Chap 7 Appropriate Problems

7.2 Calculating the Degree of Unsaturation
Calculate degrees of unsaturation 7-1 through 7-3, 7-34, 7-35, 7-67

7.3 Naming Alkenes
Naming and drawing structures 7-4 through 7-7, 7-22, 7-37 through 7-44

7.4 Cis–Trans Isomerism in Alkenes
Naming and drawing cis/trans alkenes 7-8 through 7-10

7.5 Alkene Stereochemistry and the E,Z Designation
Assigning priorities 7-11 and 7-12
Determining configuration and drawing alkenes 7-13 and 7-14, 7-23, 7-45 through 7-47, 7-53, 7-63, 7-65

7.7 Electrophilic Addition Reactions of Alkenes

7.8 Orientation of Electrophilic Additions: Markovnikov's Rule (Regioselectivity)
Predict the outcome 7-16 and 7-17, 7-57 through 7-59

7.9 Carbocation Structure and Stability
Predict C+ 7-18 and Draw C+ 7-19, 7-25, 7-54, 7-56

7.10 The Hammond Postulate
Drawing a transition state 7-20, 7-55

7.11 Evidence for the Mechanism of Electrophilic Additions: Carbocation Rearrangements
Mechanism for 7-21, 7-26 through 7-33 7-28 and 7-29 (consider the resonance contributor of the intermediate), 7-60, 7-66, 7-70

Uncategorized
7-61, 7-68, 7-69

Use **degrees of unsaturation** to determine number of π-bonds or rings in a molecule

Use IUPAC nomenclature to **name alkenes**

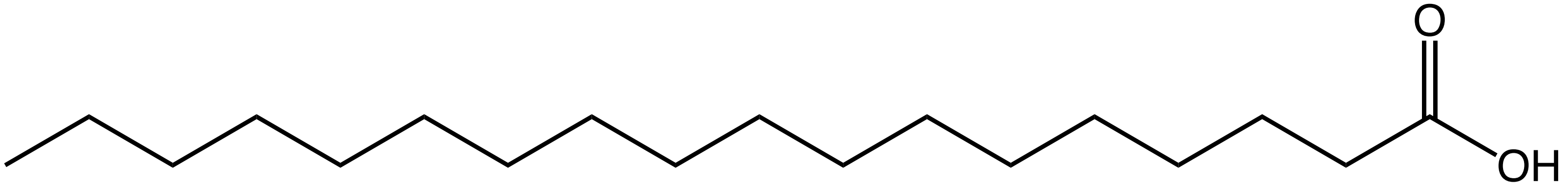
Use *cis/trans* and ***Z/E*** designations where appropriate to indicate the configurations of **alkene stereoisomers**

Explain the structure and reactivity of alkenes

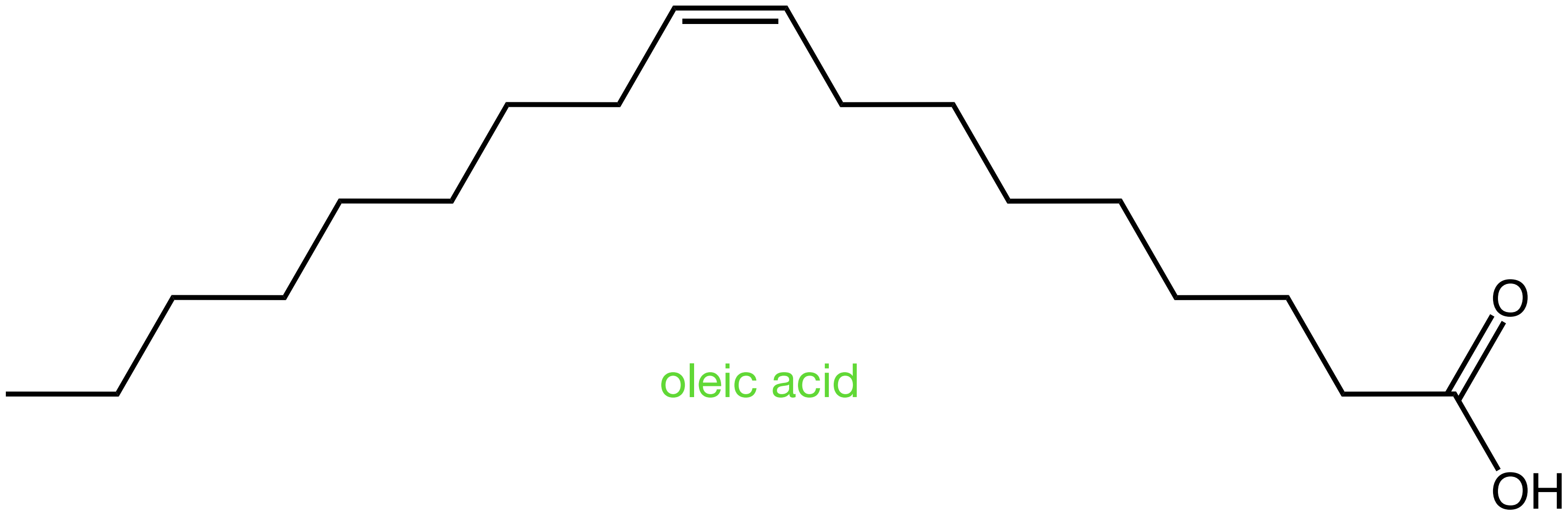
Predict the **outcome** of H^+ initiated electrophilic addition reactions

Degrees of Unsaturation: saturated vs unsaturated

Knowing the "degrees of unsaturation" can help a chemist determine the structure of an unknown compound.

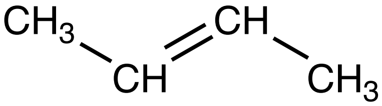


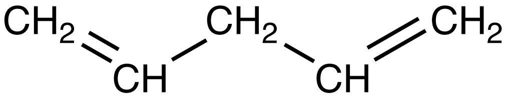
palmitic acid

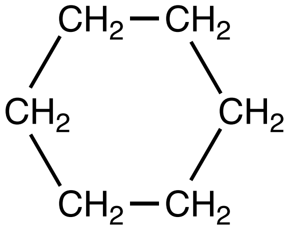


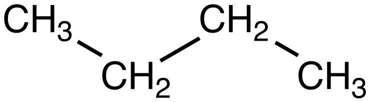
oleic acid

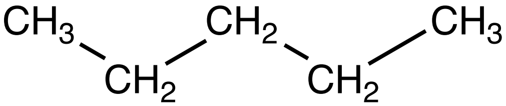
Degrees of Unsaturation: saturated vs unsaturated

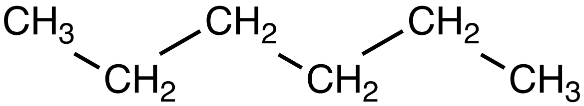










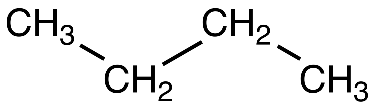


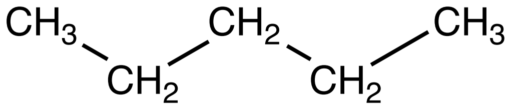
one degree of unsaturation means one π bond or one ring

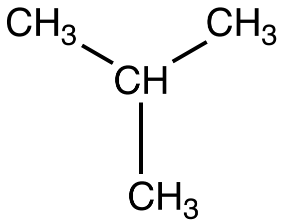
two degrees of unsaturation means two π bond, one π bond and one ring, or two rings

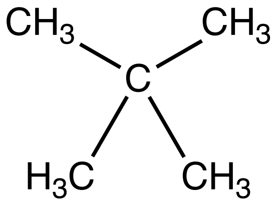
three degrees of unsaturation means three π bonds, etc...

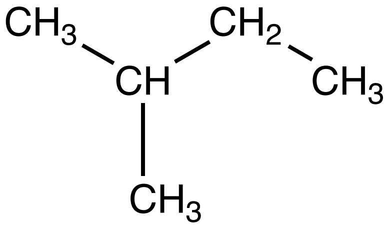
Degrees of Unsaturation: the number of H atoms needed to 'saturate' C atoms



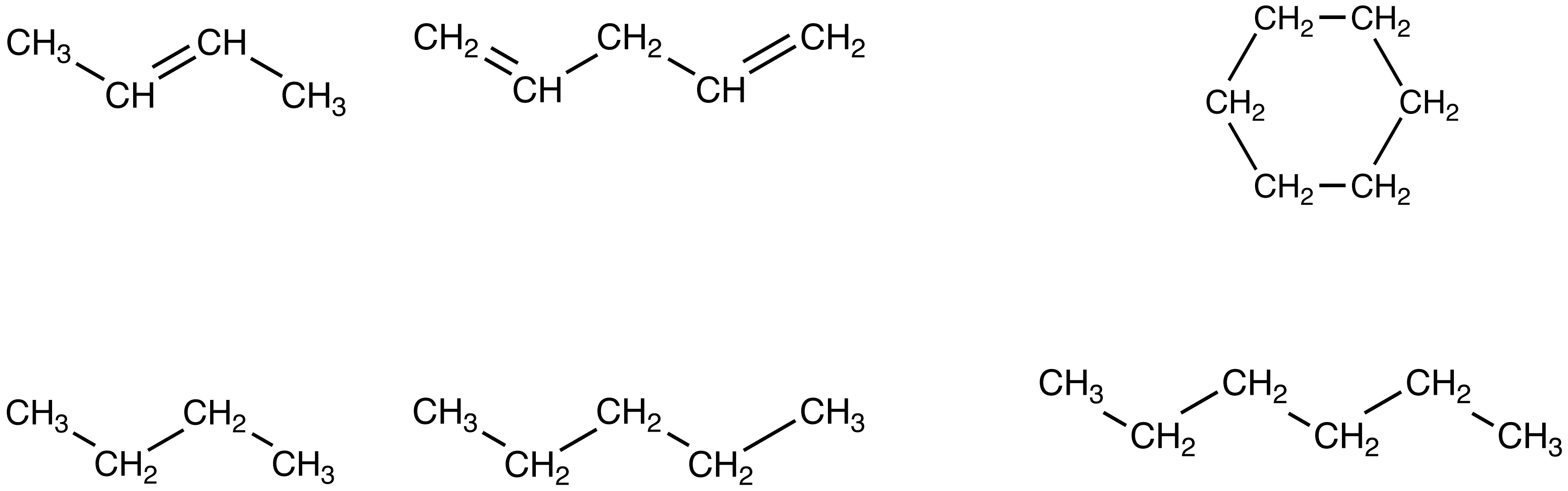








Degrees of Unsaturation

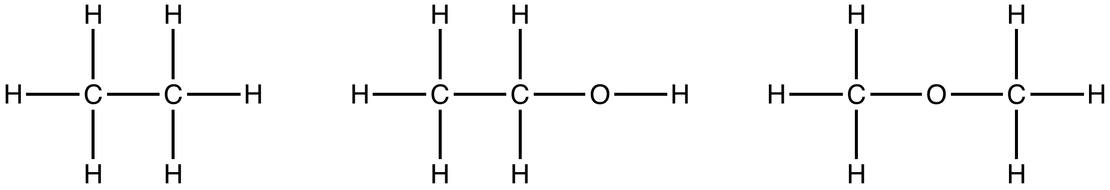


$$\frac{(\text{"expected" \# of H atoms}) - (\text{actual \# of H atoms})}{2} = \begin{array}{c}\text{degrees}\\ \text{of}\\ \text{unsaturation}\end{array}$$

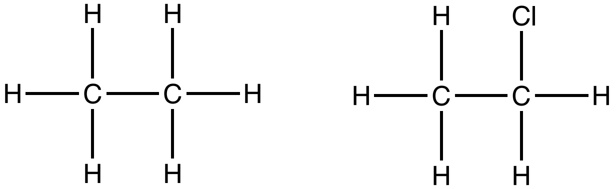
Degrees of Unsaturation: The presence of other atoms

How do other atoms effect the number of H atoms needed to saturate the C atoms?

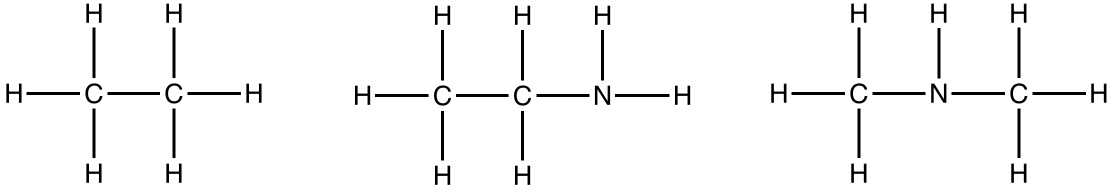
O or S atoms



Halogens



N or P atoms



Degrees of Unsaturation

$$\frac{(\text{"expected" \# of H atoms}) - (\text{actual \# of H atoms})}{2} = \text{degrees of unsaturation}$$

How do non C atoms effect the number of H atoms needed to saturated the bonding?

O or S atoms

Halogens

N or P atoms

$$(\text{"expected" \# of H atoms}) = 2 \times (\text{\# C atoms}) + 2 - (\text{\# halogen atoms}) + (\text{\# of N atoms})$$

determine degrees of unsaturation in

C_3H_7ClO

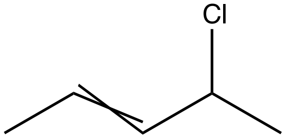
C_7H_9N

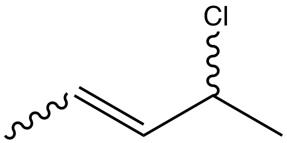
Alkene Nomenclature

A note on some special names

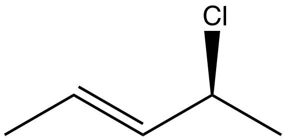
Allyl and Vinyl

A note on how structures are drawn



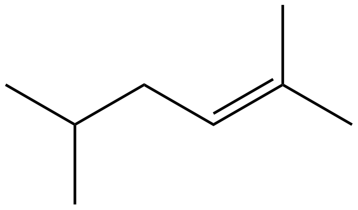


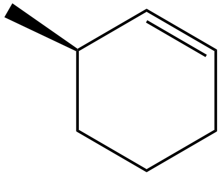
$CH_3—CH=CH—CHCl—CH_3$

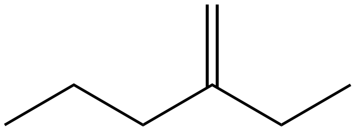


Same rules as alkanes except, alkenes are a functional group, so the position of the double bond gets the lowest number and "ane" ending of parent hydrocarbon is changed to "ene" and the double bond **must** be fully contained in the longest carbon chain.

Practice





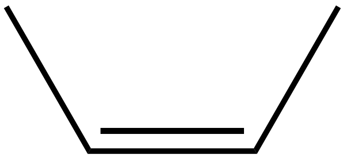


cis and *trans* Stereoisomers in alkenes

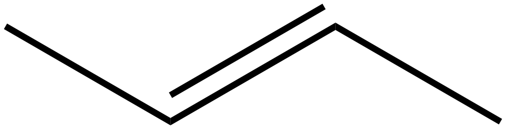
Convert $CH_3–CH=CH–CH_3$ to a skeletal structure

cis and *trans* Stereoisomers in alkenes

Convert $CH_3–CH=CH–CH_3$ to a skeletal structure



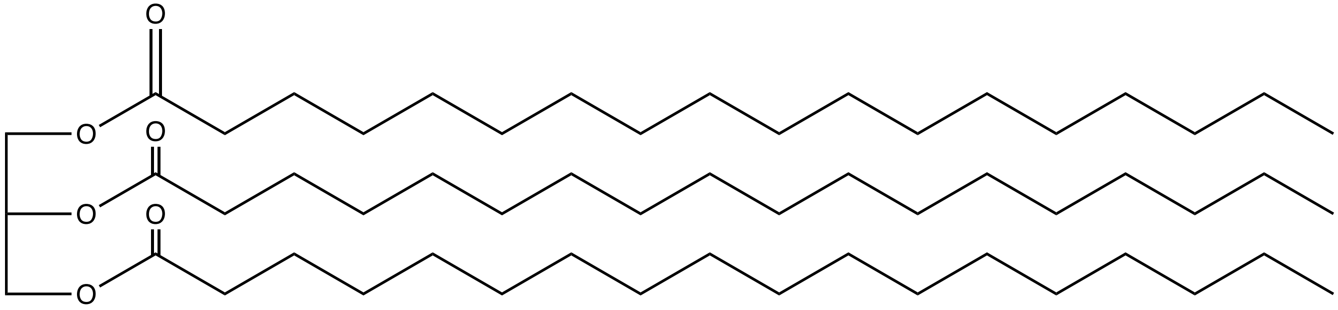
BP 3.7 °C
MP -139.0 °C

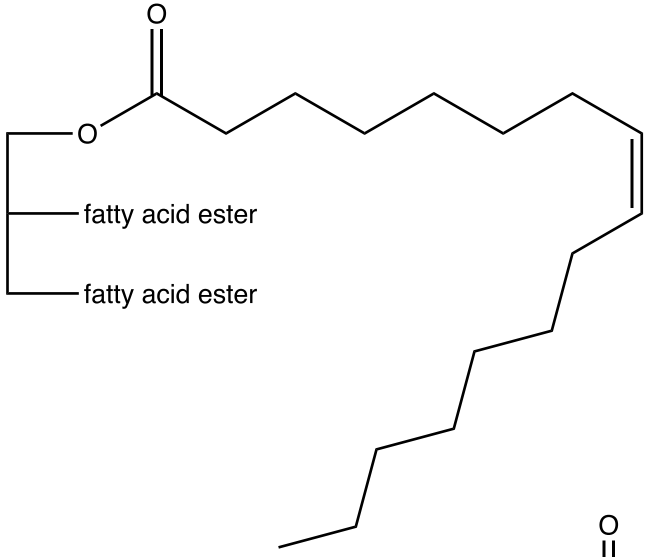


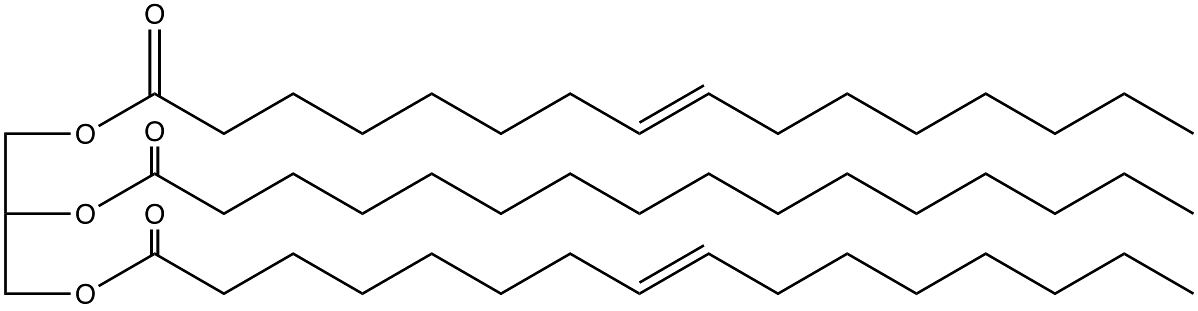
BP 1.0 °C
MP -105.0 °C

cis and *trans* Stereoisomers in alkenes

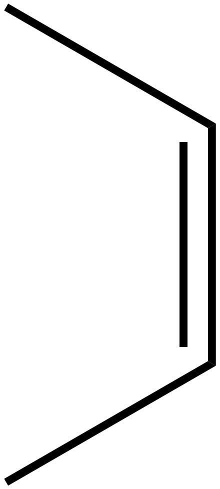
Section 7.4





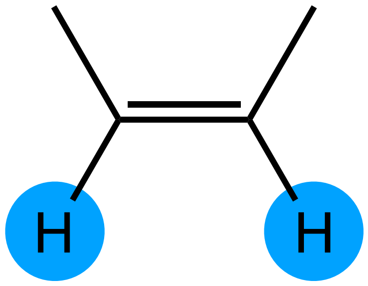


Ends, Sides, and Faces

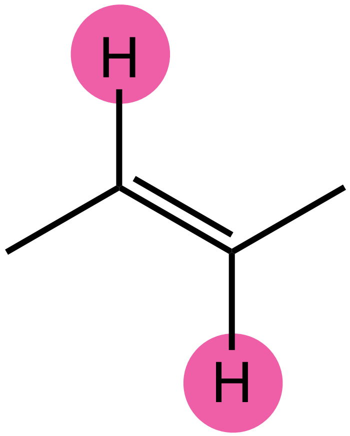


cis and *trans* Stereoisomers in alkenes

Convert $CH_3{-}CH{=}CH{-}CH_3$ to a skeletal structure



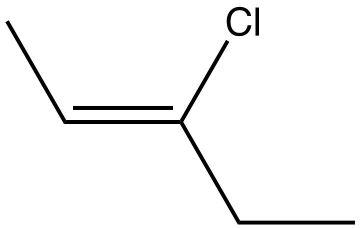
BP 3.7 °C
MP -139.0 °C

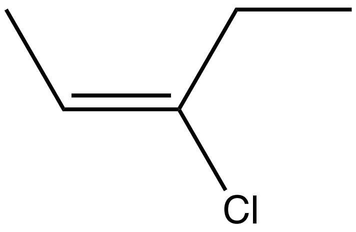


BP 1.0 °C
MP -105.0 °C

cis** and **trans nomenclature can only be used when then there are hydrogen atoms at each end of the bond

Stereoisomers in alkenes: *cis* and *trans* nomenclature doesn't work for all alkenes





The *E*, *Z* system for naming stereoisomers of alkenes

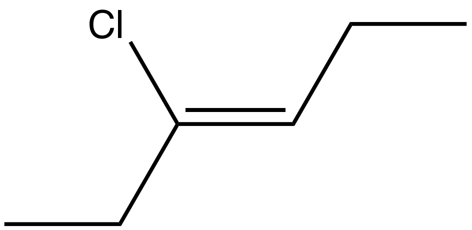
First: One end at a time, assign priority to groups at each end of double bond

- higher priority is given to the group with the higher atomic number for the atom directly bonded to the sp^2 carbon
- in a tie, consider the atomic numbers of the atoms attached to the atom that is attached to the sp^2 carbon (move one bond further out from the sp^2 hybridized C atom)

- if the atom that is attached to the sp^2 carbon has a doubly bonded or triply bonded atom attached to it the atom is treated like there are two or three atoms singly bonded to the atom that is bonded to the sp^2 carbon

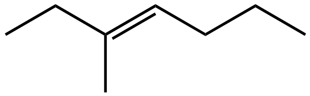
- when comparing isotopes, the mass number is used (D vs H, ^{12}C vs ^{13}C)

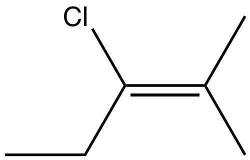
Second: If the high priority groups at each end of the double bond are on the **Zame Zide**, the proper designation is **Z**, if they are on **opposite** sides, then **E**.

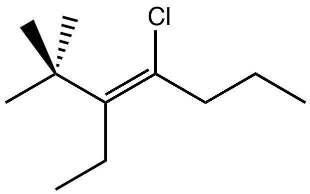


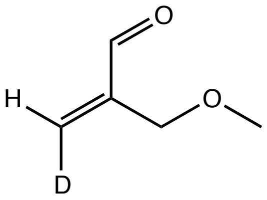
https://www.westfield.ma.edu/PersonalPages/cmasi/Z,E_priority_worksheet.pdf practice

Section 7.5



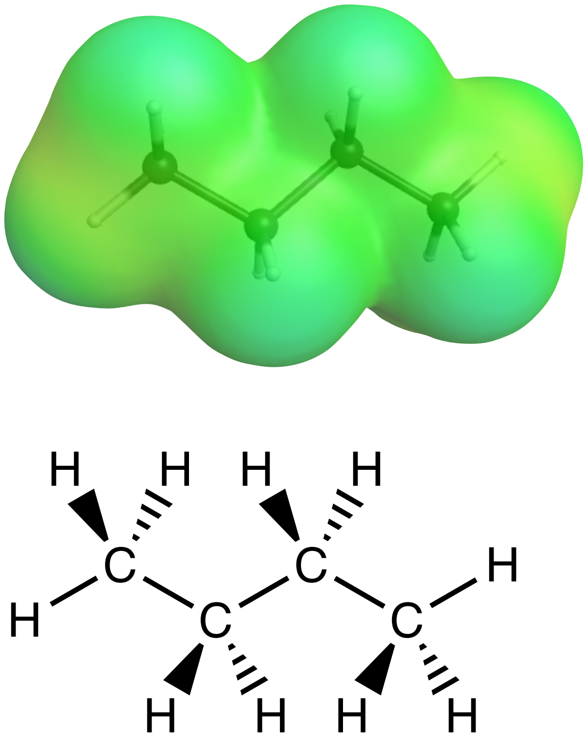


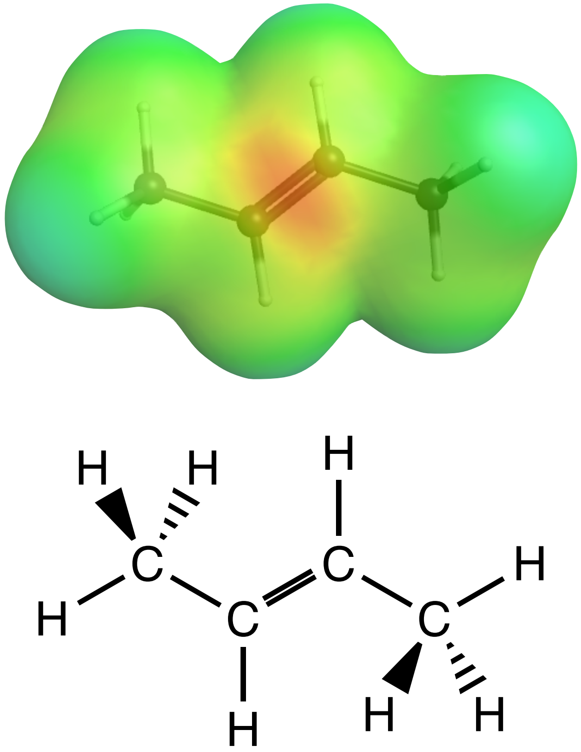




Alkene Reactivity

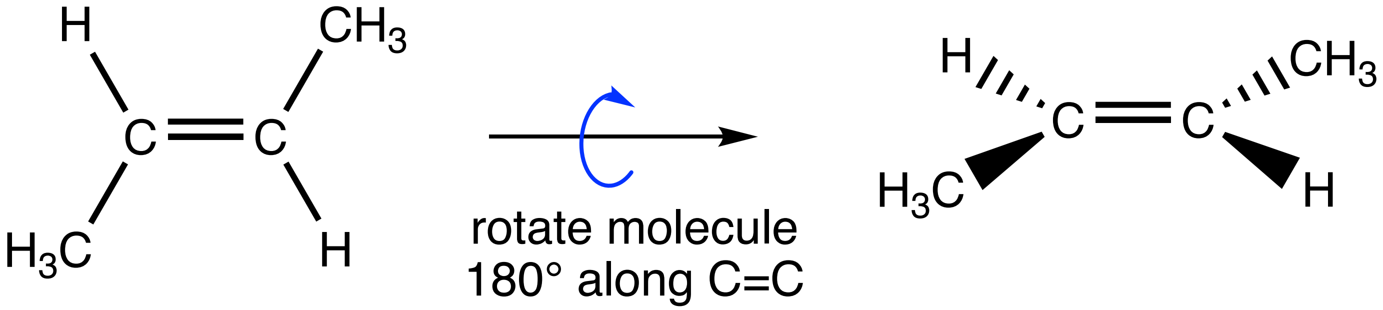
Alkenes are electron rich

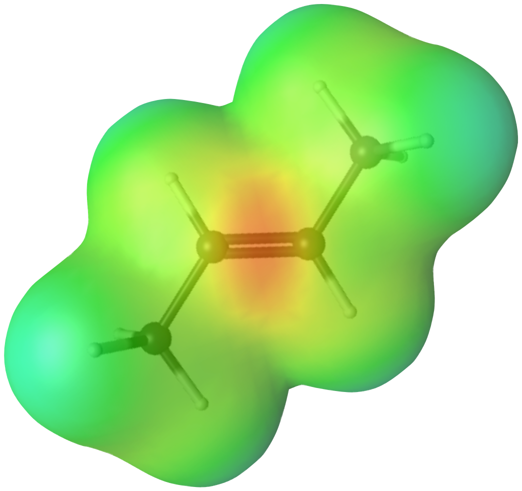


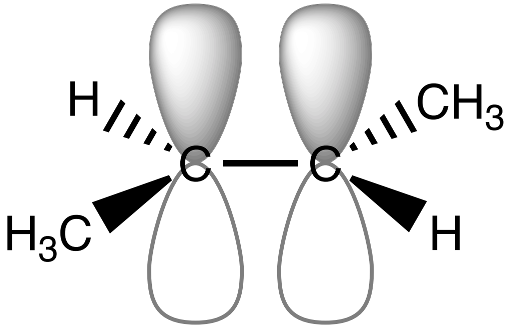


Alkene Reactivity

Alkenes are electron rich







Alkene Reactivity

Alkenes react with electrophiles…

$$H_2C{=}CH_2 \xrightarrow[\text{rxn}]{\text{E Add}} E{-}CH_2{-}CH_2{-}Nu$$

E = generic electrophile

Nu = generic nucleophile

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

Predict the outcome of electrophilic addition reactions

Draw mechanisms for electrophilic addition reactions

Know and explain the stability ordering for carbocations

Draw and, using the Hammond postulate, compare transition states for electrophilic addition reactions

Explain the stereochemical evidence for the formation of a C+ intermediate

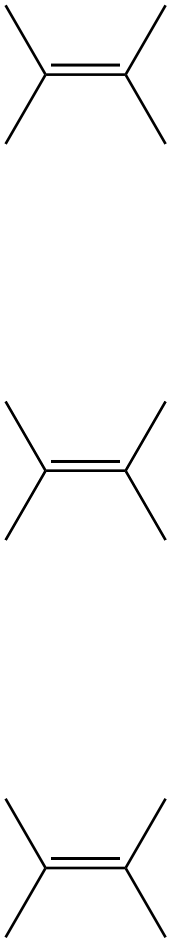
Predict products for reactions that involve C+ rearrangements

Draw mechanisms for reactions that involve C+ rearrangements

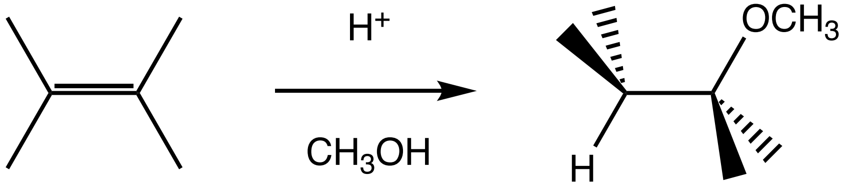
Alkene Reactivity

Section 7.7

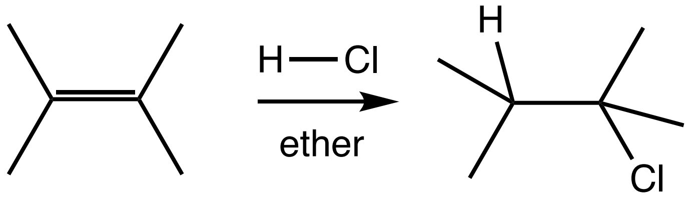
H+-based Electrophiles



What H+ producing acid to use?

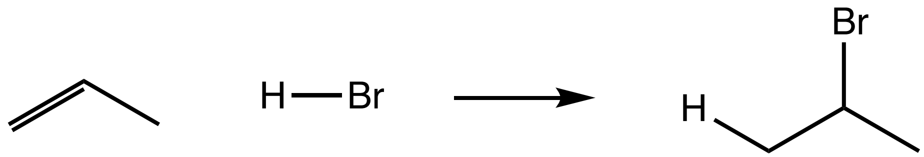


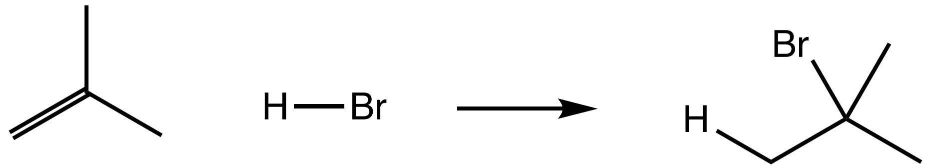
Mechanism of H+ Initiated Electrophilic Additions

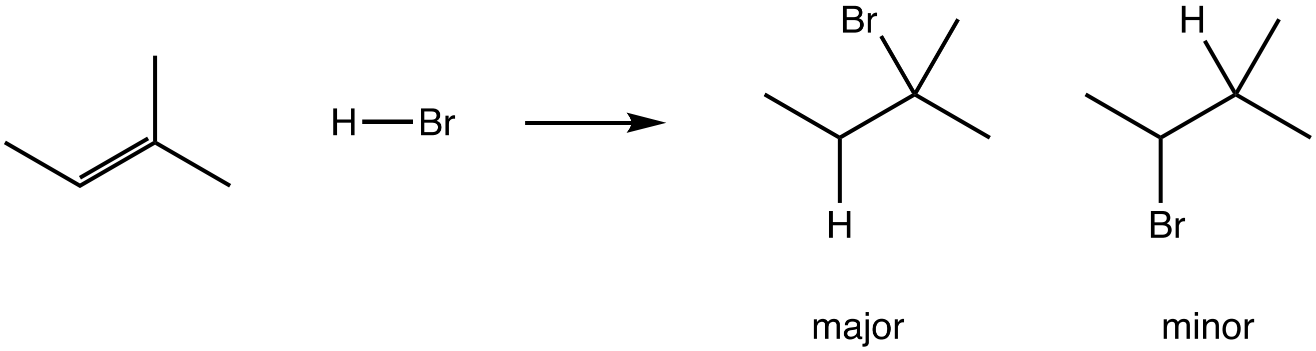


Orientation of Electrophilic Additions: Markovnikov's Rule

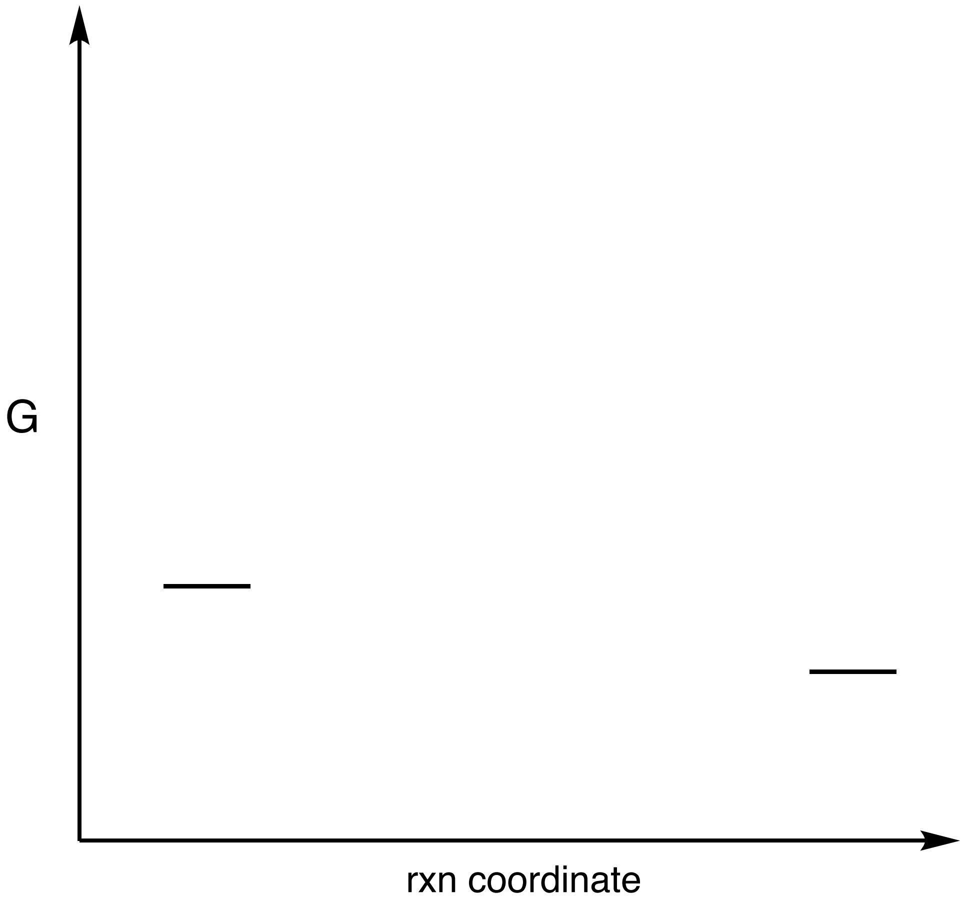
Regioselectivity: The ability of a reaction to prefer the formation of one constitutional/structural isomer over another.

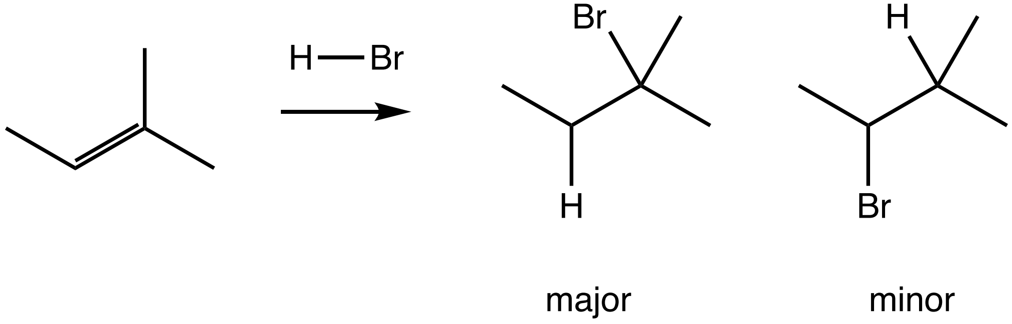






The Carbocation Intermediate, the Hammond Postulate and Regioselectivity





The Carbocation Intermediate, the Hammond Postulate and Regioselectivity

C^+ Stability

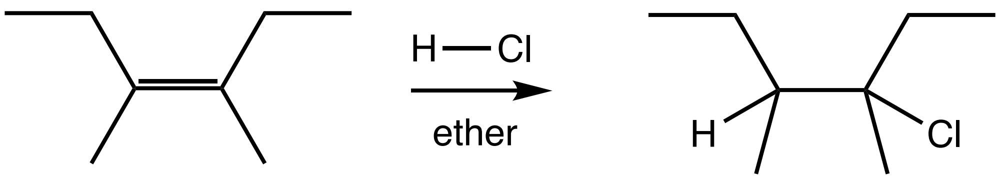
https://www.westfield.ma.edu/cmasi/organic/carbocation_stabilization/carbocation-lumo-plain.html

Restating Markovinkov's Rule

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

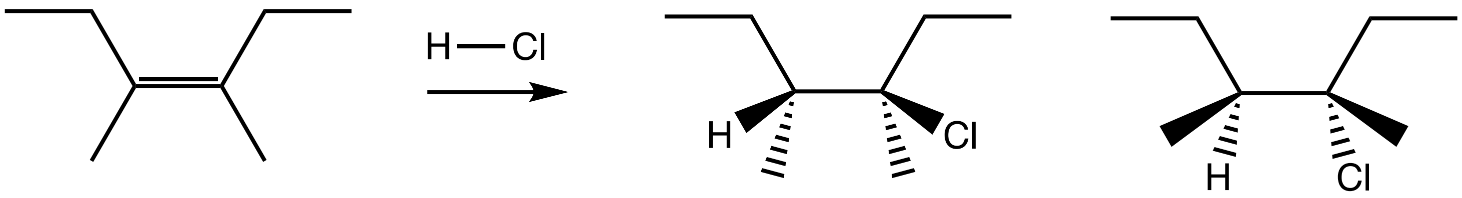
Restated: When the electrophile adds it does so such that a positive charge develops on the C atom that is better able to stabilize the positive charge.

Evidence for the C^+ based mechanism: Stereochemical Outcome



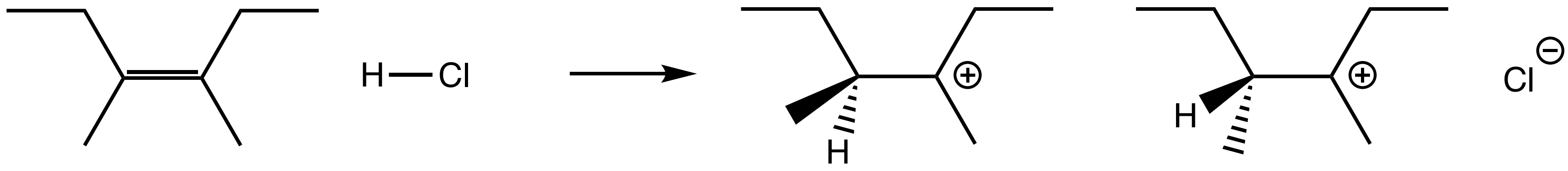
Evidence for the C+ based mechanism: Stereochemical Outcome

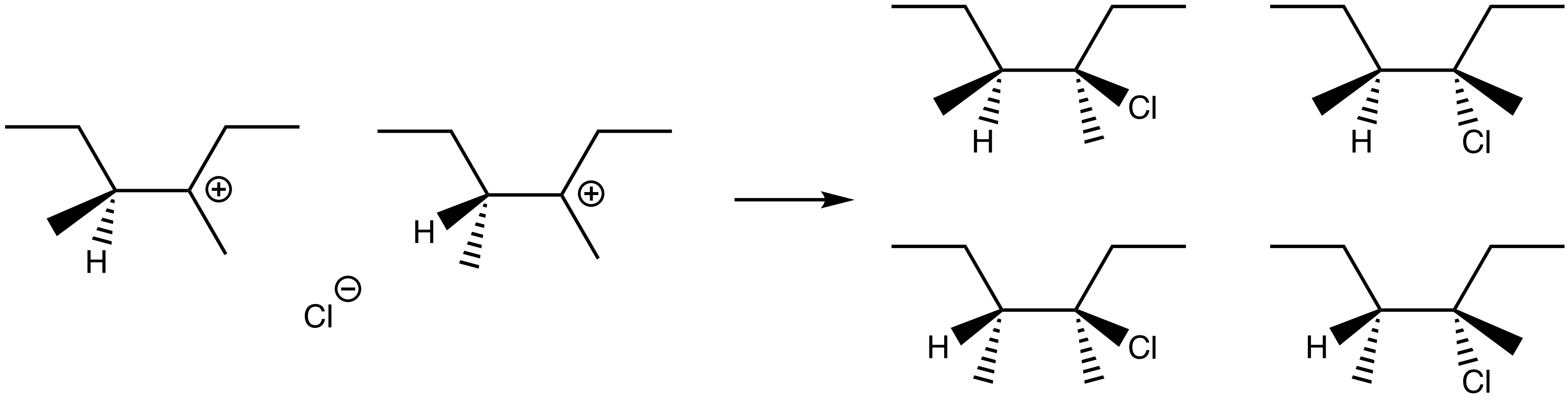
One-Step Mechanism



Evidence for the C+ based mechanism: Stereochemical Outcome

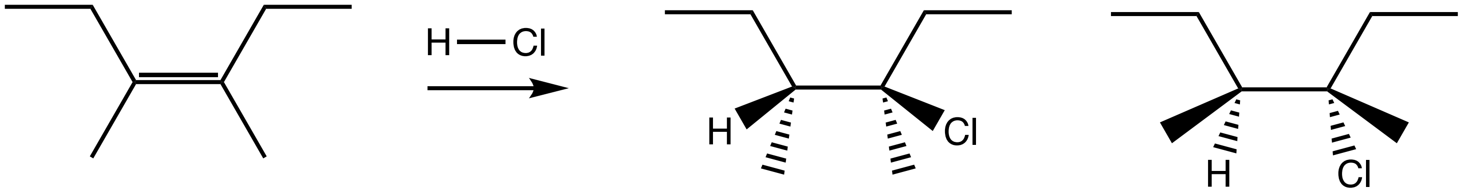
Two-Step/Carbocation Mechanism



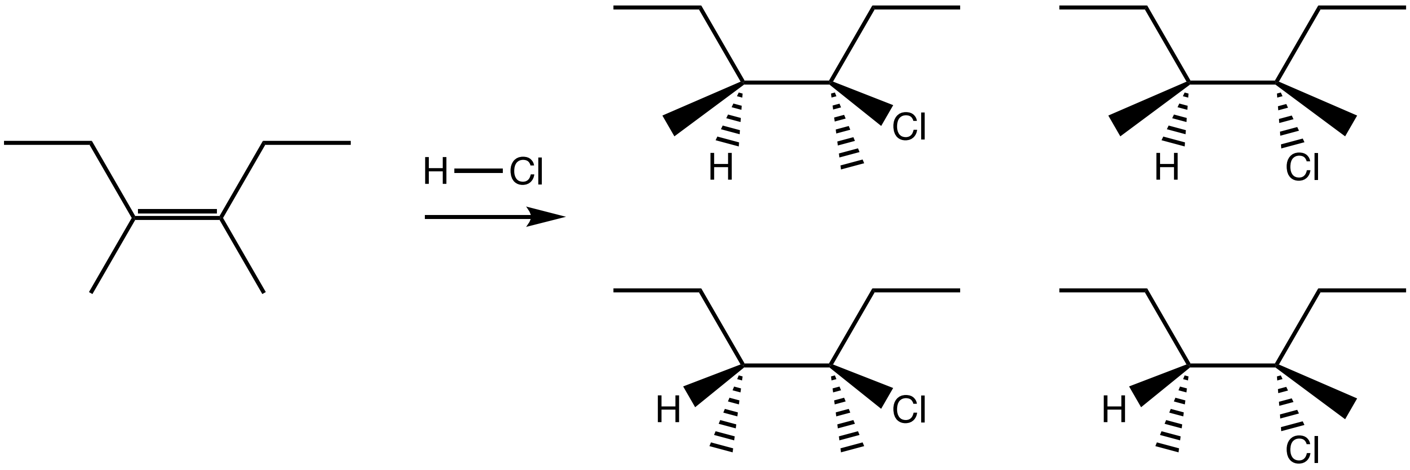


Evidence for the C^+ based mechanism in H^+ Initiated Reactions: Stereochemical Outcome

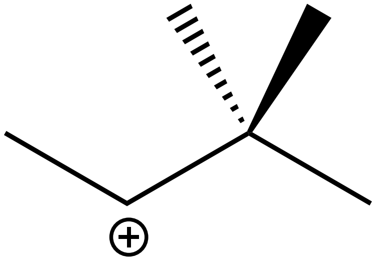
Prediction from One-Step Mechanism

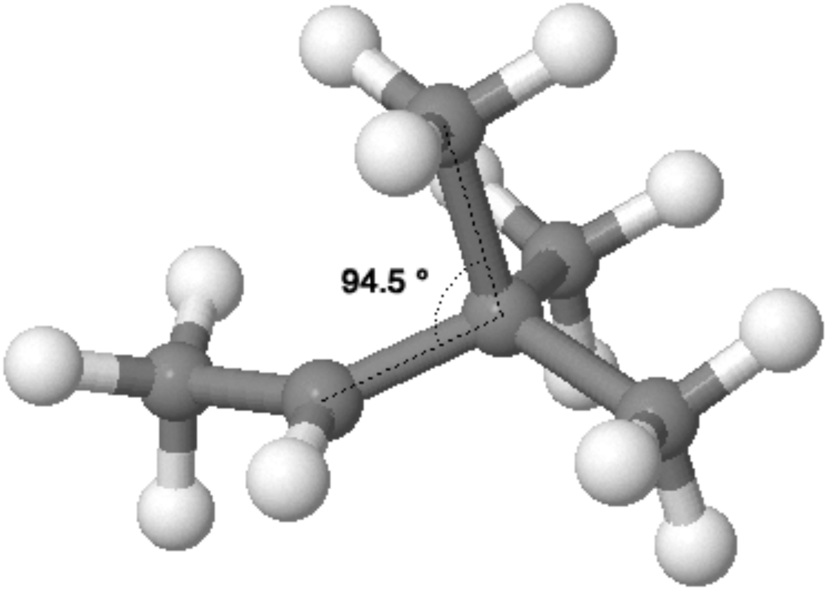


Prediction from Two-Step/Carbocation Mechanism



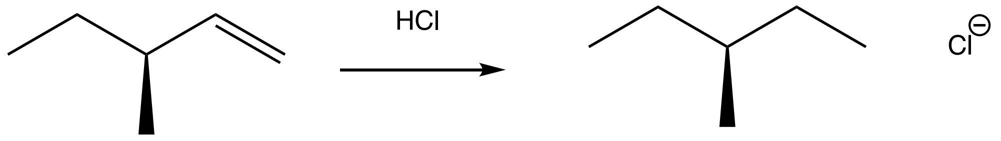
Carbocations rearrange: Evidence for the C^+ based mechanism

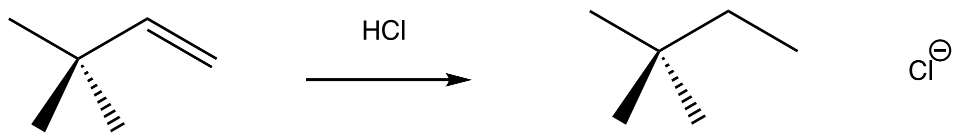


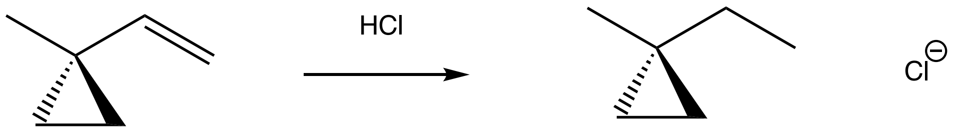


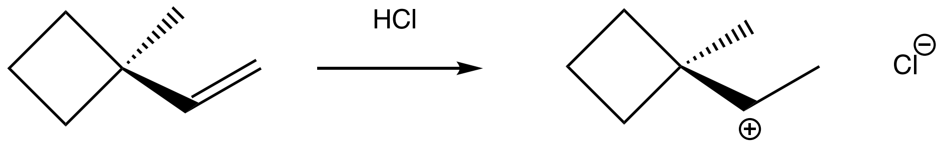
Carbocations rearrange

Section 7.11



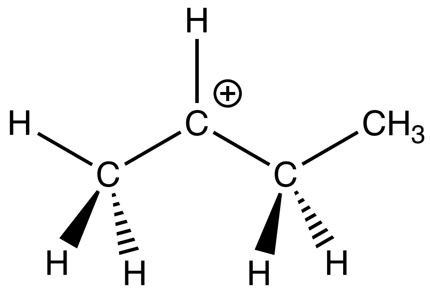






The Carbocation Summary

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+

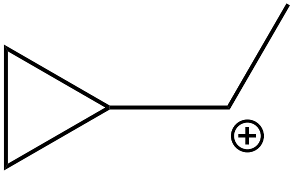
Rearranging C+'s

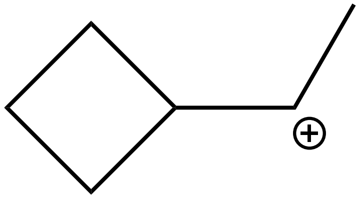
H atoms and methyl groups (CH_3's) will move from a neighboring C atom if the new C+ would be more stable

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.

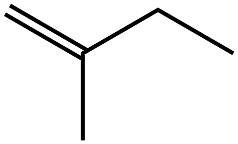
Check for carbocation rearrangement: would plus be more stable on **neighboring** C?

yes, rearrange   no   leave + where it is

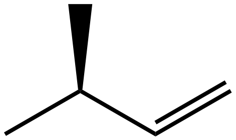
Make a bond from the nucleophile to the C with the + charge.

E Add Reactions

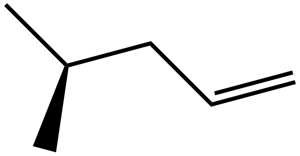
$CH_2{=}CH-CH_2-CH_3 \quad H-Cl \longrightarrow$



$H-Br \longrightarrow$



$H-I \longrightarrow$



$H-I \longrightarrow$