

## Today

Section 6.1 and 6.2  
Electrophilic Addition and Carbocation Stability

Section 6.3  
Transition state

Section 6.4  
Regioselectivity

Sections 6.5 and 6.6  
Addition of water and alcohols

Section 6.7  
Carbocations will rearrange

Section 6.8  
Hydroboration-oxidation

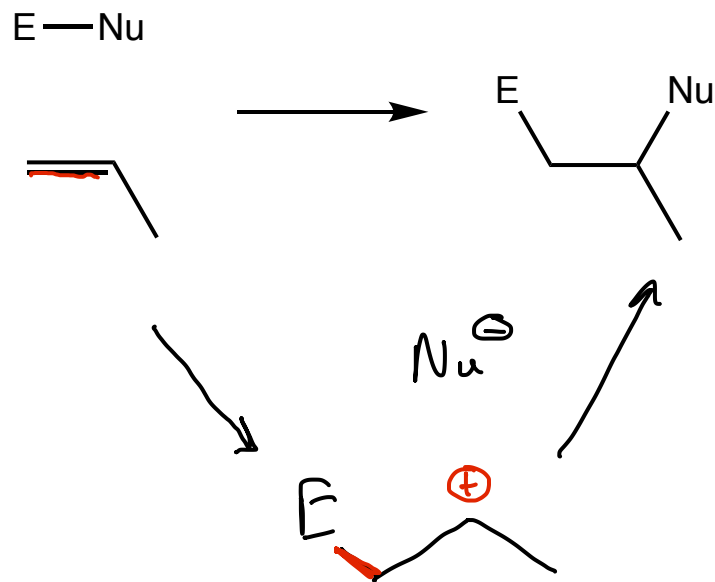
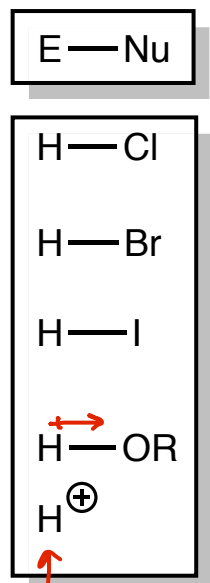
Section 6.9  
Addition of halogens

## Next Class

Sections 6.12 and 6.13  
Regio- and stereoselectivity

Section 6.16  
Reactions and synthesis





Markovnikov addition

The electrophile goes to the less substituted end of the db

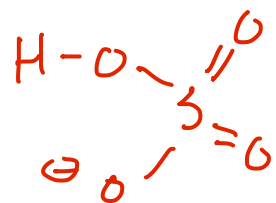
add H<sub>2</sub>SO<sub>4</sub> as a catalyst

Form the more stable intermediate

1° C<sup>+</sup> too unstable to form

2° C<sup>+</sup> will form

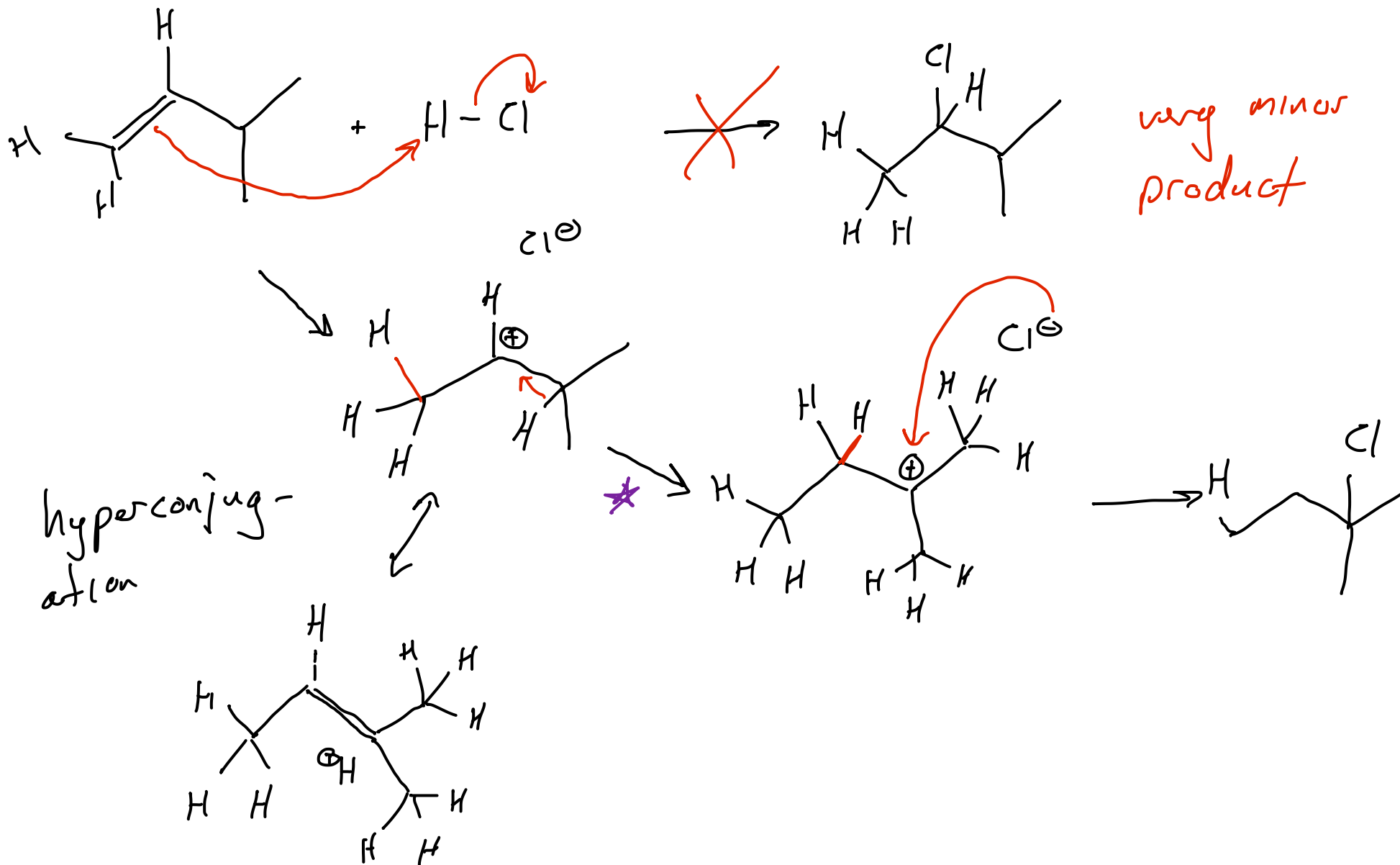
3° C<sup>+</sup> most stable of these 3



conjugate base of our acid catalyst.

delocalized e<sup>-</sup>'s makes this not nucleophilic

# The Carbocation Rearrangement

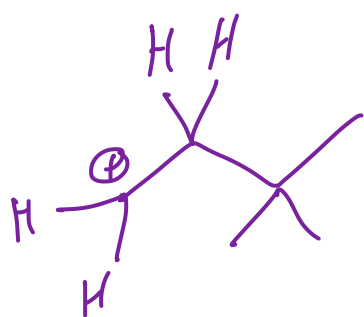
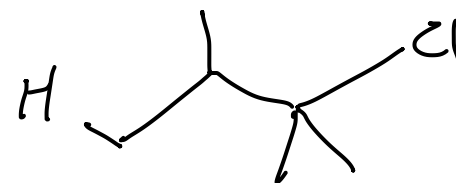
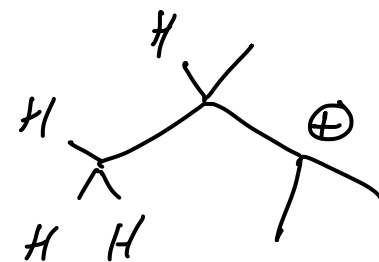
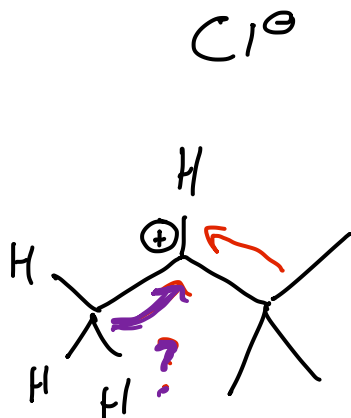
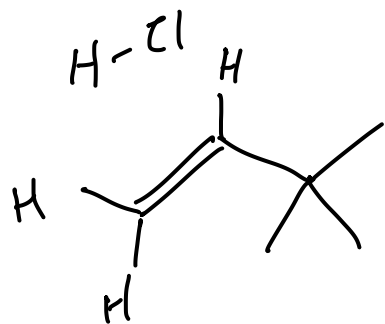


C<sup>+</sup>'s will move if they can become more stable  
 \* 1,2-hydride shift

Carbocations rearrange

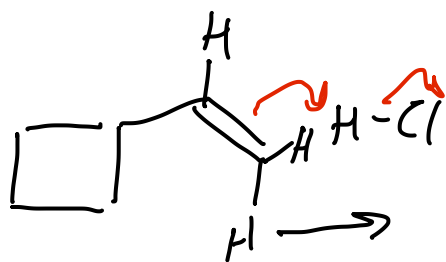
3° C<sup>+</sup> Section 6.7

yes

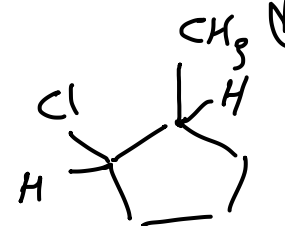
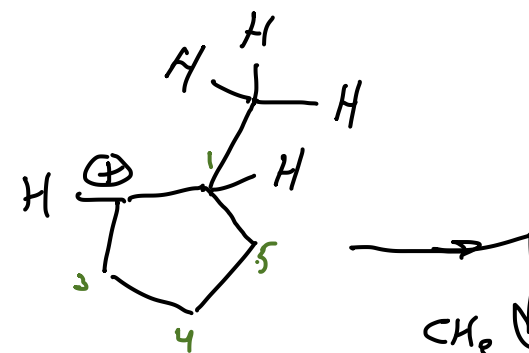
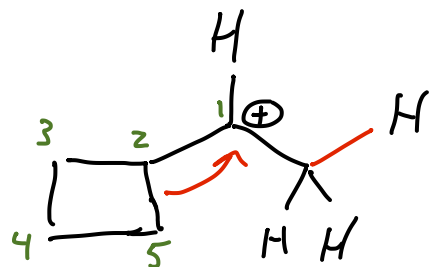


NO

1° C<sup>+</sup>



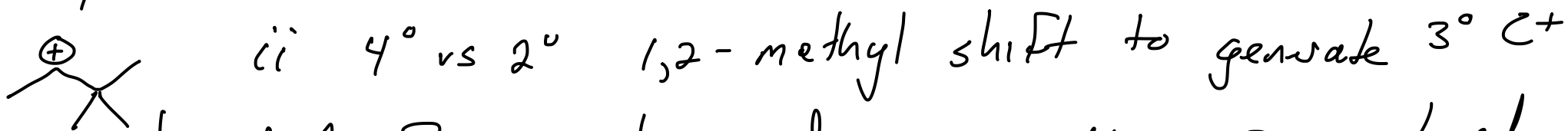
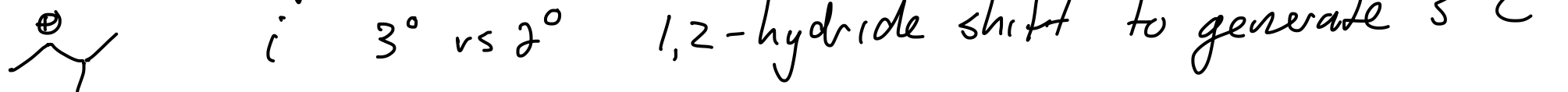
Strained ring



# Carbocation Rearrangement

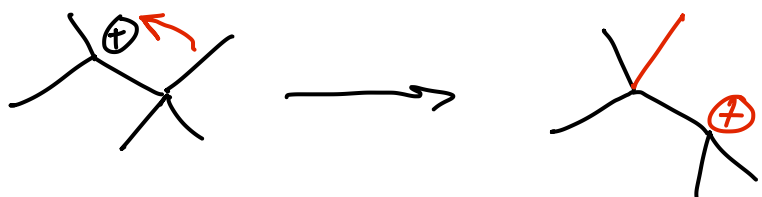
1. Form more stable  $\text{C}^+$  when adding  $\text{H}^+$  electrophile

a. look for a neighboring C with a higher degree of substitution ....



b. look for a strained ring 4 or 3 membered ring ... ring opening reaction

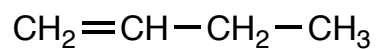
2. Add nucleophile that formed or was added in part 1



not more stable, so won't happen

# E Add Reactions

$E - Nu$

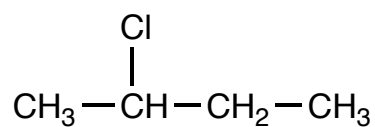
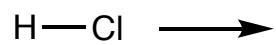


$1^\circ$  vs  $2^\circ$  /

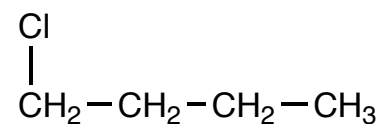
neighbor is

$2^\circ$ , so no  $E^+$  rearrangement

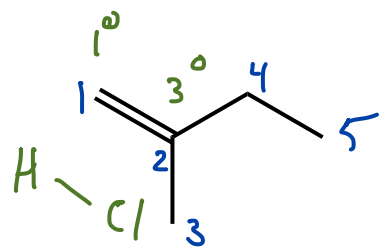
$E \quad Nu$



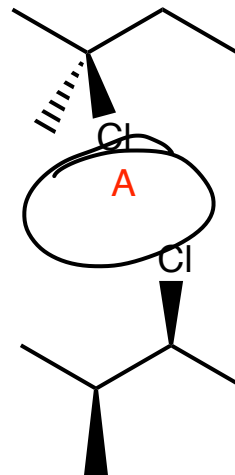
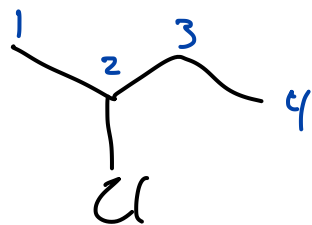
A



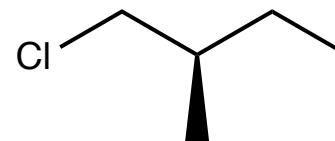
B



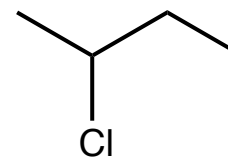
$E \quad Nu$



C

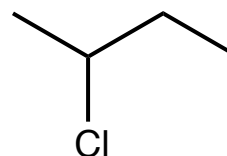
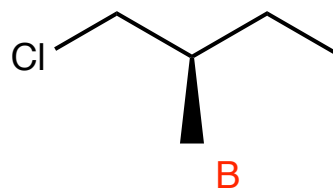
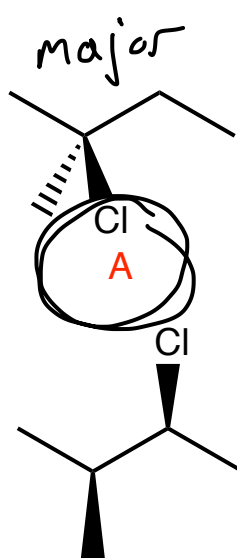
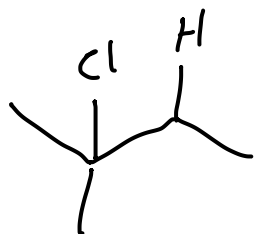
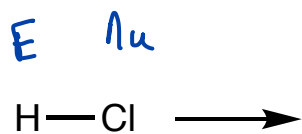
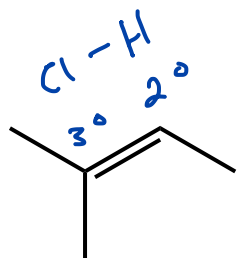


D

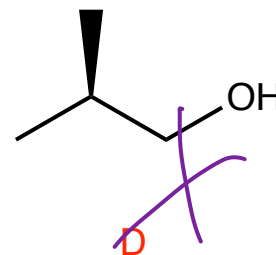
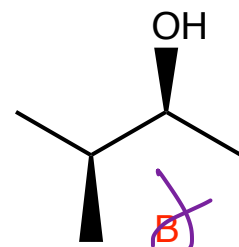
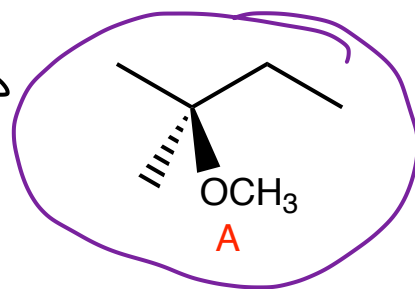
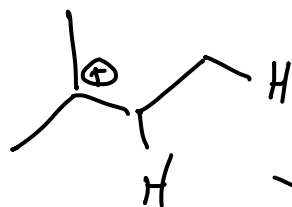
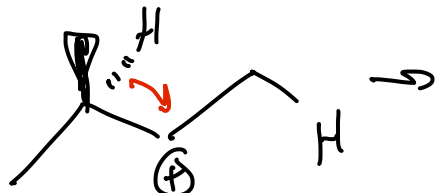


D

E Add Rxns

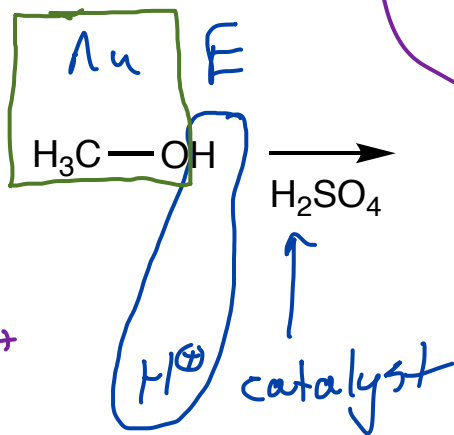


tiny amount



lost CH<sub>3</sub><sup>+</sup> from CH<sub>3</sub>OH

3° C next to 2° C<sup>+</sup> will rearrange



not this one because C<sup>+</sup> rearranged

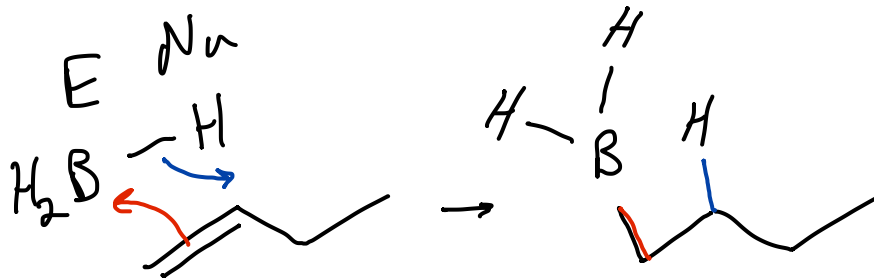
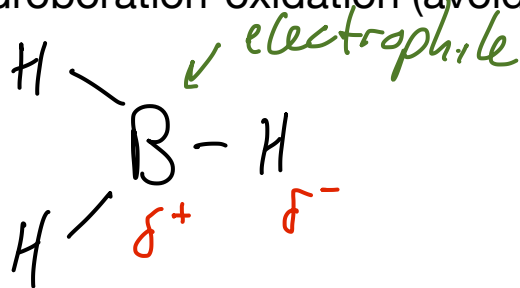
lost a CH<sub>3</sub> + put OH at wrong end



Hydroboration-oxidation (avoiding carbocation formation)

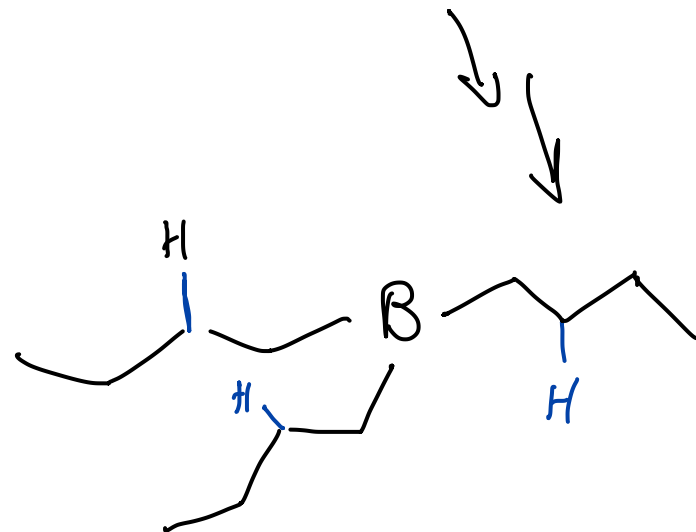
BH<sub>3</sub> is borane

Section 6.8



only 6 e<sup>-</sup> in valence shell

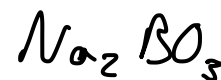
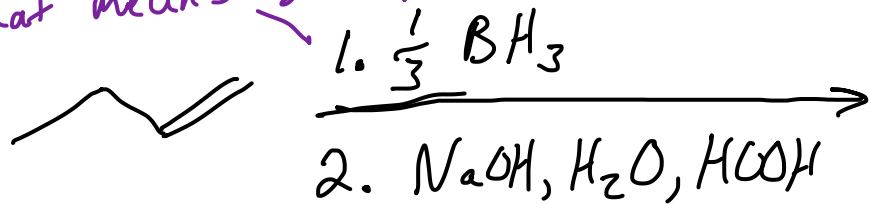
B is sp<sup>2</sup> hybridized and there is an empty p orbital on the B



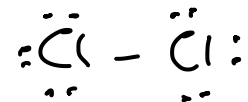
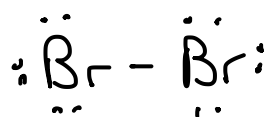
when we see Na<sub>2</sub>BO<sub>3</sub> 1., 2. over a reaction arrow that means 2 separate rxns

to remove the B  
NaOH, H<sub>2</sub>O  
HOOH

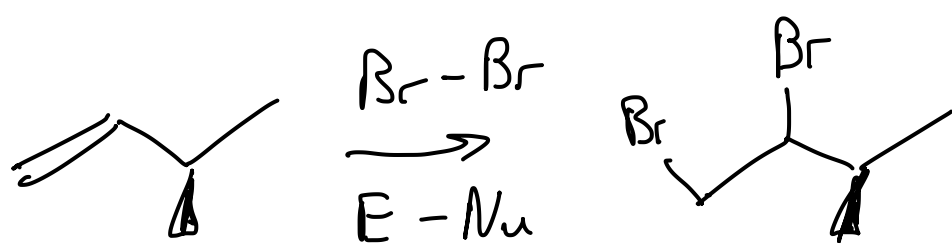
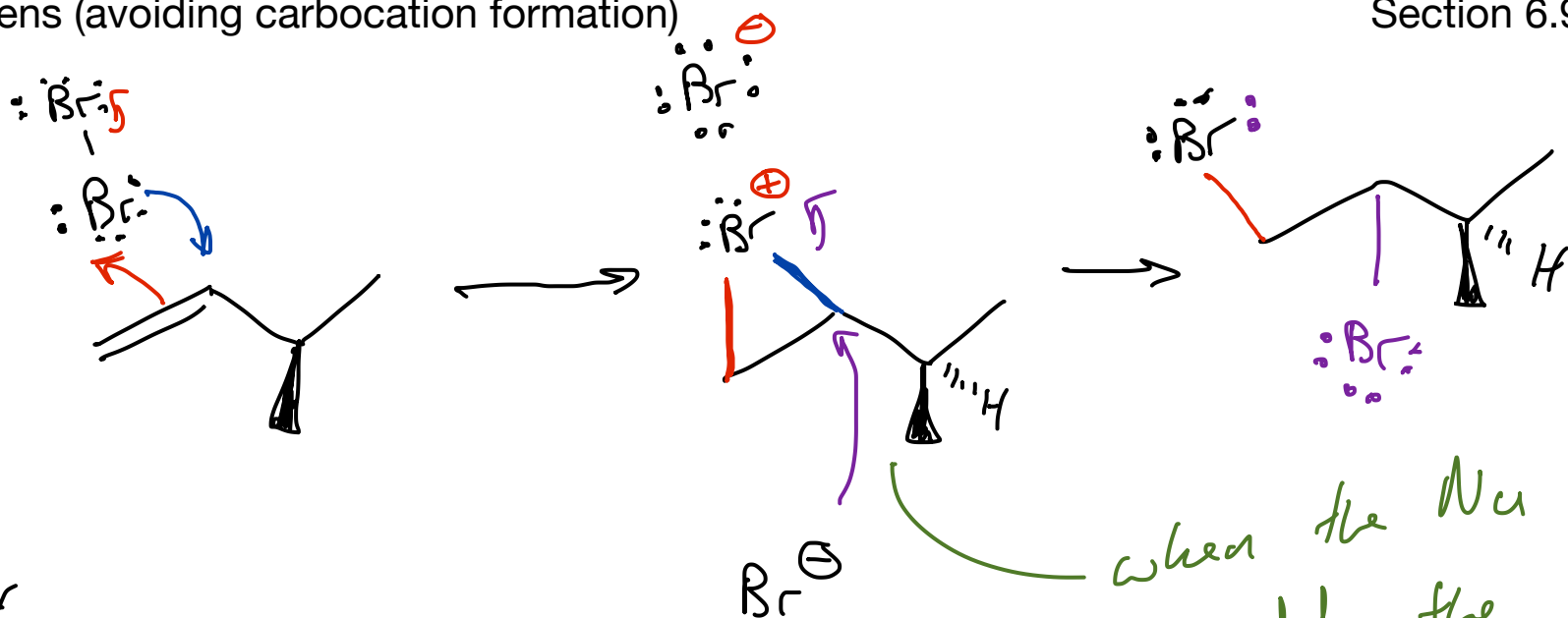
BH<sub>3</sub> can add 3x because there are 3 B to H bonds



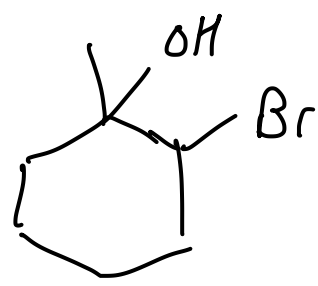
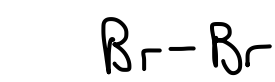
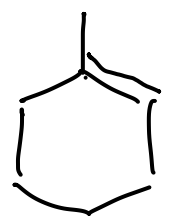
Addition of Halogens (avoiding carbocation formation)



eneg atoms  
 "fighting" over  
 $e^-$ 's will take  
 $e^-$ 's from an  
 "easier" source  
 like a  $C=C$



when the Nu  
 adds the  
 $C$  to  $\text{Br}^+$  bond  
 breaks +  
 $C$  becomes  
 a little  
 $\oplus$ . The  
 $2^\circ C$  is  
 better at  
 being  $\oplus$

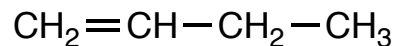


$\text{H}_2\text{O}$  added nucleophiles  
 are present at a higher concentration  
 as compared to generated Nu's

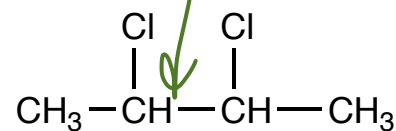
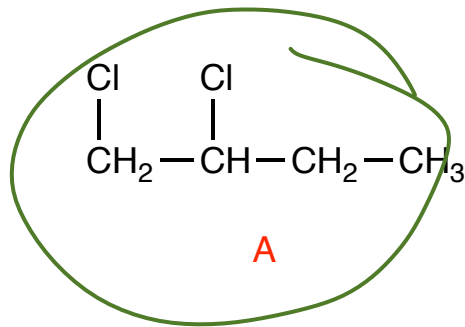
# Reactions

Section  
do wasn't  
over here

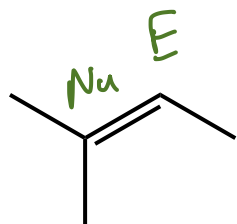
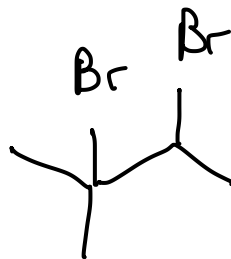
E Nu



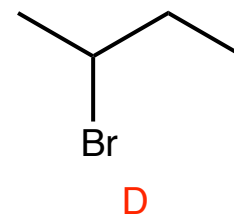
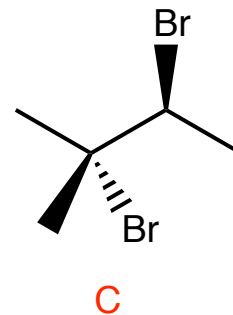
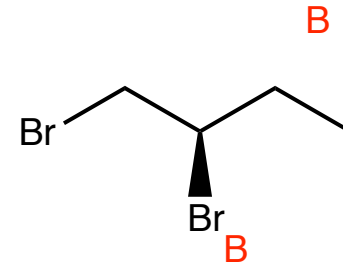
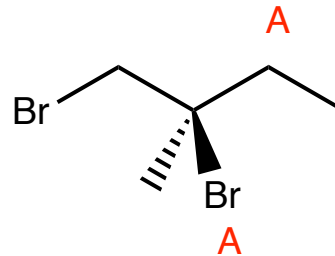
E Nu



B



E Nu



no added  
nucleophile  
so generated  
one is used

Reactions

NO  $C^+$   
 rearrangement  
 'zuz'  
 $Cl^{\oplus}$   
 intermediate

