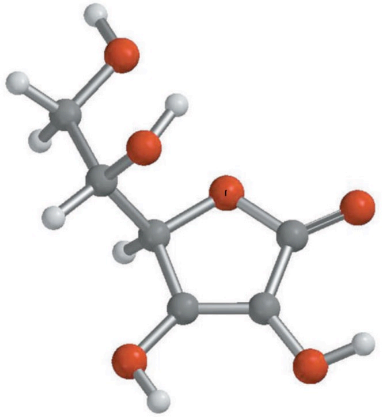
CHEM 240

PRINCIPLES OF ORGANIC CHEMISTRY I

FOR CHEMISTRY' STUDENTS, COLLEGE OF SCIENCE

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 2 (2+0)



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CHAPTER 3

ALKENES, ALKYNES

&

CONJUGATE DIENES

DEFINITION AND CLASSIFICATION

- **Alkenes** (*Olefins*) are unsaturated compounds containing carbon–carbon double bonds.
- **Alkynes** (*Acetylenes*) are unsaturated hydrocarbons containing carbon–carbon triple bonds.
- General formulas are

C_nH_{2n} Alkenes C_nH_{2n-2} Alkynes

- **Alkenes** and **Alkynes** have *physical properties* similar to those of alkanes.
- **Alkynes,** are similar to Alkenes in their *physical properties* and *chemical behavior*.
- The simplest members of the Alkenes and Alkynes series are C_2 & C_3.

	$CH_2{=}CH_2$	$HC{\equiv}CH$
Common name:	ethylene	acetylene
IUPAC name:	(ethene)	(ethyne)

DEFINITION AND CLASSIFICATION

Dienes (Alkadienes)

Compounds with two double bonds are present, the compounds are called ***alkadienes*** *or, more commonly,* ***dienes****.*

- Depending on the relative positions of the multiple bonds, double bonds are said to be:
  - **Cumulated;** when they are right next to one another.
  - **Conjugated;** when multiple bonds *alternate* with single bonds.
  - **Nonconjugated;** when more than one single bond comes between multiple bonds.

$C{=}C{=}C$

cumulated

$C{=}C{-}C{=}C$

conjugated

$C{=}C{-}C{-}C{=}C$

nonconjugated (isolated)

NOMENCLATURE

Common Names

- The simplest members of the alkene and alkyne series are frequently referred to by their older common names, ethylene, acetylene, and propylene.

$CH_2{=}CH_2$
ethylene
(ethene)

$HC{\equiv}CH$
acetylene
(ethyne)

$CH_3CH{=}CH_2$
propylene
(propene)

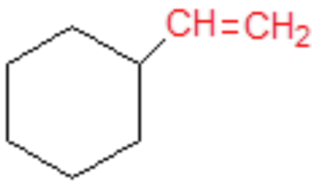
- Two important groups also have common names; They are the vinyl and allyl groups. *These groups are used in common names*.

$CH_2{=}CH{-}$
vinyl
(ethenyl)

$CH_2{=}CHCl$
vinyl chloride
(chloroethene)

$CH_2{=}CH{-}CH_2{-}$
allyl
(2-propenyl)

$CH_2{=}CH{-}CH_2Cl$
allyl chloride
(3-chloropropene)



Common name: Vinyl cyclohexane
IUPAC name: Cyclohexylethene

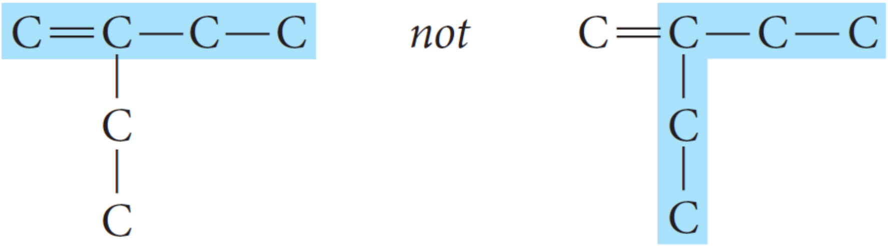
NOMENCLATURE

The IUPAC Rules

The IUPAC rules for naming alkenes and alkynes are similar to those for alkanes, but a few rules must be added for naming and locating the multiple bonds.

1. The ending *-ene* is used to a carbon–carbon double bond.
   The ending *-yne* is used for a carbon–carbon triple bond

2. Select the longest chain that includes both carbons of the double or triple bond.



3. Number the chain from the end nearest the double or triple bond so that the carbon atoms in that bond have the lowest possible numbers.

$$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C} \quad \textit{not} \quad \overset{5}{C}-\overset{4}{C}=\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$

NOMENCLATURE

The IUPAC Rules

4. Indicate the position of the multiple bond using the *lower numbered carbon atom* of that bond.

$$\overset{1}{C}H_2{=}\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$$

1-butene, *not* 2-butene

5. If more than one multiple bond is present, number the chain from the end nearest the first multiple bond.

$$\overset{1}{C}{=}\overset{2}{C}{-}\overset{3}{C}{=}\overset{4}{C}{-}\overset{5}{C} \quad \textit{not} \quad \overset{5}{C}{=}\overset{4}{C}{-}\overset{3}{C}{=}\overset{2}{C}{-}\overset{1}{C}$$

NOMENCLATURE

NOTE

- The root of the name (*eth*- or *prop*-) tells us the number of carbons, and the ending (-*ane, -ene,* or -*yne*) tells us whether the bonds are single, double, or triple.
- The **first two members** of each series are

CH_3CH_3 ethane	$CH_2{=}CH_2$ ethene	$HC{\equiv}CH$ ethyne
$CH_3CH_2CH_3$ propane	$CH_2{=}CHCH_3$ propene	$HC{\equiv}CCH_3$ propyne

  - No number is necessary in these cases, because in each instance, only one structure is possible.

NOMENCLATURE

NOTE

- With **four carbons**, a number is necessary to locate the double bond or triple bond.

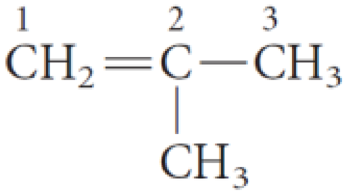
$\overset{1}{C}H_2{=}\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$
1-butene

$\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_3$
2-butene

$H\overset{1}{C}{\equiv}\overset{2}{C}\overset{3}{C}H_2\overset{4}{C}H_3$
1-butyne

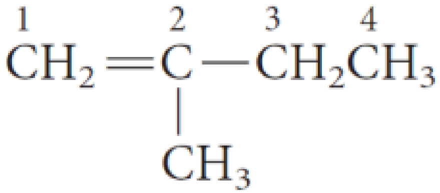
$\overset{1}{C}H_3\overset{2}{C}{\equiv}\overset{3}{C}\overset{4}{C}H_3$
2-butyne

- **Branches** are named in the usual way.



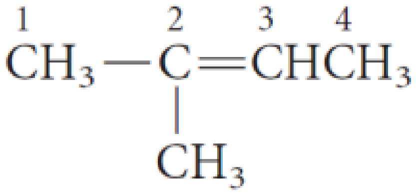
$\overset{1}{C}H_2{=}\overset{2}{\underset{\substack{|\\ CH_3}}{C}}{-}\overset{3}{C}H_3$

methylpropene
(isobutylene)



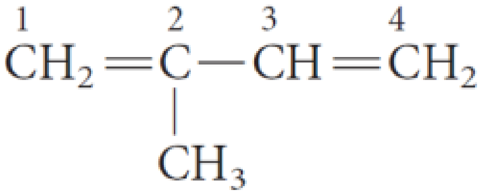
$\overset{1}{C}H_2{=}\overset{2}{\underset{\substack{|\\ CH_3}}{C}}{-}\overset{3}{C}H_2\overset{4}{C}H_3$

2-methyl-1-butene



$\overset{1}{C}H_3{-}\overset{2}{\underset{\substack{|\\ CH_3}}{C}}{=}\overset{3}{C}H\overset{4}{C}H_3$

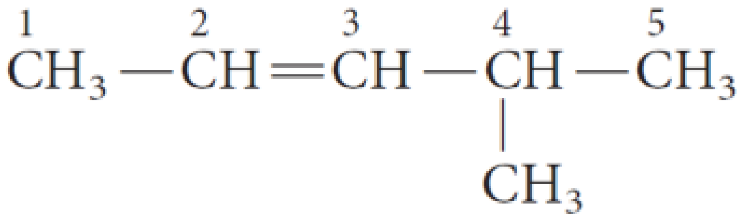
2-methyl-2-butene



$\overset{1}{C}H_2{=}\overset{2}{\underset{\substack{|\\ CH_3}}{C}}{-}\overset{3}{C}H{=}\overset{4}{C}H_2$

2-methyl-1,3-butadiene
(isoprene)

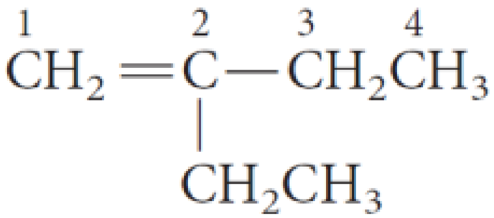
NOMENCLATURE



$$\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH}}=\overset{3}{\mathrm{CH}}-\overset{4}{\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{CH}}}-\overset{5}{\mathrm{CH_3}}$$

4-methyl-2-pentene

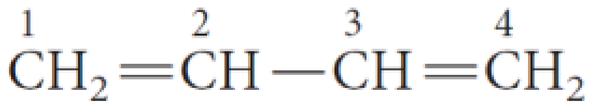
(*Not* 2-methyl-3-pentene; the chain is numbered so that the double bond gets the lower number.)



$$\overset{1}{\mathrm{CH_2}}=\overset{2}{\underset{\substack{|\\ \mathrm{CH_2CH_3}}}{\mathrm{C}}}-\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$$

2-ethyl-1-butene

(Named this way, even though there is a five-carbon chain present, because that chain does not include both carbons of the double bond.)



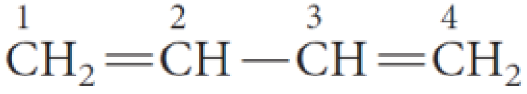
$$\overset{1}{\mathrm{CH_2}}=\overset{2}{\mathrm{CH}}-\overset{3}{\mathrm{CH}}=\overset{4}{\mathrm{CH_2}}$$

1,3-butadiene

(Note the *a* inserted in the name, to help in pronunciation.)

NOMENCLATURE

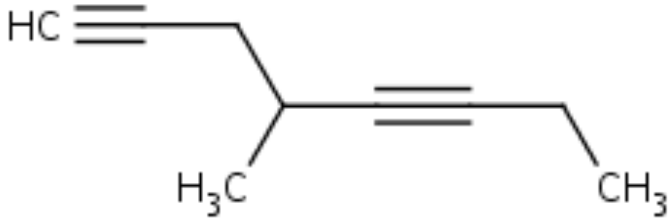
- **If a molecule contains two double bonds are (dienes)**
  - Find the longest carbon chain including both the double bonds.
  - Number the longest chain starting at the end closest to the double bond that appears first.
  - The suffix that would be used to name this molecule would be –diene.



$$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2$$

1,3-butadiene

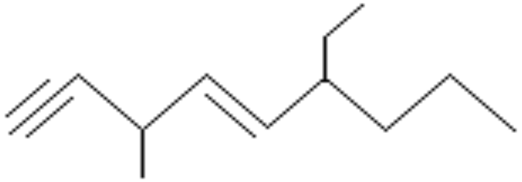
- **When there are two triple bonds in the molecule,**
  - Find the longest carbon chain including both the triple bonds.
  - Number the longest chain starting at the end closest to the triple bond that appears first.
  - The suffix that would be used to name this molecule would be –diyne.



4-methyl-1,5-octadiyne

NOMENCLATURE

- **If a molecule contains both a double and a triple bond,**
  - The carbon chain is numbered so that the first multiple bond gets a lower number.
  - If both bonds can be assigned the same number, the double bond takes precedence.
  - The molecule is then named "n-ene-n-yne“.



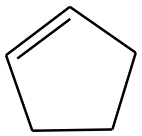
6-ethyl-3-methyl-1,4-nonenyne

6-ethyl-3-methyl-1-nonen-4-yne

NOMENCLATURE

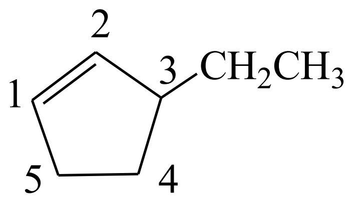
Cycloalkenes

- We start numbering the ring with the carbons of the multiple bond.
- In cyclic alkenes, a number is not needed to denote the position of the functional group, because the ring is always numbered so that the double bond is between carbons 1 and 2.



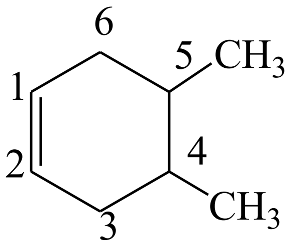
Cyclopentene

2-Cyclopentene X

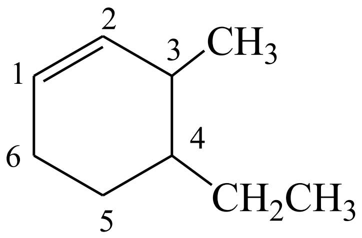


3-Ethylcyclopentene

5-Ethylcyclopentene X



4,5-Dimethylcyclohexene



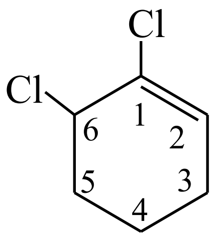
4-Ethyl-3-methylcyclohexene

NOMENCLATURE

Cycloalkenes

- Put the lowest substituent number into the name not in the direction that gives the lowest sum of the substituent numbers.
- Example;

  1,6-dichlorocyclohexene is not called 2,3-dicyclohexene because 1,6-dichlorocyclohexene has the lowest substituent number (1), even though it does not have the lowest sum of the substituent numbers (1+6=7 versus 2+3=5).

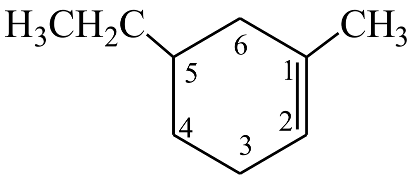


1,6-Dichlorocyclohexene

NOT

2,3-Dichlorocyclohexene

because 1<2



5-Ethyl-1-methylcyclohexene

NOT

4-Ethyl-2-methylcyclohexene

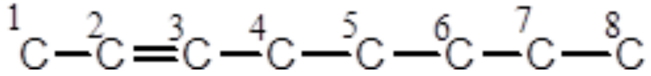
because 1<2

NOMENCLATURE

Example: Write the structural formula of 4-Isopropyl-3,5-dimethyl-2-octene.

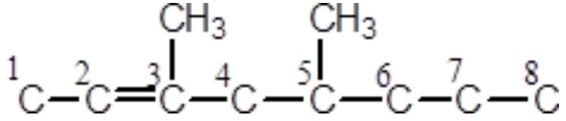
1) The parent carbon chain is an Octene.

The double bond is located between the 2nd and 3rd carbons.



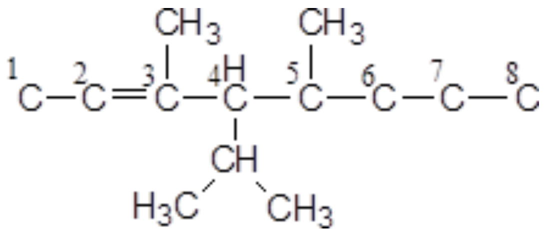
$$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}-\overset{7}{C}-\overset{8}{C}$$

2) Two methyl groups are attached on the parent carbon chain, one on carbon 3 and the other on carbon 5.



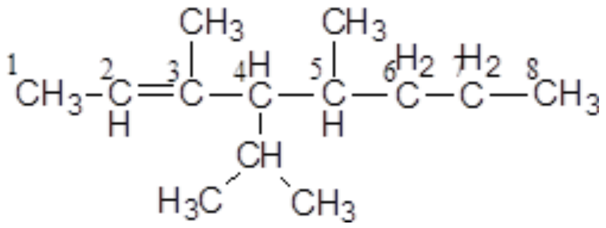
$$\overset{1}{C}-\overset{2}{C}=\overset{CH_3}{\overset{|}{\overset{3}{C}}}-\overset{4}{C}-\overset{CH_3}{\overset{|}{\overset{5}{C}}}-\overset{6}{C}-\overset{7}{C}-\overset{8}{C}$$

3) An isopropyl group is attached on carbon 4.



$$\overset{1}{C}-\overset{2}{C}=\overset{CH_3}{\overset{|}{\overset{3}{C}}}-\overset{4H}{\underset{\underset{H_3C\quad CH_3}{CH}}{\underset{|}{C}}}-\overset{CH_3}{\overset{|}{\overset{5}{C}}}-\overset{6}{C}-\overset{7}{C}-\overset{8}{C}$$

4) Put the missing hydrogens to get the correct structure.



$$\overset{1}{CH_3}-\underset{H}{\overset{2}{C}}=\overset{CH_3}{\overset{|}{\overset{3}{C}}}-\overset{4H}{\underset{\underset{H_3C\quad CH_3}{CH}}{\underset{|}{C}}}-\underset{H}{\overset{CH_3}{\overset{|}{\overset{5}{C}}}}-\overset{6H_2}{C}-\overset{7H_2}{C}-\overset{8}{CH_3}$$

PHYSICAL PROPERTIES OF ALKENES AND ALKYNES

- **Physical State**

  Alkenes and alkynes occur at room temperature are gases, liquids, and solids.

  - C2 to C4 are gases,
  - C5 to C17 are liquids,
  - C18 and larger alkenes are wax –like solids.

- **Solubility**
  - Alkenes are nonpolar compounds.
  - Alkenes are soluble in the nonpolar solvents; CCl_4 and benzene,
  - Alkenes are insoluble in polar solvents like water.

- **Boiling Points & Melting Points**
  - The boiling points and melting points of normal hydrocarbons increase with increasing molecular weight.
  - The greater the number of branches, the lower the boiling point.

Cis–Trans ISOMERISM IN ALKENES (GEOMETRIC ISOMERISM)

- Because rotation at carbon–carbon double bonds is restricted, *cis–trans* isomerism (geometric isomerism) is possible in substituted alkenes.

Geometric isomers

A. When W differs from X and Y from Z, Alkenes exist as geometric isomers

- **For example;** 1,2-dichloroethene exists in two different forms:

cis-1,2-dichloroethene
bp 60°C, mp −80°C

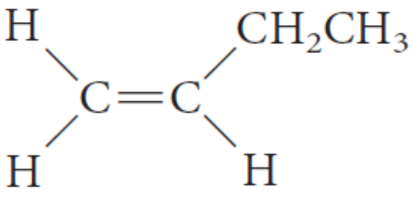
trans-1,2-dichloroethene
bp 47°C, mp −50°C

Cis–*Trans* ISOMERISM IN ALKENES (GEOMETRIC ISOMERISM)

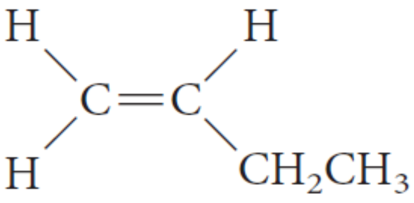
- *cis* isomer; when two similar groups are on the same side of the double bond.
- *trans* isomer; when two similar groups are on the opposite sides of the double bond.

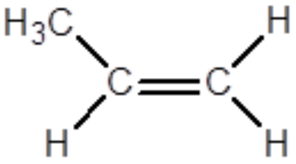
- They have different physical properties and can be separated by fractional crystallization or distillation.

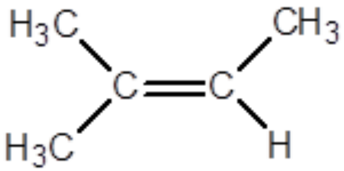
B. If (W = X or Y = Z), geometric isomerism is not possible.

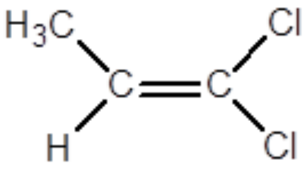

1-butene

is identical to


1-butene

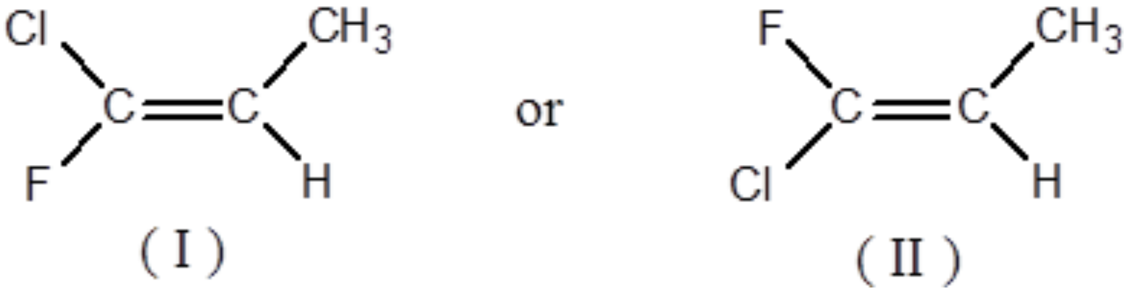

Propene


2-Methyl-2-butene


1,1-Dichloropropene

Cis–Trans ISOMERISM IN ALKENES (GEOMETRIC ISOMERISM)

- For alkenes with four different substituent such as



Cl > F, and CH_3 > H

Another system, the *E, Z* system,

- Basically, the E,Z system works as follows;
  - *Arrange the groups on each carbon of the C=C bond in order of priority (depends on atomic number)*
  - *The higher the atomic number of the atom directly attached to the double-bonded carbon, the higher the priority.*

Cis–Trans ISOMERISM IN ALKENES (GEOMETRIC ISOMERISM)

- If the two groups of higher priority are on the same side of the C=C plane,

  The isomer is labeled Z; (from the German *zusammen*, together).

- If the two groups of higher priority are on opposite sides of the C=C plane,

  The isomer is labeled E; (from the German entgegen, opposite).

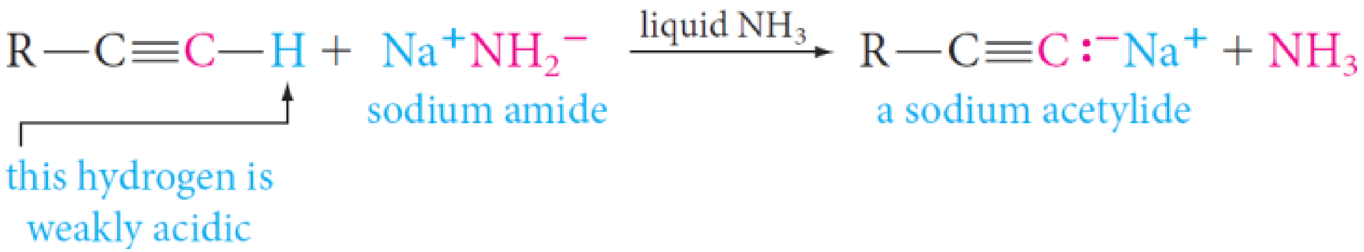
Priority: Cl > F, CH_3 > H

Z-1-Chloro-1-fluoropropene
(Cl and CH_3 on same side)

E-1-Chloro-1-fluoropropene
(Cl and CH_3 on opposite side)

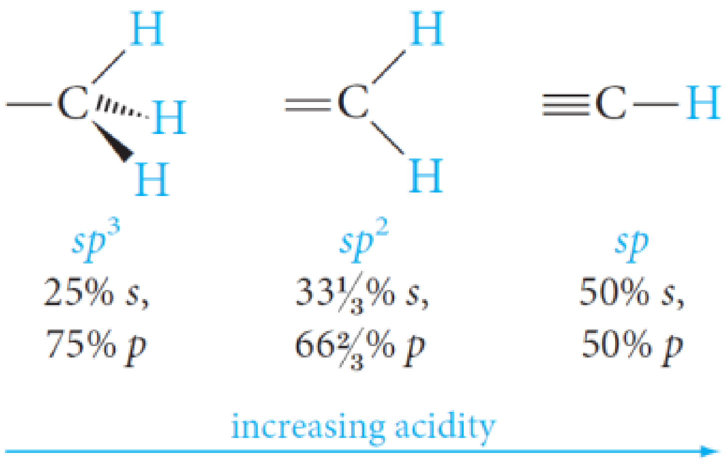
ACIDITY OF ALKYNES

- A hydrogen atom on a triply bonded carbon is weakly acidic and can be removed by a very strong base.



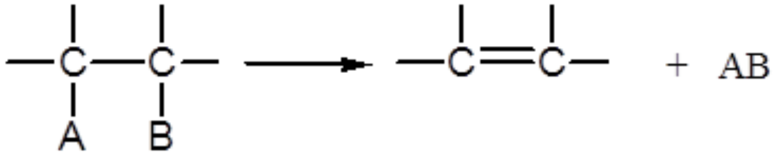
- Consider the hybridization of the carbon atom in each type of C - H bond:

Recall that *s* orbitals are closer to the nucleus than are *p* orbitals. Consequently, the bonding electrons are closest to the carbon nucleus in the triple bond, making it easiest for a base to remove that type of proton. Sodium amide is a sufficiently strong base for this purpose.



PREPARATION OF ALKENES

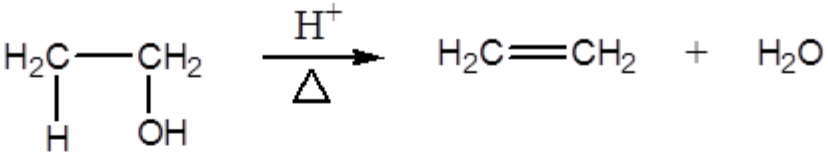
- Alkenes are prepared by *Elimination* of an atom or group of atoms from adjacent carbons to form *carbon-carbon double bond.*



(A=H or halogen;
B=OH or halogen)

1) Dehydration of Alcohols

- *When an alcohol is heated in the presence of a mineral acid catalyst, It readily loses a molecule of water to give an alkene.*

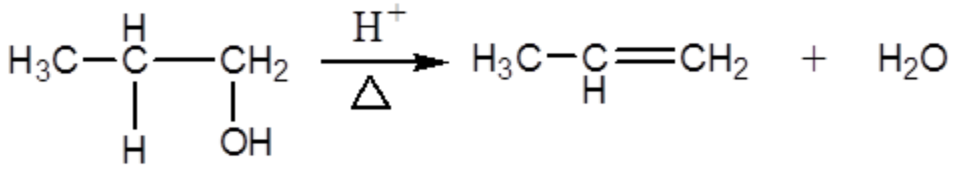


IUPAC name:	Ethanol	Ethene
Common name:	Ethyl alcohol	Ethylene

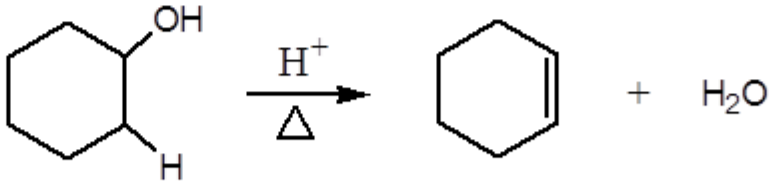
The acid catalysts most commonly used are sulfuric acid, H_2SO_4, and phosphoric acid, H_3PO_4.

PREPARATION OF ALKENES

1) Dehydration of Alcohols



IUPAC name: 1-Propanol Propene
Common name: *n*-Propyl alcohol Propylene



IUPAC name: Cyclohexanol Cyclohexene
Common name: Cyclohexyl alcohol

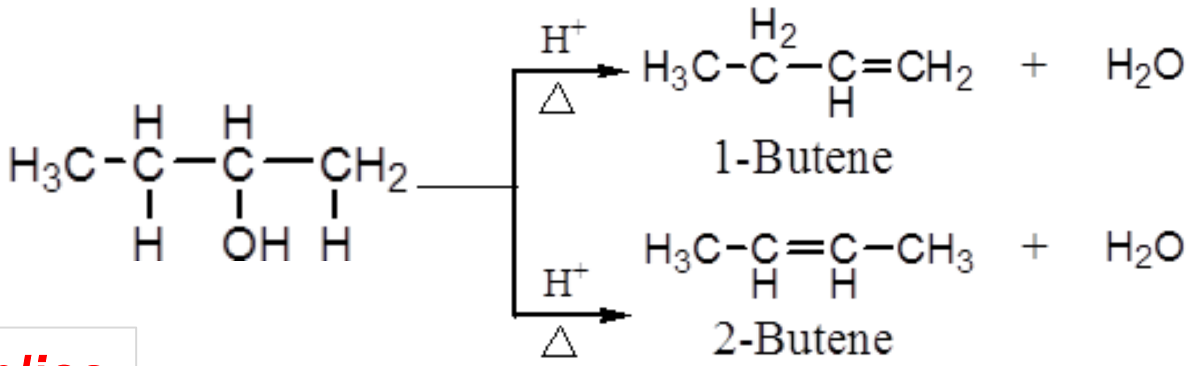
PREPARATION OF ALKENES

1) Dehydration of Alcohols

Which Alkene Predominates?; Saytzeff's Rule

The loss of water from adjacent carbon atoms, can give rise to more than one alkene.

Example: *the dehydration of 2-butanol.*



2-butene is the major (with two alkyl substituents attached to C=C)

Saytzeff's Rule applies

In every instance in which more than one Alkene can be formed

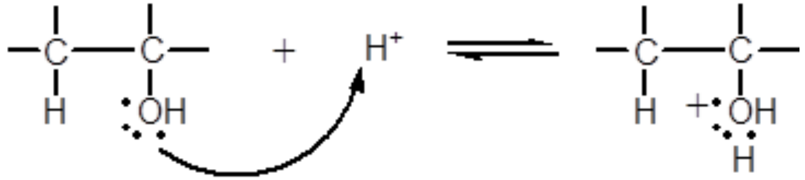
The major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.

PREPARATION OF ALKENES

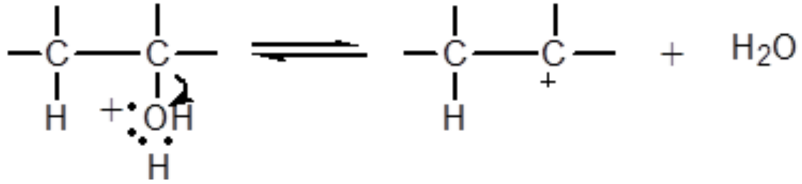
1) Dehydration of Alcohols

Mechanism of Dehydration of Alcohols

Step 1. Protonation of the alcohol.

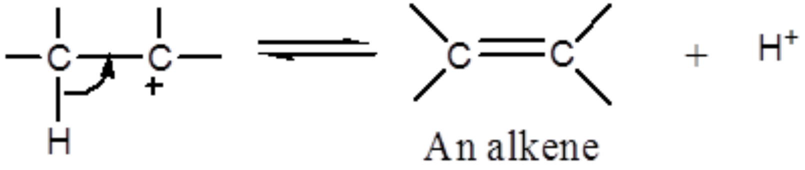


Step 2. Formation of a carbocation.



Step 3. Loss of a proton from the carbocation.

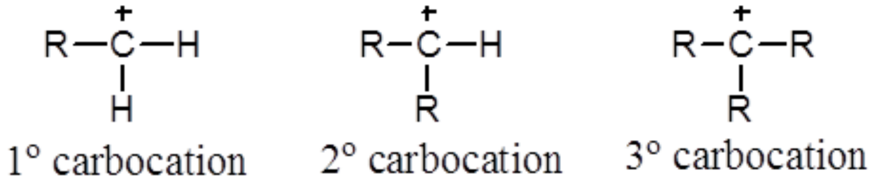
regenerates the acid catalyst and forms the alkene.



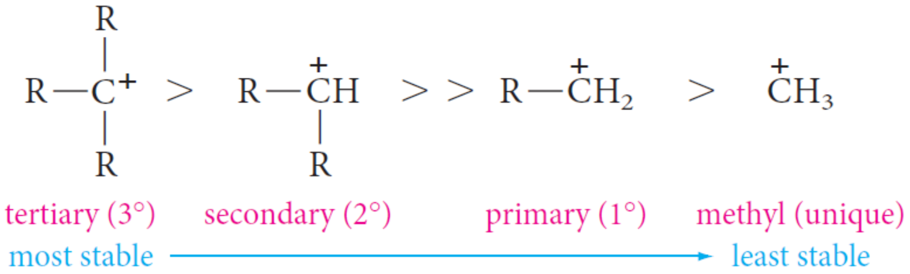
PREPARATION OF ALKENES

1) Dehydration of Alcohols

- Classes of Carbocations



according to the number of carbon atoms attached to the positively charged carbon.



Generally

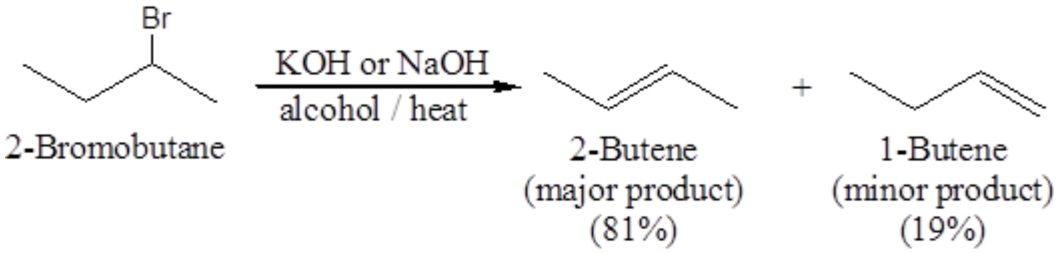
1. The dehydration of alcohols requires an acid catalyst.
2. The predominant alkene formed follows Saytzeffs rule.
3. The reaction proceeds *via* a carbocation intermediate.
4. The stabilities of carbocations and the ease of dehydration of alcohols follows the order 3° > 2° > 1°.

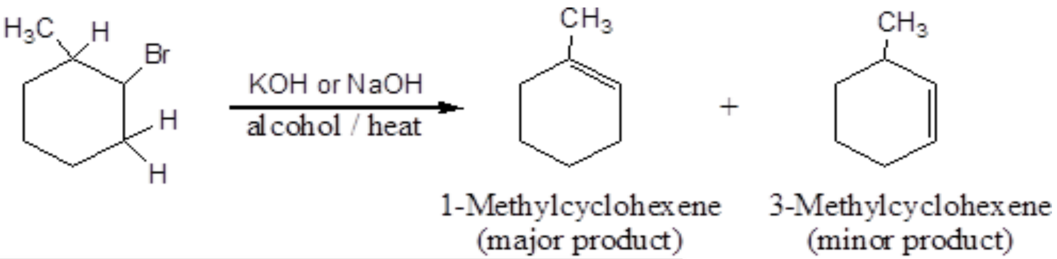
PREPARATION OF ALKENES

2) Dehydrohalogenation of Alkyl Halides

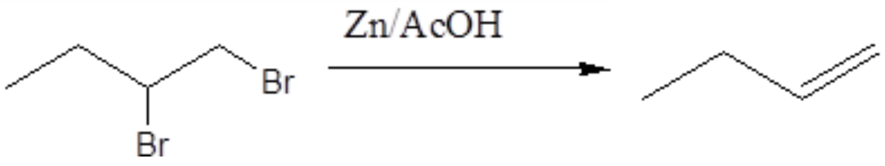
- Alkenes can also be prepared under alkaline conditions.

  heating an alkyl halide with a solution of KOH or NaOH in alcohol, yields an alkene.





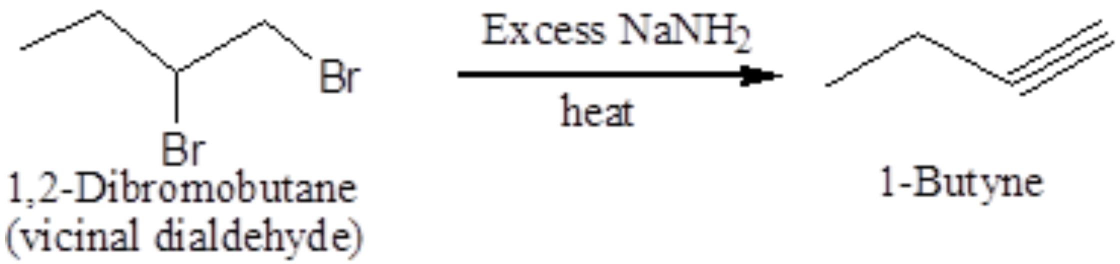
3) Dehalogenation of Vicinal Dibromides

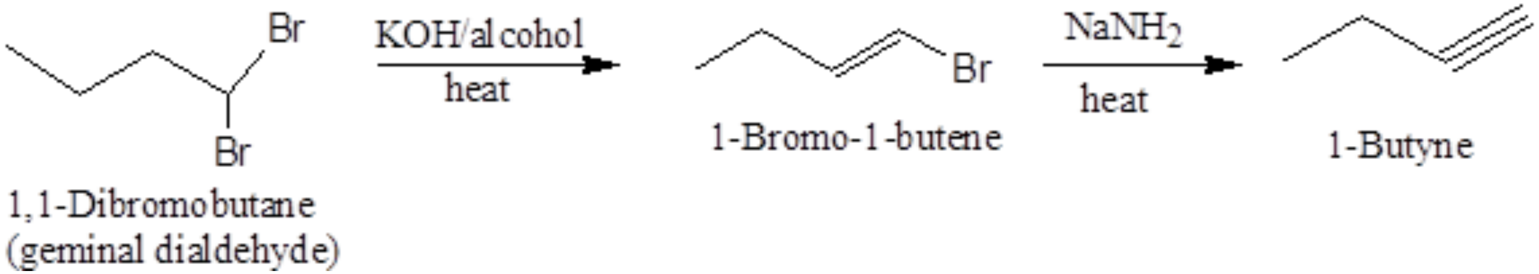


PREPARATION OF ALKYNES

1) Dehydrohalogenation of Alkyl dihalides

- Treatment of vicinal dihalides with strong base followed by sodium amide.



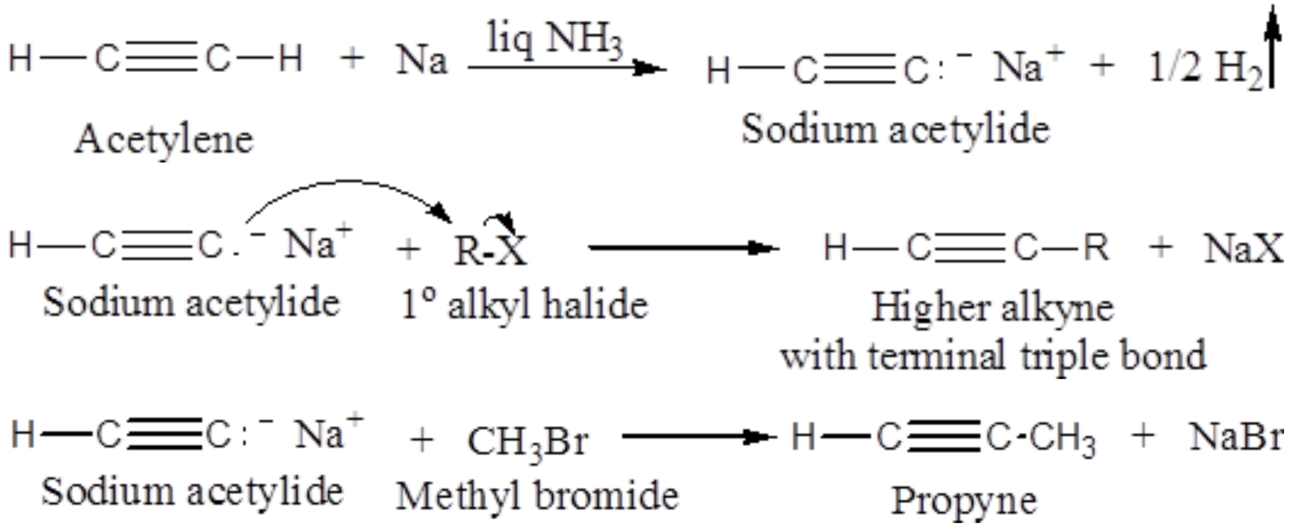


- This general method for the conversion of alkenes to alkynes.

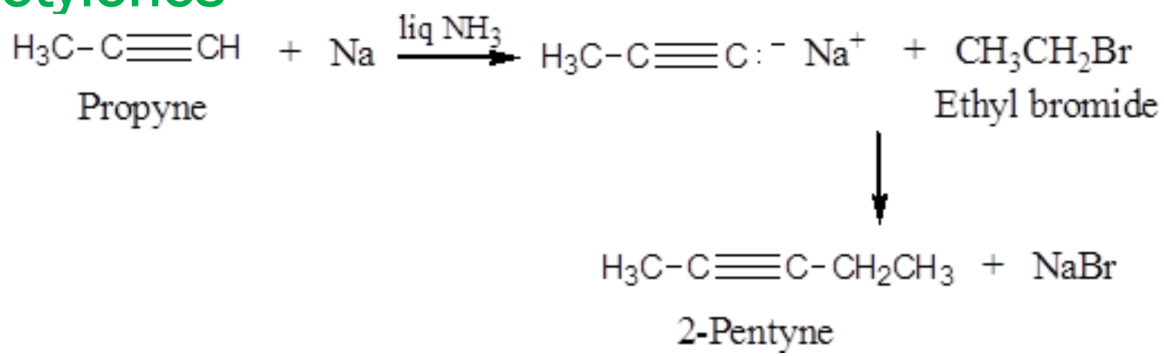
PREPARATION OF ALKYNES

2) Reaction of Sodium Acetylide with Primary Alkyl Halides

Acetylene



Monosubstituted Acetylenes



PREPARATION OF ALKYNES

3) From calcium carbide

- On industrial scale; ethyne (acetylene) is prepared by
  - Treating calcium carbide with water.
  - Calcium carbide is prepared by heating quick lime with coke.
  - Quick lime can be obtained by heating limestone.

$$\mathrm{CaCO_3} \xrightarrow{\Delta} \mathrm{CaO} + \mathrm{CO_2}$$

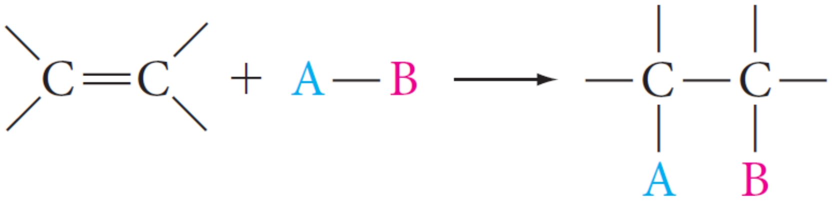
$$\mathrm{CaO} + 3\mathrm{C} \longrightarrow \underset{\text{Calcium carbide}}{\mathrm{CaC_2}} + \mathrm{CO}$$

$$\mathrm{CaC_2} + 2\mathrm{H_2O} \longrightarrow \mathrm{Ca(OH)_2} + \mathrm{C_2H_2}$$

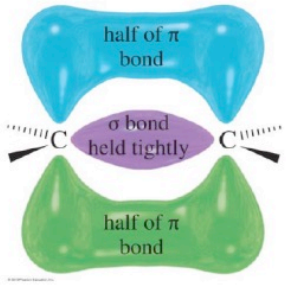
REACTIONS OF ALKENES

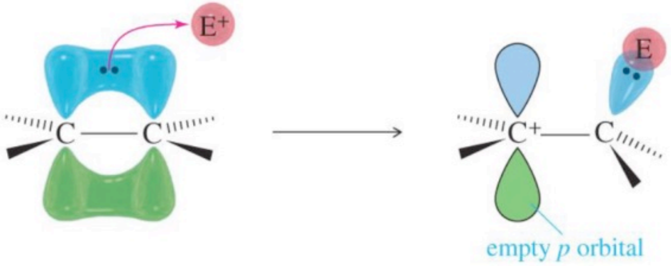
- The chemistry of alkenes can be divided into two general types of reactions:

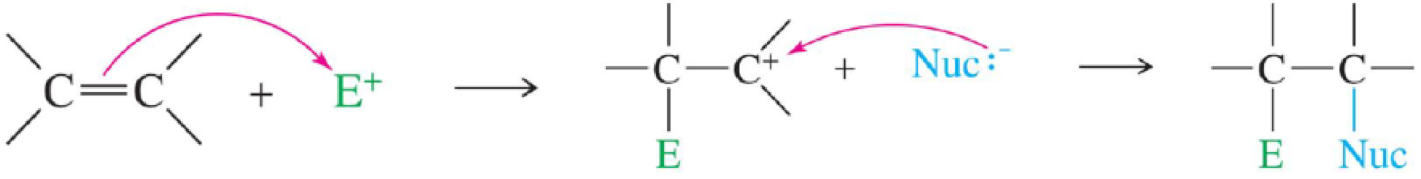
(1) Electrophilic Addition Reactions



- The π bond is localized above and below the C-C σ bond.
- The π electrons are relatively far away from the nuclei and are therefore loosely bound.







The double bond acts as a nucleophile (attacks the electrophile).

REACTIONS OF ALKENES

(1) Electrophilic Addition Reactions

Addition of Symmetric and Unsymmetric Reagents to Symmetric Alkenes.

1. Addition of Hydrogen: Catalytic Hydrogenation
2. Addition of Halogens: Halogenation

Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule.

1. Addition of Hydrogen Halides
2. Addition of Sulfuric Acid
3. Addition of Water: Hydration
4. Addition of HOX: Halohydrin Formation

(2) Oxidation Reactions

1. Ozonolysis
2. Oxidation Using $KMnO_4$

ELECTROPHILIC ADDITION REACTIONS

- Reagents and alkenes can be classified as either **symmetric** or **unsymmetric** with respect to addition reactions.
  - If a reagent and/or an alkene is symmetric, only one addition product is possible.
  - But if *both* the reagent *and* the alkene are *unsymmetric*, two products are possible.

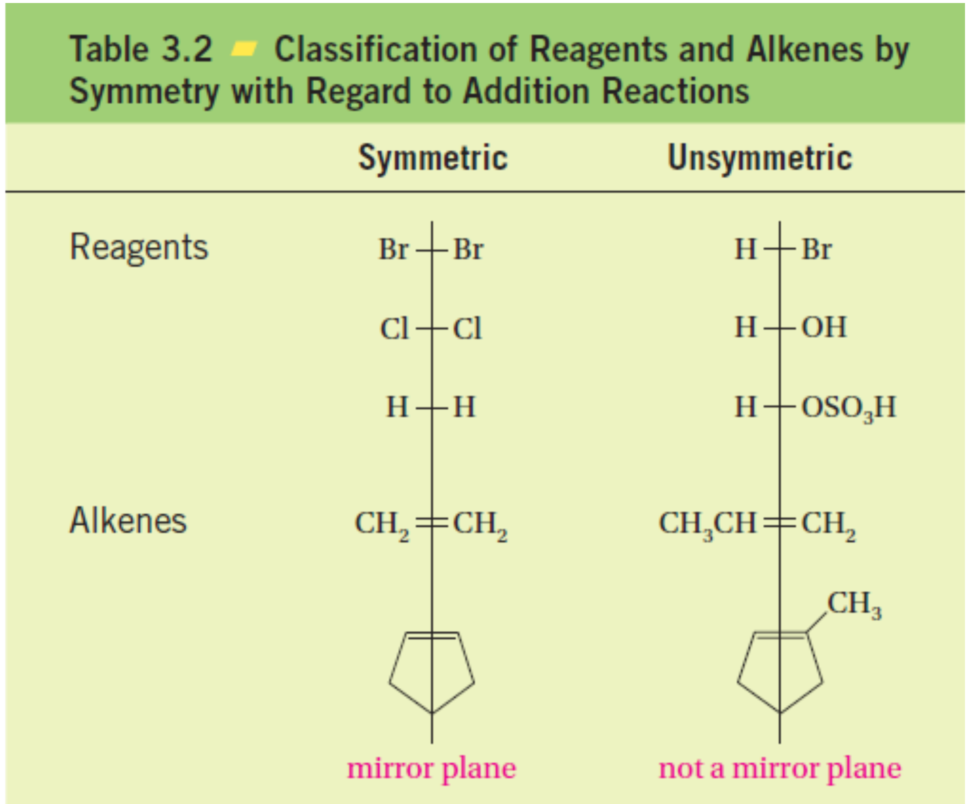
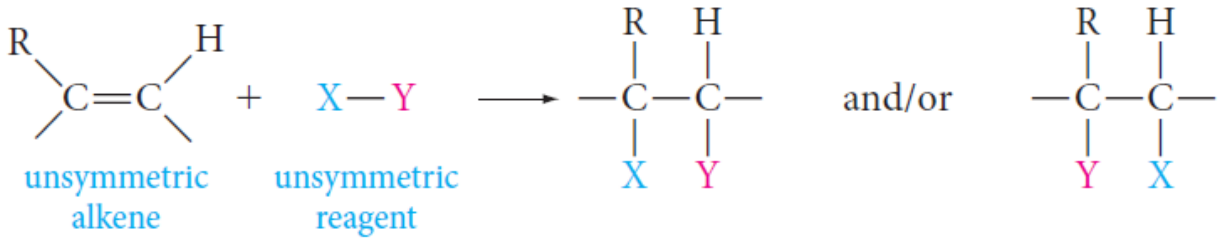


Table 3.2 Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

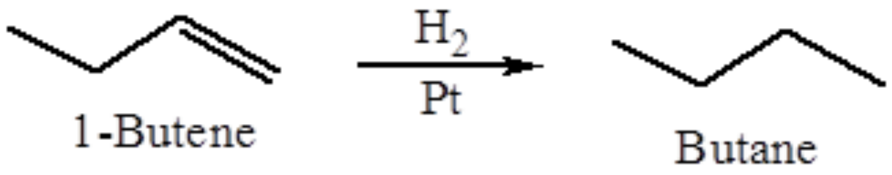
	Symmetric	Unsymmetric
Reagents	Br—Br	H—Br
	Cl—Cl	H—OH
	H—H	H—OSO_3H
Alkenes	$CH_2{=}CH_2$	$CH_3CH{=}CH_2$
		CH_3
	mirror plane	not a mirror plane

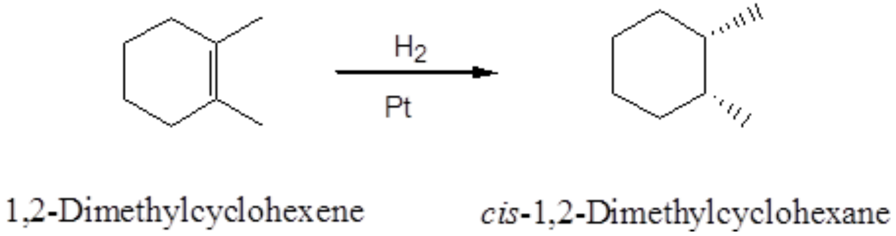


ELECTROPHILIC ADDITION REACTIONS

Addition of Hydrogen: Hydrogenation

Addition of a mole of hydrogen to carbon-carbon double bond of Alkenes in the presence of suitable catalysts to give an Alkane.

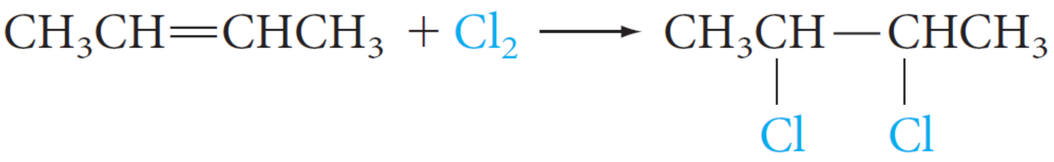




ELECTROPHILIC ADDITION REACTIONS

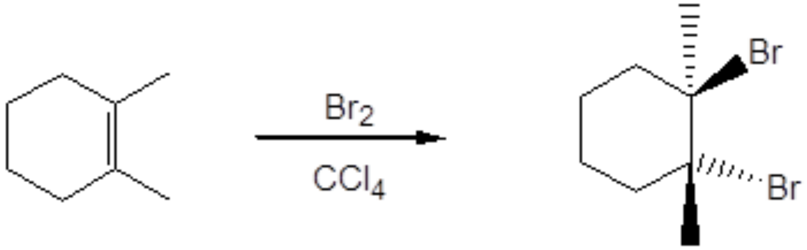
. Addition of Halogen: Halogenation

When an alkene is treated at room temperature with a solution of bromine or chlorine in carbon tetrachloride to give the corresponding vicinal dihalide (two halogens attached to adjacent carbons)



$$CH_3CH{=}CHCH_3 + Cl_2 \longrightarrow CH_3\underset{\displaystyle Cl}{\underset{|}{C}H}{-}\underset{\displaystyle Cl}{\underset{|}{C}H}CH_3$$

2-butene 2,3-dichlorobutane

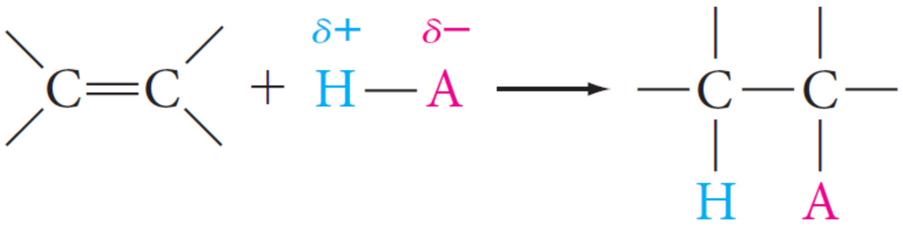


1,2-Dimethylcyclohexene *trans*-1,2-Dibromocyclohexane

ELECTROPHILIC ADDITION REACTIONS

3. Addition of Acids

- A variety of acids add to the double bond of alkenes.
  - *The hydrogen ion (or proton) adds to one carbon of the double bond, and the remainder of the acid becomes connected to the other carbon.*



$$>C{=}C< + \overset{\delta+}{H}-\overset{\delta-}{A} \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{A}{\overset{|}{\underset{|}{C}}}-$$

- Acids that add in this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I), sulfuric acid (H-OSO$_3$H) and water (H-OH).

Note that

- Any electron-deficient species is called an electrophile.

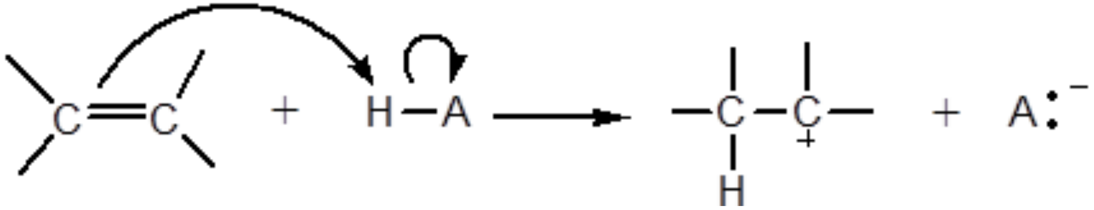
- Any electron-rich species is called a nucleophile.

ELECTROPHILIC ADDITION REACTIONS

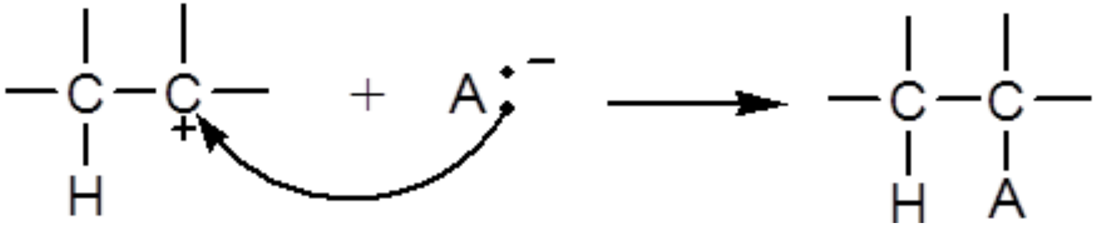
3. Addition of Acids

- The addition of H—A to an alkene is believed to be a **two-step process.**

Step 1. The hydrogen ion (the electrophile) attacks the π-electrons of the alkene, forming a C—H bond and a carbocation.



Step 2. The negatively charged species A: - (a nucleophile) attacks the carbocation and forms a new C—A bond.

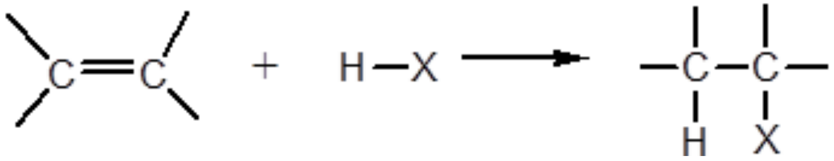


ELECTROPHILIC ADDITION REACTIONS

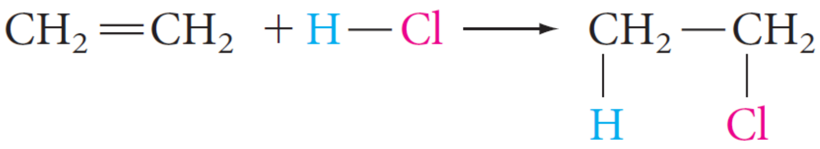
3.1. Addition of Hydrogen Halide

Alkenes react with hydrogen chloride, HC1, hydrogen bromide, HBr and hydrogen iodide, HI, to form alkyl halides, RX.

General equation



(X = Cl, Br or I)



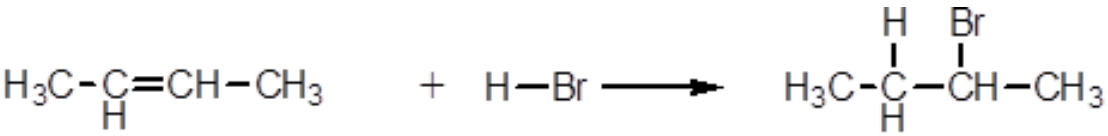
$$CH_2{=}CH_2 + H{-}Cl \longrightarrow \underset{H}{CH_2}{-}\underset{Cl}{CH_2}$$

(or CH_3CH_2Cl)

ethene

hydrogen chloride

chloroethane (ethyl chloride)



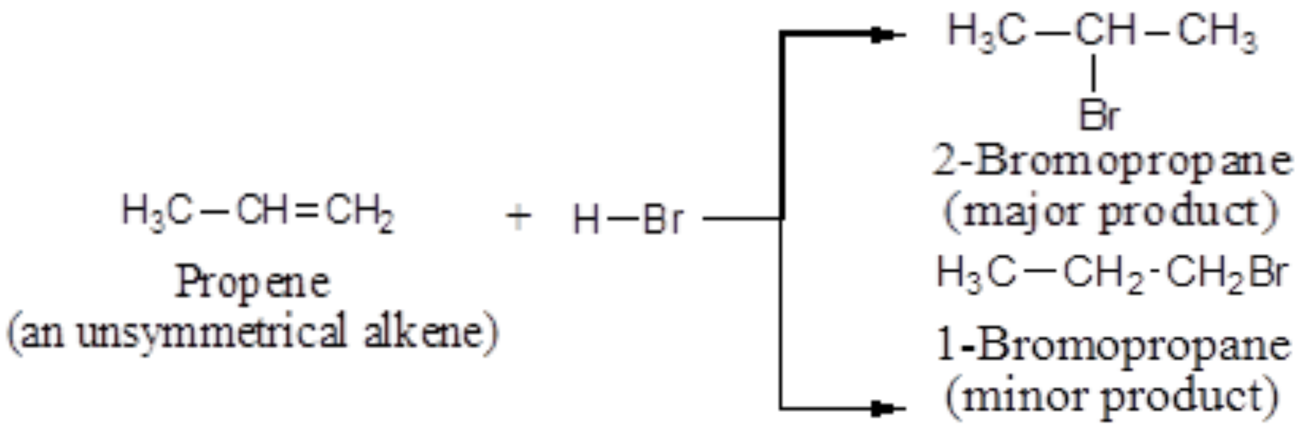
$$H_3C{-}\underset{H}{C}{=}CH{-}CH_3 + H{-}Br \longrightarrow H_3C{-}\overset{H}{\underset{H}{C}}{-}\overset{Br}{CH}{-}CH_3$$

2-Butene (a symmetrical alkene)

2-Bromobutane (only one product possible)

ELECTROPHILIC ADDITION REACTIONS

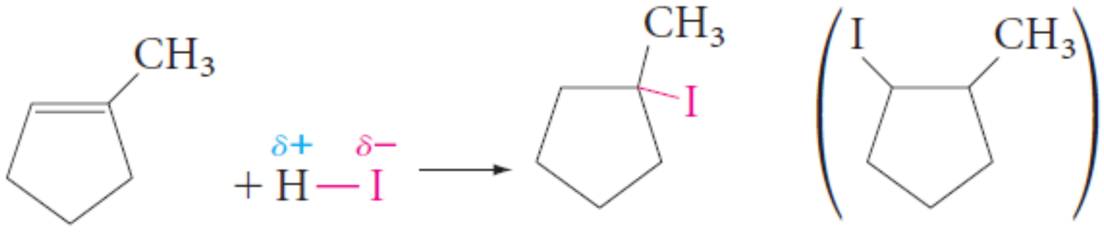
3.1. Addition of Hydrogen Halide



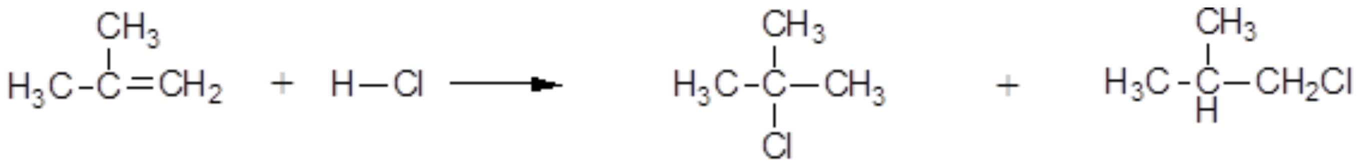
Markovnikov's Rule

In electrophilic addition of H—X *to Unsymmetrical Alkenes the hydrogen of the hydrogen halide adds to the double-bonded carbon that bears the greater number of hydrogen atoms and the negative halide ion adds to the other double-bonded carbon.*

ELECTROPHILIC ADDITION REACTIONS



not observed



$$H_3C-\overset{CH_3}{\overset{|}{C}}=CH_2 + H-Cl \longrightarrow H_3C-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 + H_3C-\underset{H}{\overset{CH_3}{\overset{|}{C}}}-CH_2Cl$$

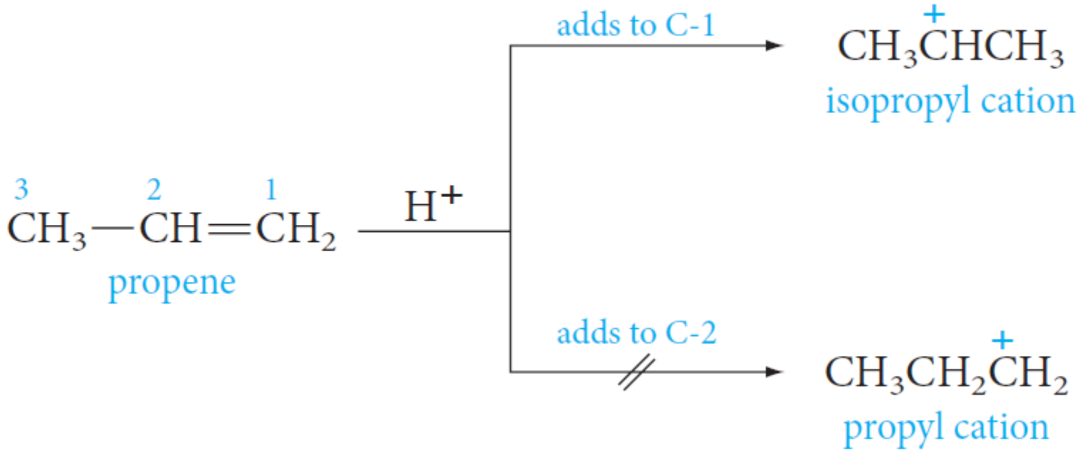
2-Chloro-2-methylpropane
(major product)

1-Chloro-2-methylpropane
(minor product)

ELECTROPHILIC ADDITION REACTIONS

Explanation for Markovnikov’s Rule

Example; the addition of HBr to propene



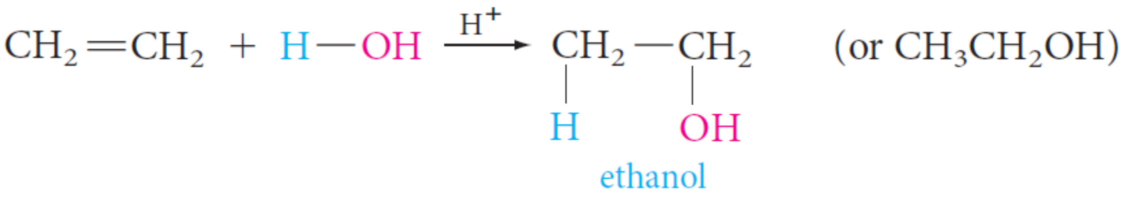
- **In modern terms Markovnikov’s rule can be restated:**

  The addition of an unsymmetrical reagent HX *to an unsymmetrical alkene proceeds in such a direction as to produce the more stable carbocation.*

ELECTROPHILIC ADDITION REACTIONS

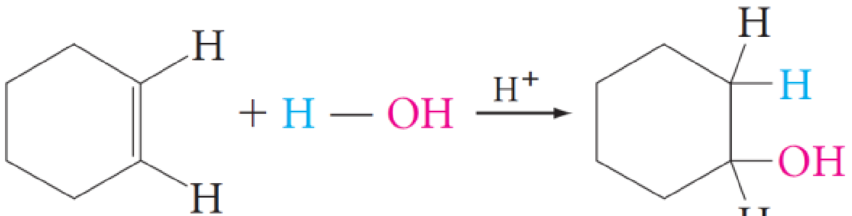
3.2. Addition of Water: Hydration

If an acid catalyst is present, water (as H-OH) adds to alkenes and the product is alcohol.



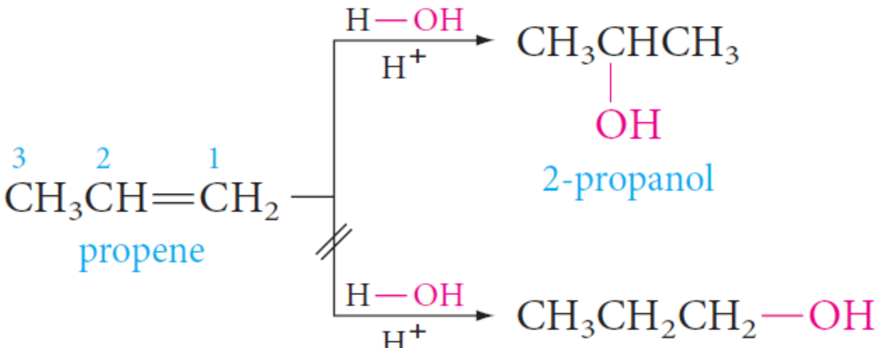
$$CH_2{=}CH_2 + H{-}OH \xrightarrow{H^+} \underset{H}{CH_2}-\underset{OH}{CH_2} \quad (\text{or } CH_3CH_2OH)$$

ethanol



cyclohexene
bp 83.0°C

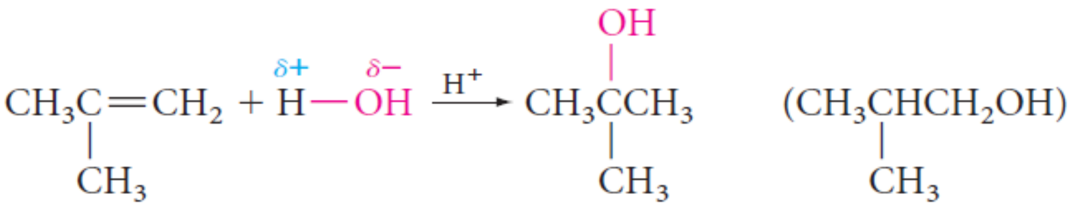
cyclohexanol
bp 161.1°C



propene

2-propanol

1-propanol



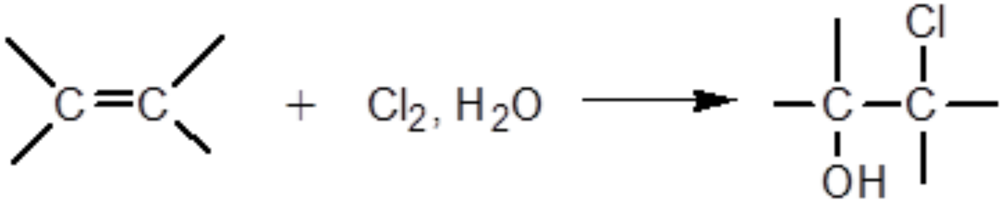
$$\underset{CH_3}{CH_3C}{=}CH_2 + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow{H^+} CH_3\overset{OH}{\underset{CH_3}{C}}CH_3 \qquad (CH_3\underset{CH_3}{CH}CH_2OH)$$

not observed

ELECTROPHILIC ADDITION REACTIONS

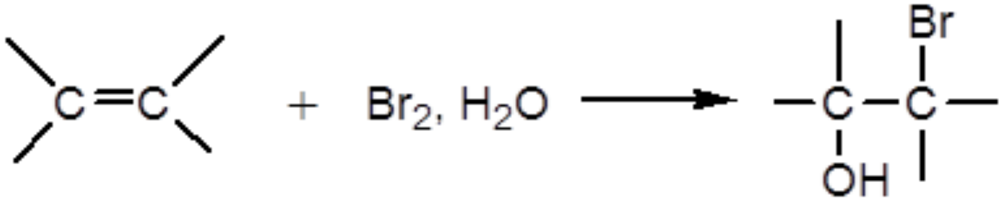
3.3. Addition of HOX: Halohydrin Formation

- When an alkene is treated with aqueous chlorine or aqueous bromine, the addition product is a halohydrin.
  - When Cl_2 is used, the product is a chlorohydrin.



A chlorohydrin

  - When Br_2 is used, the product is a bromohydrin.

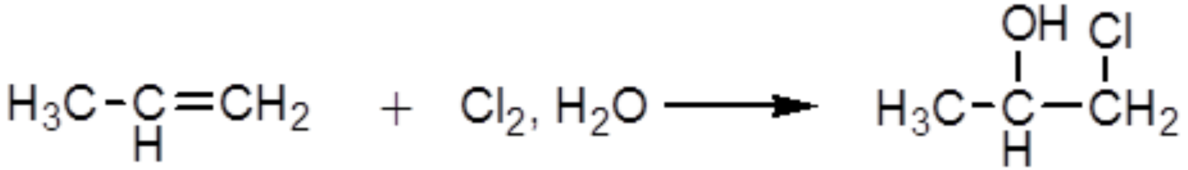


A bromohydrin

ELECTROPHILIC ADDITION REACTIONS

3.3. Addition of HOX: Halohydrin Formation

- The reaction proceeds as if hypochlorous acid, HO—Cl, or hypobromous acid, HO—Br, were the adding reagent.
  - The electrophile is chloronium ion, Cl^+, or bromonium ion, Br^+.
  - The nucleopbile is hydroxide ion, OH^-.
- Addition of HOX also follows Markovnikov's rule.



$$H_3C-\underset{H}{C}=CH_2 + Cl_2, H_2O \longrightarrow H_3C-\underset{H}{\overset{OH}{C}}-\overset{Cl}{C}H_2$$

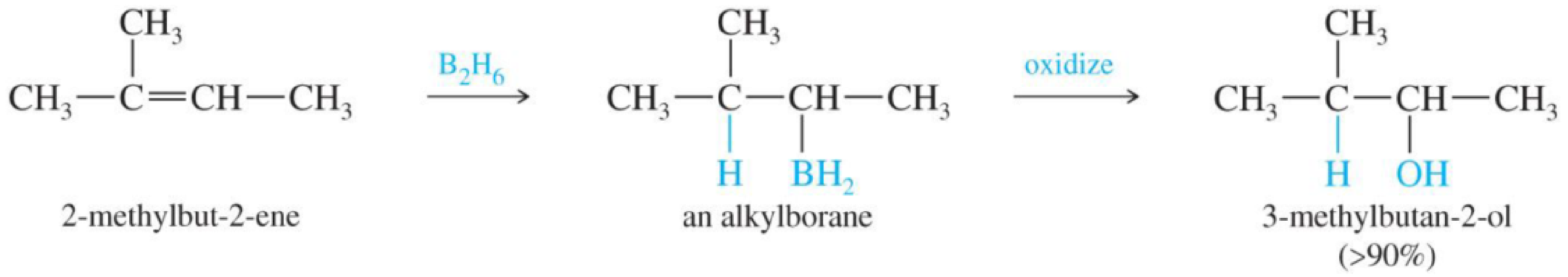
Propene

Propane chlorohydrin
(1-Chloro-2-propanol)

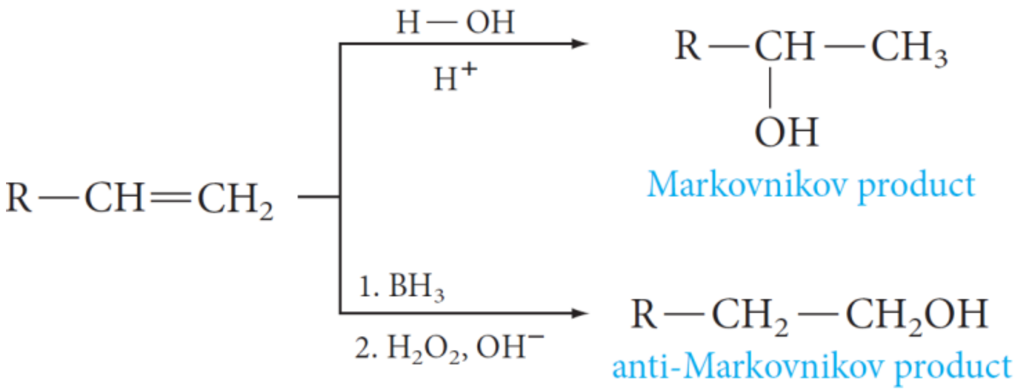
ELECTROPHILIC ADDITION REACTIONS

4. Hydroboration of Alkenes

- There is also a way to obtain anti-Markovnikov oriented alcohols: hydroboration.

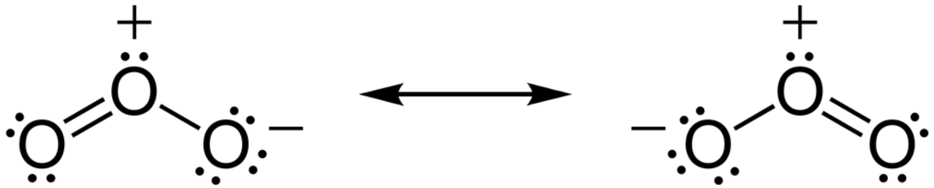


- One great advantage of this hydroboration-oxidation sequence is that it provides a route to alcohols that cannot be obtained by the acid-catalyzed hydration of alkenes.

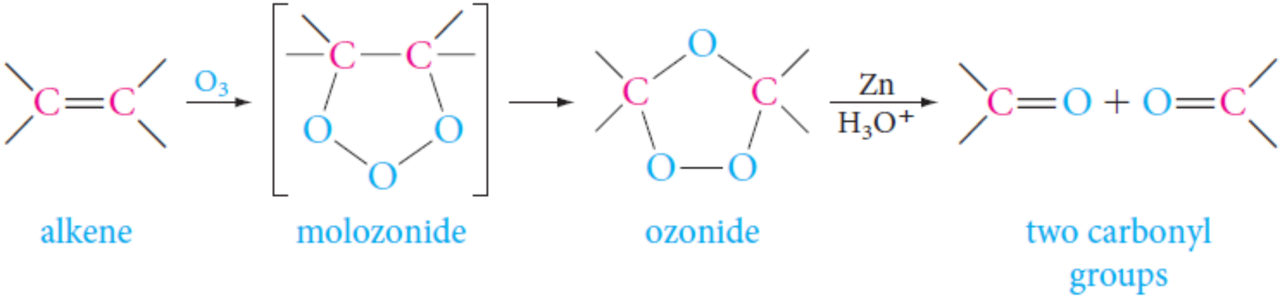


OXIDATION REACTIONS

1. Ozonolysis



- The first product, a **molozonide**, is formed by cycloaddition of the oxygen at each end of the ozone molecule to the carbon–carbon double bond.
- This product then rearranges rapidly to an **ozonide** (explosive if isolated).
- They are usually treated directly with a reducing agent, commonly zinc and aqueous acid, to give **carbonyl compounds** as the isolated products.



OXIDATION REACTIONS

1. Ozonolysis

- Ozonolysis can be used to locate the position of a double bond.
- **For example**, ozonolysis of 1-butene gives two different aldehydes, whereas 2-butene gives a single aldehyde.

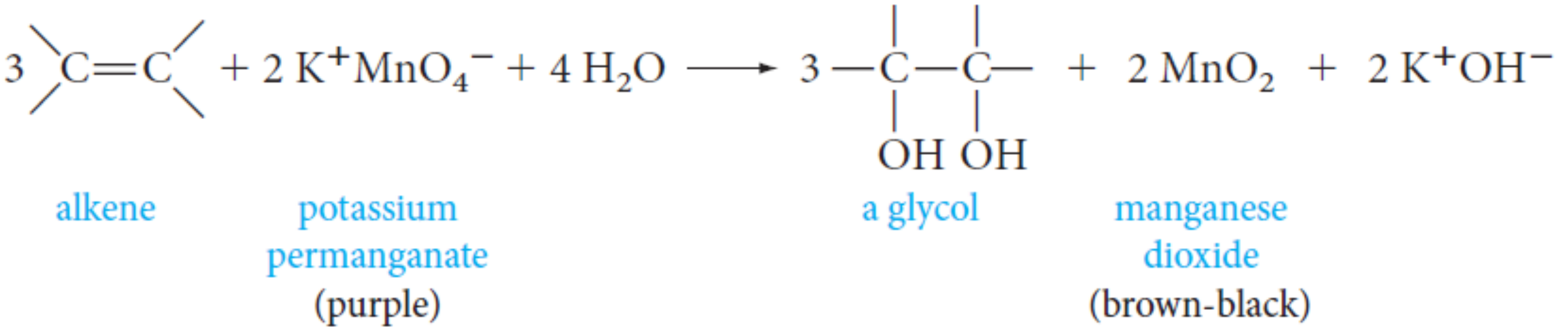
$$\underset{\text{1-butene}}{CH_2{=}CHCH_2CH_3} \xrightarrow[\text{2. Zn, } H^+]{\text{1. } O_3} \underset{\text{formaldehyde}}{CH_2{=}O} \quad \underset{\text{propanal}}{O{=}CHCH_2CH_3}$$

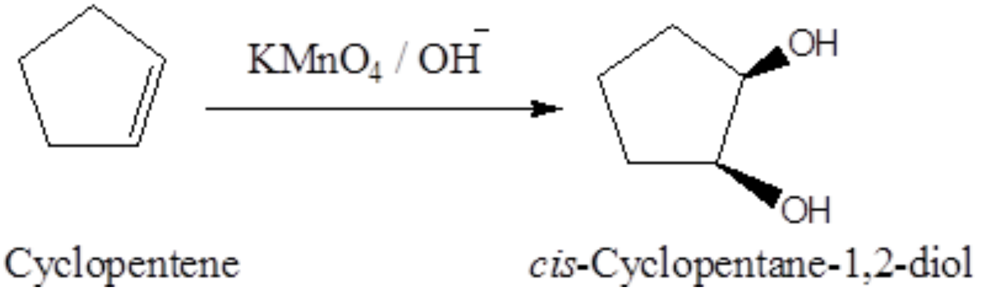
$$\underset{\text{2-butene}}{CH_3CH{=}CHCH_3} \xrightarrow[\text{2. Zn, } H^+]{\text{1. } O_3} \underset{\text{ethanal}}{2\ CH_3CH{=}O}$$

OXIDATION REACTIONS

2. Oxidation Using $KMnO_4$

Alkenes react with alkaline potassium permanganate to form **glycols** (compounds with two adjacent hydroxyl groups).





POLYMERIZATION

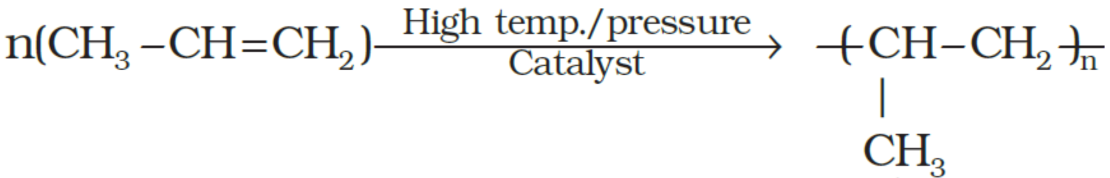
- The large molecules thus obtained are called polymers.
- This reaction is known as polymerization.
- The simple compounds from which polymers are made are called monomers.

- Examples:
  - Polyethene (polyethylene) and polypropene (polypropylene).
    They can be obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst.

$$n(CH_2{=}CH_2)\xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} -\!\!\left(CH_2-CH_2\right)\!\!-_n$$

Polythene

(13.53)



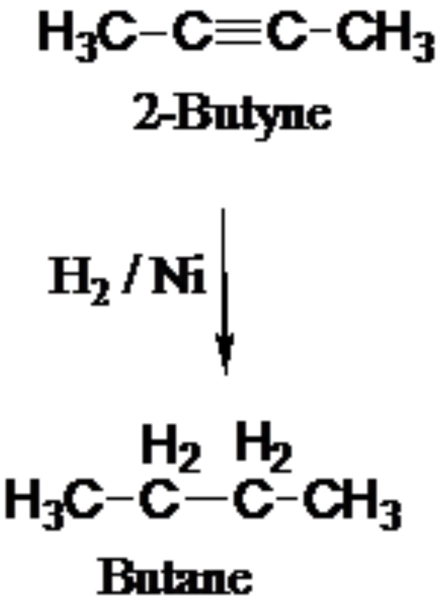
$$n(CH_3-CH{=}CH_2)\xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} -\!\!\left(\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2\right)\!\!-_n$$

Polypropene

ELECTROPHILIC ADDITION REACTIONS OF ALKYNES

1. Addition of Hydrogen: Hydrogenation

- Two hydrogen atoms are added across the double bond of an alkene, resulting in a saturated alkane.

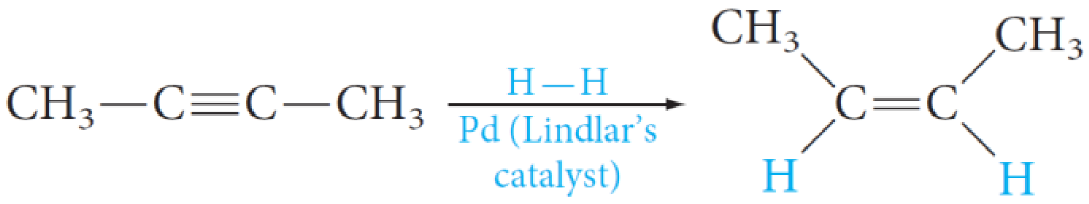


$$H_3C-C\equiv C-CH_3 \xrightarrow{H_2\,/\,Ni} H_3C-\overset{H_2}{C}-\overset{H_2}{C}-CH_3$$

ELECTROPHILIC ADDITION REACTIONS OF ALKYNES

1. Addition of Hydrogen: Hydrogenation

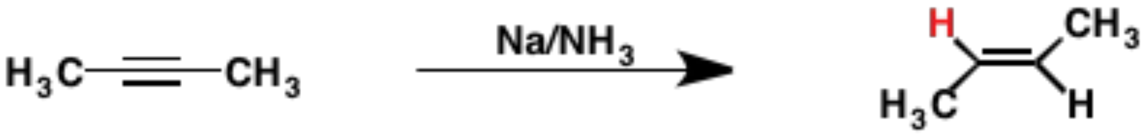
- However, a special palladium catalyst (**Lindlar's catalyst**) can control hydrogen addition so that only one mole of hydrogen adds (the product is *cis* alkene).



2-butyne
bp 27°C

cis-2-butene
bp 3.7°C

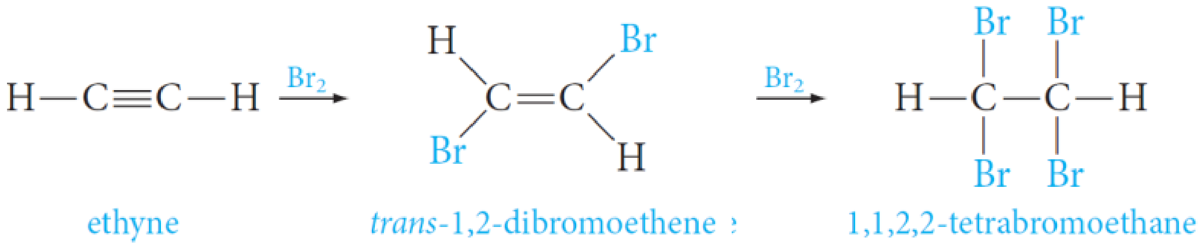
- Reduction of alkynes to *trans* alkenes using Na/NH_3.



ELECTROPHILIC ADDITION REACTIONS OF ALKYNES

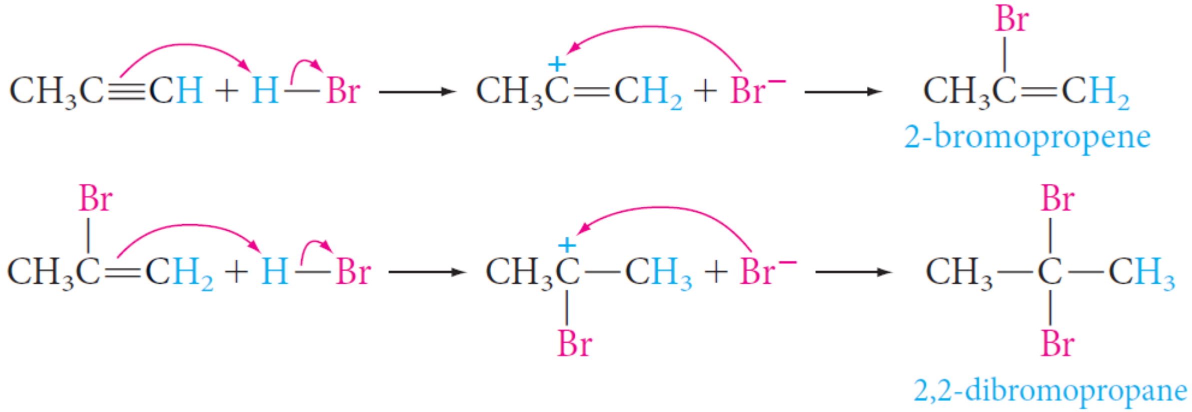
2. Addition of Halogen: Halogenation

Bromine adds as follows; In the first step, the addition occurs mainly *trans*.



3. Addition of Hydrogen Halide

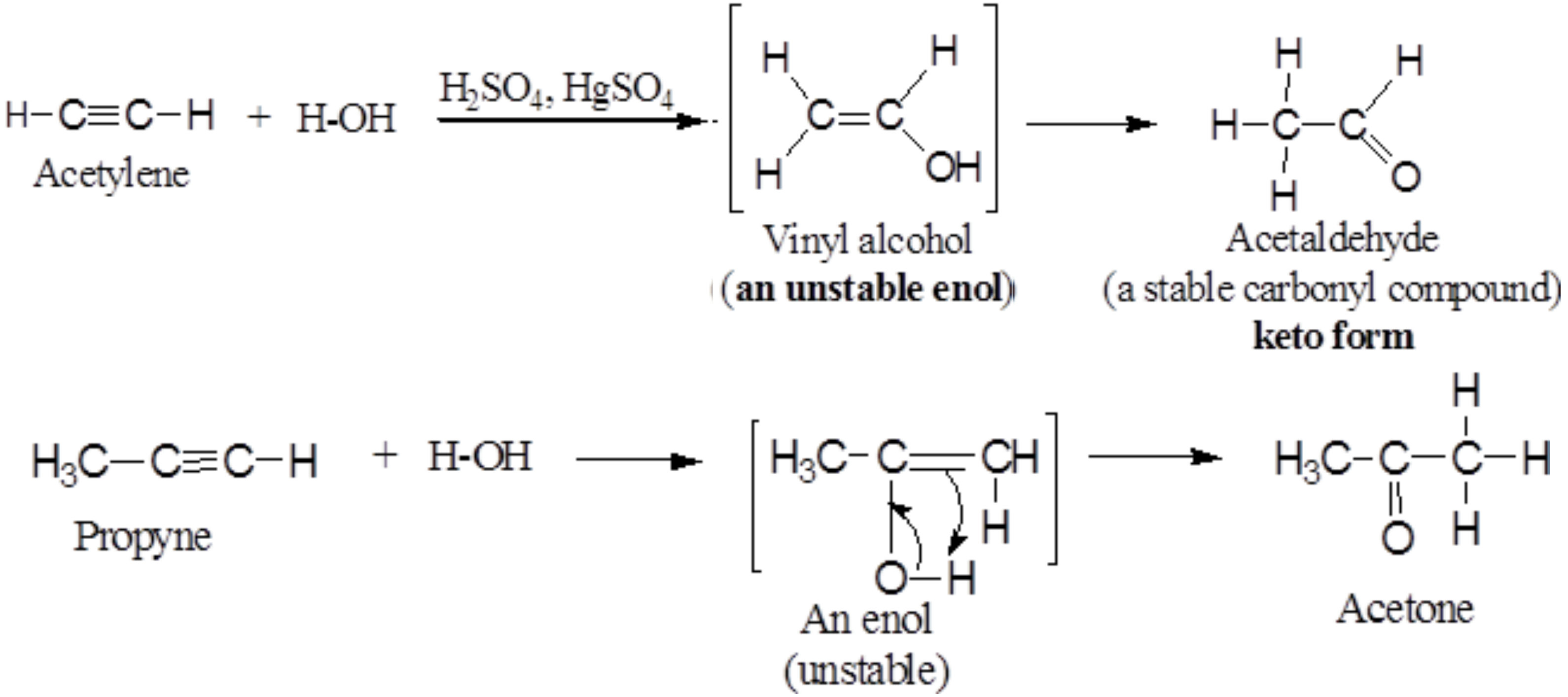
With unsymmetric triple bonds and unsymmetric reagents, Markovnikov's Rule is followed in each step.



ELECTROPHILIC ADDITION REACTIONS OF ALKYNES

4. Addition of Water: Hydration

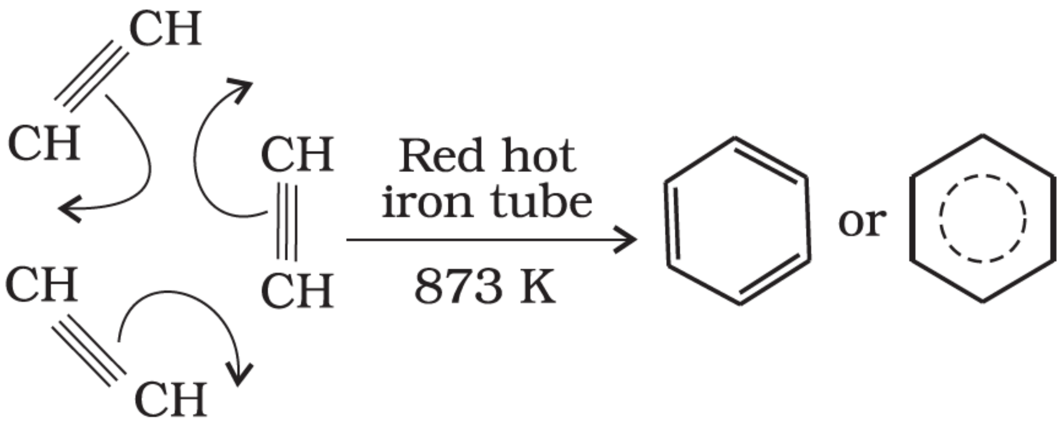
- Addition of water to alkynes requires not only an acid catalyst but mercuric ion as well.
- Although the reaction is similar to that of alkenes, the initial product—a vinyl alcohol or enol-rearranges to a carbonyl compound.



ELECTROPHILIC ADDITION REACTIONS OF ALKYNES

5. Cyclic Polymerization

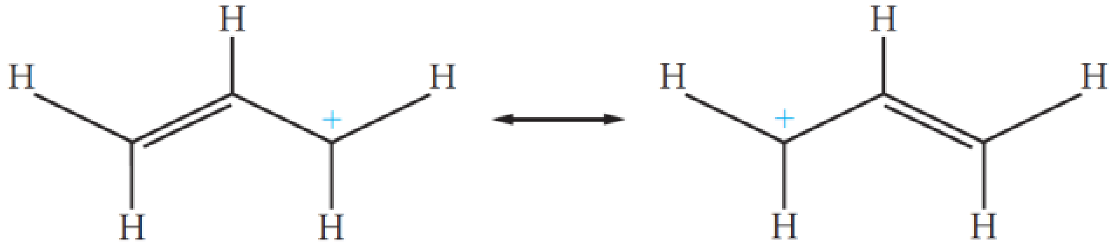
- Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization.
- Three molecules polymerize to form benzene, which is the starting molecule for the preparation of derivatives of benzene.
- This is the best route for entering from aliphatic to aromatic compounds.



ALLYLIC CATION

In an allylic cation, a carbon–carbon double bond is adjacent to the positively charged carbon atom.

- The carbocation intermediate in these reactions is a single species, a resonance hybrid.
- This type of carbocation, with a carbon–carbon double bond adjacent to the positive carbon, is called an allylic cation.
- The parent allyl cation, shown below as a resonance hybrid, is a primary carbocation, but it is more stable because its positive charge is delocalized over the two end carbon atoms.

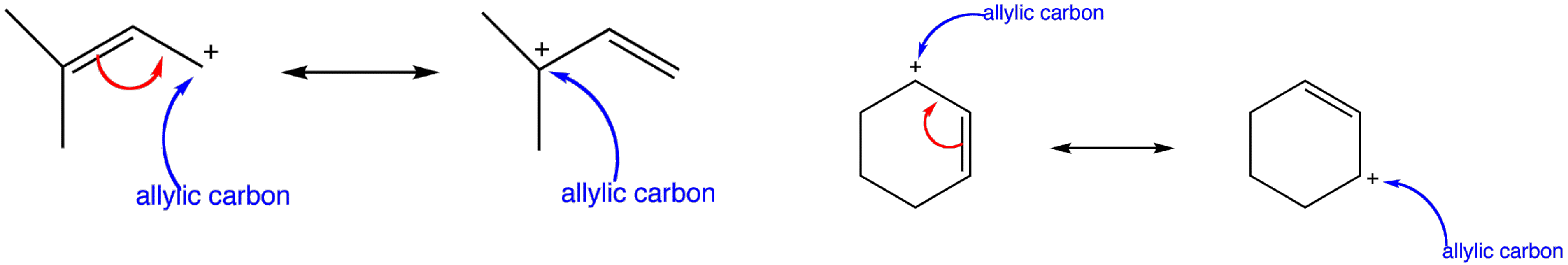


the allyl carbocation

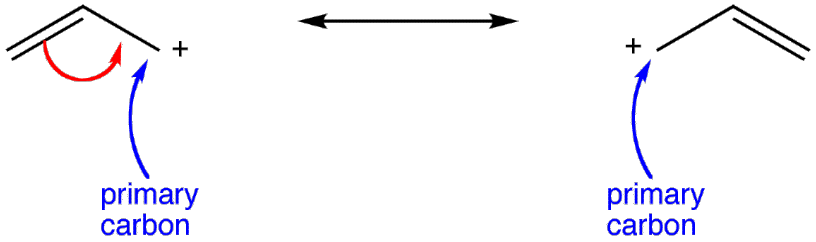
ALLYLIC CATION

Allylic Cation

An allylic cation is a resonance-stabilized carbocation in each of the two resonance forms of which the formal charge of +1 is on an allylic carbon.

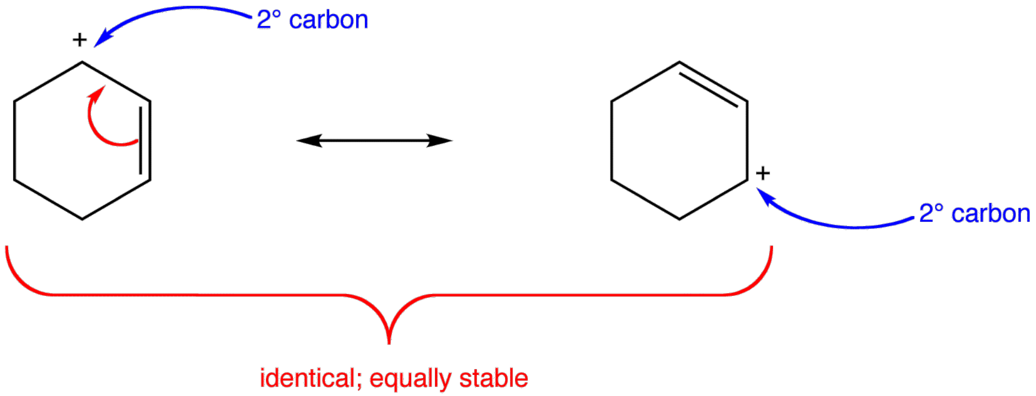


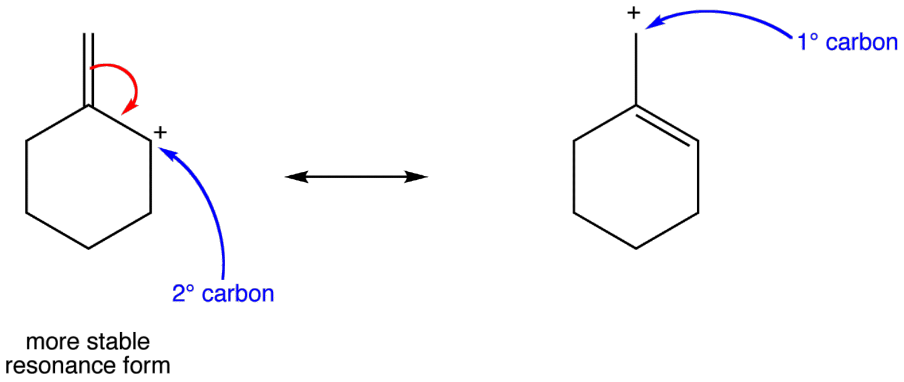
The lightest allylic carbocation (1) is called the allyl carbocation. (**Primary Allylic cation**).



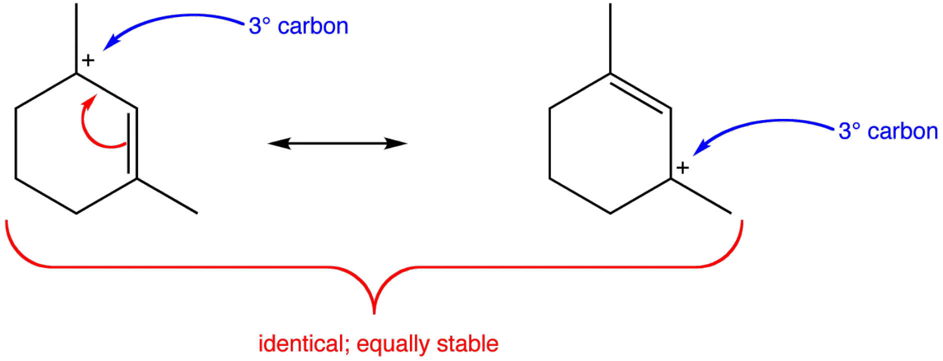
ALLYLIC CATION

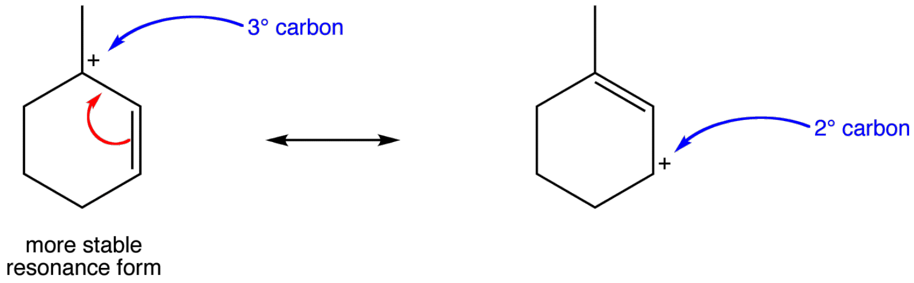
Secondary Allylic Cation





Tertiary Allylic Cation

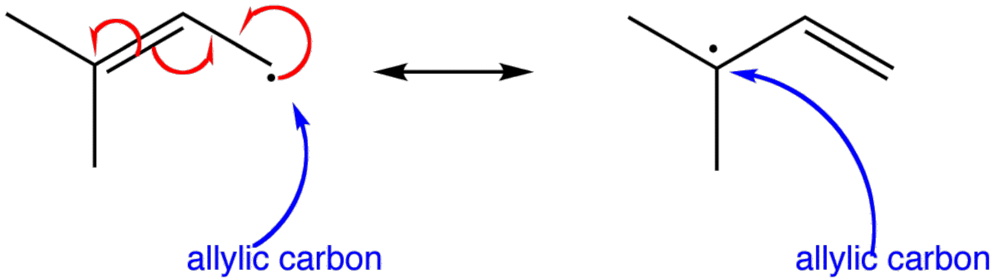




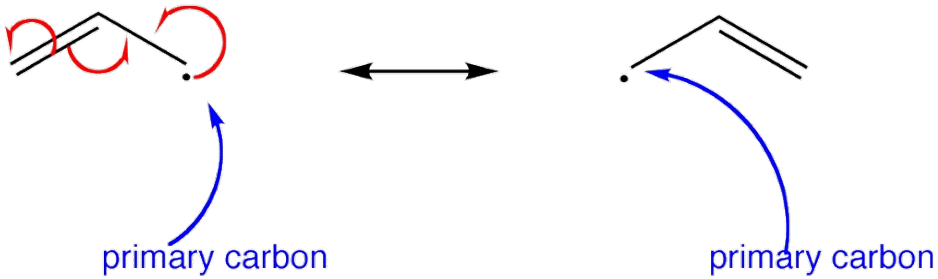
ALLYLIC RADICAL

Allylic Radical

An allylic radical is a resonance-stabilized radical in each of the two resonance forms of which the unpaired electron is on an allylic carbon.

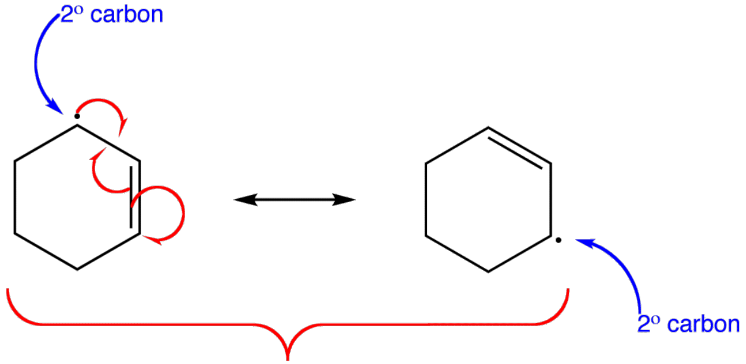


The lightest allylic radical **1** is called the allyl radical (Primary Allylic Radical).

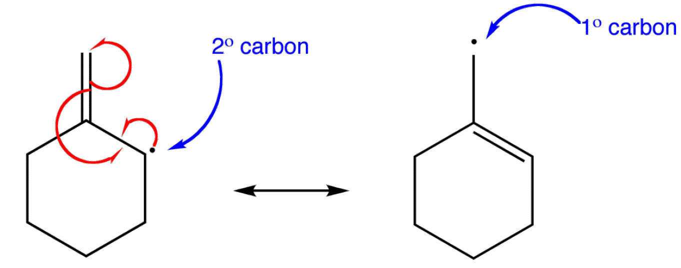


ALLYLIC RADICAL

Secondary Allylic Radical

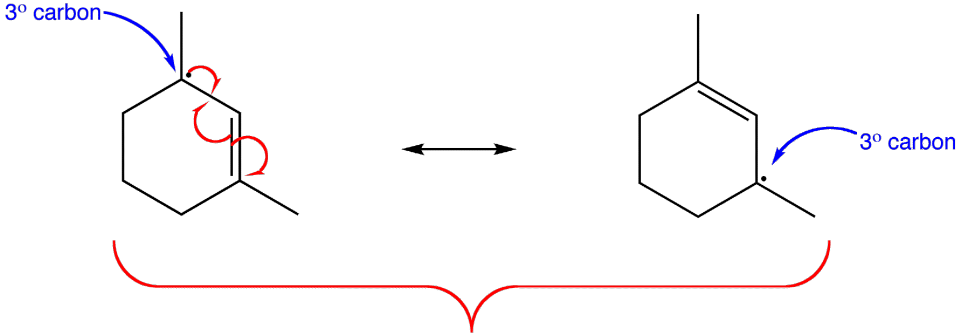


identical; equally stable

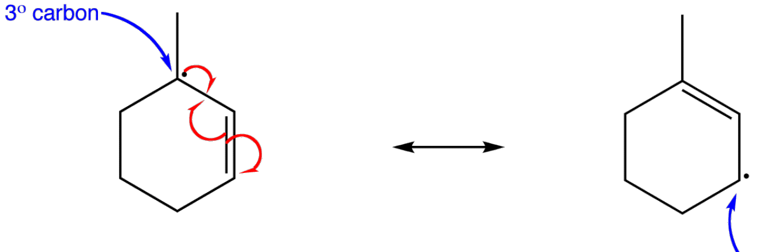


more stable
resonance form

Tertiary Allylic Radical



identical; equally stable



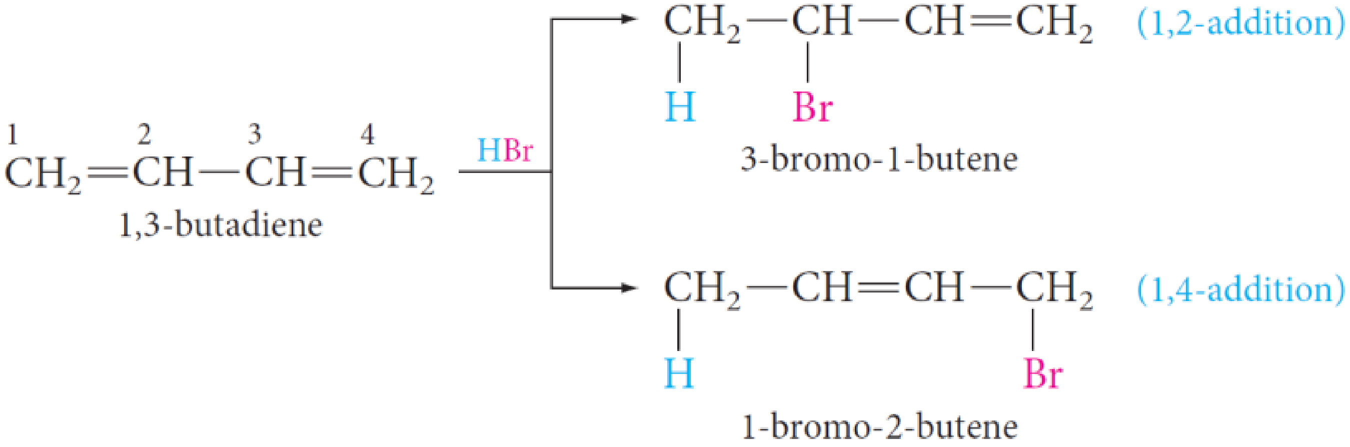
more stable
resonance form

CONJUGATED DIENES

ADDITIONS TO CONJUGATED SYSTEMS

1. Electrophilic Additions to Conjugated Dienes

- Alternate double and single bonds of conjugated systems have special consequences for their addition reactions.
- When 1 mole of HBr adds to 1 mole of 1,3-butadiene, a rather surprising result is obtained. Two products are isolated.



$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2 \xrightarrow{HBr}$$

1,3-butadiene

$$\underset{H}{CH_2}-\underset{Br}{CH}-CH=CH_2 \quad \text{(1,2-addition)}$$

3-bromo-1-butene

$$\underset{H}{CH_2}-CH=CH-\underset{Br}{CH_2} \quad \text{(1,4-addition)}$$

1-bromo-2-butene

ADDITIONS TO CONJUGATED SYSTEMS

1. Electrophilic Additions to Conjugated Dienes

- 1,2- Addition

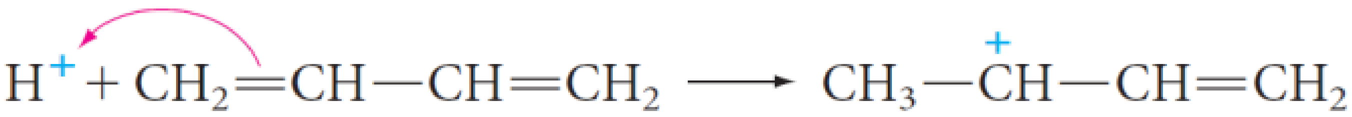
  In one of these products, HBr has added to one of the two double bonds, and the other double bond is still present in its original position.

- 1,4-Addition
  - The other product may at first seem unexpected.
  - The hydrogen and bromine have added to carbon-1 and carbon-4 of the original diene, and a new double bond has appeared between carbon-2 and carbon-3.

ADDITIONS TO CONJUGATED SYSTEMS

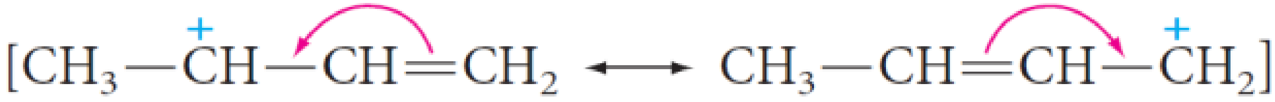
1. Electrophilic Additions to Conjugated Dienes

In the first step, the proton adds to the terminal carbon atom, according to Markovnikov's Rule.



$$H^{+} + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow CH_3{-}\overset{+}{C}H{-}CH{=}CH_2$$

- The resulting carbocation can be stabilized by resonance;
- The positive charge is delocalized over carbon-2 and carbon-4.

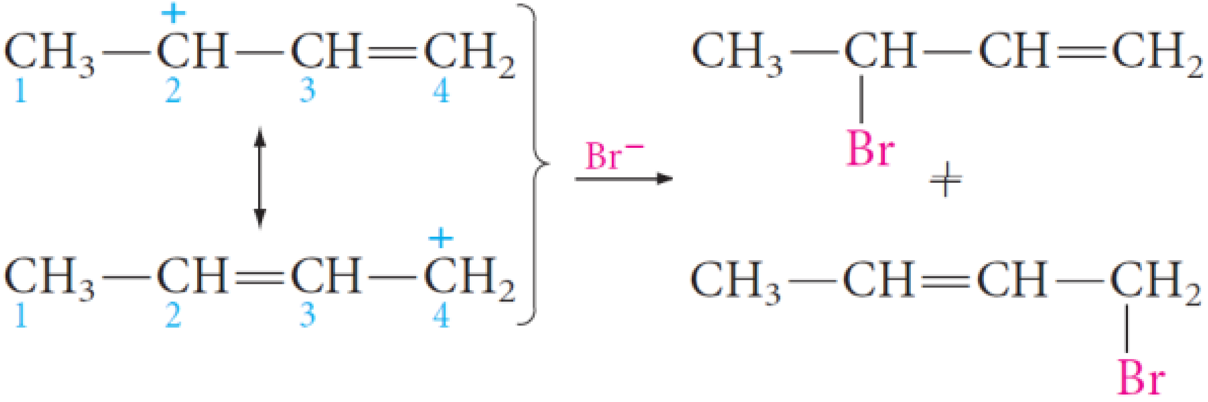


$$[CH_3{-}\overset{+}{C}H{-}CH{=}CH_2 \longleftrightarrow CH_3{-}CH{=}CH{-}\overset{+}{C}H_2]$$

ADDITIONS TO CONJUGATED SYSTEMS

1. Electrophilic Additions to Conjugated Dienes

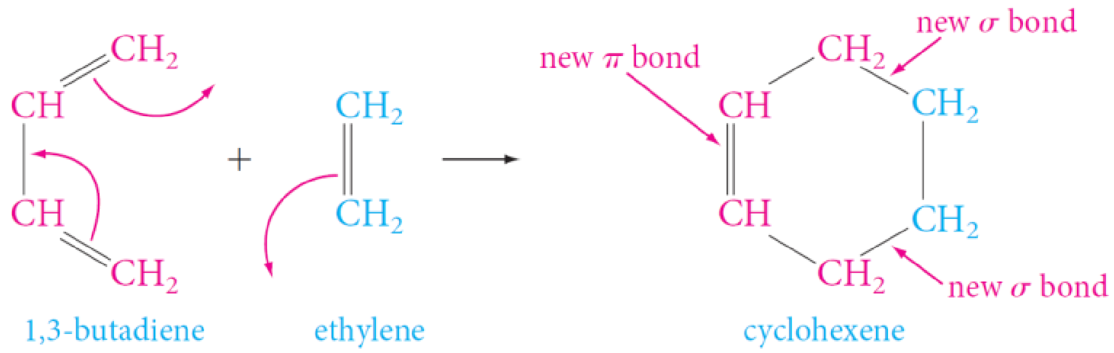
- In the next step, the carbocation reacts with bromide ion (the nucleophile);
    - it can react either at carbon-2 to give the product of **1,2-addition.**
    - or at carbon-4 to give the product of **1,4-addition.**



ADDITIONS TO CONJUGATED SYSTEMS

2. Cycloaddition to Conjugated Dienes: The Diels–Alder Reaction

- Conjugated dienes undergo another type of **1,4-addition** when they react with alkenes (or alkynes).
- **Example;** is the addition of ethylene to 1,3-butadiene to give cyclohexene.

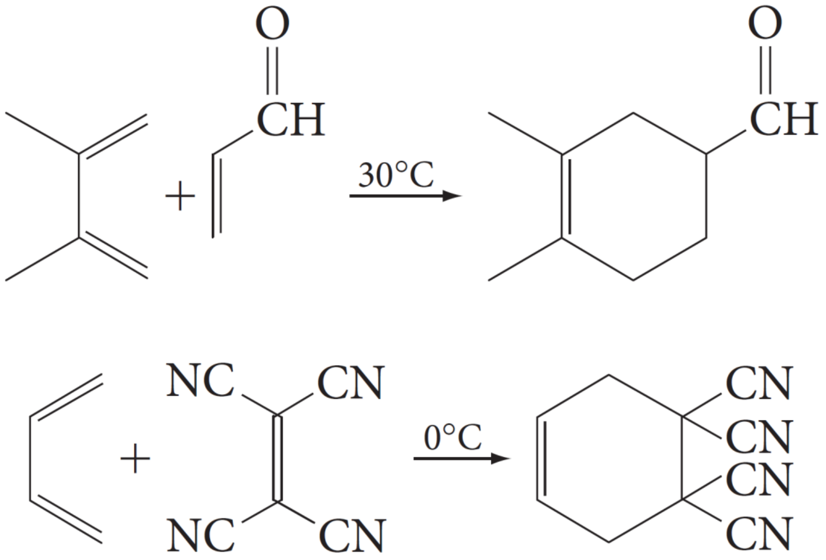


- A **cycloaddition reaction**, an addition that results in a cyclic product.
- The Diels–Alder reaction is the cycloaddition reaction of a conjugated diene and a dienophile to give a cyclic product in which three π bonds are converted to two σ bonds and a new π bond.
- All bond-breaking and bond-making occur at the same time.

ADDITIONS TO CONJUGATED SYSTEMS

2. Cycloaddition to Conjugated Dienes: The Diels–Alder Reaction

- The two reactants are a **diene** and a **dienophile** (diene lover).
- Diels–Alder Reaction gives excellent yields at moderate temperatures if the dienophile has *electron-withdrawing groups* attached.



Electron-withdrawing groups are groups of atoms that attract the electrons of the p bond, making the alkene electron poor and therefore more electrophilic toward the diene.