ORGANIC CHEMISTRY for STEM MAJORS

Part 1 of 3

Workbook designed to accompany Organic Chemistry by David Klein, 4th ed

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1: REVIEW OF GENERAL CHEMISTRY

MAIN IDEA

A molecule contains atoms connected by covalent bonds. It is often possible to find more than one way to connect a particular set of atoms to make a molecule. Two different molecules can share the same number and type of atoms, but differ in terms of the way atoms are connected. A molecule's stability and reactivity can be predicted by the unique way its atoms are connected to each other.

OBJECTIVES

☐ Understand the purpose of organic chemistry as a discipline

☐ Learn about connectivity and constitutional isomerism

☐ Review how to calculate formal charges and learn how to use formal charge to predict stability and reactivity

☐ Learn about induction

☐ Get a quick introduction to line notation

☐ Review covalent bonds, polarity, hybridization of atomic orbitals, and intermolecular forces

SKILLS TO MASTER

☐ Define "connectivity"

☐ Draw all constitutional isomers for a molecular formula

☐ Assign and interpret formal charges on a molecule

☐ Differentiate between polar and non-polar bonds

☐ Represent the unequal sharing of electrons in a polar bond

☐ Rank single, double, and triple bonds in terms of length, and explain the order

☐ Rank single, double, and triple bonds in terms of strength, and explain the order

☐ Assign hybridization to atoms in molecules

☐ Rank molecules in terms of their boiling points, and explain the order

TERMINOLOGY

- Connectivity
- Constitutional isomer
- Electronegativity
- Formal charge
- Induction
- Intermolecular forces (IMFs)
- Lone pair
- Non-polar
- Polar

1: LEWIS STRUCTURES AND FORMAL CHARGE

1. What is a covalent bond?

sharing of electrons between two atoms

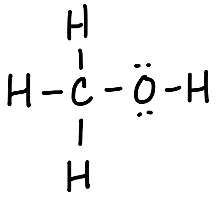
2. What are valence electrons?

electrons in the highest energy level of an atom
electrons on the outer surface of an atom

3. How many valence electrons are in C? H? O?

C: 4
H: 1
O: 6

4. Draw the Lewis structure of methanol, CH_3OH.



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & \ddot{\underset{..}{O}} & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

5. Calculate the formal charges of all the atoms in methanol. Write any non-zero formal charges onto the Lewis structure of methanol.

Formal Charge of an Atom =
Valence Electrons - Bonds - Number of Electrons in Lone Pairs

H: 1-1-0=0
C: 4-4-0=0
O: 6-2-4=0

6. The formal charge compares the number of electrons surrounding an atom in a molecule to the atom's number of valence electrons. Assuming that the ideal number of electrons for an atom is equal to its number of valence electrons, what is the ideal formal charge for any atom in a molecule?

zero

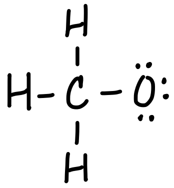
7. If an atom has a positive formal charge, what does this mean about the atom's bonds and lone pairs?

A: It has the right number of electrons in its bonds and lone pairs

B: It has too many electrons in its bonds and lone pairs

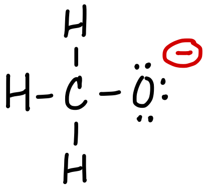
[✓ C: It does not have enough electrons in its bonds and lone pairs]

8. Draw the Lewis structure of the methoxide ion, CH_3O^-.



9. Calculate the formal charges of the atoms in methoxide. Write any non-zero formal charges onto the Lewis structure.

H: 1-1-0=0
C: 4-4-0=0
O: 6-1-6=-1



10. Many chemical reactions can be explained by atoms with non-zero formal charges attempting to reconfigure themselves into a more stable bonding environment by sharing, losing, or gaining electrons. Analyze the formal charges you calculated for methanol and methoxide. Why is methoxide more reactive than methanol?

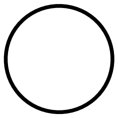
methoxide has an atom with a non-zero formal charge
methanol's atoms all have a formal charge of zero

11. Which atom of methoxide is the most "reactive"? Explain.

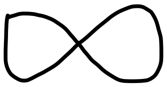
oxygen, because it is the atom with the non-zero formal charge

2: HYBRIDIZED ATOMIC ORBITALS

1. Draw an *s* orbital and a *p* orbital.



s orbital



p orbital

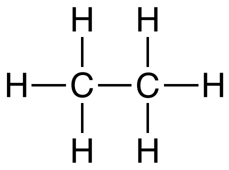
2. How many areas of electrons (bonds and/or lone pairs) are around an atom with the following types of hybridization?

sp^3 four

sp^2 three

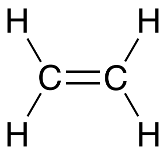
sp two

3. Identify the hybridization of each carbon atom in each of the following molecules.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

sp^3



sp^2

H—C≡C—H

sp

4. What are the C-H bond angles in each of the molecules in problem 3?

109.5°   120°   180°

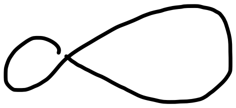
5. Rank single, double, and triple bonds from weakest to strongest. Explain your ranking.

single → double → triple

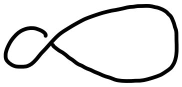
weakest → strongest

only held together by 2 electrons → held together by 6 electrons

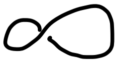
6. Draw an sp^3, an sp^2, and an sp orbital. How are they different?



sp^3 ← 75% p orbital "character" (made frome one s & three p orbitals

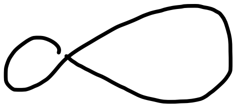


sp^2

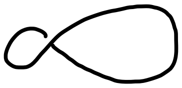


sp ← 50% p orbital "character"

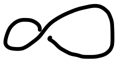
7. Rank sp^3, sp^2, and sp orbitals from shortest to longest. Explain your ranking.



sp^3 longest : more "p character" and p orbitals are longer than s orbitals



sp^2 ↓



sp shortest

8. Rank single, double, and triple bonds from shortest to longest.

single → double → triple

longest ——————→ shortest

9. What is the relationship between bond length (question 8) and hybrid orbital length (question 7)?

triple bonds use sp orbitals which are the shortest orbitals

2: RESONANCE

MAIN IDEA

In an organic molecule, the electrons in the single bonds (sigma bond) are in fixed locations. These electrons cannot move without some type of chemical reaction occurring. All the other electrons in an organic molecule, both pi bonds as well as lone pairs, can be spread around and redistributed to various locations in the molecule. This concept, called resonance, can help a molecule to stabilize an uneven distribution of electrons due to bond polarity or formal charge.

OBJECTIVES

- ☐ Interpret Lewis structures, condensed and partially-condensed structures, and line structures
- ☐ Understand the concept of resonance and delocalization
- ☐ Learn how to propose and draw resonance structures for a molecule
- ☐ Learn what makes a resonance structure “good” or “bad”
- ☐ Learn how to interpret and use curved arrows

SKILLS TO MASTER

- ☐ Draw molecules using Lewis structures, condensed and partially-condensed structures, and line structures
- ☐ Propose resonance structures for a molecule
- ☐ Draw curved arrows on resonance structures
- ☐ Interpret curved arrows on a molecule, and use them to draw a resulting resonance structure
- ☐ Identify features of good and bad resonance structures
- ☐ Evaluate sets of resonance structures, and identify the most- and least-important resonance structures in the set

TERMINOLOGY

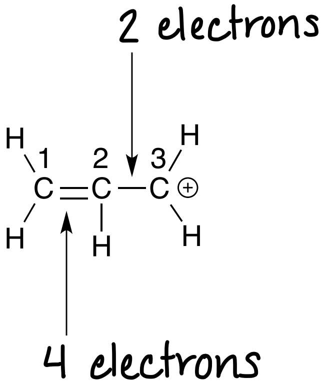
- Delocalized

- Localized

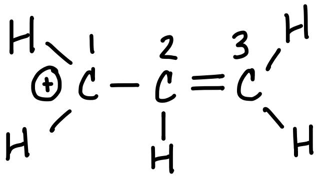
- Resonance

3: INTRODUCTION TO RESONANCE AND CURVED ARROWS

1. For the following Lewis structure, how many electrons are in the indicated carbon-carbon bonds?



2. In many molecules, the electrons are not restricted to the positions indicated by the line or Lewis structure. For the molecule in problem 1, the electrons between C1 and C2 are not *localized* (restricted) to the C1-C2 bond. Redraw the molecule in problem 1 (number the carbons 1-3 as shown in problem 1). Maintain the same connectivity (don't move any atoms) but change the position of as many electrons as possible.



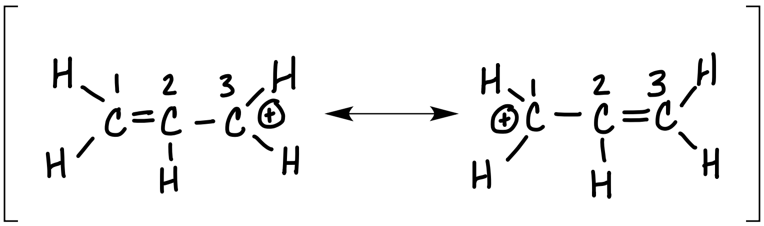
3. The molecules in problems 1 and 2 are called "resonance structures". How are resonance structures identical?

they have the same connectivity

4. The molecules in problems 1 and 2 are different in two ways. In what two ways are resonance structures different?

1: the location of the double bond
2: the location of the formal charge

5. Resonance structures are drawn in series, separated by a double-headed arrow and contained in closed brackets. Draw the resonance structures from problems 1 and 2 in the brackets below.



6. The true structure of the molecule represented in problem 5 is called a *resonance hybrid*. It cannot be drawn using a Lewis or line structure because chemists don't have a method for drawing the *delocalization* of electrons (spreading out electrons between two or more bonds). Describe the delocalization of the molecule in problem 5 using the prompts below.

*The formal charge is delocalized between C#*1 *and C#*3.

The double bond is delocalized between the C1-C2 bond and the C2-C3 *bond.*

7. Go back to the molecule in problem 1. Of all the atoms in the molecule, which would you predict to be the most unstable?

Carbon 3

8. Now look at the molecule in problem 2. Which is the most unstable atom?

carbon 1

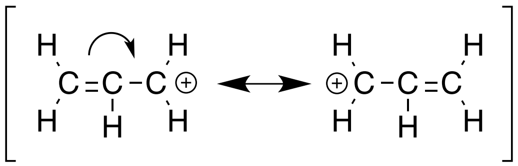
9. Resonance structures contribute to the overall stability of a molecule. Refer to your statement in problem 6 regarding the delocalization of the formal charge. Why does delocalization increase the stability of the atoms in a molecule?

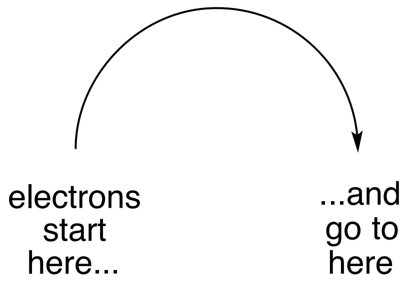
the formal charge is spread out over two atoms, which minimizes the destabilizing effect of the formal charge

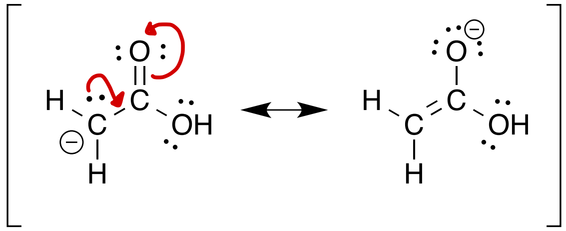
10. Resonance structures can often be used to explain the reactivity of a molecule. Look at the resonance structures in problem 5. Which atoms are the most reactive and why?

carbons 1 and 3 because they have formal charges

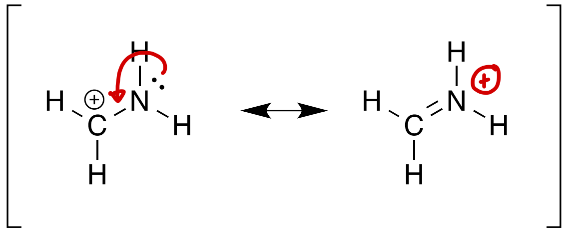
11. Curved arrows are used to show the movement of electrons in reactions and in resonance structures. They help us visualize where electrons are going, and where they are coming from. Look at the example to the right. Then, add two curved arrows to the resonance structure below.



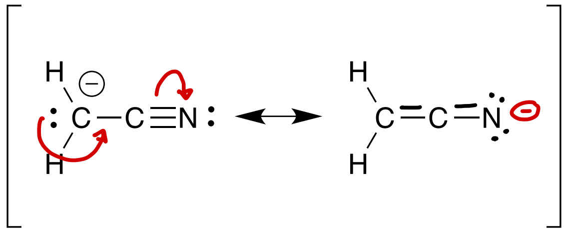




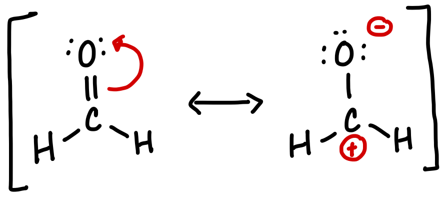
12. For this set of resonance structures, you will need to add curved arrow(s) to the structure on the left AND add the formal charge to the structure on the right.



13. For this set of resonance structures, you will need to add curved arrow(s) to the structure on the left. For the structure on the right, you will need to draw double or triple bonds as needed, and add formal charges and lone pairs.



14. Formaldehyde (CH_2O) appears to be a completely stable molecule. However, it undergoes many reactions. Its reactivity can be explained by analyzing its resonance structures. Draw the resonance structures of formaldehyde and identify its site of reactivity (the single most reactive atom in the molecule).



The carbon atom is most reactive. It has a formal charge and doesn't have an octet. The electronegativity of the oxygen makes it better at having a negative formal charge relative to carbon's positive formal charge.

4: EVALUATING RESONANCE STRUCTURES

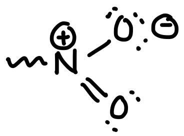
1. What are three characteristics of bad resonance structures?

   1: three or more atoms with formal charges, or atoms with formal charges that exceed $\oplus$ or $\ominus$

   2: a positively charged atom bonded to a negatively charged atom $C^{\oplus}-C^{\ominus}$ except NO_2 groups

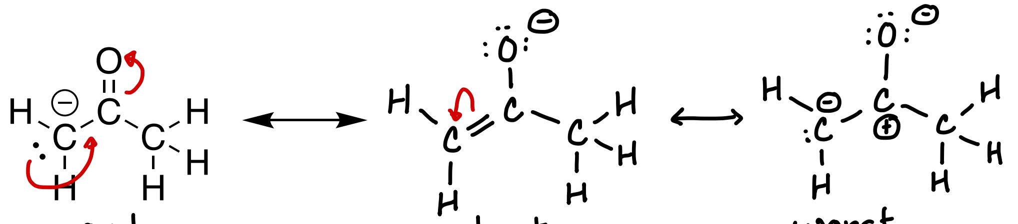
   3: electronegative atoms with less than an octet, or with positive formal charges

exception:



$-NO_2$ is good

2. Draw at least two resonance structures for the molecule below. Use curved arrow notation. Classify each resonance structure as "good" or "bad". Explain why the "bad" resonance structure(s) is/are "bad".



good

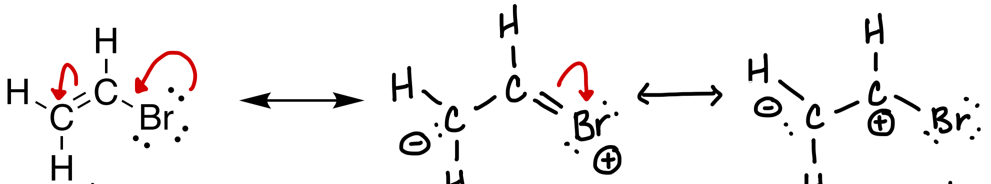
best

worst

too many formal charges, $C\ominus$ bonded to $C\oplus$

3. Draw at least two resonance structures for the molecule below. Use curved arrow notation. Classify each resonance structure as "good" or "bad". Explain why the "bad" resonance structure(s) is/are "bad".

$\oplus$ on Br



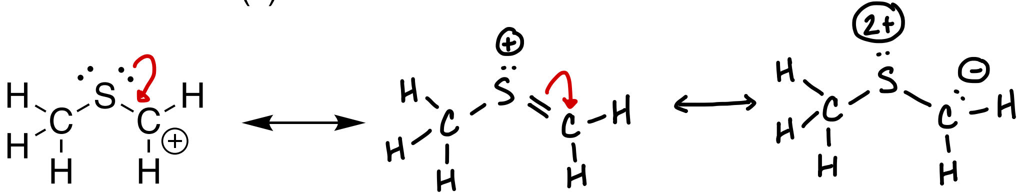
best

bad

worst

$C\oplus$ bonded to $C\ominus$

4. Draw at least two resonance structures for the molecule below. Use curved arrow notation. Classify each resonance structure as "good" or "bad". Explain why the "bad" resonance structure(s) is/are "bad".



best

bad

$\oplus$ on S

worst

too many formal charges

3: ACIDS AND BASES

MAIN IDEA

Reactions that involve the transfer of a hydrogen ion (“proton”) are classified as acid-base reactions. In this type of reaction, the molecule that loses the hydrogen ion is classified as the acid, and the molecule that gains the hydrogen ion is classified as the base. These acid-base reactions are driven by the relative stability of the reactants and products. An acid-base reaction will occur spontaneously if the products of the reaction are more stable than the reactants. In general, reactions proceed in the direction from the least stable molecule(s) toward the most stable molecule(s)

OBJECTIVES

- ☐ Learn the variables that determine a molecule’s stability
- ☐ Understand the relationship between molecular stability and molecular reactivity
- ☐ Understand the relationship between molecular stability and acidic strength or basic strength
- ☐ Understand the relationship between the stability of an acid and its conjugate base, or a base and its conjugate acid
- ☐ Understand that many organic reactions involve the transfer of a hydrogen atom from one reactant to another
- ☐ Learn how to use and interpret curved arrows in reaction mechanisms
- ☐ Learn how to predict the direction of an acid-base reaction

SKILLS TO MASTER

- ☐ Predict the relative stability of two or more molecules using “ARIO”
- ☐ Draw the structure of the conjugate base of an acid, and the structure of the conjugate acid of a base
- ☐ Predict the relative acidic strength of two or more molecules without using K_a or pK_a
- ☐ Identify the Bronsted-Lowry acid and base in an acid-base reaction
- ☐ Draw curved arrows to keep track of electron movement in an acid-base reaction
- ☐ Use the relative stability of reactants and products to predict whether a reaction will proceed from left to right, or from right to left

TERMINOLOGY

- Bronsted-Lowry acid

- Bronsted-Lowry base

- Conjugate acid

- Conjugate base

- K_a and pK_a

- Mechanism

- Proton

5: BRONSTED-LOWRY ACIDITY: A QUALITATIVE PERSPECTIVE

1. Start by reviewing the pneumonic trick “ARIO”. What does each letter represent?

A: atom (most stable structure has ⊖ on most electronegative atom)

R: resonance (more resonance = more stable)

I: induction (induction from electronegative atoms stabilizes ⊖)

O: orbital (atoms with ⊖ are more stable if sp hybrid & least stable if sp^3 hybrid)

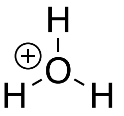
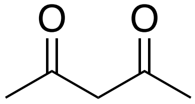
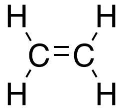
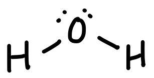
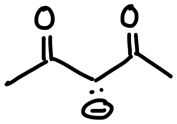
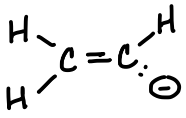
2. Recall from general chemistry the relationship between the strength of an acid and the strength of a conjugate base. Circle the correct word to complete the statements.

A strong acid produces a (strong / [✓ weak]) conjugate base.

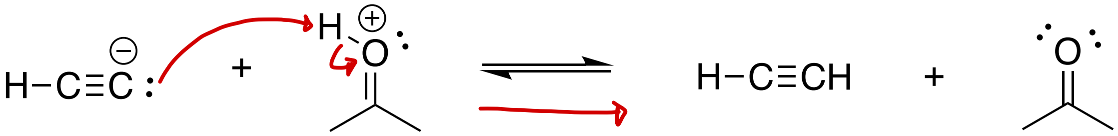
A weak acid produces a ([✓ strong] / weak) conjugate base.

3. Rank the following acids in order of increasing acidity.

    1. Draw the conjugate base of each acid.
    2. Use ARIO to rank each conjugate base according to stability.
    3. Finally, rank each acid according to stability.

Acids			
Structure of Each Acid’s Conjugate Base			
Rank the Stability of the Bases (Most=1, Least=3)	1 (no formal charge)	2 (resonance)	3
Rank the Stability of the Acids (Most=1, Least=3)	3	2	1

4. Acidic strength can be used to predict the direction of a reaction. The next problems will guide you through the process of predicting the direction of a reaction. Start by drawing curved arrows for the following reaction.



acid

least stable:
stronger

acid

most stable:
weaker

5. Identify the two acids in the above reaction. (Hint: There is one acid on the left side, and one on the right side.) Write "acid" under the two acids.

6. Use ARIO to rank the strength of the two acids. Write "stronger" under the stronger acid and "weaker" under the weaker acid.

7. In general, reactions move toward the most stable / least reactive compounds. Use this information as well as your general knowledge of acids and bases to determine the direction of the reaction in problem 4.

4: ALKANES AND CYCLOALKANES

MAIN IDEA

An alkane is a molecules that contains only carbon and hydrogen atoms, and only single bonds. The carbon atoms can be connected in a row, which is referred to as a “straight chain”. They can also be connected in a loop, which is referred to as a “ring”. Because alkane molecules contain only single bonds, the bonds are free to rotate and the molecules can twist themselves into stable shapes that minimize crowding among the hydrogen atoms.

OBJECTIVES

☐ Learn the IUPAC system of naming alkanes and cycloalkanes

☐ Understand the relationship between stability of a molecule and the relative energy of its conformation

☐ Learn how to draw Newman projections

☐ Learn how to use Newman projections to view steric hinderance

☐ Learn how to draw chair conformations

☐ Learn how to use chair conformations to view steric hinderance

☐ Understand the relationship between steric hinderance, stability, and “high-“ or “low-energy” of a molecule

SKILLS TO MASTER

☐ Name alkanes using IUPAC rules

☐ Interpret IUPAC names for alkanes

☐ Draw high- and low-energy conformations of an alkane using Newman projections

☐ Draw high- and low-energy chair conformations of cyclohexane, including substituted cyclohexane molecules, showing correct positioning of axial and equatorial substituents

TERMINOLOGY

■ Alkane

■ Anti

■ Axial

■ Bulky substituent

■ Chair conformation

■ Complex substituent

■ Conformation

■ Eclipsed

■ Equatorial

■ Gauche

■ Newman projection

■ Parent chain

- Ring Flip

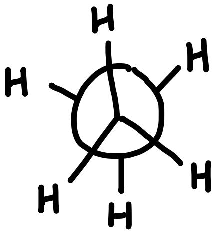
- Staggered

- Sterics

- Substituent

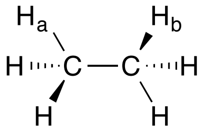
6: CONFORMATIONAL ANALYSIS OF ETHANE, PROPANE, AND BUTANE

1. Build a model of ethane. Sight down the C-C bond and arrange your model so the H atoms are evenly spaced and resemble the structures presented during lecture. Draw a Newman projection of what you see.

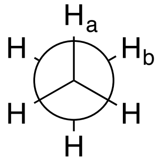


staggered
low-energy

2. The *dihedral angle* is defined as the angle of selected bond vectors and is used to describe the relative position of two atoms separated by two atoms. Confused!? Consider this:



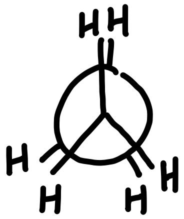
There are exactly 2 atoms (the carbon atoms) separating H_a from H_b. The *dihedral angle* is the angle between H_a and H_b as viewed in the Newman projection.



What is the dihedral angle for the Newman projection you drew in problem 1?

60°

3. Rotate the C-C bond in your ethane molecule until the dihedral angle is 0º. Draw this Newman projection.



eclipsed
high-energy

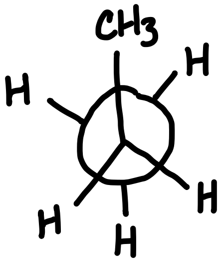
4. The Newman projections you drew in problems 1 and 3 represent two different *conformations* of ethane. Conformations only differ with respect to rotation about a bond. (In this case, the C-C bond.) Conformations are different representations or shapes of an identical molecule. (For example, a person sitting in a chair is a different conformation of a person standing up. They are the same person, and they can freely switch from standing or sitting without turning into a different person.) The two conformations of ethane are named *staggered* and *eclipsed*. Label your Newman projections in problems 1 and 3 as *staggered* or *eclipsed.*

5. *Steric hinderance* is a high-energy situation caused by atoms in a molecule coming near each other and crowding together. Why is crowding a high-energy situation? (Consider the outer surface of an atom. What subatomic particle is on the outside of an atom?)

electrons on the outer surface of an atom repel each other

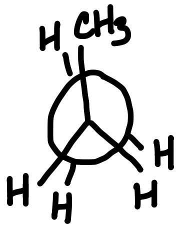
6. Use your model of ethane to determine which conformation - staggered or eclipsed - experiences the greatest amount of steric hindrance. Label this conformation as “high energy” in either problem 1 or problem 3. Label the other conformation as “low energy”.

7. Build a model of propane. Sight down the C1-C2 bond (“C1” refers to carbon number 1) and arrange your model so that it is in the staggered conformation. Draw a Newman projection of the staggered conformation of propane.



low energy

8. Rotate your model around the C1-C2 bond so that it represents the eclipsed conformation. Draw a Newman projection of the eclipsed conformation of propane.

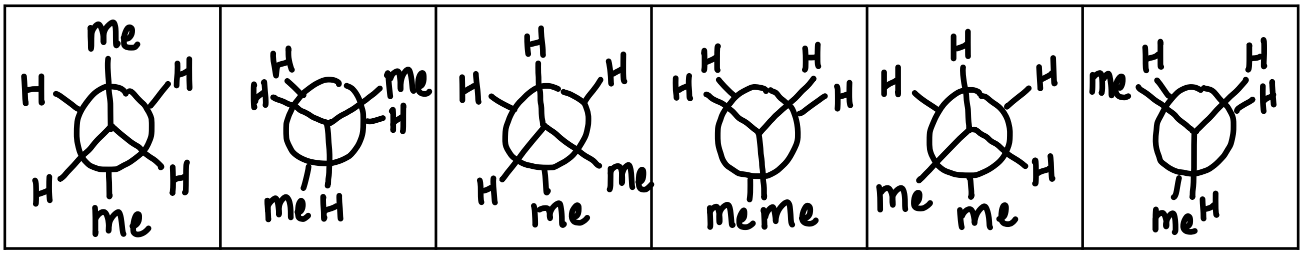


high energy

9. For the conformations in problems 7 and 8, which is higher energy? Which is lower energy? Label them.

10. Build a model of butane. Sight down the **C2-C3** bond and arrange your model so it's in a staggered conformation. Draw a Newman projection of this conformation in the first box. (There is more than one staggered conformation of butane - you can draw any one of the staggered conformations.)

me = methyl = -CH_3



lowest energy	high energy	low energy	highest energy	low energy	high energy
anti		gauche		gauche	

11. Rotate C2 (the front carbon) 60º clockwise. Draw a Newman projection of this conformation in the next box above. Continue rotating C2 60º clockwise and drawing Newman projections in the boxes until you return back to the original conformation. Make sure you always rotate the same carbon in the same direction! Some of your Newman projections will be very similar, but they should all be unique.

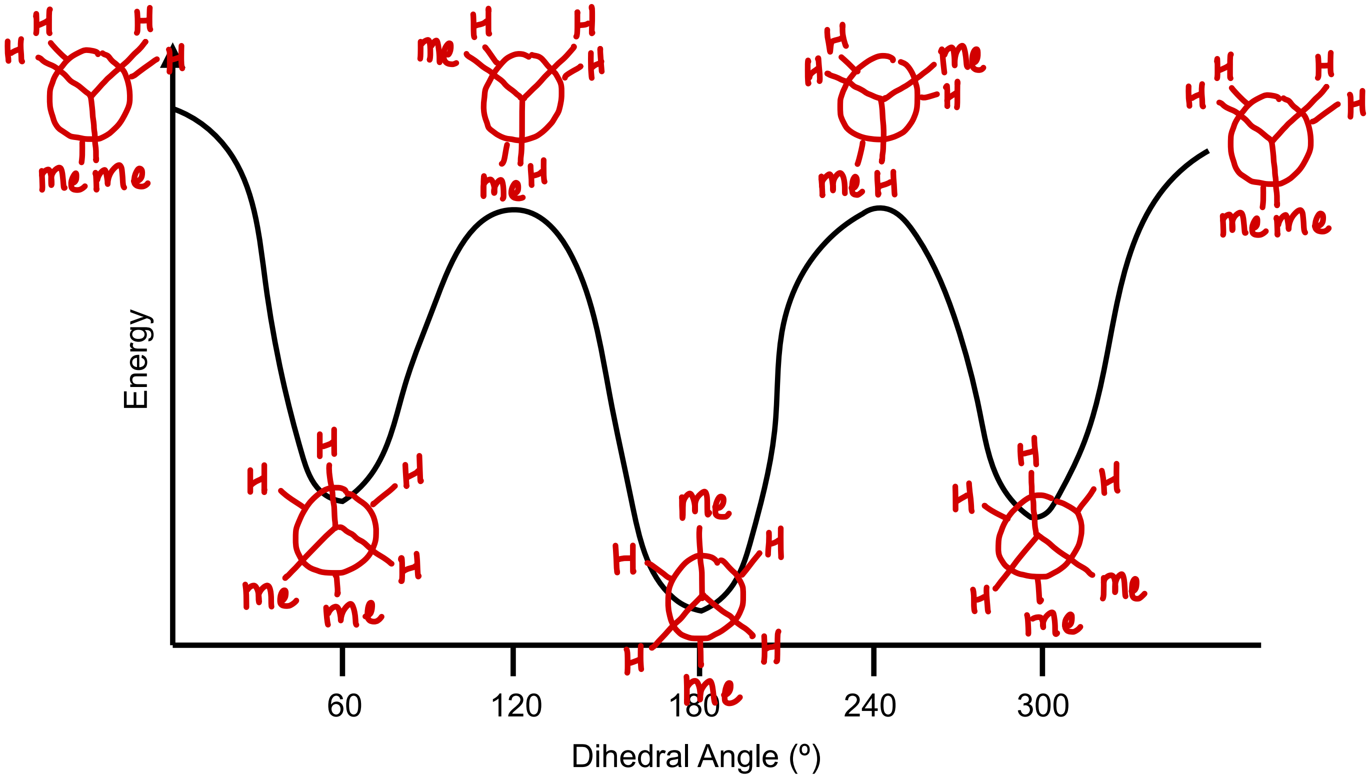
12. Of the 6 Newman projections you drew in problem 10, three of them should be eclipsed. All eclipsed conformations are high energy. However, one of the three eclipsed conformations is higher energy than the other two. Label this eclipsed conformation as "highest energy" and label the other two eclipsed conformations as "high energy".

13. The remaining 3 conformations in problem 10 are staggered. All staggered conformations are low energy. However, one of the three staggered conformations is lower energy than the other two. Label this conformation as "lowest energy" and the other two as "low energy".

14. The lowest energy conformation of butane is called "anti" which means "opposed". Label the "anti" structure.

15. The other low energy staggered conformations of butane are called "gauche" which means "awkward". Label the "gauche" structures.

16. The diagram below graphs the energy of butane as it rotates through its 6 conformations. The highest point on the graph correlates to the highest energy conformation, and the lowest energy point correlates to the lowest energy conformation. Assign the letters A-D to the structures you drew in problem 10 or draw Newman projections directly onto the graph.



7: MONO- AND DISUBSTITUTED CYCLOHEXANE

1. Build a model of cyclohexane. Use black for the carbon atoms. Add “bonds” for each of the 12 hydrogen atoms, but don’t put any hydrogen atoms onto the model yet. Twist your model into a good chair conformation. (Your chair conformation is “good” when all the axial positions are straight up or straight down.)

2. Put blue “atoms” onto each of the 6 axial bonds to represent axial hydrogen atoms. Put red “atoms” onto each of the 6 equatorial bonds to represent equatorial hydrogen atoms. Adjust your model back into a good chair conformation. (Substitute colors as needed based on your model kit.)

3. Ring-flip your model and adjust it into a good chair conformation. Notice the change in location of the colored atoms. All the blue hydrogen atoms are now equatorial and all the red hydrogen atoms are now axial. Continue playing with your model until everyone in your group can see that ***“axial becomes equatorial”*** during a ring-flip.

4. Pull all the H atoms off your cyclohexane but leave the bonds. Twist it into a good chair conformation. Place it on the table so that it sits on the three downward-pointing axial bonds. Put blue atoms on each of the 3 downward-pointing axial bonds, and put it back on the table to rest on the blue atoms.

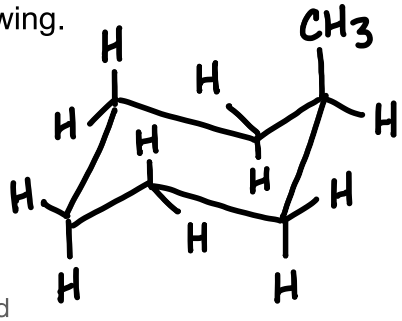
5. Notice that you have 3 upward-pointing axial bonds. Put red atoms onto each of those 3 bonds.

6. Of the 6 equatorial bonds, notice that 3 of them are angled up and 3 of them are angled down. Put red atoms on the 3 upward-pointing equatorial bonds and blue atoms on the 3 downward-pointing equatorial bonds.

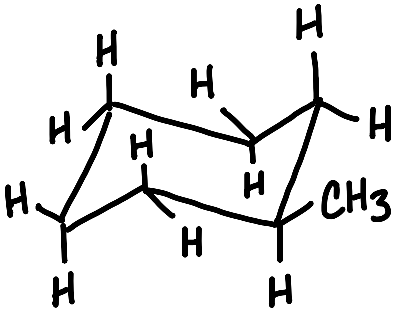
7. Notice that all your “up” bonds are red and all your “down” bonds are blue.

8. Ring-flip your model. Notice that all the “up” positions (red) have stayed “up”, and all the “down” positions (blue) have stayed “down”. Continue ring-flipping your cyclohexane until you can clearly see that ***“up stays up”*** during a ring-flip.

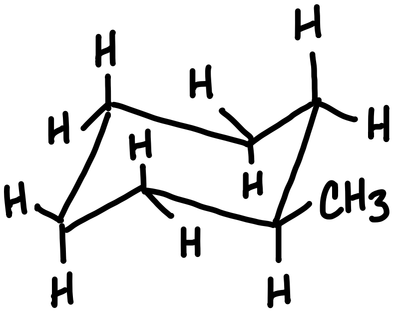
9. Turn your cyclohexane model into a methylcyclohexane by adding a -CH_3 group to any one of the carbons in the ring. Draw a chair conformation of your model. Pay attention to the position of the methyl group. Is it up or down? Axial or equatorial? Represent it accurately in your drawing.



10. Ring-flip your methylcyclohexane and draw a new chair conformation. Again, pay attention to the exact position of the methyl group and represent it accurately in your drawing. Did you show an "axial-to-equatorial" switch? Did "up stay up"?

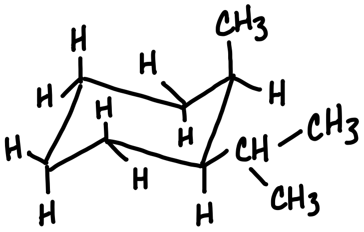


11. Put your methylcyclohexane into the lowest energy conformation. To do this, you want to minimize its steric hinderance. Find the chair conformation that puts all atoms as far apart as possible. Once you find this conformation, draw it.



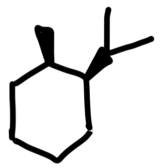
12. A mono-substituted cyclohexane (cyclohexane with one substituent) is most stable when the substituent is in an equatorial position. Is this what you found in problem 11? If not, go back to problem 11 and work with your model until you get this result.

13. Turn your cyclohexane model into 1-isopropyl-2-methylcyclohexane by adding an isopropyl group adjacent to the methyl group. When you add the isopropyl group, make sure it is pointing in the same direction as the methyl group. (Both should be "up" or both should be "down" depending on how you are holding the model.) Ring-flip your model until you find the lowest energy conformation with minimal steric hinderance. Once you find this conformation, draw it.



14. A di-substituted cyclohexane (cyclohexane with two substituents) is most stable when the *bulky substituent* is in the equatorial position. Is this what you found in problem 13? If not, go back to problem 13 and work with your model until you get this result.

15. The relative position of substituents on cyclohexane can also be represented using wedge and dash bonds on a line structure. Draw a line structure of the 1-isopropyl-2-methylcyclohexane from problem 13.



5: STEREOISOMERISM

MAIN IDEA

Carbon atoms with single bonds to four unique substituents may cause a molecule to be structurally different from its mirror image. This is a type of isomerism (called stereoisomerism) in which molecules have identical connectivity but different structures. Stereoisomers can also exist among cyclic molecules, and molecules that have carbon-carbon double bonds.

OBJECTIVES

☐ Learn what makes a carbon atom chiral or achiral

☐ Learn what makes a molecule chiral or achiral

☐ Understand the relationship between chirality and optical activity

☐ Learn how to indicate the stereochemistry of a molecule with prefixes (R), (S), (E), (Z), *cis*, and *trans*

☐ Learn how to draw Fischer projections

☐ Understand the relationship between two enantiomers

☐ Understand the difference between enantiomers and diastereomers

SKILLS TO MASTER

☐ Classify carbons at chiral or achiral

☐ Classify molecules as chiral or chiral

☐ Classify molecules as optically active or optically inactive

☐ Classify chiral carbons as (R) or (S)

☐ Draw Fischer projections with correct stereochemistry

☐ Classify alkenes as (E) or (Z)

☐ Classify alkenes and cyclic molecules as *cis* or *trans*

☐ Draw the enantiomer of a chiral molecule

☐ Draw a diastereomer of a chiral molecule

TERMINOLOGY

☐ Achiral

☐ Chiral

☐ Cis

☐ Diastereomer

☐ (E)

☐ Enantiomer

☐ Meso compound

☐ (R)

☐ (S)

☐ Stereocenter (chirality center / chiral carbon)

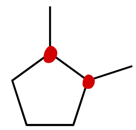
☐ Stereoisomer

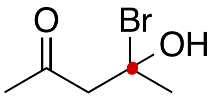
☐ Trans

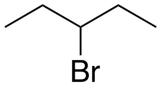
☐ (Z)

8: INTRODUCTION TO STEREOISOMERS

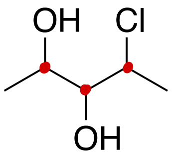
1. Find the stereocenters in each of the following molecules. Some molecules may have more than one stereocenter, and some may not have any.

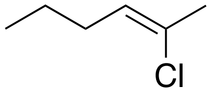






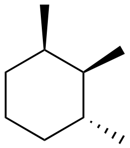
(none)

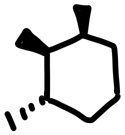


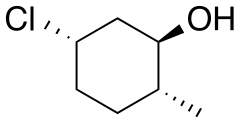


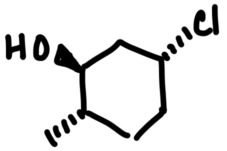
(none)

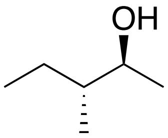
2. Draw the enantiomer of the following compounds.

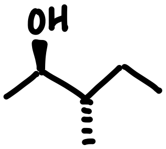


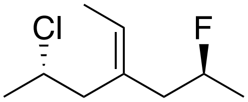


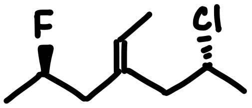




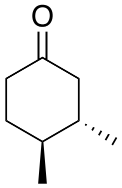


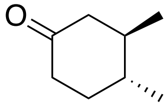




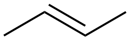


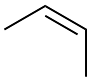
3. Classify each pair of molecules as enantiomers, identical molecules, or neither.



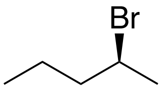


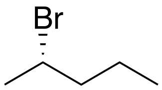
enantiomers



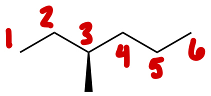


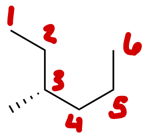
neither





identical

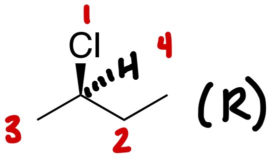


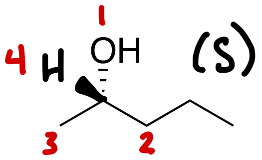


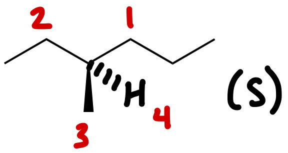
enantiomers

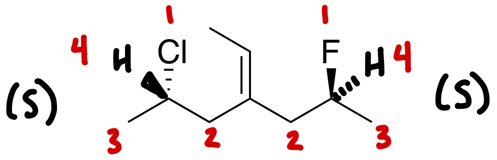
9: DESIGNATING CONFIGURATION USING (R) AND (S)

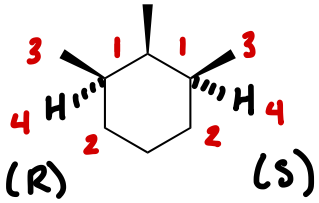
1. Designate the stereochemistry of the chiral carbons in each of the following molecules. If a molecule has more than one stereocenter, identify the stereochemistry of each chiral carbon.



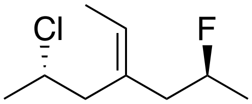


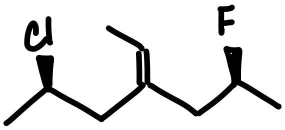


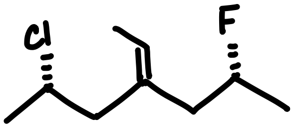


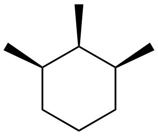


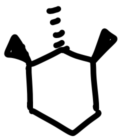
2. Draw two diastereomers of each of the following molecules.

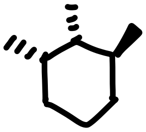




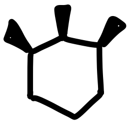






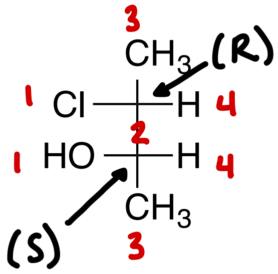


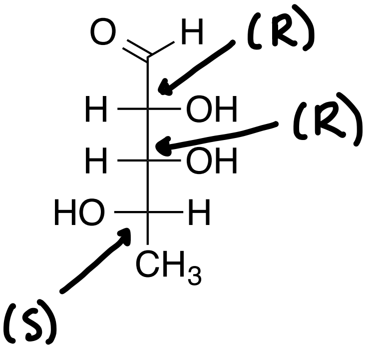
3. Identify the meso compound in problem 1.



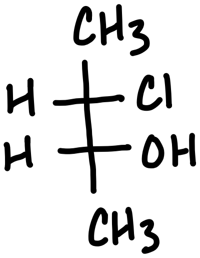
10: FISCHER PROJECTIONS

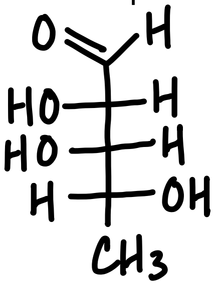
1. Designate the stereochemistry of each of the chiral carbons in the following molecules.



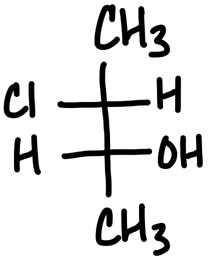


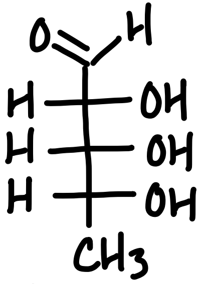
2. Draw the enantiomer of each molecule from problem 1.



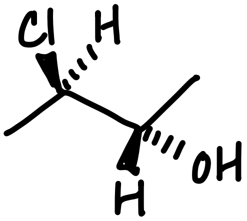


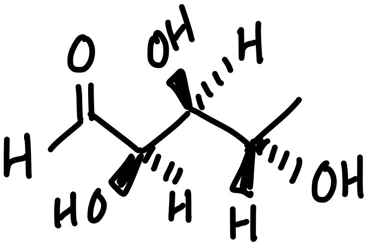
3. Draw a diastereomer of each molecule from problem 1.





4. Convert each molecule from problem 1 into wedge-dash notation such that each chiral carbon is shown with one wedge bond, one dash bond, and two straight-line bonds.





6: CHEMICAL REACTIVITY AND MECHANISMS

MAIN IDEA

Chemical reactions occur when unstable molecules attempt to become more stable. This process requires a reactant to proceed through an unstable transition state, and often also requires molecules to temporarily exist as slightly unstable intermediates. This process, and the stability of transition states and intermediates, is illustrated in energy diagrams.

OBJECTIVES

- ☐ Interpret and understand an energy diagram
- ☐ Learn how to propose the structure of a transition state
- ☐ Understand what makes a molecule nucleophilic or electrophilic
- ☐ Learn what features contribute to the stability of a carbocation
- ☐ Learn how to predict when a carbocation will undergo rearrangement
- ☐ Learn how to predict the structure of a carbocation after it undergoes rearrangement

SKILLS TO MASTER

- ☐ Label the location of reactants, products, transition states, and intermediates on an energy diagram
- ☐ Label the activation energies on an energy diagram
- ☐ Use an energy diagram to determine if a reaction is exothermic or endothermic
- ☐ Use an energy diagram to predict the number of steps in a chemical reaction
- ☐ Use the Hammond Postulate to predict the structure of a transition state
- ☐ Classify molecules as nucleophiles or electrophiles
- ☐ Predict the relative stability of carbocations
- ☐ Draw the structure of a carbocation after it undergoes rearrangement

TERMINOLOGY

- Activation energy

- Carbocation

- Electrophile

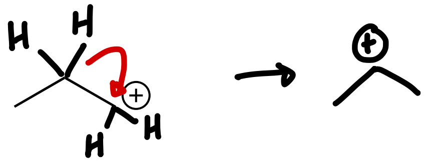
- Intermediate

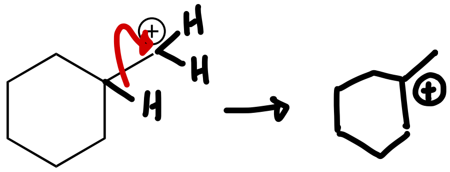
- Nucleophile

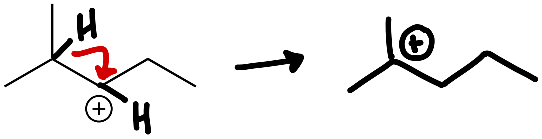
- Transition state

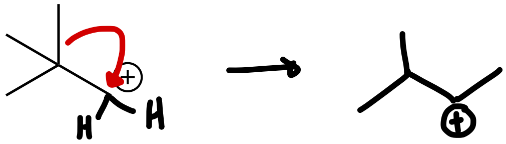
11: CARBOCATION REARRANGEMENT

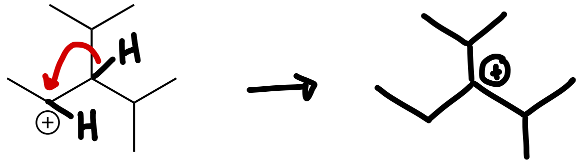
Rearrange the following carbocations to form a more stable carbocation.

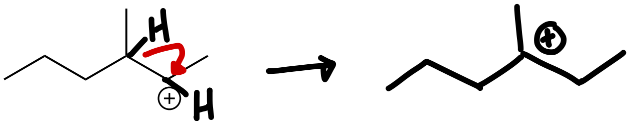


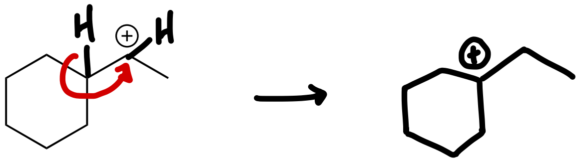












7: ALKYL HALIDES: NUCLEOPHILIC SUBSTITUTION AND ELIMINATION REACTIONS

MAIN IDEA

Alkanes with one or more halogen atoms are called “alkyl halides”. Halogen atoms are relatively easy to remove from an alkyl halide. A halogen atom can be replaced with a different atom (or group of atoms) in a type of reaction called “nucleophilic substitution”. A halogen atom can also be removed, along with a hydrogen atom, in a type of reaction called “elimination”.

OBJECTIVES

- ☐ Learn how to name alkyl halides
- ☐ Understand nucleophilic substitution
- ☐ Learn the conditions that cause a reaction to proceed via S_N1 or S_N2
- ☐ Understand the differences between the S_N1 and S_N2 mechanisms, and how these differences dictate the product(s) of these mechanisms
- ☐ Understand elimination
- ☐ Learn the conditions that cause a reaction to proceed via E1 or E2
- ☐ Understand the differences between the E1 and E2 mechanisms, and how these differences dictate the product(s) of these mechanisms
- ☐ Learn how to predict whether an alkyl halide will undergo substitution, elimination, or both

SKILLS TO MASTER

- ☐ Name alkyl halides using IUPAC rules
- ☐ Draw the mechanisms of S_N1 and S_N2 reactions and predict the product(s) of the reaction with correct stereochemistry
- ☐ Draw the mechanisms of E1 and E2 reactions and predict the product(s) of the reaction with correct stereochemistry
- ☐ Predict the mechanism of a reaction of an alkyl halide (S_N1, S_N2, E1, and/or E2) by analyzing the reactant, nucleophile, and solvent

TERMINOLOGY

- Abstract / abstracted

- Allylic alkyl halide

- Anti-coplanar

- Benzylic alkyl halide

- Bulky base

- Hofmann product

- Inversion of configuration

- Leaving group

- Polar aprotic

- Polar protic

- Primary alkyl halide

- Protonate

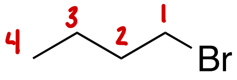
- Secondary alkyl halide

- Tertiary alkyl halide

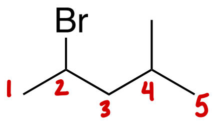
- Zaitsev product

12: ALKYL HALIDES

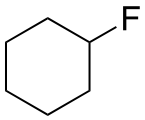
1. Alkyl halides are alkanes with a halogen substituent. To name an alkyl halide, follow the same rules as naming alkanes. Name the halogen substituent as “fluoro” or “bromo” or “chloro” or “iodo”. Provide IUPAC names for the following alkyl halides.



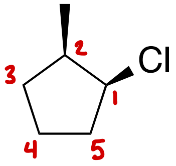
1-bromobutane



2-bromo-4-methylpentane



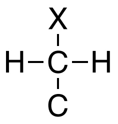
fluorocyclohexane



(1S,2R)-1-chloro-2-methylcyclopentane

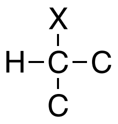
2. Did you remember to include stereochemistry? One of the molecules in problem 1 should have stereochemistry in its name.

3. Alkyl halides are classified as primary, secondary, or tertiary based on the number of additional carbon atoms directly attached to the C-X bond. Classify each of the following molecules as primary, secondary, or tertiary.



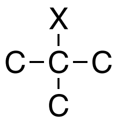
$\begin{array}{c} X \\ | \\ H-C-H \\ | \\ C \end{array}$

primary



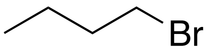
$\begin{array}{c} X \\ | \\ H-C-C \\ | \\ C \end{array}$

secondary

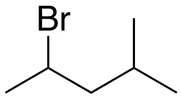


$\begin{array}{c} X \\ | \\ C-C-C \\ | \\ C \end{array}$

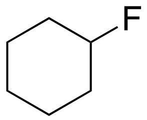
tertiary



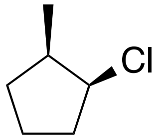
primary



secondary

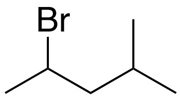


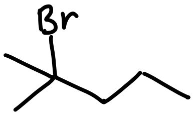
secondary



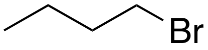
secondary

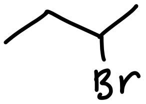
4. Draw a constitutional isomer of the following molecule that is a tertiary alkyl halide.



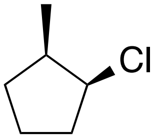


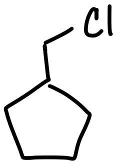
5. Draw a constitutional isomer of the following molecule that is a secondary alkyl halide.





6. Draw a constitutional isomer of the following molecule that is a primary alkyl halide.



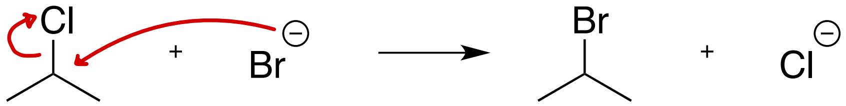


13: POSSIBLE MECHANISMS FOR SUBSTITUTION

1. Define "reaction mechanism".

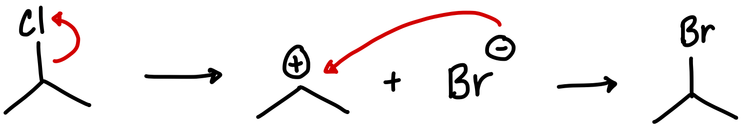
a detailed description of a reaction using curved arrow notation to show the movement of electrons

2. Propose a reaction mechanism for the following generic substitution reaction. Use curved arrows to show the movement of all electrons.



one step (one →)
zero intermediates (reactants → products)

3. Propose a *different* mechanism for the reaction in problem 2. You cannot change the bonds that are broken and formed, but you can change the order in which bonds are broken and formed.



two steps (two → →)
one carbocation intermediate
(reactant → carbocation intermediate → product)

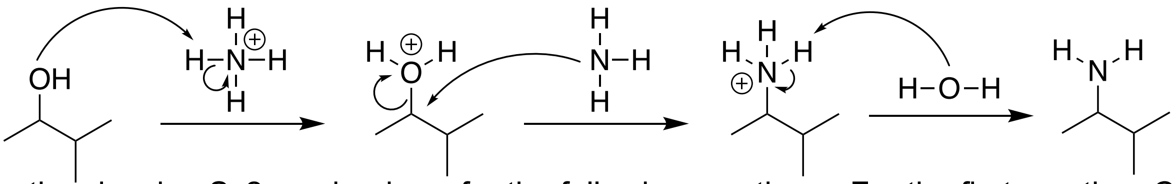
4. Your mechanisms from problems 2 and 3 should differ in terms of the number of steps it takes to get from reactant to product. Go back up to problem 2 and write down the number of steps in the proposed mechanism. Do the same for problem 3.

5. Your mechanisms should also differ in terms of reaction intermediates. Go back up to problem 2 and describe the reaction intermediate (if applicable). Do the same for problem 3.

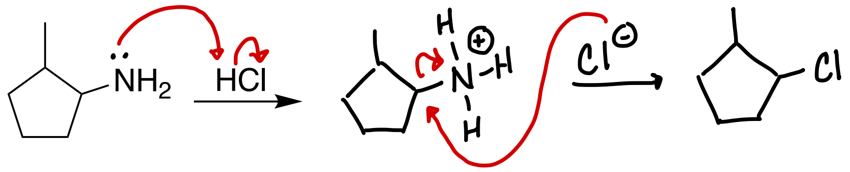
14: DRAWING THE S_N2 MECHANISM

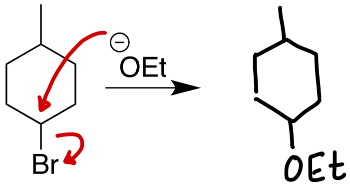
Step	**Always Happens** *These steps happen in all S_N2 reactions*	**Sometimes Happens** *These steps are not always necessary - it depends on the structure of the reactant and type of nucleophile*
1	Make sure the alkyl halide is CH_3X, primary, or secondary. (Tertiary alkyl halides can't do S_N2.)	
2		If the leaving group is -OH or $-NH_2$, protonate it with an acid.
3	Attack the carbon with a nucleophile and make the leaving group leave.	
4		If the nucleophile was charge-neutral before attacking, the product will have a positive formal charge. Deprotonate the product using another nucleophile or the leaving group.

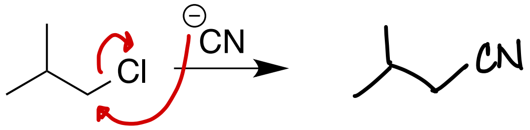
Example:



Practice drawing S_N2 mechanisms for the following reactions. For the first reaction, Cl^- is the nucleophile.

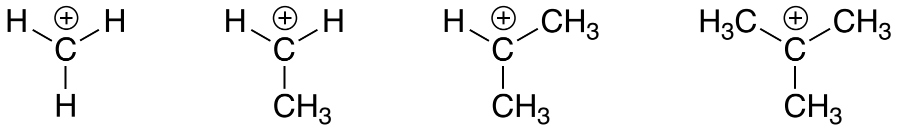






15: ALKENE STABILITY

1. Rank the following carbocations in order of increasing stability.



least ⟶ most

2. Explain your answer to problem 1. What increases the stability of a carbocation?

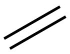
alkyl groups are electron donors, so they help stabilize the positive charge

3. What is the hybridization of the positively-charged carbon atom in a carbocation?

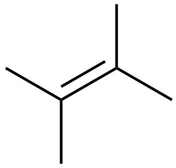
sp^2

4. What is the hybridization of the carbon atoms of an alkene? Rank these two molecules in order of increasing stability.

sp^2

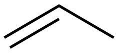


least

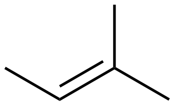


most

5. Rank these two molecules in order of increasing stability. How does their stability compare to the molecules in problem 4?

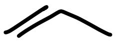


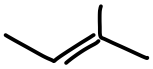
least



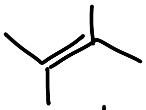
most

least



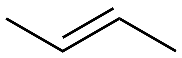


⟶

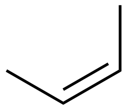


most

6. Rank these two alkenes in terms of stability. *This comparison is different from the previous two examples, so you will need to use a different concept to rank their stability. It might help to build models or draw Lewis structures of the two molecules with all their hydrogen atoms fully expanded.*



most



least

7. What is the general trend for predicting the stability of an alkene?

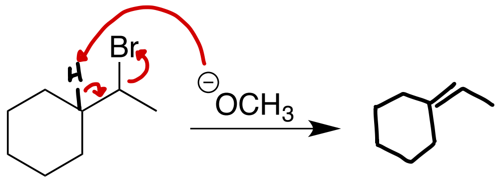
Like carbocations, alkyl groups increase the stability of an alkene.

For disubstituted alkenes, the trans isomer is more stable because it has less steric hinderance.

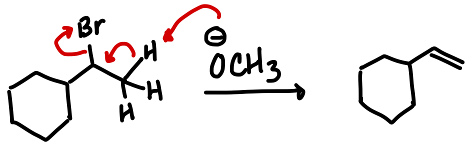
16: THE E2 MECHANISM

Step	**Always Happens** *These steps happen in all E2 reactions*	**Sometimes Happens** *These steps are not always necessary - it depends on the structure of the reactant*
1	Make sure the hydrogen and leaving group are on adjacent carbon atoms.	
2		If both carbon atoms (from step 1) are chiral, make sure the hydrogen and leaving group are anti-coplanar.
3		If both of the carbon atoms are part of a cyclohexane ring, make sure the hydrogen and leaving group are axial.
4	Attack the hydrogen atom with a base. Move the C-H electrons to the C-C bond to form the double bond. Break the bond between the C and leaving group.	
5	Attack the carbon with a nucleophile and make the leaving group leave.	

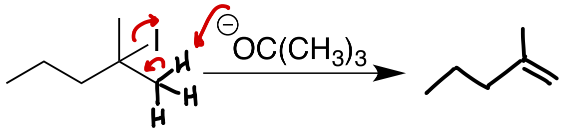
1. In the E2 mechanism, the size of the base ("bulky" or not) dictates the position of the double bond in the major product. Predict the major and minor E2 products of the following reactions.



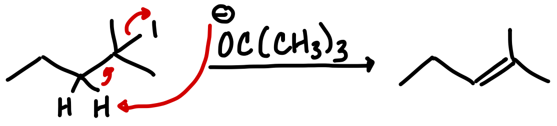
major / Zaitsev



minor / Hofmann



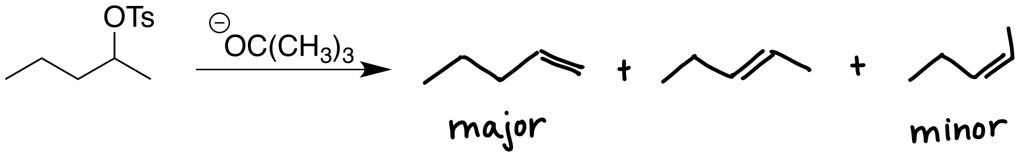
major / Hofmann

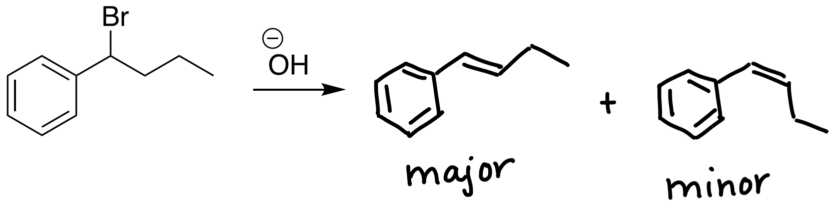


minor / Zaitsev

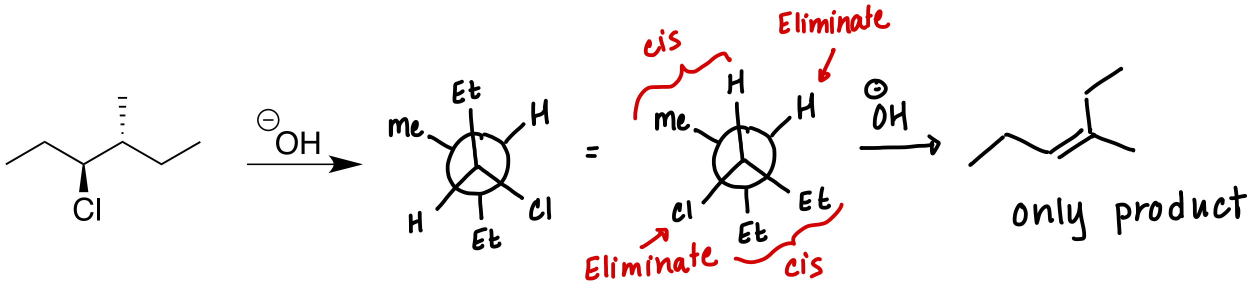
2. Go back to problem 1 and label all products as Zaitsev or Hofmann.

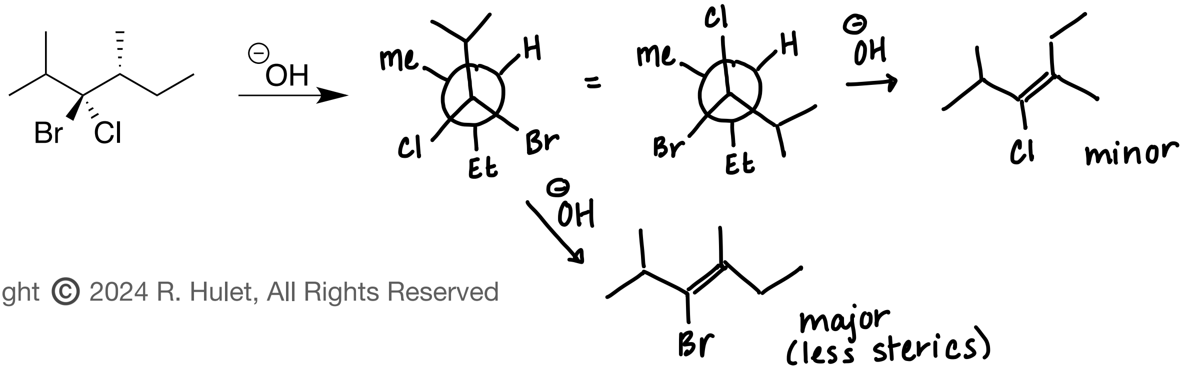
3. If an E2 reaction involves at least one achiral carbon atom, the reaction is *stereoselective,* meaning that is has a preference for producing the *trans* isomer over the *cis* isomer, although both isomers are formed. Predict all possible E2 products for the following reactions. For each reaction, identify the major product and minor product.



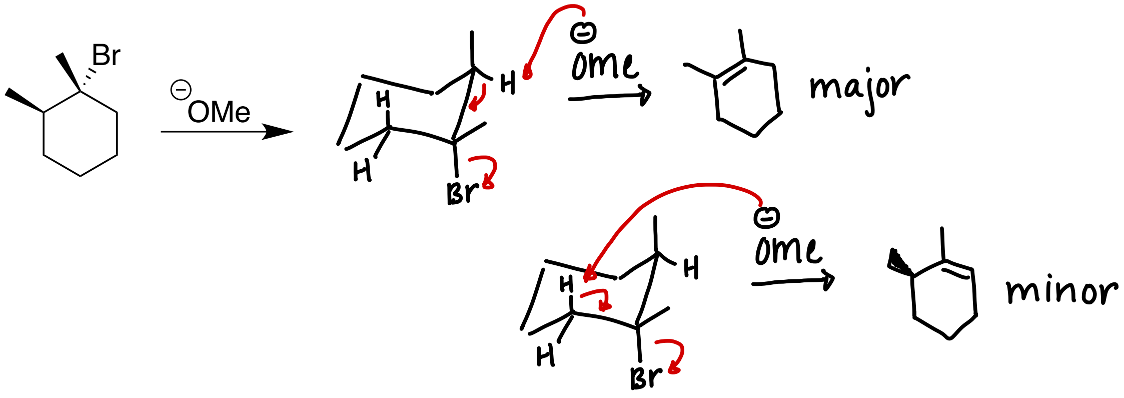


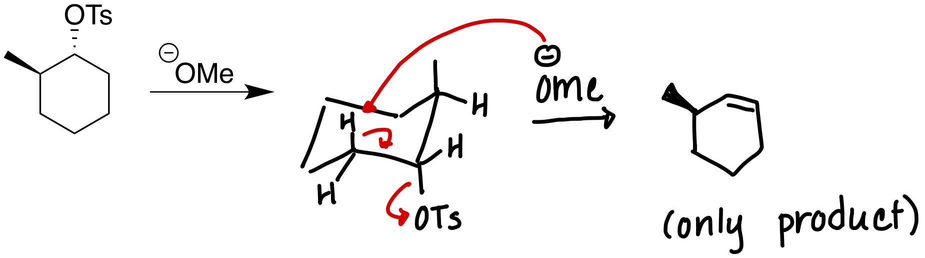
4. If an E2 reaction occurs between two chiral carbon atoms, the reaction is *stereospecific*, meaning that is produces either the (*E*) or (*Z*) isomer. Predict all possible E2 products of the following reactions. For each reaction, identify the major and minor product.



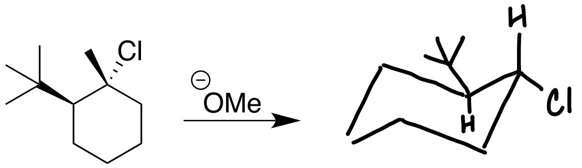


5. If an E2 reaction occurs between two carbon atoms in a ring, the reaction is also *stereospecific.* Predict all possible E2 products of the following reactions. For each reaction, identify the major and minor product.

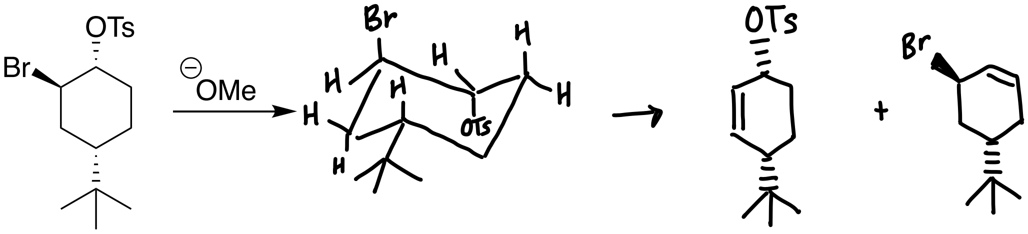




6. Because of its size, a *t*-butyl group can only be in an equatorial position of a cyclic molecule. Predict all possible E2 products of the following reactions. For each reaction, identify the major and minor product.



can't react because Cl can't be in an axial position

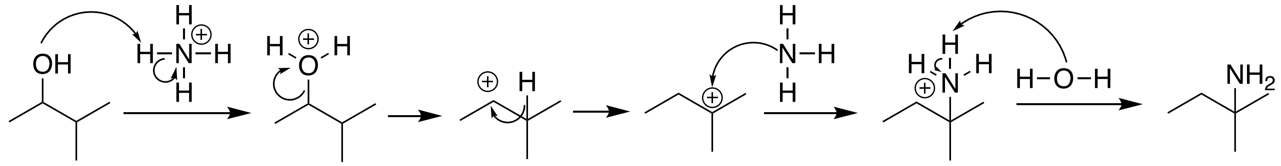


Both are equally formed

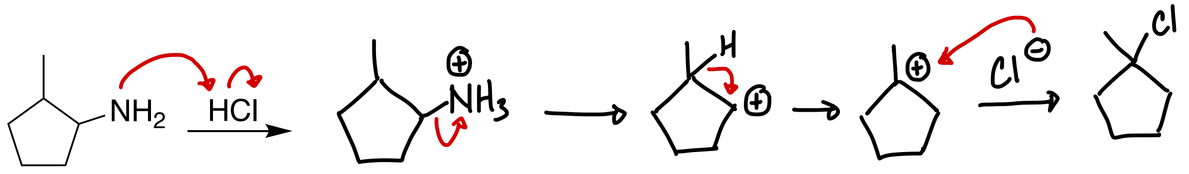
17: DRAWING THE S_N1 MECHANISM

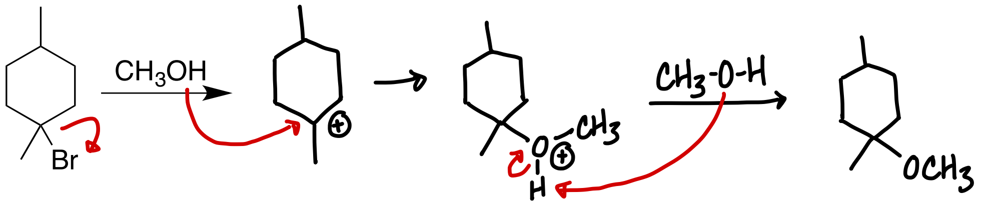
Step	**Always Happens** *These steps happen in all S_N1 reactions*	**Sometimes Happens** *These steps are not always necessary - it depends on the structure of the reactant and type of nucleophile*
1	Make sure the alkyl halide is secondary or tertiary. (Methyl or primary alkyl halides can't do S_N1.)	
2		If the leaving group is -OH or -NH_2, protonate it with an acid.
3	Make the leaving group leave and form a carbocation.	
4		Rearrange the carbocation to form a more-stable carbocation.
5	Attack the carbocation with a nucleophile.	
6		If the nucleophile was charge-neutral, the product will have a positive formal charge. Deprotonate the product using another nucleophile or the leaving group.

Example:



Practice drawing S_N1 mechanisms for the following reactions. For the first reaction, Cl^- is the nucleophile.

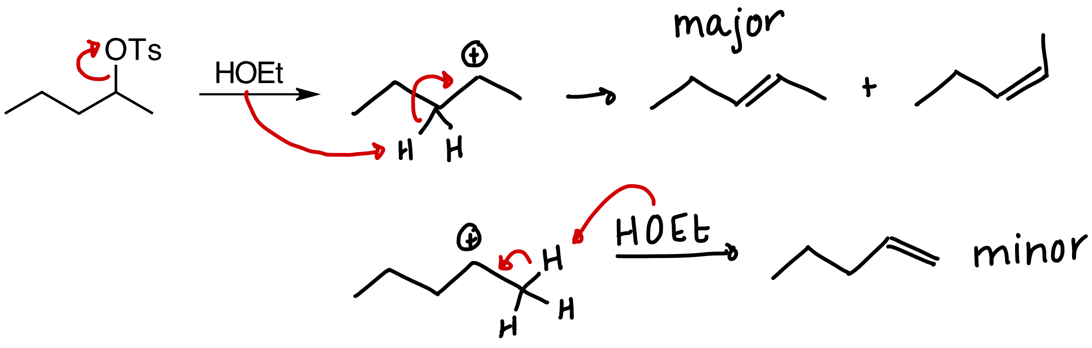


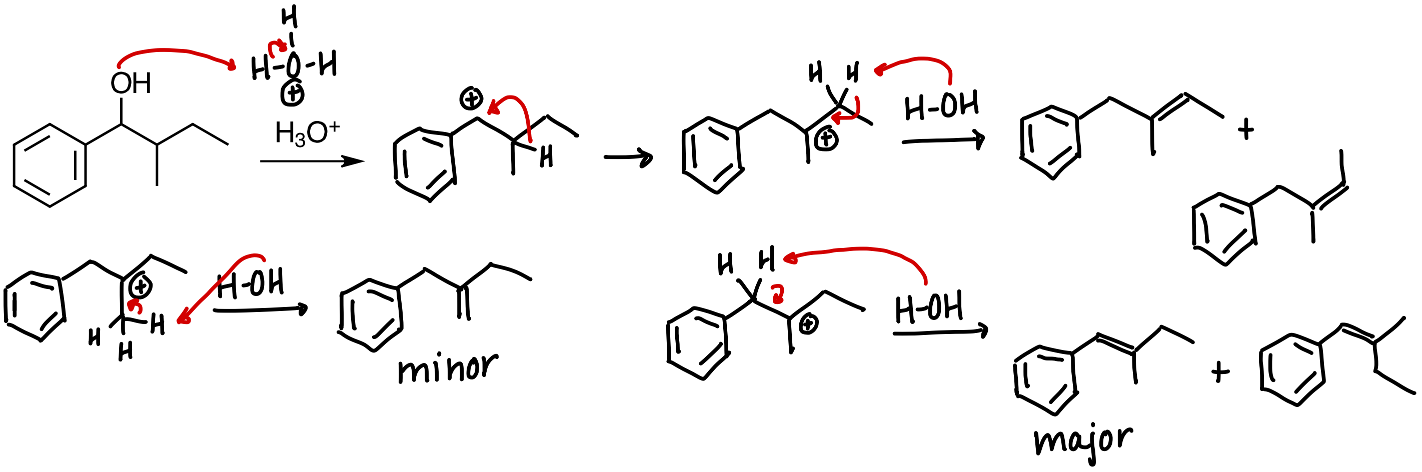


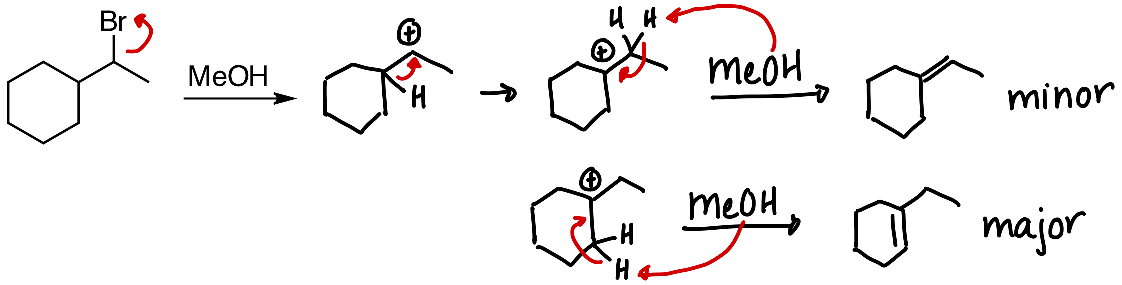
18: THE E1 MECHANISM

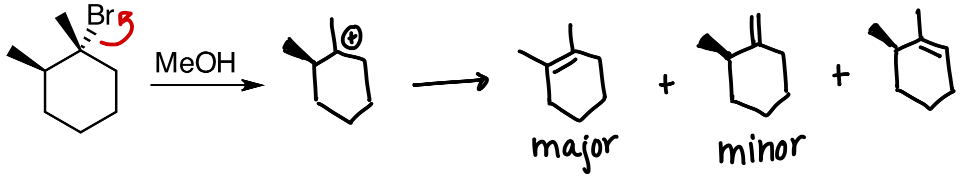
Step	**Always Happens** *These steps happen in all E1 reactions*	**Sometimes Happens** *These steps are not always necessary - it depends on the structure of the reactant*
1	Make sure the alkyl halide is secondary or tertiary. (Methyl or primary alkyl halides can't do E1.)	
2		If the leaving group is -OH or -NH_2, protonate it with an acid.
3	Make the leaving group leave and form a carbocation.	
4		Rearrange the carbocation to form a more-stable carbocation.
5	Attack an adjacent hydrogen with the base. (An "adjacent hydrogen" is one that is attached to a carbon that is bonded directly to the carbocation.) Move the C-H electrons to the C-C bond to form the double bond.	

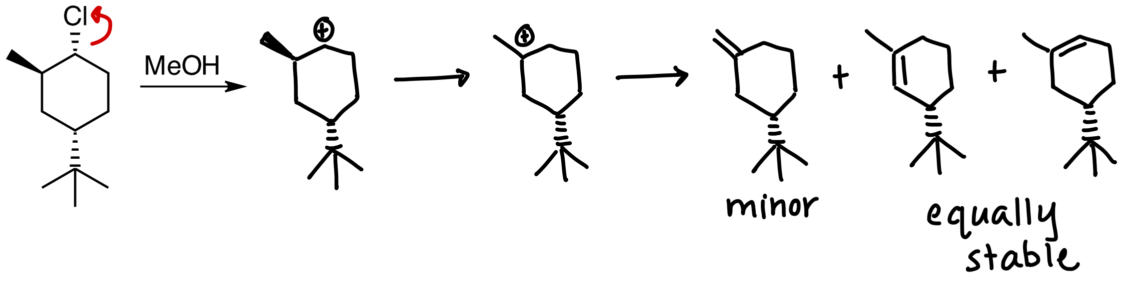
Predict all possible E1 products for the following reactions. For each reaction, identify the major product and minor product.




OH
H-O-H
H
H₃O⁺
H
H H
H-OH
H H H
H-OH
minor
H H
H-OH
major


Br
MeOH
H
H H
MeOH
minor
H
H
MeOH
major


Br
MeOH
major
minor


Cl
MeOH
minor
equally stable

8: ADDITION REACTIONS OF ALKENES

MAIN IDEA

The double bond of an alkene has a large amount of electron density, which makes it nucleophilic. Because the double bond is nucleophilic, it attracted to positively-charged ions, such as H^+, or partially-positive atoms, such as hydrogen atoms in a polar bond. This attraction is the motivation for a class of reactions called addition reactions. Addition reactions convert alkenes to alkanes while simultaneously adding two new atoms or functional groups, typically to the two alkene carbons.

OBJECTIVES

- ☐ Learn how to name alkenes
- ☐ Understand Markovnikov's Rule
- ☐ Learn the difference between syn- and anti-addition
- ☐ Learn how to predict the products of alkene addition reactions, including stereochemistry
- ☐ Learn how to convert alkenes to alkyl halides, alcohols, and alkanes

SKILLS TO MASTER

- ☐ Name alkenes using IUPAC rules
- ☐ Draw the mechanisms for the following alkene addition reactions:
    - ☐ Hydrohalogenation
    - ☐ Acid-catalyzed hydration
    - ☐ Halogenation
    - ☐ Formation of a halohydrin
- ☐ Draw the products with correct stereochemistry for the following alkene addition reactions.
    - ☐ Hydrohalogenation
    - ☐ Radical hydrobromination
    - ☐ Acid-catalyzed hydration

    - ☐ Oxymercuration-demercuration
    - ☐ Hydroboration-oxidation
    - ☐ Catalytic hydrogenation
    - ☐ Halogenation
    - ☐ Formation of a halohydrin
    - ☐ Anti-dihydroxylation
    - ☐ Syn-dihydroxylation
    - ☐ Oxidative cleavage
- ☐ Identify the reagents needed for the following alkene addition reactions:
    - ☐ Hydrohalogenation
    - ☐ Radical hydrobromination
    - ☐ Acid-catalyzed hydration
    - ☐ Oxymercuration-demercuration
    - ☐ Hydroboration-oxidation
    - ☐ Catalytic hydrogenation
    - ☐ Halogenation
    - ☐ Formation of a halohydrin
    - ☐ Anti-dihydroxylation
    - ☐ Syn-dihydroxylation
    - ☐ Oxidative cleavage

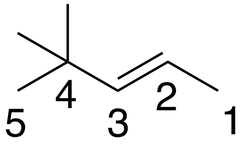
TERMINOLOGY

- Anti addition
- Epoxide
- Halohydrin
- Markovnikov’s rule
- Peroxide
- Peroxy acid
- Syn addition

19: NOMENCLATURE OF ALKENES

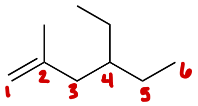
Step	Naming a Straight-Chain Alkene	Things to Consider
1	Find the longest continuous chain of carbon atoms that includes the double bond.	This may not be the longest chain of carbons in the molecule.
2	Number the chain to give the double bond the smallest possible number.	Don't pay attention to the numbers you are assigning to the other substituents. The double bond takes priority and gets the smallest possible number.
3	If applicable, determine stereochemistry and start the name with either *cis*-, *trans*-, (*E*)-, or (*Z*)-.	
4	If applicable, locate and name the substituents.	Remember that substituents are listed in alphabetical order.
5	State the location of the double bond.	The double bond is located by stating only the first number. For example, if a double bond spans carbons 2 and 3, it is considered to be located at carbon 2.
6	Name the parent chain, but change the ending of the name from "-ane" to "-ene" to indicate that it is an alk<u>ene</u> and not an alk<u>ane</u>.	Alternatively, you can place the location of the double bond in the middle of the name of the parent chain, immediately before the "-ene" ending.

Example:

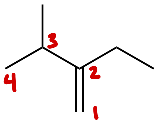


The molecule to the left has a five-carbon chain with a double bond. Numbering the chain from right to left will give the double bond the smallest possible number. The molecule has *trans* or (*E*) stereochemistry. It has two methyl groups, both located on carbon 4. Its name is: *trans*-4,4-dimethyl-2-pentene or *trans*-4,4-dimethylpent-2-ene or (*E*)-4,4-dimethyl-2-pentene or (*E*)-4,4-dimethylpent-2-ene.

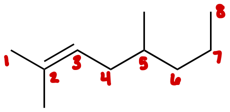
Practice naming the following alkenes:



4-ethyl-2-methyl-1-hexene



2-ethyl-3-methyl-1-butene

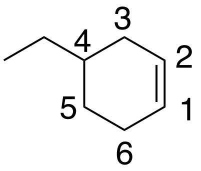


2,5-dimethyl-2-octene

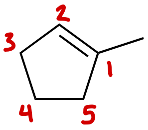
Step	Naming a Cyclic Alkene	Things to Consider
1	Make sure the double bond is part of the ring. If not, it should be named as a straight-chain alkene.	This may not be the longest chain of carbons in the molecule.
2	Number the ring such that the double bond contains carbons 1 and 2.	Choose your numbering direction (clockwise or counterclockwise) to give the other substituents the smallest possible numbers, but make sure the alkene contains carbons 1 and 2.
3	If applicable, locate and name the substituents.	Remember that substituents are listed in alphabetical order.
4	Name the parent chain, but change the ending of the name from "-ane" to "-ene" to indicate that it is an alk<u>ene</u> and not an alk<u>ane</u>.	It is not necessary to locate the position of the double bond, because it is always located on carbon 1.

Example:

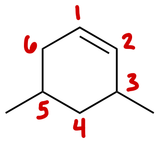
The molecule to the right has a six-carbon ring with a double bond. Numbering the double bond counter-clockwise will put the ethyl substituent on the smallest possible number. (If it is numbered clockwise, the ethyl would be on carbon 5.) Its name is: 4-ethylcyclohexene.



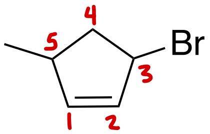
Practice naming the following alkenes:



1-methylcyclopentene



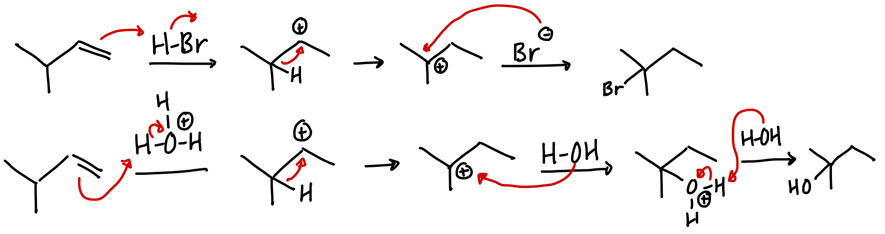
3,5-dimethylcyclohexene

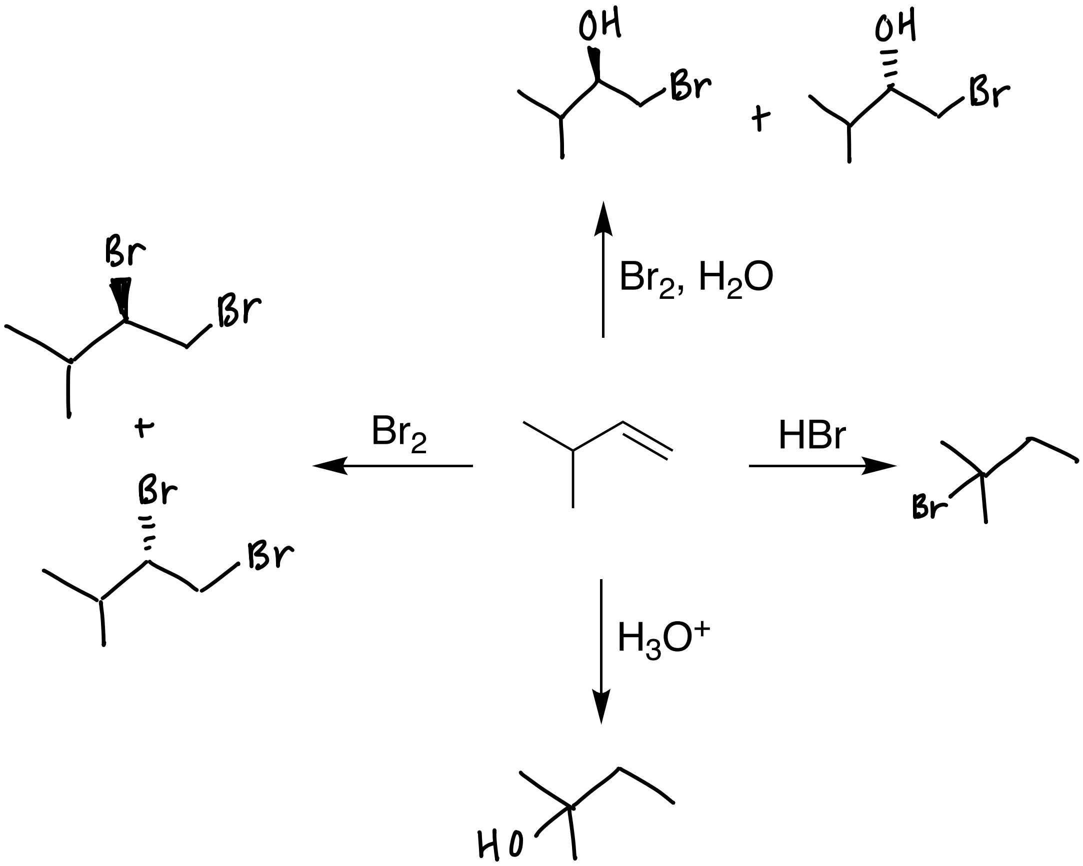


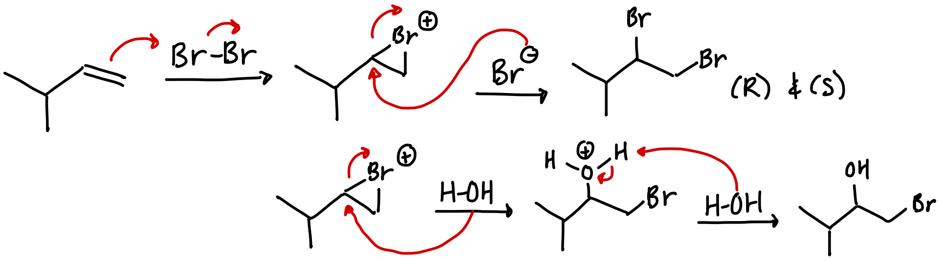
3-bromo-5-methylcyclopentene

20: ALKENE ADDITION REACTIONS

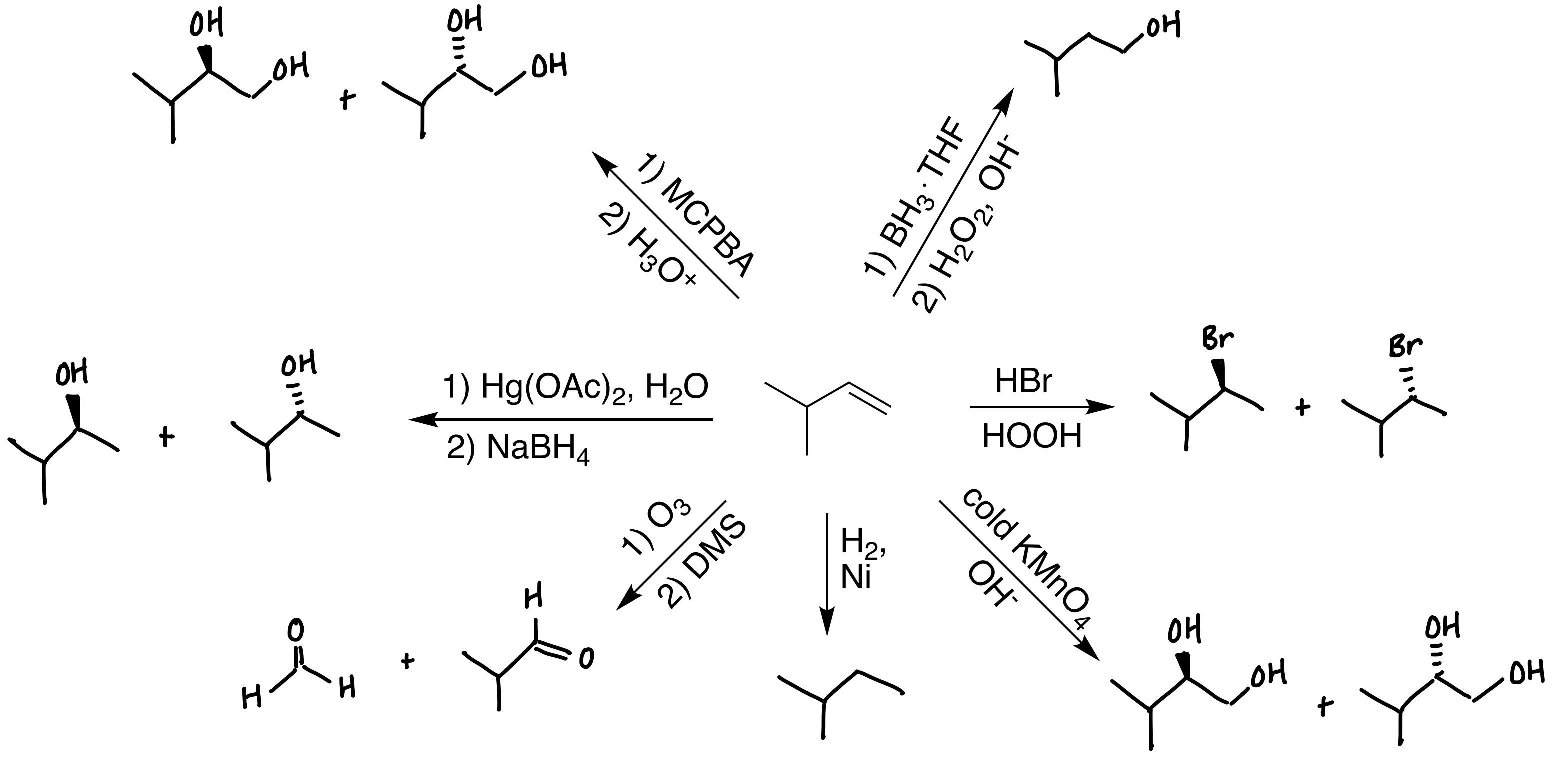
Draw mechanisms and predict the products of the following reactions. Show all stereochemistry.



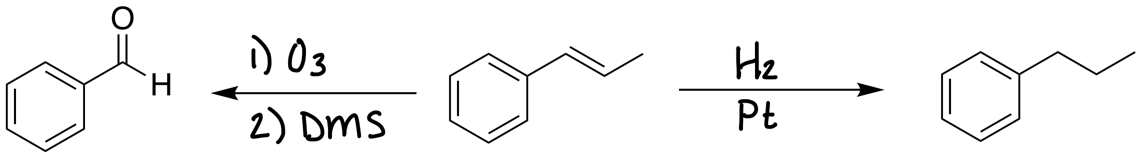


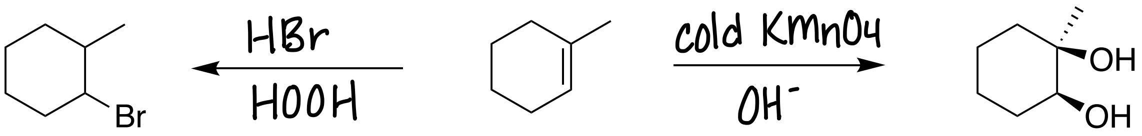


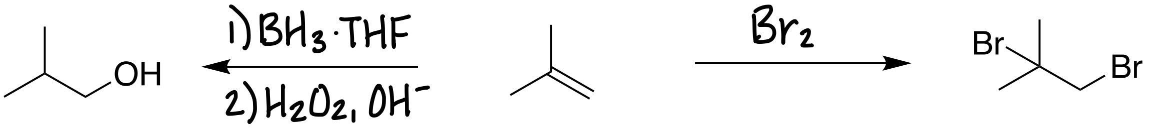
Predict the products of the following reactions. Show all stereochemistry.

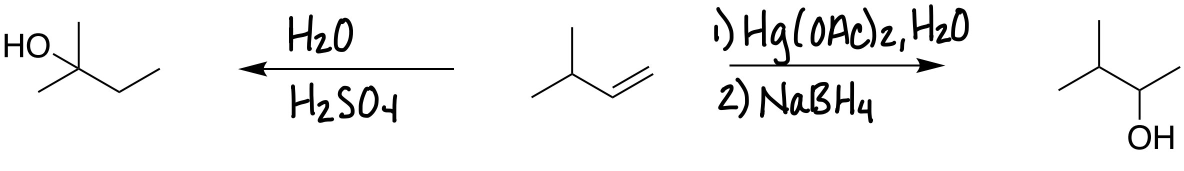


Provide the reagents necessary to perform each reaction.









9: ALKYNES

MAIN IDEA

A triple bond between two carbon atoms is referred to as the alkyne functional group. Alkynes are structurally very similar to alkenes. They are synthesized by elimination reactions, and they undergo many of the same addition reactions as alkenes. Due to the increased strength and stability of a triple bond (compared to that of a double bond), alkynes are not as reactive as alkenes. Despite this, a hydrogen atom attached to an alkyne is surprisingly easy to remove in an acid-base reaction. This allows for the creation of a carbanion - a carbon atom with a negative formal charge.

OBJECTIVES

- ☐ Learn how to name alkynes
- ☐ Understand tautomerization
- ☐ Learn how to synthesize alkynes
- ☐ Learn how to increase the carbon chain of an alkyne
- ☐ Learn how to predict the products of alkyne addition reactions, including stereochemistry
- ☐ Learn how to convert alkynes to alkanes, alkenes, alkyl halides, ketones, aldehydes, and carboxylic acids

SKILLS TO MASTER

- ☐ Name alkynes using IUPAC rules
- ☐ Draw the products with correct stereochemistry for the following reactions involving alkynes as either reactants or products.
    - ☐ Dihalide elimination
    - ☐ Catalytic hydrogenation
    - ☐ Poisoned catalytic hydrogenation
    - ☐ Dissolving metal hydrogenation
    - ☐ Hydrohalogenation
    - ☐ Hydrohalogenation in excess

☐ Radical hydrobromination

☐ Acid-catalyzed hydration

☐ Hydroboration-oxidation

☐ Halogenation

☐ Ozonolysis

☐ Alkylation of terminal alkyne

☐ Identify the reagents needed for the following reactions involving alkynes as either reactants or products

☐ Dihalide elimination

☐ Catalytic hydrogenation

☐ Poisoned catalytic hydrogenation

☐ Dissolving metal hydrogenation

☐ Hydrohalogenation

☐ Hydrohalogenation in excess

☐ Radical hydrobromination

☐ Acid-catalyzed hydration

☐ Hydroboration-oxidation

☐ Halogenation

☐ Ozonolysis

☐ Alkylation of terminal alkyne

TERMINOLOGY

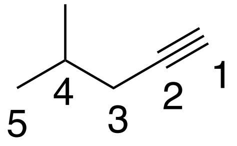
- Enol
- Internal alkyne
- Tautomerization
- Terminal alkyne

21: NOMENCLATURE OF ALKYNES

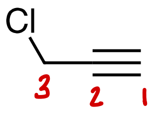
Step	Naming an Alkyne	Things to Consider
1	Find the longest continuous chain of carbon atoms that includes the triple bond.	This may not be the longest chain of carbons in the molecule.
2	Number the chain to give the triple bond the smallest possible number.	Don't pay attention to the numbers you are assigning to the other substituents. The triple bond takes priority and gets the smallest possible number.
3	If applicable, locate and name the substituents.	Remember that substituents are listed in alphabetical order.
4	State the location of the triple bond.	The triple bond is located by stating only the first number. For example, if a triple bond spans carbons 2 and 3, it is considered to be located at carbon 2.
5	Name the parent chain, but change the ending of the name from "-ane" to "-yne" to indicate that it is an alkyne and not an alkane.	Alternatively, you can place the location of the double bond in the middle of the name of the parent chain, immediately before the "-yne" ending.

Example:

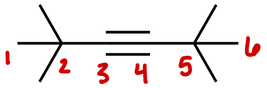
The molecule to the left has a five-carbon chain with a triple bond. Numbering the chain from right to left will give the triple bond the smaller possible number. It has a methyl group on carbon number 4. Its name is: 4-methyl-1-pentyne or 4-methylpent-1-yne



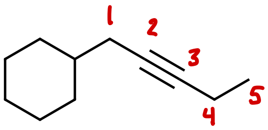
Practice naming the following alkynes:



3-chloro-1-propyne



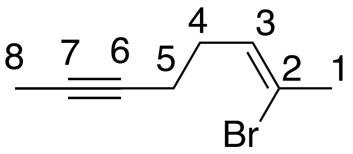
2,2,5,5-tetramethyl-3-hexyne



1-cyclohexyl-2-pentyne

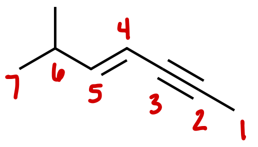
Step	Naming an Alkene-Alkyne	Things to Consider
1	Find the longest continuous chain of carbon atoms that includes both the double and triple bonds.	This may not be the longest chain of carbons in the molecule.
2	Number the chain starting at the end closest to either the double or triple bond.	If both bonds are equally distant from the end of the carbon chain, number the chain to give the double bond the smaller number.
3	If applicable, determine stereochemistry and start the name with either *cis*-, *trans*-, (*E*)-, or (*Z*)-.	
4	If applicable, locate and name the substituents.	Remember that substituents are listed in alphabetical order.
5	State the prefix of the parent chain.	
6	Locate the double bond, followed by “-en-“.	Do not use “-ene” in this instance. The final “-e” is only used at the end of the molecule’s name.
7	Locate the triple bond, followed by “-yne”.	

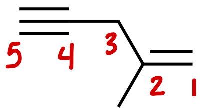
Example:



The molecule to the left has an eight-carbon chain with a triple bond and a double bond. Numbering the chain from left to right or from right to left puts a multiple bond on carbon number 2. In this instance, the double bond gets numbering priority, and the chain is numbered from right to left. The double bond has (*Z*) stereochemistry. There is a bromine on carbon 2. The alkene is on carbon 2 and the alkyne is on carbon 6. Its name is: (*Z*)-2-bromooct-2-en-6-yne

Practice naming the following molecules:





(E)-6-methylhept-4-en-2-yne

2-methylpent-1-en-4-yne