

Today

Section 6.1 and 6.2
Electrophilic Addition and Carbocation Stability

Section 6.7
Carbocations will rearrange

Sections 6.5 and 6.6
Addition of water and alcohols

Today

Wednesday

Next Classes

today Section 6.9
Addition of halogens

today Section 6.8
Hydroboration-oxidation

Sections 6.12 and 6.13
Regio- and stereoselectivity

Section 6.16
Reactions and synthesis

We are going to have class on Wednesday. You can attend over Zoom.

We do not have a Wednesday lab; classes end at 12:20.

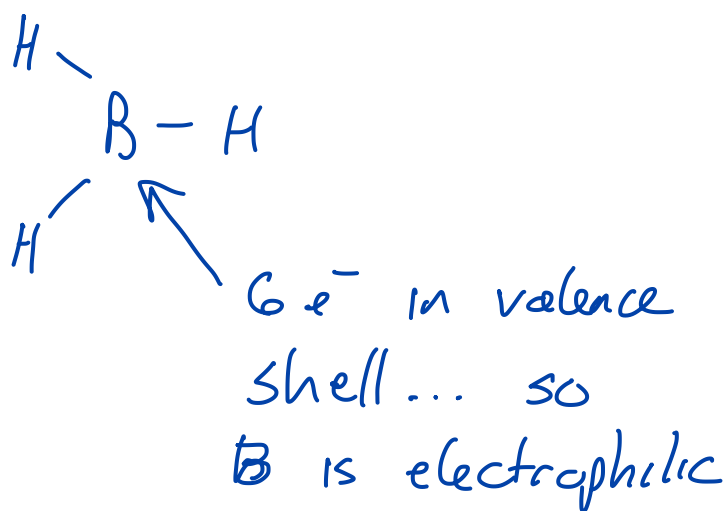
We will look at three kinds of electrophilic addition reactions each of them have similar regioselectivity (section 6.7) due to similarities in their transition states, but there each have different mechanisms based on the specific class of electrophile.

Sections 6.1, 6.2, 6.5, 6.6, 6.7 focus on using strong acids, H^+ , as the electrophile.

Section 6.9 focuses on using Cl_2 and Br_2 as the electrophile.

Section 6.8 focuses on the reaction of the electrophile BH_3 .

We will mix sections 6.12 and 6.13 in with sections that discuss regioselectivity, stereoselectivity, and stereospecificity in with our discussion of the various mechanisms and summarize at the end.



$Cl-Cl + Br-Br$ ~~F_2~~

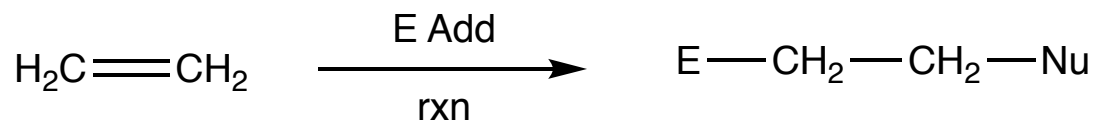
F_2 too reactive

looking for an easier source of electrons instead of fighting over e^- 's with another energy atom

I_2 less energy than Cl

Definitions

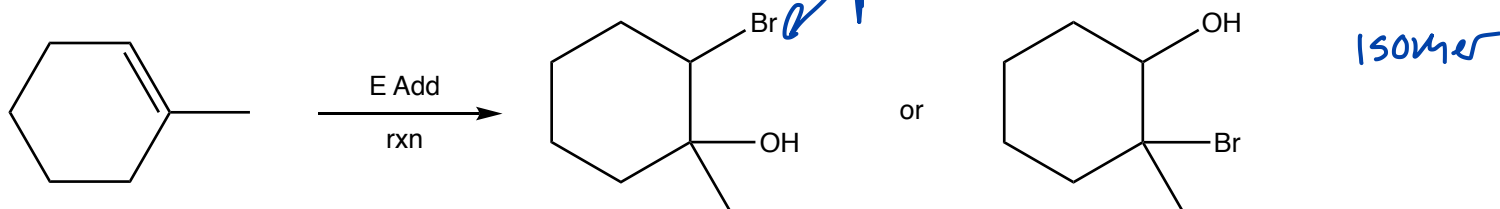
The reactions are called **electrophilic additions** because they are initiated by an electrophile and two groups/atoms are added across the double bond.



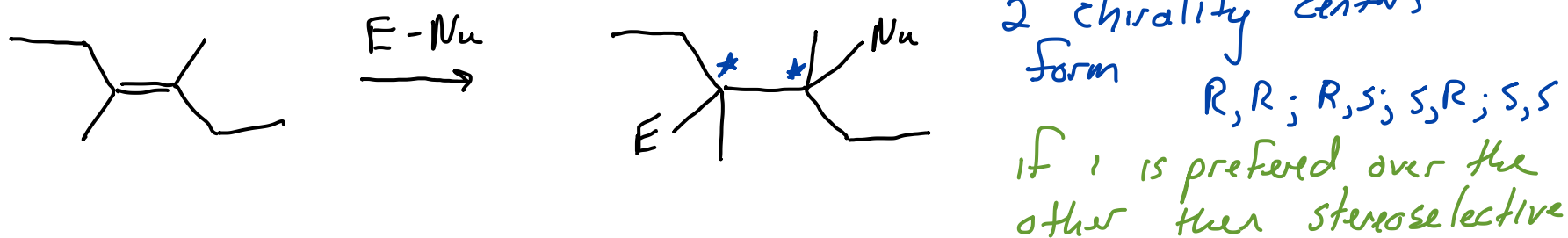
E = generic electrophile

Nu = generic nucleophile

Regioselectivity: The ability of a reaction to prefer the formation of one constitutional/structural isomer over another.

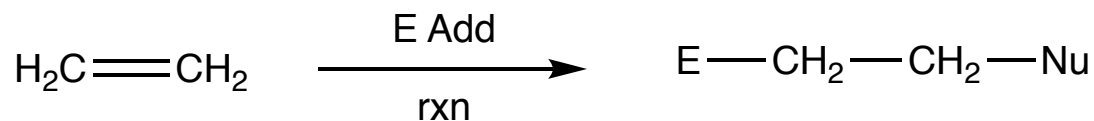


Stereoselectivity: The ability to prefer the formation of one stereoisomer over another.



Definitions

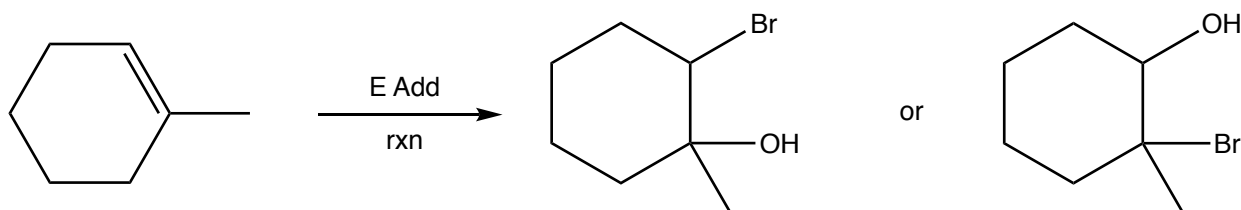
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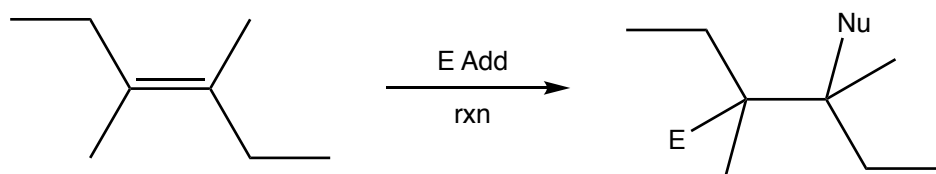
E = generic electrophile

Nu = generic nucleophile

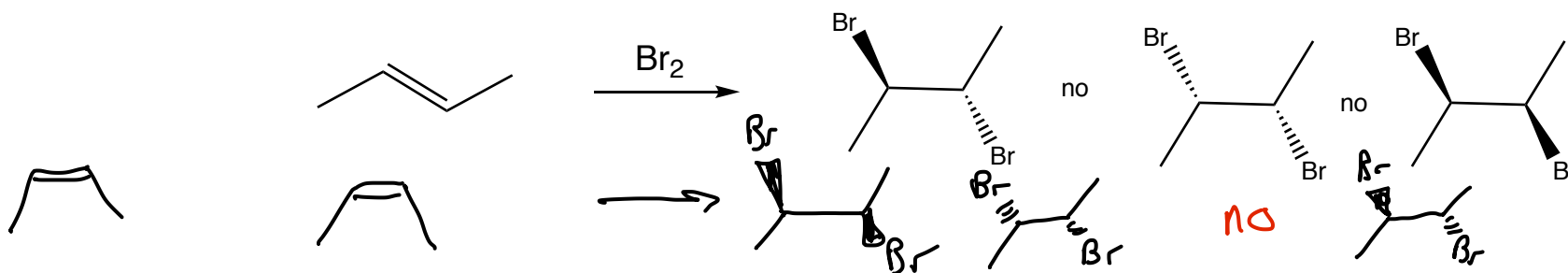
Regioselectivity: The ability of a reaction to prefer the formation of one constitutional/structural isomer over another.



Stereoselectivity: The ability to prefer the formation of one stereoisomer over another.



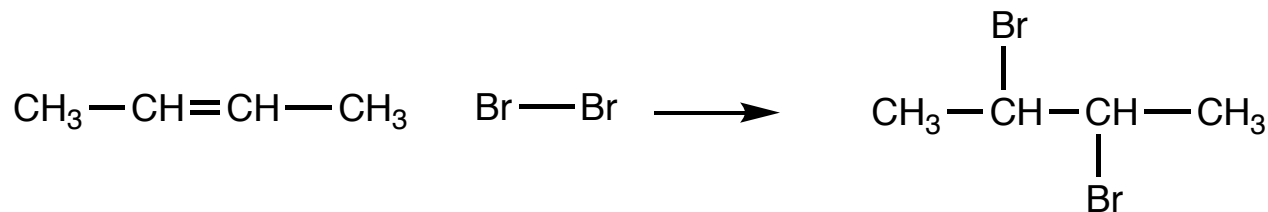
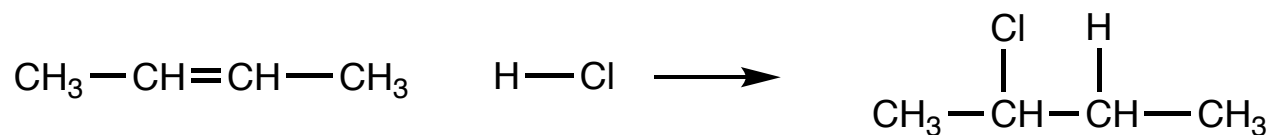
Stereospecificity: The ability of a reaction to form only **specific stereoisomers** from one **stereoisomeric reactant**.



Electrophilic Addition Reactions

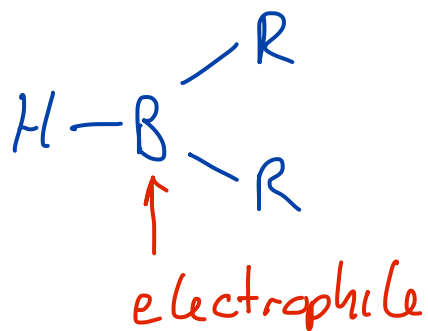
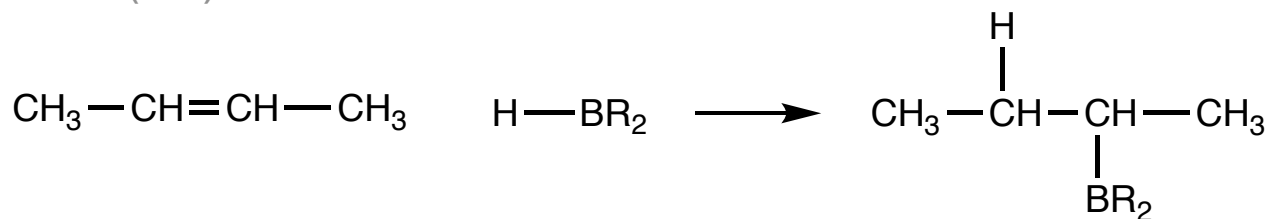
Section 6.1

Two step mechanism (6.1, 6.5, 6.6)

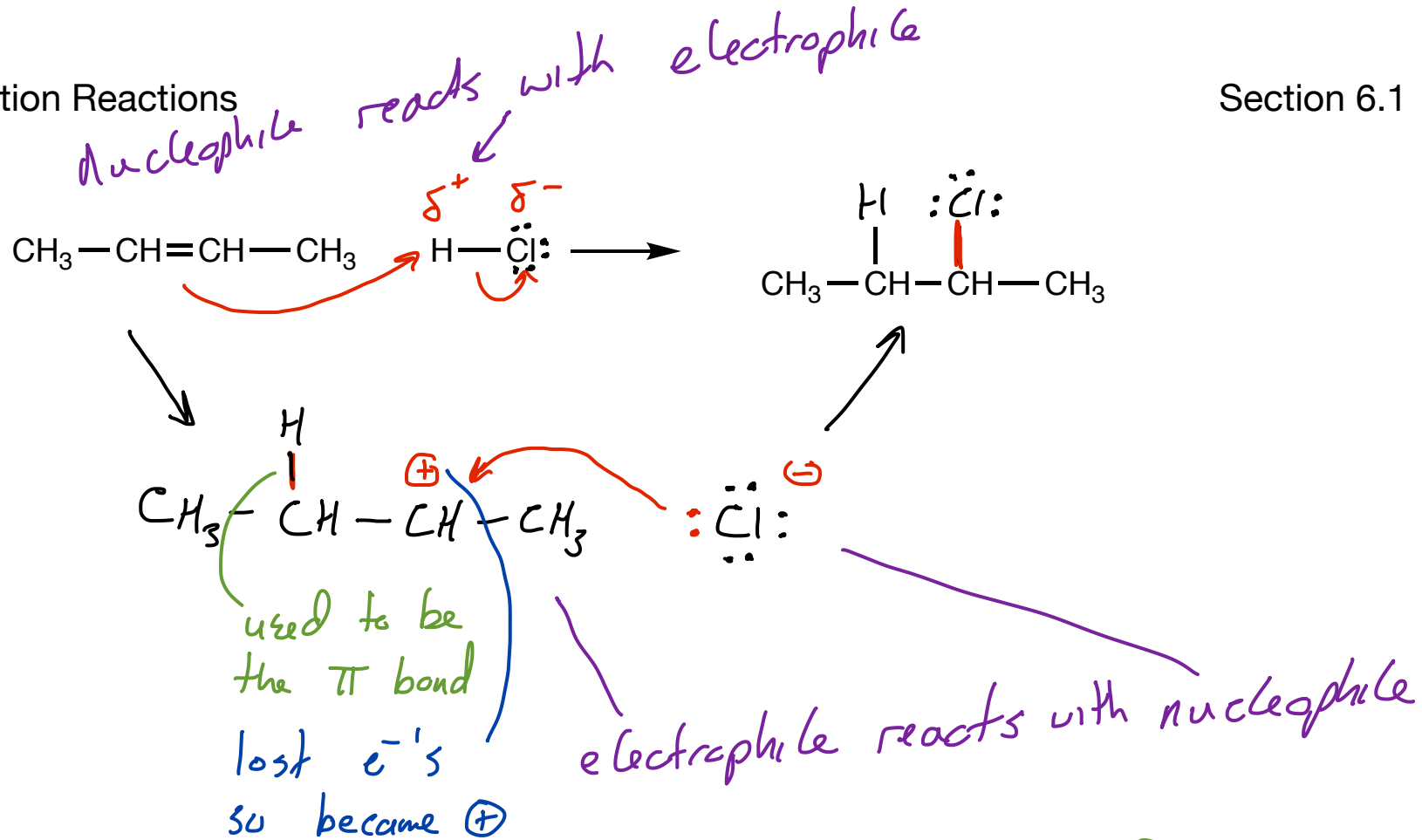


alkene reacts with E \longrightarrow reactive intermediate reacts with Nu \longrightarrow products

One step mechanism (6.8)



Electrophilic Addition Reactions



With H^+ electrophiles, carbocation intermediates form
 Strong acids required. . . weak acids like acetic acid

(vinegar) can't initiate the reaction

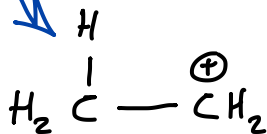
though dangerous not strong enough for this rxn

pKa	H-Cl	H-I	H-Br	H-F
	-6	-11	-9	4

The Carbocation Intermediate and Regioselectivity

Sections 6.2 and 6.4

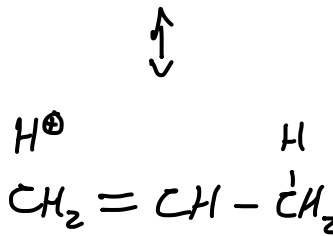
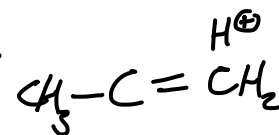
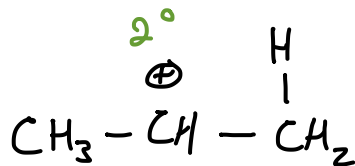
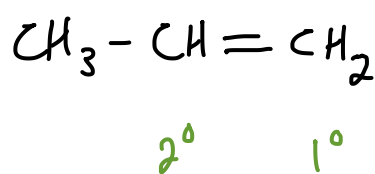
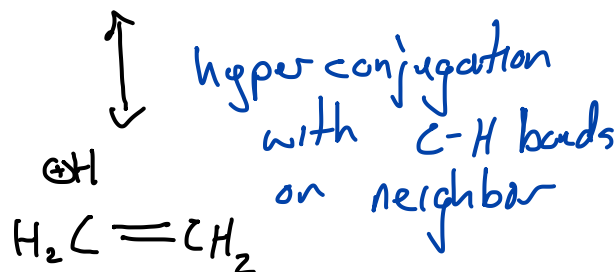
least stable
not made ...



1°

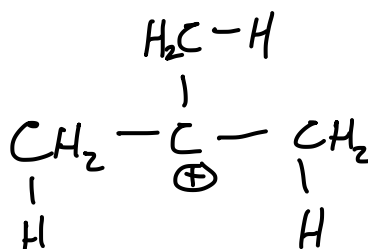
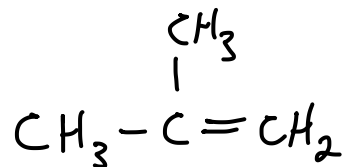
1° C⁺

too unstable to form under typical lab conditions



6 neighboring σ bonds to do hyperconjugation (in this case 6 C-H bonds)

most stable

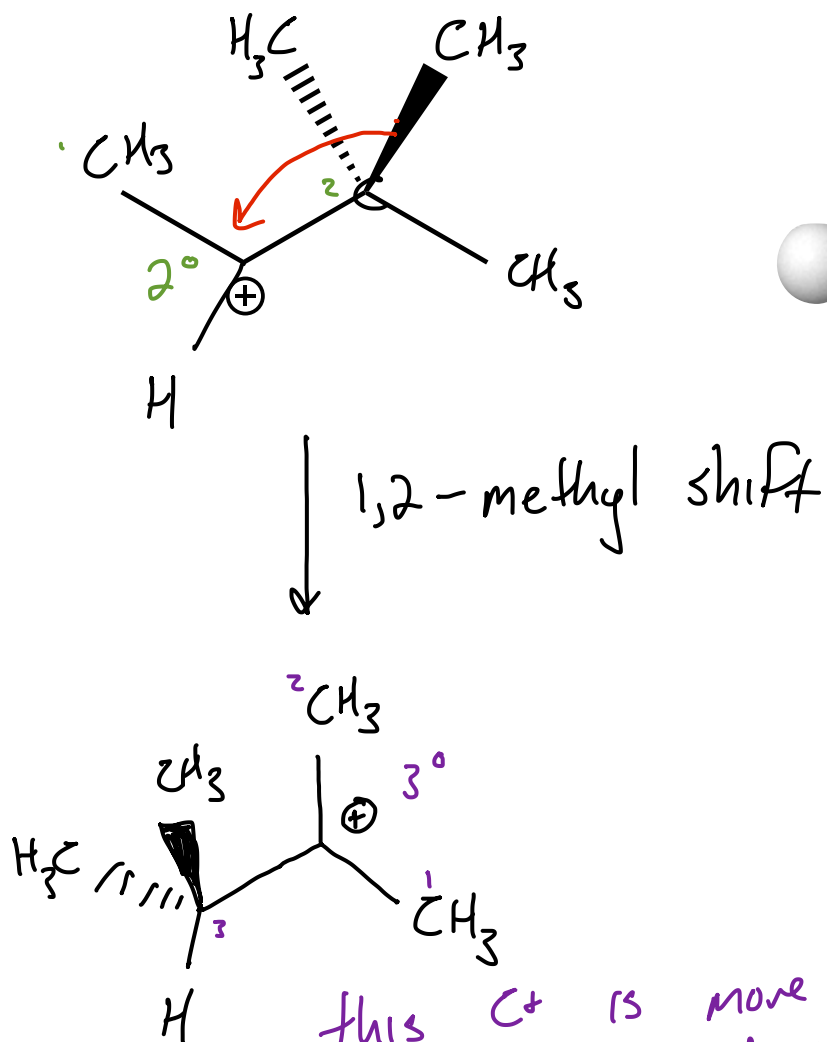


9 neighboring σ bonds to do hyperconjugation

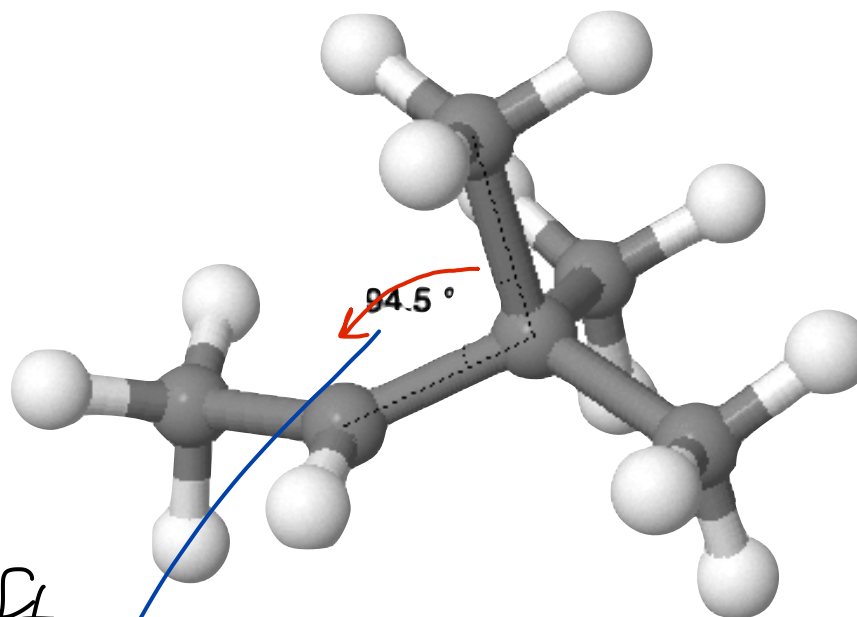
easiest to form

Carbocations rearrange if doing more stable C^+

so results in a



this C^+ is more stable so we don't go back to the $2^\circ C^+$



lowest energy structure for this C^+

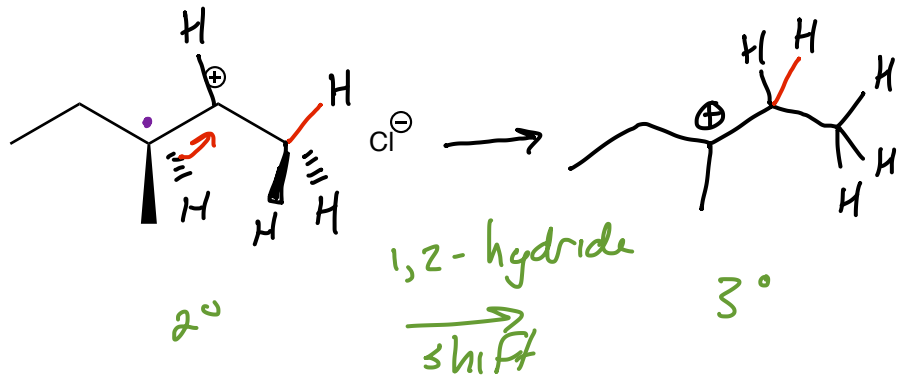
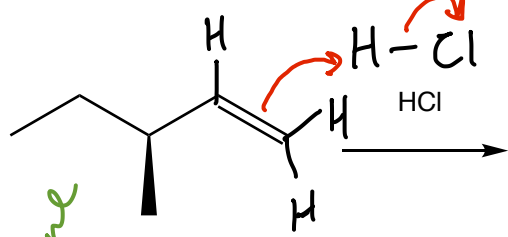
This bond angle is not $109.5 - 112^\circ$

2° C^+ forms initially because 1° C^+ is too unstable

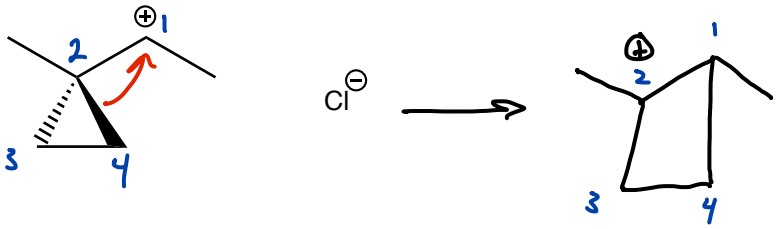
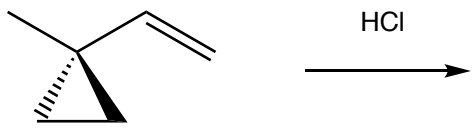
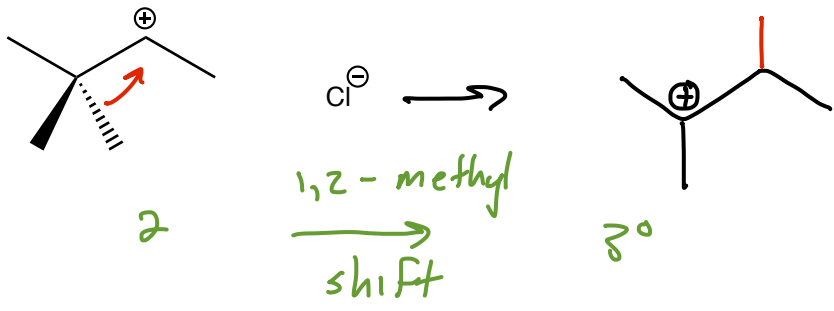
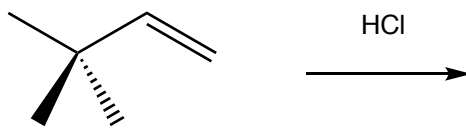
Carbocations rearrange

Section 6.7

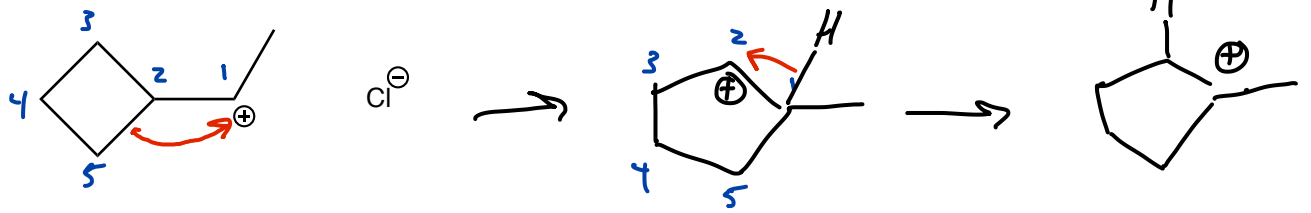
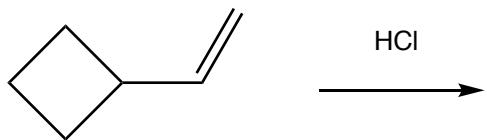
predict outcome



• what is bonded to this C?
~~ethyl group~~
 methyl groups
 hydrogen easiest to move



• e^- 's in bond from C_2 to C_4 are going to leave C_2 and move to C_1 forming a new bond from C_1 to C_4



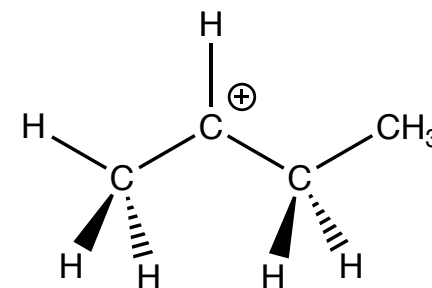
The Carbocation Summary

Sections 6.2, 6.4, and 6.7

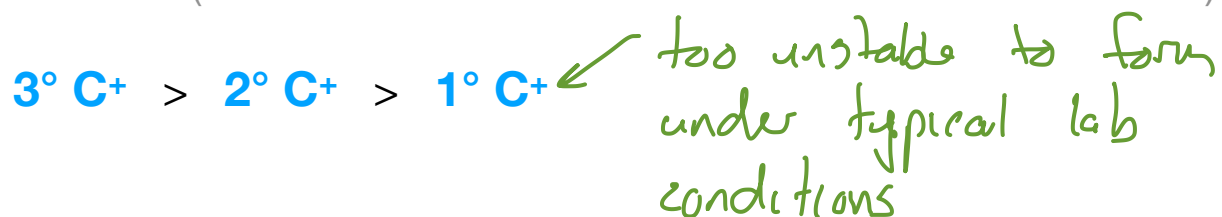
Stability

Getting electron density to a C⁺ helps stabilize the C⁺

e⁻'s in σ-bonds on neighboring carbon atoms stabilize C⁺'s by hyperconjugation



Stability order based on degree of substitution (there are other ways to stabilize C⁺'s that we will see later)



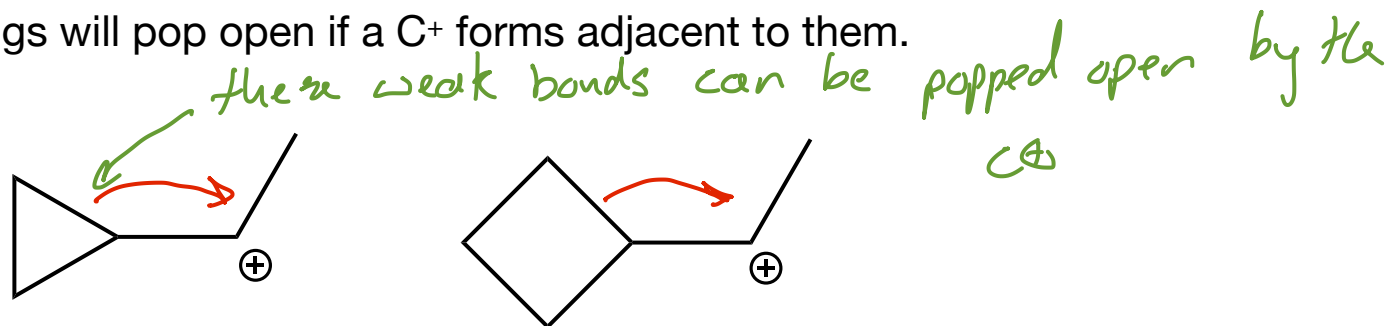
Rearranging C⁺'s

H atoms and methyl groups (CH₃'s) will move from a neighboring C atom if the new C⁺ would be more stable

1° C⁺ will rearrange to a 2° C⁺ or 3° C⁺

2° C⁺ will rearrange to a 3° C⁺

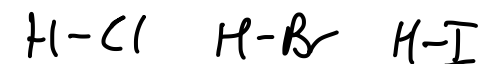
Three- and four-membered rings will pop open if a C⁺ forms adjacent to them.



Summary, so far..

Reaction starts at π bond: π bond is lost and σ bonds to electrophile and nucleophile form

Identify the electrophile: so far the H^+ of a strong acid



Identify the nucleophile: so for the conjugate base of the strong acid, the X^- of the HX

Create intermediate: open π bond and determine where the $+$ goes (based on stability of $+$) and attach electrophile to other end.

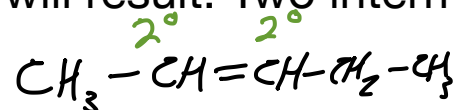
Are the ends of the double bond identical?

Yes. It doesn't matter; put the $+$ at either end and move on.

No. Is there a reason to prefer making one end of the bond $+$?

Yes. Major and minor products will form. Place the $+$ at the end where it will be more stable and move on.

No. ~1:1 mixture of products will result. Two intermediates form each one with a $+$ at one end.



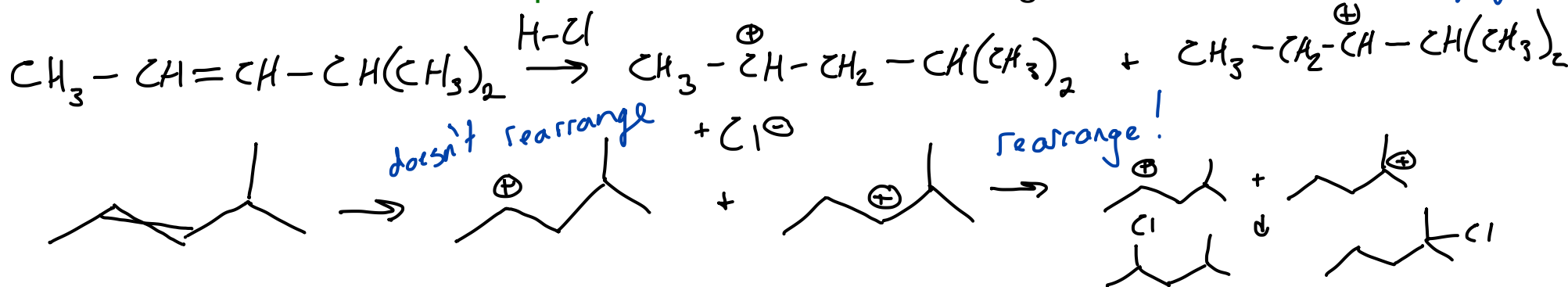
Check for carbocation rearrangement: would plus be more stable on neighboring C?

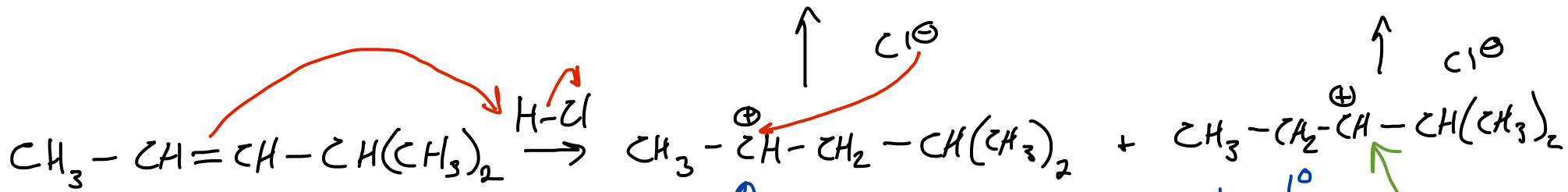
yes, rearrange

no

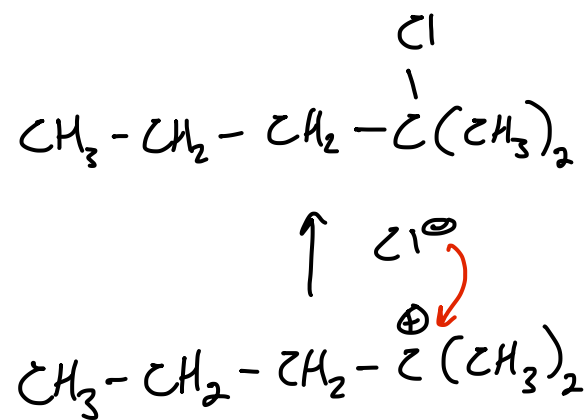
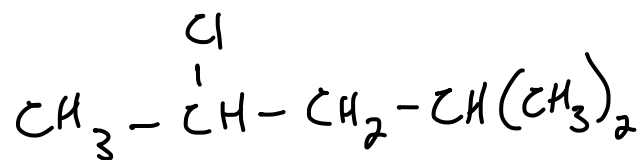
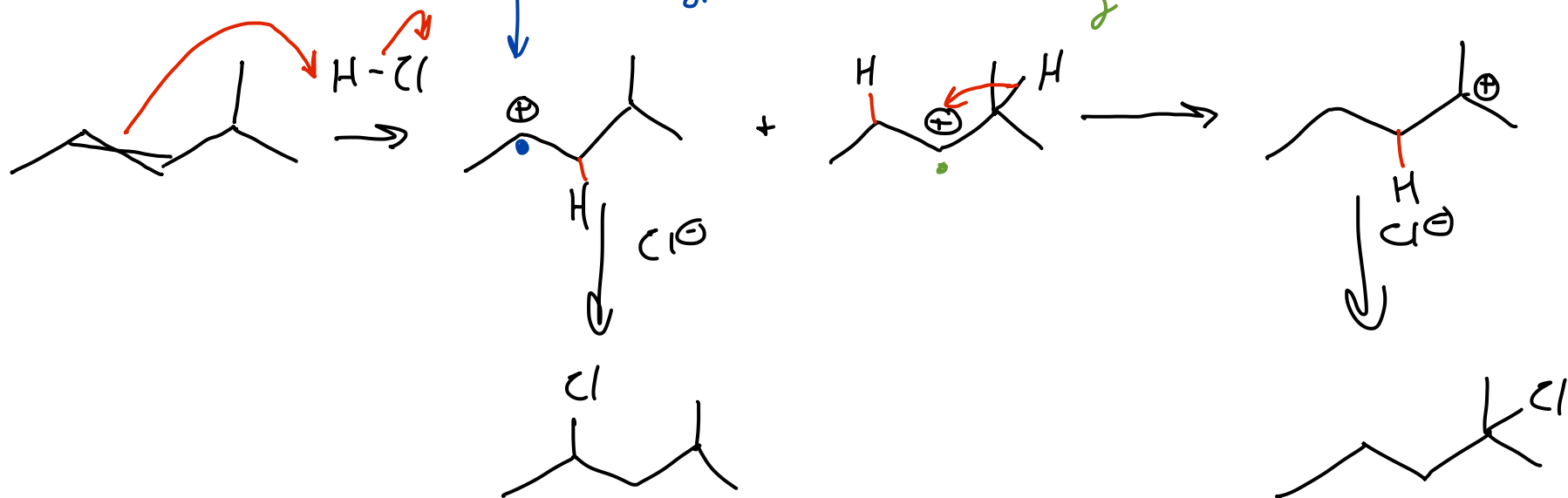
leave + where it is

Make a bond from the nucleophile to the C with the $+$ charge.

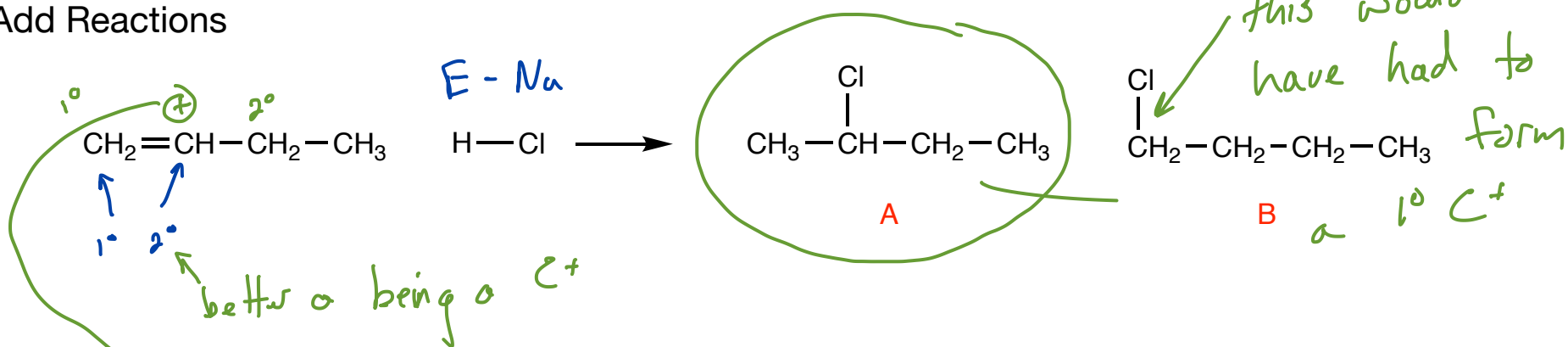




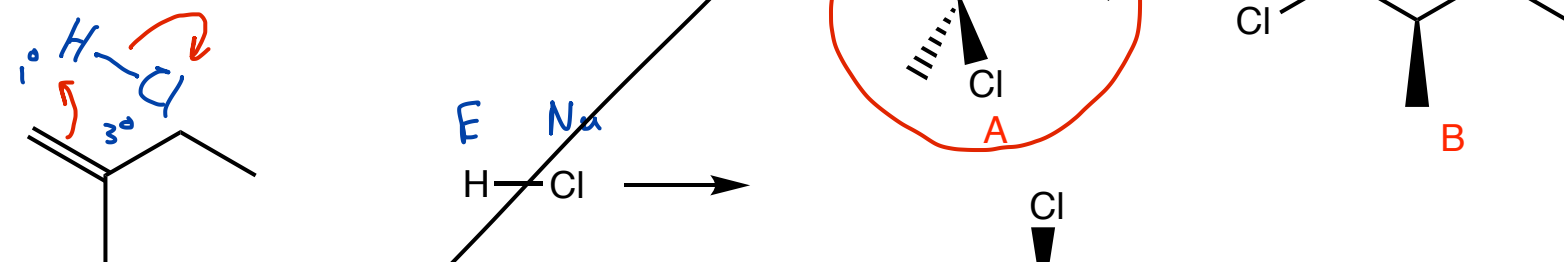
• not going to rearrange to another 2° or to another 2°
 • 2° to 2° no
 2° to 3° yes



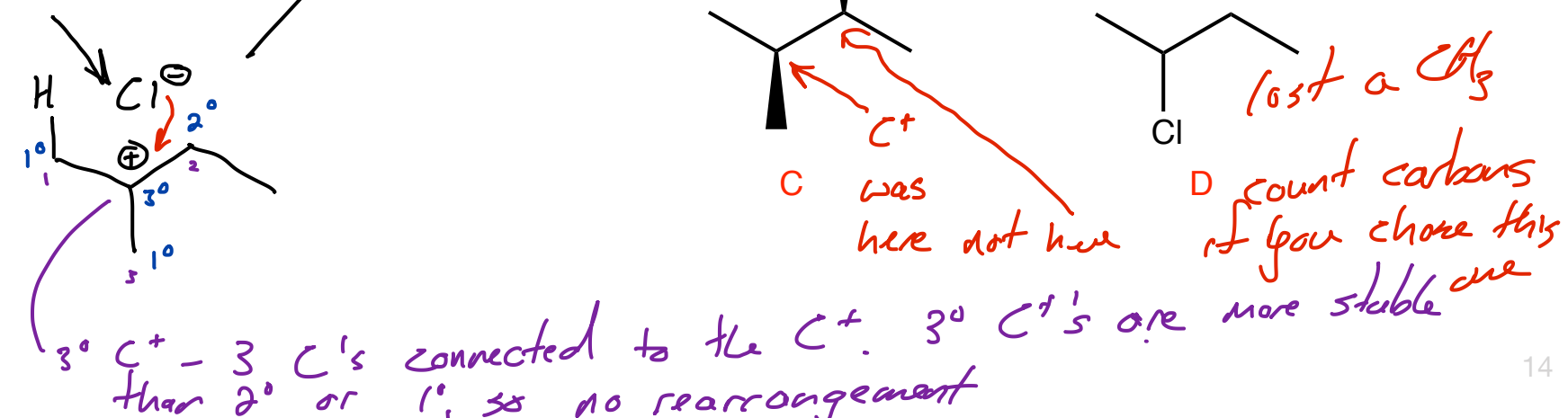
E Add Reactions



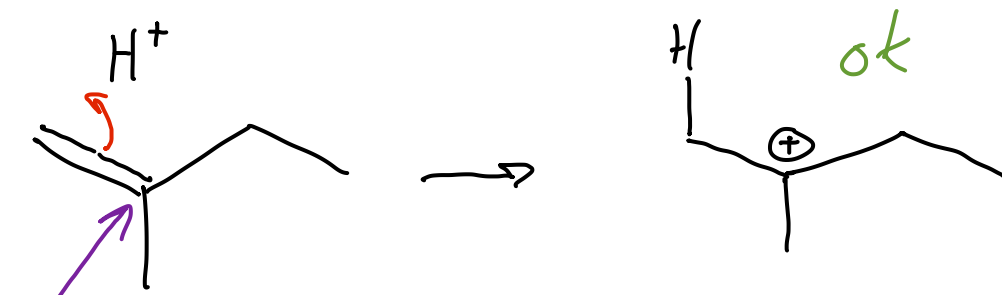
would a C^+ here rearrange? No neighbors are $1^\circ + 2^\circ$



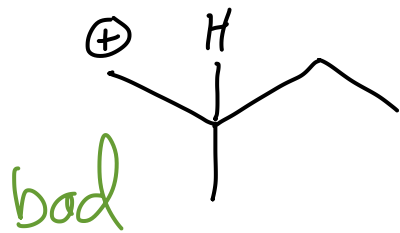
H^+ was electrophile 1°C^+ so it should be here



the H^+ is \oplus , but it pulls the e^- 's toward itself and becomes \ominus



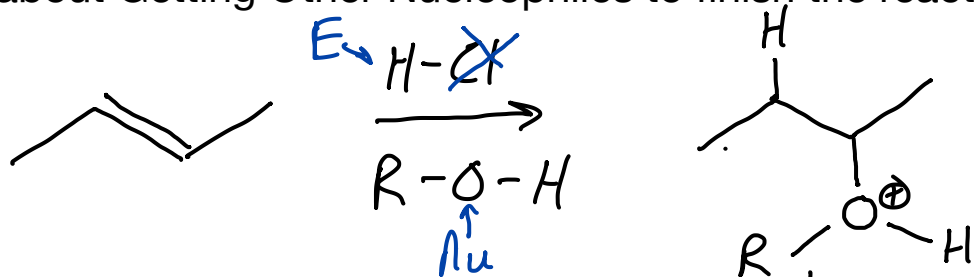
one of the ends of the db has to lose the e^- 's so a C to H bond can form



the 3° C atom is surrounded by σ bonds (more so than the 1°) so it is easier for the H^+ to pull the e^- 's away from the 3° C $^+$

How about Getting Other Nucleophiles to finish the reaction

add a nucleophile Section 6.7

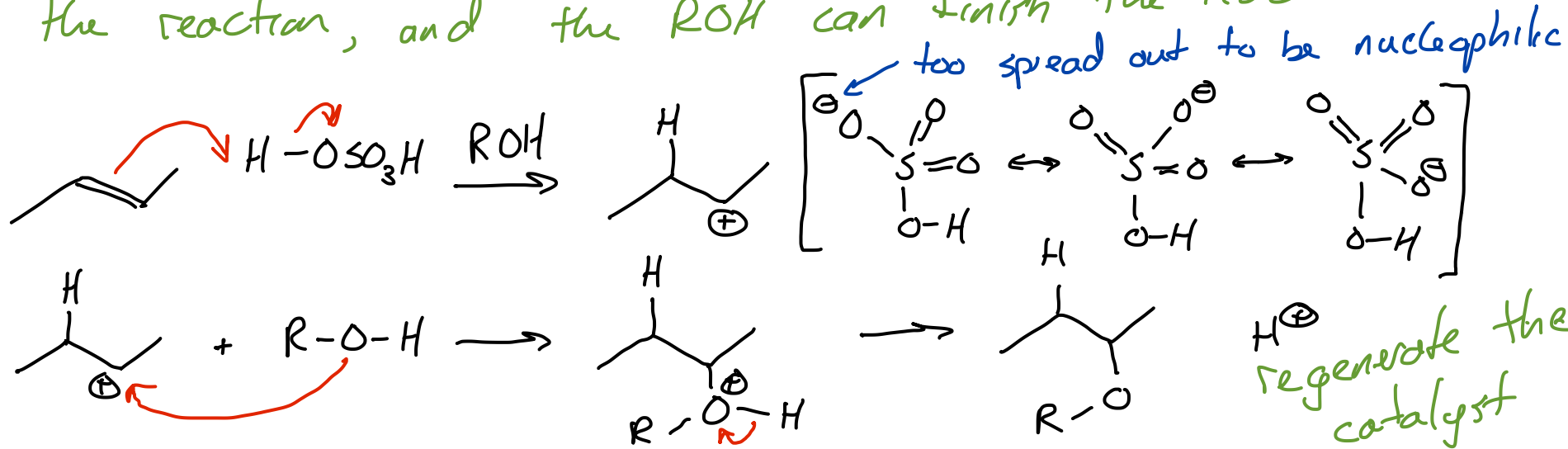


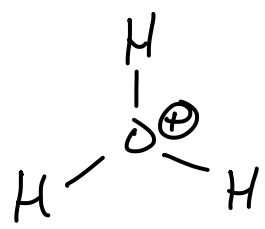
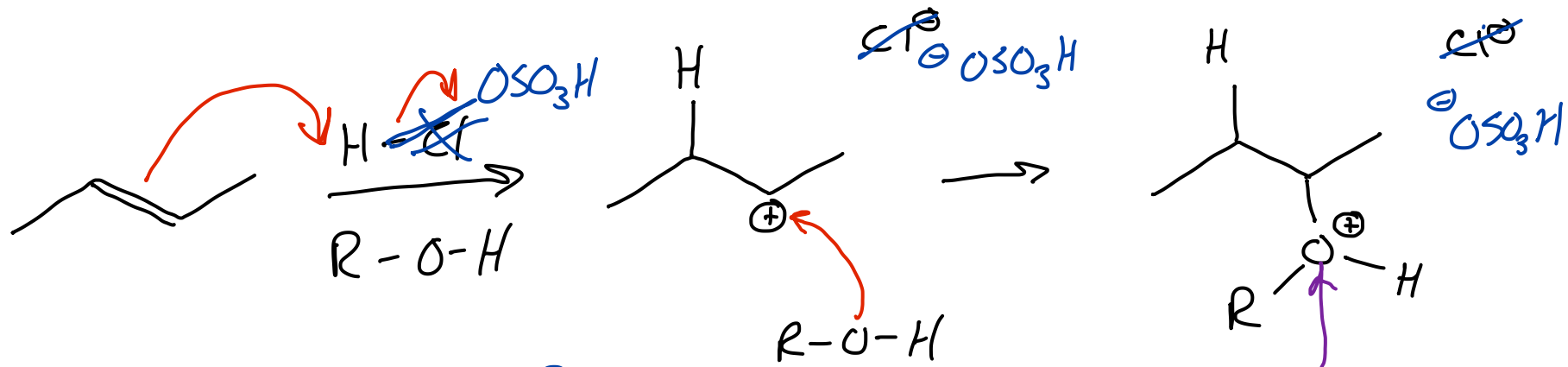
choose one that won't react with the HCl... strong or weak base?

we should choose a weak base so the HCl isn't neutralized

NaI or NaBr for each step 1 Cl^- is formed from the HCl but the added nucleophile is present at a much higher conc

$\text{R}=\text{H} = \text{H}_2\text{O}$ $\text{R}=\text{CH}_3$ CH_3OH The H of the acid starts the reaction, and the ROH can finish the reaction.



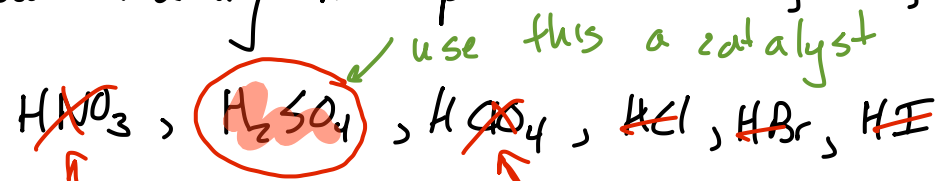


if $[\text{ROH}] > [\text{Cl}^-]$
 then ROH wins
 the competition

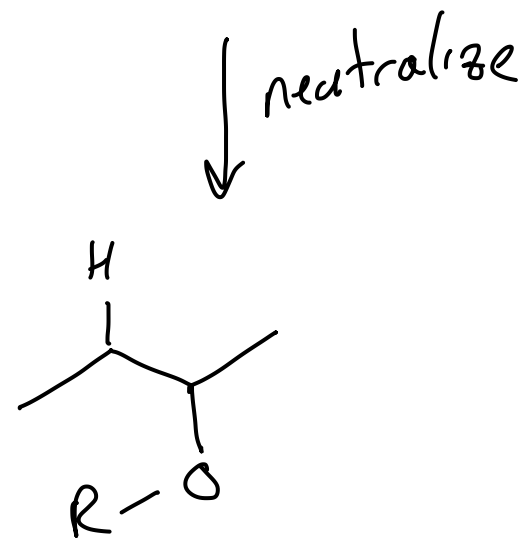
if $\text{R} = \text{H}$
 alcohol
 if $\text{R} = \text{C}$
 ether

we don't need 1:1 acid we can use an acid
catalyst

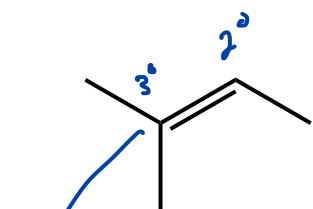
our catalyst
 needs to be a strong acid
 but ideally not produce Cl^- , Br^- , or I^- ~~HF~~



too strongly oxidizing to be useful

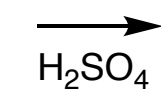
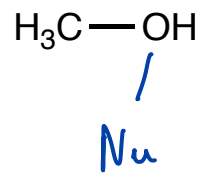
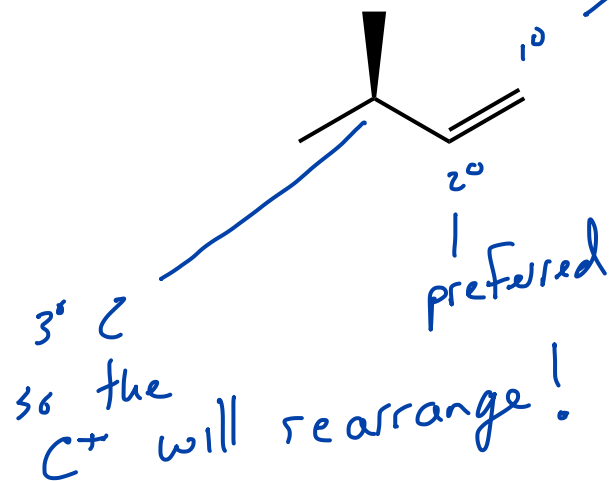
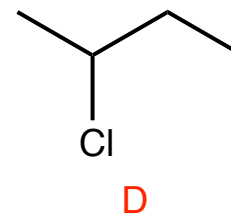
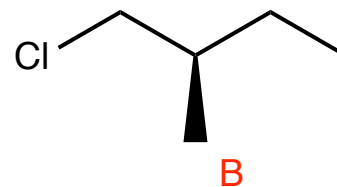
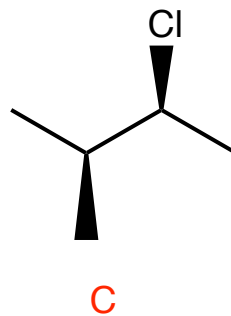
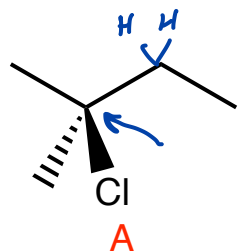
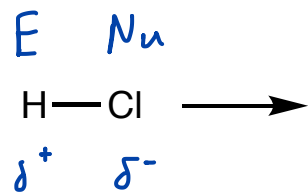


E Add Rxns

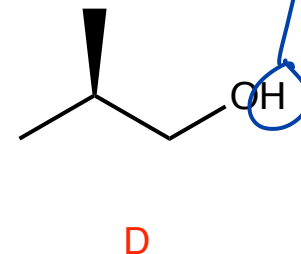
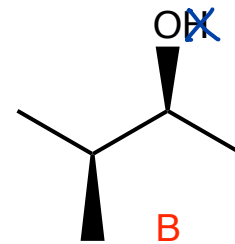
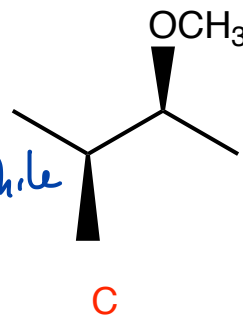
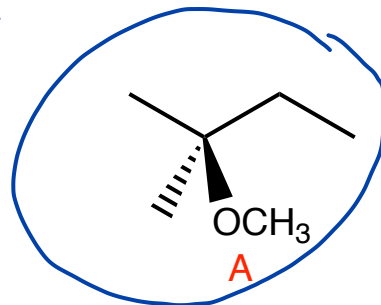
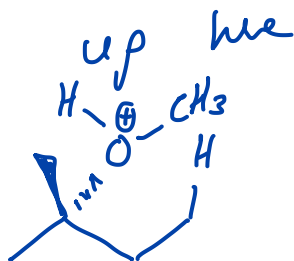


C^+ forms here
check rearrangement?

no rearranging so the ends



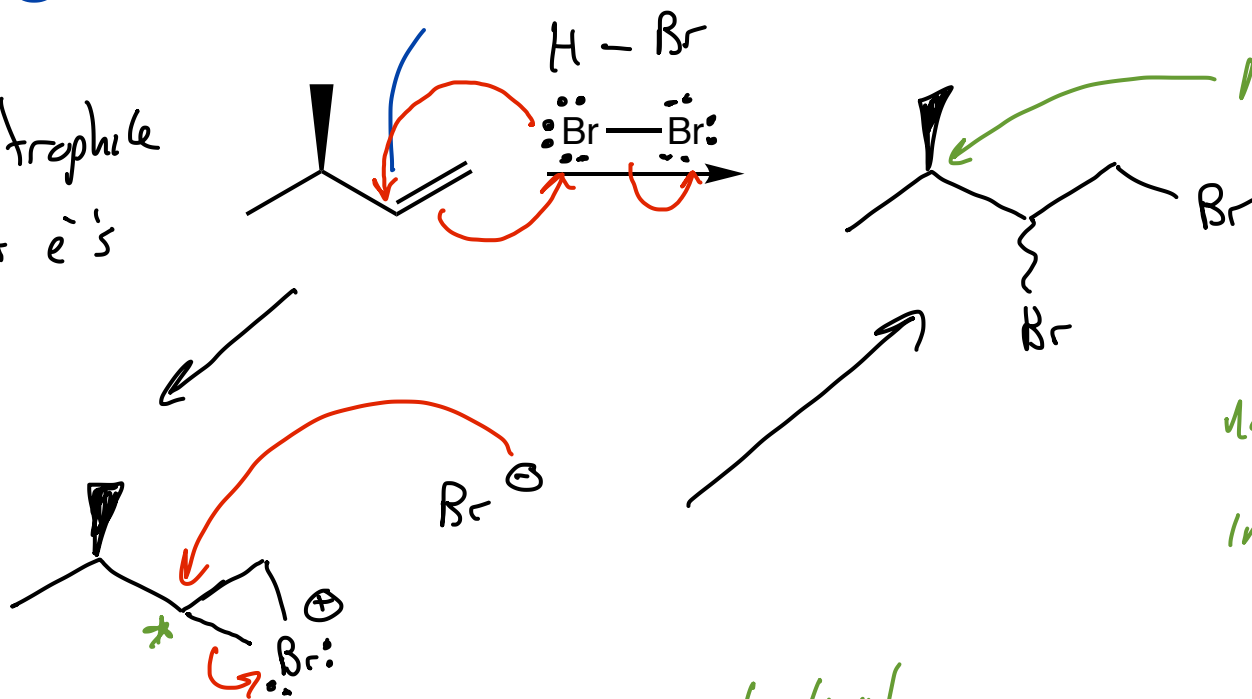
H^+ electrophile
 HSO_4^- not a nucleophile



H^+ has to come off to regenerate C^+

if a C^+ were to form here then it would rearrange

The Br electrophile has lone-pair e⁻'s



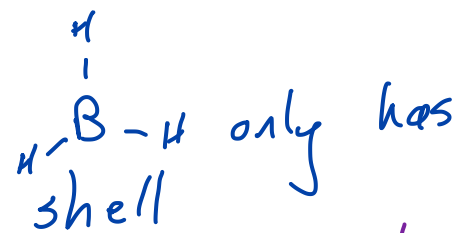
the half of the reaction didn't go here so there must not be a C^+ intermediate

a bromonium ion forms... same thing happens with Cl_2

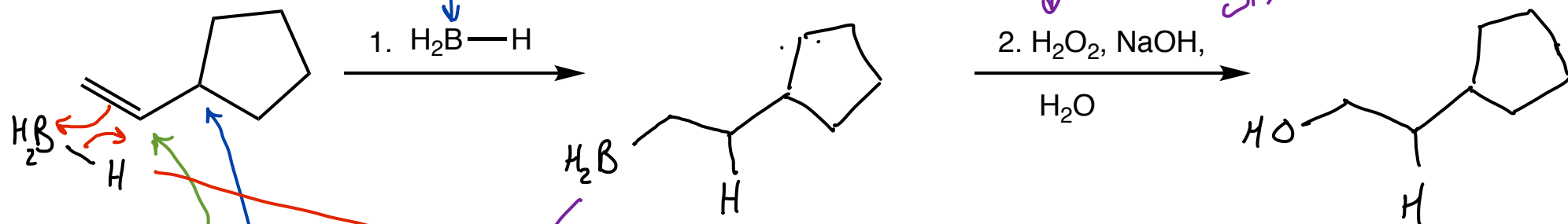
same regioselectivity because the C to Br^+ bond has to break and as it does the C becomes δ^+

Hydroboration-oxidation (avoiding carbocation formation)

B is an electrophile because
6 e⁻ in its valence shell



This just knocks this
B off and replaces it
with an OH



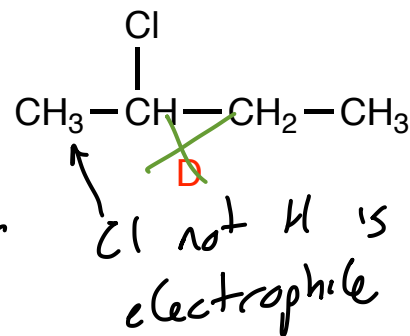
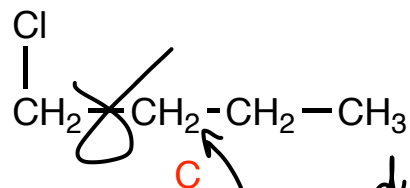
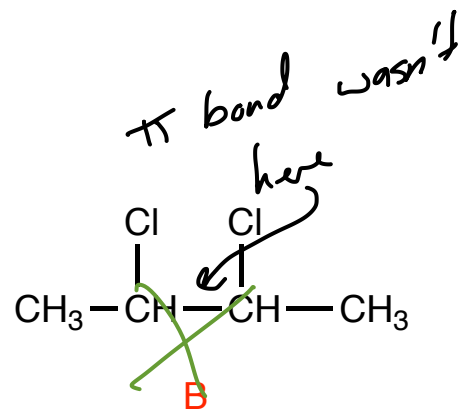
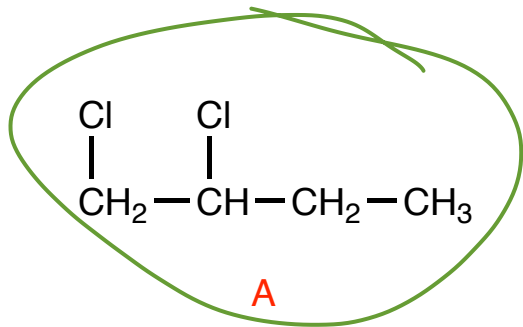
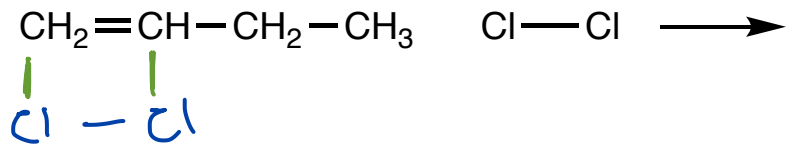
if c⁺
formed
here,
it would
rearrange
to here

reacts 2 more
times
BH₃ can react
3 times, once
for each of its
3 B-H bonds

this reaction is a
one step mechanism...
B adds to the less substituted
end and H (the nucleophile)
goes to the more substituted
end

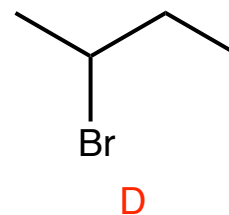
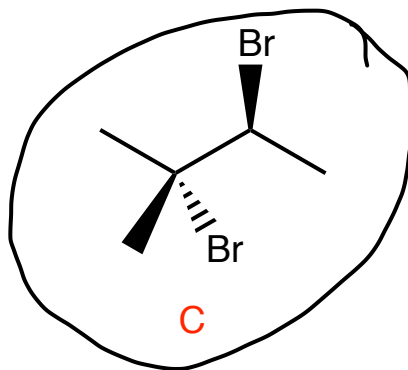
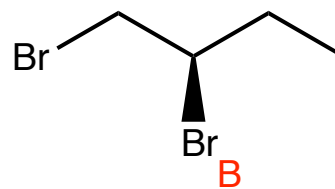
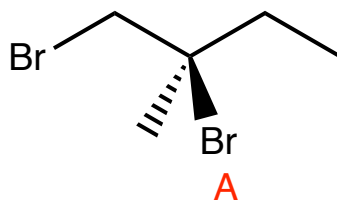
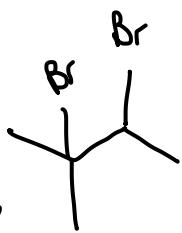
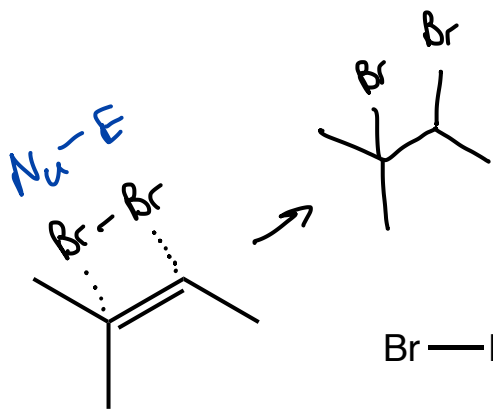
Reactions

reacts at π bond.
 Chloronium intermediate means no worrying about rearranging
 E Nu



where did we get an H from?

Cl not H is electrophile



Reactions

