(33) **Today** (a)

7.11 Evidence for the Mechanism of Electrophilic Additions: Carbocation Rearrangements
Practice Predicting Outcome of H+ Initiated Electrophilic Addition Reactions

Next Class (34)

8.2 Halogenation of Alkenes: Addition of X_2

8.3 Halohydrins from Alkenes: Addition of HO-X

(35) **Second Class from Today**

8.4 Hydration of Alkenes: Addition of H_2O by Oxymercuration

8.5 Hydration of Alkenes: Addition of H_2O by Hydroboration

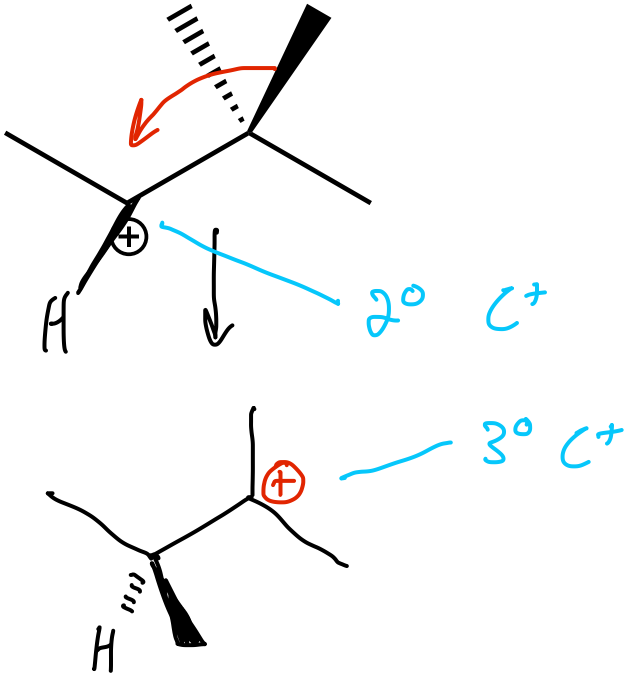
8.6 Reduction of Alkenes by Hydrogenation

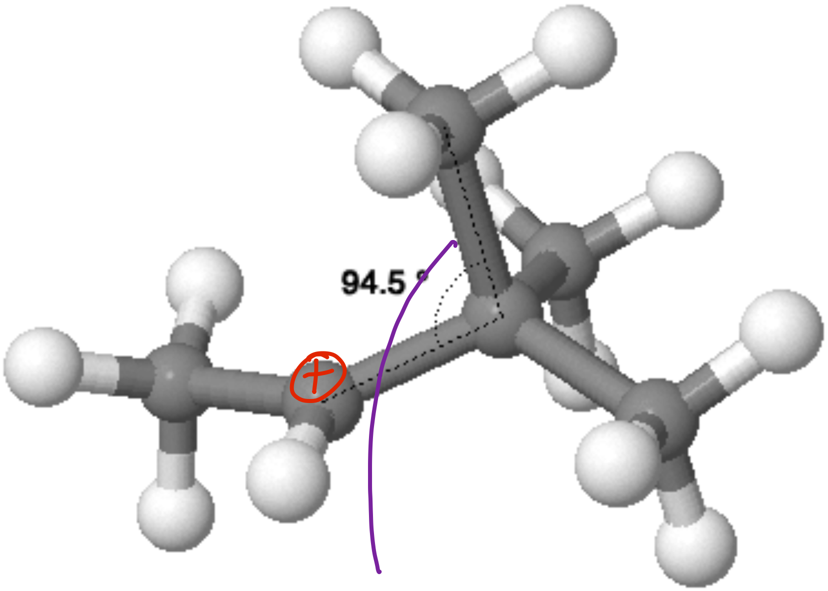
8.12 and 13: Stereochemistry of addition reactions

Third Class from Today (36)

11.1 - 11.6: Substitution Reactions
10.5, 17.6: Alcohols in Nucleophilic Substitution Reactions

Carbocations rearrange: Evidence for the C^+ based mechanism





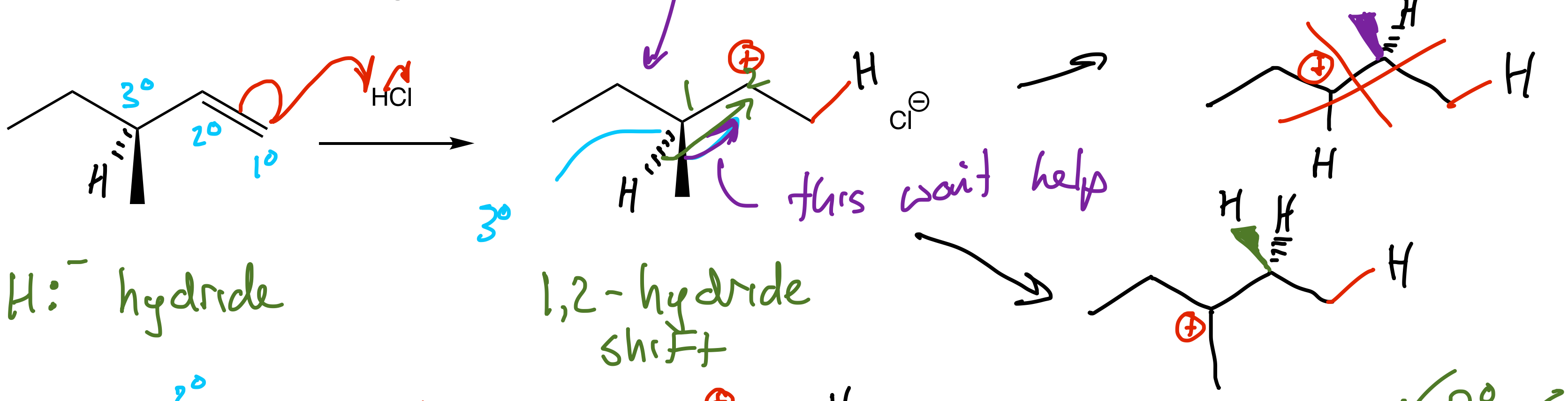
bond angle is < 112° because e^- in the bond are being attracted to the empty p orbital

C^+ can & do rearrange when they can form a more stable C^+ 1 bond away

Carbocations rearrange

Section 7.11

this bond won't move Et + larger groups are too big to move



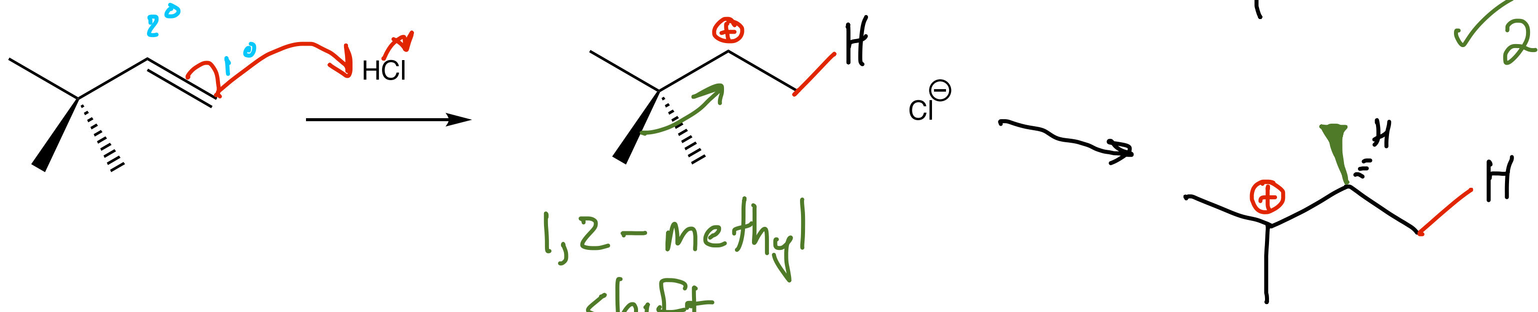
this won't help

2° C+ to 2° C+ is unlikely... not more stable

H:⁻ hydride

1,2-hydride shift

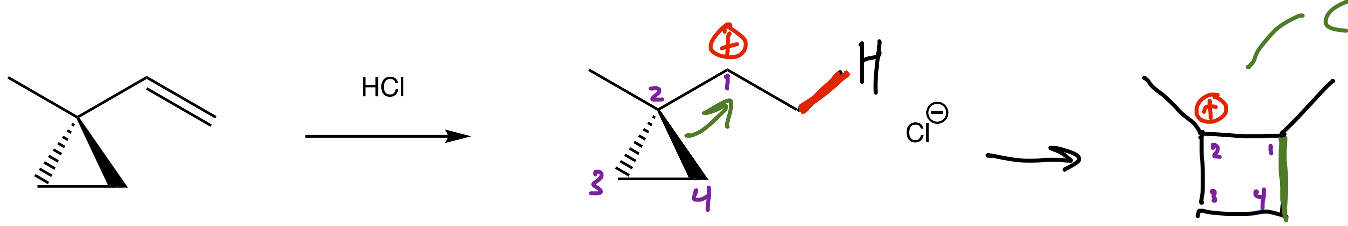
✓2° C+ → 3° C+



2° C+ → 3° C+

1,2-methyl shift

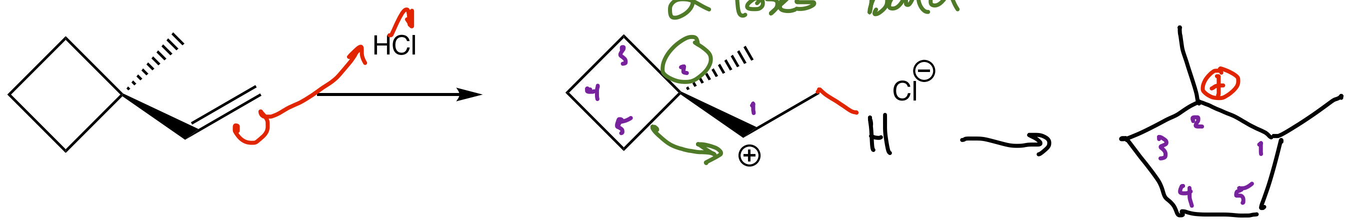
C₂ lost the bond so it became ⊕



- 3-membered to 4 strain reduced
- 2° C+ → 3° C+

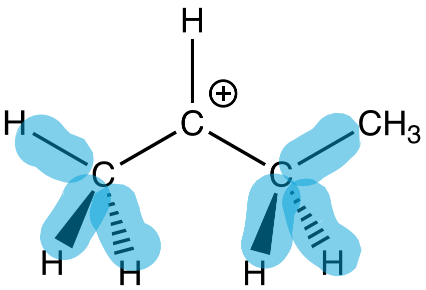
ring expanding rearrangement

2 loses bond



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^+~~ not stable enough to form under typical lab conditions

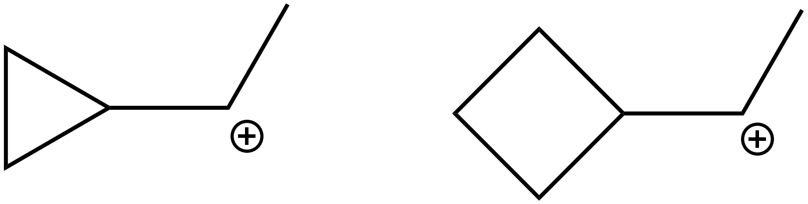
Rearranging C^+'s

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 $R\ddot{\underset{\cdot\cdot}{O}}H$ $H\ddot{\underset{\cdot\cdot}{O}}H$

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.

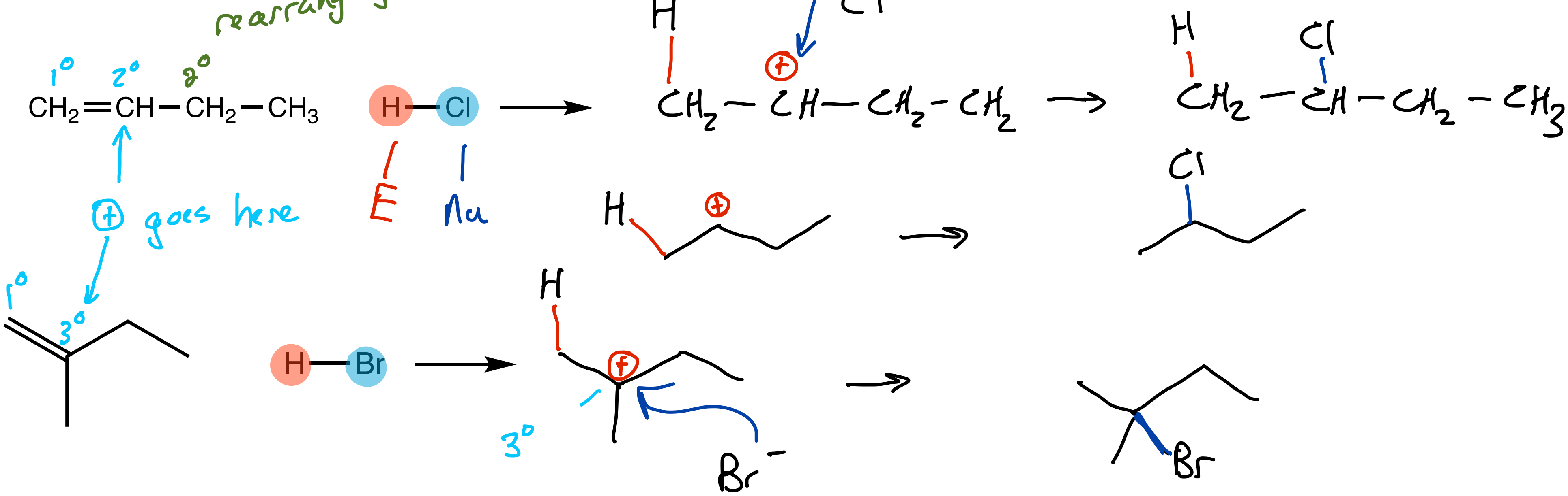
- Are the ends of the double bond identical?
  - Yes. It doesn't matter; put the + at either end and move on.
  - No. Is there a reason to prefer making one end of the bond + ?
    - Yes. Major and minor products will form. Place the + at the end where it will be more stable and move on.
    - No. ~1:1 mixture of products will result. Two intermediates form, each one with a + at one end.

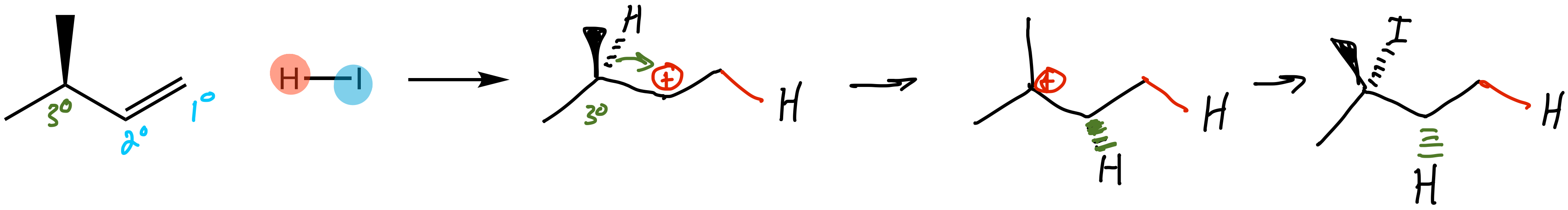
Check for carbocation rearrangement: would plus be more stable on **neighboring** C?

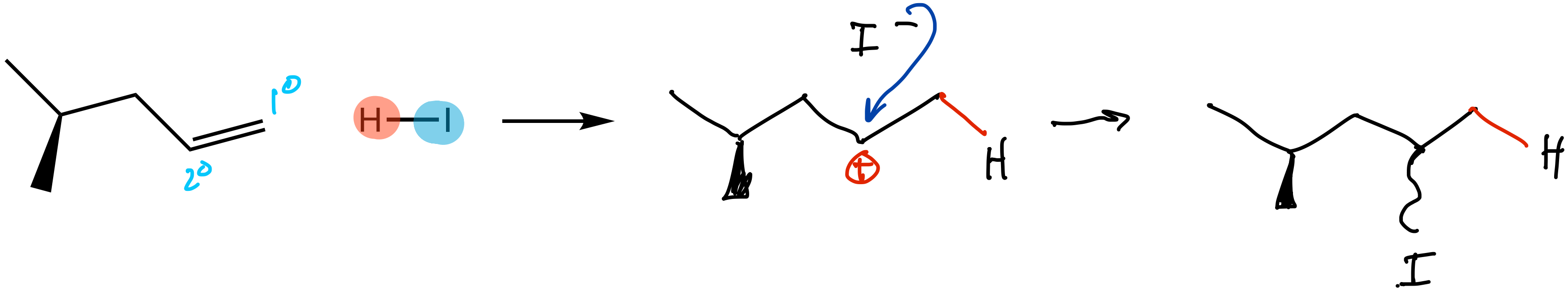
yes, rearrange no leave + where it is

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

E Add Reactions

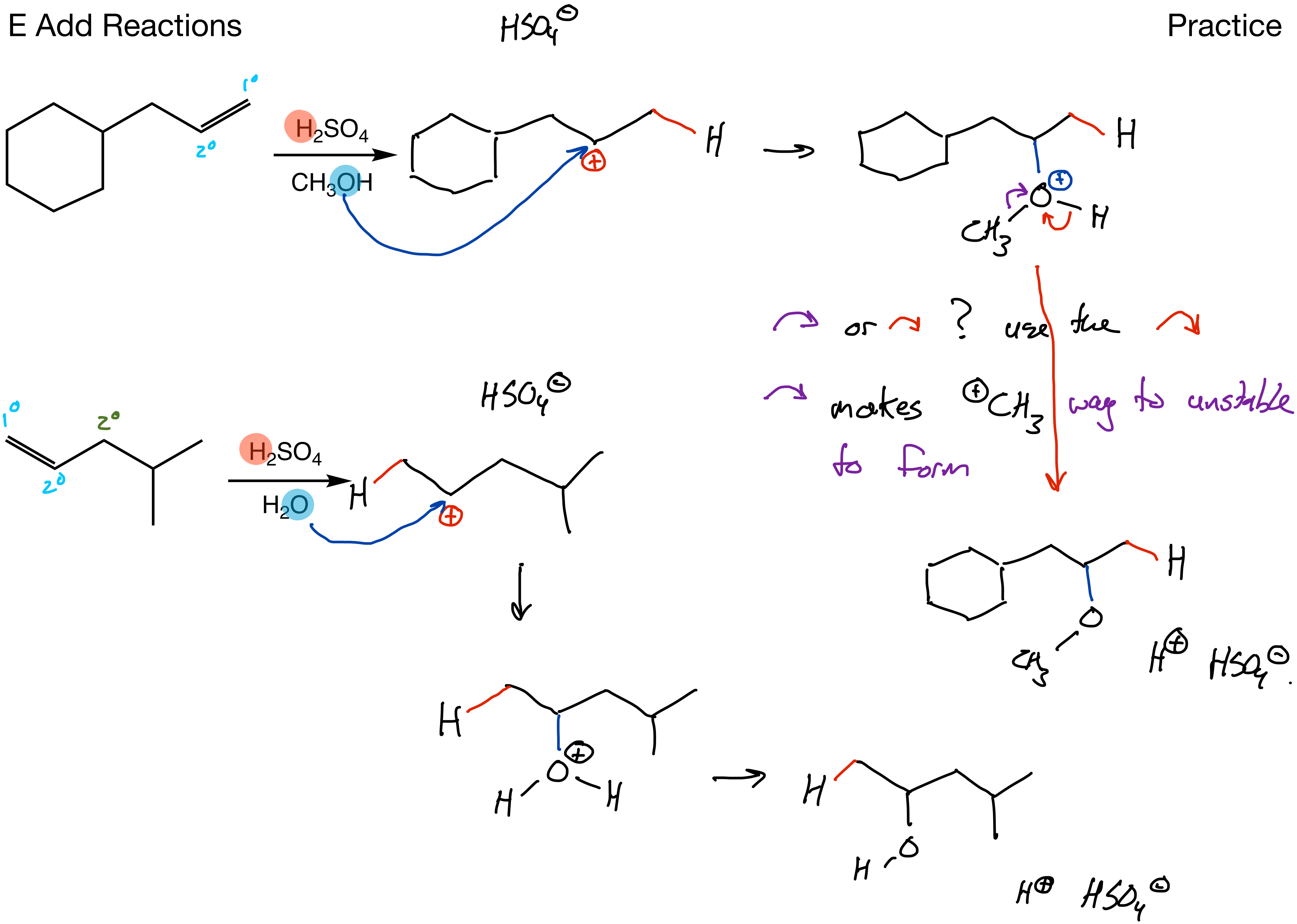






E Add Reactions

Practice



↷ or ↷ ? use the ↷ way to unstable

↷ makes $^{\oplus}CH_3$ to form