

Today: Reactions!

Tomorrow (Fri.),

Review 3-5 pm SC C

Monday exam

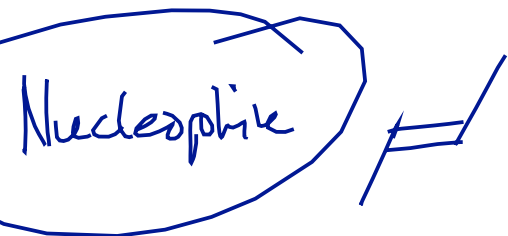
8:10 am - 9:20

lecture 9:30.

Sunday Help Room SC 302
2-6 pm.

An Introduction to Reactions of Alkenes

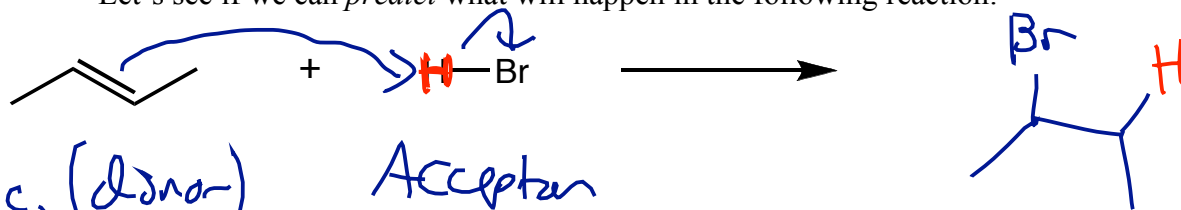
- A review: What are the important orbitals in an alkene?



HOMO: $\pi_{C=C} \rightarrow$ good donor

LUMO: $\pi^*_{C=C} \rightarrow$ not good acceptor

- Let's see if we can predict what will happen in the following reaction:

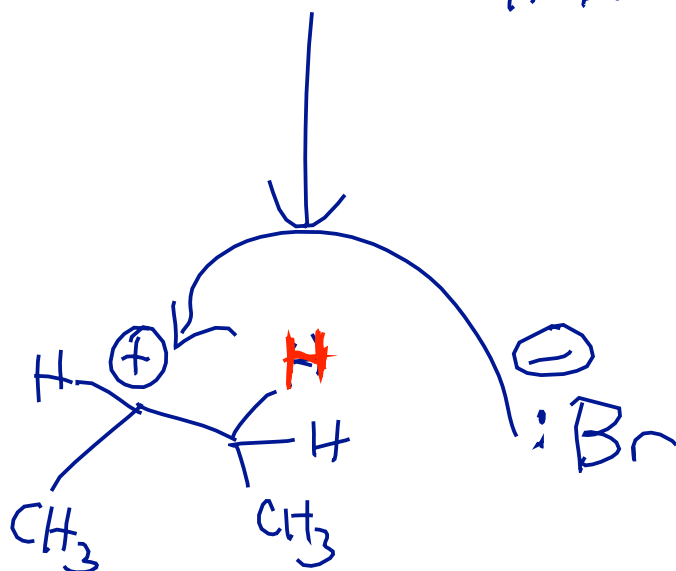


Nuc. (donor)

Acceptor

$\pi_{C=C}$

σ^*_{H-Br}



Acceptor
C vacant
p

Donor
Br lp

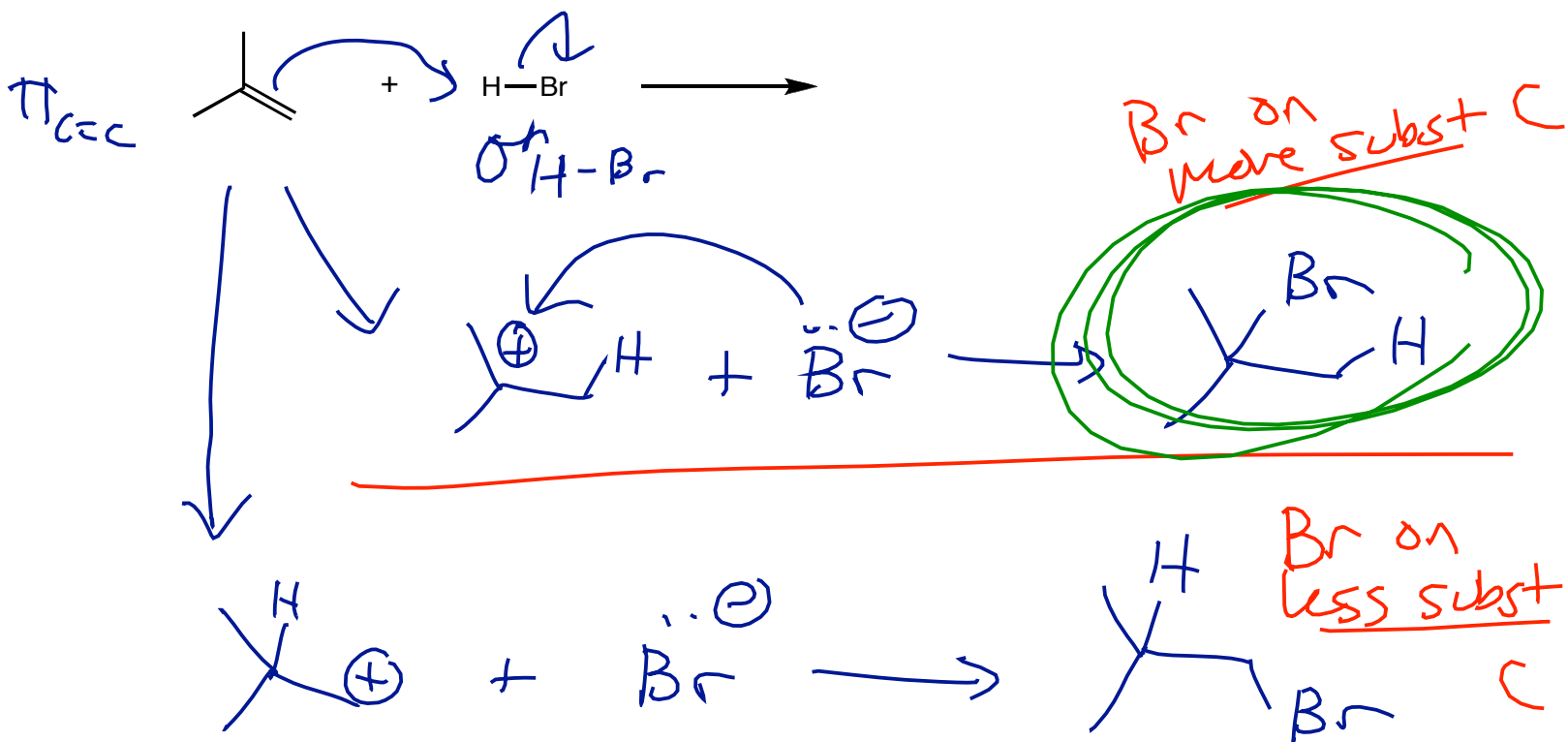
Alkene
addition;

Add H and Br
"across" $\pi_{C=C}$

Reading: Section 4.7

Regioselectivity: "Markovnikov's Rule"

- Now consider the following reaction. Can you *predict* what will happen?

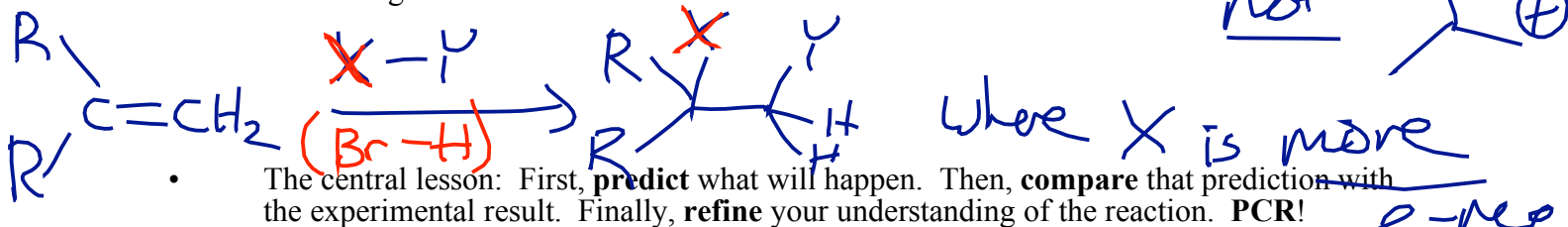


- What is the *observed* product of this reaction? What does this observation tell you about the *mechanism* of this reaction?

Product has Br on more subst. C

Therefore intermediate carbocation was 

- Is there a general *rule* that we can formulate about alkene additions?



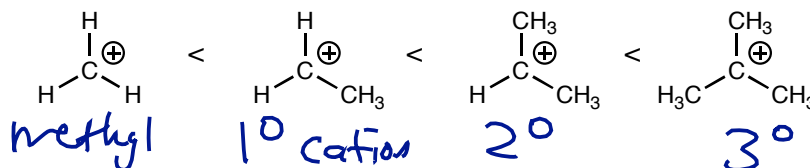
Reading: Section 4.7

More e-req atom \rightarrow more subst. carbon

The Stability of Carbocations

- The relative stability of carbocations exhibits the following trend:

less
stable



more
stable

less
substituted

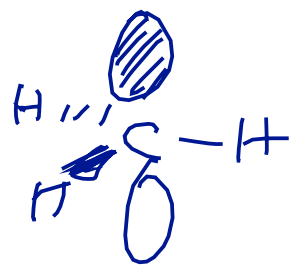
more
substituted

$\sigma_{CH} \leftrightarrow$ vacant p

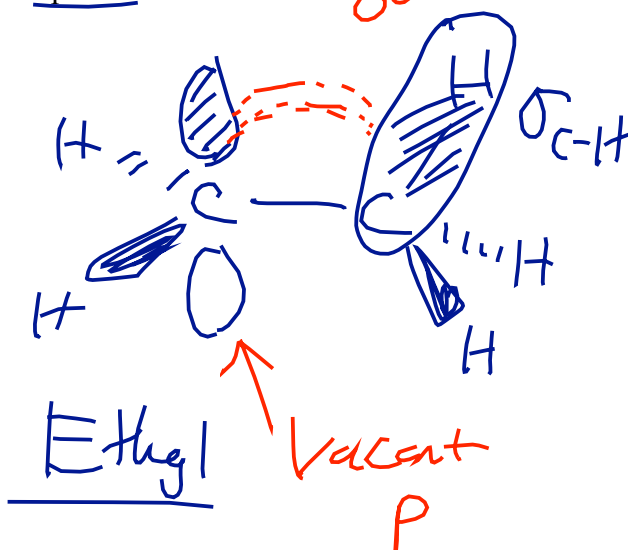
Hyperconjugation

Weak overlap

How can we explain this trend?



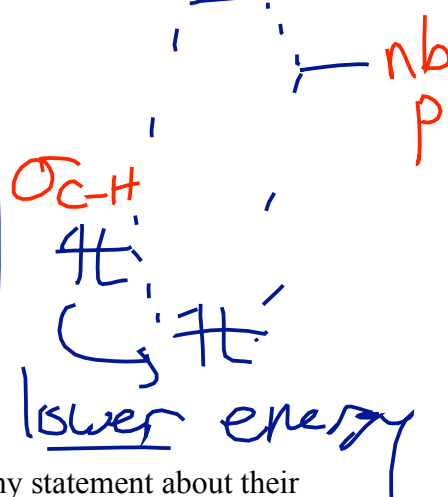
Methyl



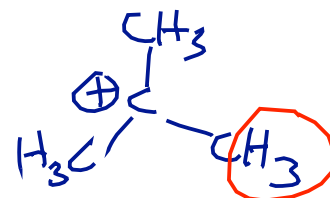
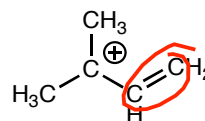
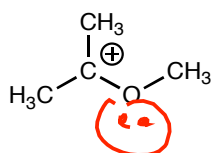
Ethyl

vacant p

MO
Filled / Unfilled



- Here are two other examples of "carbocations." Can you make any statement about their stability, relative to the carbocations above (and relative to each other)?



MO:

Donor lp O

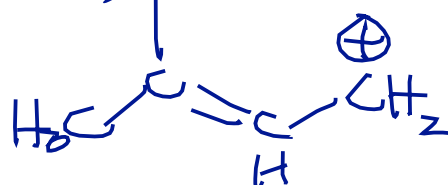
[Best]

most stable

$\pi C=C$

\updownarrow

H₃C



σ_{C-H}

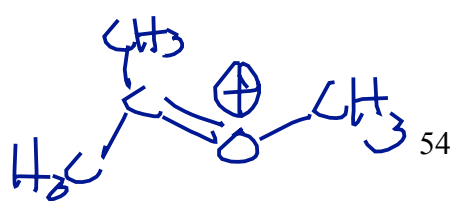
[Worst]

least stable

Reading: Section 4.7

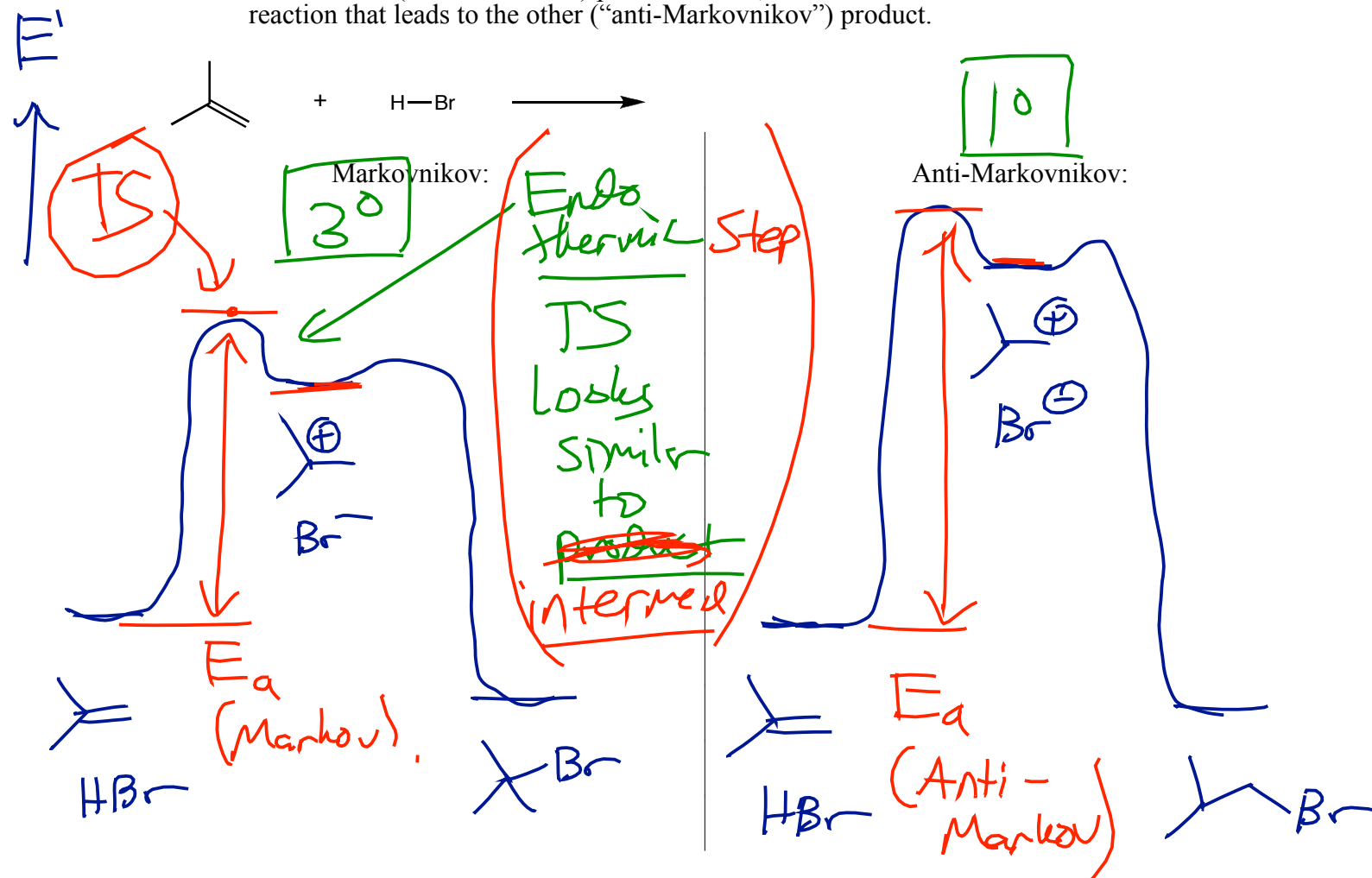
(no)

Resonance:



Reactive Intermediates and Hammond's Postulate

- For the following reaction, draw out the **reaction coordinate** for the reaction that leads to the observed ("Markovnikov") product. Then, draw the reaction coordinate for the reaction that leads to the other ("anti-Markovnikov") product.



- How can we analyze these reaction coordinate diagrams?

$$E_a(\text{Markov}) < E_a(\text{Anti-Markov})$$

Faster

Slower

Lower intermediate

- Does this help to explain why the Markovnikov product is the one that is observed?

Hammond's postulate

Lower TS

Faster reaction

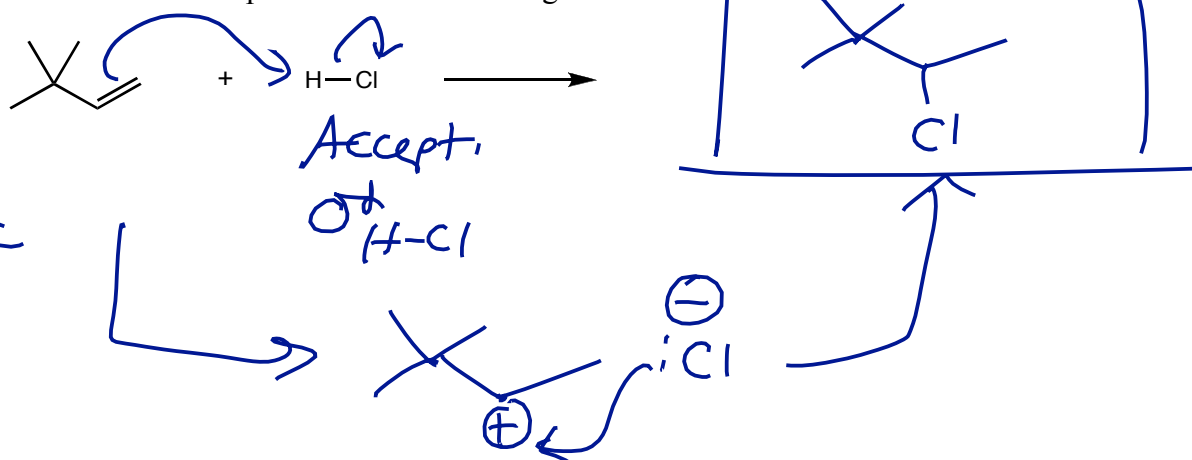
More stable cation

Markovnikov prod.

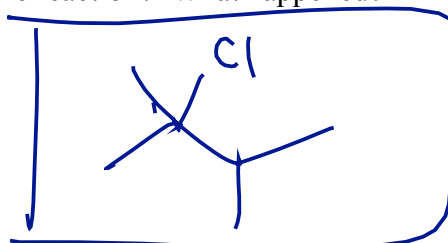
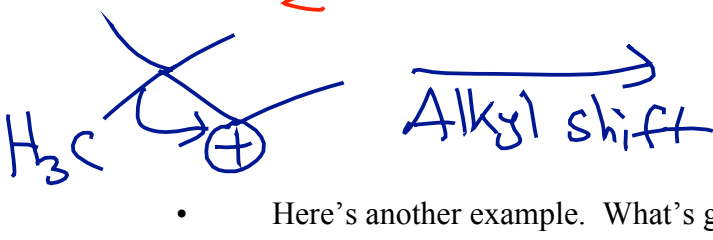
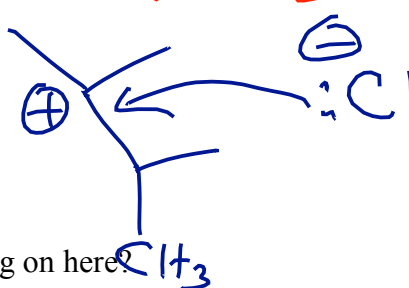
Reading: Section 4.8

Rearrange!**Carbocations Do Funky Things**

- Predict the product of the following reaction:



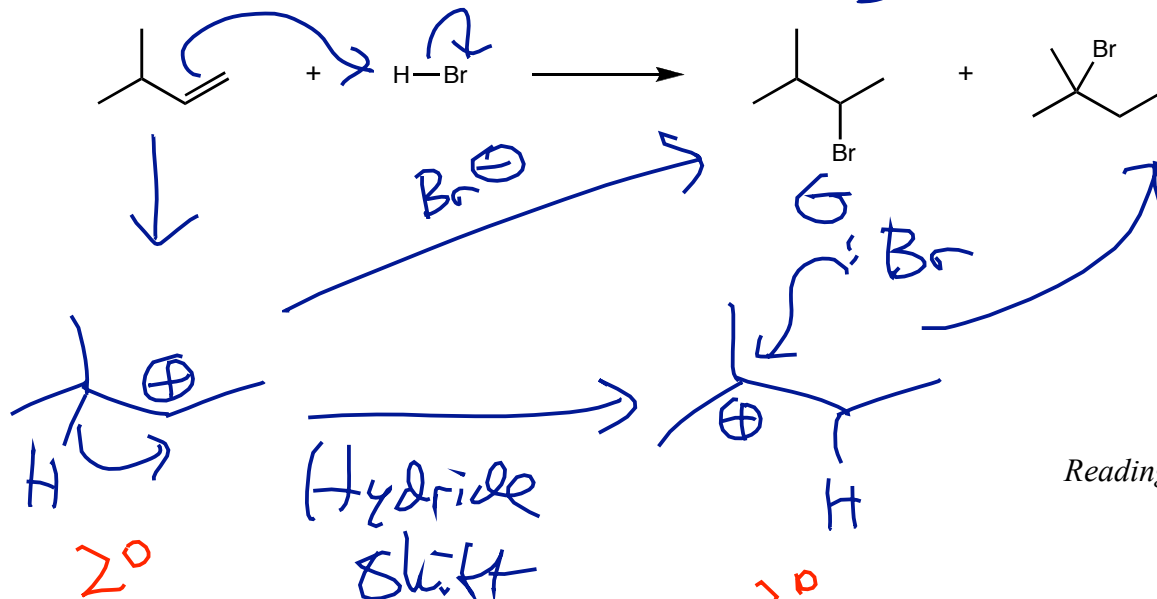
- What is the *actual* product of the reaction? What happened?

In Lab:Consider cation:
2°**3° more stable**

product.

Generally you should predict alkyl shifts,

- Here's another example. What's going on here?

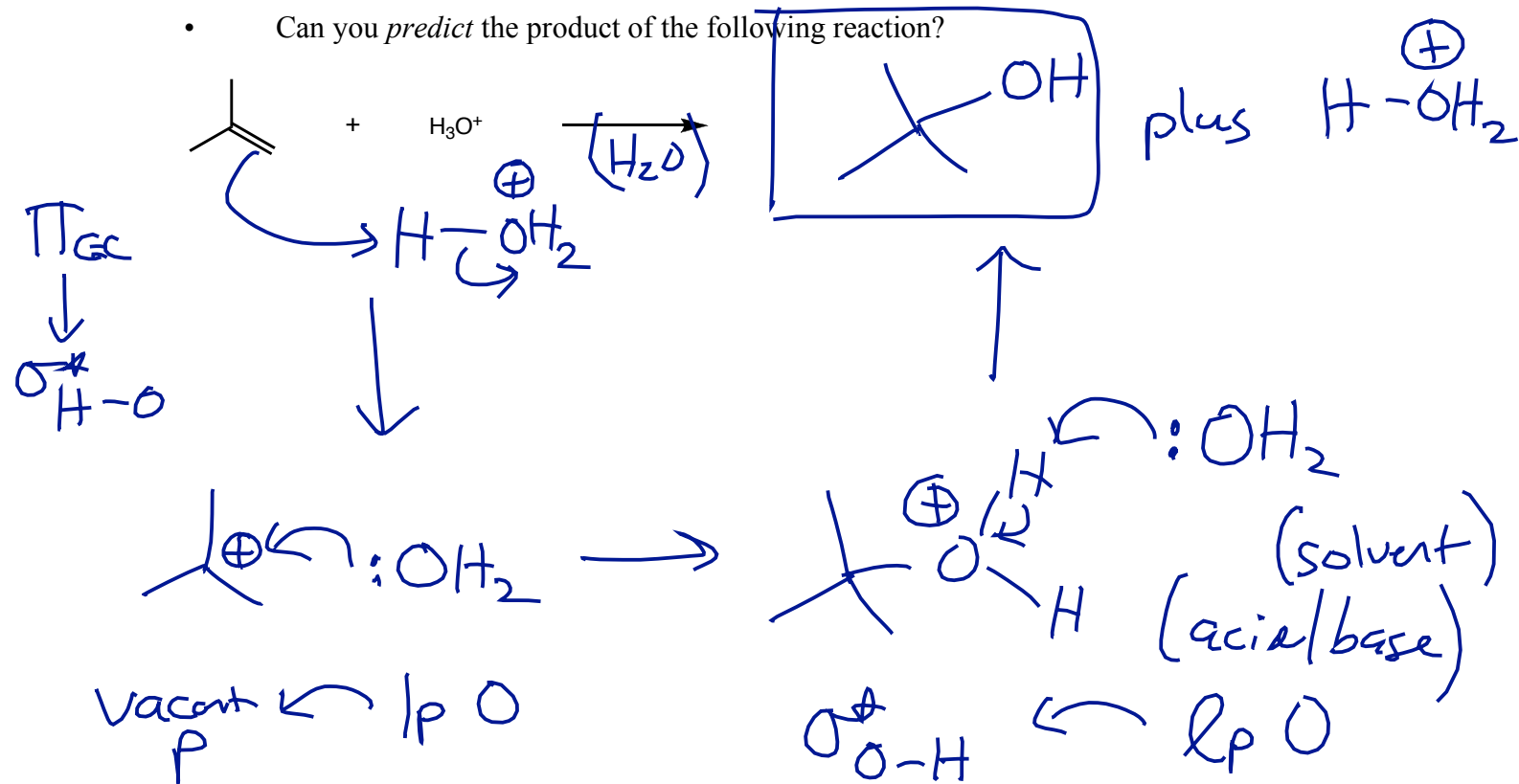


but don't "predict" hydride shifts.

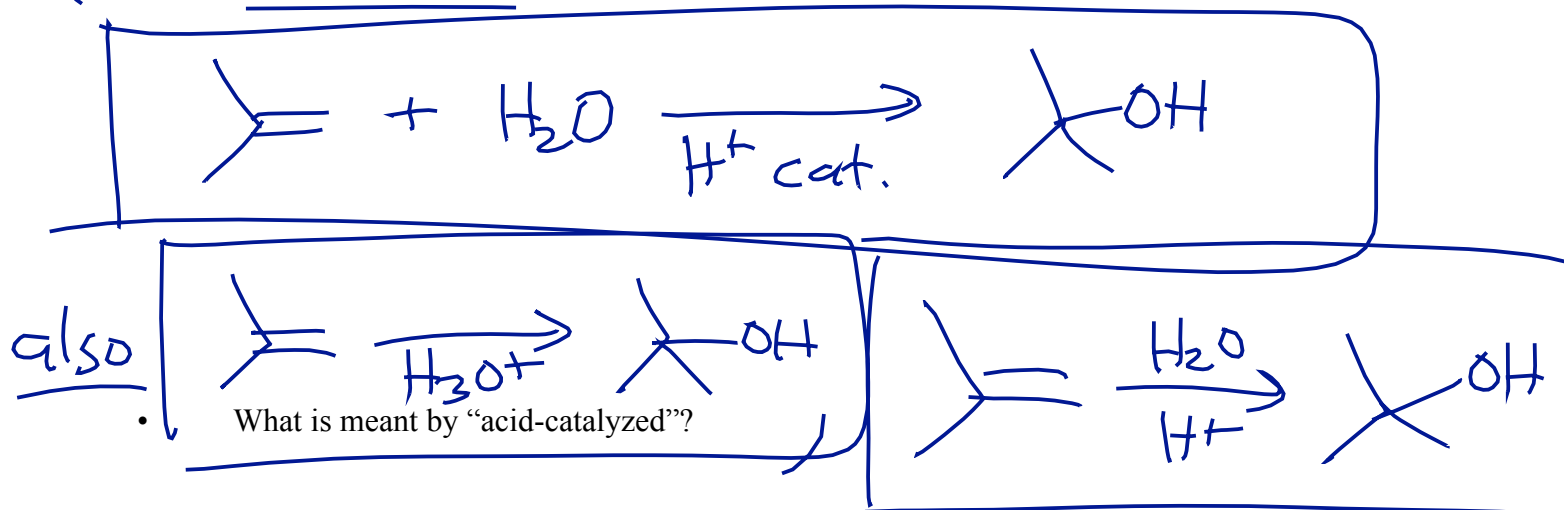
Reading: Section 4.7

More Reactions of Alkenes

- Can you *predict* the product of the following reaction?



- What's really going on here? Why would this reaction be described as "the acid-catalyzed addition of water to an alkene"? How would we ordinarily write this reaction?



because H^+ (H_3O^+) is not consumed

Reading: Section 4.9

\rightarrow regenerated in final step

Still More Reactions of Alkenes

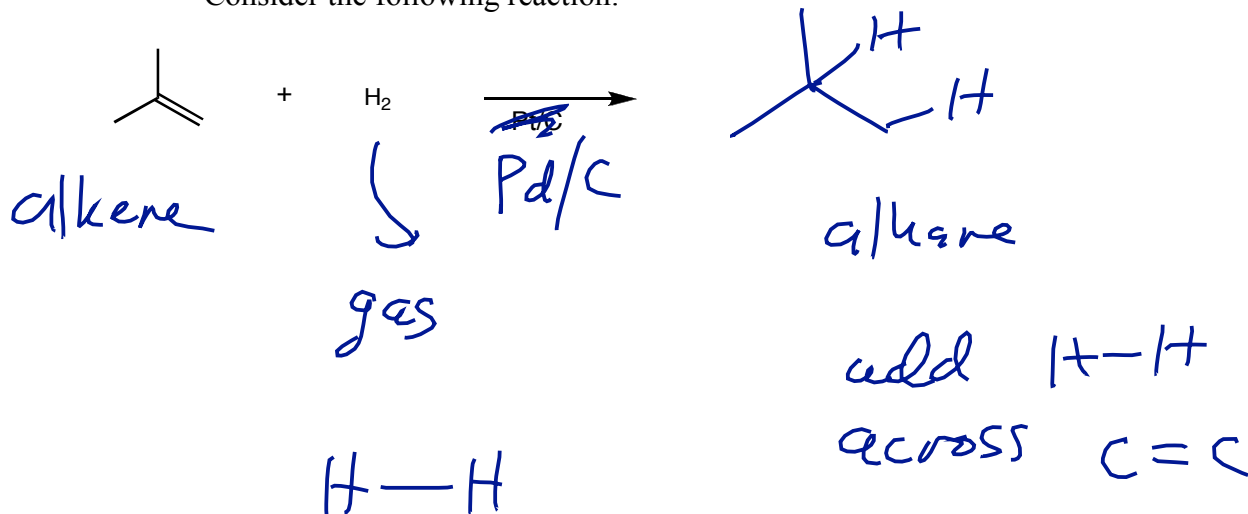
- You try this one: Can you predict the product of the following reaction?



Reaction to learn, no mech!

Wow, There Are Lots of Reactions of Alkenes

- Consider the following reaction:

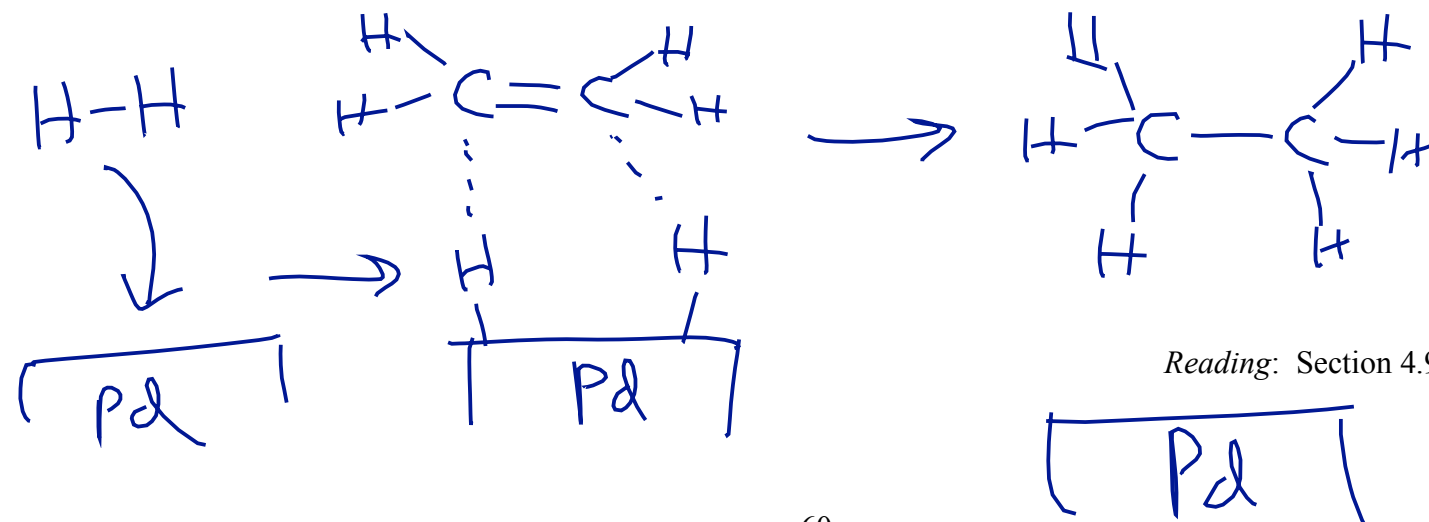


- Is there any way you could have predicted the product of this reaction? Does this reaction even make sense?

not really

Needs Pd catalyst
(solid)

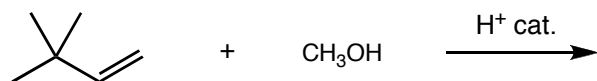
- How does this reaction take place? What is the *mechanism* of this reaction?



Reading: Section 4.9

Test Yourself Now!

- Can you write a curved-arrow mechanism and predict the product of the following reaction?

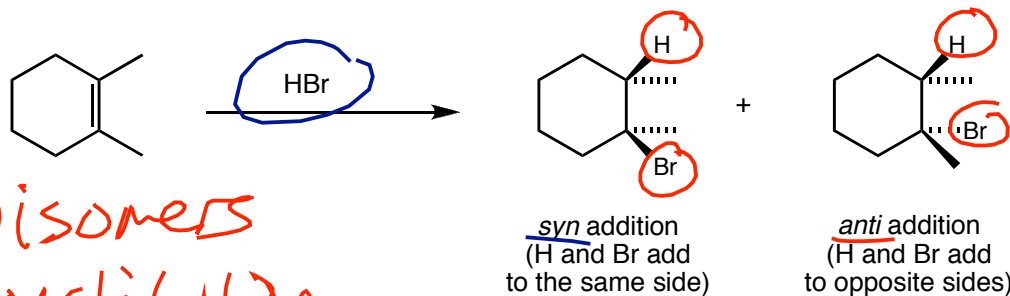


just did this . . .

examples: E vs. Z alkenes

Stereochemistry of Alkene Additions

- Consider adding HBr to a *cyclic* alkene, like the one shown below. The two new groups that are added (H and Br) could be added in two different ways: *syn* (both added to the same face of the alkene) or *anti* (added to opposite faces of the alkene):



get
a
mix

(Recall that we used the term *stereoisomers* before to refer to *cis* and *trans* alkenes.)

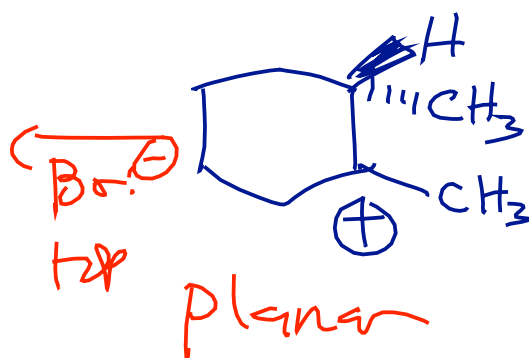
Work through the mechanism of HBr addition. Which is preferred: *syn* or *anti*?



H adds to top face of ring.

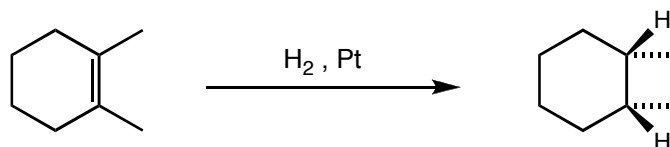


Syn



anti

- The addition of H₂ to the same cyclic alkene gives *only one* product. What type of addition is this, and why is only one product observed?



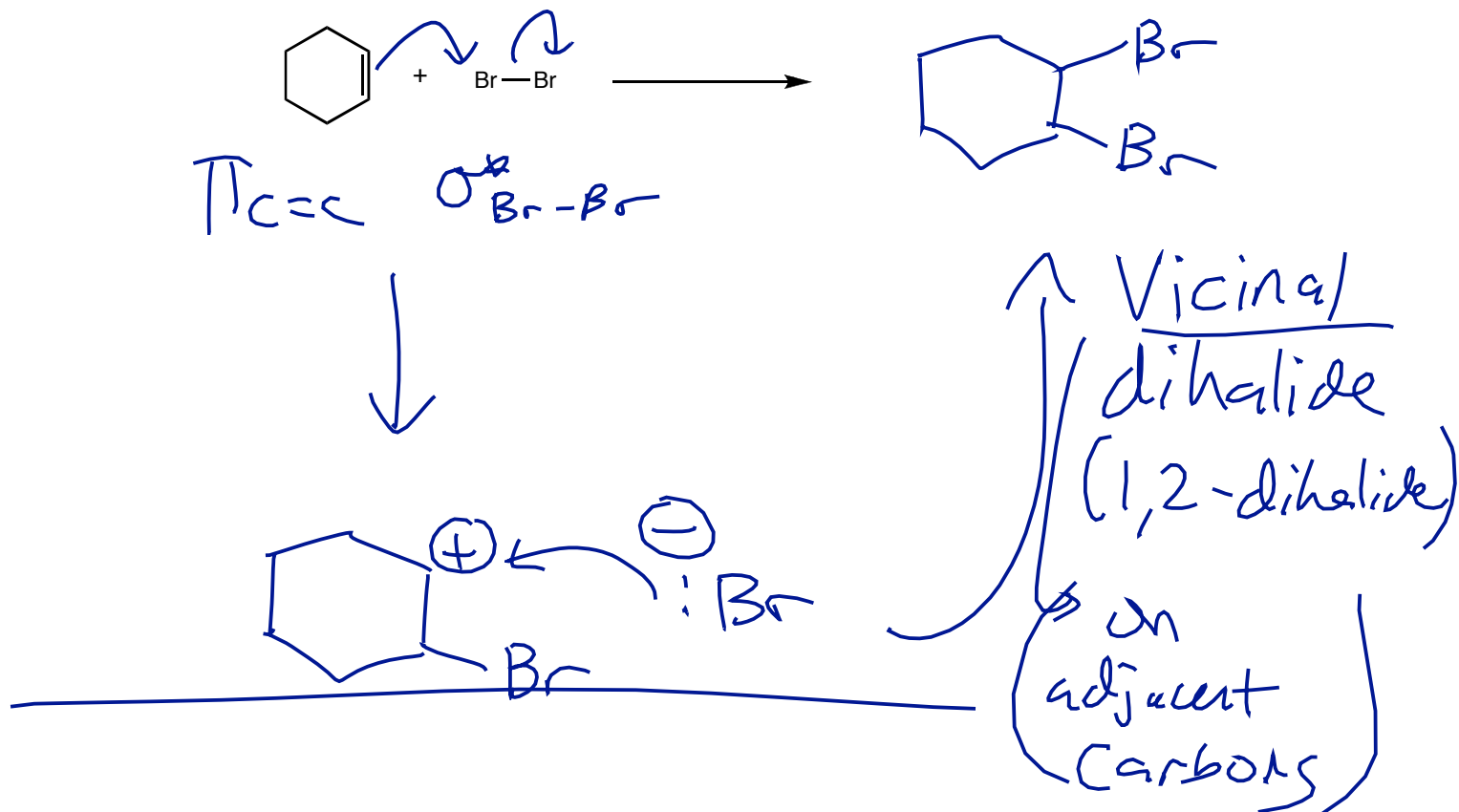
always syn

Reading: Section 7.9

(general: X_2) $X = Cl, Br, I$

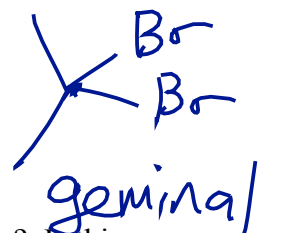
Addition of Br_2 or Cl_2 to Alkenes

- First, let's *predict* what we expect to happen when an alkene reacts with Br_2 . How do we make such a prediction?

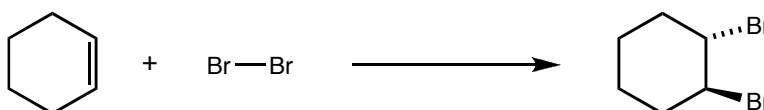


- What would your proposed mechanism predict about the *stereochemistry* of the outcome?

Predict both, carbocation is planar.



- The actual outcome of the reaction is shown below. What type of addition is this? Is this stereochemical outcome consistent with your proposed mechanism?

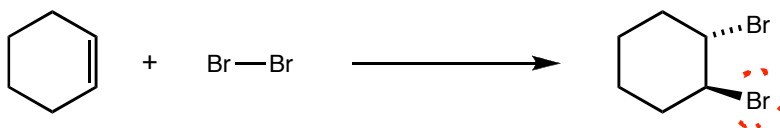


always anti

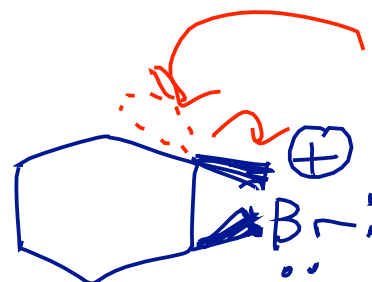
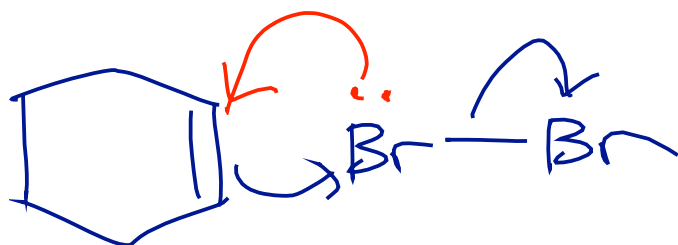
Reading: Section 5.1

The Mechanism of Br₂ or Cl₂ Addition

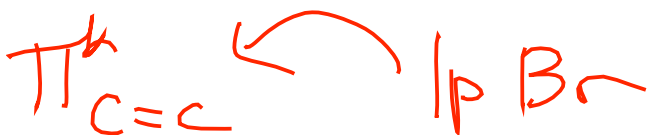
- Is there a mechanism of Br₂ addition that is consistent with the observed stereochemistry?



from bottom



bromonium ion

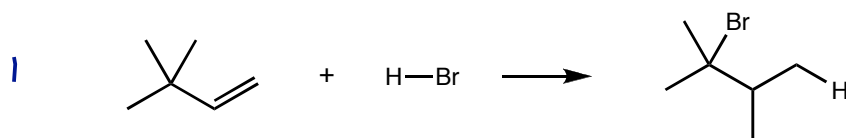


Acceptor

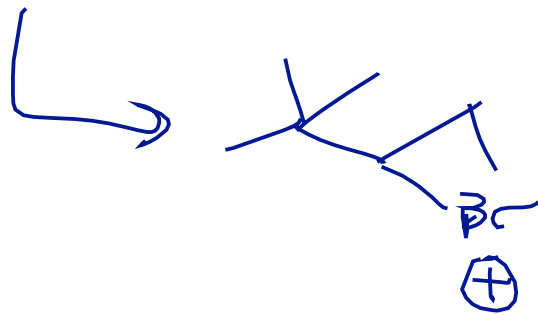
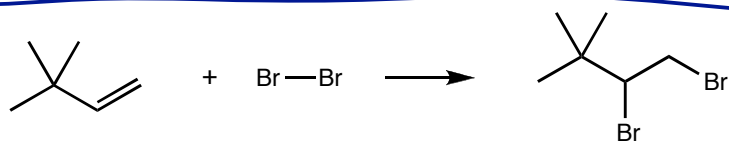
on bottom of ring!

Never have a carbocation!

- Consider the following alkene additions. Rearrangement is observed in one case but not in the other. Can you explain why?



Rearrangements!

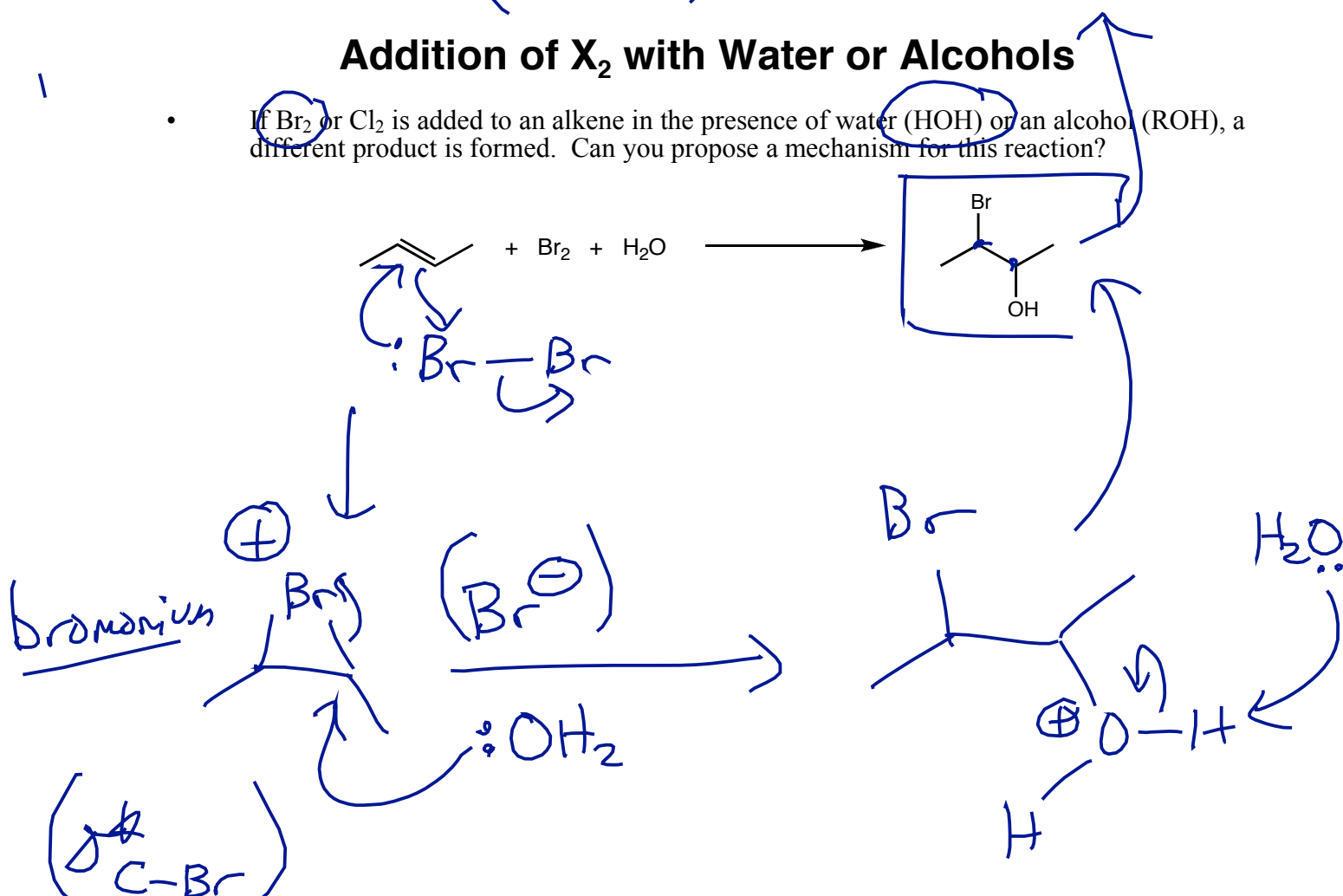


Not a carbocation Reading: Section 5.1

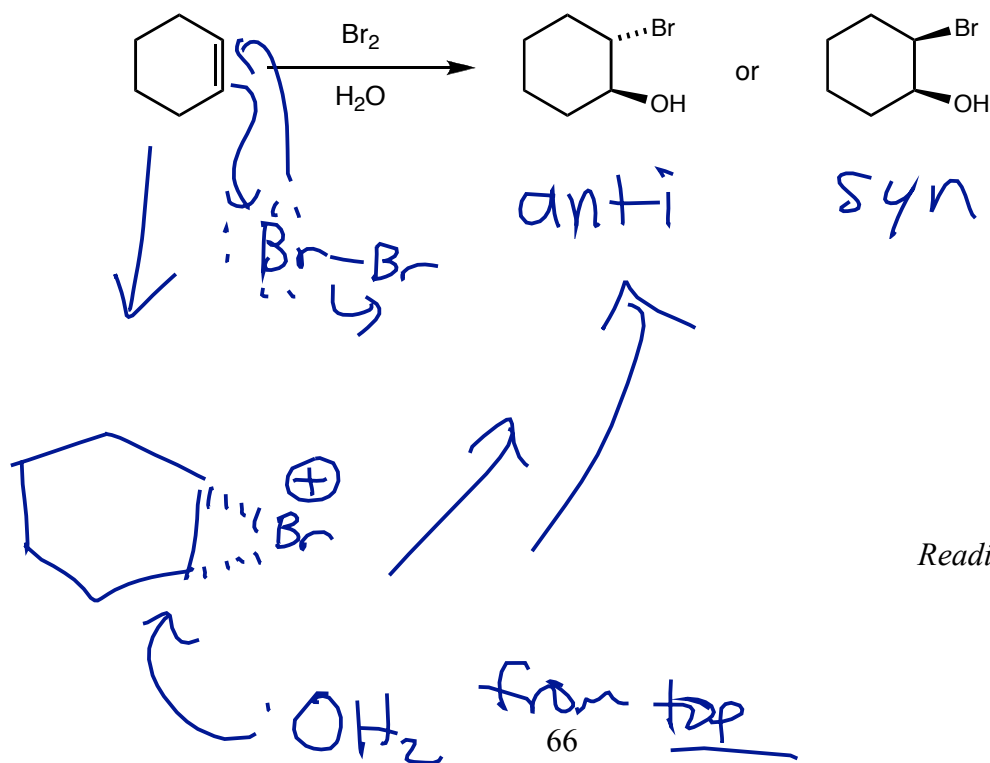
(vicinal) halohydrin

Addition of X_2 with Water or Alcohols

- If Br_2 or Cl_2 is added to an alkene in the presence of water (HOH) or an alcohol (ROH), a different product is formed. Can you propose a mechanism for this reaction?



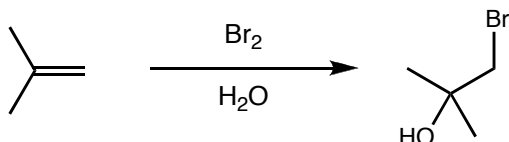
- Now that you've seen the mechanism, can you predict which of the following products will be produced in the reaction of cyclohexene with bromine in water?



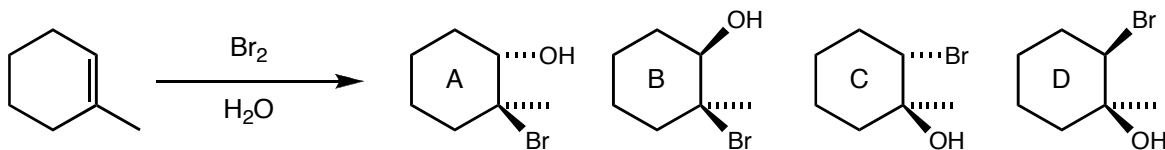
Reading: Section 5.1

The Structure of the Bromonium Ion

- Explain why *only one product* is observed in the following reaction:



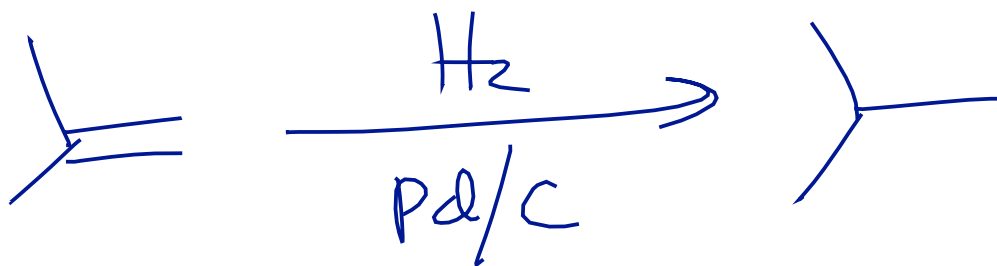
- Is this observation consistent with Markovnikov's Rule? Why or why not?
- Given all that you know about the addition of Br_2 to alkenes, *predict* which of the four products shown below would be the main product observed in the addition of bromine to 1-methylcyclohexene in the presence of water:



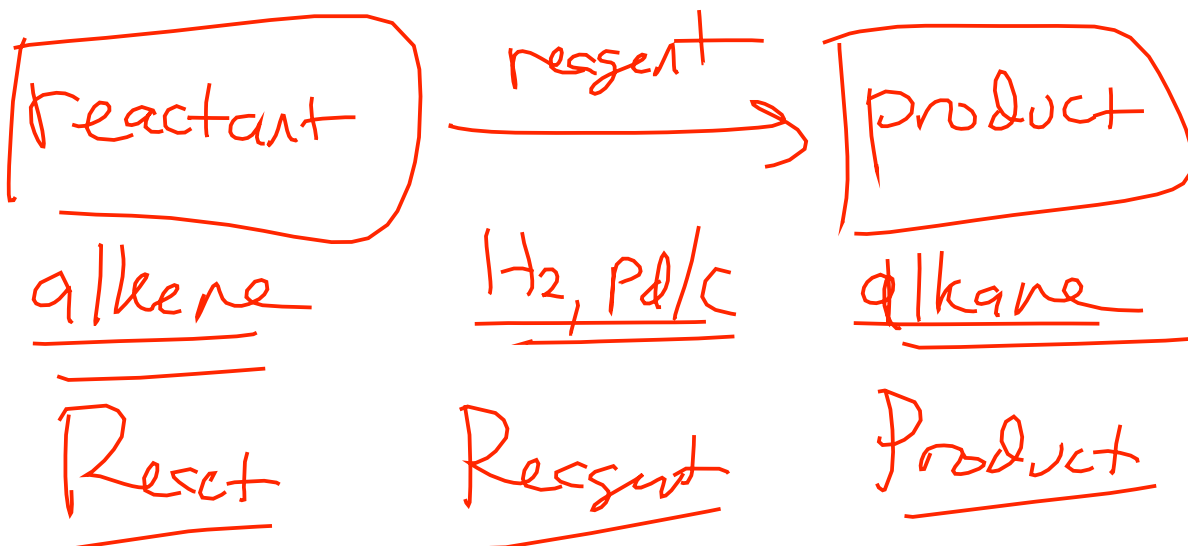
Reading: Section 5.1

How Can I Possibly Learn All of These Reactions?

Hydrogenation,



Syn
addition
on
surface
of
Pd



Comments
and
Mechanism

Mech