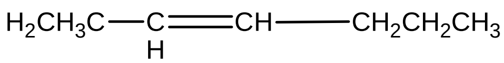
Alkenes

Alkenes-hydrocarbons with a carbon-carbon double bond. Alkenes have the formula C_nH_{2n}.

Nomenclature

Alkenes are named in the same manner as alkanes with the following adjustments.

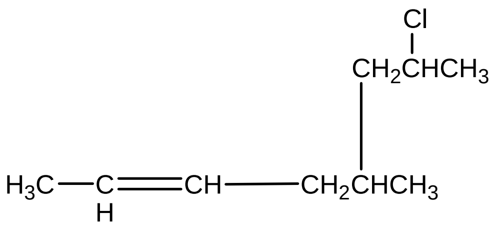
1. Find the longest continuous chain of carbons containing the double bond.
2. Number the carbons so that the carbon-carbon double bond gets the lowest numbers possible.
3. Indicate the location of the carbon-carbon double bond by placing the lower of the two double bond C numbers in front of the parent name.
4. Change the ending from -ane to -ene.



3-heptene

Practice Problem

1. What is the name of:



Answer

Calculating Degrees of Unsaturation

The degree of unsaturation is the number of rings and/or multiple bonds present in the molecule. To calculate the degree of unsaturation take the number of H's in saturated molecule – (number of H's in the molecule + 1 for every halogen and - 1 for every nitrogen in the molecule) all divided by 2:

Ignore oxygens in calculating degrees of unsaturation.

$$\text{Number of degrees of unsaturation} = \text{\# H's in saturated compound having the given number of C's} - \left(\text{\# H's actually in molecule} + \text{\# of halogens in molec.} - \text{\# of N's in molec.} \right)$$

Practice Problems

2. Calculate the degree of unsaturation of a hydrocarbon with the formula: C_3H_6.

Answer

3. Calculate the degree of unsaturation in $C_8H_9Br_3$.

Answer

<u>Isomerism in Alkenes</u>

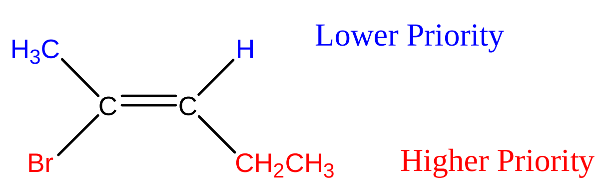
Rotation around a double bond is restricted. Therefore, substituted alkenes can exist as cis-trans isomers. A substituted alkene’s specific geometry can be notated by specifying whether it is E or Z.

Guidelines for Determining E, Z for alkenes:

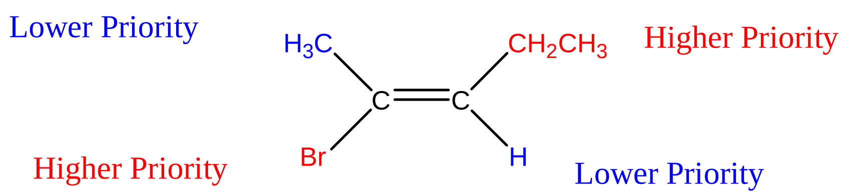
E is when highest priority atoms bonded to double bonded carbons are on opposite sides. Z is when highest priority atoms are on the same side.

1. Consider each of the carbons of the double bond individually. Identify which atom directly bonded to each of the carbons has the highest priority (highest atomic number).
2. If no decision can be made by looking at the first atoms in the substituents, look at the second, then third, etc. until the first difference can be found.
3. Atoms bonded through multiple bonds are treated as though they are bonded to the same number of single bonded atoms.

Example



(Z)-2-bromo-2-pentene

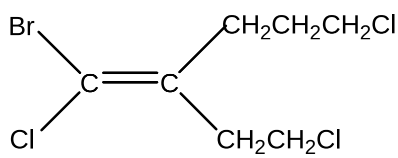


(E)-2-bromo-2-pentene

Practice Problem:

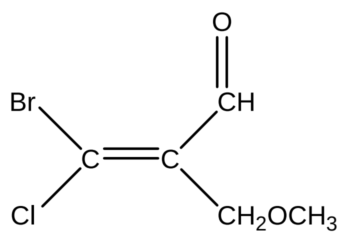
4. Designate the following as E or Z:

a.



Answer

b.



Answer

Reactions to Know

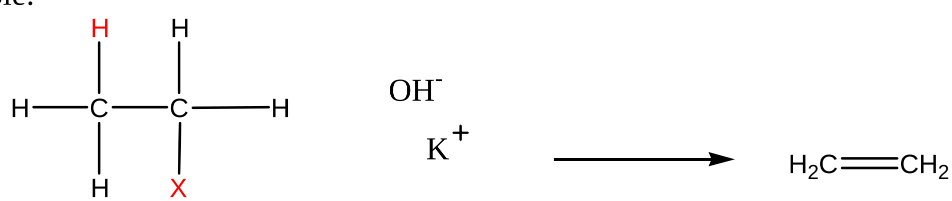
<u>Preparation of Alkenes</u>

1. Dehydrohalogenation

   General Reaction:

   Alkyl halide + alcoholic KOH → alkene

   Example:



2. Dehydration

General Reaction:

Alcohol + strong acid (e.g. sulfuric acid) → alkene

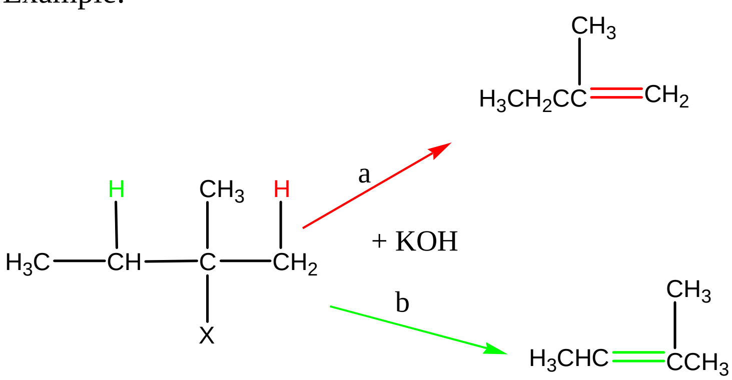
Example:

In situations where a double bond can form in more than one location, keep in mind that the more stable alkene will form in greater amounts.

Stability of Substituted Alkenes:

Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted

Example:



disubstituted
(2 alkyl groups bonded to double bond carbon)

trisubstituted
(3 alkyl groups bonded to double bond carbon)

Path **a** forms a less stable alkene than the alkene formed in path **b**. Therefore there should be more of the trisubstituted alkene formed in this reaction.

<u>Reactions of Alkenes</u>

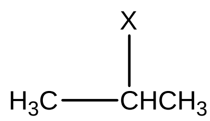
The same argument used to explain why the more stable alkene forms can also be used to explain which products form in the reactions involving carbocations.

1. Addition of HX.

General Reaction:

Alkene + HX → alkyl halide

Example:

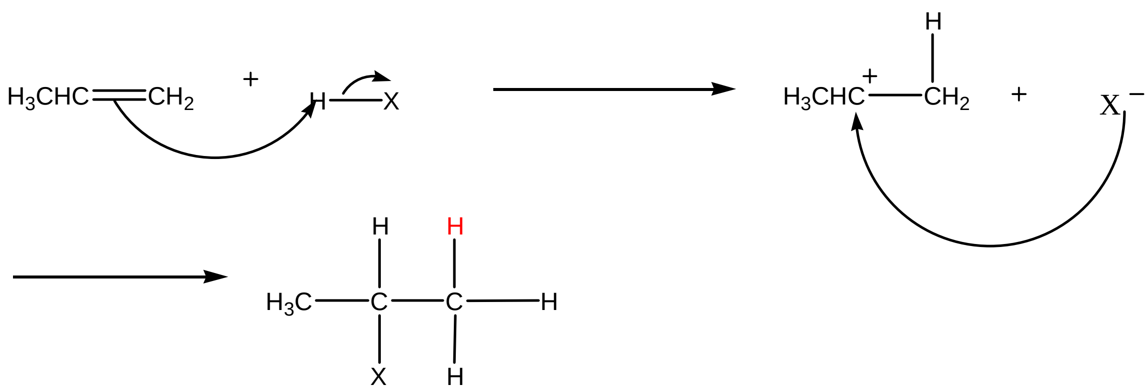
$CH_3CH{=}CH_2$ + HX → 

Follows Markovnikov's Rule. The X goes to the more highly substituted carbon, and the H goes to the least substituted carbon (i.e. the one with the most H's).

Carbocation stability:
Tertiary > Secondary > Primary > methyl carbocations

Why? Each alkyl group that a carbon is bonded to helps to stabilize a positive charge on that carbon because alkyl groups have an electron releasing effect. The more alkyl groups bonded to a carbon with a positive charge, the more the charge is stabilized. Thus, the transition state to form a more stable carbocation is lower in energy. It has a lower energy of activation, which means that more collisions leading to the formation of that carbocation are successful per unit of time.

Mechanism:

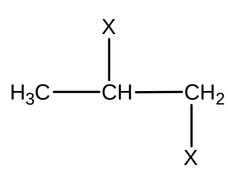


2. Addition of X_2.

General Reaction:

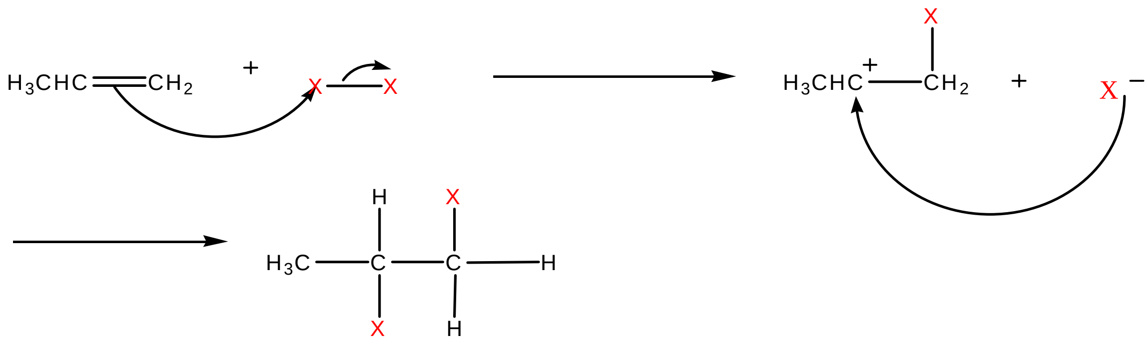
Alkene + X_2 → dihalide

Example:

$CH_3CH{=}CH_2$ + X_2 → 

X's add anti to each other.

Mechanism:

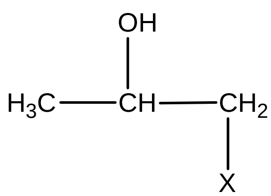


3. Formation of halohydrin.

General Reaction:

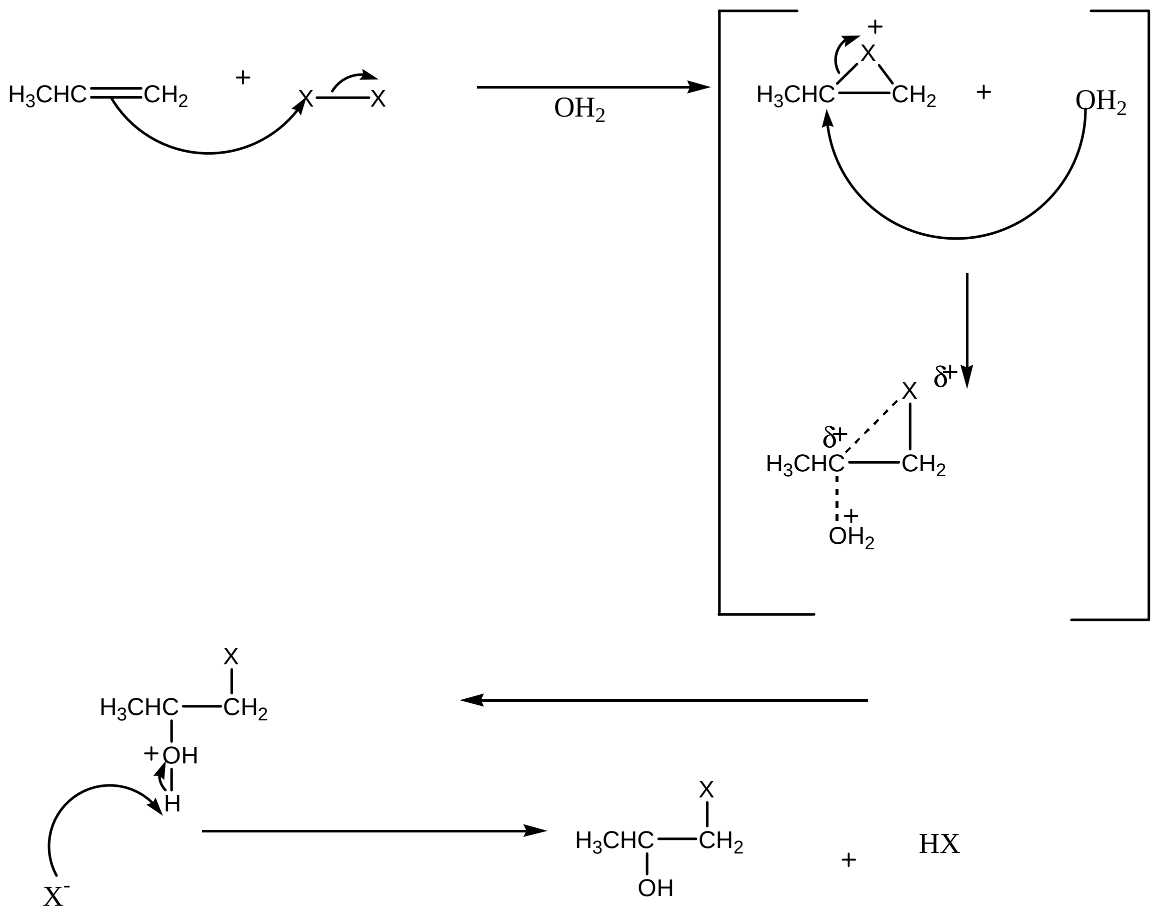
Alkene + X_2 in water → halohydrin

Example:



$CH_3CH{=}CH_2$ + X_2 + H_2O →

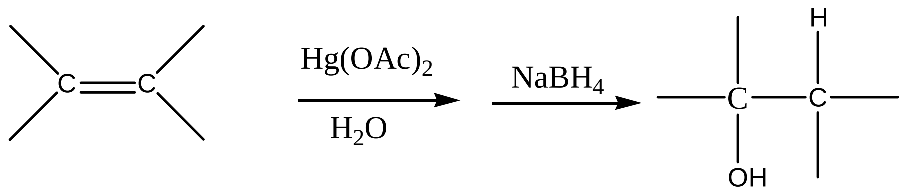
Mechanism:



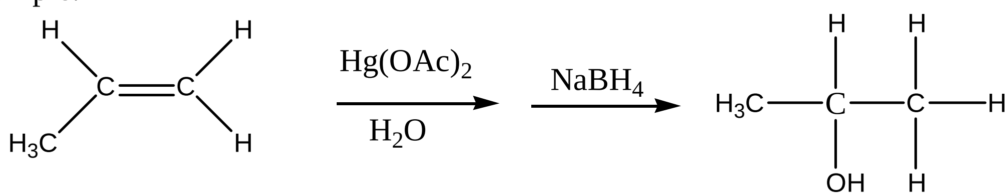
The OH goes to the most highly substituted carbon because a partial positive charge develops on the carbon where the OH is donating electrons. This partial charge forms because water is a poor nucleophile. It donates electrons to the carbon more slowly than the carbon loses electrons to the halogen.

4. Oxymercuration-demercuration.

General Reaction:

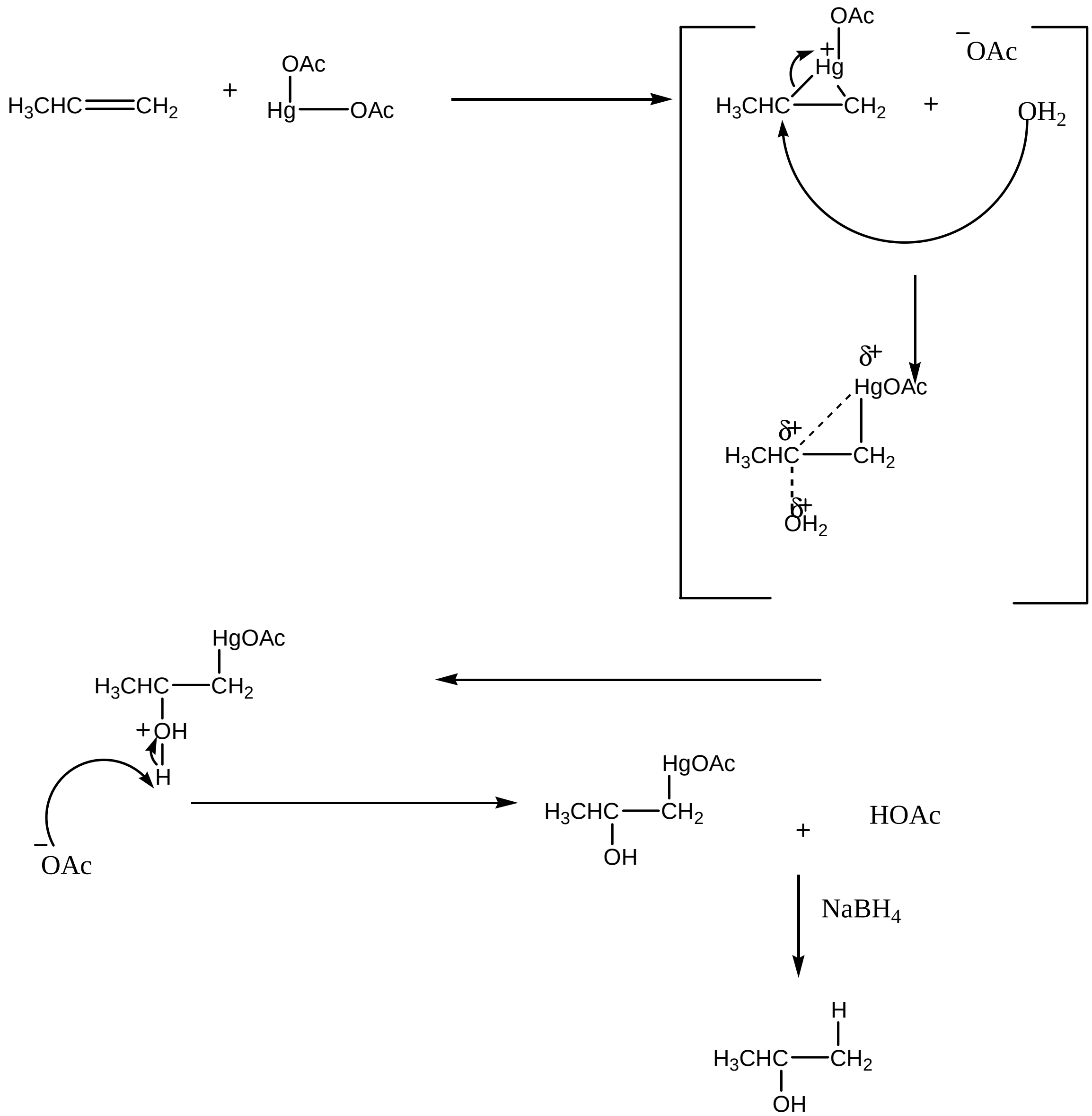


Example:



Follows Markovnikov's rule. OH goes to most highly substituted carbon. H goes to carbon with most H's.

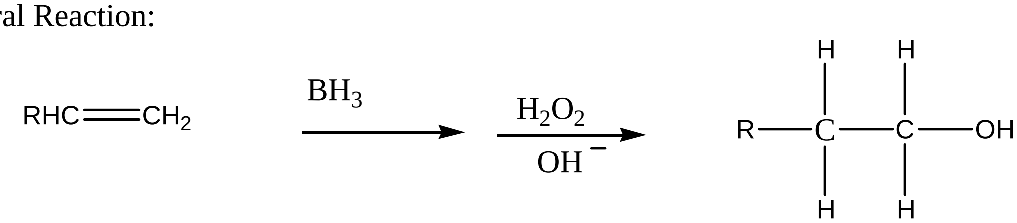
Mechanism:



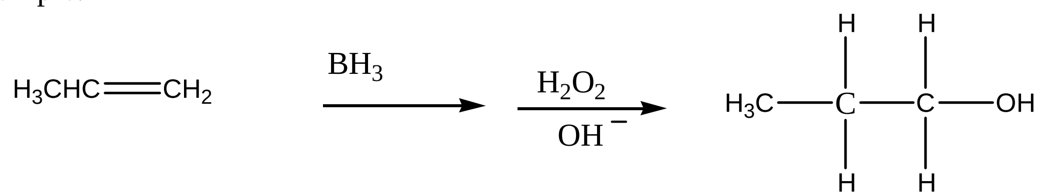
The OH goes to the most highly substituted carbon because a partial positive charge develops on the carbon where the OH is donating electrons. This partial charge forms because water is a poor nucleophile. It donates electrons to the carbon more slowly than the carbon loses electrons.

5. Hydroboration-Oxidation.

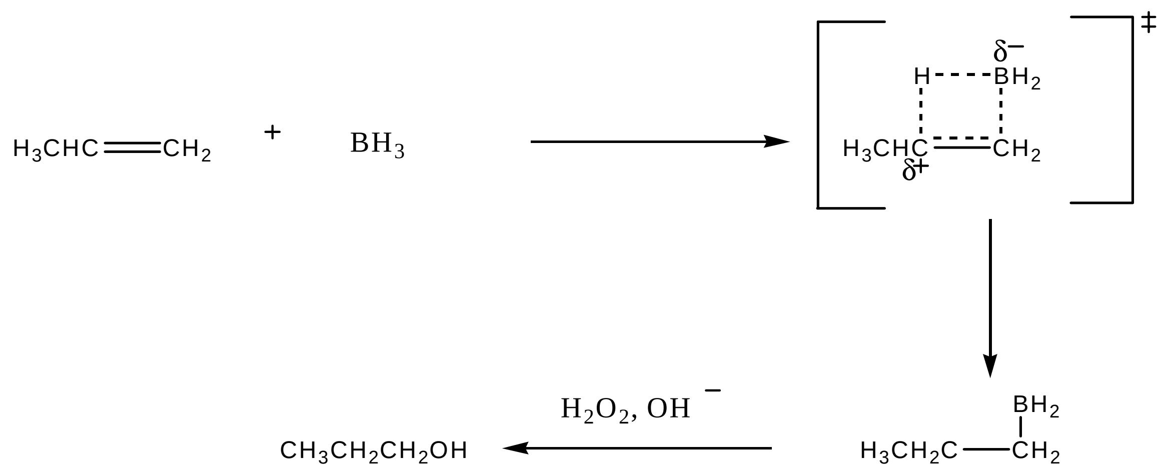
General Reaction:



Example:



Mechanism:



Anti Markovnikov's rule. The boron-containing molecule goes to the least sterically crowded carbon making up the double bond. Why? A similar argument used to explain carbocation stability applies here. A partial positive charge forms on the carbon that is diagonal to the boron. The partial positive forms on this carbon and the partial negative forms on the boron because boron gains electrons faster than it loses them in this reaction while carbon loses electrons faster than it gains them. When boron goes to the least sterically crowded carbon, the carbon on which the partially positive charge forms is the more highly substituted carbon. More R groups bonded to that carbon make it a more stable location for the partially positive charge, because R groups have an electron releasing effect that stabilizes the charge. This transition state is more stable than the transition state for the reaction with the partially positive charge forming on the least substituted carbon. Therefore, the more stable transition state has a lower energy of activation, and more collisions per unit of time are successful.

Note that oxymercuration-demercuration and hydroboration oxidation complement each other. One forms a more substituted alcohol and the other forms a less substituted alcohol

6. Hydrogenation

General Reaction:

Alkene + H_2 with catalyst (Pd/C) → alkane

Example:

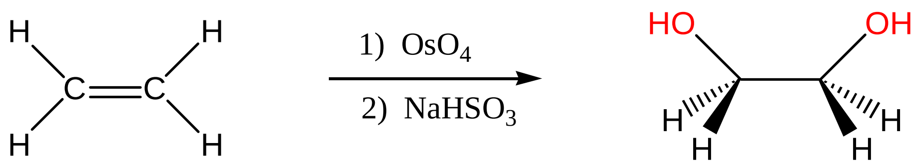
Syn addition

7. Hydroxylation

General Reaction:

Alkene + 1) OsO_4 2) $NaHSO_3$ → vicinal diol

Example:



(Vicinal diol)

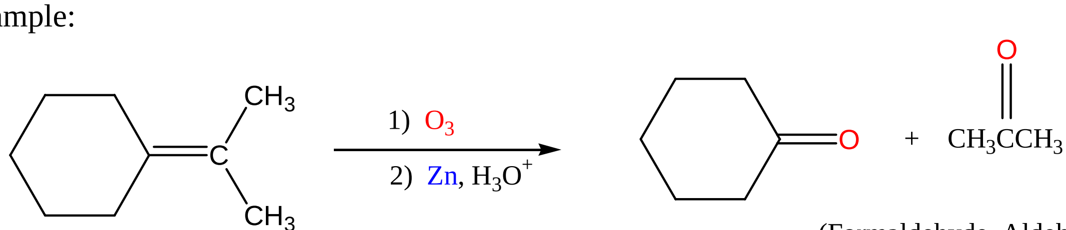
Syn addition

8. Ozonolysis

General Reaction:

Alkene + 1) O_3 2) Zn, H_3O^+ → Formaldehyde, aldehyde or ketone (depending upon the number of R groups in the original alkene)

Example:



(Formaldehyde, Aldehyde, or Ketone)

In this reaction, the carbon-carbon double bond is broken and each carbon ends up being double bonded to an oxygen.

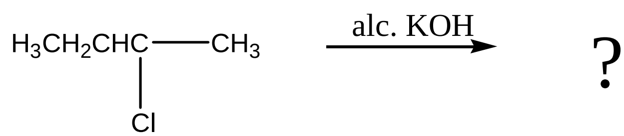
9. Cleavage with $KMnO_4$

Depending on the product obtained from ozonolysis (Reaction #8), cleavage with $KMnO_4$ will result in the following products:

- CO_2 if the ozonolysis product is formaldehyde.
- Carboxylic acid if the ozonolysis product is an aldehyde.
- Ketone if the ozololysis product is a ketone.

Practice Problems

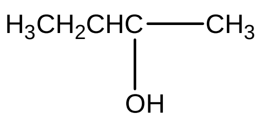
5.



a. What are the products?
b. Which product forms in greater amounts?

Answer

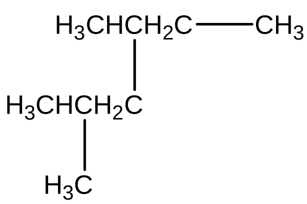
6. Prepare:



From $H_3CH_2CHC{=}CH_2$ and any other needed reagents.

Answer

7. Prepare:



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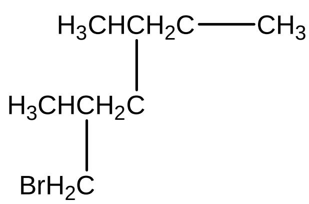


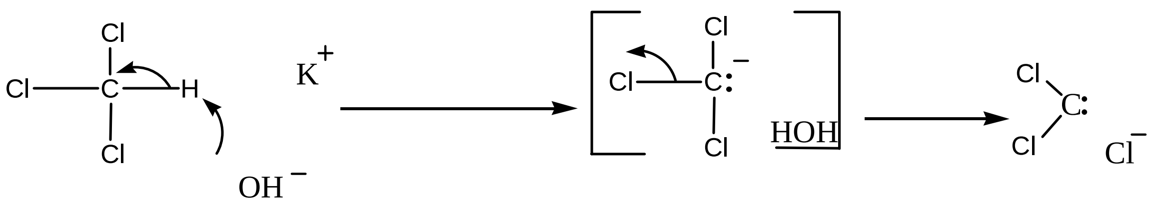
and any other needed reagents.

Answer

Formation of Carbenes

Carbenes (R_2C:) are neutral molecules containing a carbon with only 6 electrons in its valence shell. Therefore, carbenes are very reactive. Carbenes react with alkenes to form cyclopropanes.

1. $CHCl_3 + KOH \rightarrow [\,^{-}\!:CCl_3] \rightarrow :CCl_2$



2. Simmons-Smith Reaction

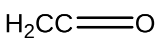
$CH_2I_2 + Zn(Cu) \xrightarrow{\text{ether}} ICH_2ZnI = :CH_2$

3.

CH_2N_2 —uv→ $:CH_2$ + N_2

diazomethane

4.



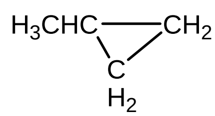
ketone

—uv→ $:CH_2$ + N_2

<u>Reaction of Carbenes</u>

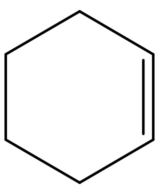
1. Alkene + carbene = cyclopropane

CH3CH=CH2 + CH2I2 + Zn(Cu) —ether→



Practice Problems

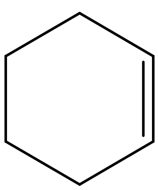
8.



+ CH_2I_2 + Zn(Cu) —ether→ ?

Answer

9.

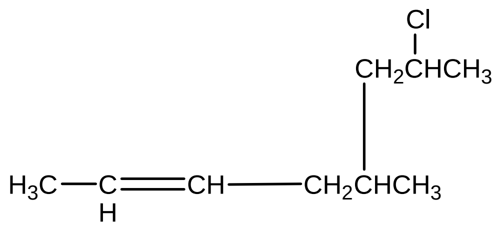


+ $CHCl_3$ + KOH ——→ ?

Answer

Answer

1. What is the name of:



7-chloro-5-methyl-2-octene

Return to Problem

Answer

2. Calculate the degree of unsaturation of a hydrocarbon with the formula C_3H_6.

8 hydrogens in saturated molecule (C_nH_{2n}+2 where n = 3).
(8 - 6)/2 = 1
1 degree of unsaturation

Return to Problem

Answer

3. Calculate the degree of unsaturation in $C_8H_9Br_3$

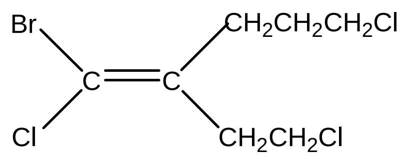
18 hydrogens in saturated molecule
9 hydrogens in molecule + (1 x 3 halogens) = 12
(18 -12)/2 = 3
3 degrees of unsaturation

Return to Problem

Answer

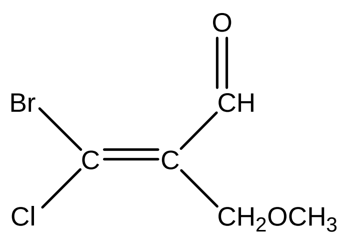
4. Designate the following as E or Z:

a.



E

b.

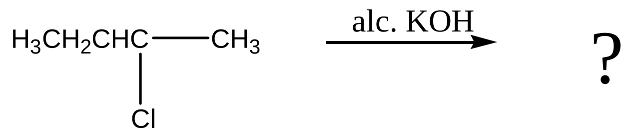


Z

Return to Problem

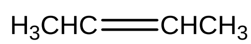
Answer

5.



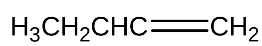
a. What are the products?

A



and

B



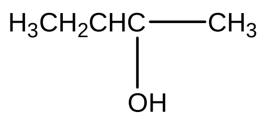
b. Which product forms in greater amounts?

A is the major product.

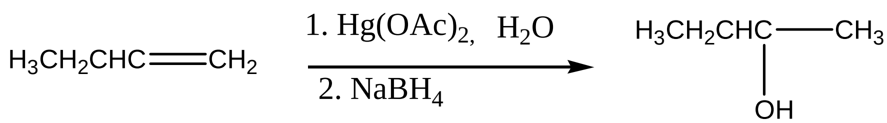
Return to Problem

Answer

6. Prepare:



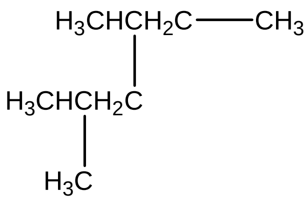
From $H_3CH_2CHC{=}CH_2$ and any other needed reagents.

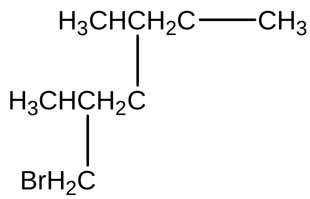


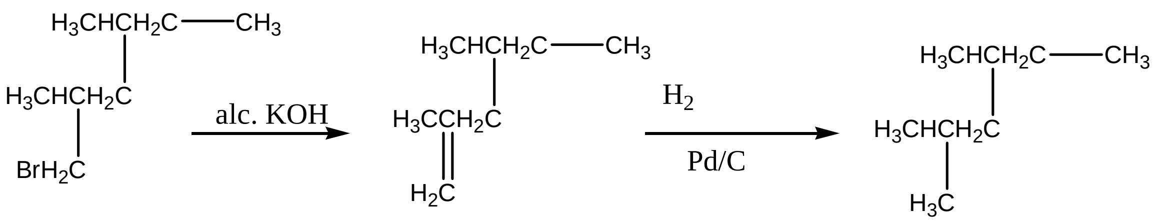
Return to Problem

Answer

7. Prepare:



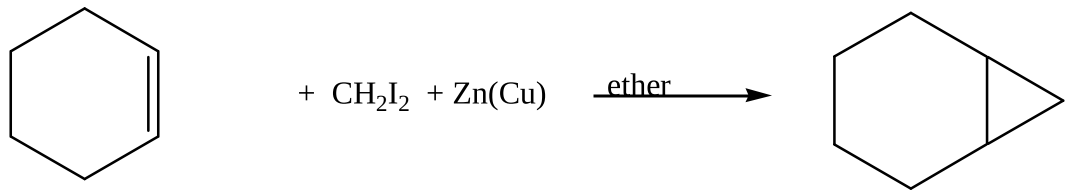
From :  and any other needed reagents.



Return to Problem

Answer

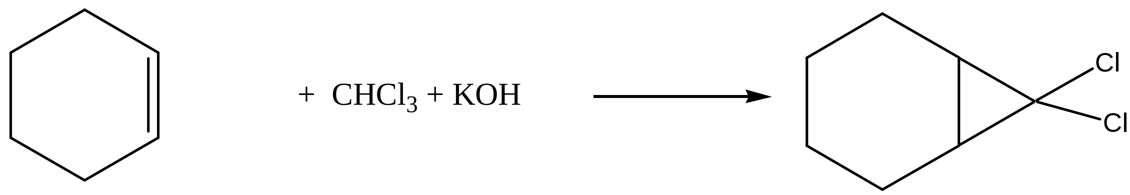
8.



Return to Problem

Answer

9.



Return to Problem