

(33) Today

Next Class (34)

7.8 Orientation of Electrophilic Additions:
Markovnikov's Rule (Regioselectivity)

8.1 Preparing Alkenes:
A Preview of Elimination Reactions

7.9 Carbocation Structure and Stability

8.2 Halogenation of Alkenes:
Addition of X_2

7.10 The Hammond Postulate
Drawing a transition state

8.3 Halohydrins from Alkenes:
Addition of HO-X

7.11 Evidence for the Mechanism of
Electrophilic Additions: Carbocation
Rearrangements

(35) Second Class from Today

Third Class from Today (36)

8.3 Halohydrins from Alkenes:
Addition of HO-X

8.4 Hydration of Alkenes:
Addition of H_2O by Oxymercuration

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8.5 Hydration of Alkenes:
Addition of H_2O by Hydroboration

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Addition of H_2O by Hydroboration

8.8 Oxidation of Alkenes: Cleavage to
Carbonyl Compounds

Reworked Test 3 Due Monday, December 9.

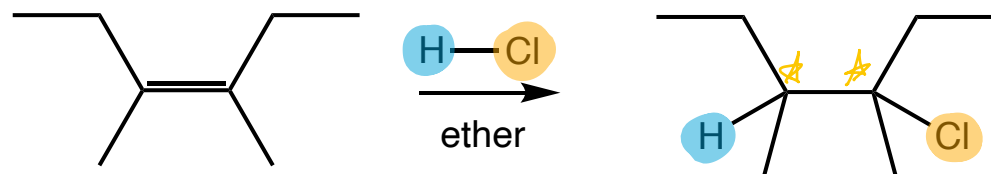
On a separate piece of paper, provide answers for any question for which you did not receive full credit. I do NOT need the test itself back.

Restating Markovnikov's Rule

Original: The electrophile adds to the less substituted end of the double bond.

Restated: When the electrophile adds it does so such that a positive charge develops on the C atom that is better able to stabilize the positive charge.

Evidence for the C⁺ based mechanism: Stereochemical Outcome

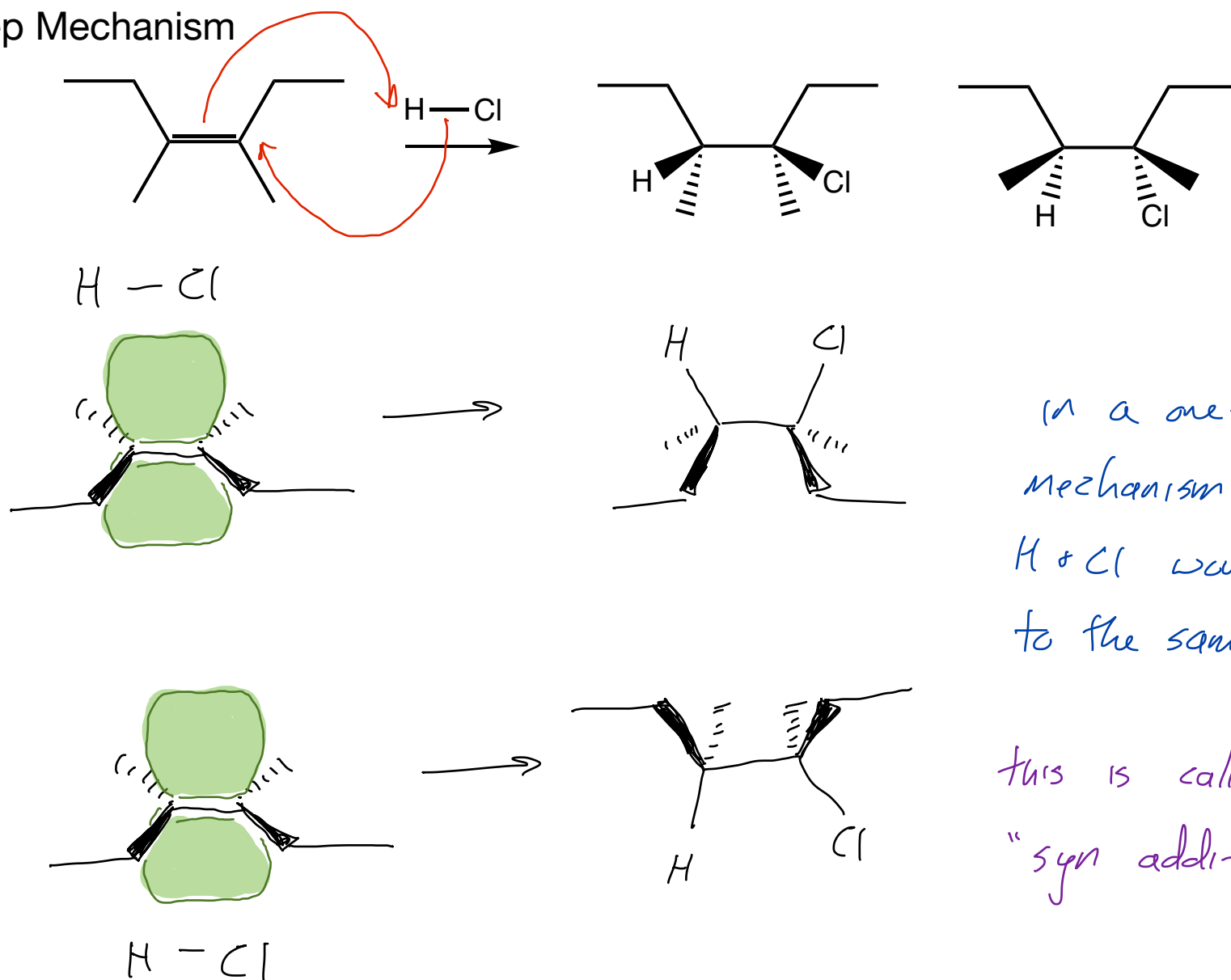


$2^n = \text{maximum number of stereoisomers}$

$$2^2 = 4$$

Evidence for the C⁺ based mechanism: Stereochemical Outcome

One-Step Mechanism

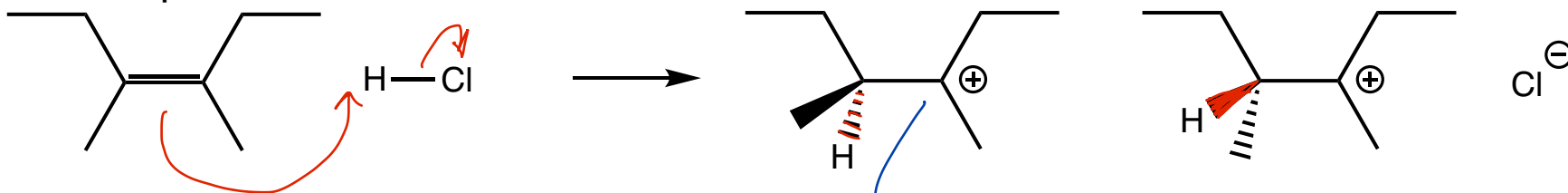


In a one-step mechanism the H + Cl would add to the same face

this is called a "syn addition"

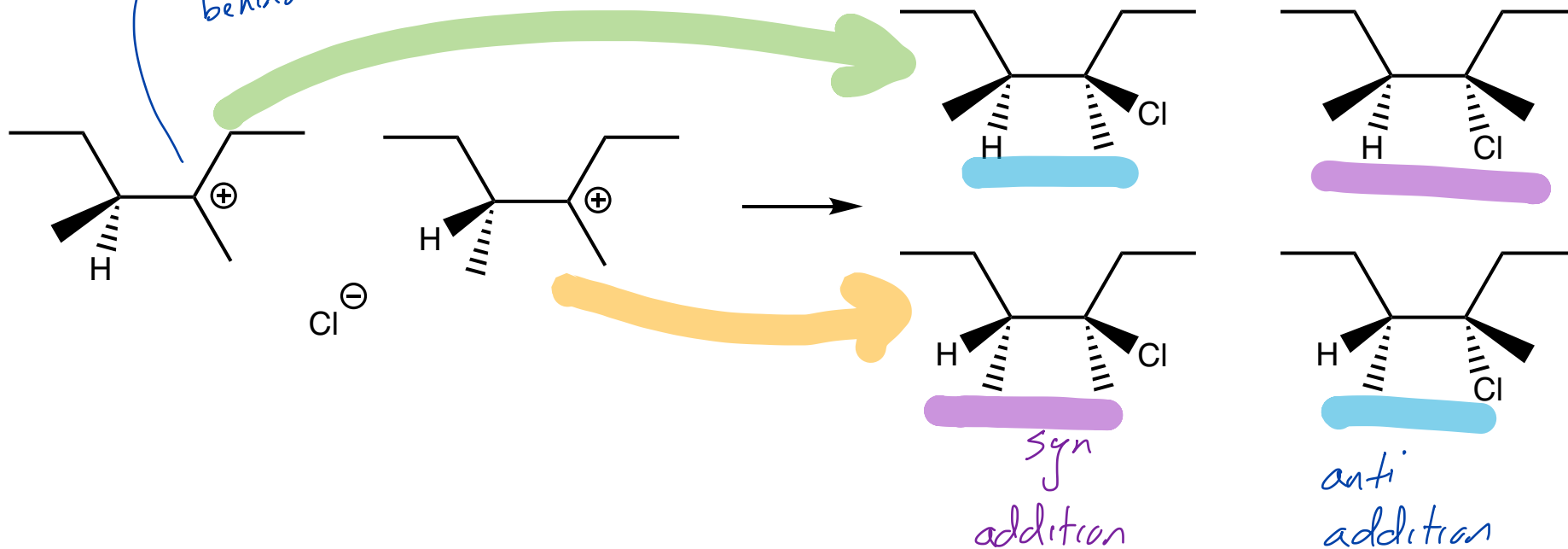
Evidence for the C⁺ based mechanism: Stereochemical Outcome

Two-Step/Carbocation Mechanism



the C⁺ has 3 σ bonds so sp^2 hybridized so it's planar, and it has an empty p orbital

p orbital has a lobe in front of the screen + one behind the screen

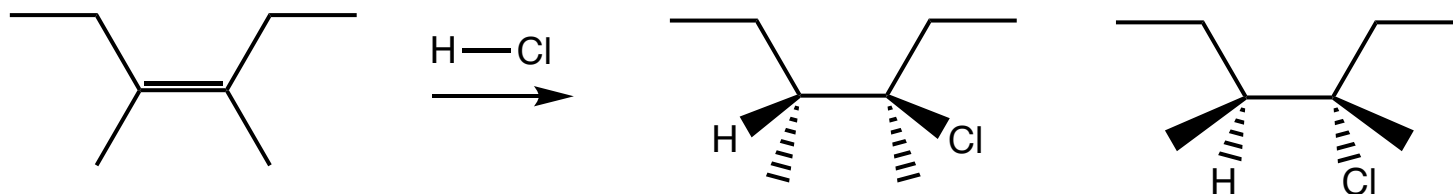


syn addition

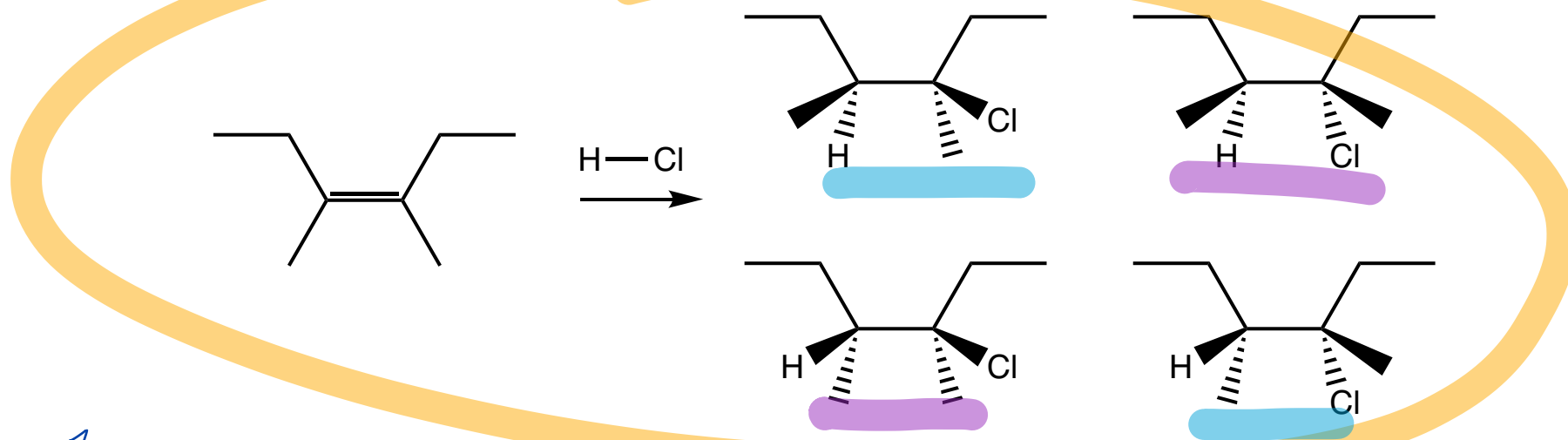
anti addition

Evidence for the C⁺ based mechanism: Stereochemical Outcome

Prediction from One-Step Mechanism



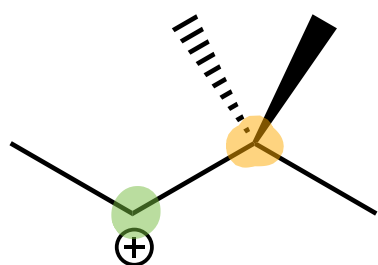
Prediction from Two-Step/Carbocation Mechanism



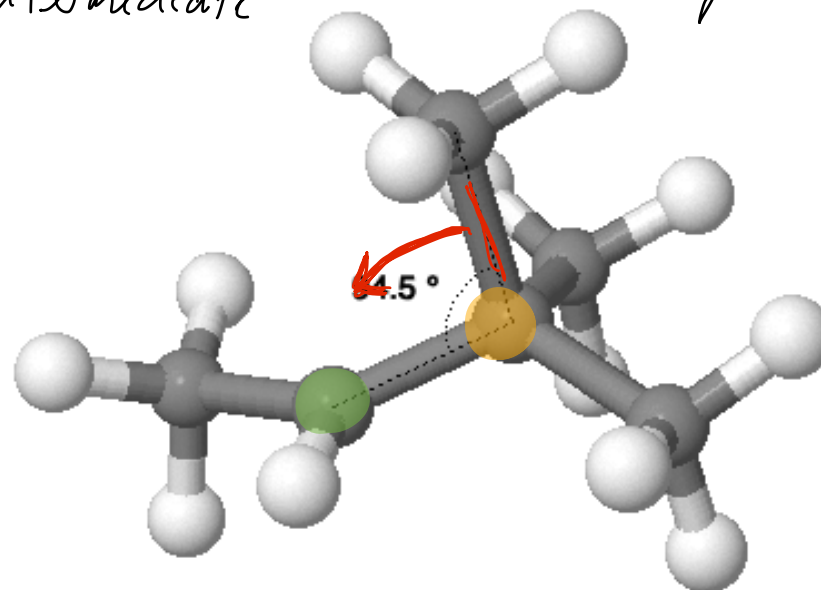
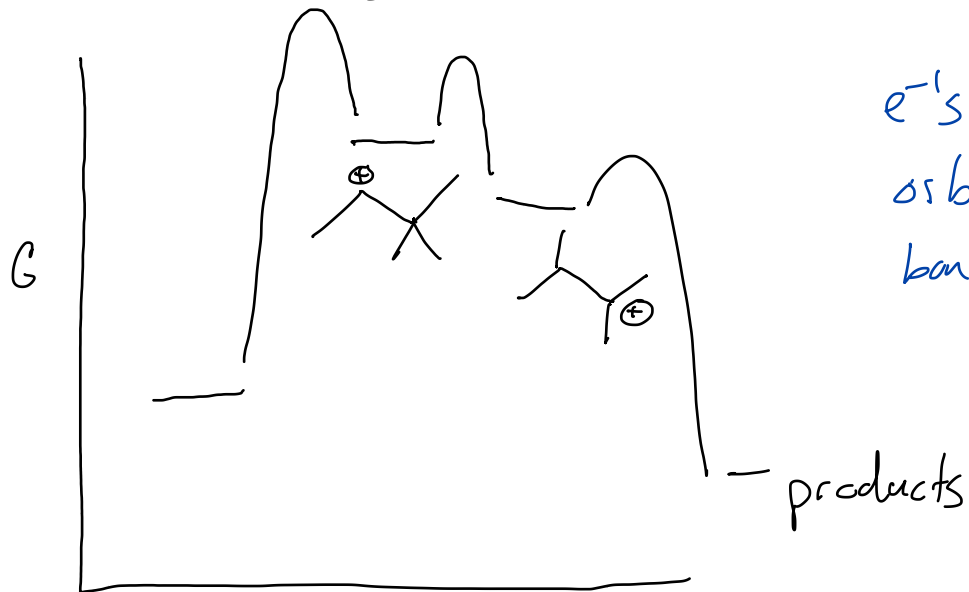
The C^+ intermediate allows us to do both **syn** **anti** additions, which gives us all 4 possible stereoisomers

Carbocations rearrange: Evidence for the C⁺ based mechanism

1° vs 2° of the neighboring C atom would be a more stable C⁺, the intermediate can rearrange to form that C⁺



2° better



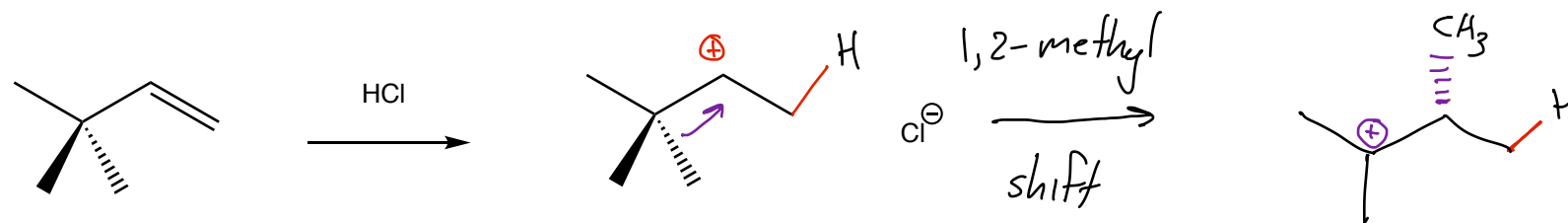
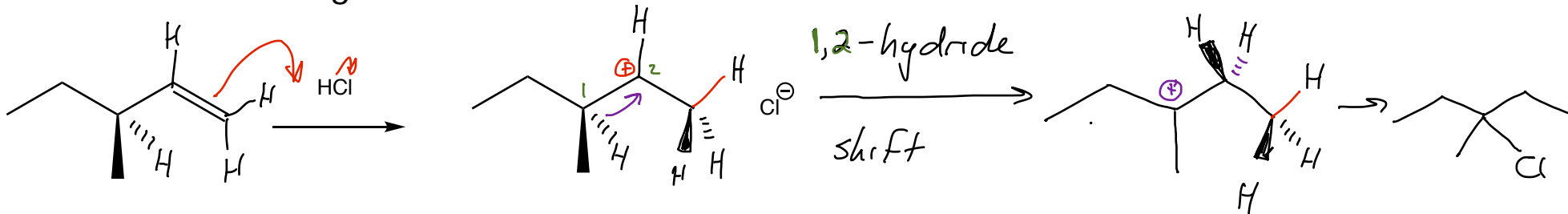
e⁻s are being drawn to the empty p orbital to stabilize the C⁺, so the bond angle is tighter than expected



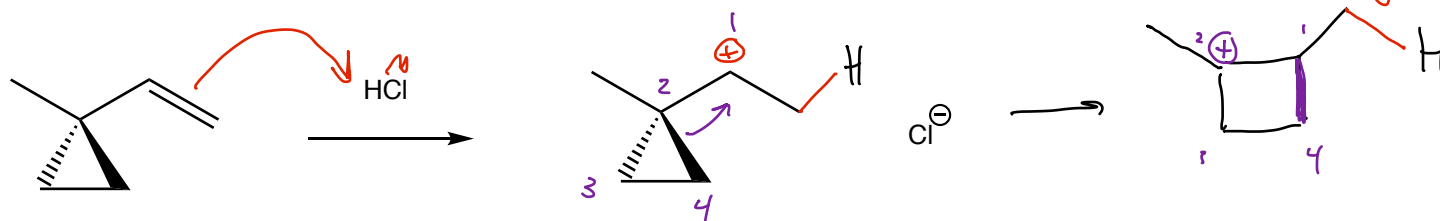
Carbocations rearrange

$H:^{\ominus}$ hydride ion

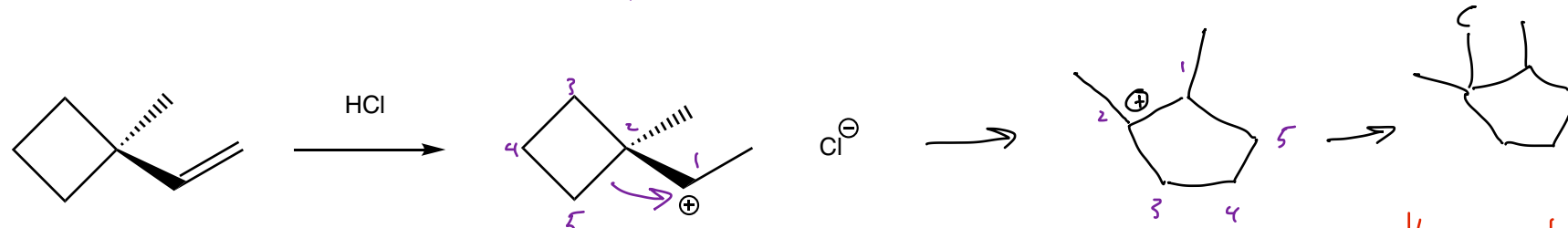
Section 7.11



H's and CH₃'s can shift ... nothing bigger



the bond from 4 to 2 slides over to be between 4 and 1



3- and 4-membered rings can open ... nothing bigger

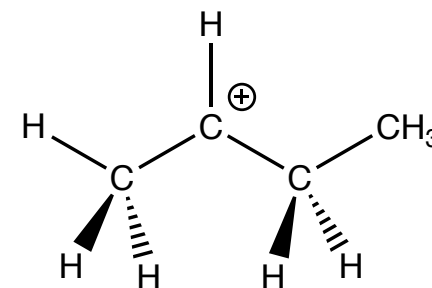
The Carbocation Summary

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)



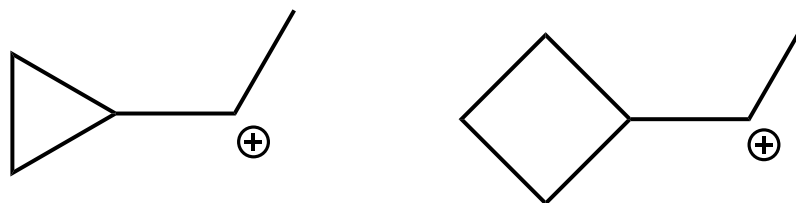
Rearranging C⁺'s

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.

E Add Reactions

