CHEM 240

Chapter 3

Unsaturated Hydrocarbons

Alkenes, alkynes and Dienes

Definition and Classification

- Alkene (Olefins) : C_nH_{2n} Crabon-Carbon double bond

- Cycloalkene : C_nH_{2n-2} Single ring with one or more double bond

- Alkynes (Acetylenes) : C_nH_{2n-2} Crabon-Carbon Trible bond

- Compounds with two double bonds are present, the compounds are called alkadienes or, more commonly, dienes. There are also trienes, tetraenes, and even polyenes .
- Depending on the relative positions of the multiple bonds, double bonds are said to be:

C=C=C	C=C—C=C	C=C—C—C=C
cumulated	conjugated	nonconjugated (isolated)

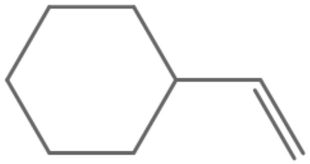
Nomenclature : Common Name

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

$CH_2{=}CH_2$	$HC{\equiv}CH$	$CH_3CH{=}CH_2$
ethylene	acetylene	propylene
(ethene)	(ethyne)	(propene)

- Two important groups also have common names. They are the vinyl and allyl groups, these groups are used in common names.

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

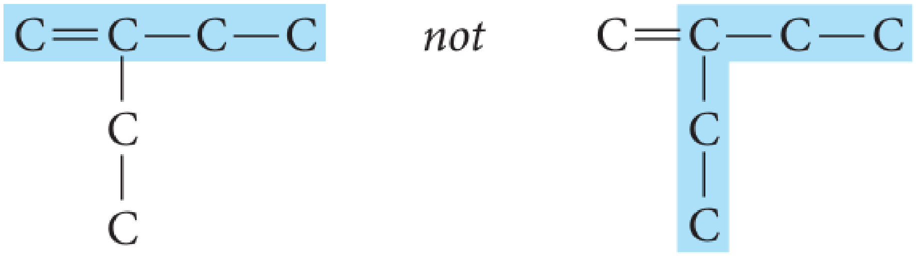
$CH_2{=}CHCl$	$CH_2{=}CH{-}CH_2Cl$	
vinyl chloride	allyl chloride	Vinylcyclohexane
(chloroethene)	(3-chloropropene)	

Nomenclature : IUPAC Name

- The IUPAC rules for naming alkenes and alkyne 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 designate a carbon–carbon double bond. When more than one double bond is present, the ending is *-diene*, *-triene*, and so on.
   - The ending *-yne* (rhymes with wine) is used for a triple bond (*-diyne* for two triple bonds and so on).
   - Compounds with a double and a triple bond are *-enynes*.

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

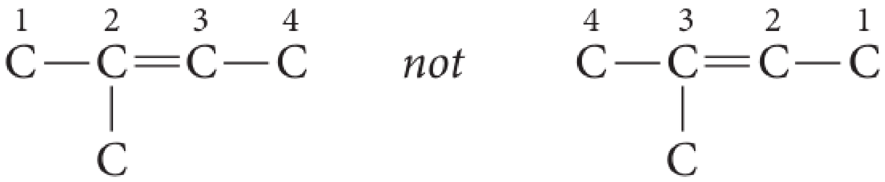


named as a butene, not as a pentene

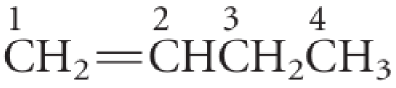
Nomenclature : IUPAC Name

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

If the multiple bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.



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



1-butene, *not* 2-butene

Nomenclature : IUPAC Name

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

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

If a double and a triple bond are equidistant from the end of the chain, the double bond receives the lowest numbers.

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

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

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

Nomenclature : IUPAC Name

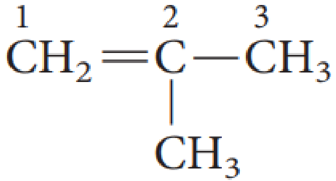
Examples

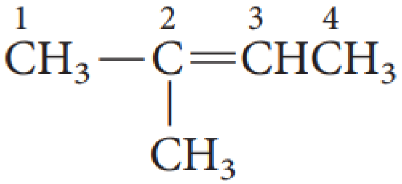
$\overset{1}{C}H_2{=}\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$
1-butene

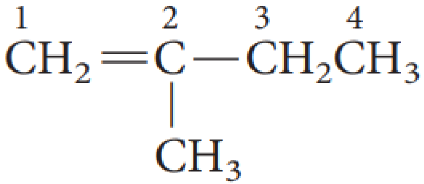
$\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_3$
2-butene

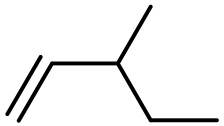
$H\overset{1}{C}{\equiv}\overset{2}{C}\overset{3}{C}H_2\overset{4}{C}H_3$
1-butyne

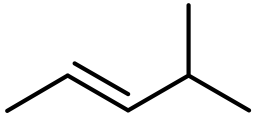
$\overset{1}{C}H_3\overset{2}{C}{\equiv}\overset{3}{C}\overset{4}{C}H_3$
2-butyne

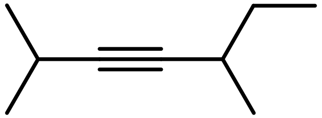

methylpropene
(isobutylene)

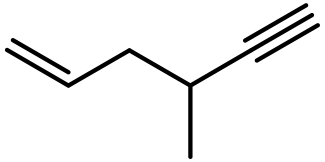

2-methyl-2-butene

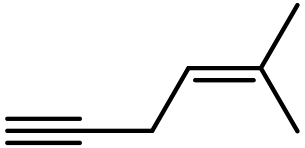

2-methyl-1-butene


2-ethyl-1-butene


4-methyl-2-pentene


2,5-dimethyl-3-heptyne

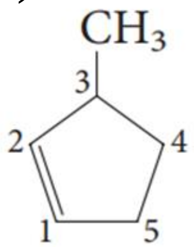

4-Methyl-1-hexen-5-yne


5-Methyl-4-hexen-1-yne

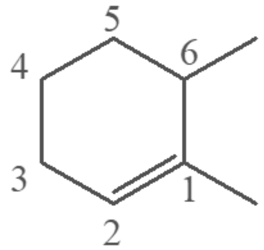
Nomenclature : Cycloalkenes

- In cycloalkenes, the double is always found between carbon 1 and carbon 2. It is therefore not necessary to specify the position of the double bond with a number.
- If substituents are present, the ring must numbered, starting from the double bond, in the direction that gives the substituents the lowest number(s).

cyclopentene

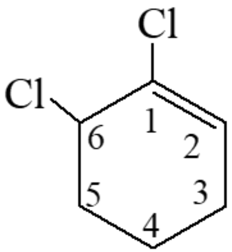


3-methylcyclopentene

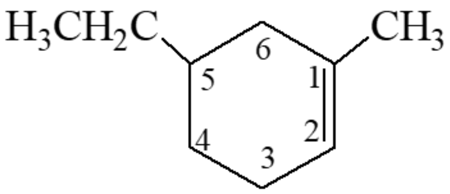


1,6-Dimethylcyclohexene

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



1,6-Dichlorocyclohexene
Not
2,3-Dichlorocyclohexene

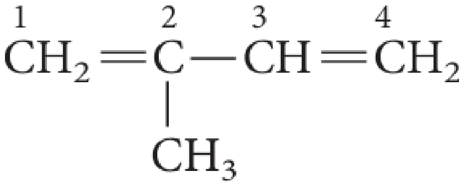


5-Ethyl-1-methylcyclohexene
Not
4-Ethyl-2-methylcyclohexene

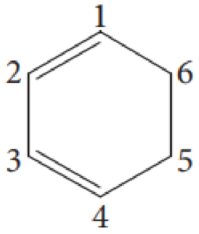
Nomenclature : Dienes

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

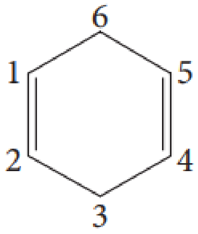
1,3-butadiene



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



1,3-cyclohexadiene



1,4-cyclohexadiene

Physical properties

Physical States

C_1-C_4	gases
C_5-C_{18}	liquids
More than C_{18}	solids

Solubilities

- Alkenes and alkynes are nonpolar compounds. Thus alkenes are soluble in the nonpolar solvents such as carbon tetrachloride (CCl_4) and benzene (C_6H_6), but they are insoluble in polar solvents such as 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.

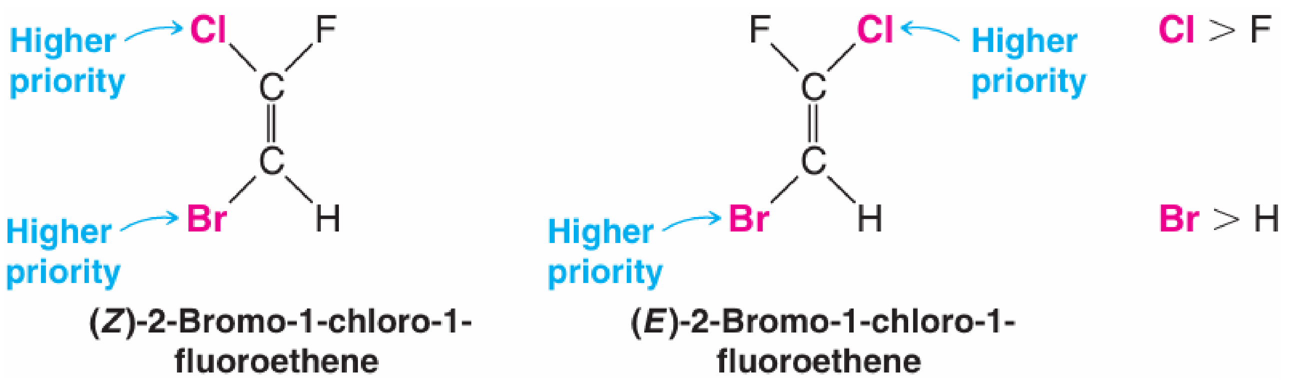
Geometric Isomerism in Alkene

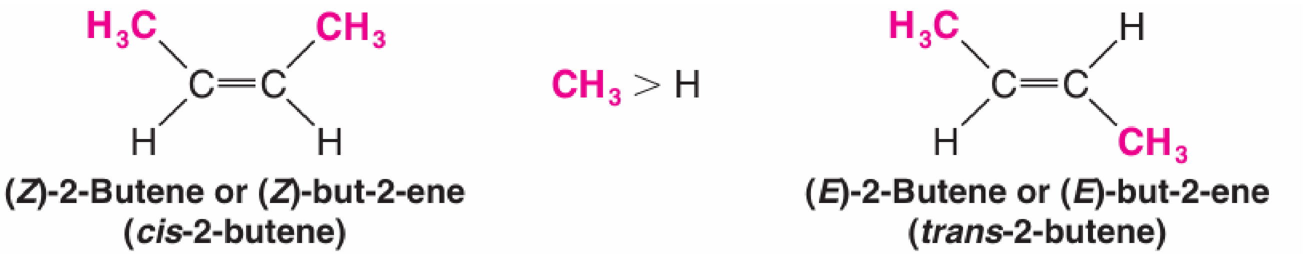
The (E)–(Z) System for Designating Alkene Diastereomers

- The terms cis and trans are ambiguous and not applicable for tri- and tetrasubstituted alkenes. The universal solution is the (*E*)-(*Z*) system, which uses the Cahn-Ingold-Prelog priority rules to designate alkene stereochemistry.
- In the (*E*)-(*Z*) system, we examine the two groups attached to one carbon atom of the double bond and decide which has higher priority. Then we repeat that operation at the other carbon atom.
- Compare it with the group of higher priority on the other carbon atom.
- If the two groups of higher priority are on the same side of the double bond, the alkene is designated (Z) (from the German word zusammen, meaning together).
- If the two groups of higher priority are on opposite sides of the double bond, the alkene is designated (E) (from the German word entgegen, meaning opposite).

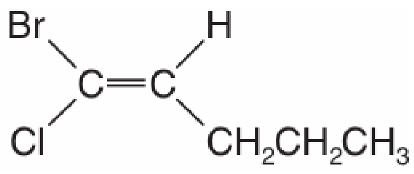
Geometric Isomerism in Alkene

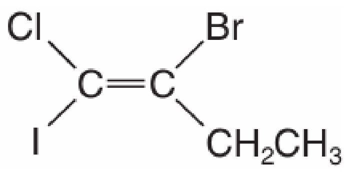
The (E)–(Z) System for Designating Alkene Diastereomers

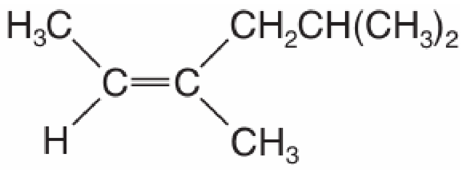


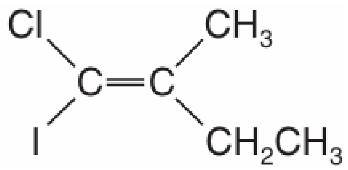


- Practice Problem: Using the (*E*)–(*Z*) designation for the following:

(a) 

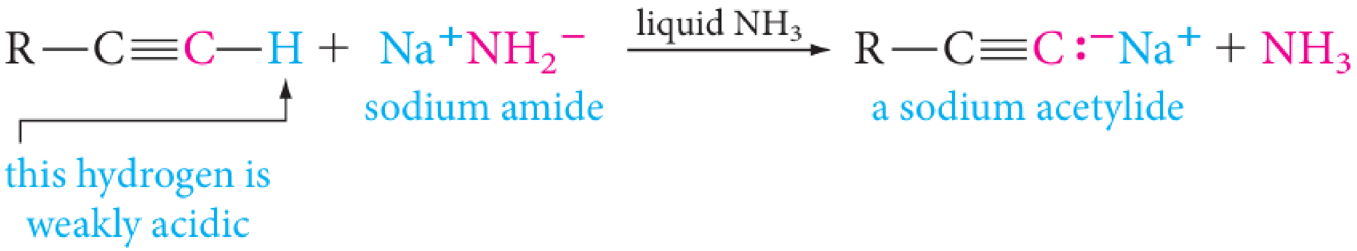
(b) 

(c) 

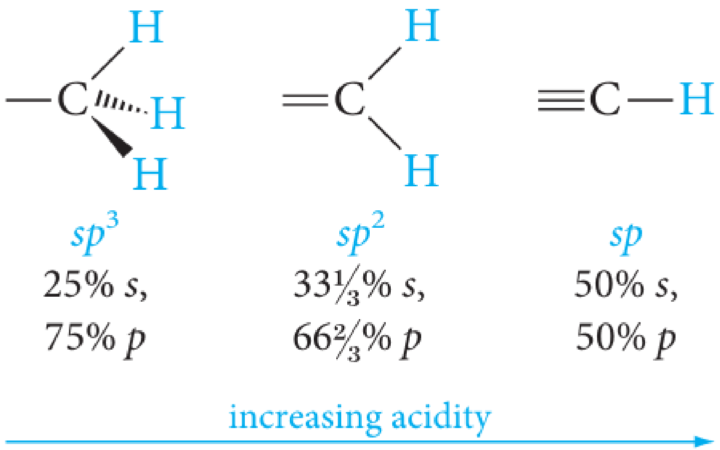
(d) 

Acidity of Terminal Alkynes

- The hydrogen bonded to the carbon of a terminal alkyne, called an acetylenic hydrogen atom, is considerably more acidic and can be removed by a very strong base. Sodium amide, for example, converts acetylenes to acetylides.



- This type of reaction occurs easily with a hydrogen attached to a carbon-carbon triple bond (i.e., RC≡C—H), but less so when the hydrogen is adjacent to a double or single bond because of the hybridization of the carbon atom in each type of C-H bond:

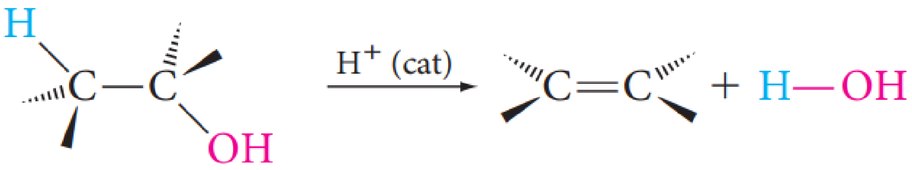


Preparation of alkenes

- Alkenes are prepared from alcohols and alkyl halides by Elimination Reactions.

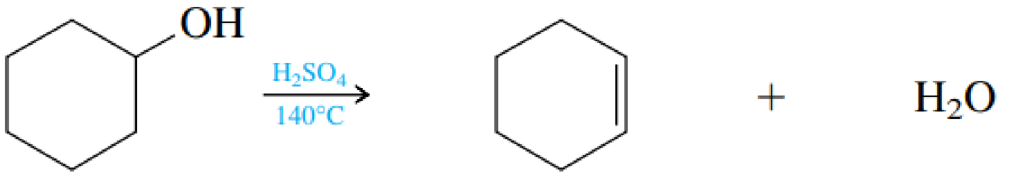
1- Dehydration of Alcohols

- Most alcohols undergo dehydration (lose a molecule of water) to form an alkene when heated with a strong acid.
- The acid catalysts most commonly used are sulfuric acid, H_2S0_4, and phosphoric acid, H_3P0_4 .
- It is an elimination reaction and can occur by either an E1 or an E2 mechanism, depending on the class of the alcohol.



$$CH_3CH_2OH \xrightarrow[160°C]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

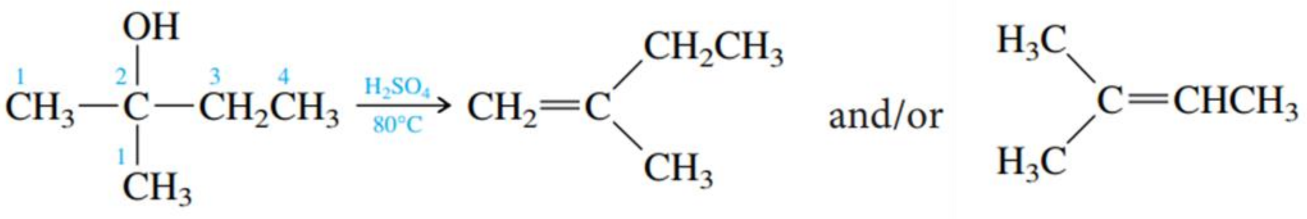
Ethyl alcohol — Ethylene — Water



Cyclohexanol — Cyclohexene (79–87%) — Water

Preparation of alkenes

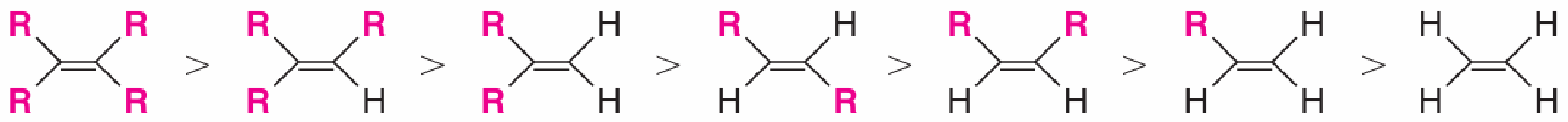
Regioselectivity in Dehydration of Alcohols: Zaitsev’s Rule



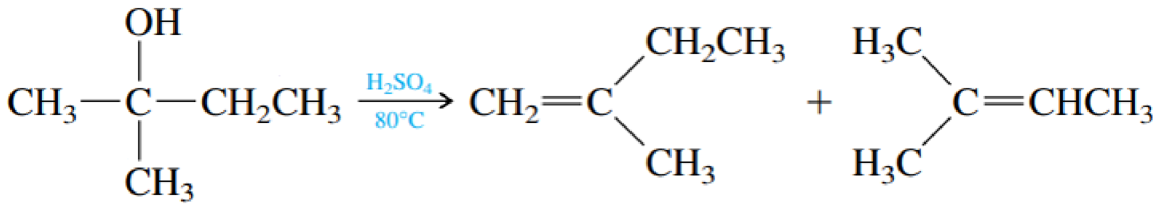
2-Methyl-2-butanol — 2-Methyl-1-butene — 2-Methyl-2-butene

Zaitsev’s Rule:

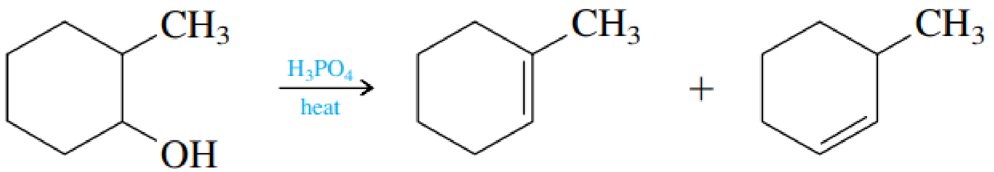
Hydrogen is preferably removed from the carbon with least no. of hydrogen since the alkene formed is more highly branched and is energetically more stable.



Tetrasubstituted — Trisubstituted — ⟵ Disubstituted ⟶ — Monosubstituted — Unsubstituted



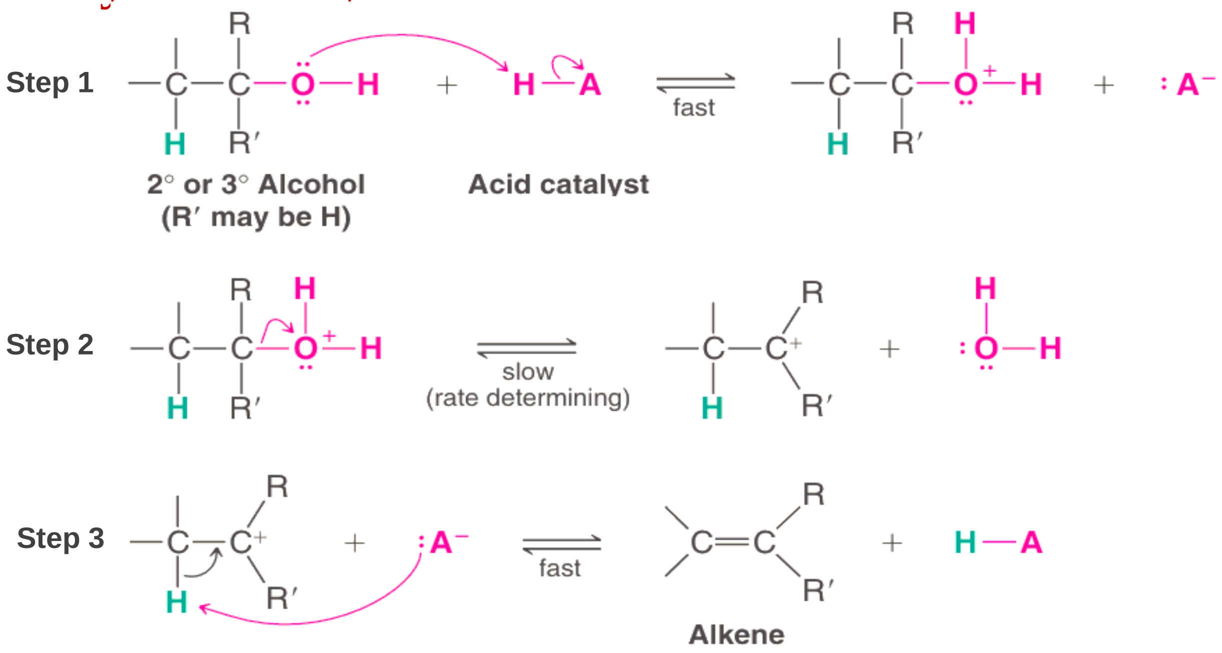
2-Methyl-2-butanol — 2-Methyl-1-butene (10%) — 2-Methyl-2-butene (90%) major



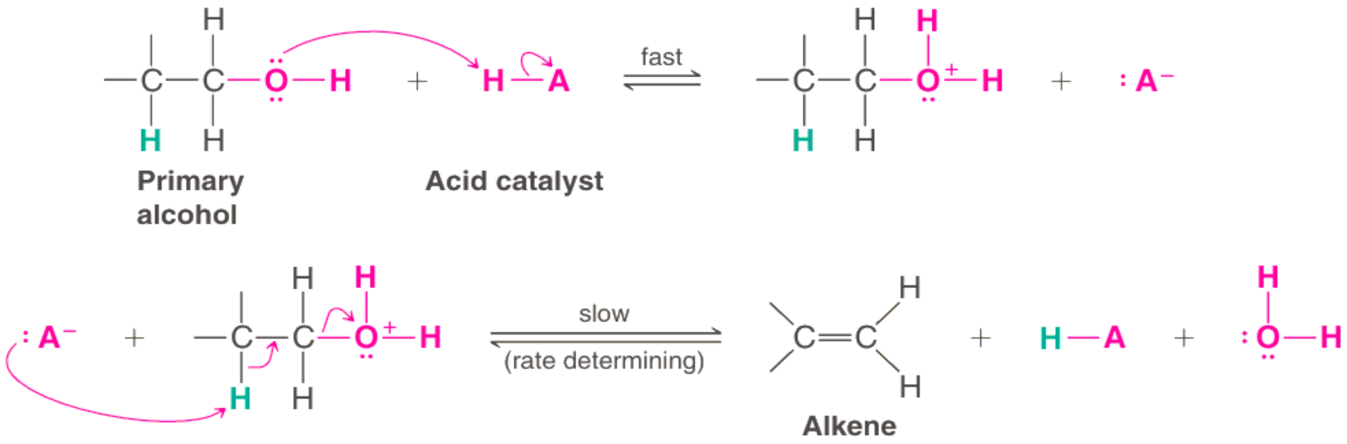
2-Methylcyclohexanol — 1-Methylcyclohexene (84%) major — 3-Methylcyclohexene (16%)

Preparation of alkenes

Dehydration of a Secondary or Tertiary Alcohol: An E1 Mechanism

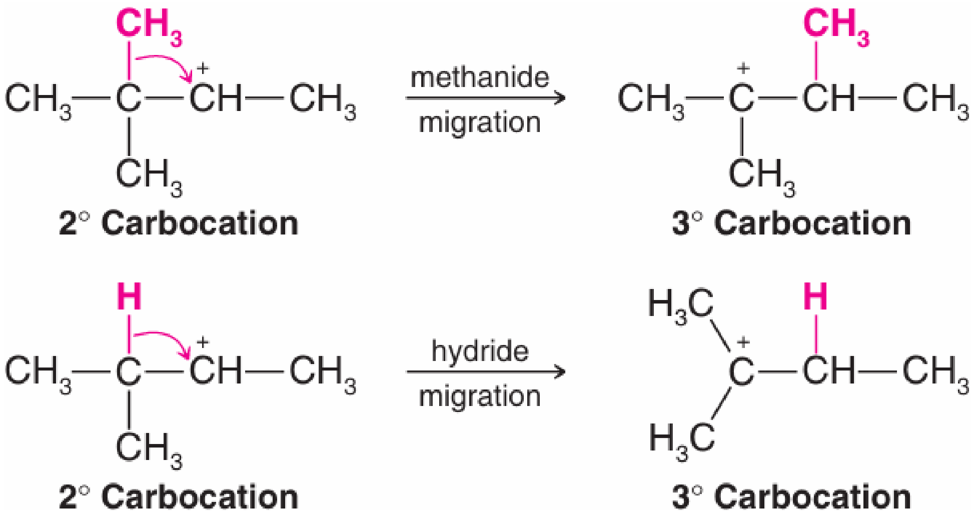


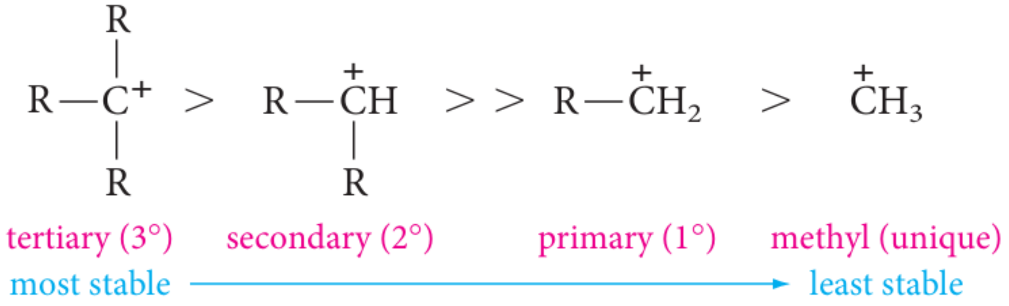
Dehydration of a Primary Alcohol: An E2 Mechanism

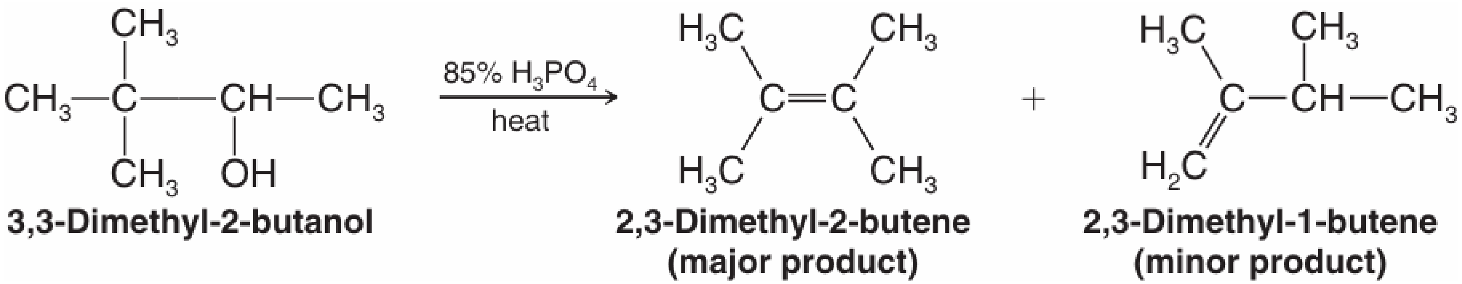


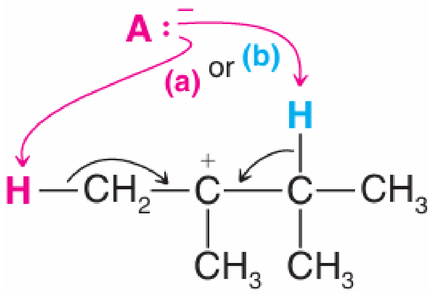
Preparation of alkenes

Rearrangement during Dehydration of Secondary Alcohols





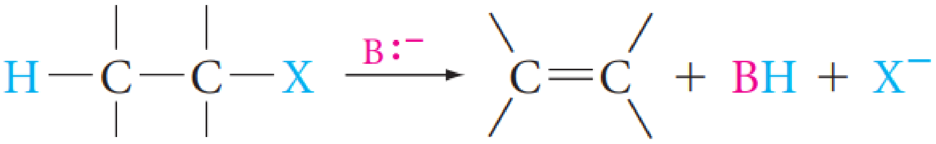


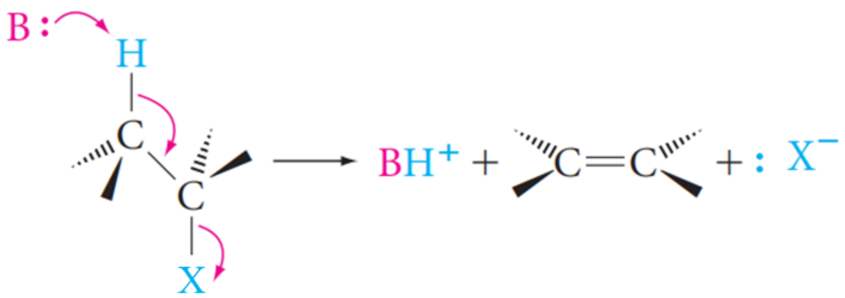


Preparation of alkenes

2- Dehydrohaloganation of Alkyl halides

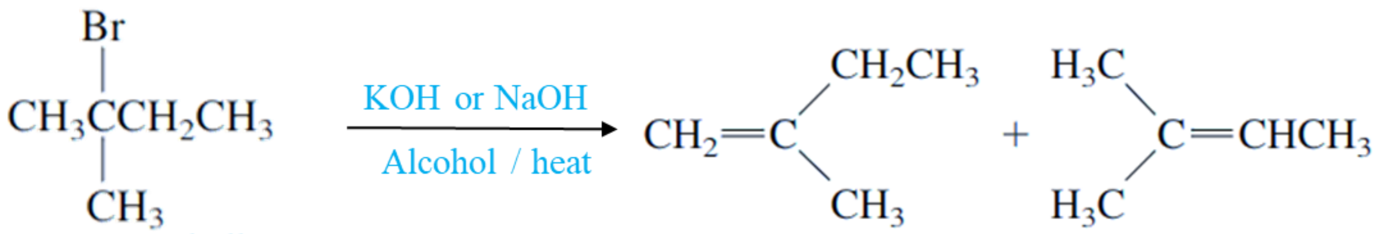
- Alkenes can be prepared by heating an alkyl halide with a solution of KOH or NaOH in alcohol.
- The best reaction conditions by dehydrohalogenation are those that promote an E2 mechanism.





E2: Bimolecular Elimination:

$$\underset{\text{1-bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[\text{Alcohol / heat}]{\text{KOH or NaOH}} \underset{\text{1-butene}}{CH_3CH_2CH=CH_2}$$



2-Bromo-2-methylbutane 2-methyl-1-butene 2-methyl-2-butene major

Zaitsev's Rule

Preparation of alkynes

1) Industrial

- From Calcium carbide

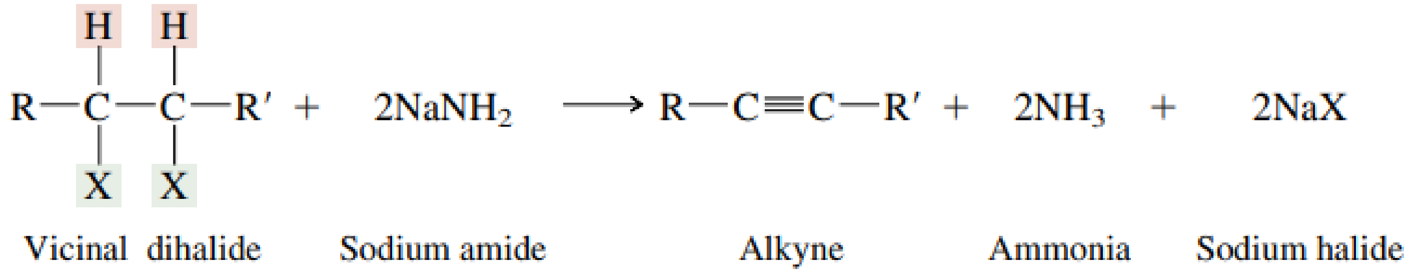
$$\underset{\substack{\text{Calcium oxide}\\ \text{(from limestone)}}}{CaO} + \underset{\substack{\text{Carbon}\\ \text{(from coke)}}}{3C} \xrightarrow{1800\text{–}2100°C} \underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Carbon monoxide}}{CO}$$

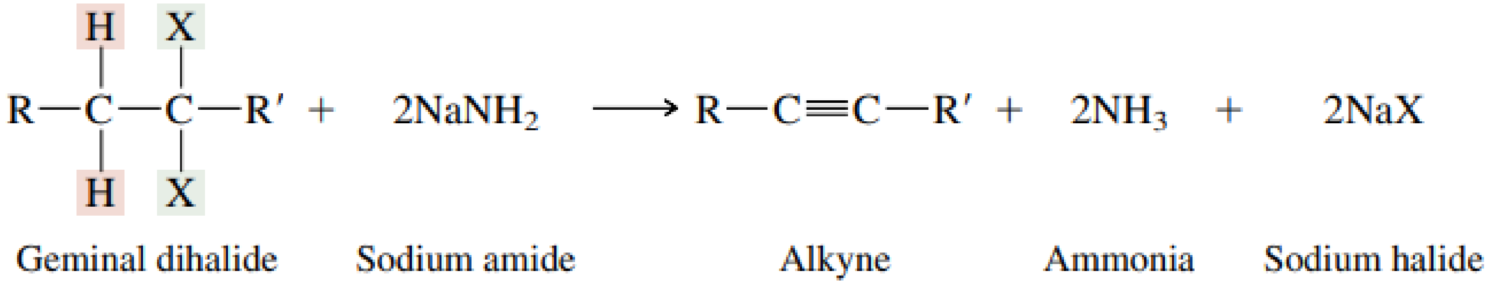
$$\underset{\text{Calcium carbide}}{Ca^{2+}\left[\begin{matrix}\ddot{C}\\ |||\\ \underset{\cdot\cdot}{C}\end{matrix}\right]^{2-}} + \underset{\text{Water}}{2H_2O} \longrightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Acetylene}}{HC{\equiv}CH}$$

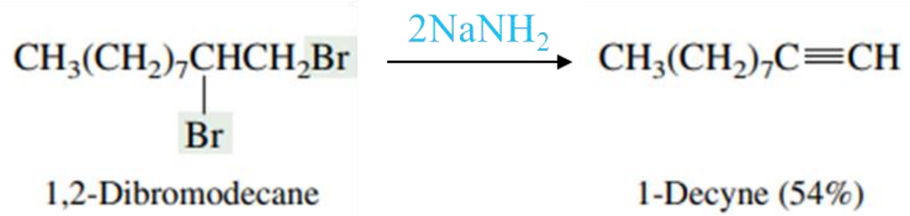
Preparation of alkynes

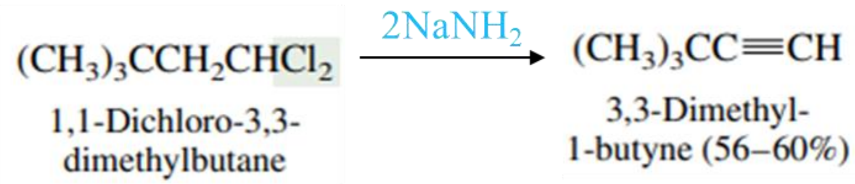
2- Dehydrohalogenation of Alkyl Dihalide

- Treatment of vicinal or germinal dihalides with strong base followed by sodium amide (liq NH_3, Na).









Preparation of alkynes

3- Alkylation of Acetylene and Terminal Acetylene

- By attaching alkyl groups to acetylene, more complex alkynes can be prepared.
- By treating the sodium alkynide with a primary alkyl halide.

$$\underset{\text{Acetylene}}{HC{\equiv}CH} + \underset{\text{Sodium amide}}{NaNH_2} \longrightarrow \underset{\text{Sodium acetylide}}{HC{\equiv}CNa} + \underset{\text{Ammonia}}{NH_3}$$

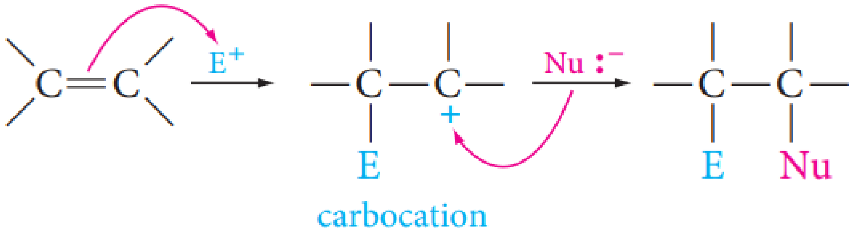
$$\underset{\text{Sodium acetylide}}{HC{\equiv}CNa} + \underset{\text{Alkyl halide}}{RX} \longrightarrow \underset{\text{Alkyne}}{HC{\equiv}CR} + \underset{\text{Sodium halide}}{NaX} \quad \text{via} \quad HC{\equiv}C\!:^{-} \;\; R{-}X$$

$$\underset{\text{Sodium acetylide}}{HC{\equiv}CNa} + \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow{NH_3} \underset{\text{1-Hexyne (70–77\%)}}{CH_3CH_2CH_2CH_2C{\equiv}CH}$$

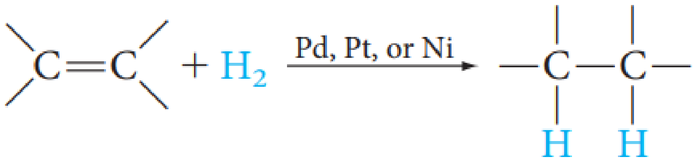
$$\underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow[\text{2. } CH_3CH_2Br]{\text{1. } NaNH_2,\ NH_3} \underset{\text{1-Butyne}}{HC{\equiv}CCH_2CH_3} \xrightarrow[\text{2. } CH_3Br]{\text{1. } NaNH_2,\ NH_3} \underset{\text{2-Pentyne (81\%)}}{CH_3C{\equiv}CCH_2CH_3}$$

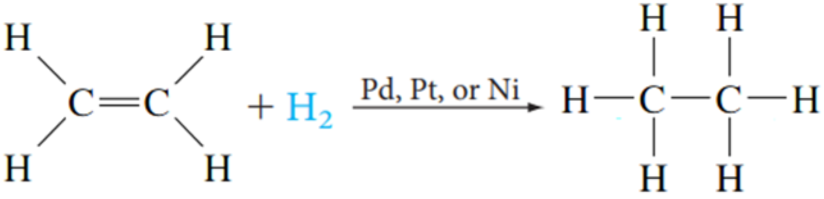
Reaction of alkenes

- Electrophilic Addition reactions on the carbon-carbon double bond.



1- Addition of Hydrogen: Catalytic Hydrogenation





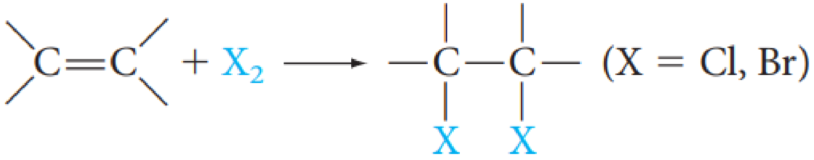
Ethylene   Ethane

$$(CH_3)_2C{=}CHCH_3 + H_2 \xrightarrow{Pt} (CH_3)_2CHCH_2CH_3$$

2-Methyl-2-butene   2-Methylbutane

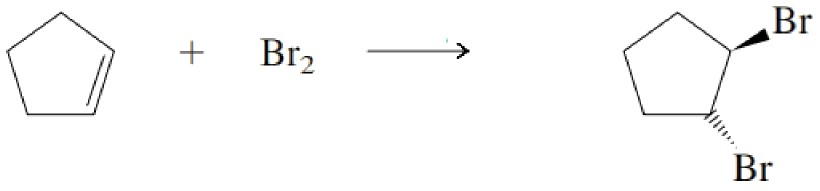
Reaction of alkenes

2- Addition of Halogens: Halogenation



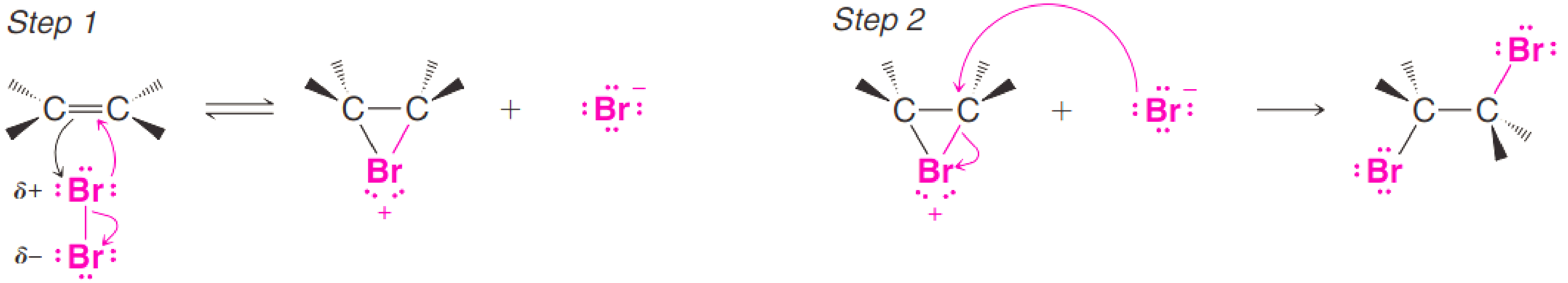
$$CH_3CH{=}CHCH_3 + Cl_2 \longrightarrow CH_3\underset{\substack{|\\Cl}}{CH}-\underset{\substack{|\\Cl}}{CH}CH_3$$

2-butene — 2,3-dichlorobutane



Cyclopentene — *trans*-1,2-Dibromocyclopentane

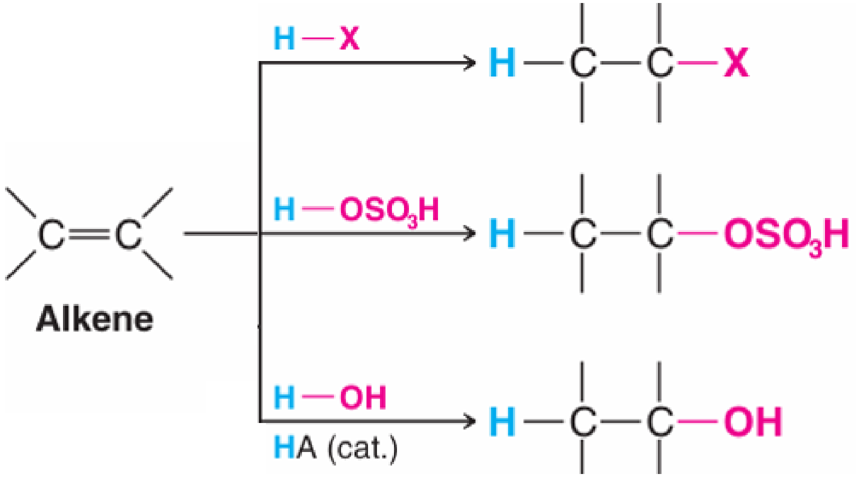
The Mechanism:



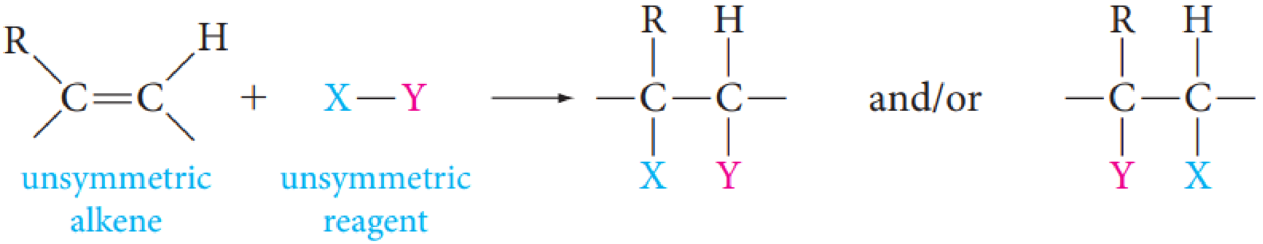
Reaction of alkenes

3- Addition of Acids:

- Acids that add in this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I), sulfuric acid (H-OSO_3H) and water (H-OH) .



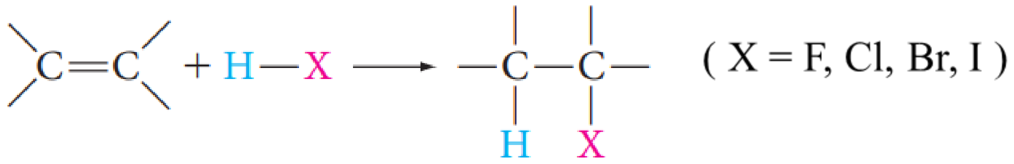
- Addition of Unsymmetric Reagents to Unsymmetric Alkenes; **Markovnikov's Rule**

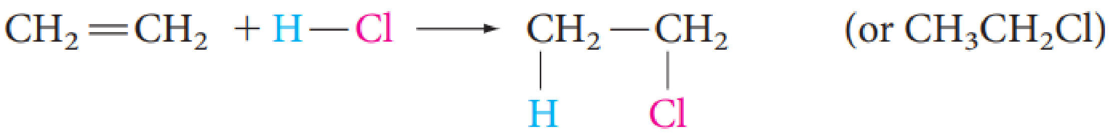


- When an unsymmetric reagent adds to an unsymmetric alkene, the electropositive part of the reagent adds to the carbon of the double bond that has the greater number of hydrogen substituents .

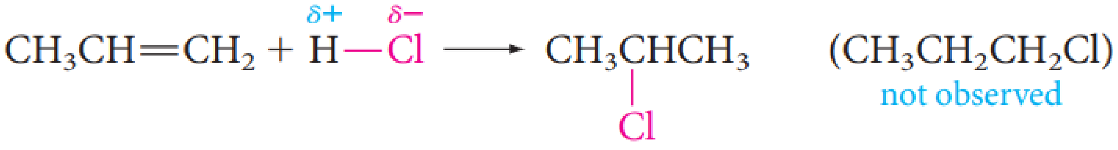
Reaction of alkenes

3.1- Addition of hydrogen halides



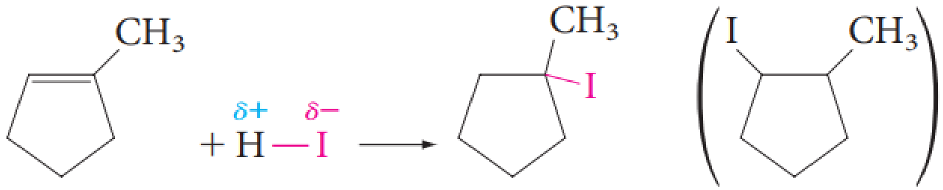


ethene | hydrogen chloride | chloroethane (ethyl chloride)



not observed

Markovnikov addition

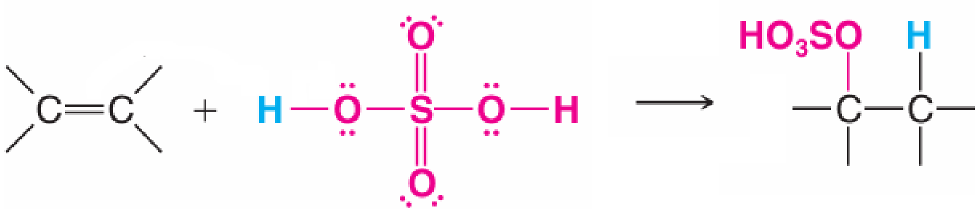


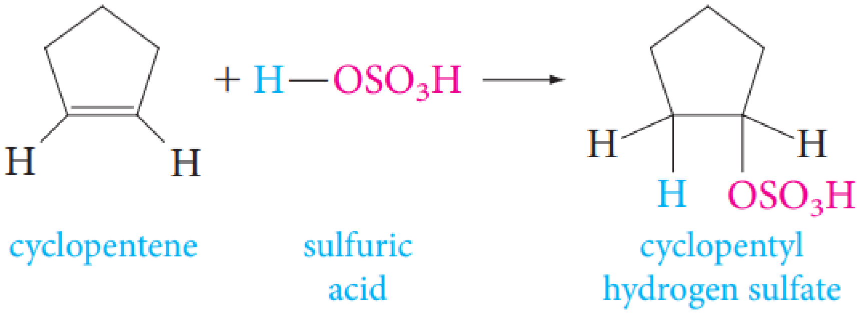
not observed

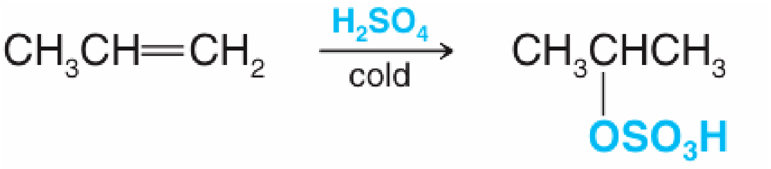
Markovnikov addition

Reaction of alkenes

3.2- Addition of Sulfuric Acid



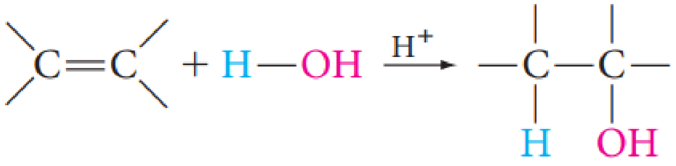




Markovnikov addition

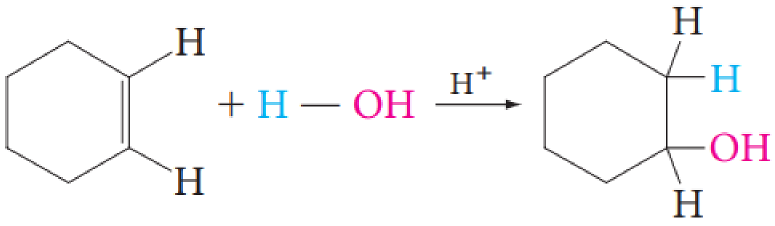
Reaction of alkenes

3.3- Addition of Water : Hydration

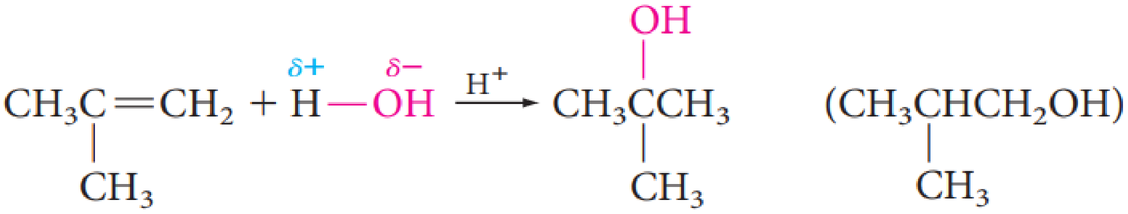


$$CH_2{=}CH_2 + H{-}OH \xrightarrow{H^+} \underset{\displaystyle H}{\underset{|}{CH_2}}{-}\underset{\displaystyle OH}{\underset{|}{CH_2}} \quad (\text{or } CH_3CH_2OH)$$

ethanol



cyclohexene cyclohexanol



not observed

Markovnikov addition

Reaction of alkenes

4- Hydroboration

- Hydroboration-oxidation reactions are regioselective; the net result of hydroboration-oxidation is anti Markovnikov addition of water to an alkene.

$$3\ RCH{=}CH_2 \xrightarrow{BH_3} (RCH_2CH_2)_3B \xrightarrow[HO^-]{H_2O_2} 3\ RCH_2CH_2OH$$

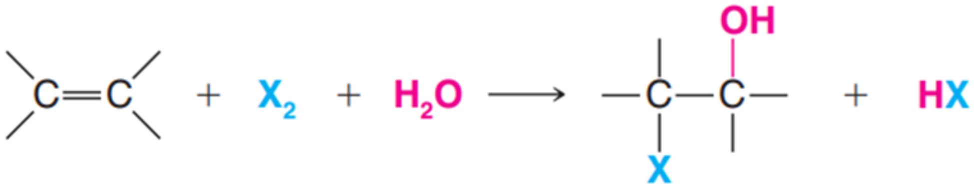
$$\underset{\text{propene}}{3\ CH_3CH{=}CH_2} + \underset{\text{borane}}{BH_3} \longrightarrow \underset{\text{tri-}n\text{-propylborane}}{CH_3CH_2CH_2{-}B(CH_2CH_2CH_3)_2}$$

$$\underset{\text{tri-}n\text{-propylborane}}{(CH_3CH_2CH_2)_3B} + 3\ H_2O_2 + 3\ NaOH \longrightarrow \underset{n\text{-propyl alcohol}}{3\ CH_3CH_2CH_2OH} + \underset{\text{sodium borate}}{Na_3BO_3} + 3\ H_2O$$

$$3\ CH_3{-}C(CH_3){=}CH_2 \xrightarrow{BH_3} (CH_3{-}CH(CH_3){-}CH_2)_3B \xrightarrow[OH^-]{H_2O_2} 3\ CH_3{-}CH(CH_3){-}CH_2OH$$

5- Addition of HOX : Halohydrin Formation

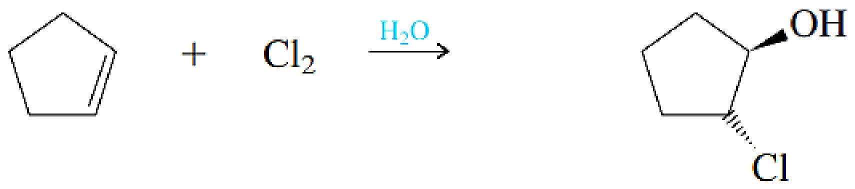
- When the halogenation of an alkene is carried out in aqueous solution, the major product is a halohydrin (also called a halo alcohol)



X_2 = Cl or Br

Halohydrin

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{Bromine}}{Br_2} \xrightarrow{H_2O} \underset{\text{2-Bromoethanol (70\%)}}{HOCH_2CH_2Br}$$



Cyclopentene | Chlorine | *trans*-2-Chlorocyclopentanol

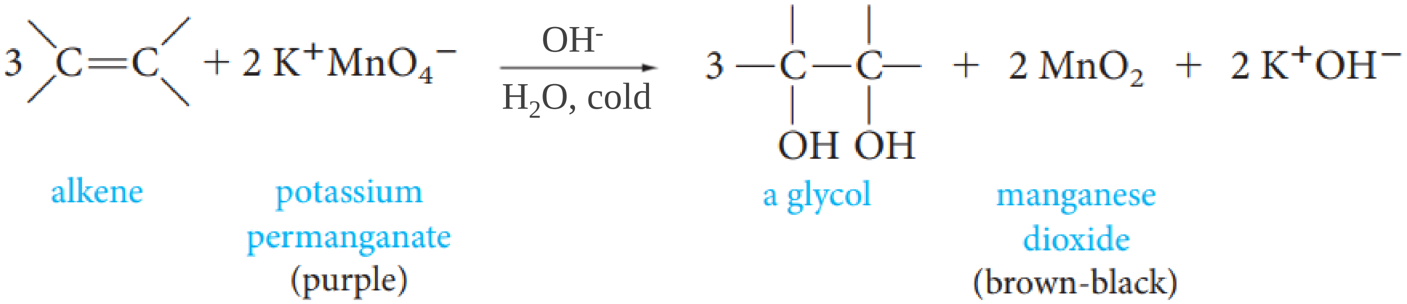
Reaction of alkenes

6- Oxidation of alkenes

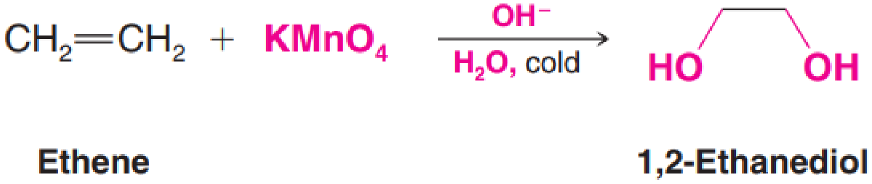
- Oxidation of alkenes to Diols or Carbonyl-Containing Compounds.

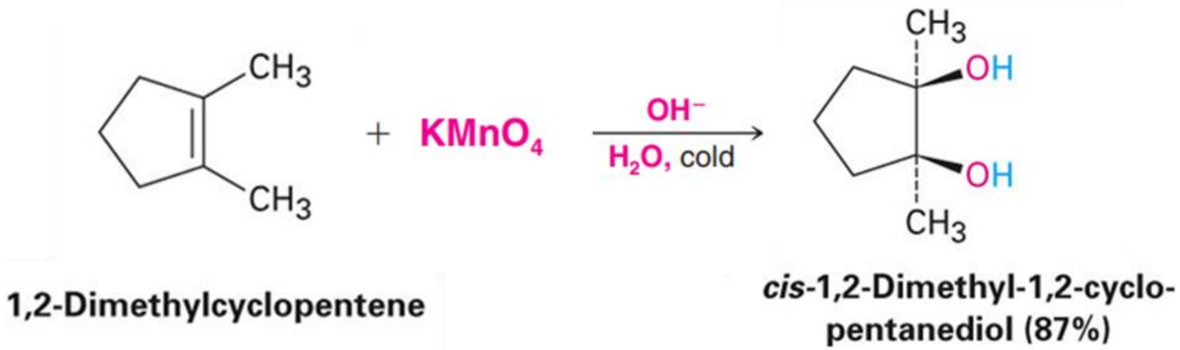
6.1- Oxidation of alkenes with Permanganate

- Alkenes react with alkaline potassium permanganate to form glycols.



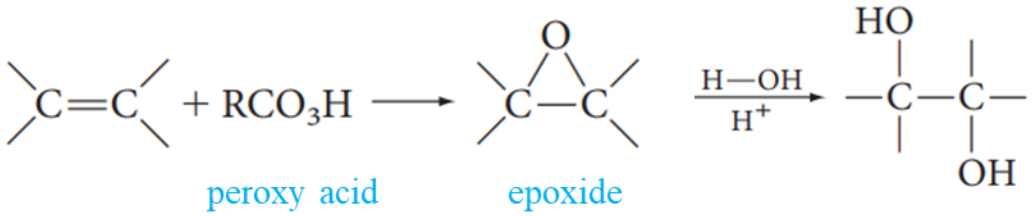
syn hydroxylation



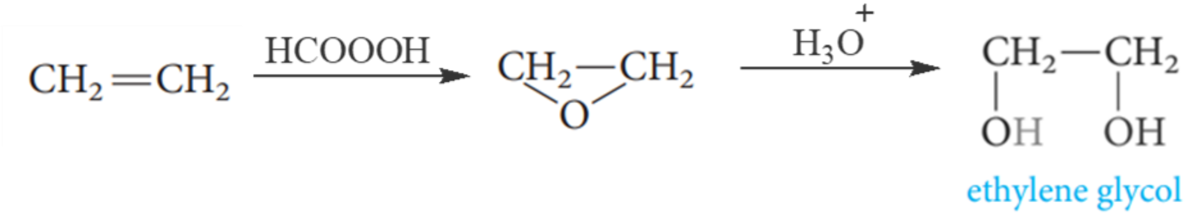


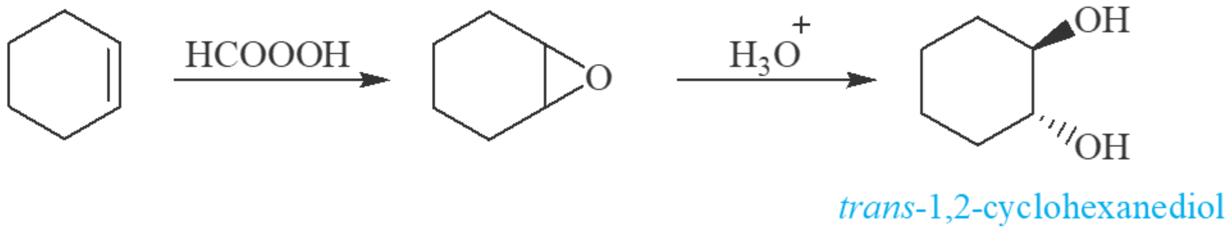
Reaction of alkenes

6.2- Oxidation of alkenes with peroxy acid



anti hydroxylation

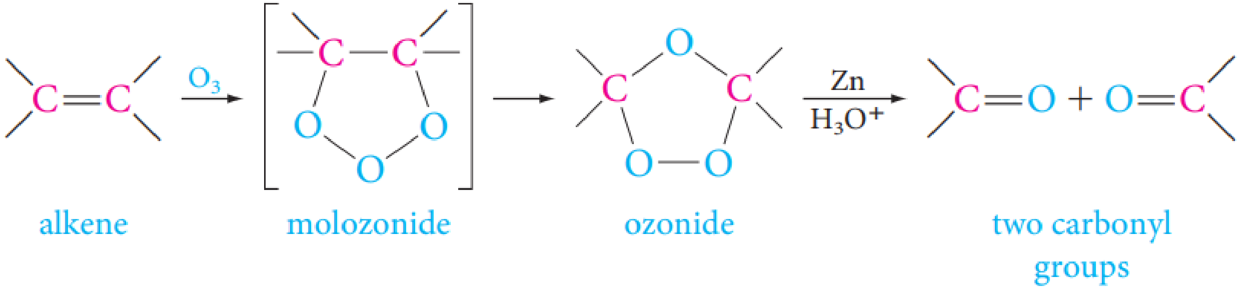




Reaction of alkenes

6.3- Ozonolysis:

- Oxidation of alkenes by ozone O_3.

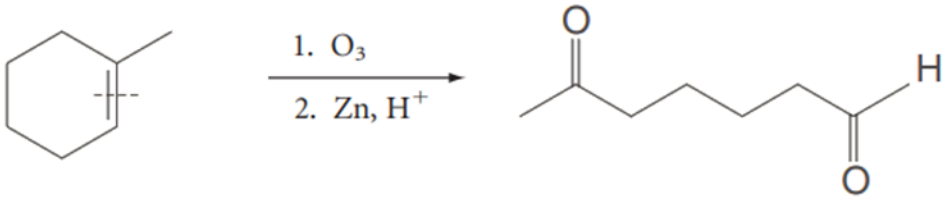


$$CH_2{=}CHCH_2CH_3 \xrightarrow[\text{2. Zn, H}^+]{\text{1. } O_3} CH_2{=}O \quad O{=}CHCH_2CH_3$$

1-butene — formaldehyde — propanal

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

2-butene — ethanal



Reaction of alkenes

7- Free-Radical Additions; polymerization

- A polymer is a large molecule containing a repeating unit derived from small molecules called monomers. The process of polymer formation is called polymerization.
- The free-radical polymerization of ethylene gives polyethylene, a material that is produced on a very large scale (more than 150 billion pounds worldwide annually).

$$\underset{\text{ethylene}}{CH_2{=}CH_2} \xrightarrow[\text{1000 atm, >100°C}]{\text{catalyst}} \underset{\substack{\text{polyethylene} \\ (n\,=\,\text{several thousand})}}{-\!\!\left(CH_2{-}CH_2\right)\!\!-_n}$$

Reaction of alkynes

1- Addition of Hydrogen: Hydrogenation

$$\underset{\text{Alkyne}}{RC{\equiv}CR'} \xrightarrow[\text{catalyst}]{H_2} \underset{\text{Alkene}}{RCH{=}CHR'} \xrightarrow[\text{catalyst}]{H_2} \underset{\text{Alkane}}{RCH_2CH_2R'}$$

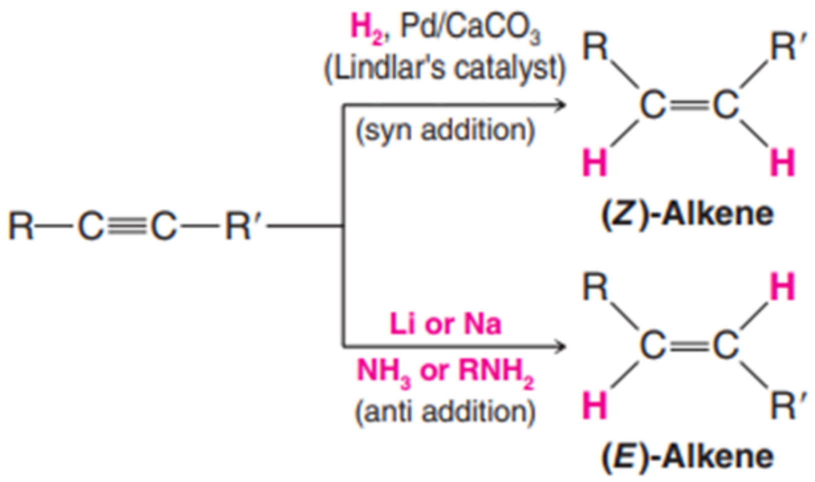
$$\underset{\text{Alkyne}}{RC{\equiv}CR'} + \underset{\text{Hydrogen}}{2H_2} \xrightarrow{\text{Pt, Pd, Ni, or Rh}} \underset{\text{Alkane}}{RCH_2CH_2R'}$$

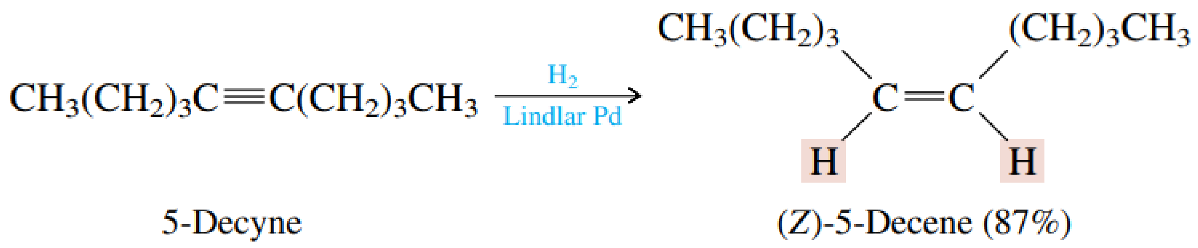
$$\underset{\text{4-Methyl-1-hexyne}}{CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2C{\equiv}CH} + \underset{\text{Hydrogen}}{2H_2} \xrightarrow{\text{Ni}} \underset{\text{3-Methylhexane (77\%)}}{CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2CH_3}$$

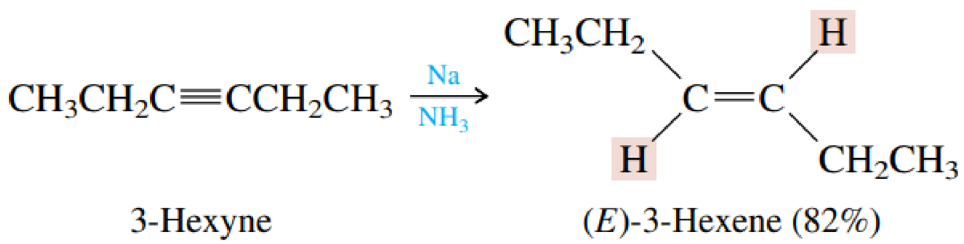
Reaction of alkynes

1- Addition of Hydrogen: Hydrogenation

- Hydrogenation of an alkyne to an alkene can be accomplished through the use of special catalysts or reagents. Moreover, these special methods allow the preparation of either (E)- or (Z)-alkenes from disubstituted alkynes.

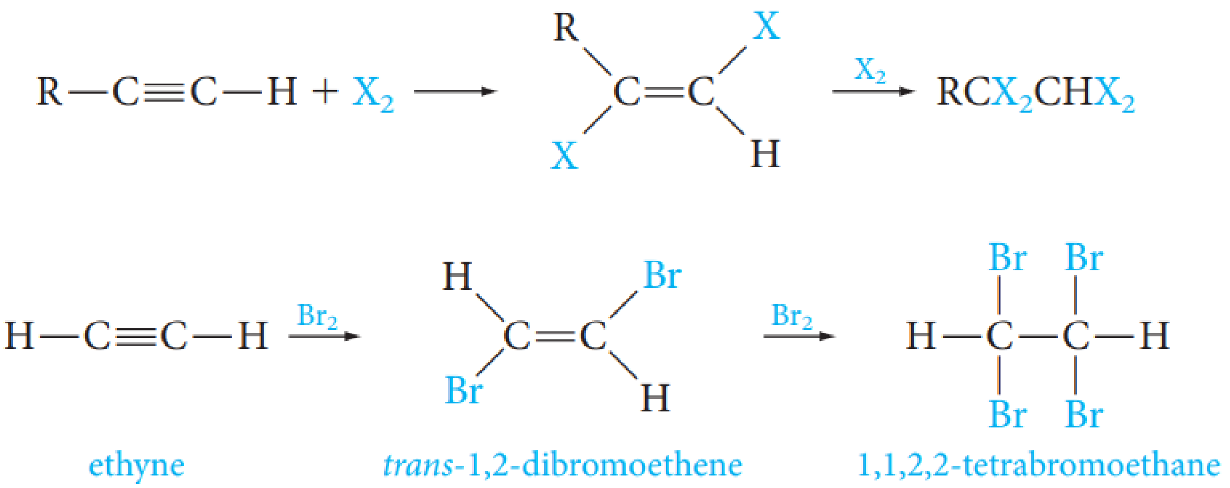




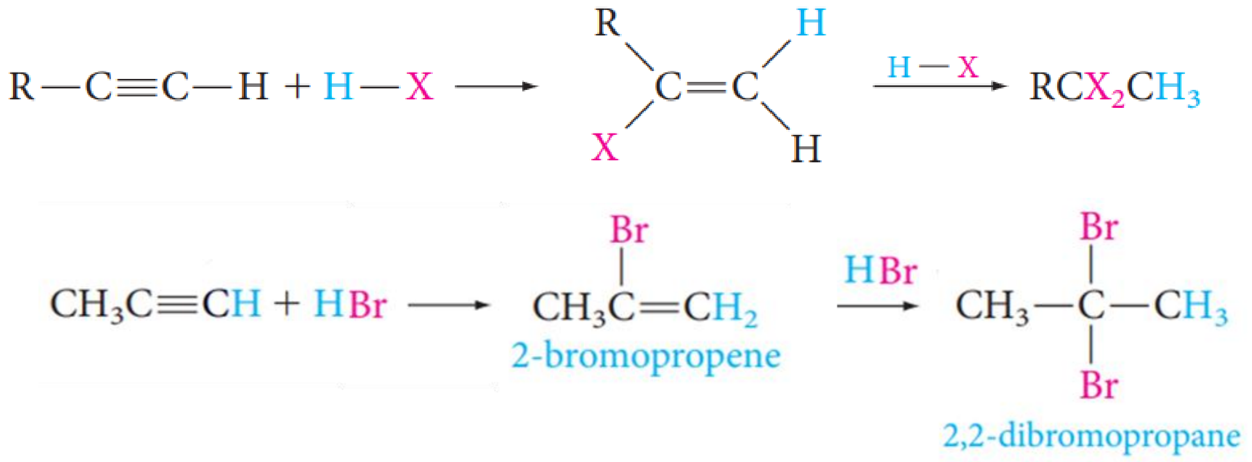


Reaction of alkynes

2- Addition of Halogen: Halogenation



3- Addition of Hydrogen Halide: Hydrohalogenation

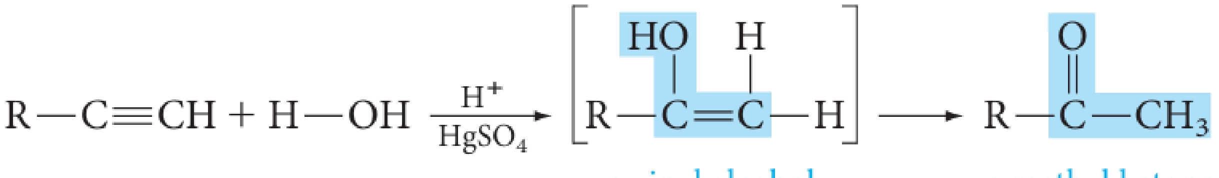


Markovnikov addition

Reaction of alkynes

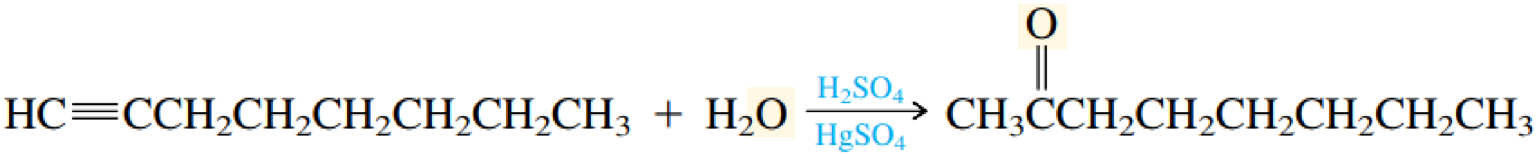
4- Addition of Water : Hydration

- Addition of water to alkynes requires not only an acid catalyst but mercuric ion as well.



a vinyl alcohol, a methyl ketone

Markovnikov addition



1-Octyne 2-Octanone (91%)

Reaction of alkynes

5- Ozonolysis of alkynes

- Treating alkynes with ozone followed by acetic acid, leads to cleavage at the carbon–carbon triple bond. The products are carboxylic acids.

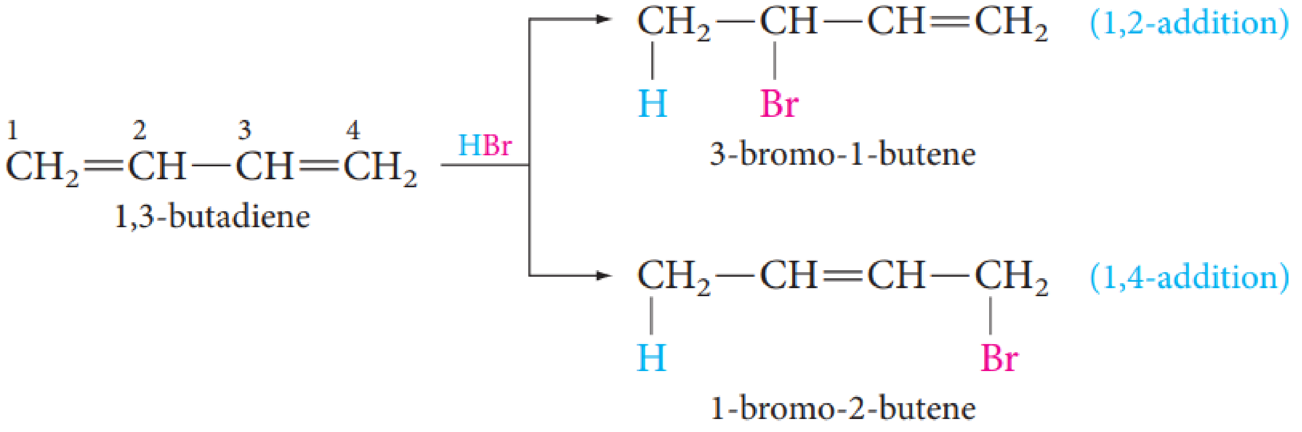
$$RC{\equiv}CR' \xrightarrow[\text{2. } CH_3COOH]{\text{1. } O_3} RCOH \;(\text{C=O}) + HOCR' \;(\text{C=O})$$

$$\underset{\text{2-Hexyne}}{CH_3CH_2CH_2C{\equiv}CCH_3} \xrightarrow[\text{2. } CH_3COOH]{\text{1. } O_3} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}OH} + \underset{\text{Acetic acid}}{HO\overset{\displaystyle O}{\overset{\|}{C}}CH_3}$$

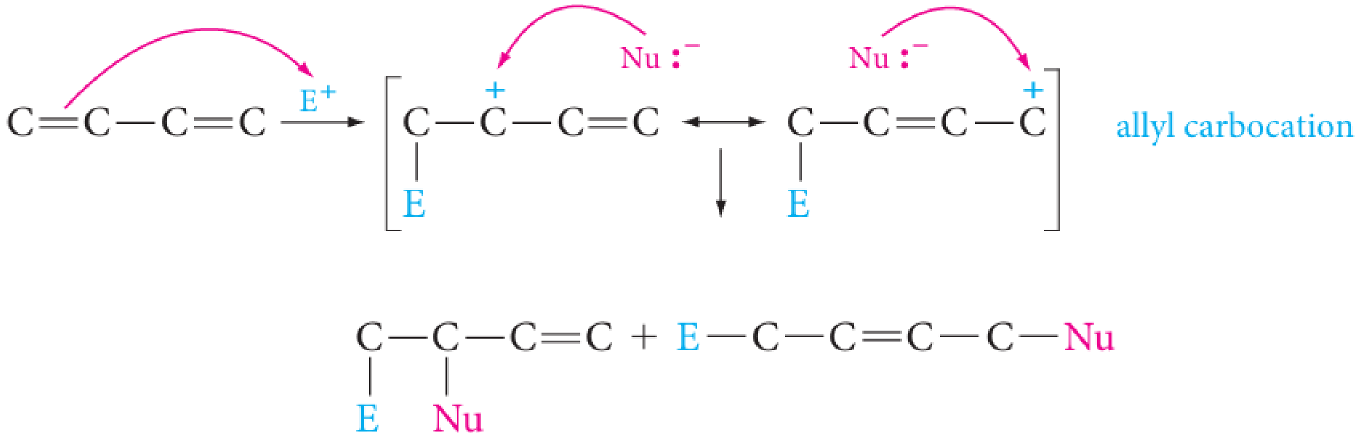
$$\underset{\text{1-Hexyne}}{CH_3CH_2CH_2CH_2C{\equiv}CH} \xrightarrow[\text{2. } CH_3COOH]{\text{1. } O_3} \underset{\text{Pentanoic acid (51\%)}}{CH_3CH_2CH_2CH_2CO_2H} + \underset{\text{Carbonic acid}}{HO\overset{\displaystyle O}{\overset{\|}{C}}OH}$$

Reactions of Dienes

1- Electrophilic Additions to Conjugated Dienes:



The Mechanism:

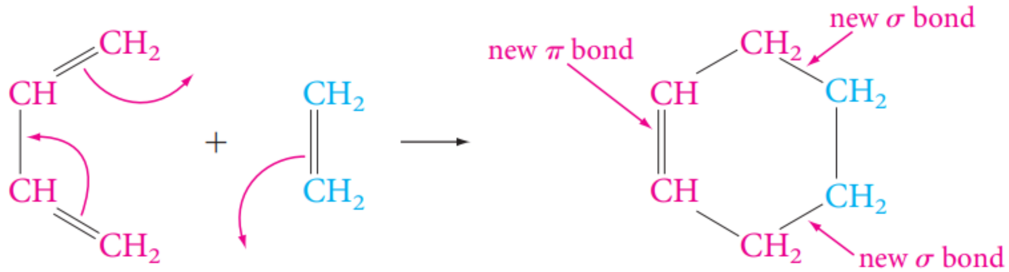


1,2-product 1,4-product

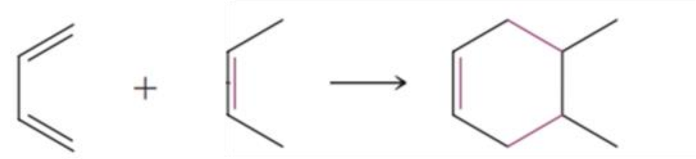
Reactions of Dienes

2- The Diels-Alder reaction

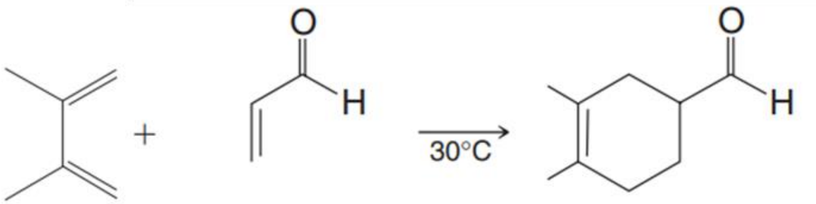
- The Diels–Alder reaction is the cycloaddition reaction of a conjugated diene and a dienophile (alkene) to give a cyclic product in which three π bonds are converted to two σ bonds and a new π bond.



1,3-butadiene ethylene cyclohexene



1,3-Butadiene



2,3-Dimethyl-1,3-butadiene Propenal 100%