(32) **Today**

7.8 Orientation of Electrophilic Additions: Markovnikov's Rule (Regioselectivity)
7.9 Carbocation Structure and Stability
7.10 The Hammond Postulate
Drawing a transition state
7.11 Evidence for the Mechanism of Electrophilic Additions: Carbocation Rearrangements
Practice Predicting Outcome of H+ Initiated Electrophilic Addition Reactions

Next Class (33)

Test 3 on Chap 5, 6 and Chap 7.3 – 7.5

(34) **Second Class from Today**

8.2 Halogenation of Alkenes: Addition of X2
8.3 Halohydrins from Alkenes: Addition of HO-X

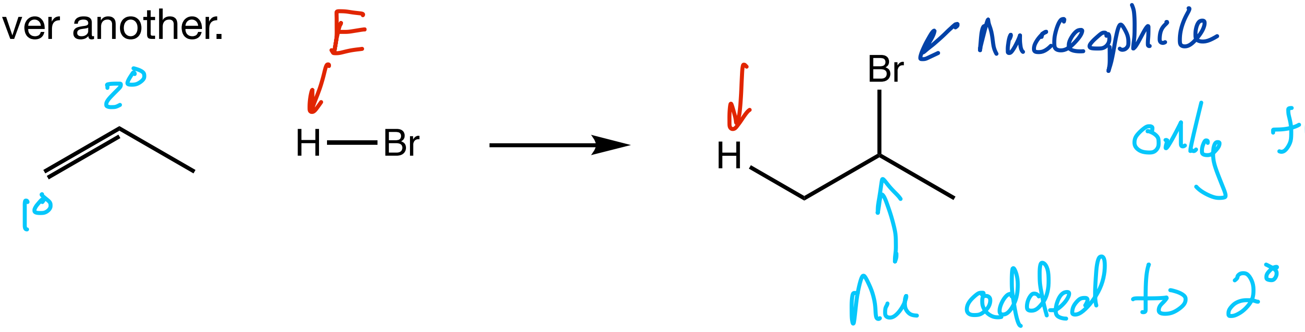
Third Class from Today (35)

8.4 Hydration of Alkenes: Addition of H_2O by Oxymercuration
8.5 Hydration of Alkenes: Addition of H2O by Hydroboration
8.6 Reduction of Alkenes by Hydrogenation
8.12 and 13: Stereochemistry of addition reactions

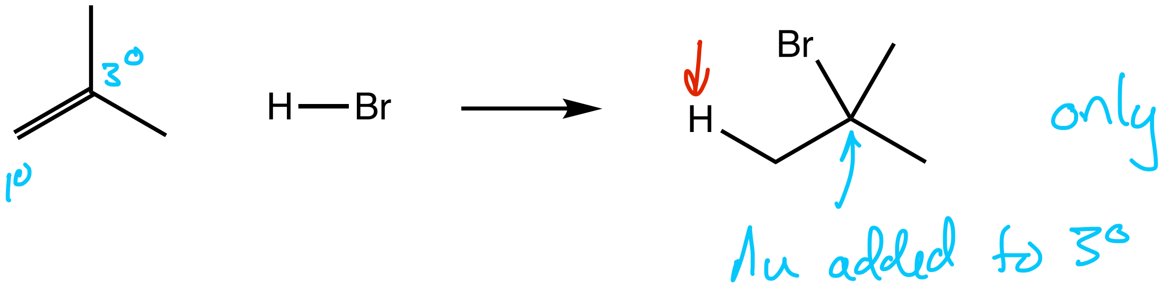
Review session from 2:00 to 3:30 this afternoon in Wilson 309. Any questions answered during the review will be posted on the "Sample Tests" Webpage.

Orientation of Electrophilic Additions: Markovnikov's Rule

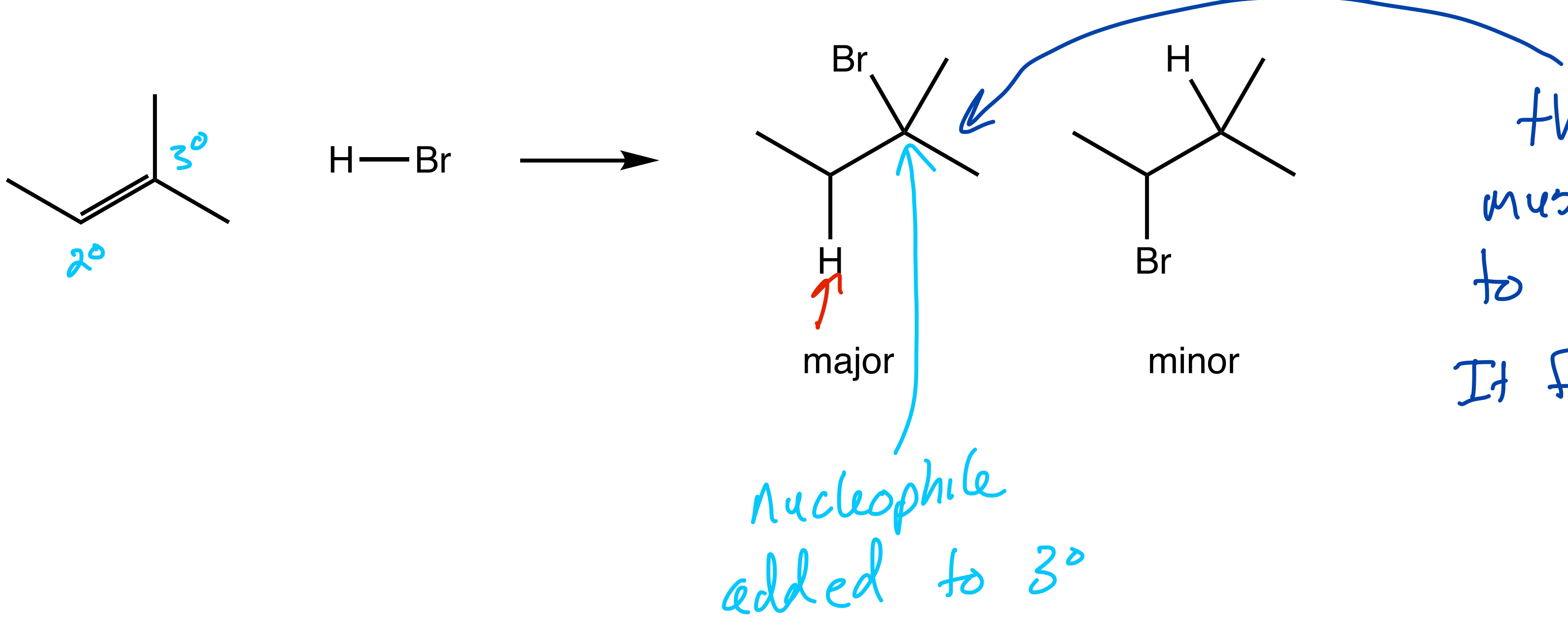
Regioselectivity: The ability of a reaction to prefer the formation of one constitutional/structural isomer over another.



only this one forms

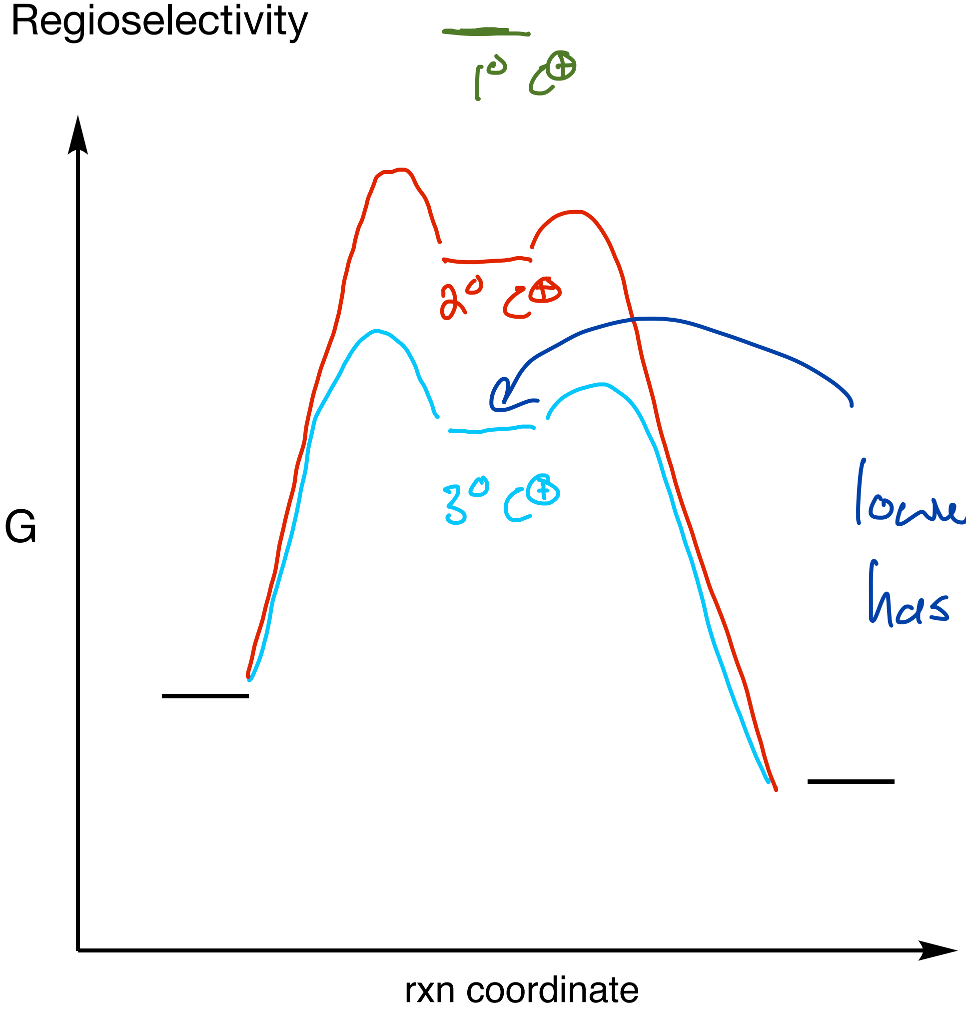


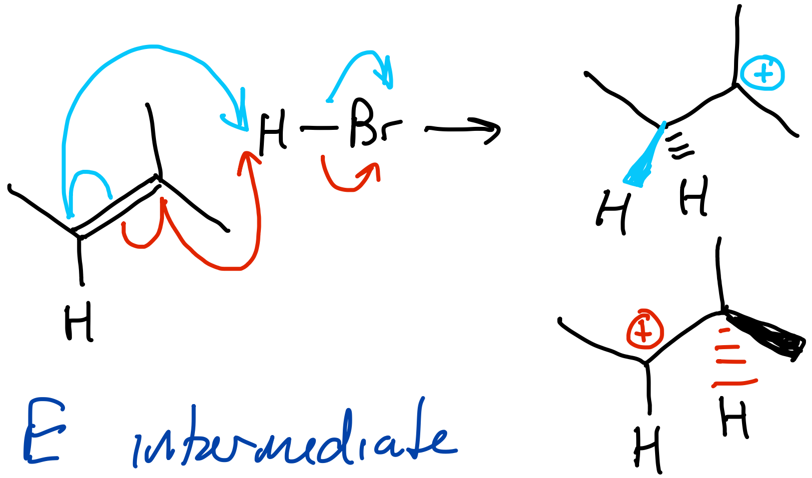
only this one forms



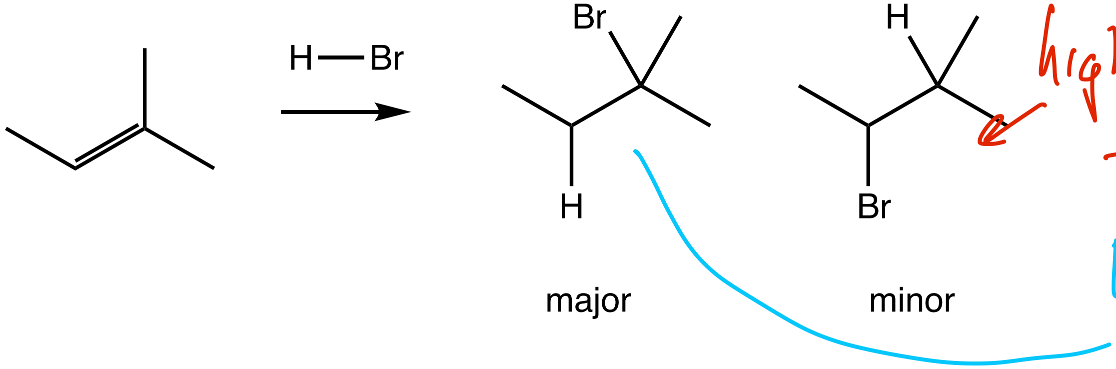
this one
must be easier
to make...
It forms faster

The Carbocation Intermediate, the Hammond Postulate and Regioselectivity





lower E intermediate has a low E transition state so more product forms from the 3° C⊕



high E pathway... hard/slow to do

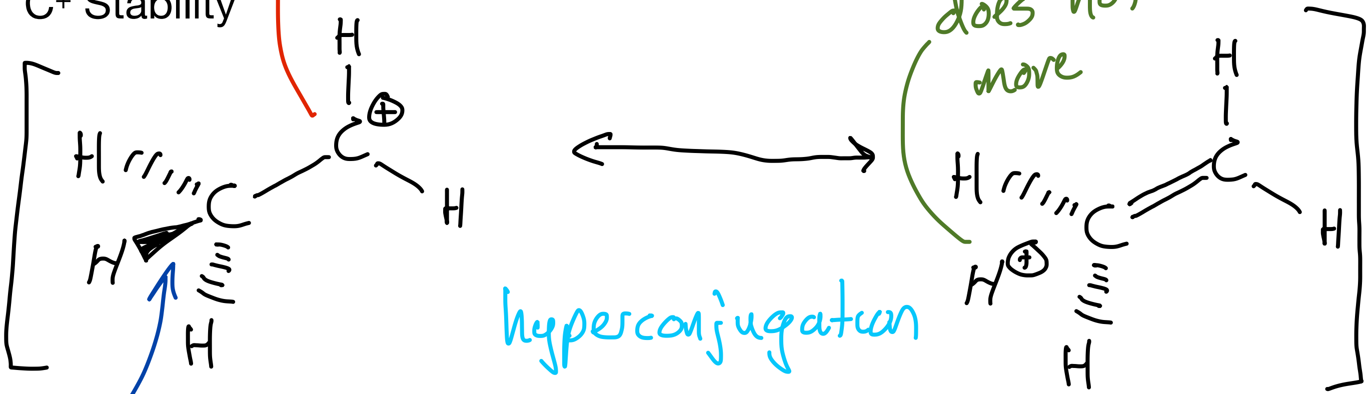
low E pathway... easier/faster to do

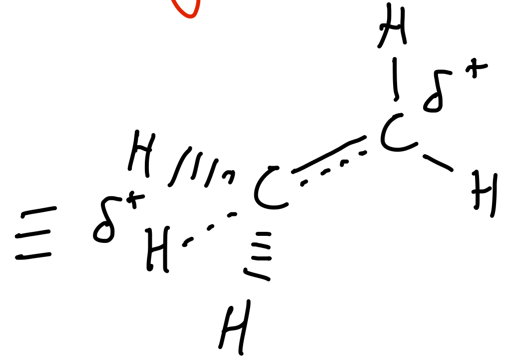
The Carbocation Intermediate, the Hammond Postulate and Regioselectivity

Section 7.9 - 11

sp^2 hybridized C⊕... and it has an empty 2p orbital

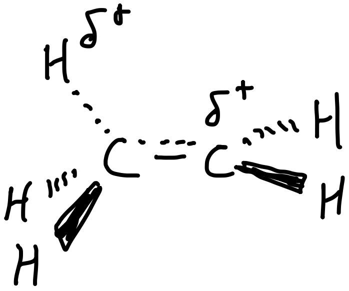
C+ Stability



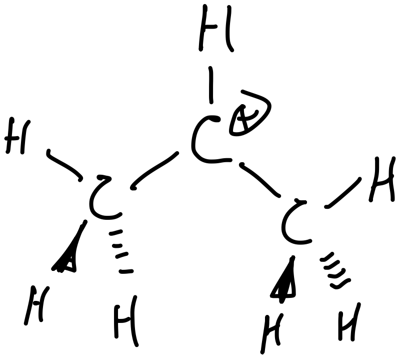


hyperconjugation

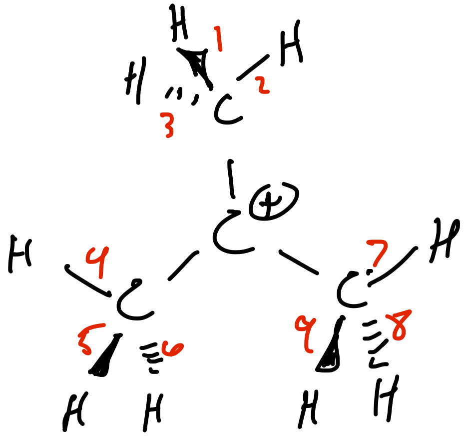
these e⁻'s align with empty p orbital & are attracted to it



only 3 σ-bonds helping and that's not enough to make 1° C+ form under typical lab conditions



6 σ-bonds help out



9 σ-bonds help out

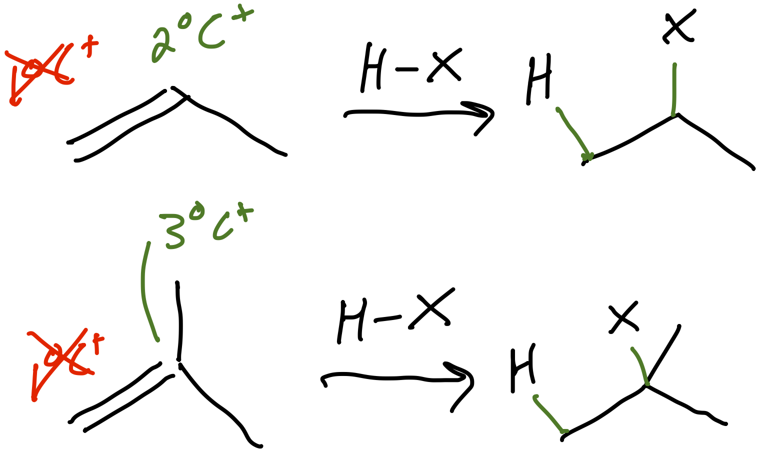
https://www.westfield.ma.edu/cmasi/organic/carbocation_stabilization/carbocation-lumo-plain.html

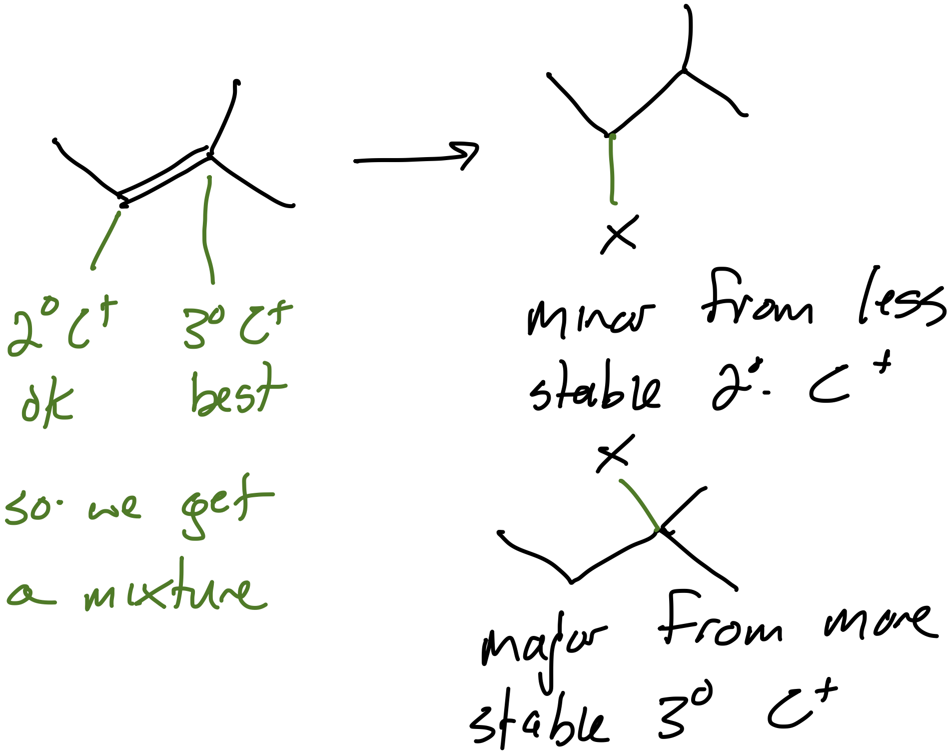
Restating Markovinkov's Rule

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.

1° C⊕ nope... to unstable 2° ok 3° was best





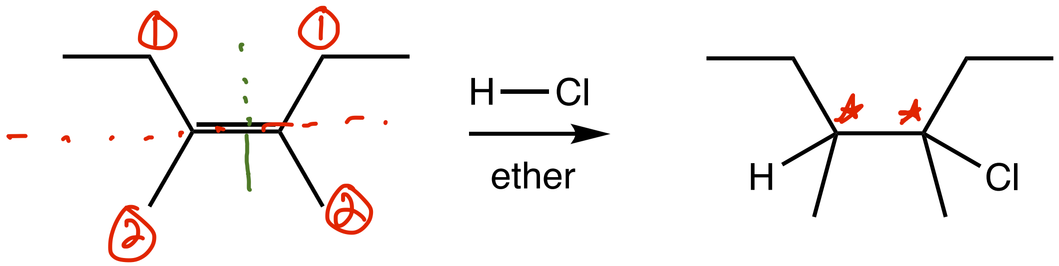
so we get a mixture

minor from less stable 2° C+

major from more stable 3° C+

Evidence for the C+ based mechanism: Stereochemical Outcome

2^n



R, R

R, S

S, R

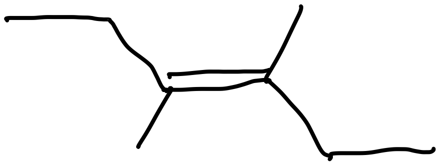
S, S

(Z)-3,4-dimethyl-3-hexene

product exists as 4 stereoisomers

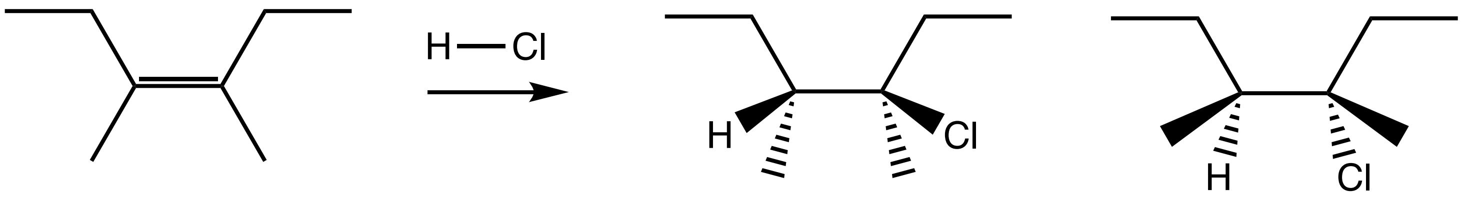
which does form? ....

The mechanism must be consistent with the outcome



Evidence for the C+ based mechanism: Stereochemical Outcome

One-Step Mechanism is not correct...



What does 1 step mechanism predict?

H + Cl must add simultaneously.

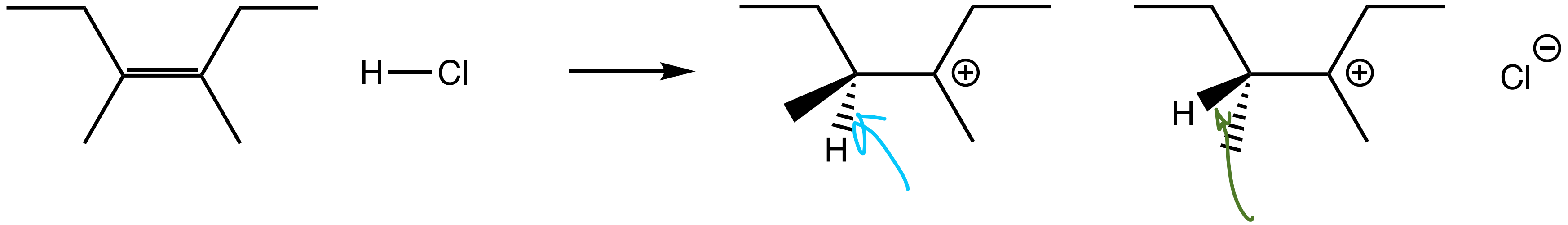
Can H + Cl add the the front and back face simultaneously? No

The H + Cl must add to the same face

prediction... 2 stereoisomers form

Evidence for the C⁺ based mechanism: Stereochemical Outcome

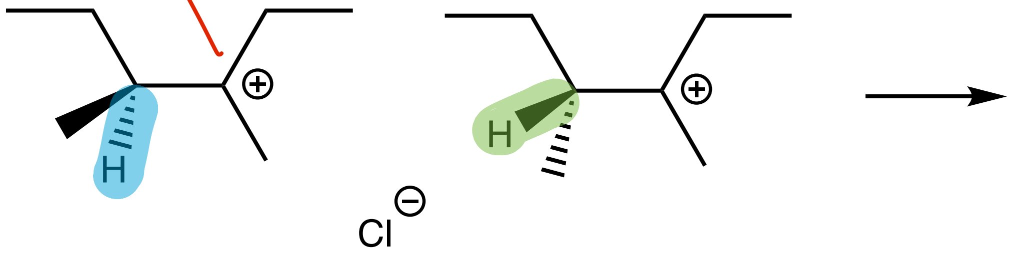
Two-Step/Carbocation Mechanism

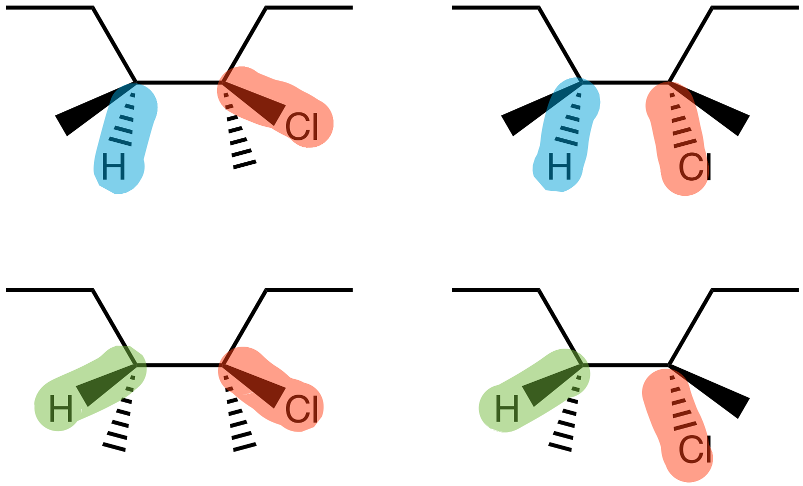


H^+ adds to back face

H^+ adds to front face

sp^2 C⊕
empty 2p orbital
exists in front and in back of screen



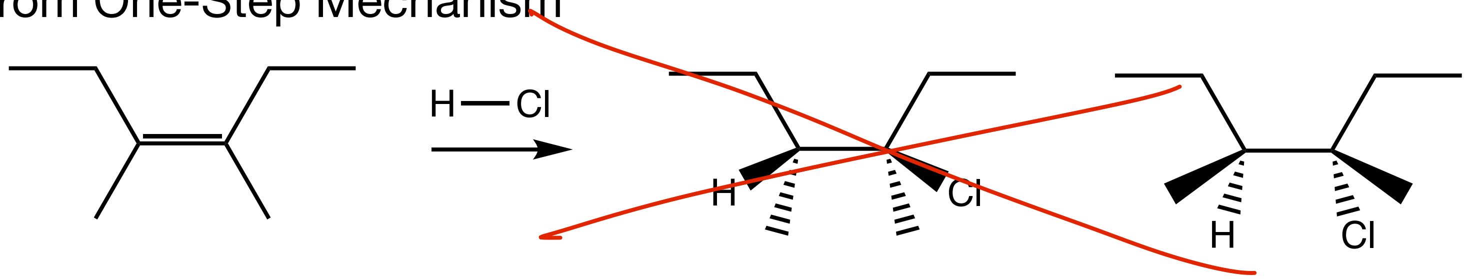


mechanism predicts 4 stereoisomers

Evidence for the C^+ based mechanism in H^+ Initiated Reactions: Stereochemical Outcome

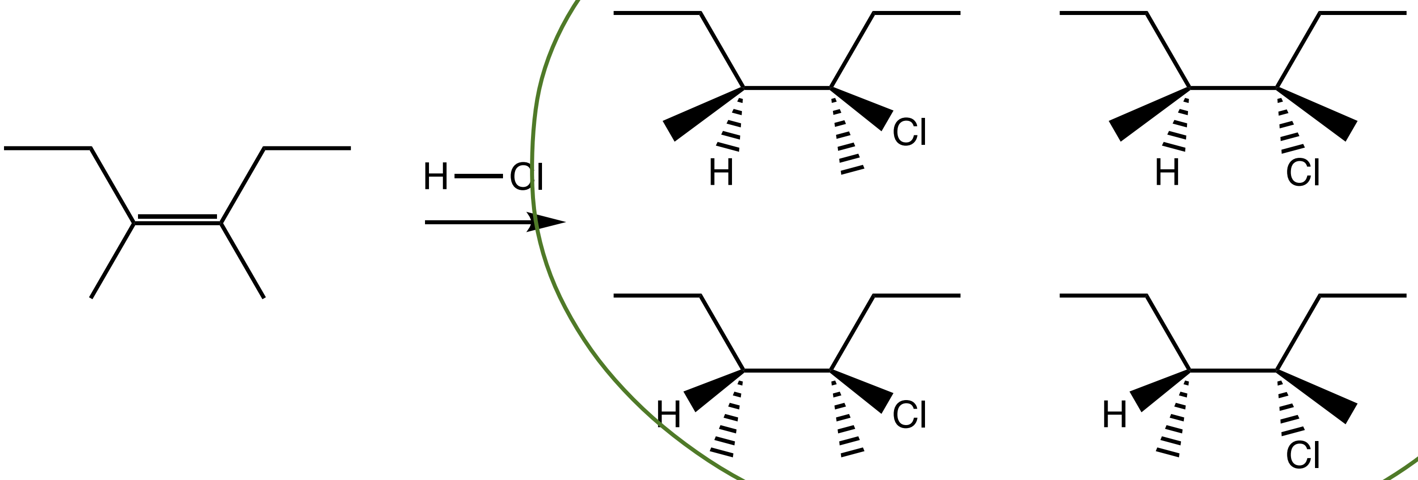
mechanism disproved

Prediction from One-Step Mechanism



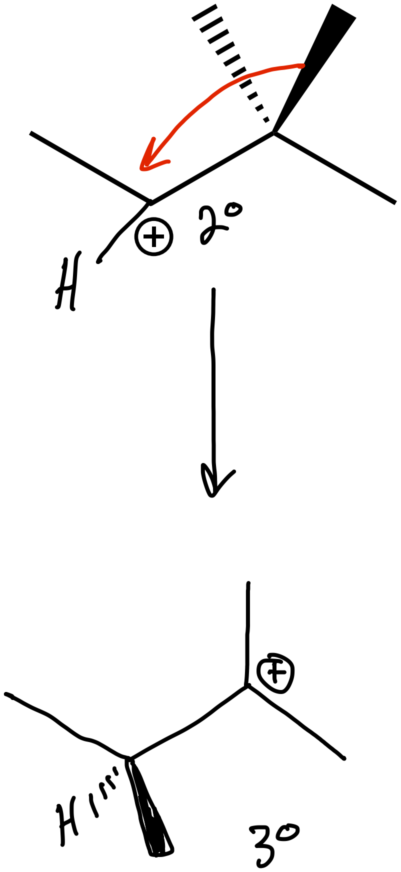
all 4 stereoisomers form

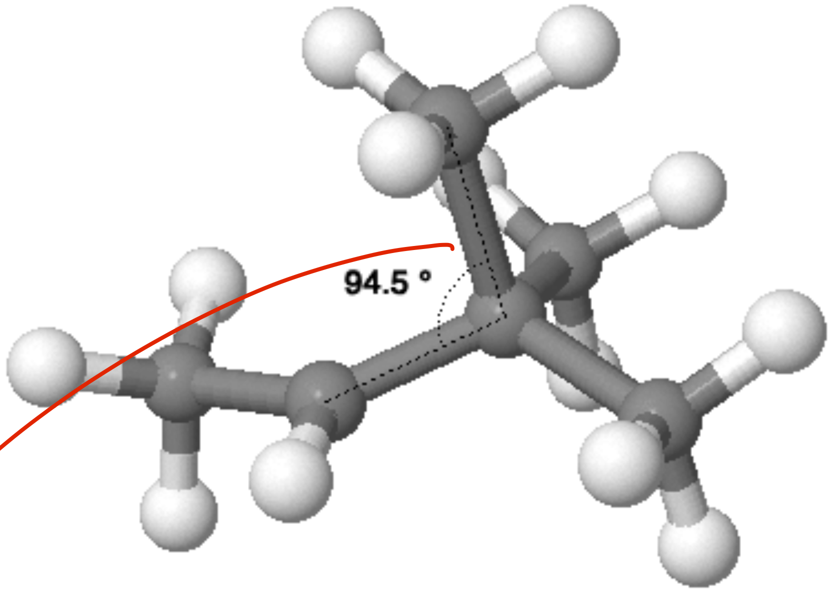
Prediction from Two-Step/Carbocation Mechanism



evidence supports 2 step C^+ mechanism

Carbocations rearrange: Evidence for the C+ based mechanism



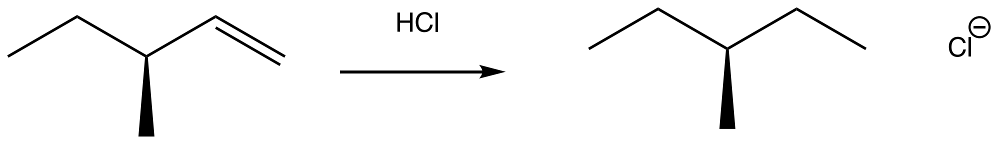


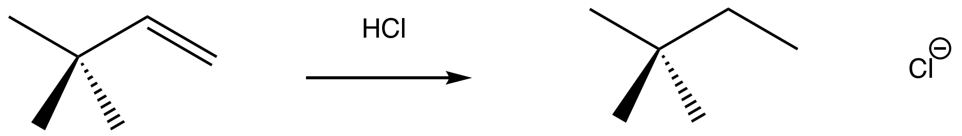
e⁻'s in this bond are being attracted to the empty p orbital

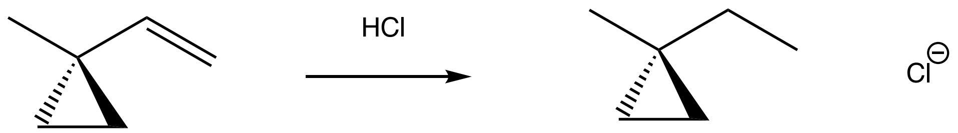
yep... C+ can and do rearrange when going from less stable to a more stable C⊕

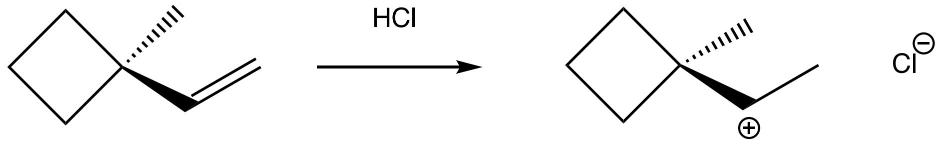
Carbocations rearrange

Section 7.11



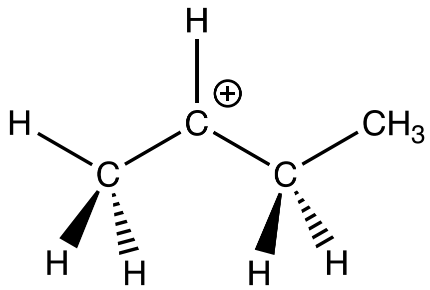






The Carbocation Summary

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^+

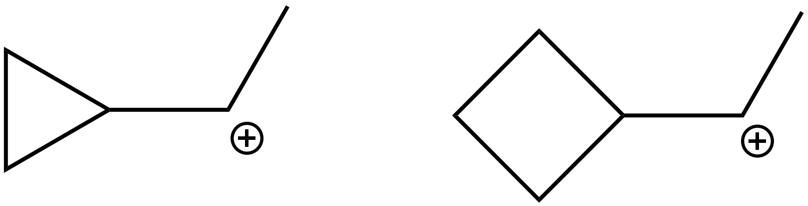
Rearranging C^+'s

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

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

$CH_2{=}CH{-}CH_2{-}CH_3 \quad H{-}Cl \longrightarrow$