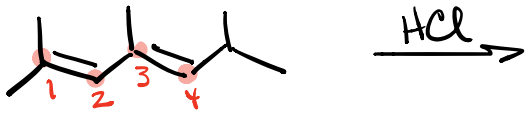
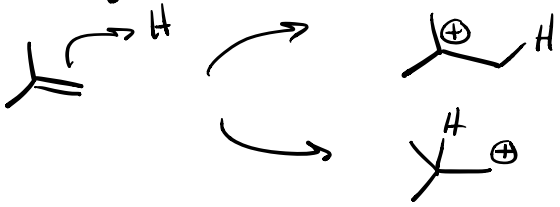
major product

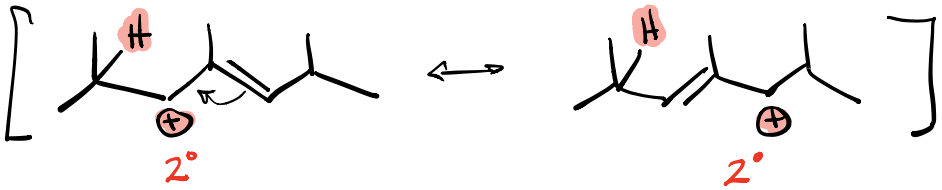


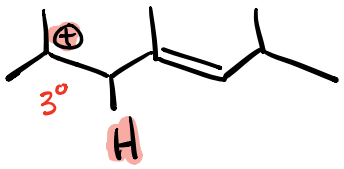
① How many locations can the H^+ add?



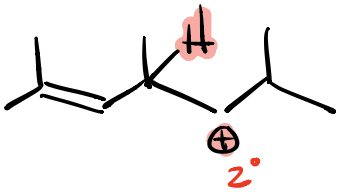
= 4 locations

② Draw each resulting cation from all 4 additions

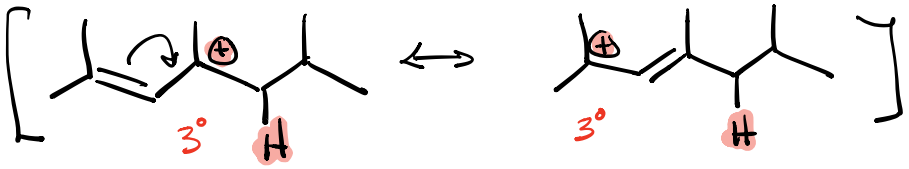
① 

② 

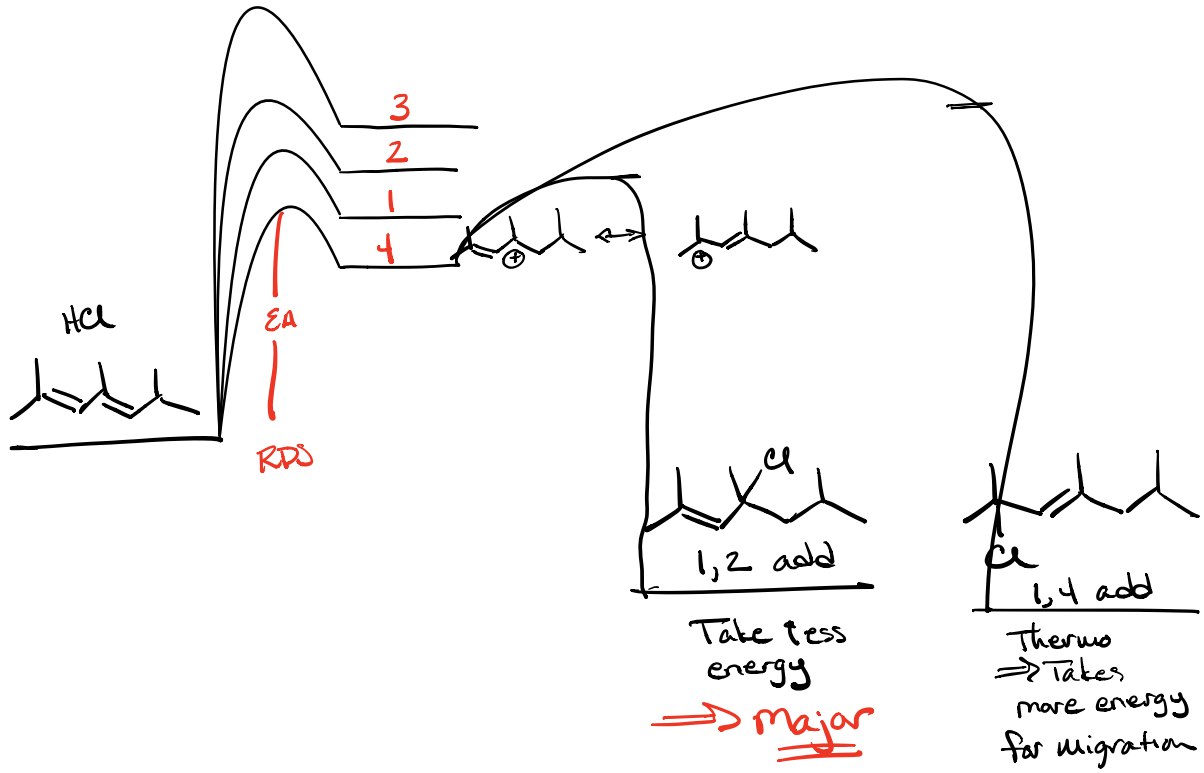
No Resonance Isolated

③ 

No Resonance Isolated

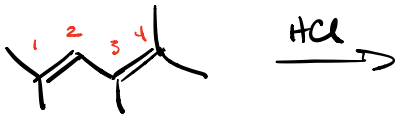
④ 

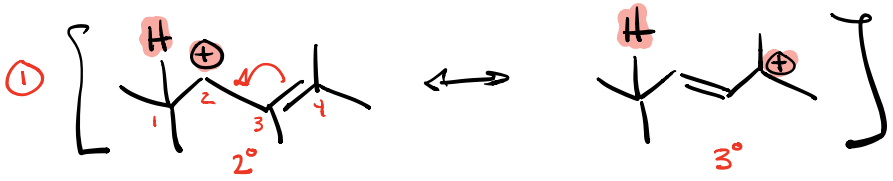
most stable

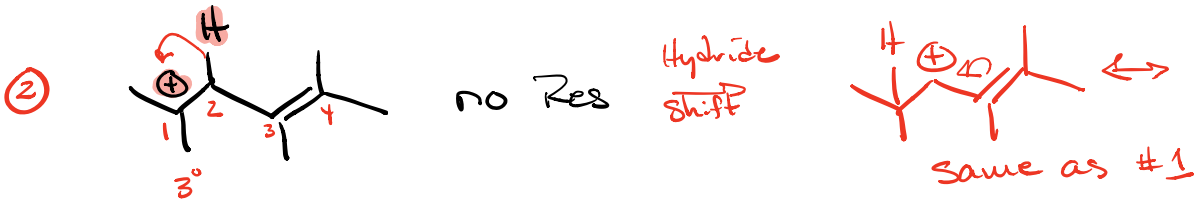


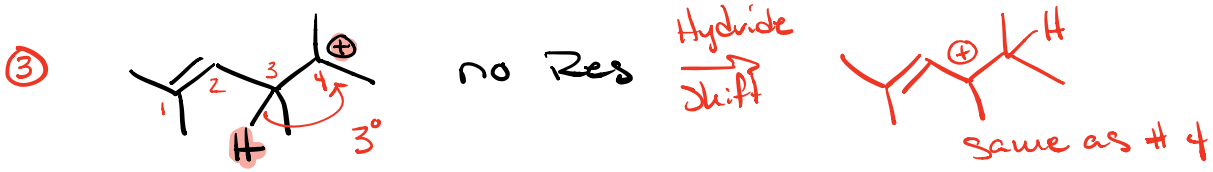
① Substitution of double bond
⇒ more substituted = more stable

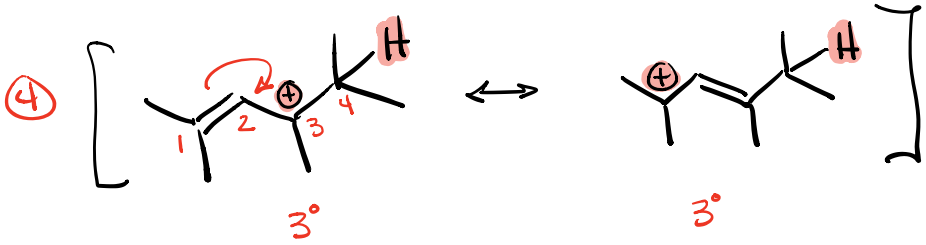
② Direct (1,2-add) vs. Conjugate (1,4-add)
⇒ 1,2 - requires less energy for addition
⇒ 1,4 - requires more energy to allow for migration of the nucleophile.


1
2
3
4
HCl

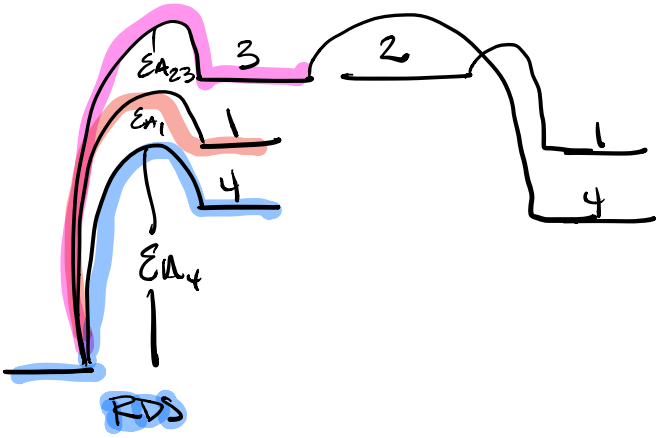

①
H
1
2
3
4
2°
3°

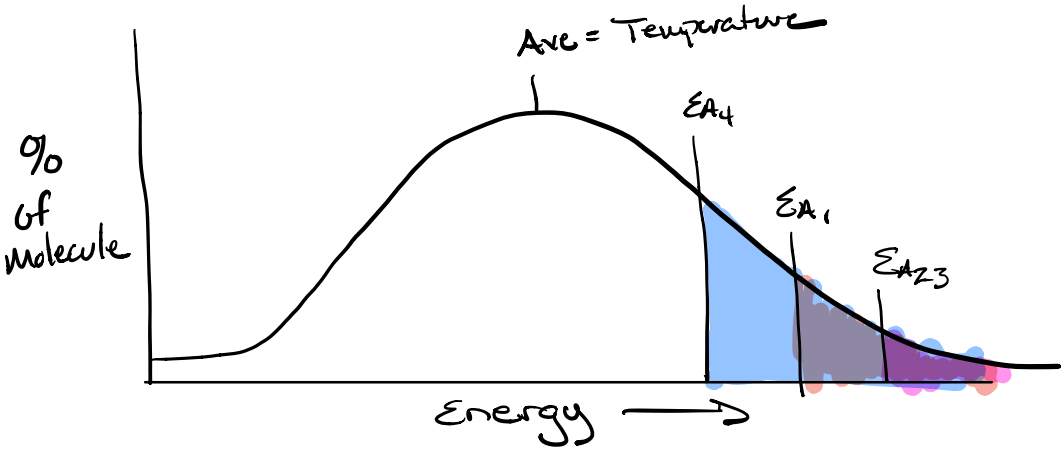

②
H
1
2
3
4
3°
no Res
Hydride
Shift
H
same as #1

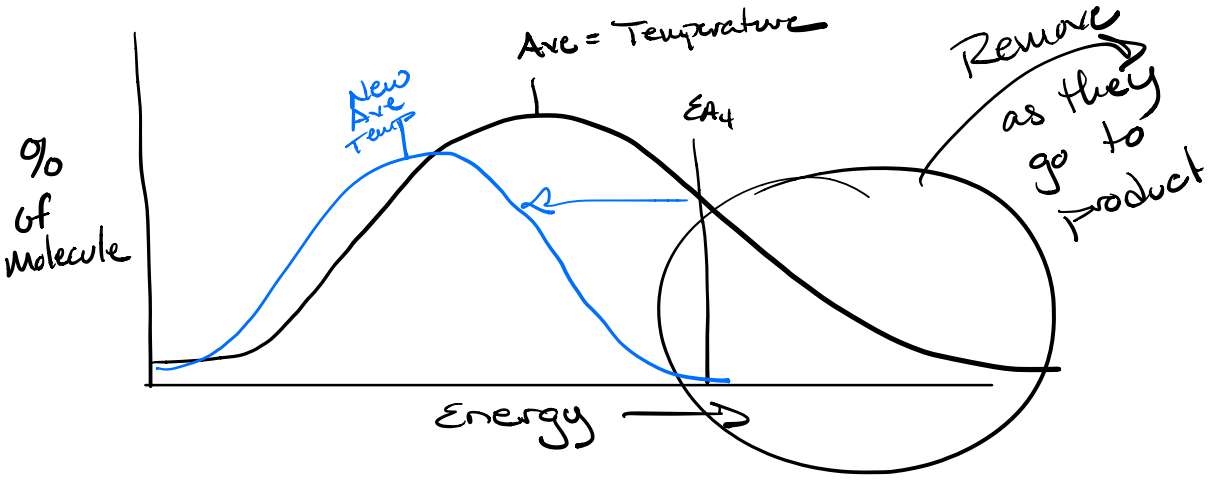

③
1
2
3
4
H
3°
no Res
Hydride
Shift
H
same as # 4


④
H
1
2
3
4
3°
3°

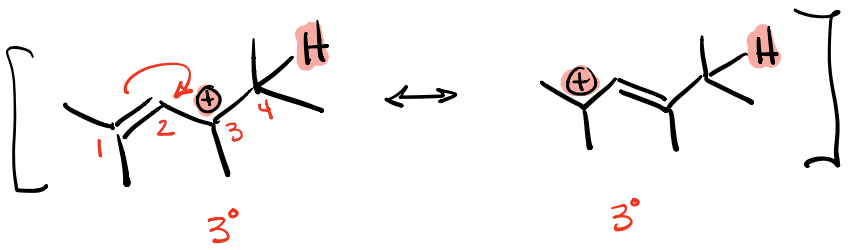
4 > 1 > 2 ≈ 3


$E_{A_{23}}$
3
2
E_{A_1}
1
1
4
4
E_{A_4}
RDS

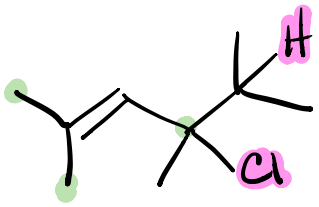

Ave = Temperature
E_{A_4}
E_{A_1}
$E_{A_{23}}$
% of Molecule
Energy



$\Longrightarrow$ possible products from # 4

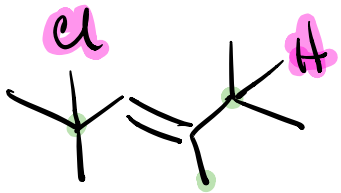


Cl^- Cl^-



direct
1,2-add

Trisubstituted



Conjugate
1,4-add

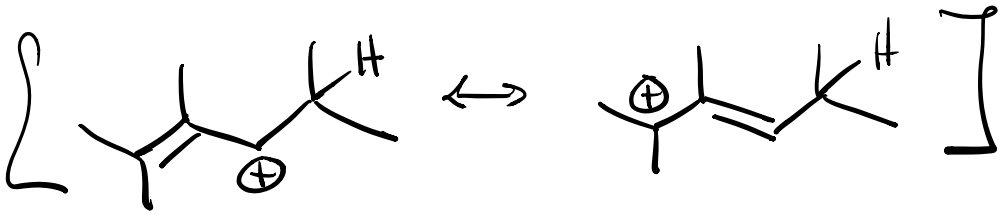
Trisubstituted

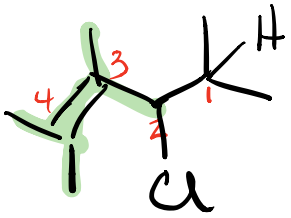
If

1,2 direct
more Sub

1,4 Conjugate
Less Sub

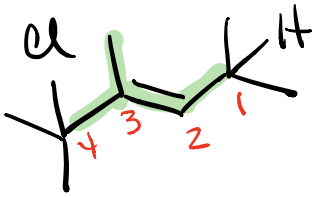
which one is thermodynamic & which is kinetic





A

tetra
1,2-add



B

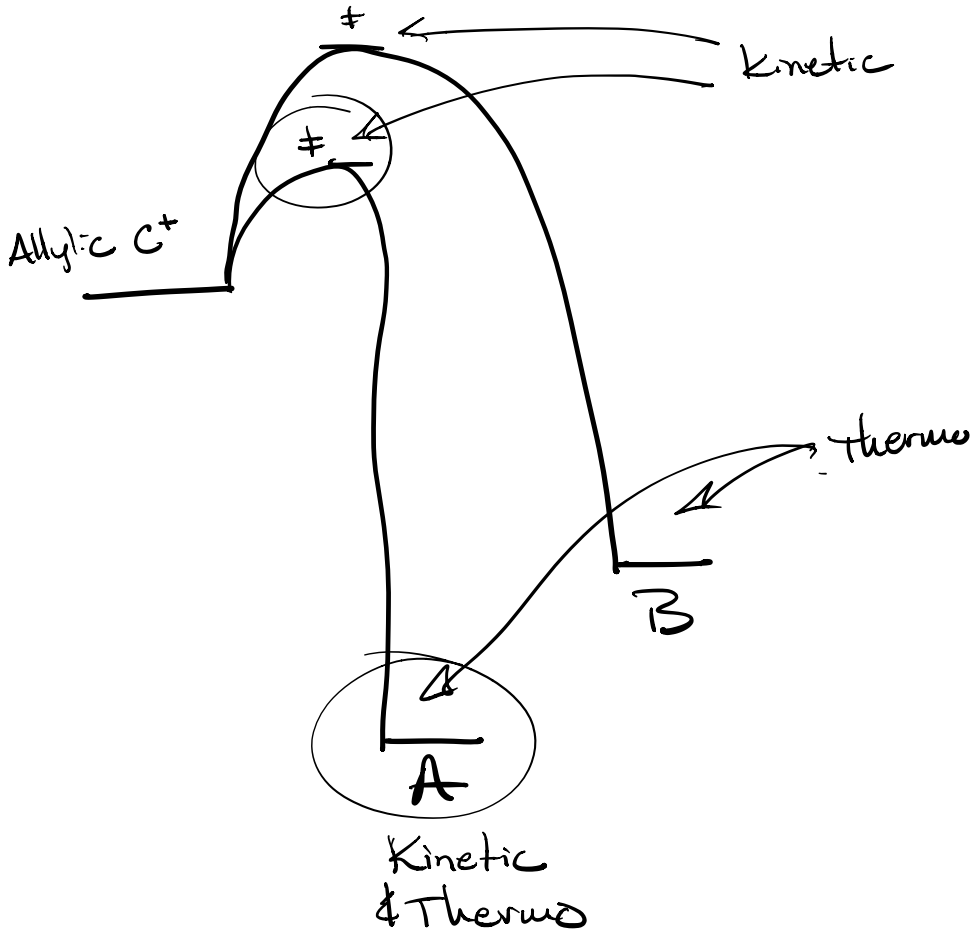
tri
1,4-add

⇒ more stable

⇒ Less Energy to form

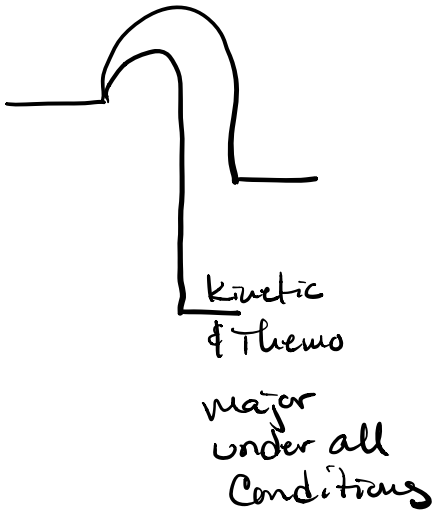
⇒ less Stable

⇒ took more energy



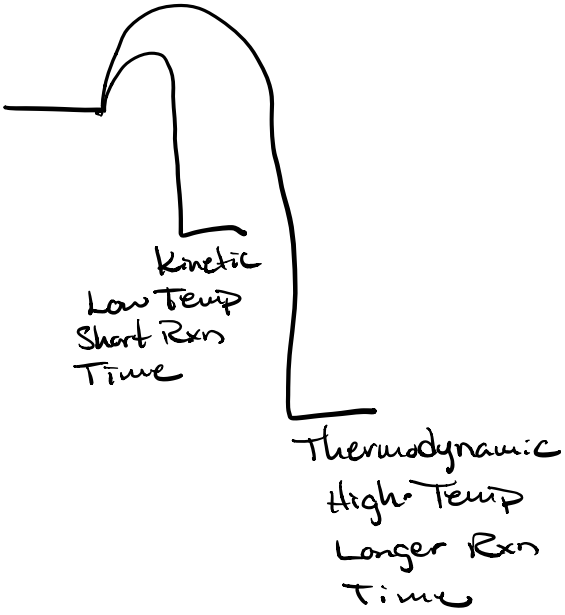
A is major under all Conditions

Most Reactions



Special Case

Kinetic vs Thermodynamic



How do you decide kinetic conditions from Thermodynamic Conditions?

Easy

$\xrightarrow[0^\circ C]{HCl}$ Kinetic Condition

$\xrightarrow[80^\circ C,\ 4\ hrs]{HCl}$ Thermodynamic Conditions

Temp

$\leq 0^\circ C$

Time in minutes

$\Rightarrow$ Kinetic

Temp

Reflux temp for Solvent

Time in hours

$\Rightarrow$ Thermodynamic

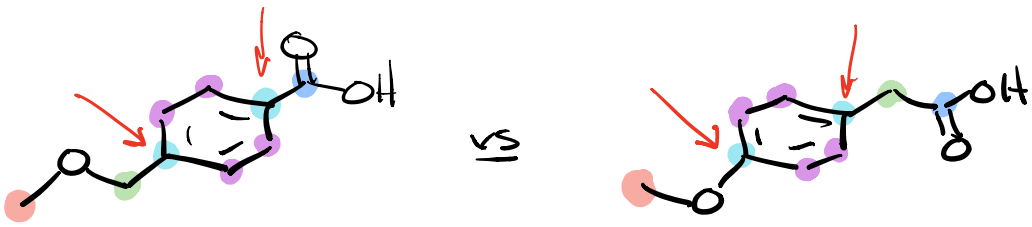
⇒ If no temp or time given

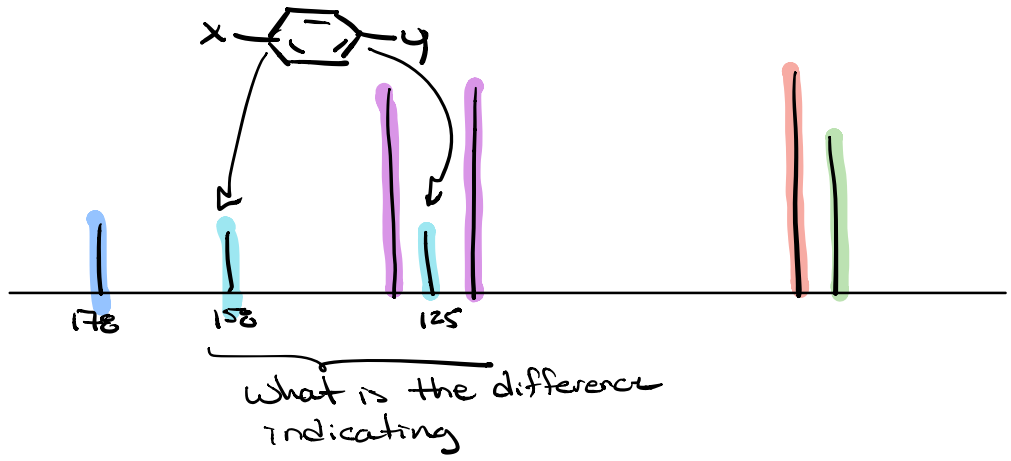
⇒ Assume Thermo Conditions

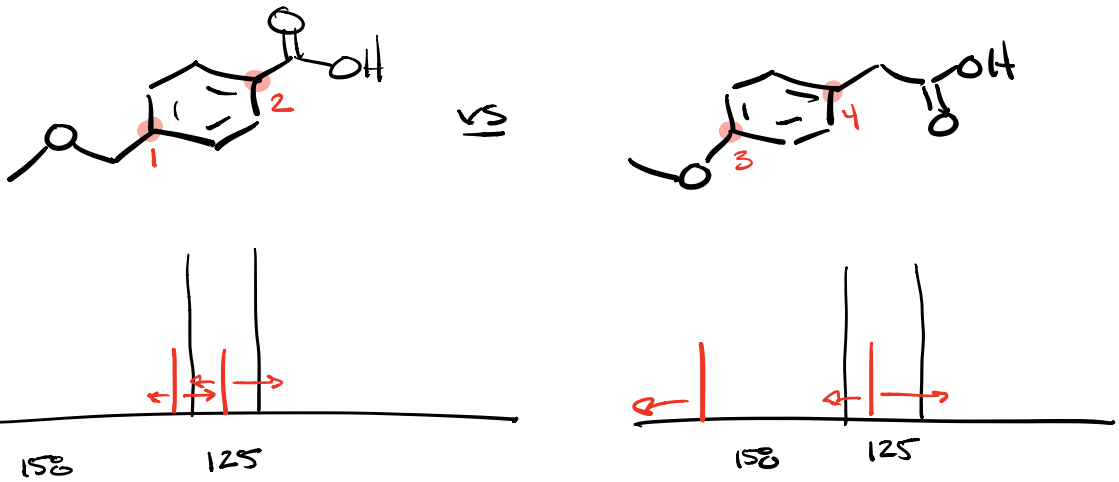
EtOH — Bp 78°C

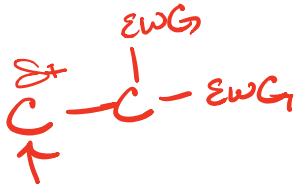
MeOH — Bp 66°C

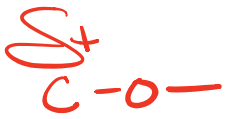
Toluene — Bp 110°C

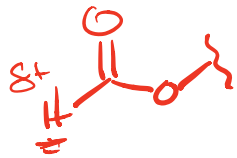

OH
vs
OH


X
Y
178
158
125
what is the difference indicating

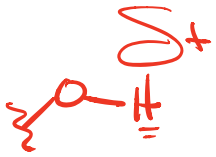

OH
2
1
vs
OH
4
3
158
125
158
125


EWG
EWG

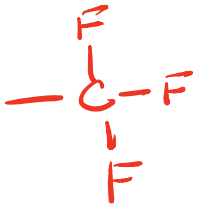

C-O



Aldehyde
not labile
⇒ not protic

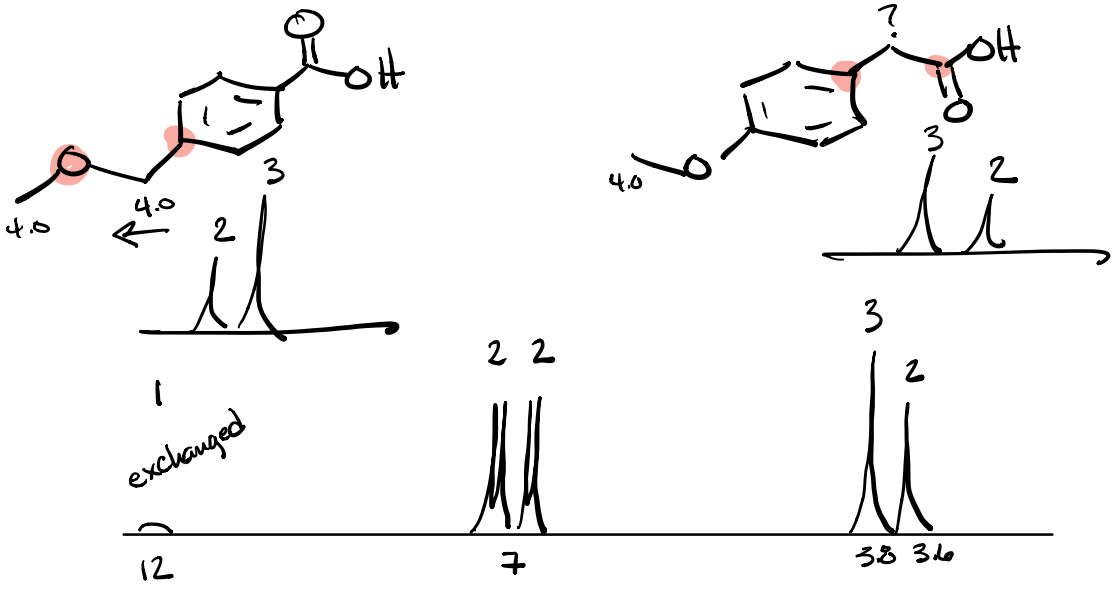


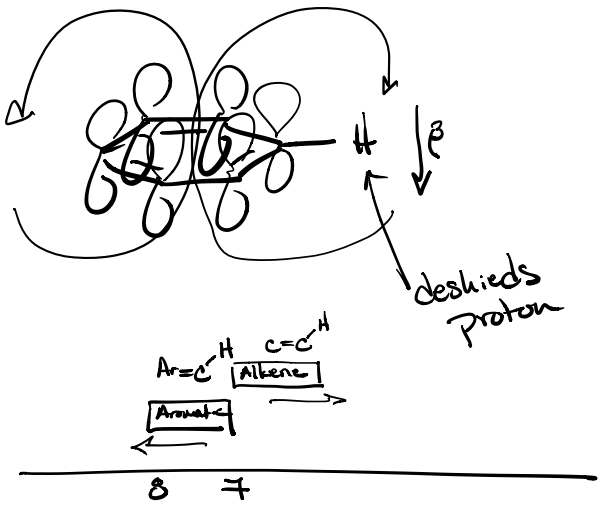
alcohol
H-bonds
protic
labile



Rare

Common




H
B
deshieds proton
Ar=C H
C=C H
Alkene
Aromatic
8
7