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

Next Classes

Section 6.9
Addition of halogens

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.

Wednesday lab notebooks will be returned on Monday. Stop by my office if you really want it back today.

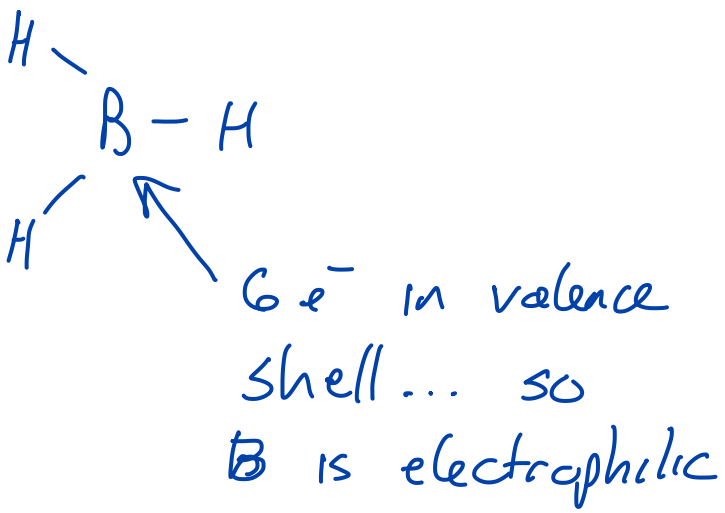
We will look at three kinds of electrophilic addition reactions each of them have similar regioselectivity (section 6.7) due to similarities in their transition states, but there each have different mechanisms based on the specific class of electrophile.

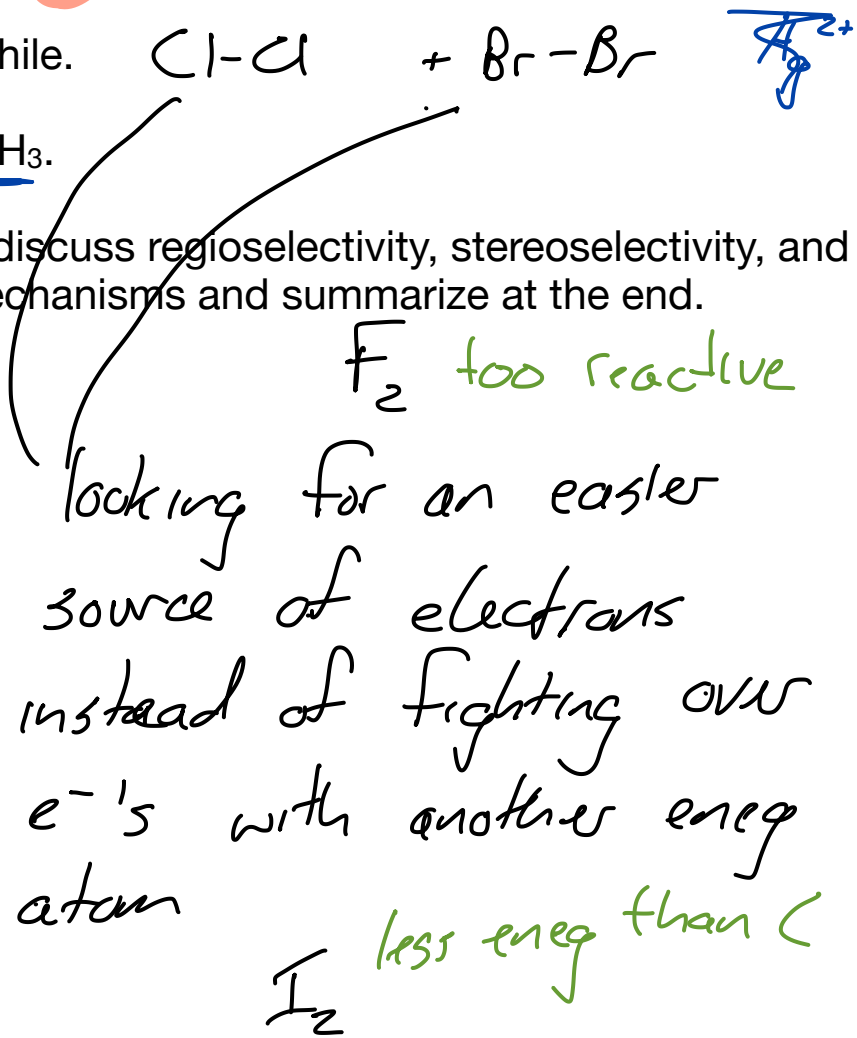
Sections 6.1, 6.2, 6.5, 6.6, 6.7 focus on using strong acids, H^+, as the electrophile.

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.

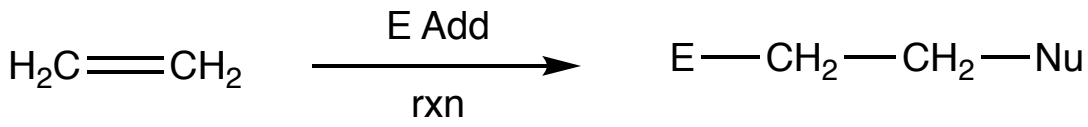
We will mix sections 6.12 and 6.13 in with sections that discuss regioselectivity, stereoselectivity, and stereospecificity in with our discussion of the various mechanisms and summarize at the end.





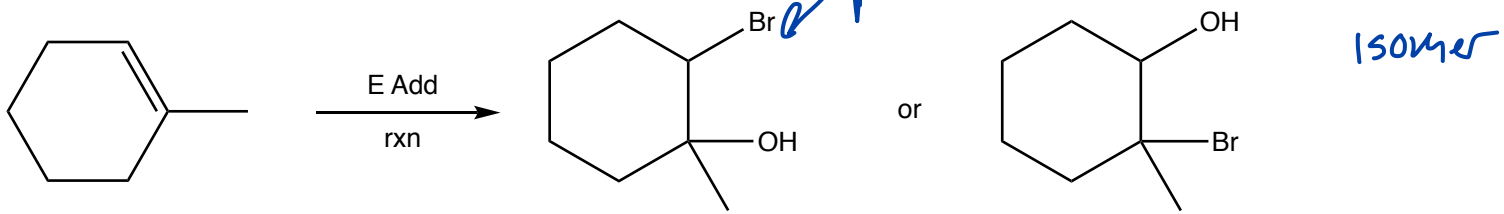
Definitions

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



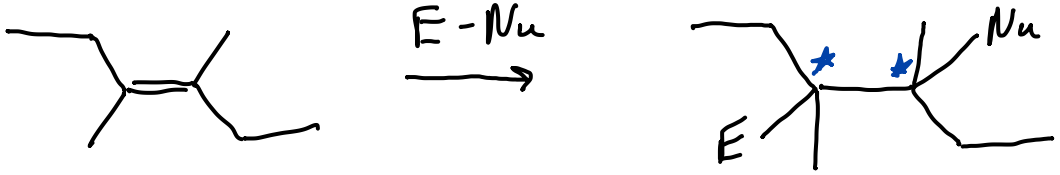
E = generic electrophile Nu = generic nucleophile

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



preferental formation of this isomer

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



2 chirality centers form

R,R ; R,S ; S,R ; S,S

if 1 is prefered over the other then stereoselective

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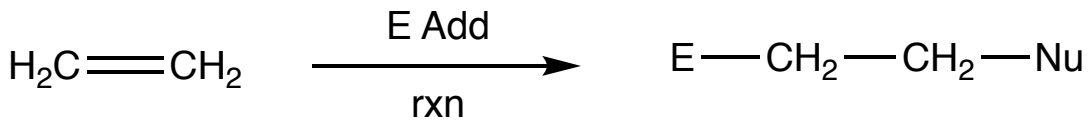

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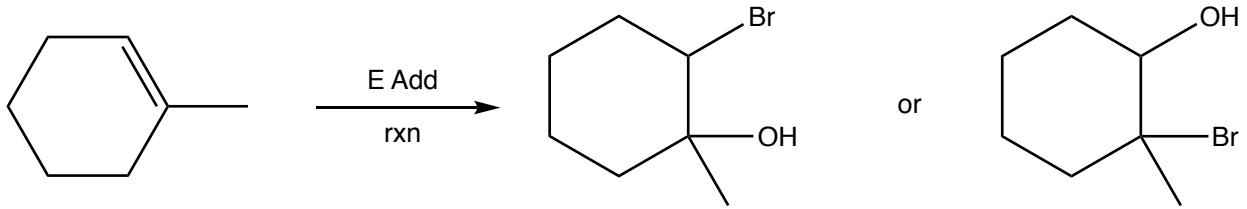
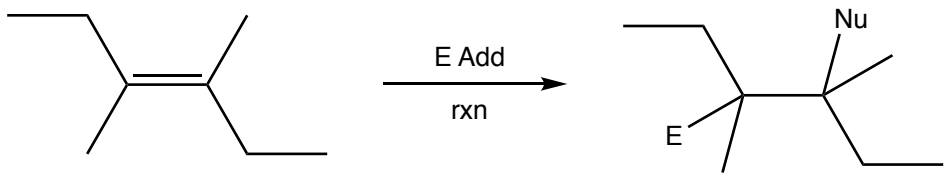
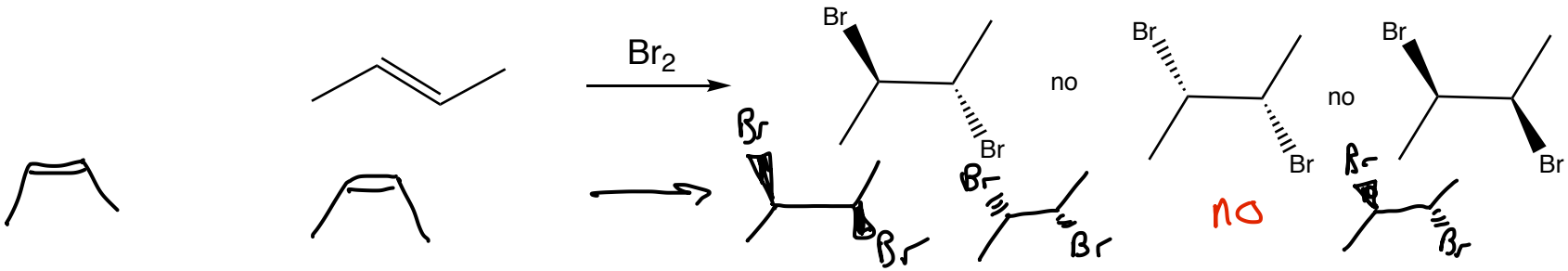


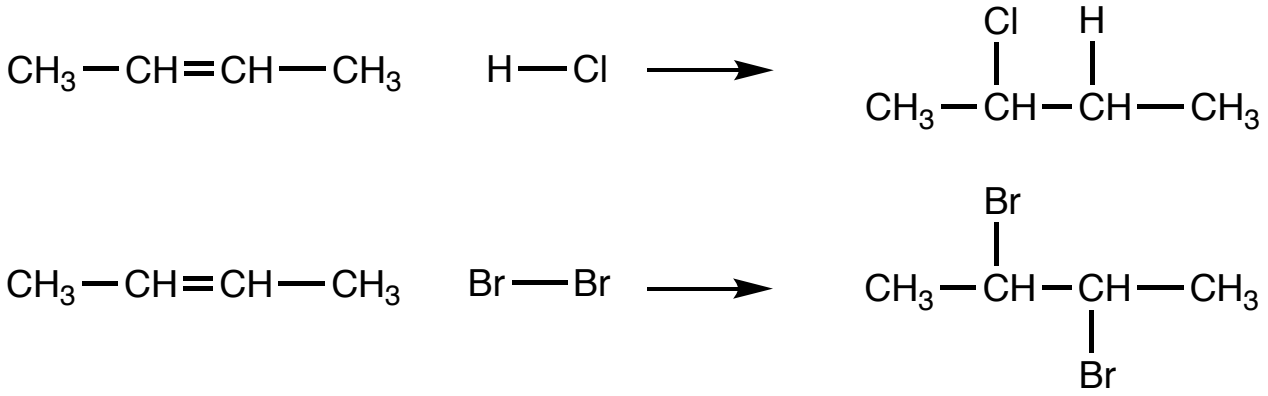
Stereoselectivity: The ability to prefer the formation of one stereoisomer over another.



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

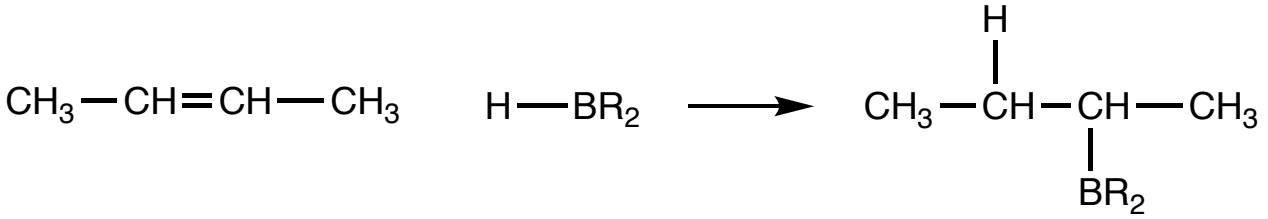


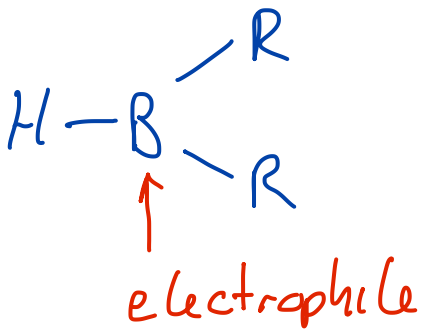
Two step mechanism (6.1, 6.5, 6.6)

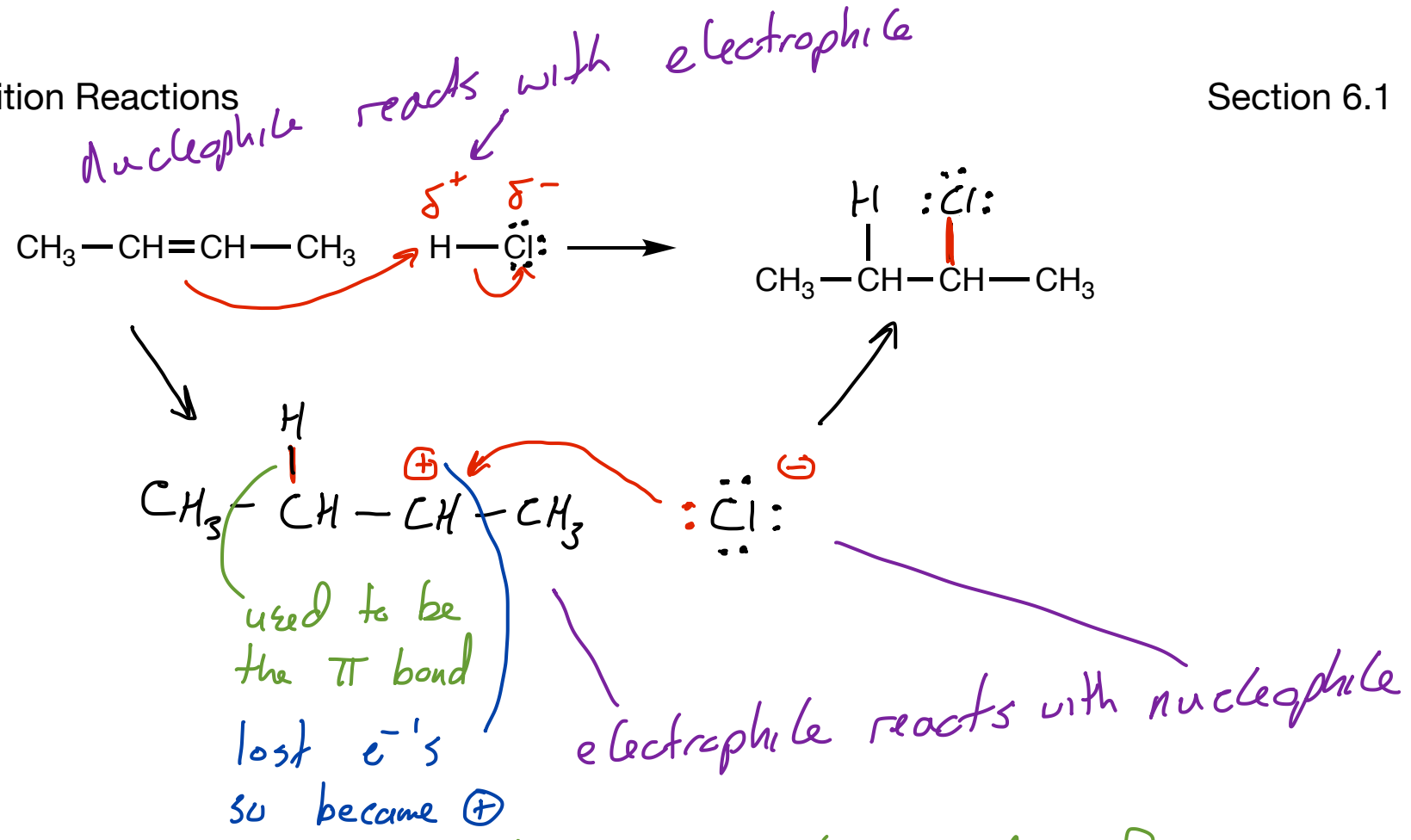


alkene reacts with E → reactive intermediate reacts with Nu → products

One step mechanism (6.8)







With H^+ electrophiles, carbocation intermediates form

Strong acids required.. weak acids like acetic acid

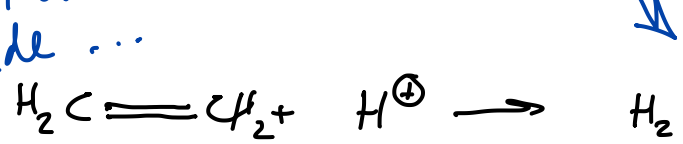
vinegar) can't initiate the reaction

though dangerous not strong enough for this rxn

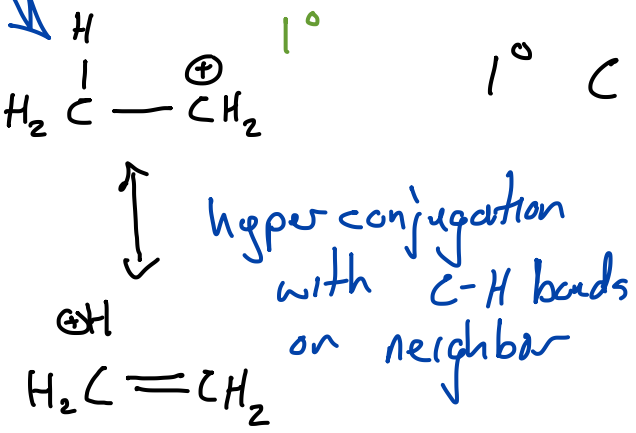
H-Cl, H-I, H-Br, ~~H-F~~

pKa -6 -11 -9 ~~4~~

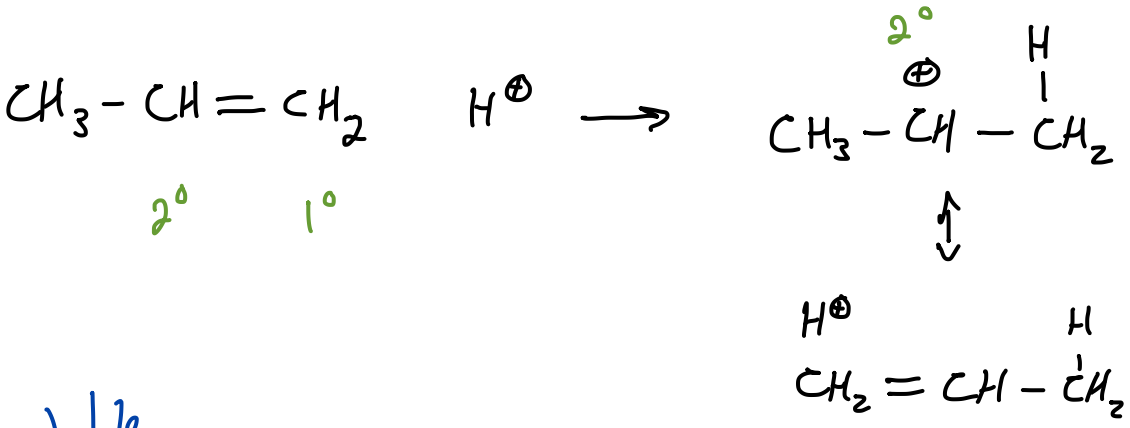
least stable not made ...



1° 1° C+ too unstable to form under typical lab conditions



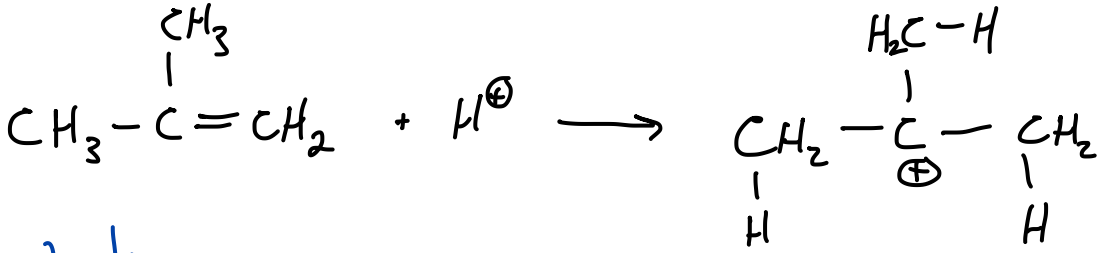
hyperconjugation with C-H bonds on neighbor



2° 1°

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

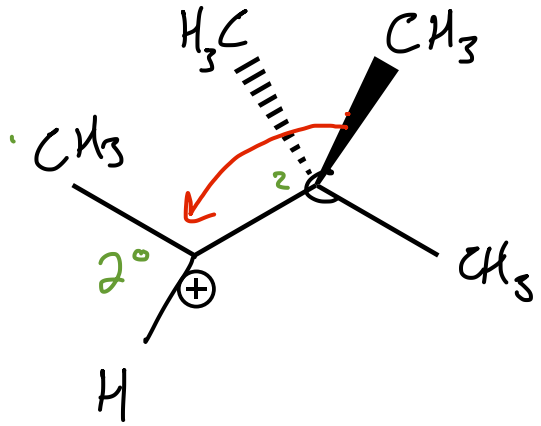
most stable



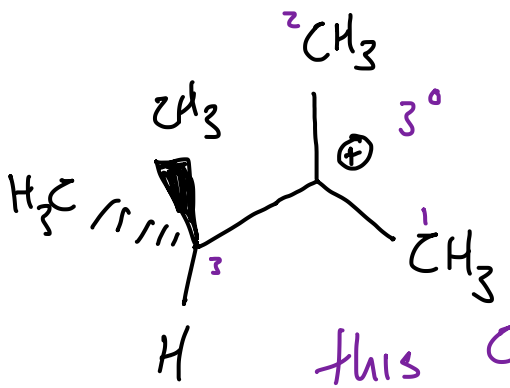
easiest to form

9 neighboring σ bonds to do hyperconjugation

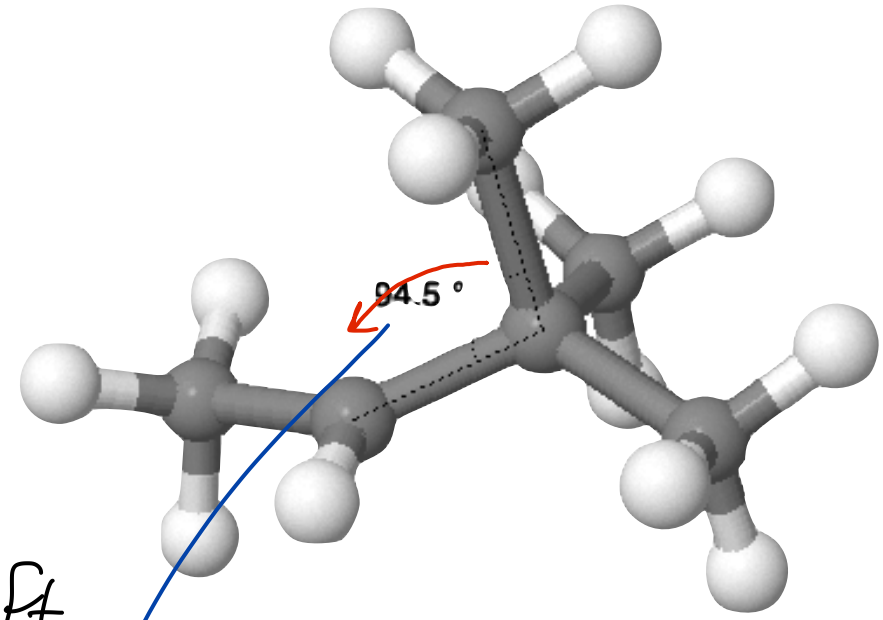
if doing so results in a more stable C⊕



1,2-methyl shift



this C+ is more stable so we don't go back to the 2° C⊕



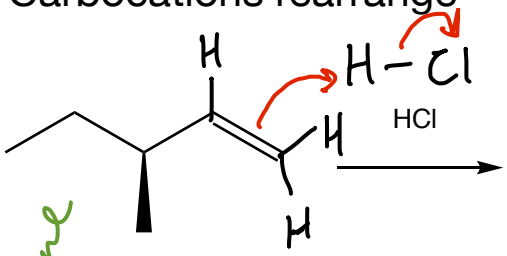
lowest energ structure for this C⊕

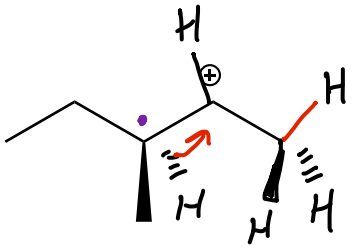
This bond angle is not 109.5 - 112°

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

Carbocations rearrange

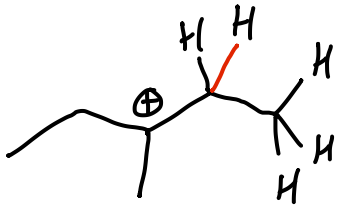
predict outcome





2°

1,2-hydride shift

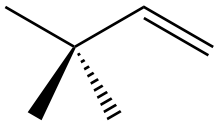


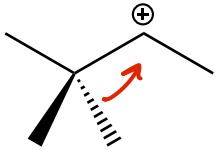
3°

- what is bonded to this C?

~~ethyl group~~

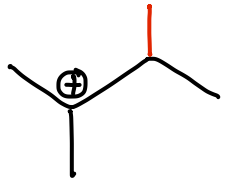
methyl group hydrogen easiest to move



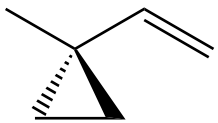


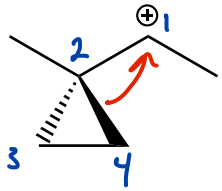
2

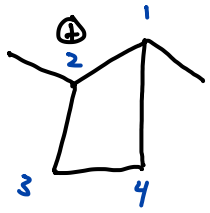
1,2-methyl shift



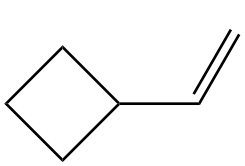
3°

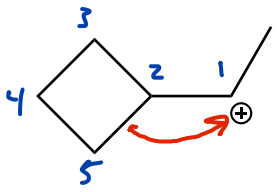


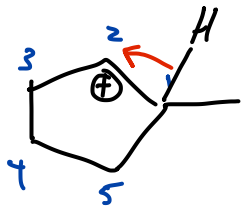


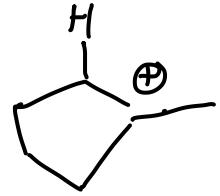


- e⁻'s in bond from C_2 to C_4 are going to leave C_2 and move to C_1 forming a new bond from C_1 to C_4

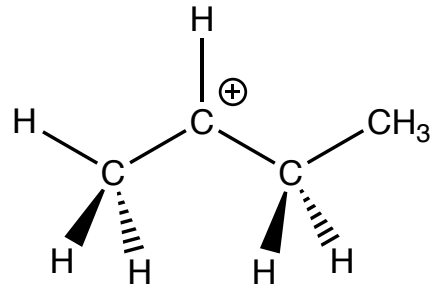








Stability



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 was to stabilize C+'s that we will see later)

3° C+ > 2° C+ > 1° C+ ← too unstable to form under typical lab conditions

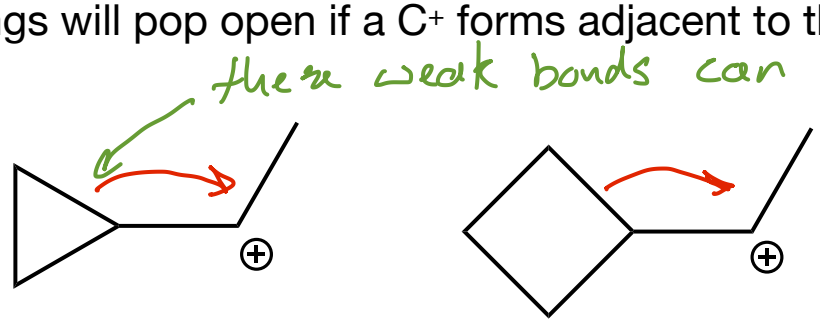
Rearranging C+'s

H atoms and methyl groups (CH_3'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 H-Cl H-Br H-I

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.

$CH_3-CH=CH-CH_3$

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.

$CH_2=C(CH_3)_2$

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

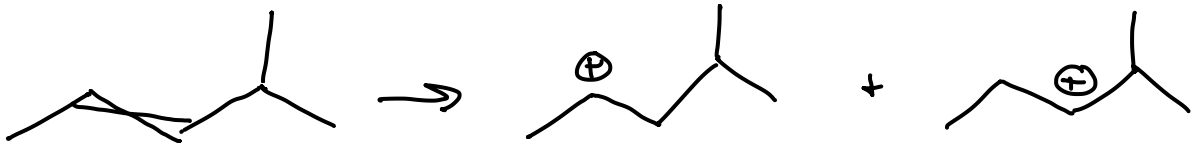
$CH_3-\overset{2^\circ}{C}H=\overset{2^\circ}{C}H-CH_2-CH_3$

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.

$CH_3-CH=CH-CH(CH_3)_2 \xrightarrow{H-Cl} CH_3-\overset{\oplus}{C}H-CH_2-CH(CH_3)_2 + CH_3-CH_2-\overset{\oplus}{C}H-CH(CH_3)_2$



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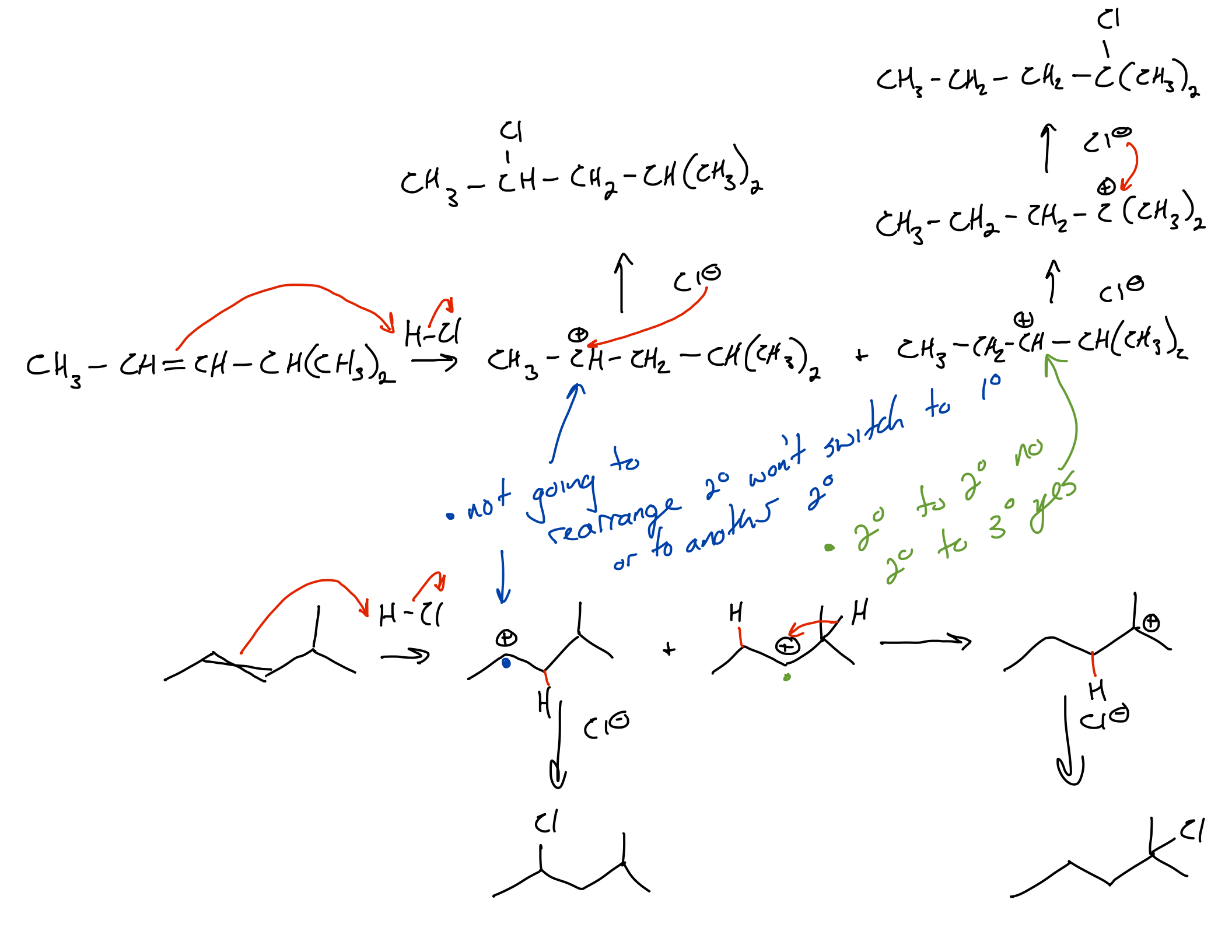
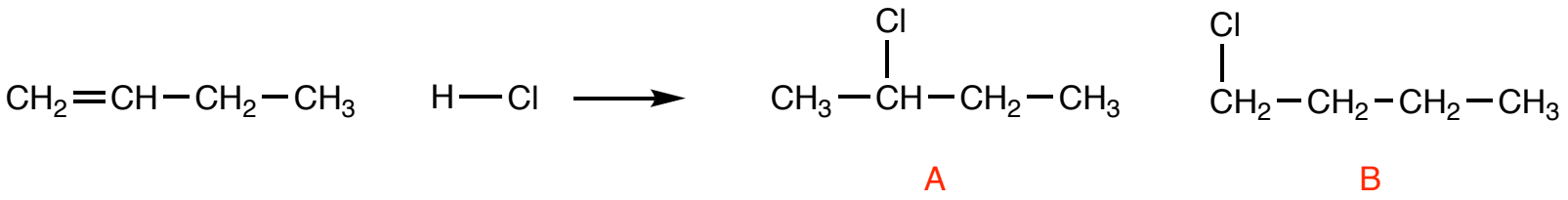
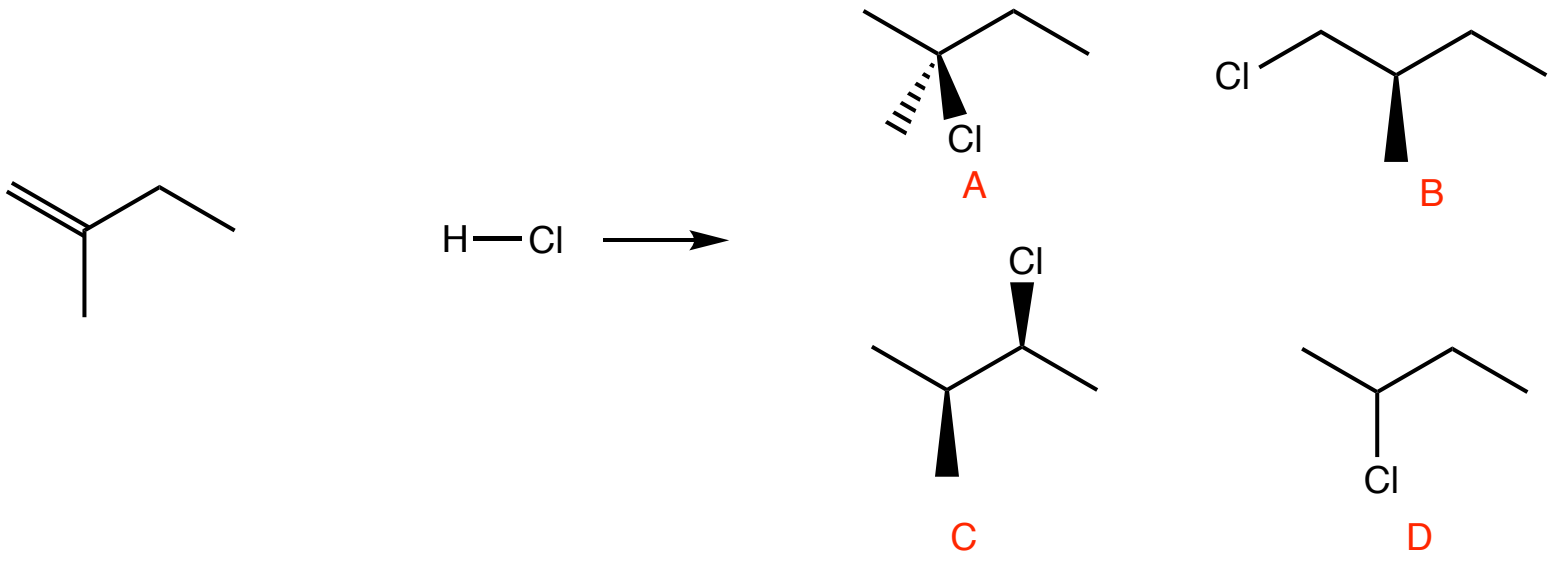

CH3 – CH = CH – CH(CH3)2
H–Cl
CH3 – CH – CH2 – CH(CH3)2
Cl
Cl⊖
CH3 – CH2 – CH2 – C(CH3)2
CH3 – CH2 – CH – CH(CH3)2
• not going to rearrange 2° won't switch to 1° or to another 2°
• 2° to 2° no
2° to 3° yes
H–Cl
H
Cl⊖
Cl

E Add Reactions

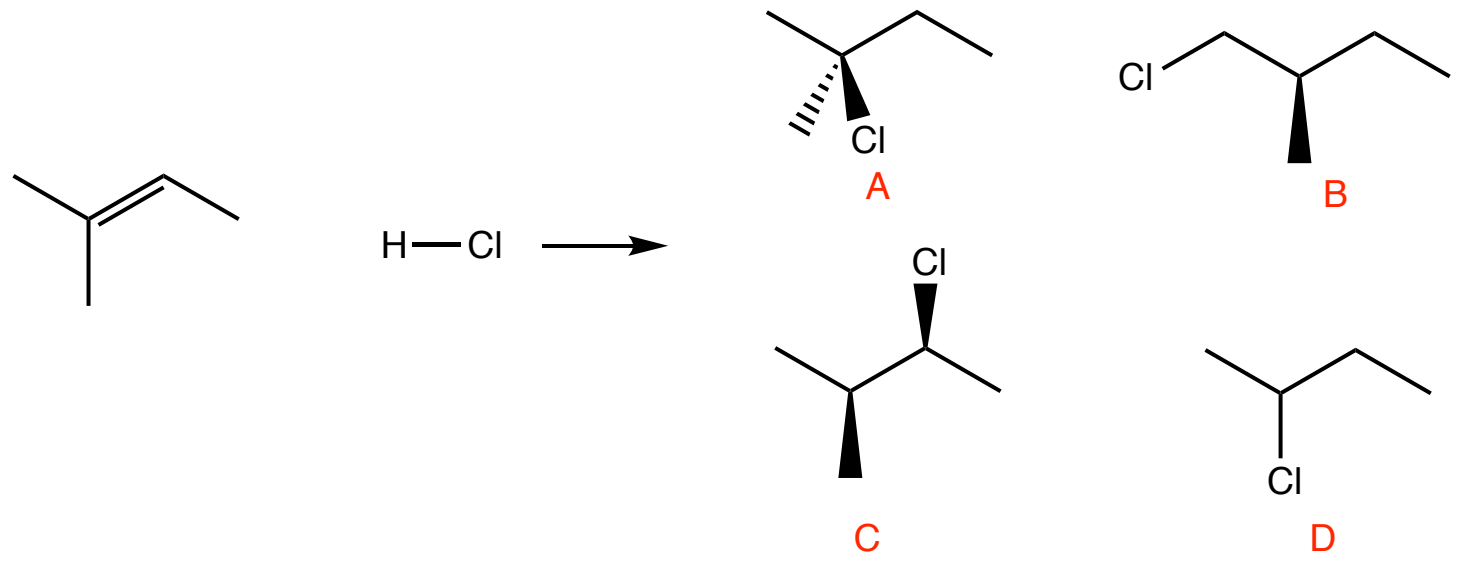


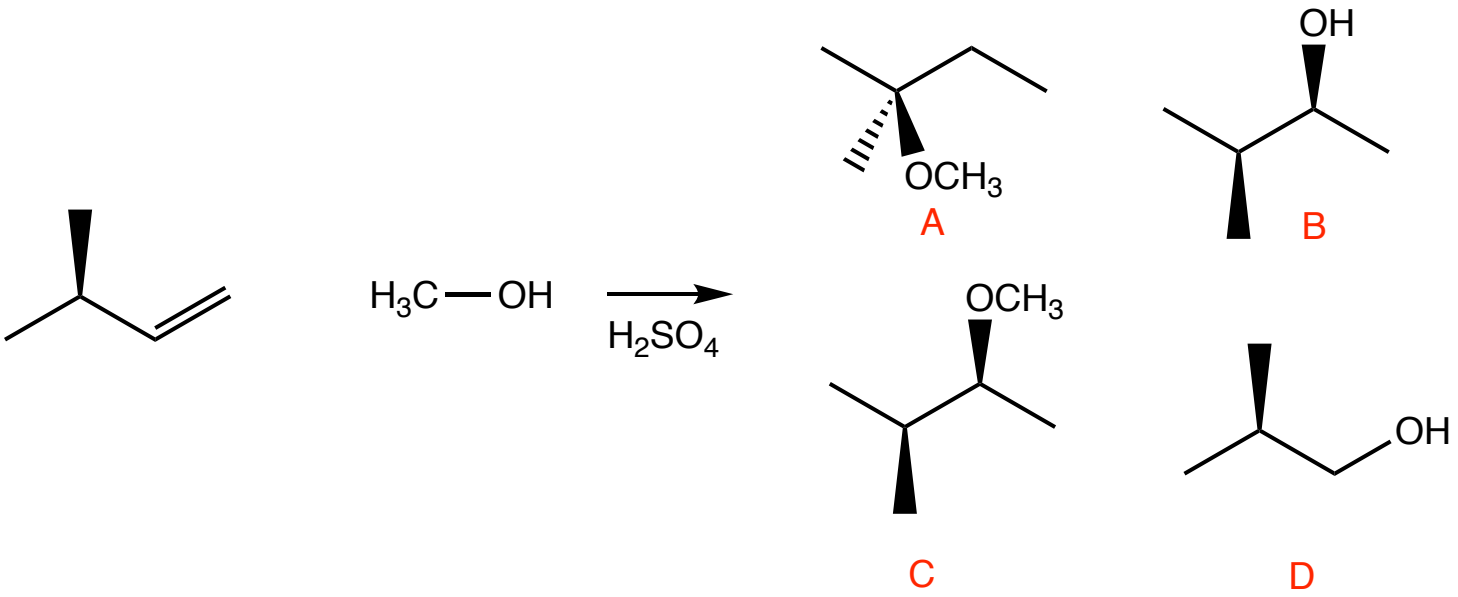
A B



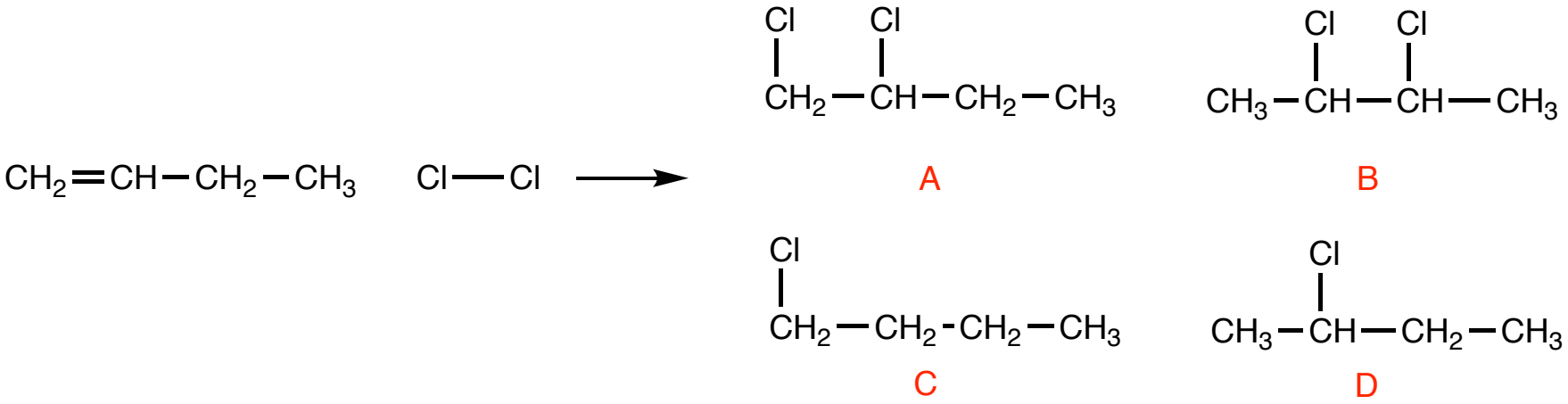
A B C D

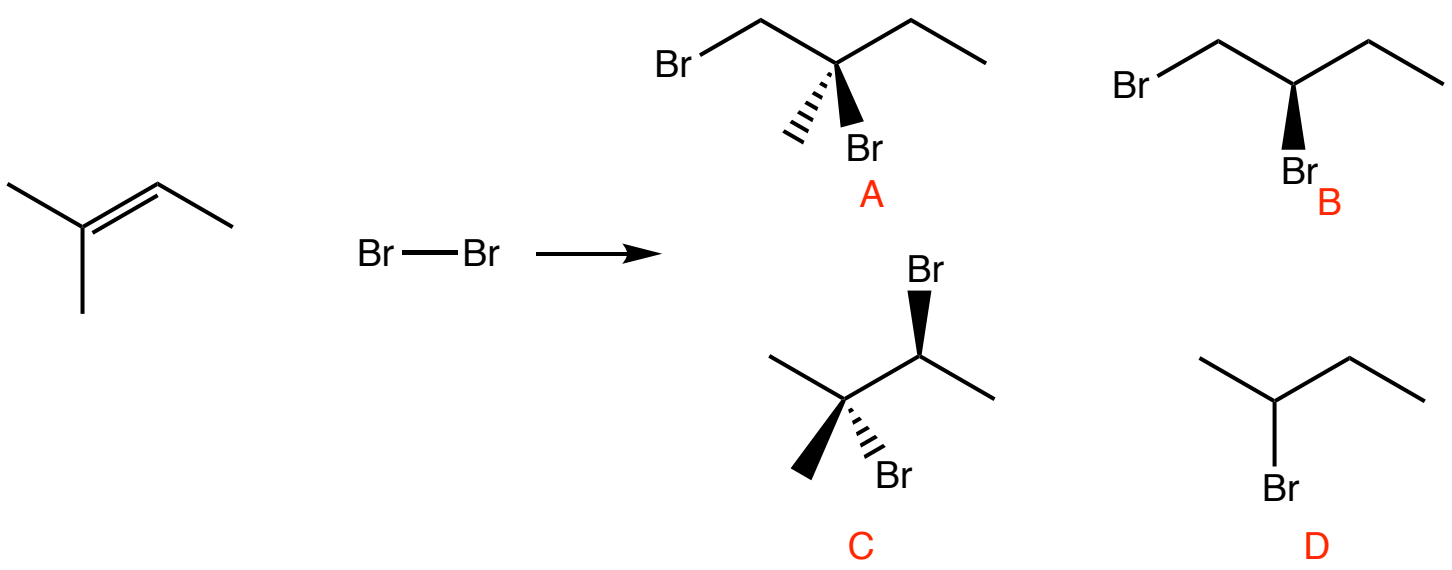
E Add Rxns



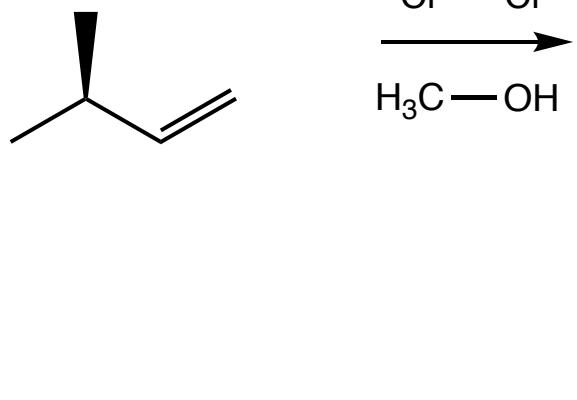


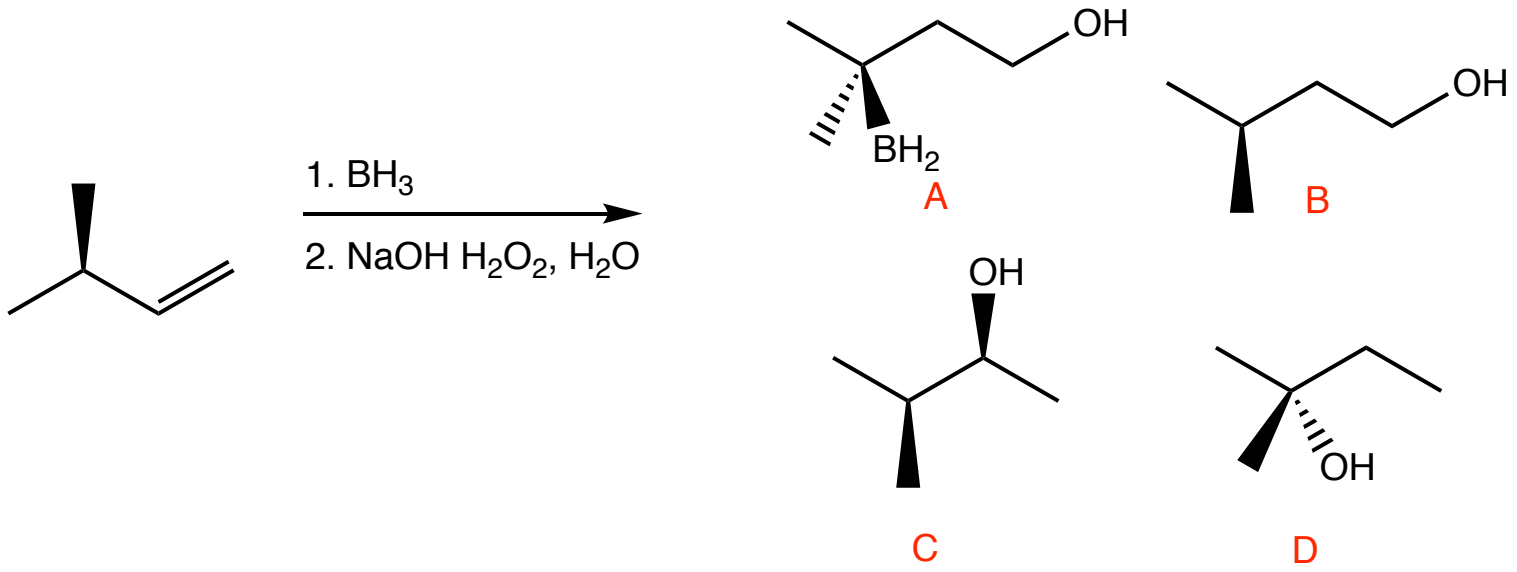
Reactions


CH2=CH–CH2–CH3
Cl–Cl
Cl Cl
CH2–CH–CH2–CH3
A
Cl Cl
CH3–CH–CH–CH3
B
Cl
CH2–CH2–CH2–CH3
C
Cl
CH3–CH–CH2–CH3
D


Br–Br
Br
Br
A
Br
Br
B
Br
Br
C
Br
D

Reactions


Cl—Cl
H3C—OH
Cl
OCH3
A
OH
Cl
B
OCH3
C
OCH3
Cl
D


1. BH3
2. NaOH H2O2, H2O
OH
BH2
A
OH
B
OH
C
OH
D