

Chapter 6 – Alkenes I

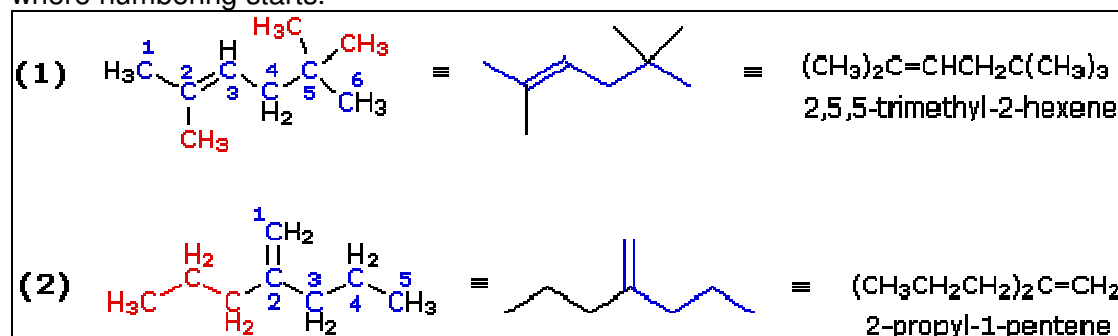
Naming Alkenes

General Rule: replace ane with ene.

No. of Carbons	IUPAC Name	Common Name	Formula C_nH_{2n}	Structure
2	Ethane	ethylene	C_2H_4	$CH_2=CH_2$
3	Propene	propylene	C_3H_6	$CH_2=CHCH_3$
4	1-Butene	butylene	C_4H_8	$CH_2=CHCH_2CH_3$
5	1-Pentene	“	C_5H_{10}	$CH_2=CHCH_2CH_2CH_3$

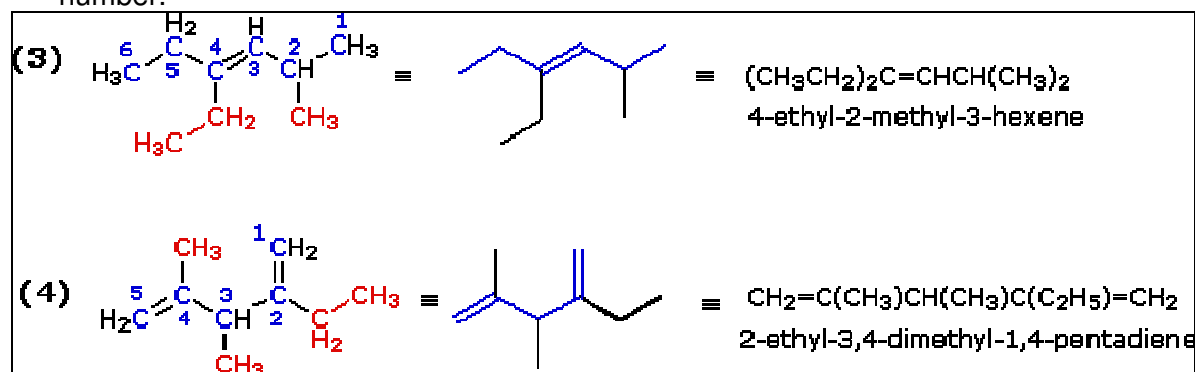
IUPAC Rules for Alkene and Cycloalkene Nomenclature

1. Find the longest chain; will end in -ene.
2. The longest chain chosen for the root name must include both carbon atoms of the double bond.
3. The longest chain must be numbered from the end nearest a double bond carbon atom. If the double bond is in the center of the chain, the nearest substituent rule is used to determine the end where numbering starts.



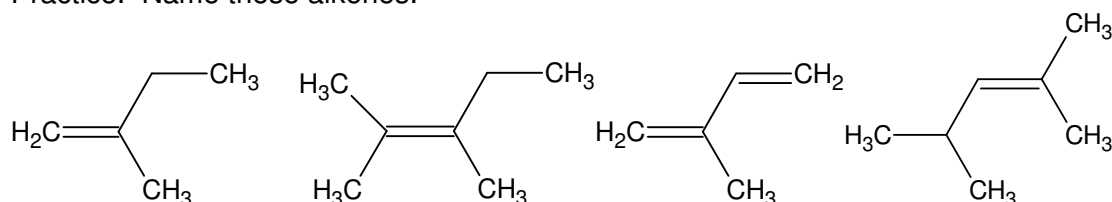
<http://www.cem.msu.edu/~reusch/VirtualText/nomen1.htm#nom3>

4. The smaller of the two numbers designating the carbon atoms of the double bond is used as the double bond locator.
5. If more than one double bond is present the compound is named as a diene, triene or equivalent prefix indicating the number of double bonds, and each double bond is assigned a locator number.

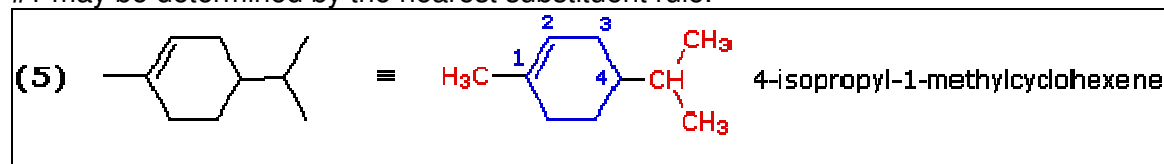


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Practice. Name these alkenes:

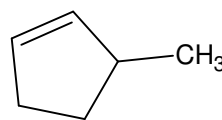
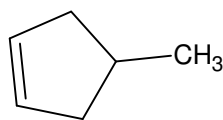
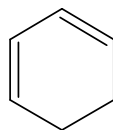


In cycloalkenes the double bond carbons are assigned ring locations #1 and #2. Which of the two is #1 may be determined by the nearest substituent rule.



<http://www.cem.msu.edu/~reusch/VirtualText/nomen1.htm#nom3>

Practice. Name these alkenes:



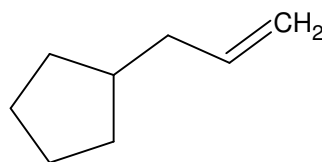
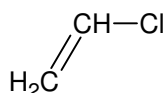
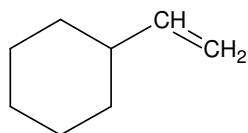
Alkene as substituent

Substituent groups containing double bonds are:

$\text{H}_2\text{C}=\text{CH}-$ Vinyl group

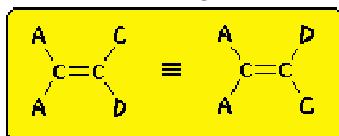
$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-$ Allyl group

Application:

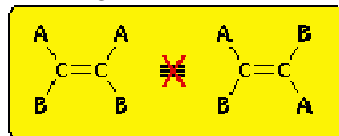


Cis/Trans

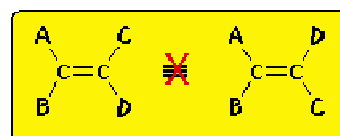
Consider the arrangement of groups arranged around a double bond:



Example 1

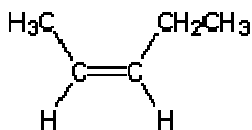


Example 2

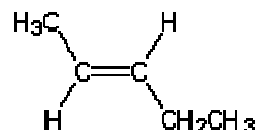


Example 3

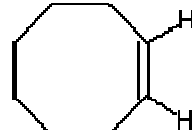
In example 2 and 3, the connectivity (name) is the same. This type of isomer is called stereoisomerism. Here are some real cases: Notice the cis or trans designation.



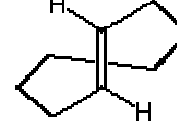
cis-2-pentene



trans-2-pentene

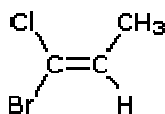


cis-cyclooctene

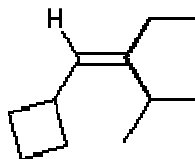


trans-cyclooctene

Here it's all OK, but there are cases in which the cis/trans rules are useless. How would you assign cis/trans here?



Compound A
(one isomer)



Compound B
(one isomer)

<http://www.cem.msu.edu/~reusch/VirtualText/sterisom.htm#isom1>

We order groups on each side of the = and then evaluate which is on the same side (Z) – kind of like cis – or the opposite sides (E) – kind of like trans.

The Sequence Rule for Assignment of Alkene Configurations

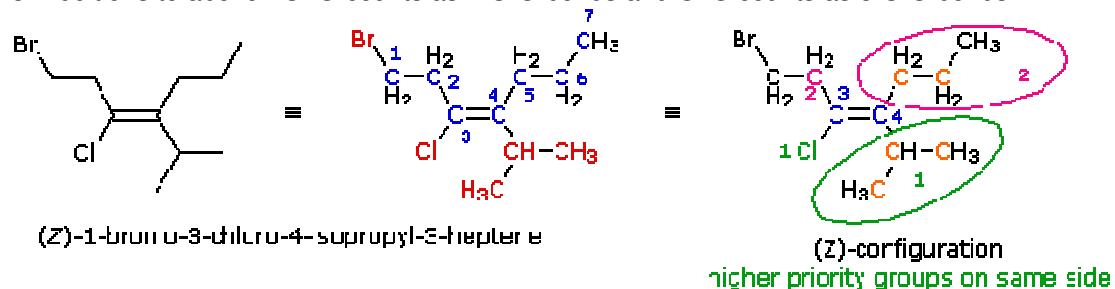
Assign priorities to double bond substituents by looking at the atoms attached directly to the double bond carbons.

1. The higher the atomic number of the immediate substituent atom, the higher the priority. For example, H- < C- < N- < O- < Cl-. (priority increases left to right) (Different isotopes of the same element are assigned a priority according to their atomic mass.)

2. If the two substituents are the same, go to FPD (1st point of difference).

For example, CH₃- < C₂H₅- < ClCH₂- < BrCH₂- < CH₃O

3. Additions to above: C=O counts as 2 C-O bonds and C≡C counts as 3 C-C bonds.

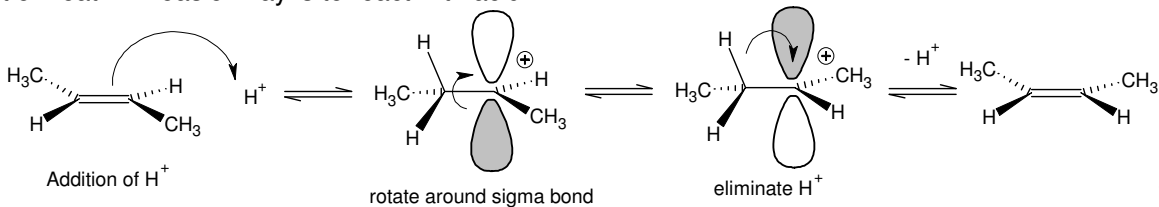
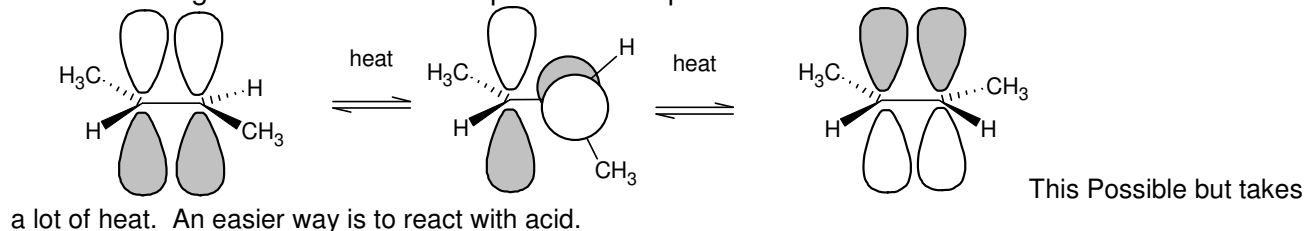


<http://www.cem.msu.edu/~reusch/VirtualText/sterisom.htm#isom1>

Rotation around the double bond

There is normally no rotation around the double bond, but it is chemically possible to randomize the positions.

- Heating the alkene to the point that the pi bond is broken rotates and reforms.



Unsaturation

Alkane R-CH₂-CH₂-R C_nH_{2n+2}

Cycloalkane (CH₂)_n Each ring or cyclic reduces the # of hydrogen atoms by 2.

Alkene R-CH=CH-R C_nH_{2n} Each double bond reduces the # of hydrogen atoms by 2.

Formula Unsaturation

C₅H₁₂ 0 Take C₅H₈O. What is the unsaturation.

C₅H₁₀ 1

C₅H₈ 2

C₅H₆ 3

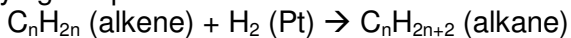
How many isomers of the formula C₄H₆?

This formula may be extended beyond hydrocarbons by a few simple corrections:

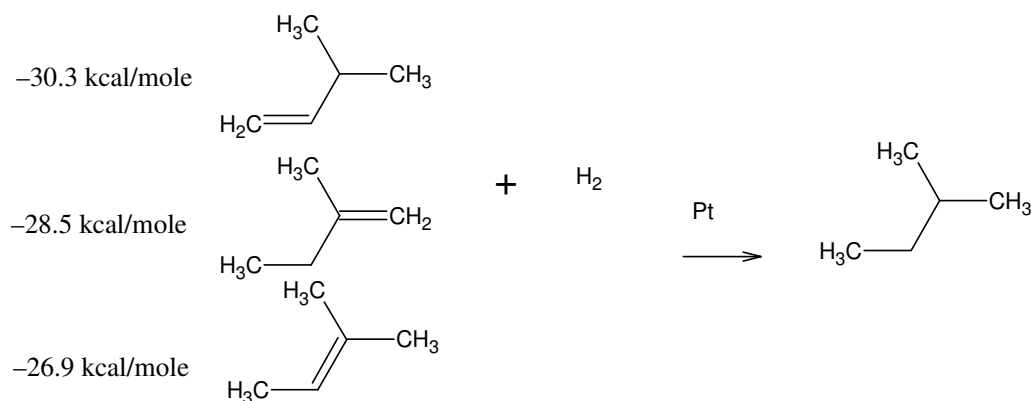
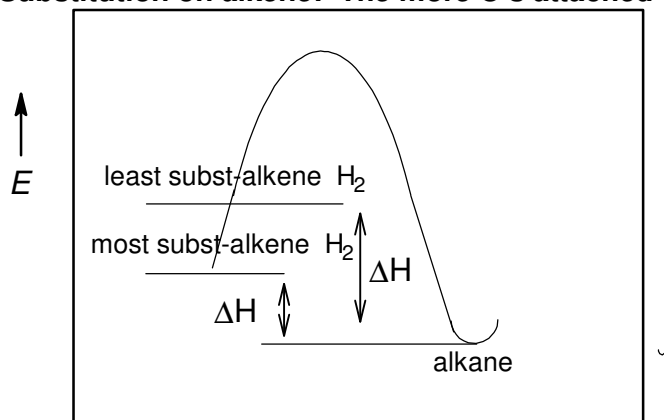
- **The presence of oxygen does not alter the relationship.**
- **All halogens present in the molecular formula must be replaced by H count.**
- **Each nitrogen in the formula must be replaced by a CH moiety.**

Not all alkenes have the same stabilities, because the pi bond is very sensitive to the electronics of the groups attached.

The standard method is to compare a standard reaction for the same chemical structure, but varying the position of the double bond.



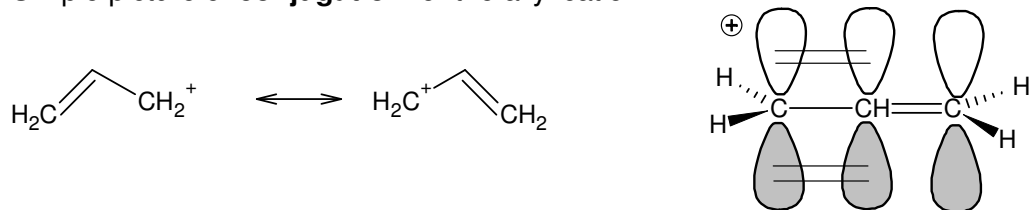
Substitution on alkene: The more C's attached to the alkene.



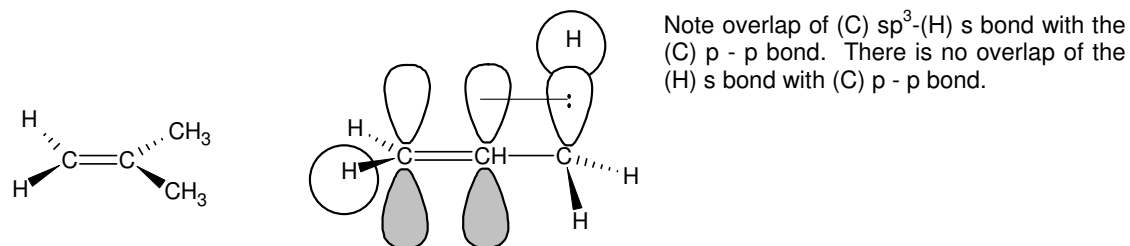
To a rough approximation, we see that each alkyl substituent on a double bond stabilizes the alkene about ___ kcal/mole. The Russian chemist Alexander Zaitsev (Saytzeff) discovered this trend. We call it: **The Zaitsev Rule:**

Hyperconjugation vs Conjugation

Simple picture of **conjugation** for the allyl cation:

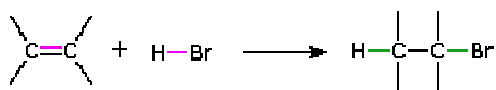


picture of **hyperconjugation** for propene. <http://chemistry.boisestate.edu/rbanks/organic/resonance.html>



Addition Reactions of Alkenes

- Generally exothermic because the energy of breaking a strong acid bond is low.
- $\Delta H = \text{Energy}(\text{Bonds Broken}) - \text{Energy}(\text{Bonds Formed})$.
- the C-C pi-bond is relatively weak (ca. 63 kcal/mole) relative to the sigma-bonds formed



Bonds Broken : π C=C & H-Br Sum = 150.5 kcal/mole
63 87.5

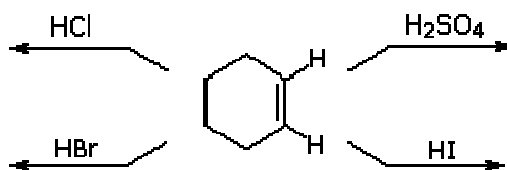
Bonds Formed : H-C & Br-C Sum = 167.0 kcal/mole
99 68

Heat of Reaction = (150.5) - (167.0) = -16.5 kcal/mole

<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1a>

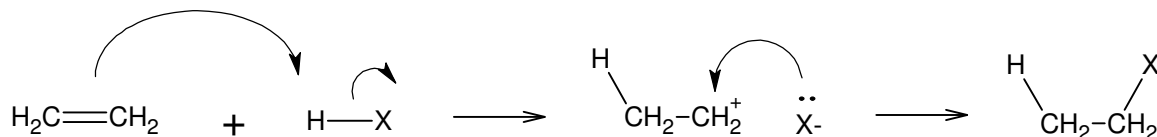
1. Addition of Strong Brønsted Acids

As illustrated by the preceding general equation, strong Brønsted acids such as HCl, HBr, HI & H₂SO₄, rapidly add to the C=C functional group of alkenes to give products in which new covalent bonds are formed to hydrogen and to the conjugate base of the acid. Using the above equation as a guide, write the addition products expected on reacting each of these reagents with cyclohexene.



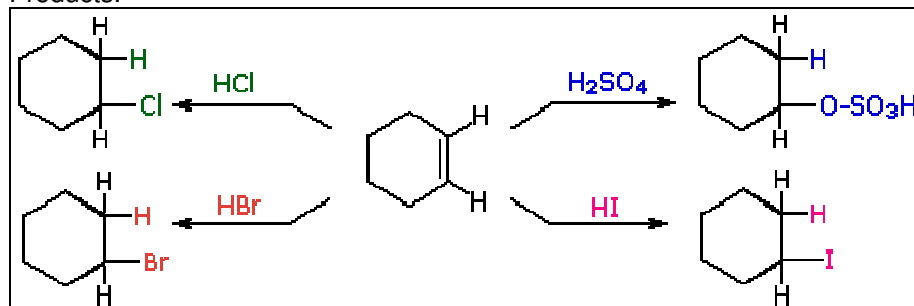
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Mechanism



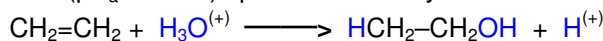
Mechanism shown at

Products.



Notes:

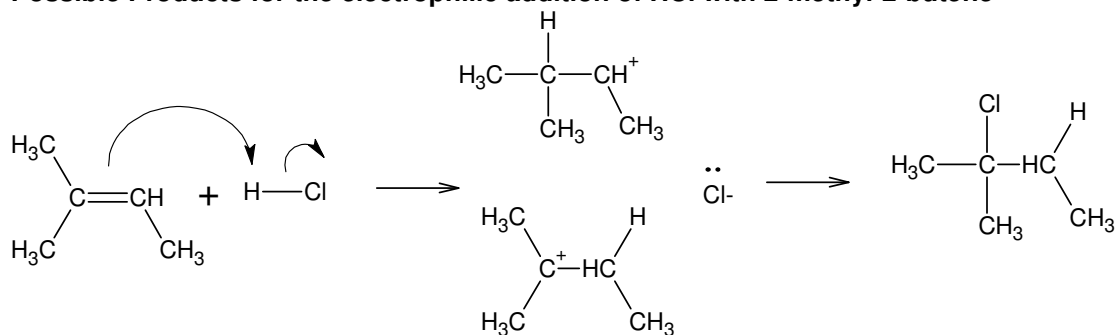
- Weak Brønsted acids such as water ($pK_a = 15.7$) and acetic acid ($pK_a = 4.75$) do not normally add to alkenes.
- Strong acid diluted in water serves to catalyze the addition of water, and in this way alcohols may be prepared from alkenes. For example, if sulfuric acid is dissolved in water it is completely ionized to the hydronium ion, H₃O⁽⁺⁾, and this strongly acidic ($pK_a = -1.74$) species effects hydration of ethene and other alkenes.



<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1>

Electrophilic addition gives one product when the alkene has the same substitution pattern. Because the H can go to either C2 or C3, there are two possible products.

Possible Products for the electrophilic addition of HCl with 2-methyl-2-butene

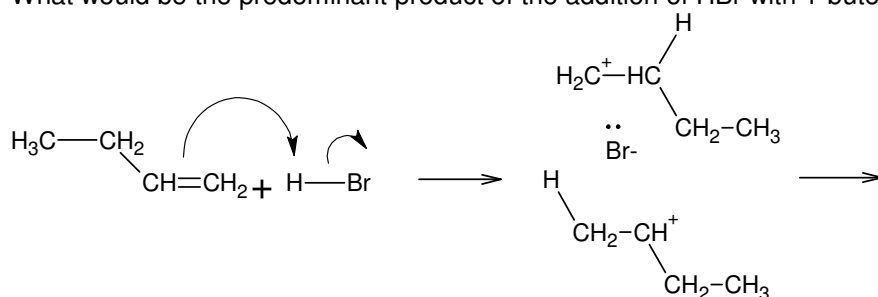


2-methyl-2-butene

2-chloro-3-methylbutane or 2-chloro-2-methylbutane

Since only 2-chloro-2-methylbutane is formed. The product is called **regioselective**.

What would be the predominant product of the addition of HBr with 1-butene:

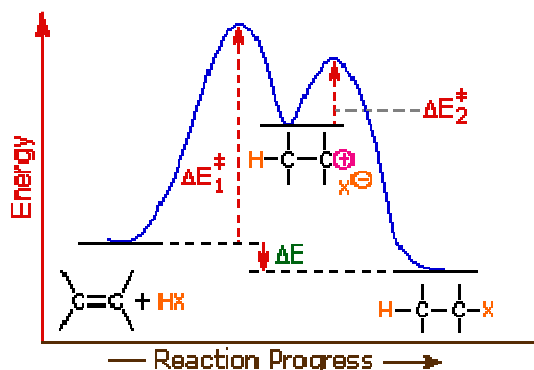
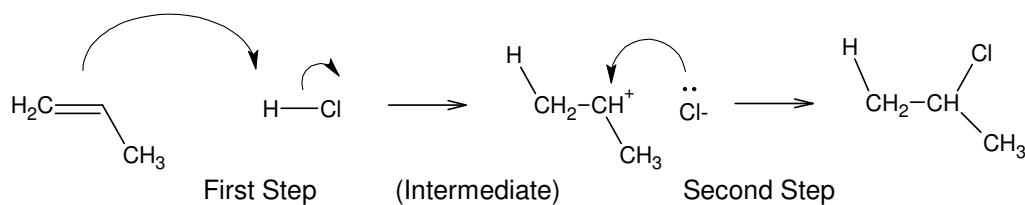


The Russian chemist Vladimir Markovnikov discovered this trend. We name this phenomenon for him and call it: **The Markovnikov Rule:**

When a Brønsted acid, HX, adds to an unsymmetrically substituted double bond, the acidic hydrogen of the acid bonds to that carbon of the double bond that has the greater number of hydrogen atoms already attached to it.

Some people say it's like the phrase, "**Them that has gits – meaning the H of course.**"

Mechanism of Markovnikov Addition



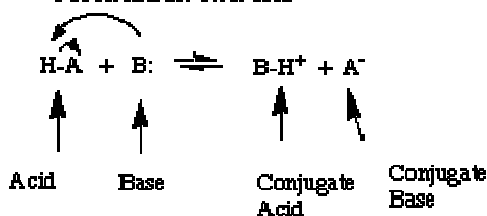
Identify the rate-determining step
 Identify the two ΔE^\ddagger ?
 What is the intermediate?

<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1>

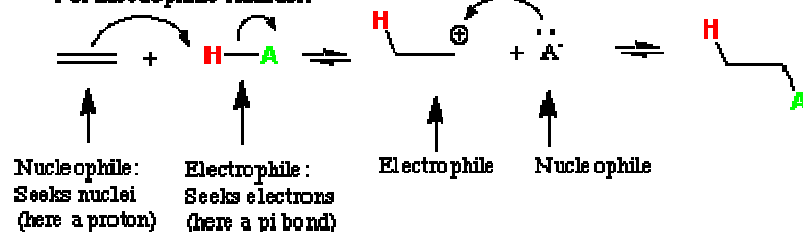
Let's go through the general reaction.

General Reactions

For Acid/Base Reactions

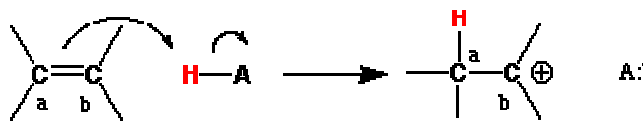


For Electrophilic Addition

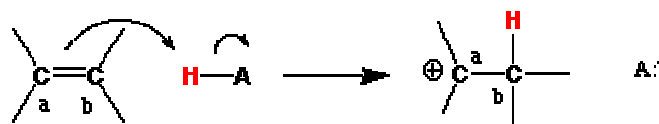


Consider the possibilities

Pivot on carbon-a:



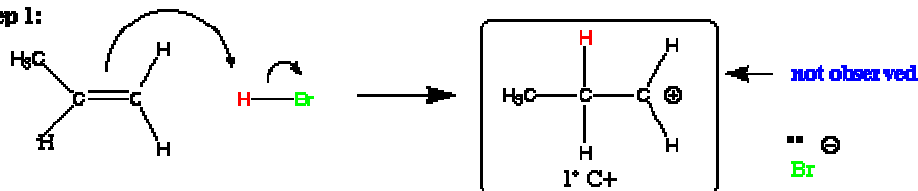
Pivot on carbon-b:



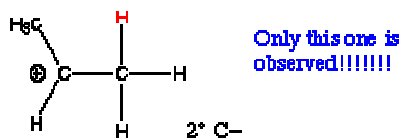
We will see soon why it makes a difference which way the bond pivots! !!

Add in the Markovnikov dilemma.

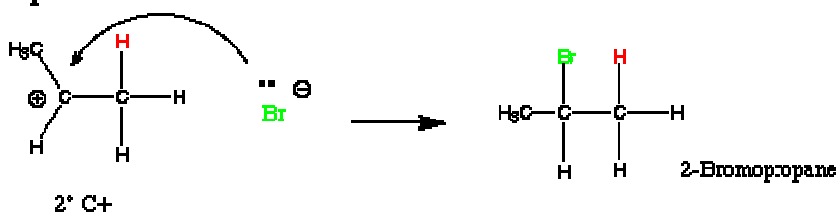
Step 1:



C⁺ or carbocations are reactive intermediates that can be stabilized but usually are not isolated. The stability of C⁺ is 3° > 2° > 1° > methyl. Here only the 2° C⁺ is formed.

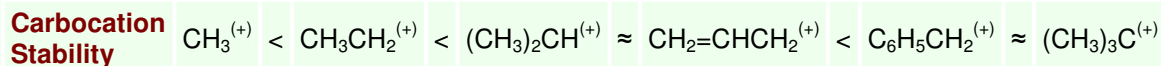


Step 2:

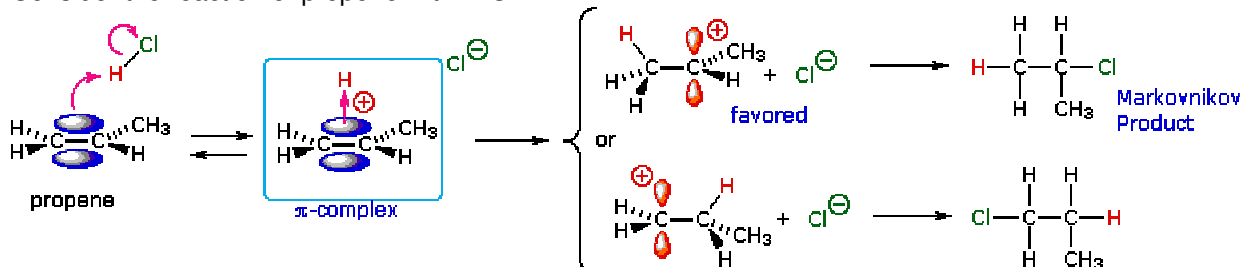


In general, the most substituted C⁺ is more stable.

More exactly stated, the most conjugated C⁺ is the most stable.



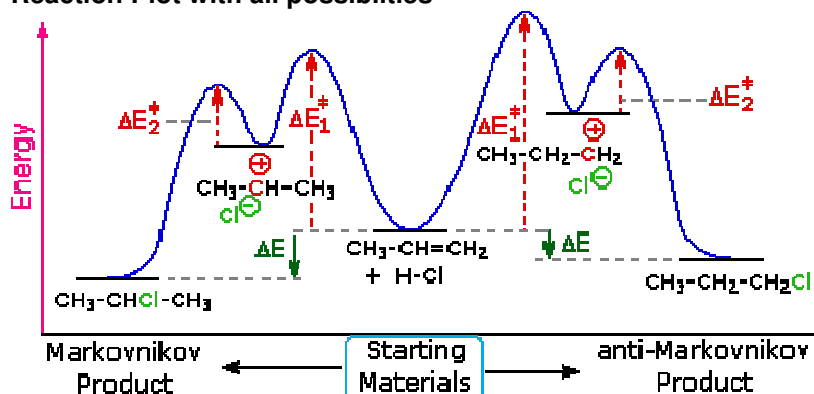
Consider the reaction of propene with H-Cl.



<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1>

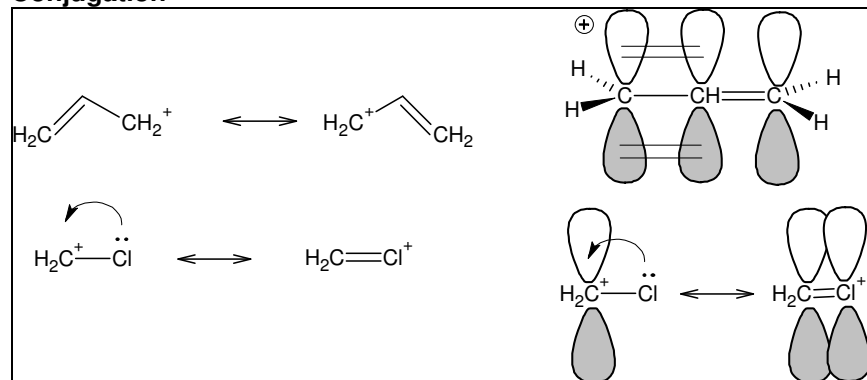
The following energy diagram summarizes these features. Note that the pi-complex is not shown, since this rapidly and reversibly formed species is common to both possible reaction paths.

Reaction Plot with all possibilities

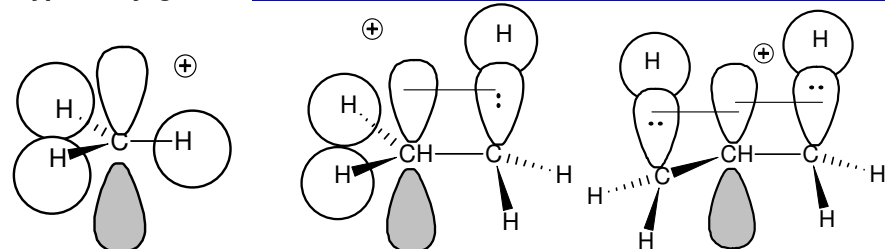


<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1>

Conjugation

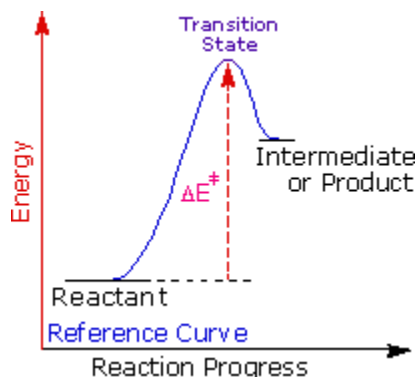


Hyperconjugation <http://chemistry.boisestate.edu/rbanks/organic/resonance.html>



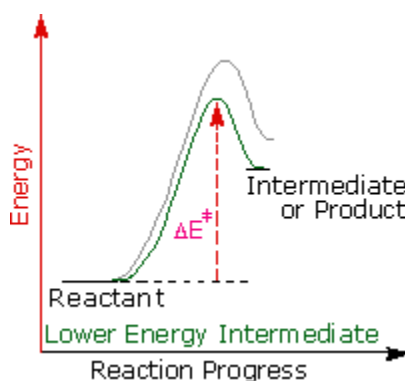
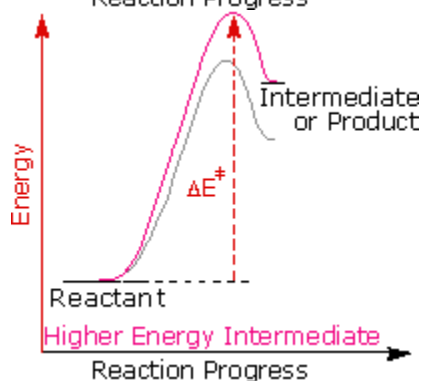
Methyl Cation (no overlap) One Methyl (C) sp³-(C) p Two Methyls (C) sp³-(C) p
 Draw the structure for the trimethyl cation.

George Hammond formulated a useful principle that relates the nature of a transition state to its location on the reaction path. This **Hammond Postulate** states that a **transition state will be structurally and energetically similar to the species (reactant, intermediate or product) nearest to it on the reaction path**. In strongly



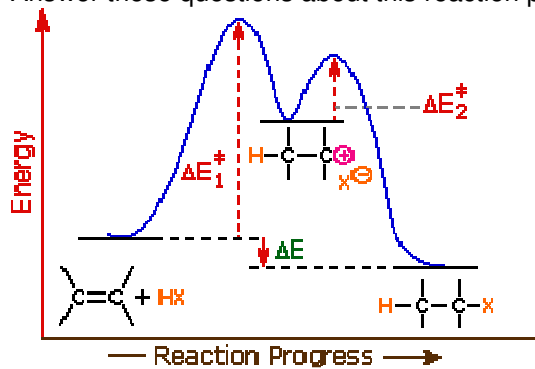
exothermic reactions the transition state will resemble the reactant species. In strongly endothermic conversions, such as that shown to the right, the transition state will resemble the high-energy intermediate or product, and will track the energy of this intermediate if it changes. This change in transition state energy and activation energy as the stability of the intermediate changes may be observed by clicking the higher or lower buttons to the right of the energy diagram. Three examples may be examined, and the reference curve is changed to gray in the diagrams for higher (magenta) and lower (green) energy intermediates.

<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1>



<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1>

Answer these questions about this reaction plots:



<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1>

Describe the geometry of the reactants.

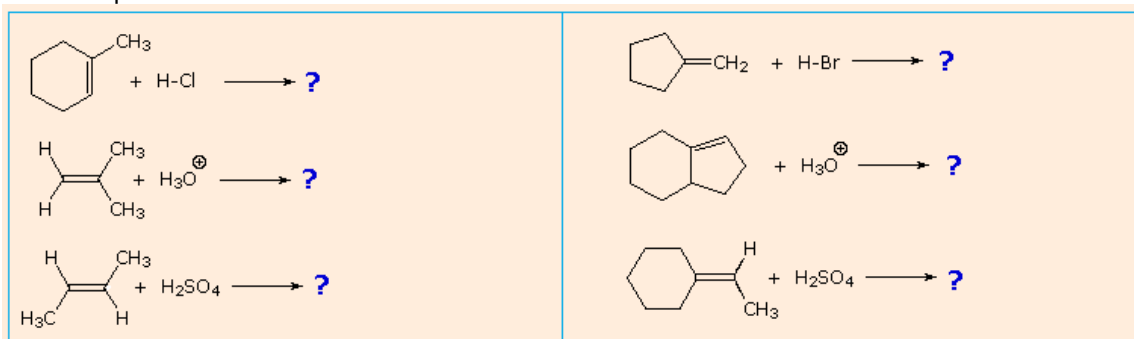
Describe the geometry of TS1:

Describe the geometry of the intermediate.

Describe the geometry of TS2.

Describe the geometry of the product.

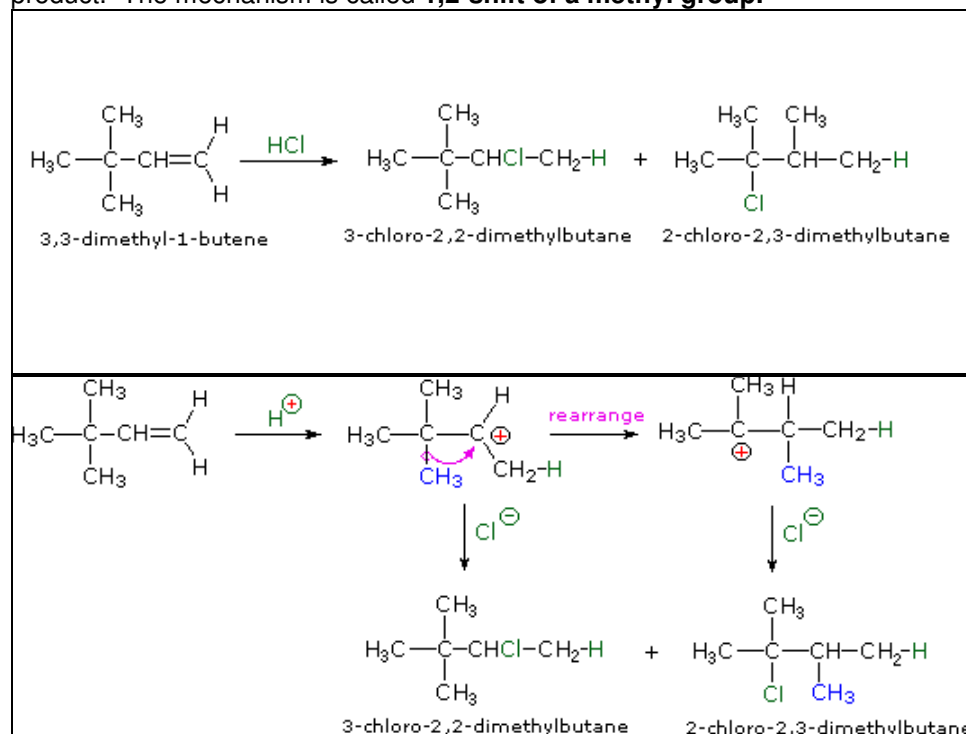
Reaction practice:



answers at <http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1>

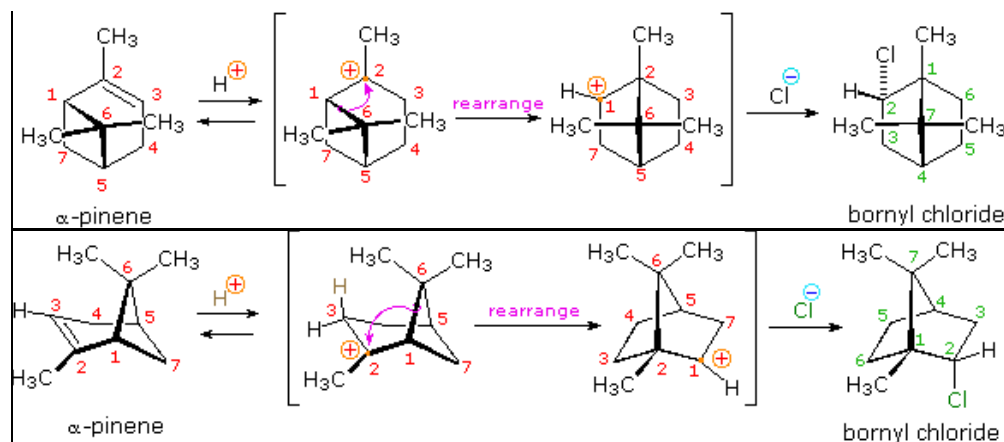
Rearrangement of Carbocations

The addition of HCl to 3,3-dimethyl-1-butene, for example, leads to an unexpected product, 2-chloro-2,3-dimethylbutane, in somewhat greater yield than 3-chloro-2,2-dimethylbutane, the expected Markovnikov product. The mechanism is called **1,2-shift of a methyl group**.



<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1c>

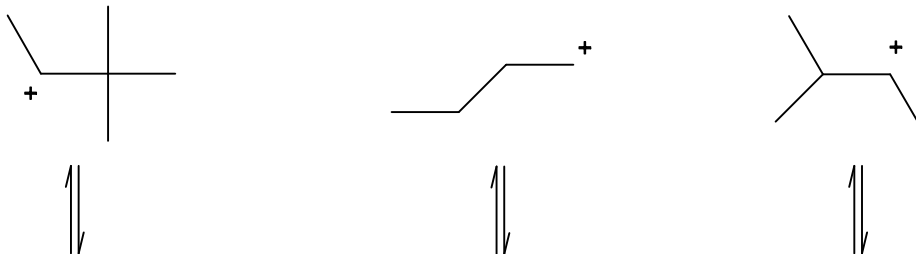
Here are two views of the reaction of pinene with acid



<http://www.cem.msu.edu/~reusch/VirtualText/addene1.htm#add1c>

What is the driving force for this reaction?

Practice: If the cation(s) below would undergo a 1,2-hydride or methyl shift, show the product from the rearrangement.



BioMolecules

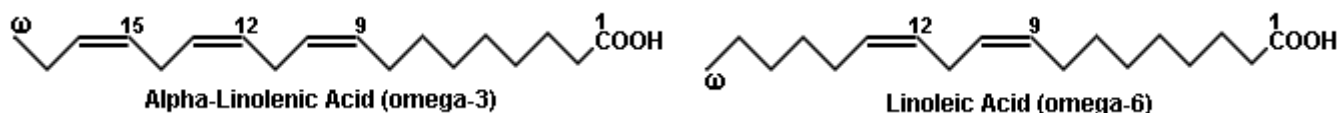
Unsaturated fatty acids:

9,12-octadecadienoic acid (Linoleic Acid)

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$

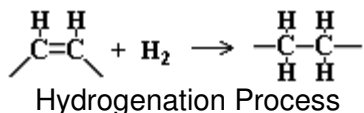
abbreviated as $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

Alpha and omega nomenclature depends on the position of the double bonds and the ends of the chain.



What is Hydrogenation and Partial Hydrogenation?

Unsaturated fats exposed to air oxidize to create compounds that have rancid, stale, or unpleasant odors or flavors. Hydrogenation is a commercial chemical process to add more hydrogen to natural unsaturated fats to decrease the number of double bonds and retard or eliminate the potential for rancidity. Unsaturated oils, such as soybean oil, which contain unsaturated fatty acids like oleic and linoleic acid, are heated with metal catalysts in the presence of pressurized hydrogen gas. Hydrogen is incorporated into the fatty acid molecules and they become saturated with hydrogen.



Fully saturated fats are too waxy and solid to use as food additives, so manufacturers use **partially hydrogenated** oils. These oils are also produced at high temperatures with metal catalysts and pressurized hydrogen, but the process is stopped when the oil has the proper consistency for its application. The high temperatures and catalysts used for this chemical reaction weaken the double bonds and, as a side effect, cause a large percentage of the natural *Cis* double bonds to change to *Trans* double bonds. *Trans* fatty acids are present mainly in partially hydrogenated fats, but they are also present in hydrogenated fats because chemical reactions never achieve 100% efficiency.

quoted verbatim from author(s) at <http://www.scientificpsychic.com/fitness/fattyacids.html>

Summaries:

1. Name alkenes. Draw alkenes from names.
2. Distinguish between cis and trans alkenes.
3. Distinguish between E/Z alkenes.
4. Be able to use unsaturation numbers to determine the number of double bonds in a formula.
5. What is the chemistry of breaking the C-C pi double bond.
6. Zaitsev's rule. Substitution and what is the most stable double bond?
7. Hyperconjugation and Conjugation. How do they work? What is the result?
8. Electrophilic addition. Addition of an electrophile to an alkene.
9. Regioselectivity. Stability of different intermediates leads to ONE product.
10. Carbocations. What are they? Why are some more stable than others?
11. Hammond Postulate: The relationship between transition states and stability of intermediates and products.
12. Reaction profiles of the electrophilic addition.
13. Be able to predict the products of the reaction of alkenes with simple Bronsted Lowry acids.
14. Be able to predict the reaction profile for the reaction of alkenes with simple Bronsted Lowry acids.
15. Be able to predict when C⁺ will undergo rearrangements.
16. Predict rearrangement products.