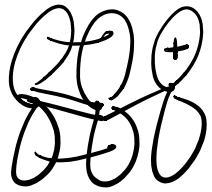




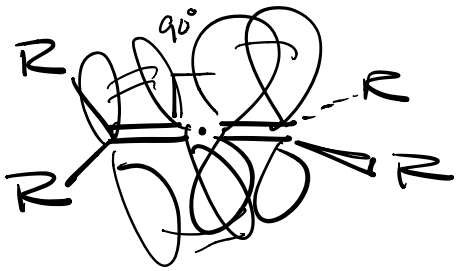
Conjugated Systems



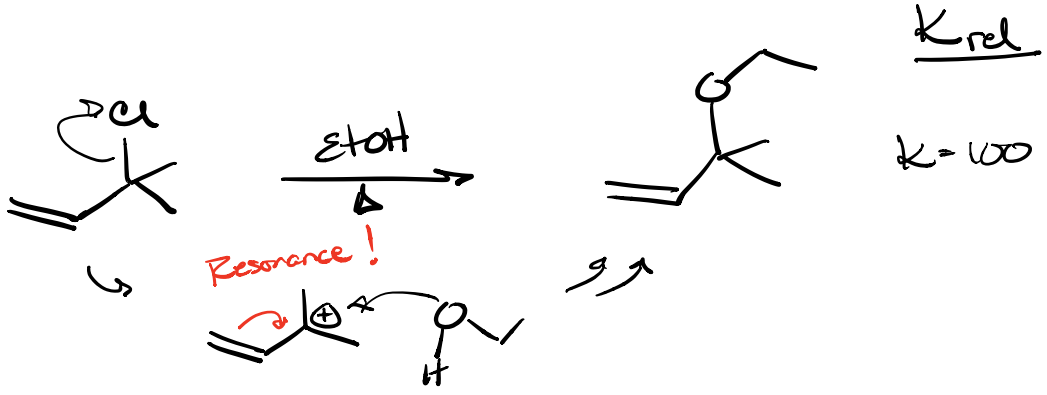


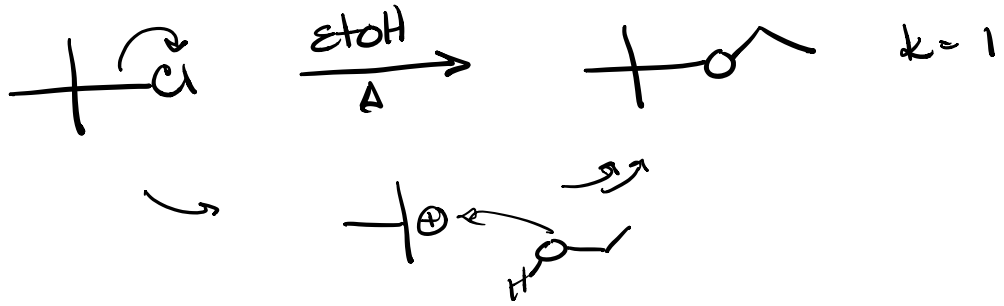


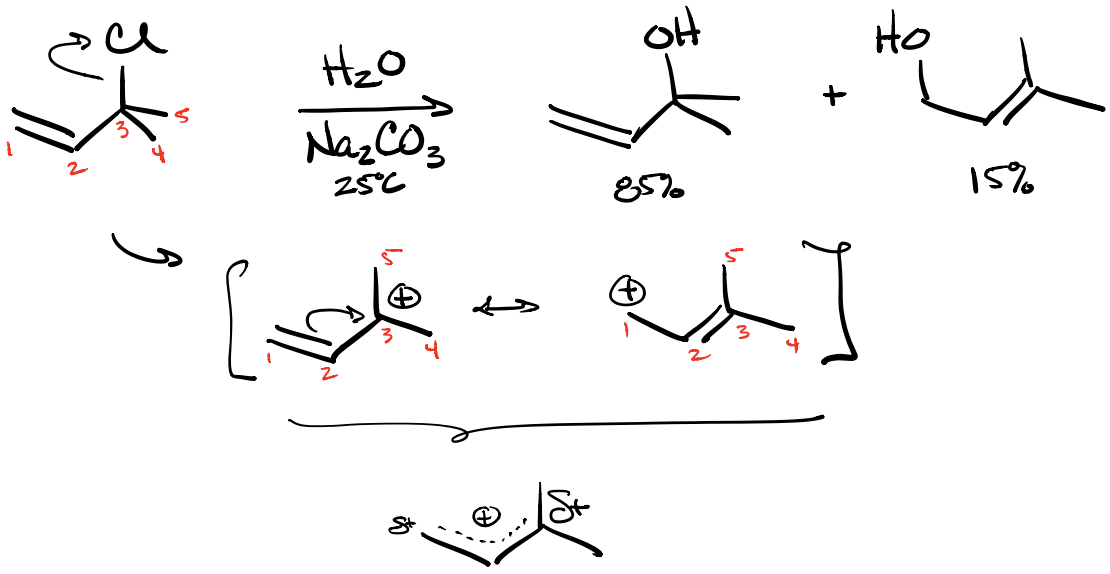
Allylic Cation
orbitals Coplaner

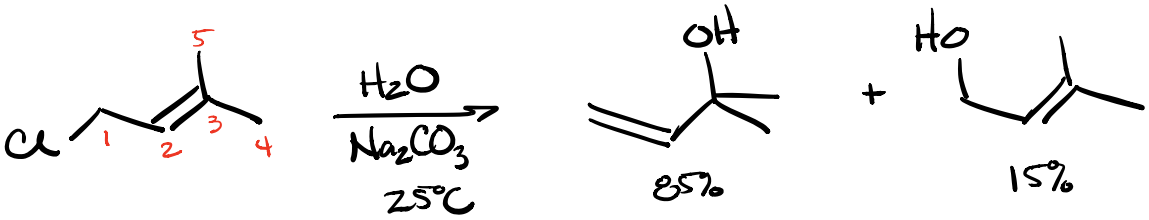


Solvolysis Rxns S_N1 Resonance > Induction



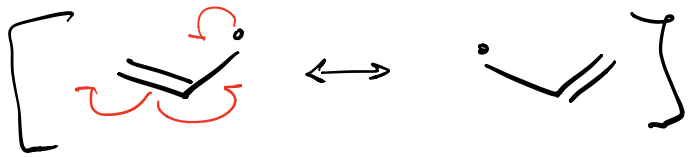


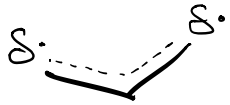


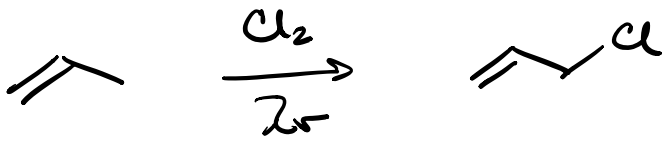


⇒ Same Carbocation

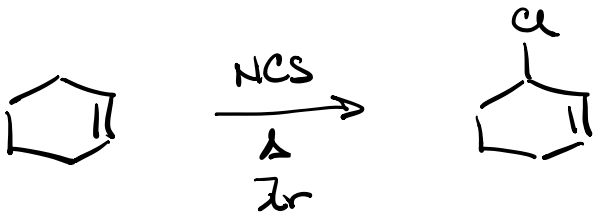
Remember that free radical stability closely follows carbocation stability

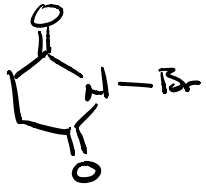


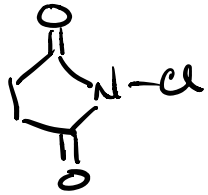




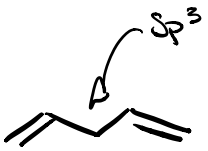
Allylic Chlorination



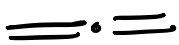
NBS 

NCS 

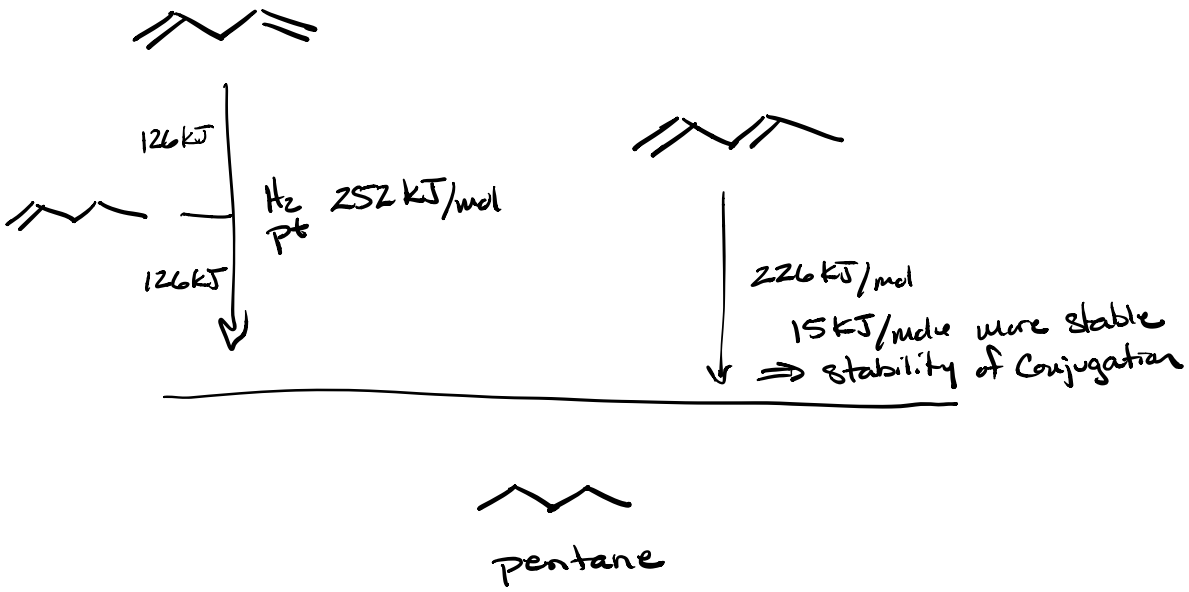
Dienes

Isolated 

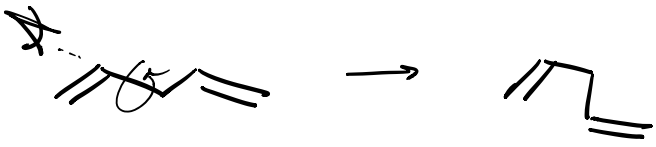
Conjugate  all sp^2

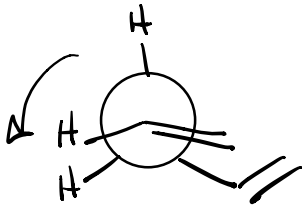
Cummulate  (allenes)

Conjugated more stable than isolated

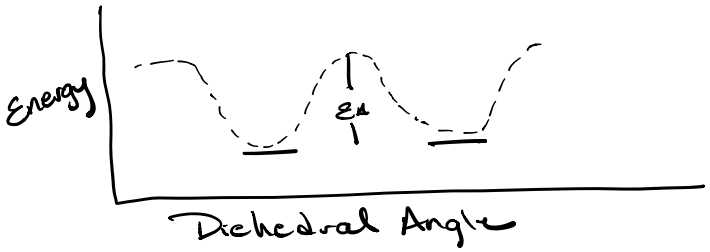


Isolated System





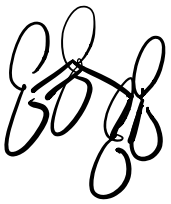
Some small energy barrier due to Sterics



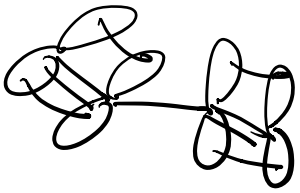
Conjugated System

Much higher energy barrier to rotation

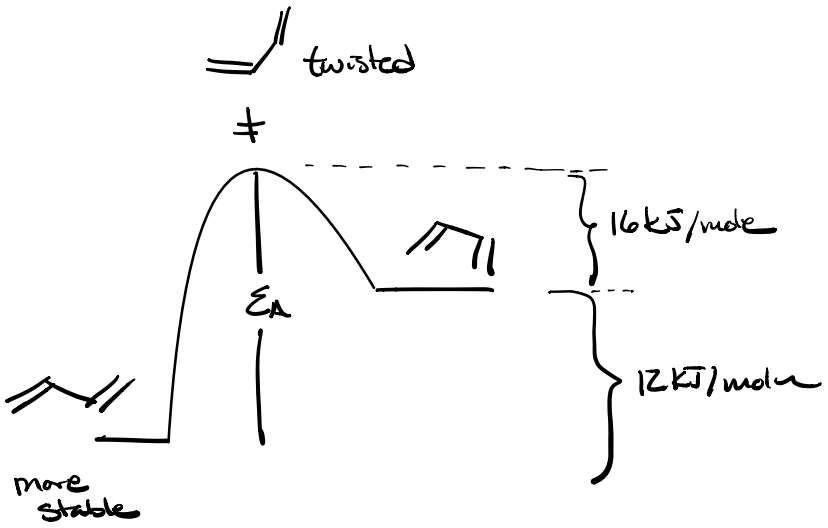
Pseudo trans

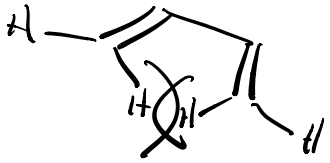


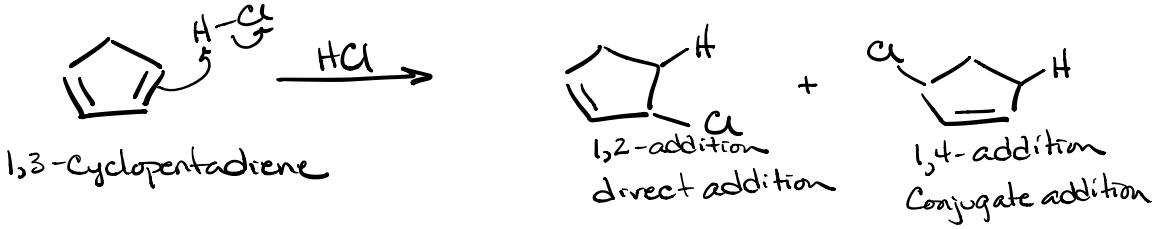
Pseudo Cis

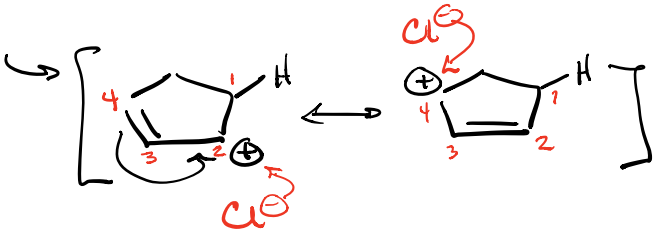


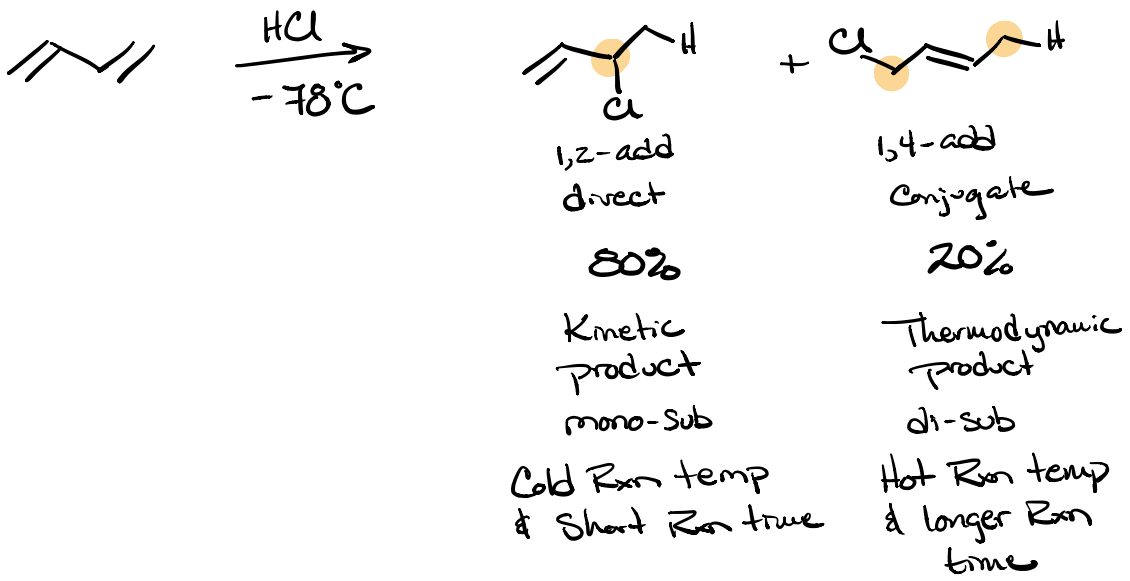
Must go through an isolated System to rotate

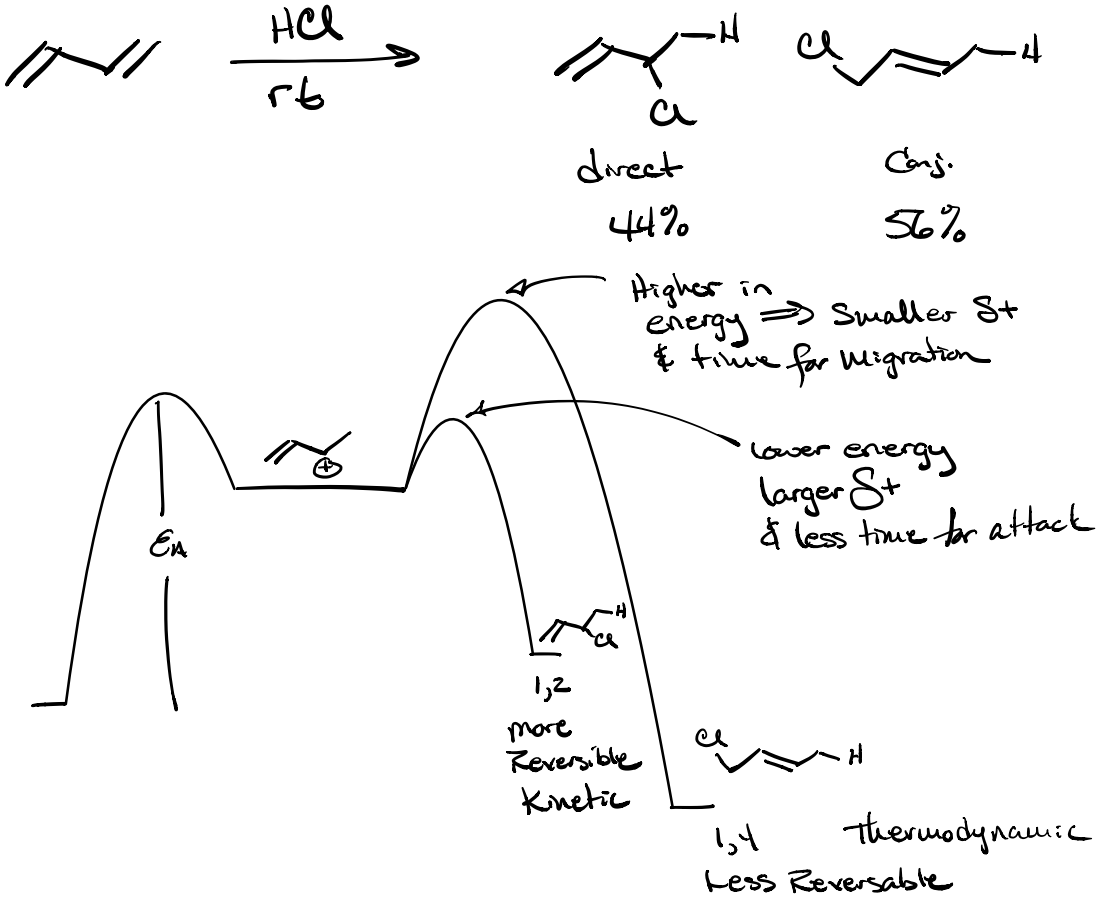

twisted
‡
16kJ/mole
E_A
12kJ/mole
more stable

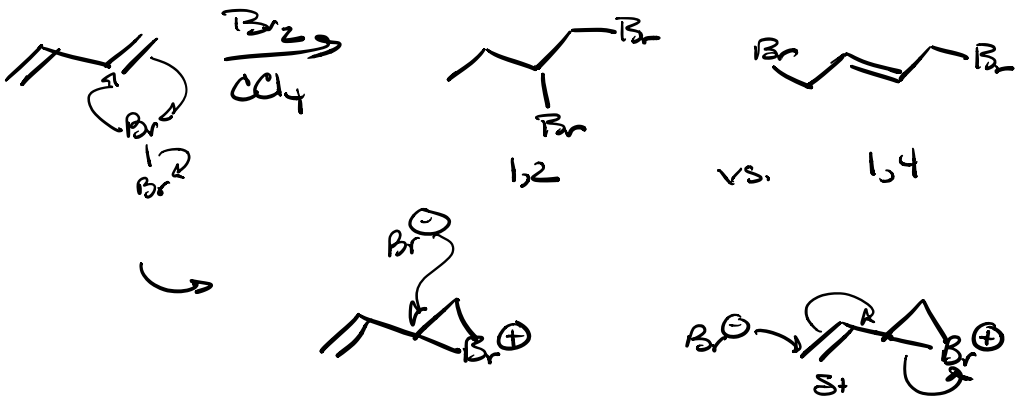



HCl
1,3-Cyclopentadiene
1,2-addition
direct addition
+
1,4-addition
Conjugate addition

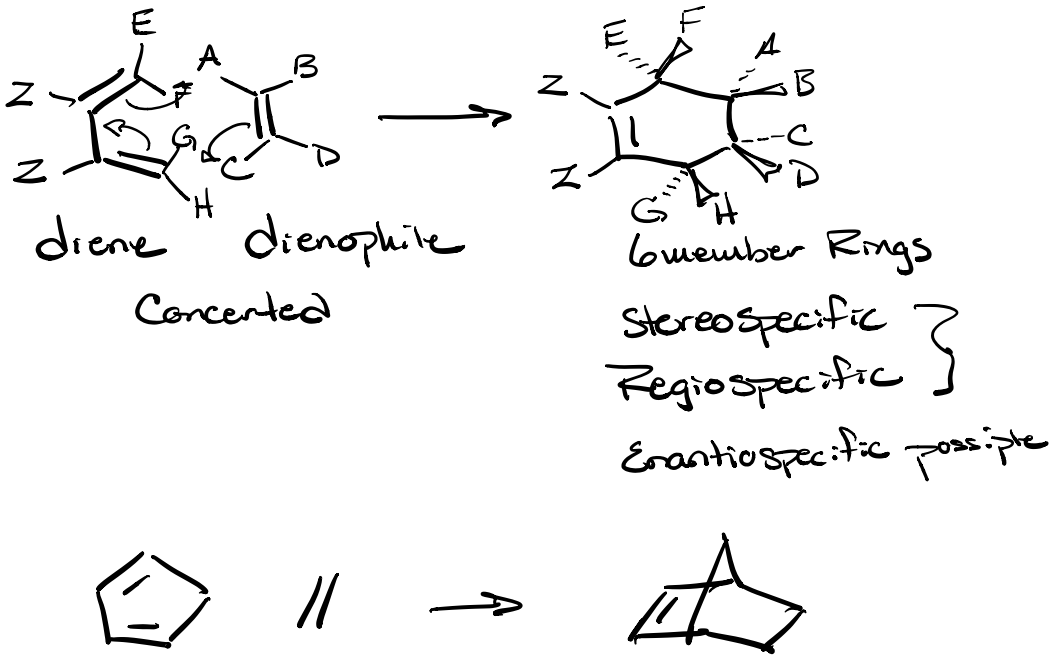



HCl
-78°C
1,2-add
direct
80%
Kinetic
product
mono-sub
Cold Rxn temp
& Short Rxn time
1,4-add
Conjugate
20%
Thermodynamic
Product
di-sub
Hot Rxn temp
& longer Rxn
time


HCl
rt
direct
44%
Conj.
56%
Higher in
energy ⇒ Smaller S+
& time for migration
lower energy
larger S+
& less time for attack
E_A
1,2
more
Reversible
Kinetic
1,4
Less Reversable
Thermodynamic


Br2
CCl4
1,2
vs.
1,4

Diels-Alder


diene
dienophile
Concerted
6 member Rings
Stereospecific
Regiospecific
Enantiospecific possible