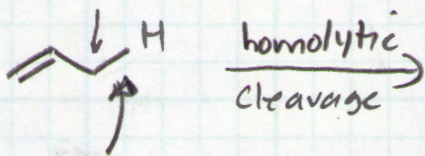


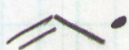
Delocalized π bond electrons $\rightarrow$ effect of π bond e^-

e^- like to "flow" from regions of high e^- density to those of lower e^- density

allylic carbon



homolytic
cleavage

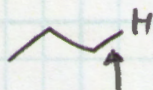


$\uparrow$
removal of allylic $\cdot H$

bde
(bond dissociation E)

$DH^\circ = 87 \text{ kcal mol}^{-1}$ adjacent π bond lowers bde of C-H bond

Compare



$DH^\circ = 101 \text{ kcal mol}^{-1}$

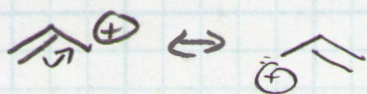


$DH^\circ = 96.5$



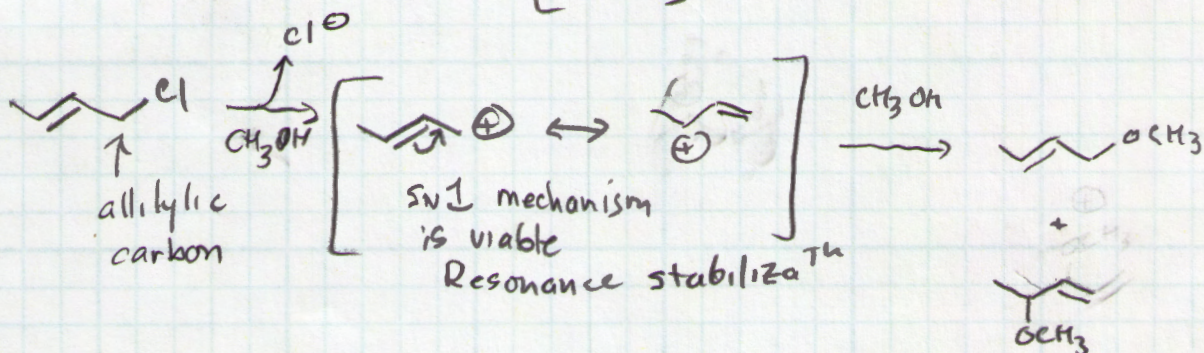
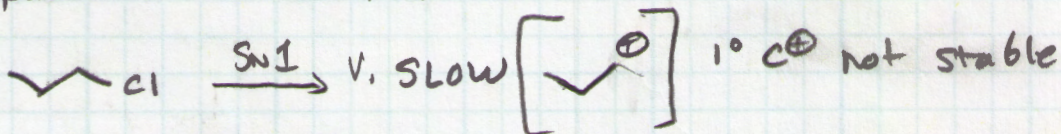
$DH^\circ = 98.5$

π bonds stabilize adjacent $C^\oplus$

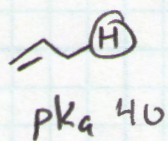


"conjugated" system

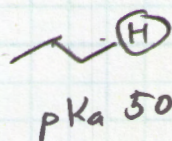
Compare S_N1 mechanism rates



Adjacent π e⁻s lower pKa



compare



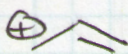
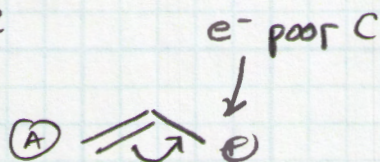
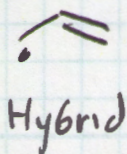
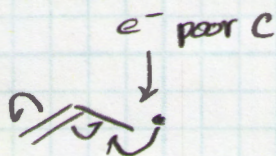
eval rel. stabilities of conj bases



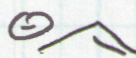
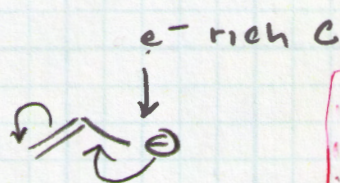
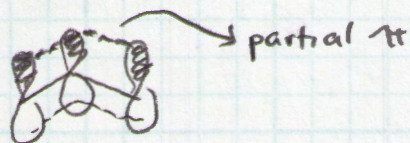
Res stabilized



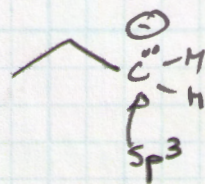
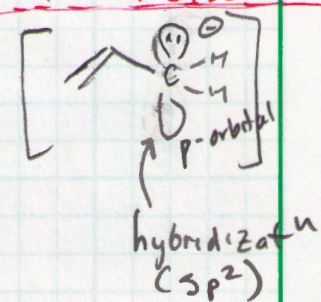
Not res. stabilized



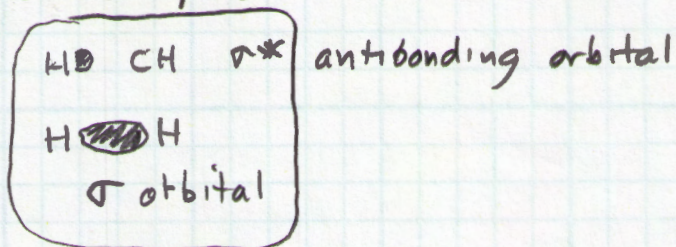
Hybrid



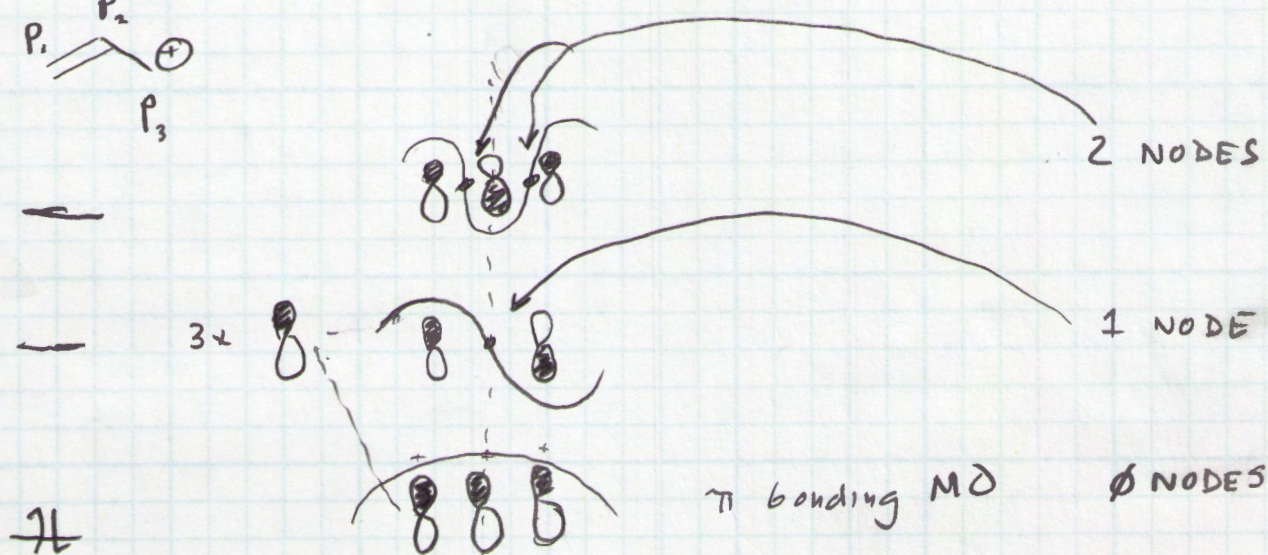
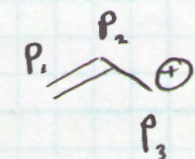
ASIDE



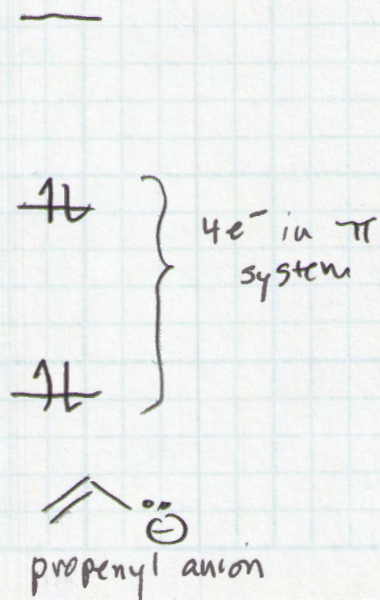
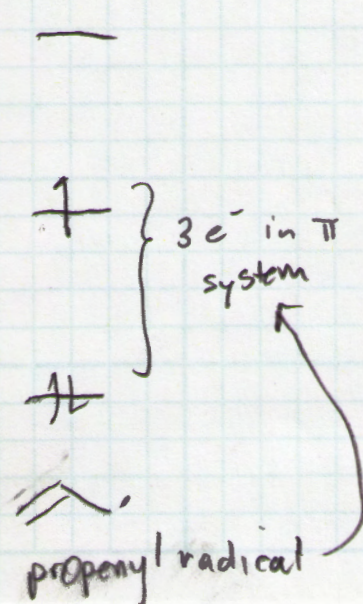
Recall atomic orbitals combine to yield molecular orbitals in a molecular structure.



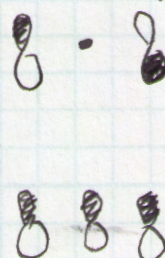
p-orbitals combine mathematically to form molecular orbitals



propenyl C^+
has 2 π e^- in π system

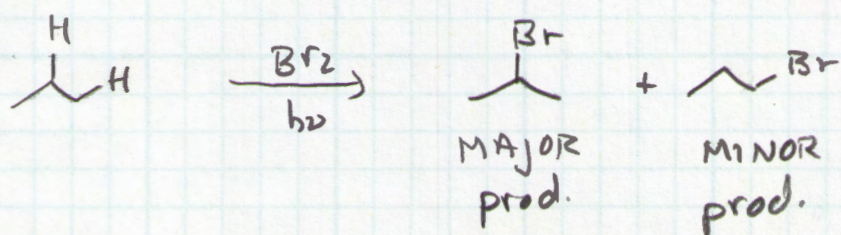


e^- for radical and anion will occupy to end C's.



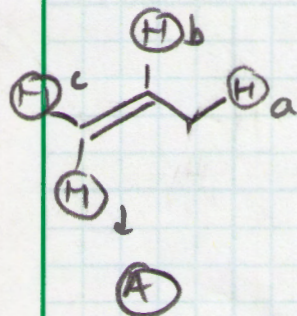
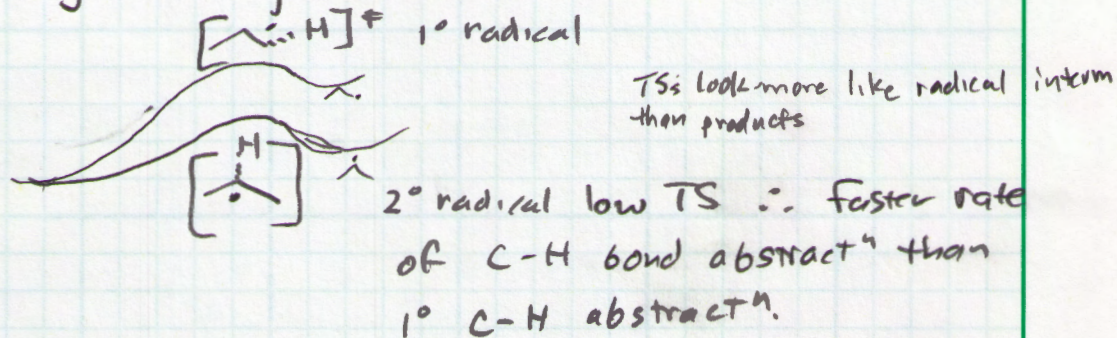
Radical Based Allylic Bromination

Recall

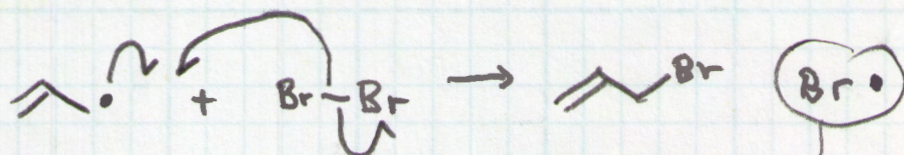
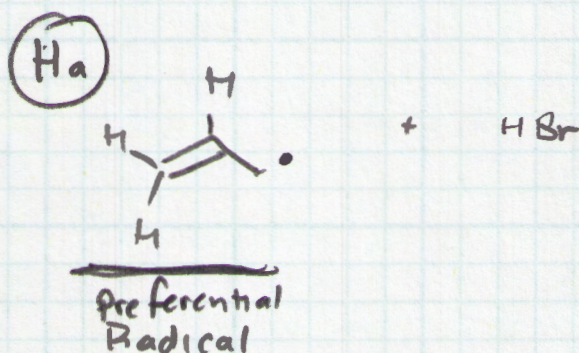


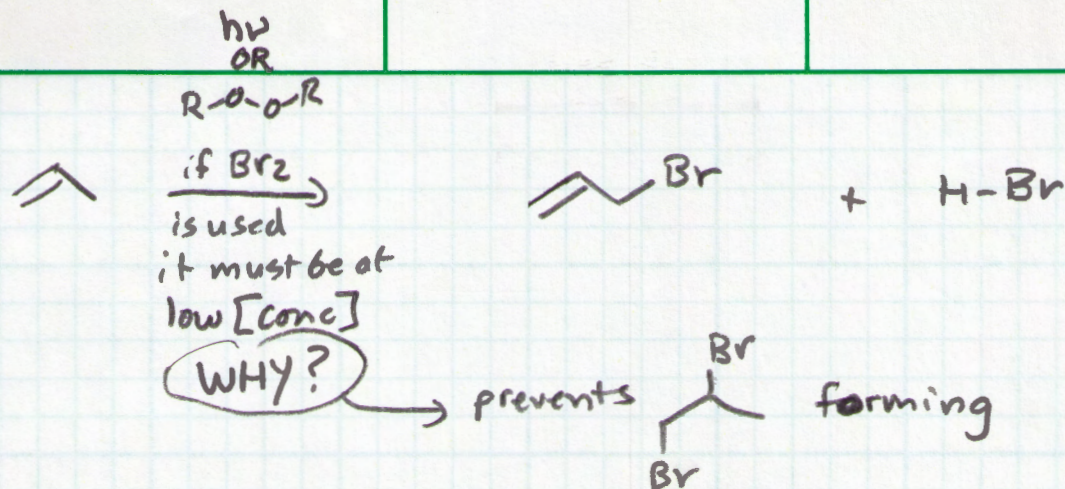
Why is the 2° bromo product Major?

TS rel E are governed by radical stabilities.

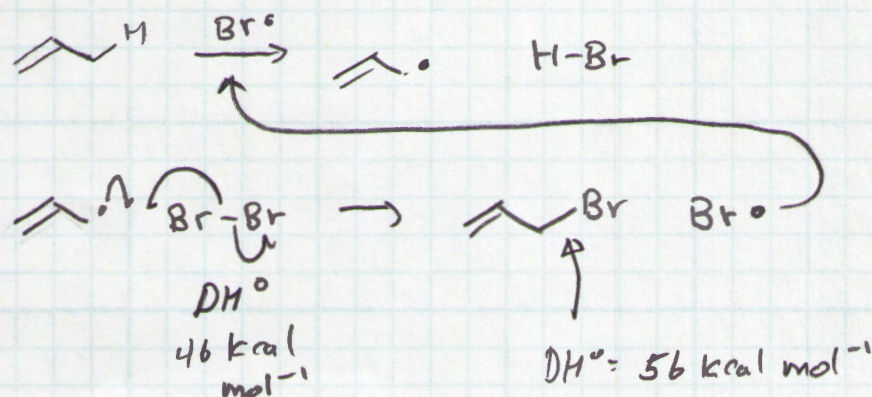
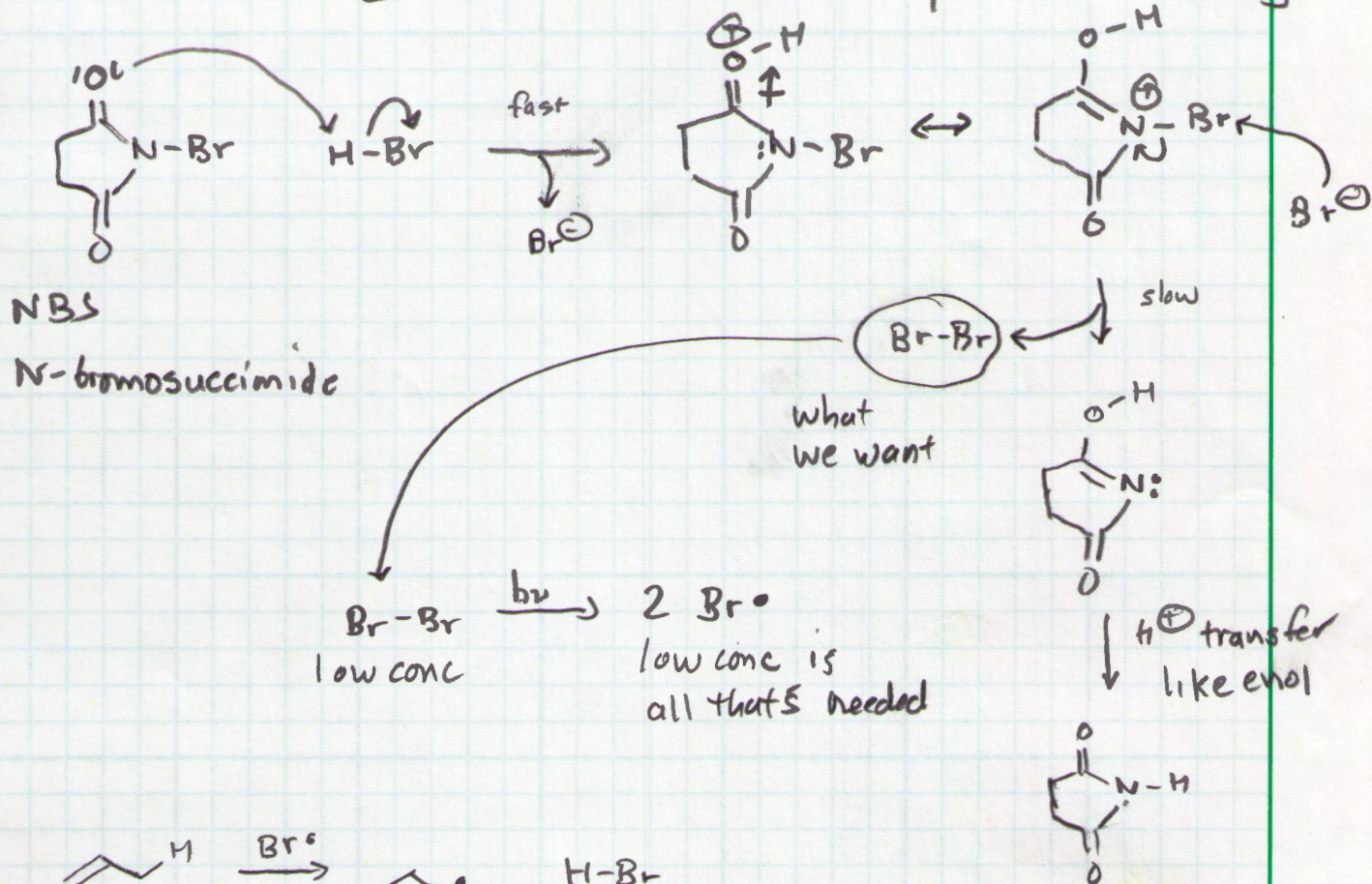


which proton abstraction by a $Br\cdot$ from structure A has lower E TS

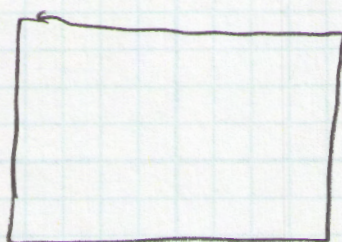
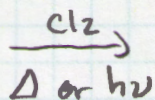
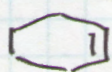
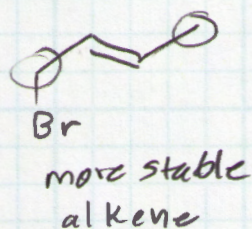
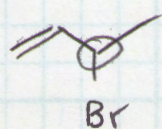
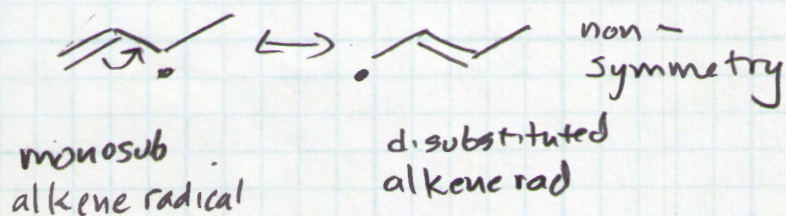
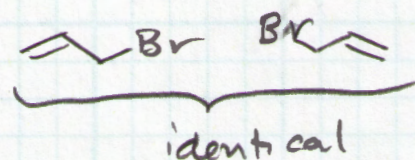
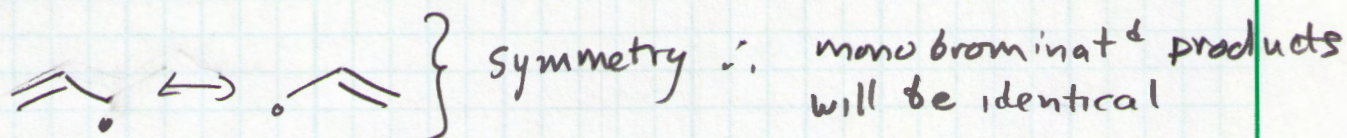




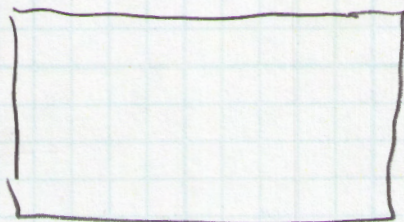
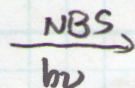
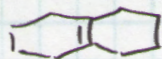
Alternative Br_2 source so it's always at low $[\text{Br}_2]$



Initial terminal
 Lets say Resonance show Radical alkene intermediates are not symmetrical

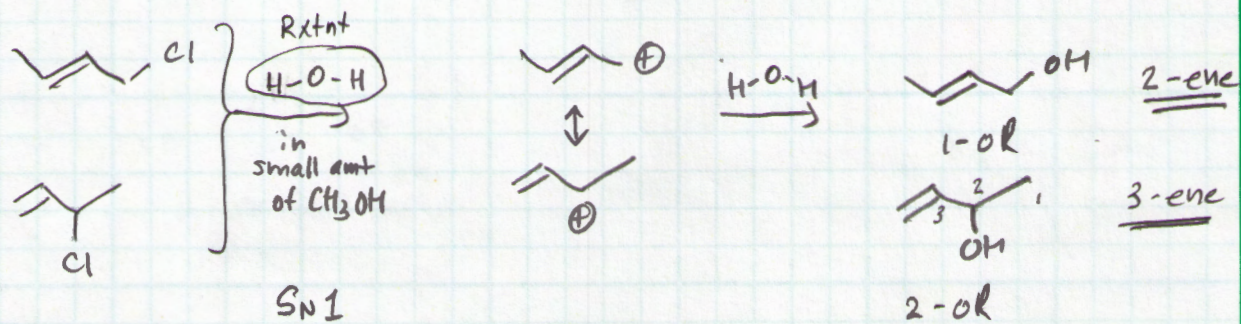


List unique mono Cl products

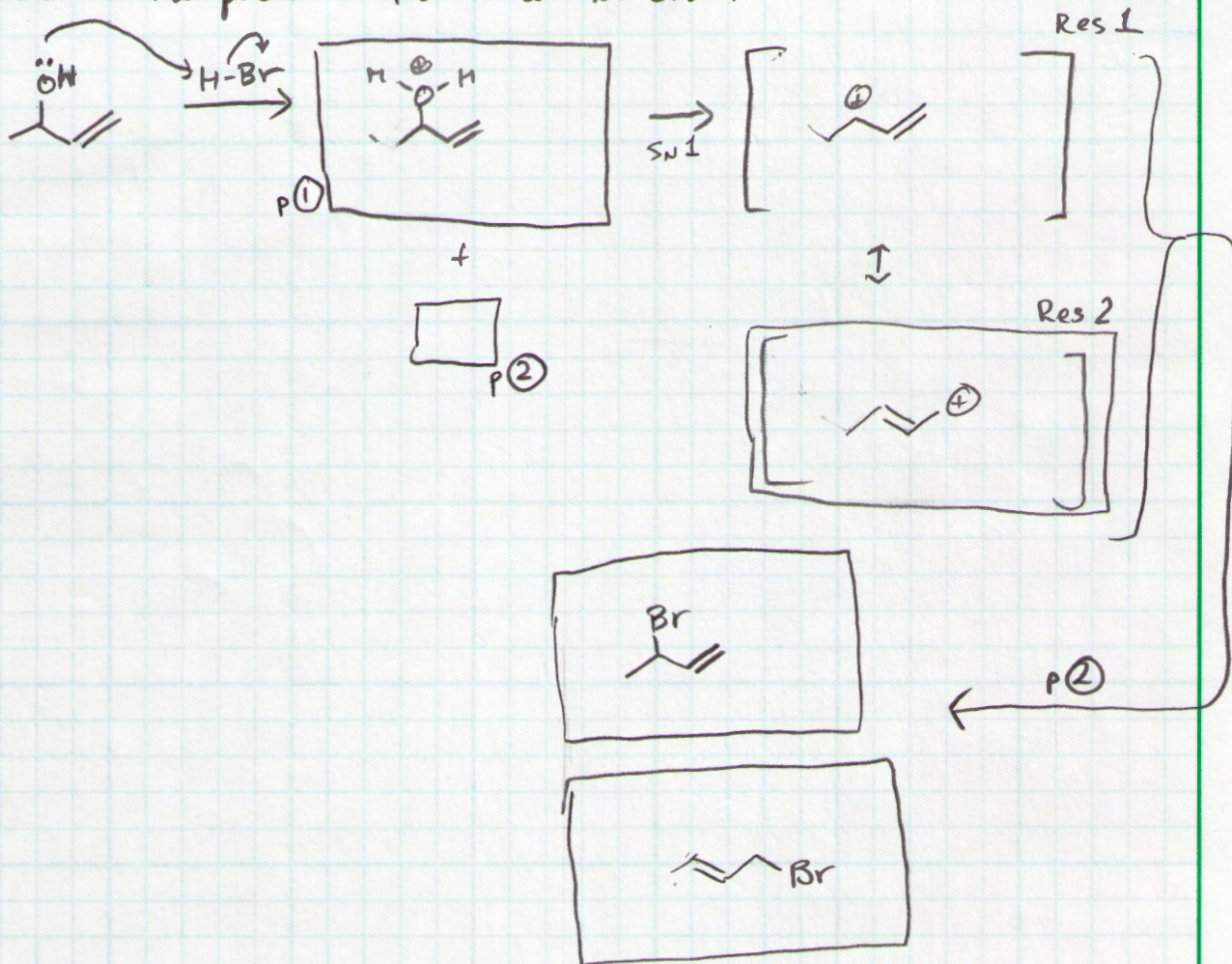


All mono Br (unique) products

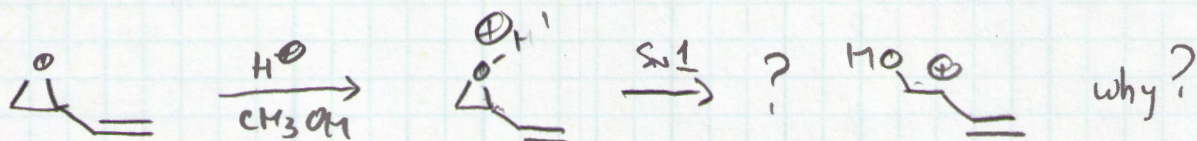
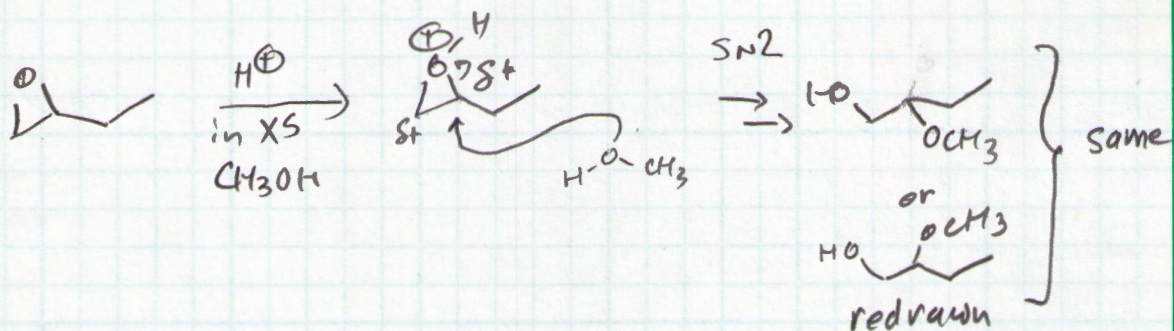
SN1 and SN2 rxns with allylic halides



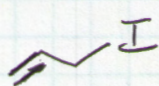
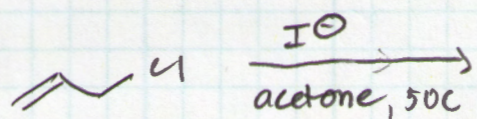
Predict the products from the monobrominatⁿ rxn below



Recall



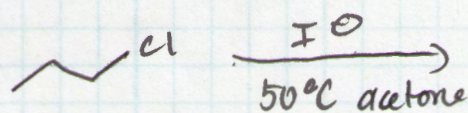
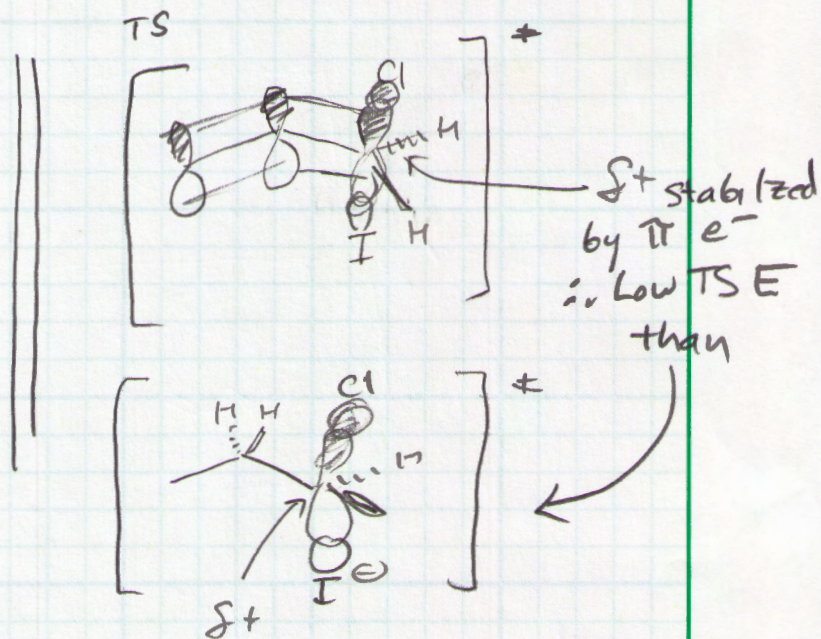
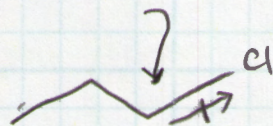
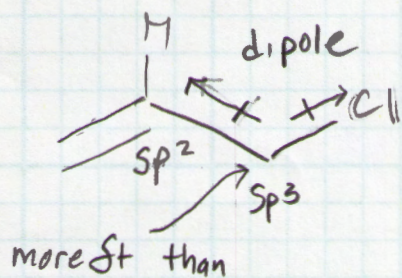
SN2 w/ Allylic Halides



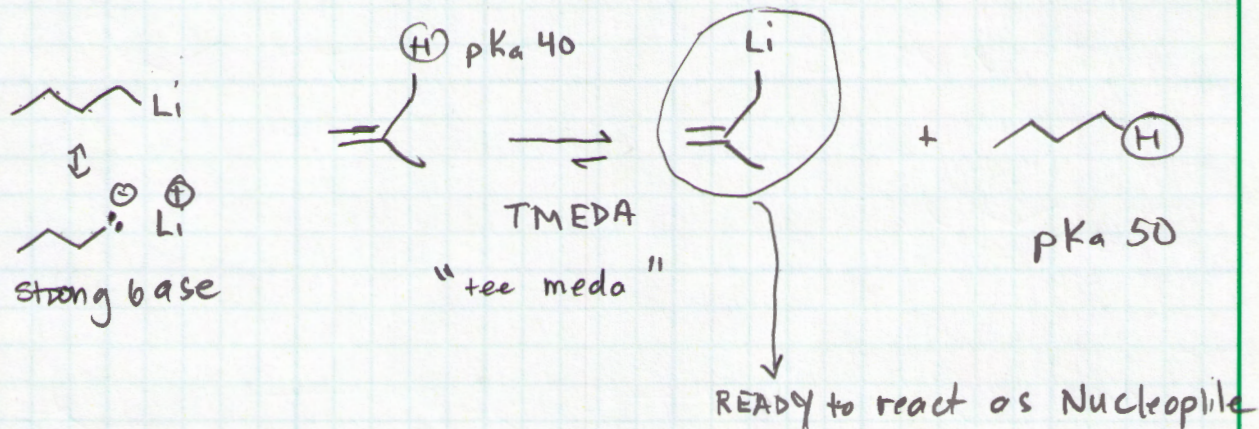
Rel Rates

73 s⁻¹

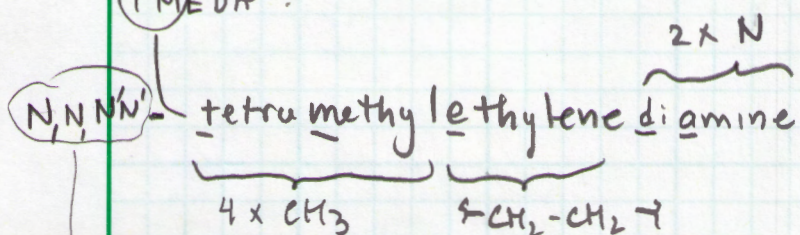
why

1 s⁻¹

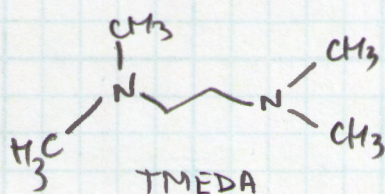
Allylic Organometallic Reagents



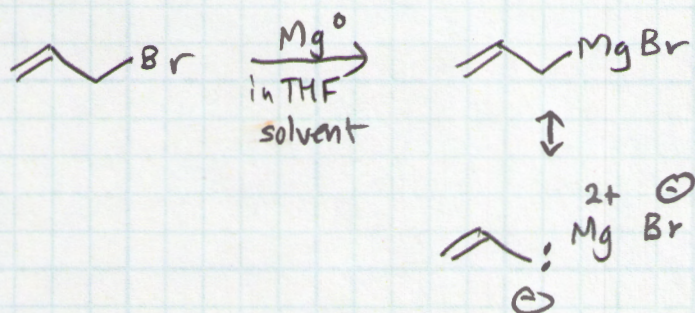
TMEDA:



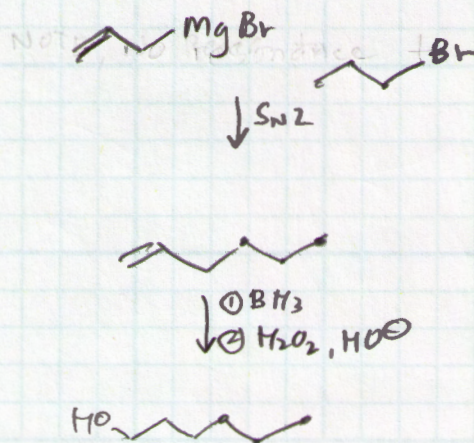
N,N - means one of the 2 amines has 2-CH₃ groups attached
 N,N' " the other amine also has 2-CH₃ groups attached.



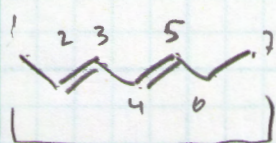
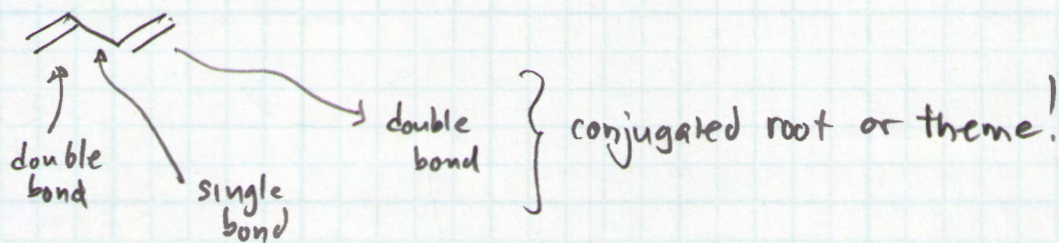
good solvent for lithiated molecules



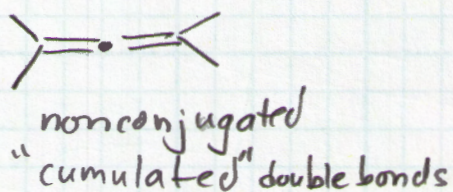
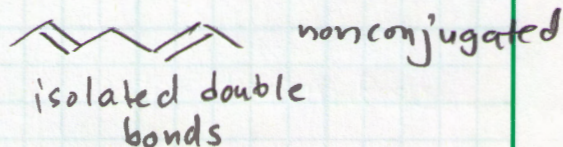
Example



Conjugated Dienes



conjugated system



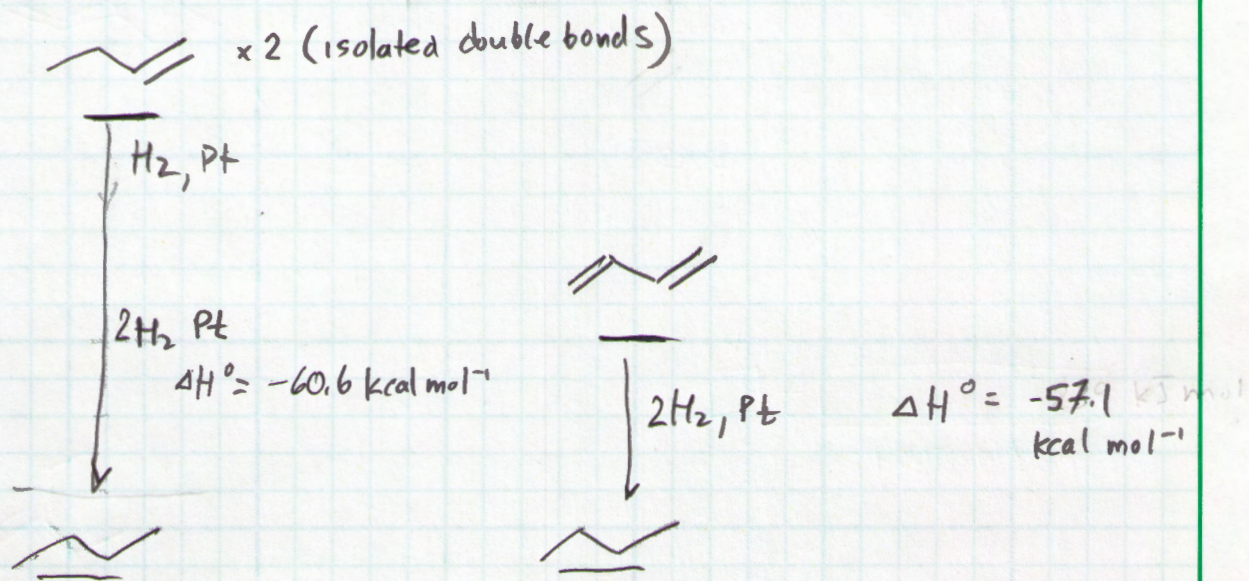
Brief, naming ① Longest C chain; it may or may not include double bonds
 └ heptane family, but contains 2 dbl bonds
 └ heptadiene

② Dienes appear at 2 and 4 positions
 2,4-heptadiene

③ double bond stereoisomerism

 └ (2E, 4E) -
 └ (2E, 4E) - 2,4-heptadiene

Heats of Hydrogenation of Conjugated Dienes
show they are more stable than Non Conjugated Dienes



conj
 The diene is $\sim 3.5 \text{ kcal mol}^{-1}$ more stable than 2 isolated double bonds