Organic Chemistry
244 CHEM

Unsaturated Hydrocarbons
Alkenes & Alkynes

Dr. Hany El-Hamshary

Alkenes & Alkynes

Alkenes are hydrocarbons whose molecules contain the C=C double bond

also known as olefins: (oleum = oil, facere = make)

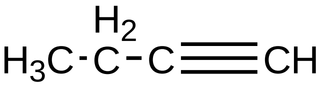
Formula: C_nH_{2n}

	$CH_2{=}CH_2$	$H_3C{-}CH{=}CH_2$
Common name:	Ethylene	Propylene
IUPAC name:	Ethene	Propene

Alkynes are hydrocarbons whose molecules contain the $C\equiv C$ triple bond.

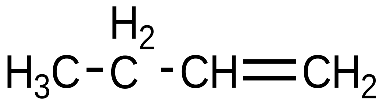
These compound are called: acetylenes: or Alkynes

$H-C\equiv C-H$	
Acetylene	Common name
Ethyne	IUPAC

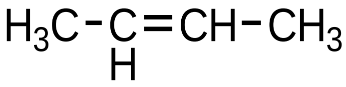
	$HC\equiv CH$	$H_3C-C\equiv CH$	 $H_3C-\overset{H_2}{C}-C\equiv CH$	$H_3C-C\equiv C-CH_3$
IUPAC name:	Ethyne	Propyne	1-Butyne	2-Butyne
Common name:	Acetylene			

Nomenclature of Alkenes

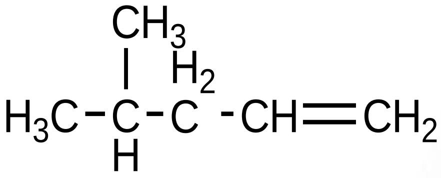
1. To name alkenes, *select the longest carbon* chain which **includes** the carbons of the double bond. Remove the **-ane** suffix from the name of the alkane which corresponds to this chain. Add the suffix **-ene**.
2. Number this chain so that the first carbon of the double bond has the lowest number possible, even if it results in the substituting getting higher numbers**.**


$H_3C-\overset{H_2}{C}-CH=CH_2$

1-Butene
(*not* 3-Butene)

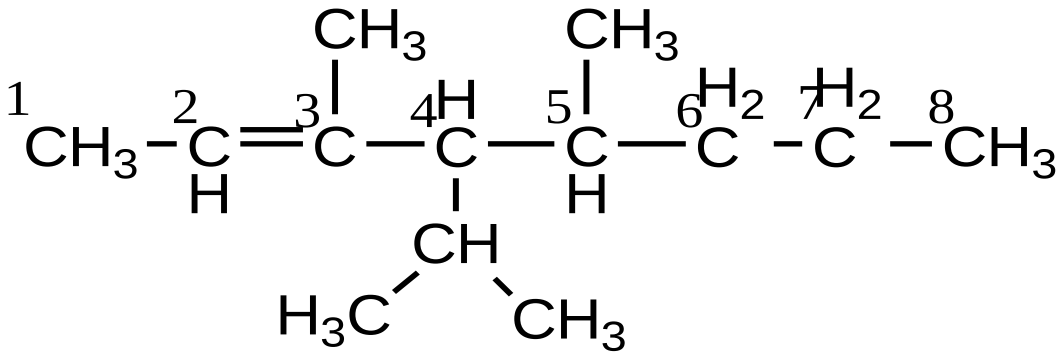

$H_3C-\underset{H}{C}=CH-CH_3$

2-Butene


$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{H}{C}}-\overset{H_2}{C}-CH=CH_2$

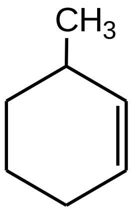
4-Methyl-1-pentene
(*not* 2-Methyl-4-pentene)

3. Indicate the location of the substituent groups by numbering of the carbon atoms to which they are attached.

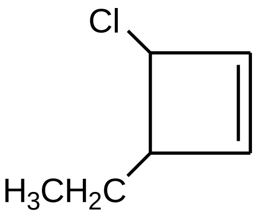


3,5-Dimethyl-4-isopropyl-2-octene

4. Number substituted cycloalkenes in the same way that gives the carbon atoms of the double bond the 1 and 2 positions and that also gives the substituent groups the lower numbers at the first point of difference.

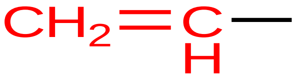


3-Methylcyclohexene
(*not* 1-Methyl-2-cyclohexene)



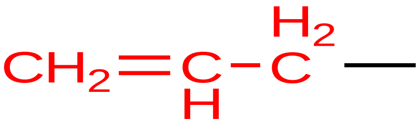
3-Chloro-4-ethylcyclobutene
(*not* 1-Chloro-2-ethyl-3-cyclobutene)

5. Two frequently encountered alkenyl groups are the ***vinyl*** group and ***allyl*** group.



$CH_2{=}\underset{H}{C}-$

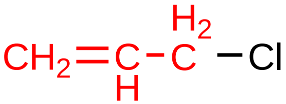
Vinyl



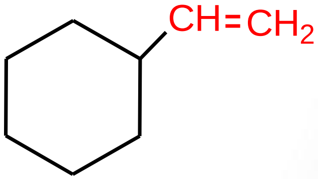
$CH_2{=}\underset{H}{C}-\overset{H_2}{C}-$

Allyl

$CH_2{=}\underset{H}{C}-Br$



$CH_2{=}\underset{H}{C}-\overset{H_2}{C}-Cl$



Common name:	Vinyl bromide	Allyl chloride	Vinyl cyclohexane
IUPAC name:	Bromoethene	3-Chloro-1-propene	Cyclohexylethene

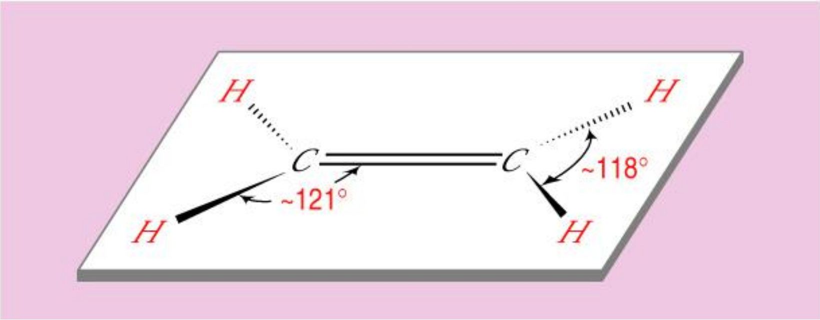
Geometry of Unsaturated Hydrocarbones

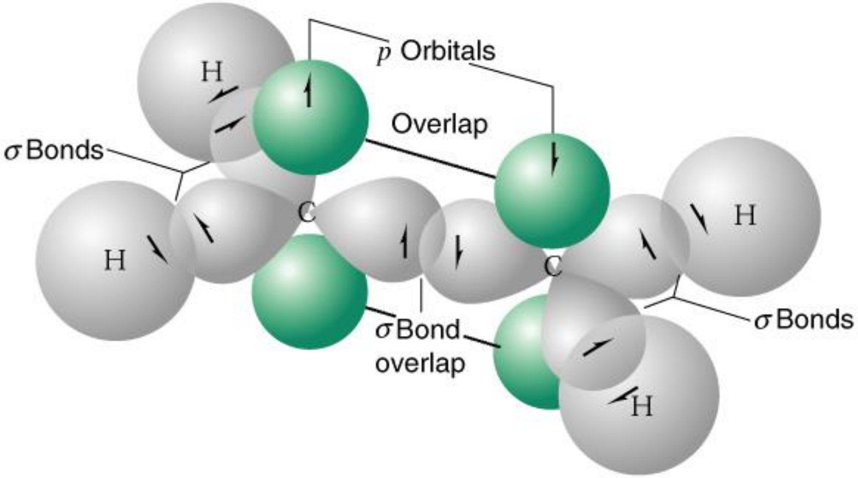
Geometry of the Carbon-Carbon Double Bond:

sp^2 Hybridization

- The *2s* orbital and only two of the three *2p* orbitals hybridize.
- The result is three equivalent *sp*^{2} hybrid orbitals and one unhydridized $2p_z$ orbital.
- The three *sp*^{2} orbitals get as far away from each other by assuming a ***planar*** arrangement with angle of 120°.
- This type of arrangement is also known as **trigonal *planar*** geometry.

The Structure of Ethene (Ethylene):
sp^2 Hybridzation





A model for the bonding molecular orbitals of ethane formed from two *sp*^{2}-hybridized carbon atoms and four hydrogen atoms.

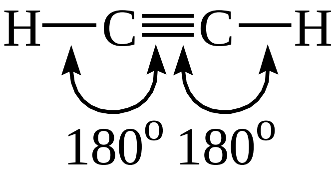
Geometry of the Carbon-Carbon Triple Bond:

sp Hybridization

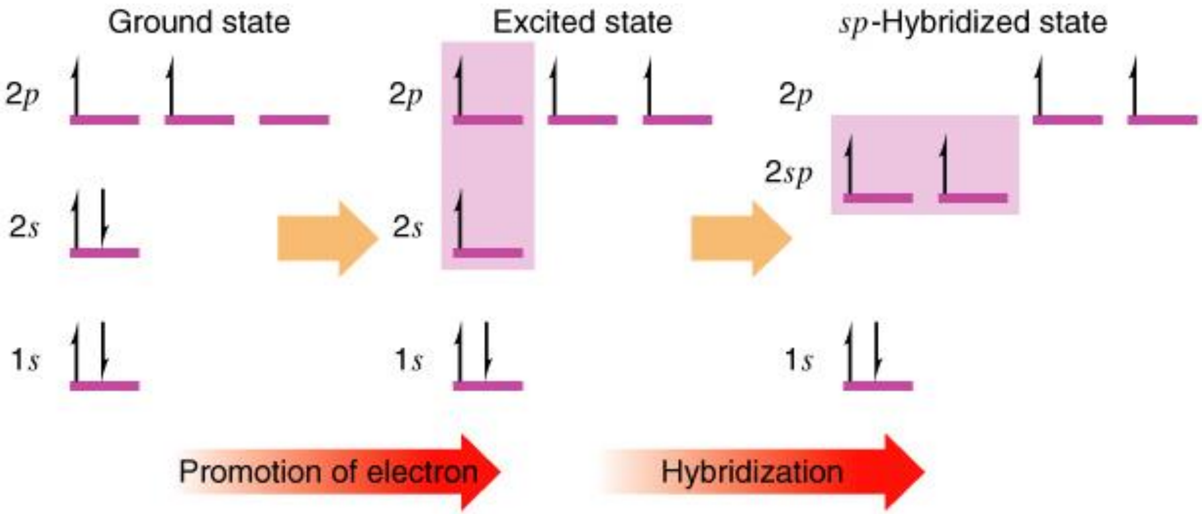
- **Acetylene is a linear molecule with a bond angle of 180°.**

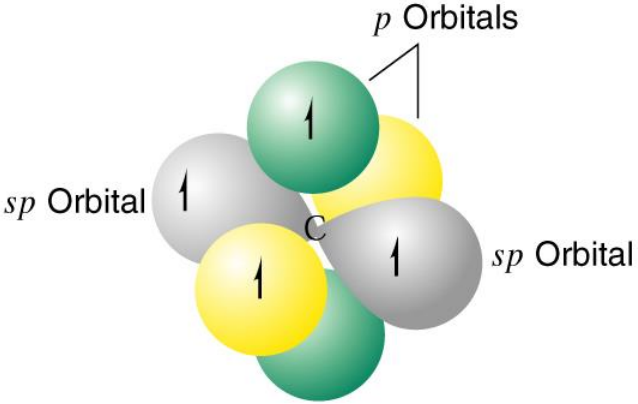
The *sp* hybrid orbitals have their large positive lobes oriented at an angle of 180° with respect to each other

$$H-C\equiv C-H$$

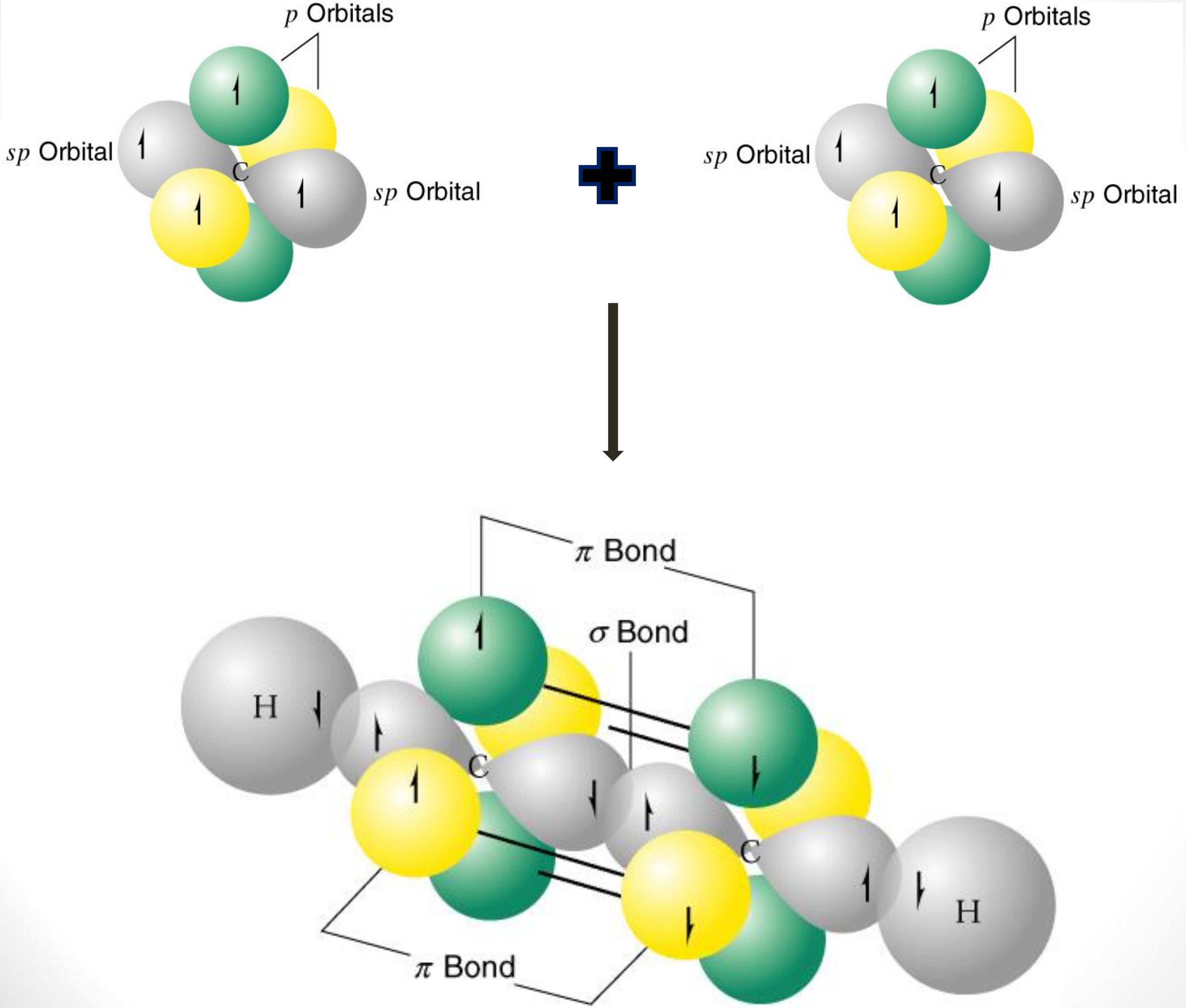


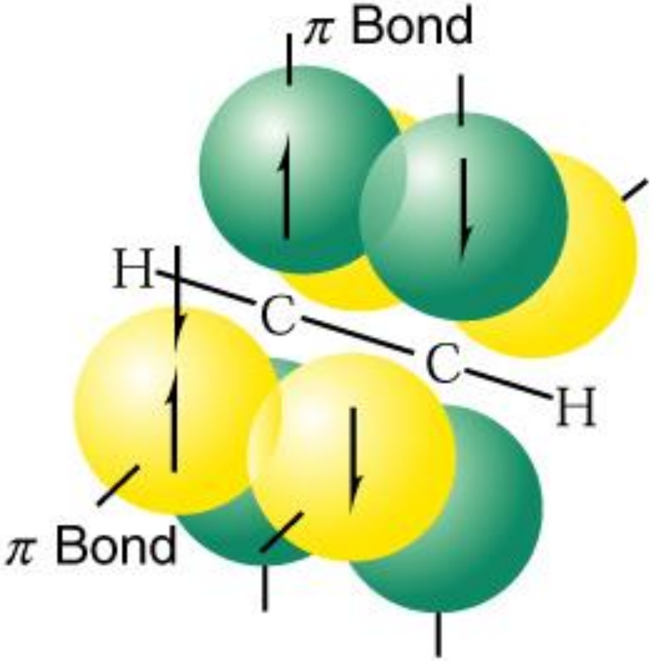
sp Hybridization:





An *sp*-hybridized carbon atom.

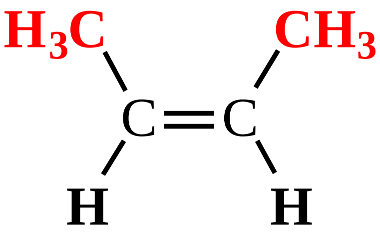

p Orbitals
sp Orbital
C
sp Orbital
p Orbitals
sp Orbital
C
sp Orbital
π Bond
σ Bond
H
C
C
H
π Bond



(*a*)

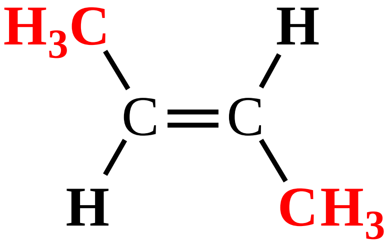
Geometric Isomerism in Alkenes

If two identical groups are on the same side of the double bond, the compound can be designated ***cis***; if they are on the opposite sides it can be designated ***trans***



cis-2-Butene

mp= - 139°C
bp = 3.7°C



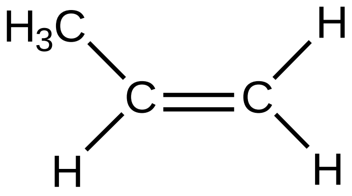
trans-2-Butene

mp= - 106°C
bp = 0.9°C

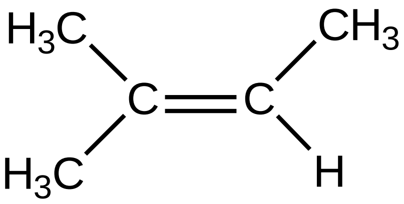
cis- and ***trans*** isomers have different physical properties and can be separated by fractional crystallization or distillation.

If similar groups are present at the double bond, geometric isomerism is not possible.

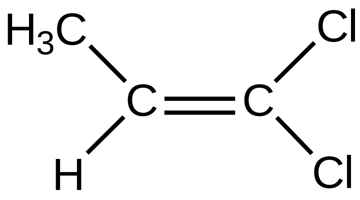
The following compounds have no geometric isomers



Propene

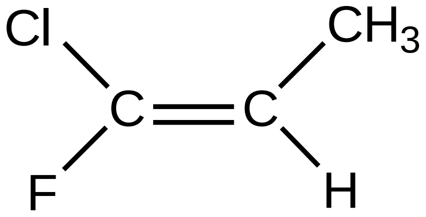


2-Methyl-2-butene



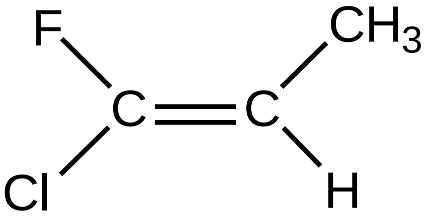
1,1-Dichloropropene

For alkenes with four different substituent such as



(I)

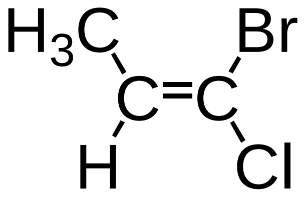
or



(II)

cis/trans problems

Naming alkenes using the cis and trans nomenclature can be confusing if an alkene is tri-or tetrasubstituted. One has to determine which two atoms or groups to compare as being cis or trans to each other.



This molecule is a 1-bromo-1-chloropropene but is it *cis* or *trans* ?

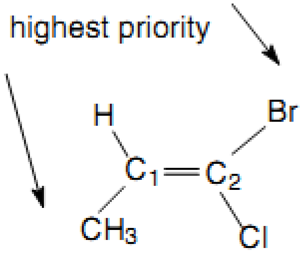
To avoid confusion, the E/Z system is used. E is derived from the German word entgegen, meaning opposite, and Z is derived from the German word zusammen, meaning together or on the same side.

It is important to determine which atoms or groups to compare as being on the same or opposite side for assigning E or Z designations.

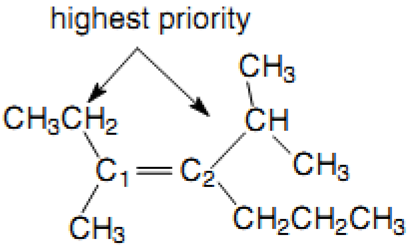
Basically, the E,Z system works as follows;

Arrange the groups on each carbon of the C=C bond in order of priority (The priority depends on atomic number) :

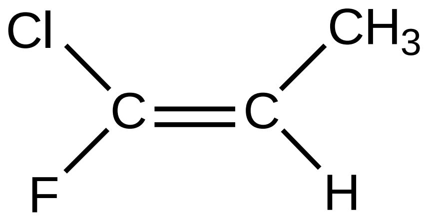
The higher the atomic number of the atom directly attached to the double-bonded carbon, the higher the priority.



E isomer

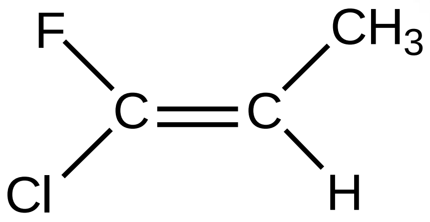


Z isomer



(I)

or



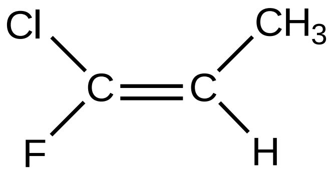
(II)

Thus, in structure (I), Cl > F, and CH_3 > H.

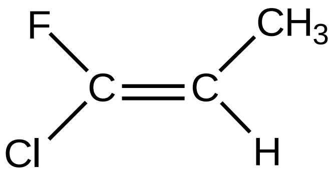
If the two groups of higher priority are on the same side of the C=C plane the isomer is labeled *Z*

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



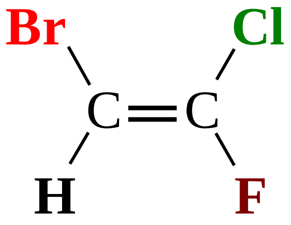
Z-1-Chloro-1-fluoropropene
(Cl and CH_3 on same side)



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

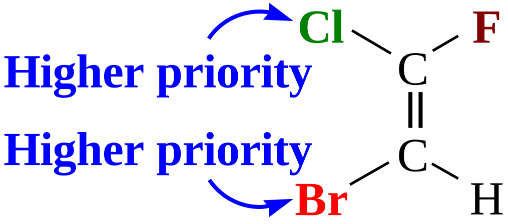
THE (*E*)-(*Z*) SYSTEM FOR DESIGNATING ALKENE DIASTEREOMERS

1. *Cis*- and *trans*- designations the stereochemistry of alkene diasteroemers are unambiguous only when applied to disubstituted alkenes.



A

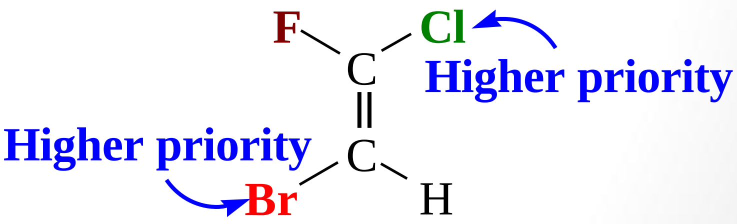
2. The (*E*)-(*Z*) system:



(*Z*)-2-Bromo-1-chloro-1-fluroethene

Cl > F

Br > H

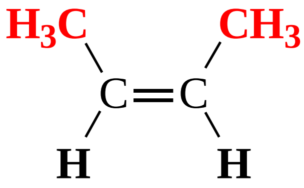


(*E*)-2-Bromo-1-chloro-1-fluroethene

3. The group of higher priority on one carbon atom is compared with the group of higher priority on the other carbon atom:

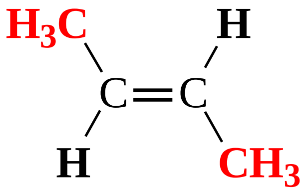
ii-(*Z*)-alkene: If the two groups of higher priority are on the same side of the double bond (German: *zusammen*, meaning together).

ii- (*E*)-alkene: If the two groups of higher priority are on opposite side of the double bond (German: *entgegen*, meaning opposite).

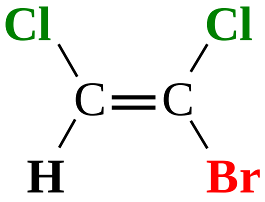


(*Z*)-2-Butene
(*cis*-2-butene)

$CH_3 > H$

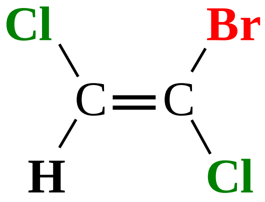


(*E*)-2-Butene
(*trans*-2-butene)



(*E*)-1-Bromo-1,2-dichloroethene

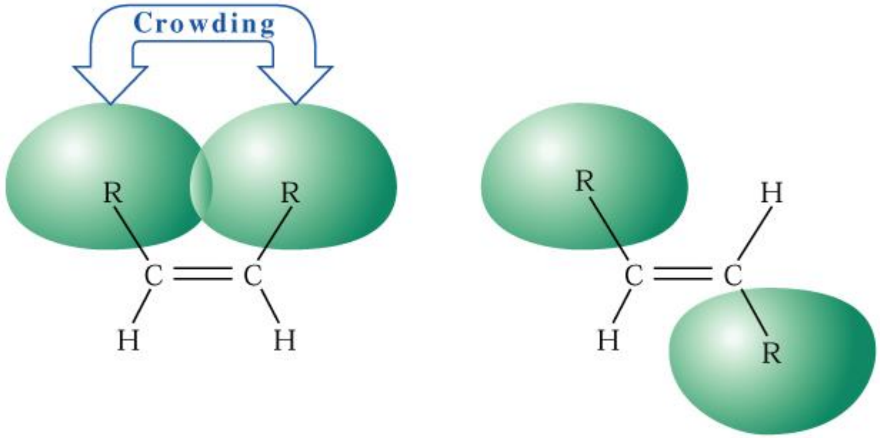
Cl > H
Br > Cl



(*Z*)-1-Bromo-1,2-dichloroethene

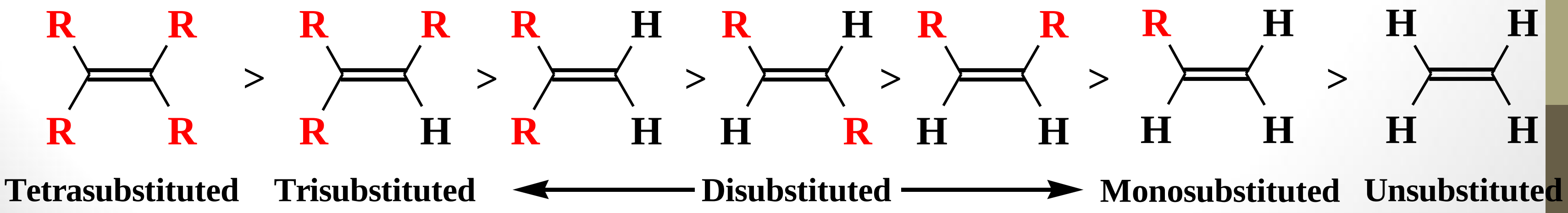
Relative stabilities of alkenes

- Cis isomers are generally less stable than trans isomers due to strain caused by crowding of the two alkyl groups on the same side of the double bond



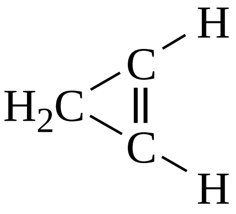
cis- and *trans*-Alkene isomers. The less stable *cis* isomer has greater strain

In general, The greater the number of attached alkyl groups (i.e., the more substituted the carbon atoms of the double bond), the greater is the alkene’s stability.

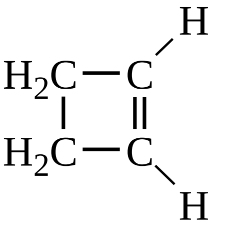


Cycloalkenes

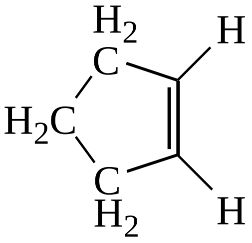
The rings of cycloalkenes containing five carbon atoms or fewer exist only in the *cis* form.



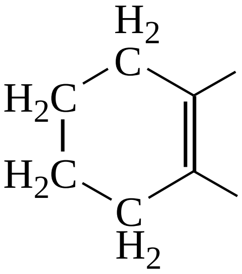
Cyclopropene



Cyclobute



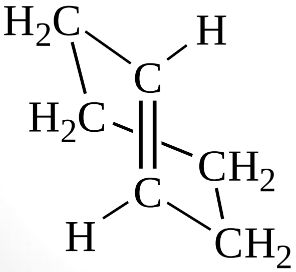
Cyclopentene



Cyclohexene

cis-Cycloalkenes

There is evidence that *trans*-cyclohexene can be formed as a very reactive short-lived intermediate in some chemical reactions.

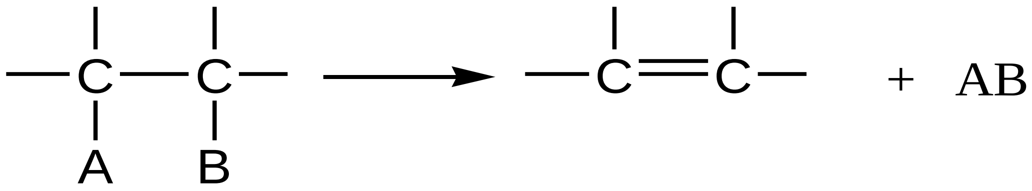


Hypothetical *trans*-cyclohexene. This molecule is apparently too highly strained to exist at room temperature.

Synthesis of alkenes

Elimination reactions

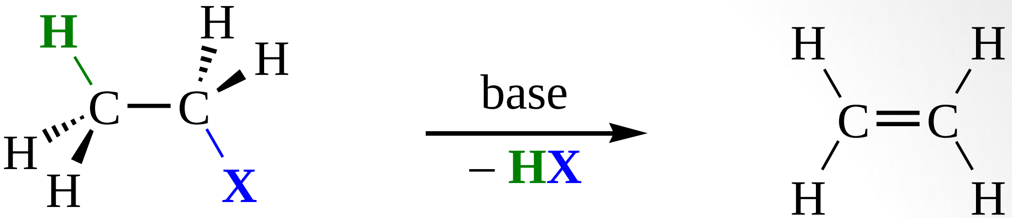
Alkenes are prepared by elimination of an atom or group of atoms from adjacent carbons to form carbon-carbon double bond



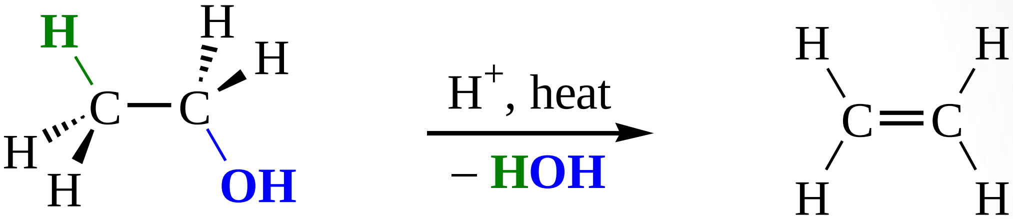
$$-\underset{A}{\overset{|}{\underset{|}{\mathrm{C}}}}-\underset{B}{\overset{|}{\underset{|}{\mathrm{C}}}}- \longrightarrow -\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}- \quad + \quad \mathrm{AB}$$

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

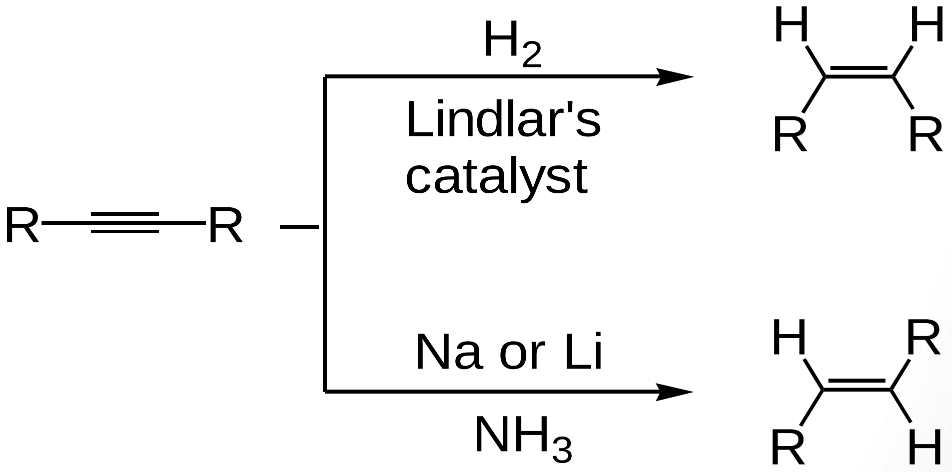
Dehydrohalogenation



Dehydration of alcohols



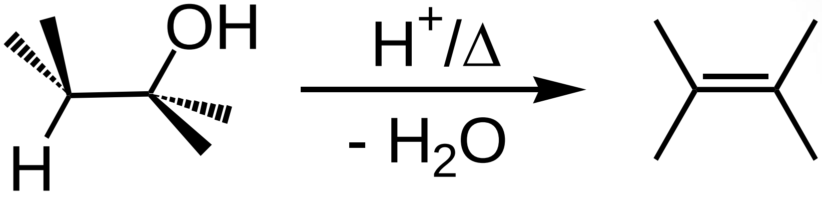
Hydrogenation of alkynes

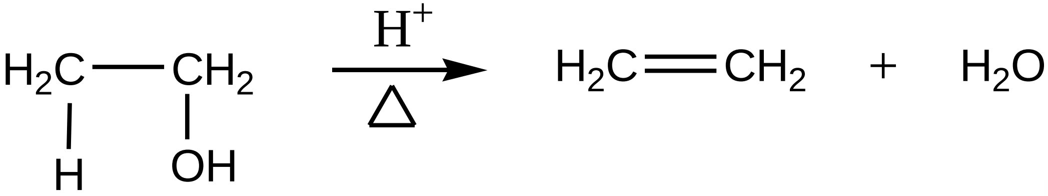


Lindlar catalyst:
$Pd/CaCO_3/Pb(OAc)_2$/quinoline

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

Dehydration of alcohols:

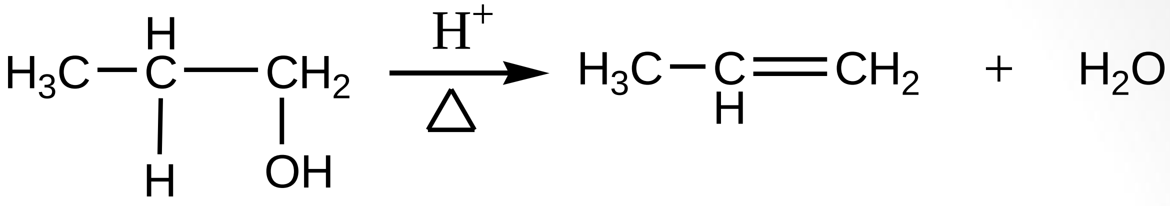




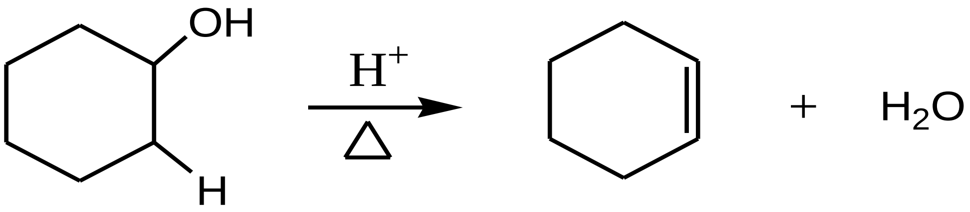
$$\underset{H}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH_2}} \xrightarrow[\Delta]{H^+} H_2C=CH_2 + H_2O$$

IUPAC name:	Ethanol	Ethene
Common name:	Ethyl alcohol	Ethylene

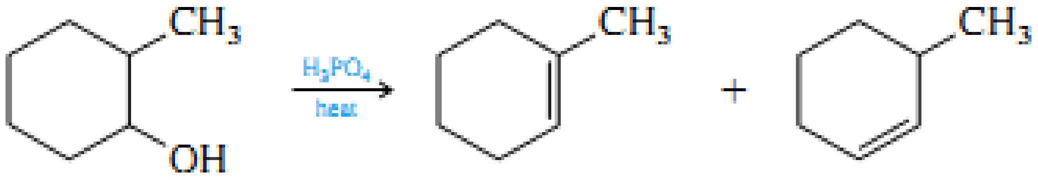
The acid catalysts most commonly used are sulfuric acid, H_2S0_4, and phosphoric acid, H_3P0_4 or Al_2O_3.



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



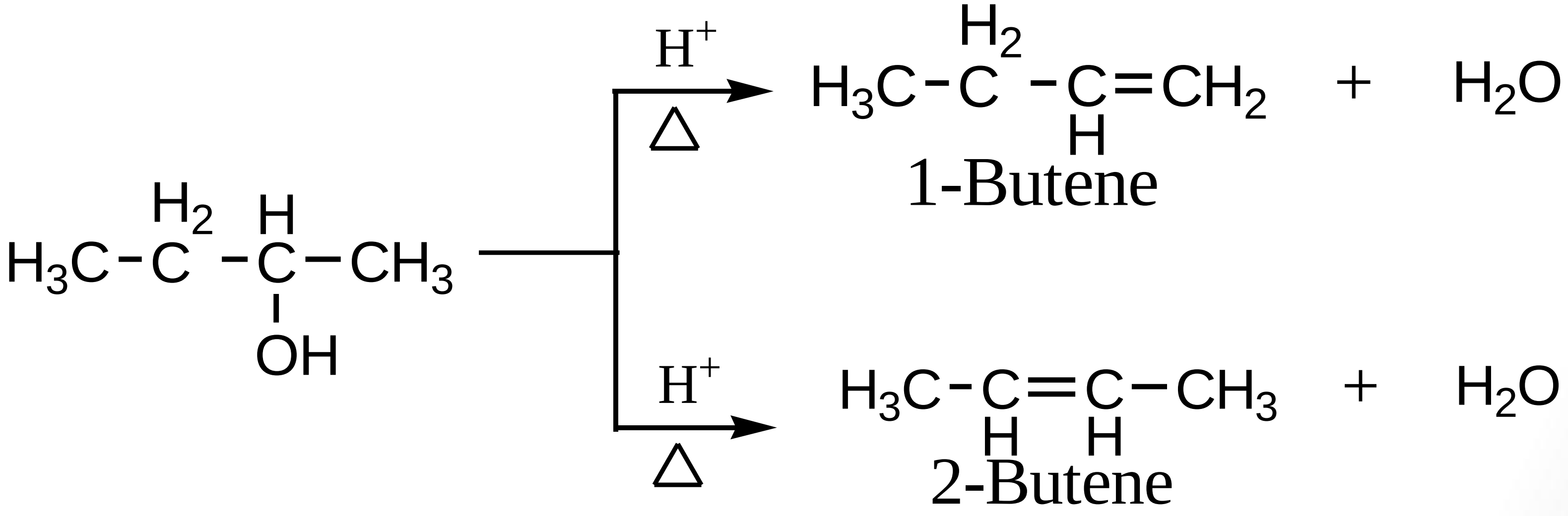
IUPAC name: Cyclohexanol Cyclohexene
Common name: Cyclohexyl alcohol



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

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

Example: the dehydration of 2-butanol.



Which Alkene Predominates?

Saytzeff's Rule

Saytzeff's Rule applies:

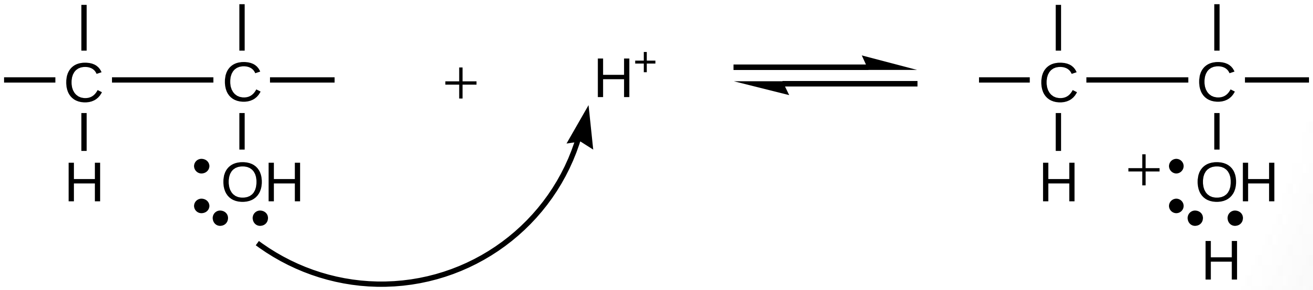
- Saytzeff's rule states that elimination reactions tend to give the most highly substituted alkene as the major product.
- **Applying Saytzeff's Rule to dehydration of 2-butanol**

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

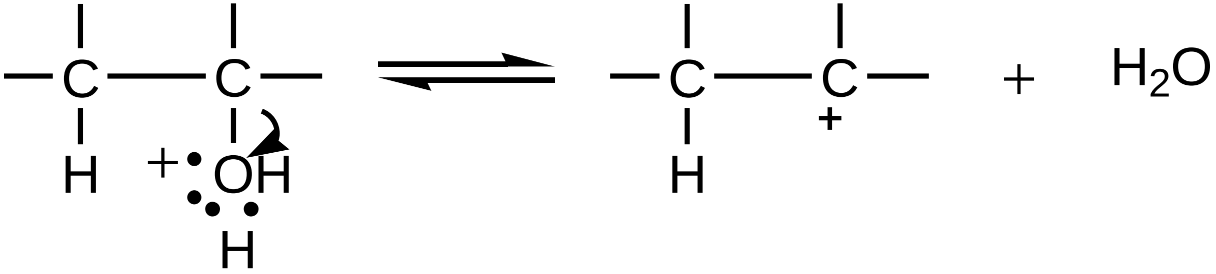
Mechanism of Dehydration of Alcohols

- **The dehydration of alcohols involves a carbocation, a reaction intermediate.**
- **The mechanism of dehydration basically involves the following three steps.**

Step 1. Protonation of the alcohol.

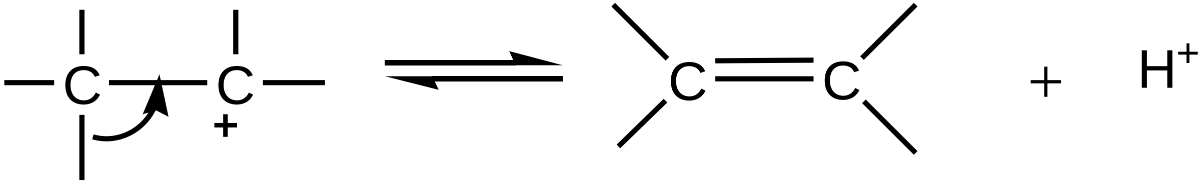


Step 2. Formation of a carbocation.



Step 3. Loss of a **proton** from the carbocation.

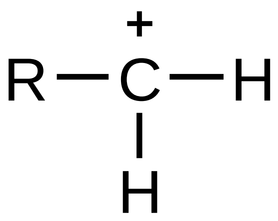
regenerates the acid catalyst and forms the alkene.



An alkene

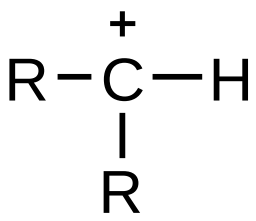
Classes of Carbocations and Ease of Dehydration of Alcohols

- **Carbocations are classified as**



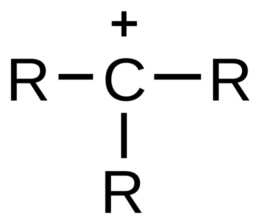
$$\mathrm{R}-\overset{+}{\underset{\substack{|\\ \mathrm{H}}}{\mathrm{C}}}-\mathrm{H}$$

1^{o} carbocation



$$\mathrm{R}-\overset{+}{\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C}}}-\mathrm{H}$$

2^{o} carbocation



$$\mathrm{R}-\overset{+}{\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C}}}-\mathrm{R}$$

3^{o} carbocation

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

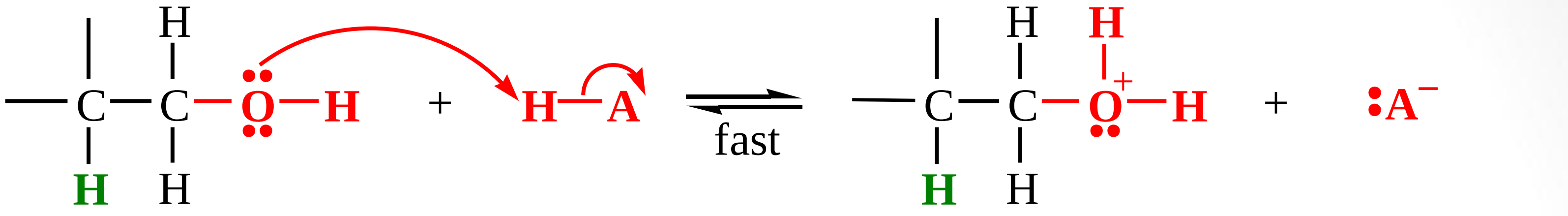
The ease of formation and the stabilities of carbocations follow the order

$$3^{o} > 2^{o} > 1^{o}$$

$$\xleftarrow{\qquad\qquad\qquad\qquad\qquad\qquad}$$

Ease of formation and stabilities of carbocations

Dehydration of a Primary Alcohol:



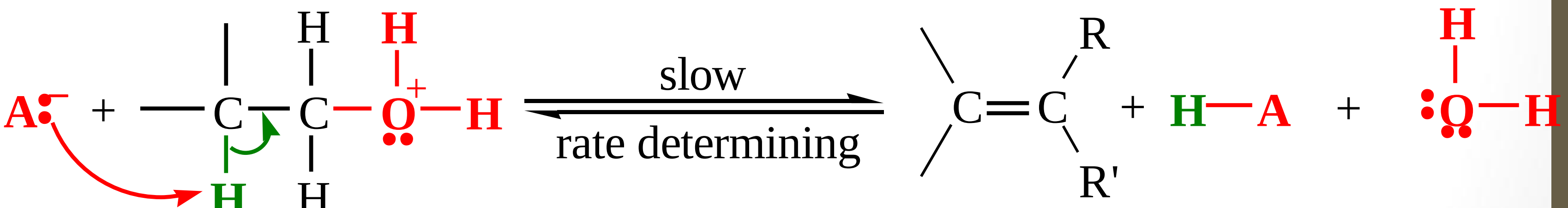
Primary alcohol

Strong acid (typically sulfuric or phosphoric acid)

Protonated alcohol

Conjugate base

The alcohol accepts a proton from the acid in a fast step.

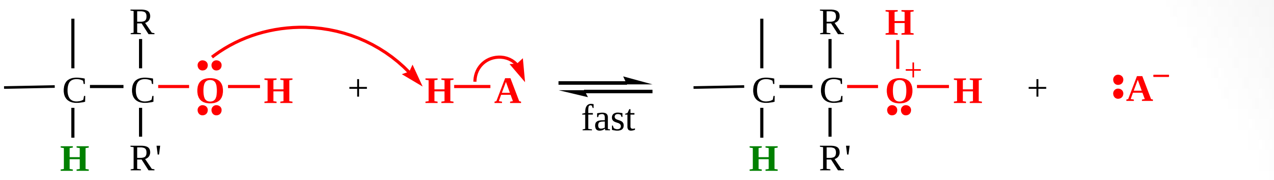


Alkene

A base removes a hydrogen from the β carbon as the double bond forms and the protonated hydroxyl group departs. (The base may be another molecule of the alcohol or the conjugate base of the acid)

Acid-Catalyzed Dehydration of Secondary or Tertiary Alcohols

Step 1



2^o or 3^o Alcohol (R' may be H)

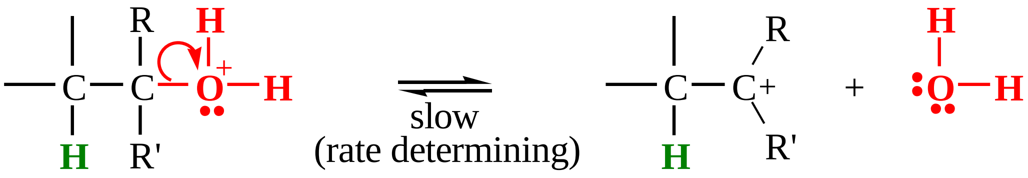
Strong acid (typically sulfuric or phosphoric acid)

Protonated alcohol

Conjugate base

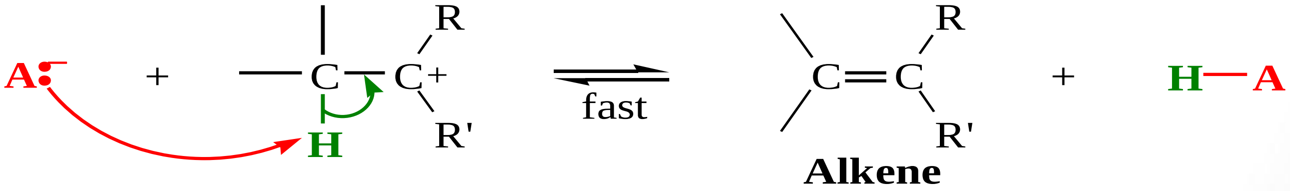
The alcohol accepts a proton from the acid in a fast step.

Step 2



The protonated alcohol loses a molecule of water to become a carbocation.
This step is slow and rate determining

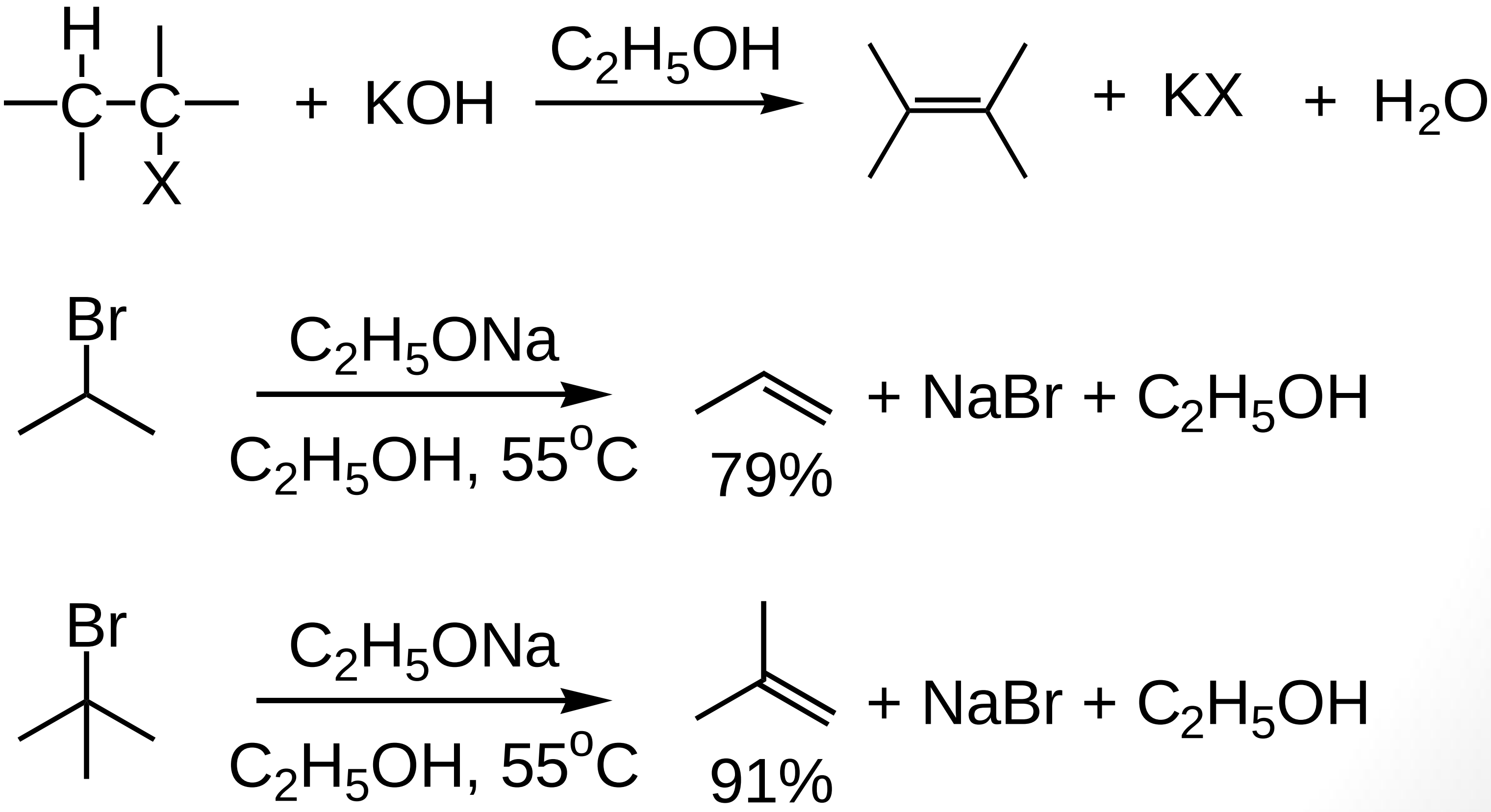
Step 3



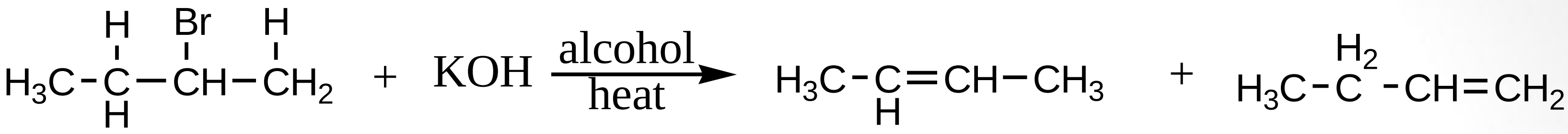
The carbocation loses a proton to a base. In this step, the base may be another molecule of the alcohol, water, or the conjugate base of the acid. The proton transfer results in the formation of the alkene. Note that the overall role of the acid is catalytic (it is used in the reaction and regenerated).

DEHYDROHALOGENATION OF ALKYL HALIDE

Dehydrohalogenation is the loss of a hydrogen and a halogen from an alkyl halide.



Apply Saytzeff's Rule

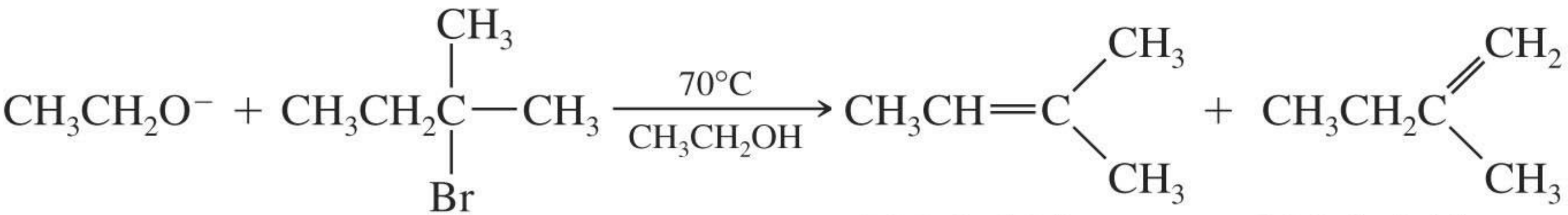


$$H_3C-\underset{H}{\overset{H}{C}}-\overset{Br}{CH}-\overset{H}{CH_2} + KOH \xrightarrow[heat]{alcohol} H_3C-\underset{H}{C}=CH-CH_3 + H_3C-\overset{H_2}{C}-CH=CH_2$$

2-Bromobutane

2-Butene
(major product)
(81%)

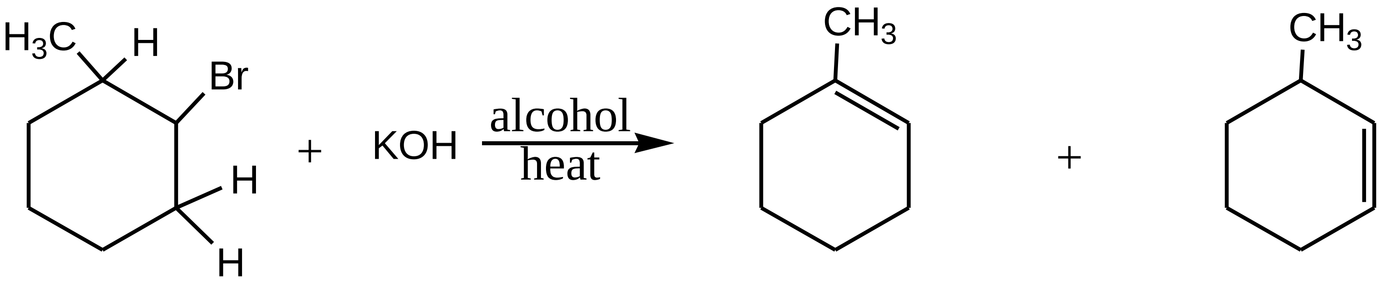
1-Butene
(minor product)
(19%)



$$CH_3CH_2O^- + CH_3CH_2\underset{Br}{\overset{CH_3}{C}}-CH_3 \xrightarrow[CH_3CH_2OH]{70°C} CH_3CH=C\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} + CH_3CH_2C\begin{matrix}\diagup\!\!\!\diagup CH_2\\ \diagdown CH_3\end{matrix}$$

2-Methyl-2-butene
(69%)
(more stable)

2-Methyl-1-butene
(31%)
(less stable)



1-Methylcyclohexene
(major product)

3-Methylcyclohexene
(minor product)

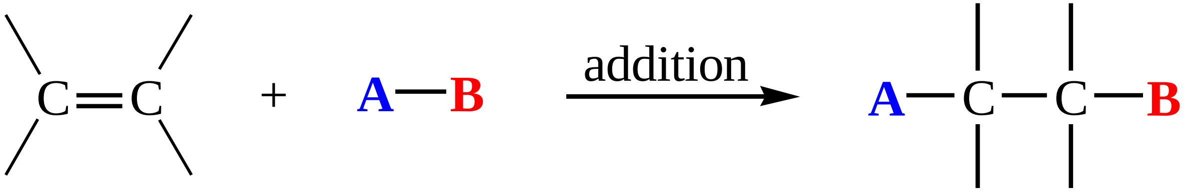
Reactions of Alkenes

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

  (1) Addition reactions that involve the carbon—carbon double bond

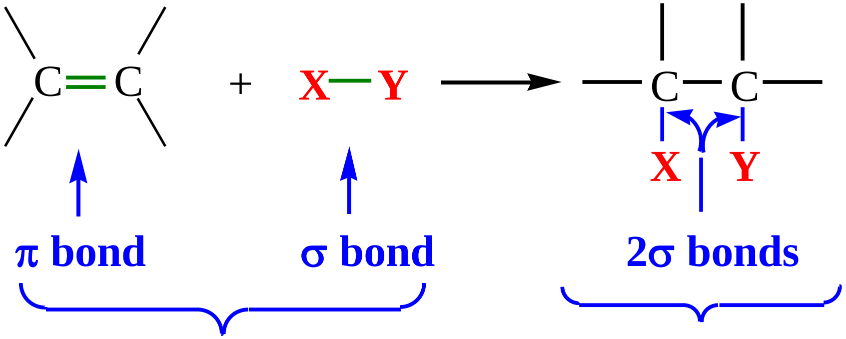
  (2) Substitution reactions that usually involve the saturated alkyl chain.

Additions to Alkenes



Characteristics of the double bond:

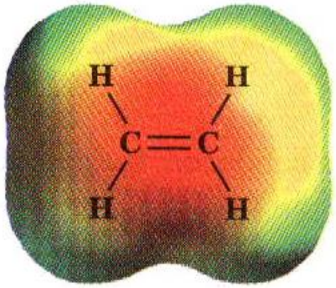
1. An addition results in the conversion of one p bond and one s bond into two s bonds:
   i- pi bonds are weaker than that of sigma binds ⇒ energetically favorable.



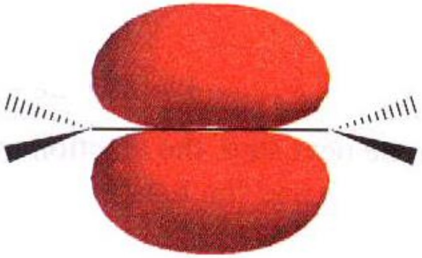
π bond **σ bond** **2σ bonds**

Bonds broken **Bond formed**

2. The electrons of the p bond are exposed ⇒ the **p bond is particularly susceptible to electrophiles** (electron-seeking reagents).



An electrostatic potential map for ethane shows the higher density of negative charge in the region of the π bond.



The electron pair of the π bond is distributed throughout both lobes of the π molecular orbital.

1) **Electrophilic**: means electron-seeking.

Examples of Electrophilic:

i) **Positive reagents**: protons (H^+), alkyl group R^+ , nitronium ion (NO_2^+), etc.…

ii) **Neutral reagents having positively polarized centers**: HCl, bromine (because it can be polarized so that one end is positive).

iii) **Lewis acids**: molecules or ions that can accept an electron pair ⇒ BF_3 and $AlCl_3$.

iv) **Metal ions** that contain vacant orbitals: the silver ion (Ag^+), the mercuric ion (Hg^{2+}), and the platinum ion (Pt^{2+}).

A **nucleophile:** is a reagent that seeks **positive center.** It is a species with an **unshared electron pair** (**lone-pair electrons)**

A ***nucleophile*** is any **negative ion** or any **neutral molecule** that has at least **one unshared electron pair**.

a) Negative ions :

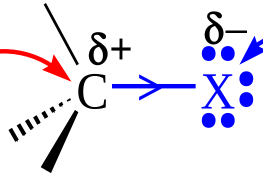
e.g. $H\ddot{\underset{\cdot\cdot}{O}}\colon^{-}$ Hydroxide ion, $H\ddot{\underset{\cdot\cdot}{S}}\colon^{-}$ Hydrosulphide ion, $R\ddot{\underset{\cdot\cdot}{O}}\colon^{-}$ Alkoxide ions,

$\colon N\equiv C\colon^{-}$ Cyanide ion, $\colon\ddot{\underset{\cdot\cdot}{X}}\colon^{-}$ Halide ions, ...etc.

b) Neutral molecules :

e.g. $H_2\ddot{\underset{\cdot\cdot}{O}}$, $R—\ddot{\underset{\cdot\cdot}{O}}—H$, $R—\ddot{\underset{\cdot\cdot}{O}}—R$, $H_3\ddot{N}$, $R_3\ddot{N}$, ...etc.

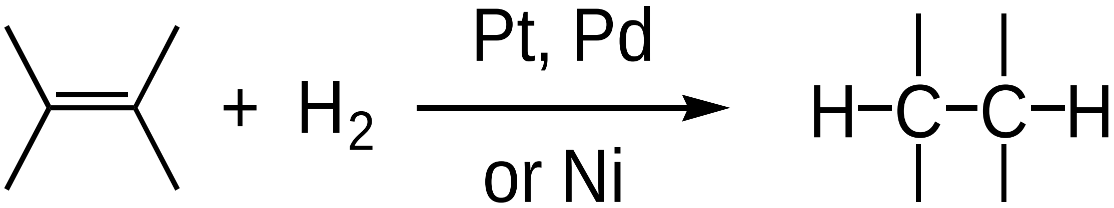
This is the postive center that the nuceophile seeks.



The electronegative halogen polarizes the C–X bond.

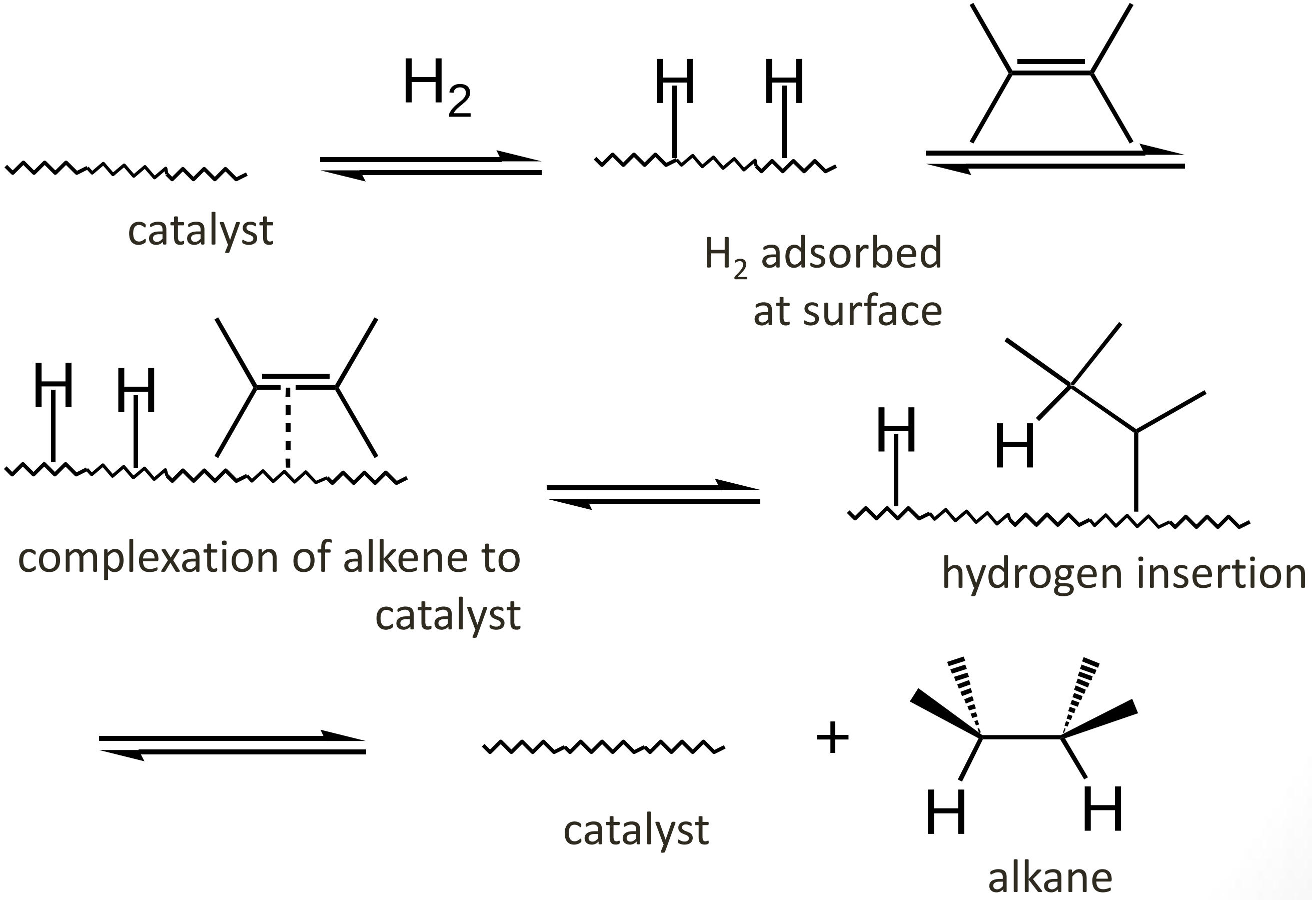
1. Addition of Hydrogen: Catalytic Hydrogenation

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



Heat of hydrogenation : the heat liberated during this reaction. ΔH is ~125 kJ/mol for each double bond in the compound.

Mechanism of alkene hydrogenation



catalyst

H_2 adsorbed at surface

complexation of alkene to catalyst

hydrogen insertion

catalyst

alkane

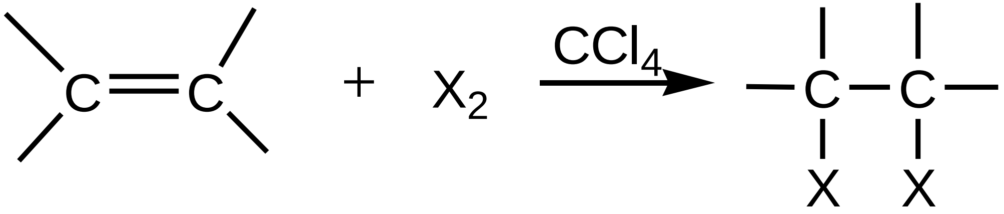
2. Addition of Halogens: Halogenation

- **When an alkene is treated at room temperature with a solution of bromine or chlorine in carbon tetrachloride.**

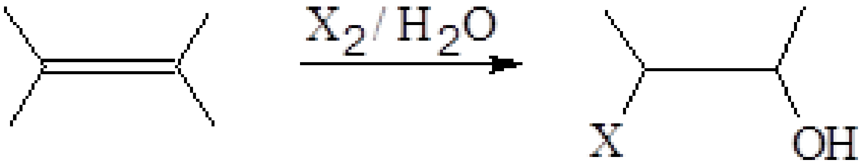
the halogen adds rapidly to the double bond of the alkene to give the corresponding vicinal dihalide

(two halogens attached to adjacent carbons).

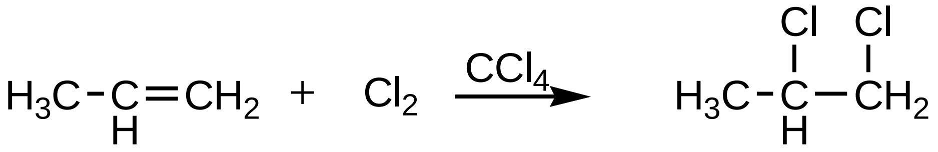
General equation



(X = Cl or Br)

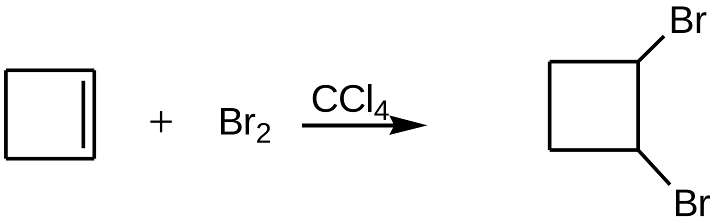


Specific examples;



$$H_3C-\underset{H}{C}=CH_2 + Cl_2 \xrightarrow{CCl_4} H_3C-\underset{H}{\overset{Cl}{C}}-\overset{Cl}{C}H_2$$

Propene 1,2-Dichloropropane

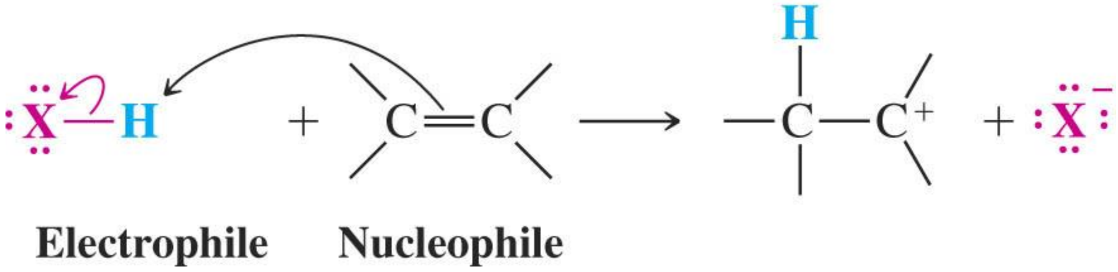


Cyclobutene 1,2-Dibromocyclobutane

- **Iodine** is **too unreactive** and will not add to the double bond of an alkene.

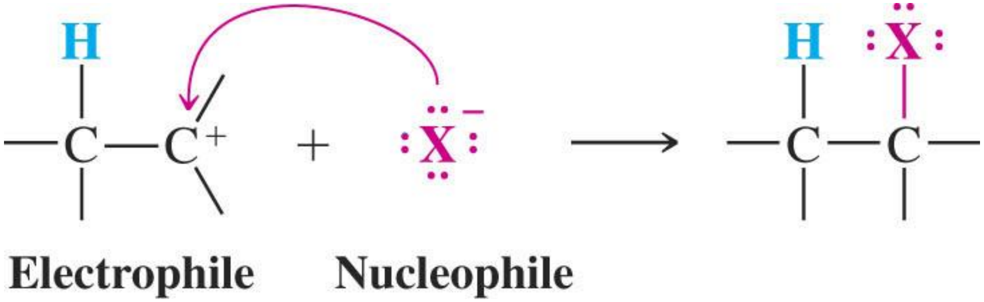
- **Fluorine** is **too reactive** and reacts explosively with an alkene.

3. Electrophilic Addition to Alkenes: Addition of Acids



$HX = HCl, HBr, HI$

In addition reactions the alkene changes from a nucleophile in the first step to an electrophile in the second



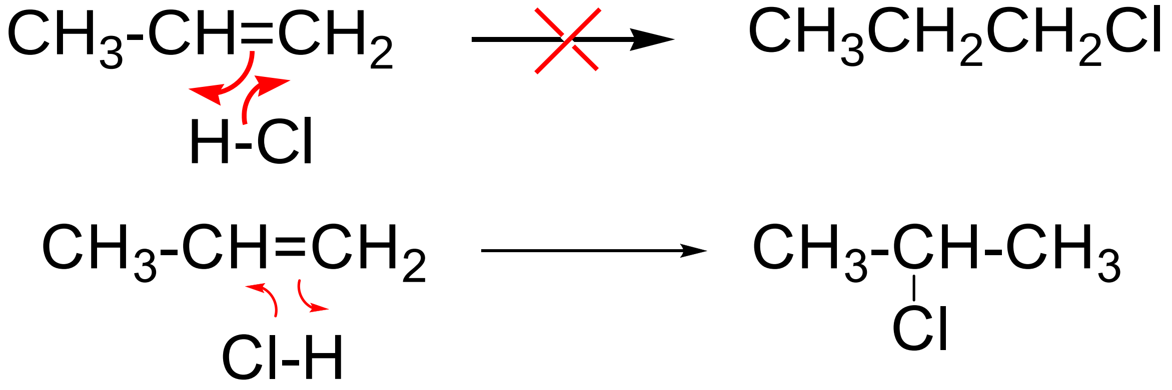
Addition of hydrogen halides

$$H_2C{=}CH_2 \;+\; HCl \longrightarrow CH_3CH_2Cl$$

only one product is possible, chloroethane

but....

$$CH_3\text{-}CH{=}CH_2 \longrightarrow ?$$

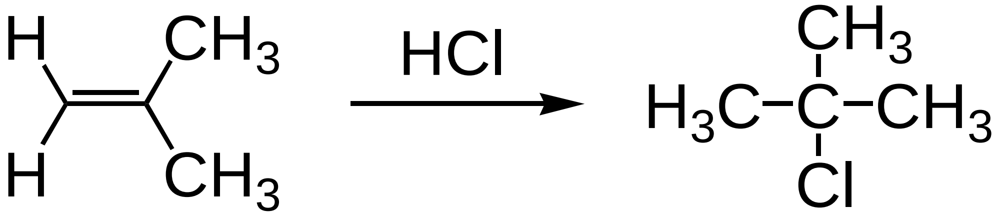


$$\underset{H\text{-}Cl}{CH_3\text{-}CH{=}CH_2} \;\not\longrightarrow\; CH_3CH_2CH_2Cl$$

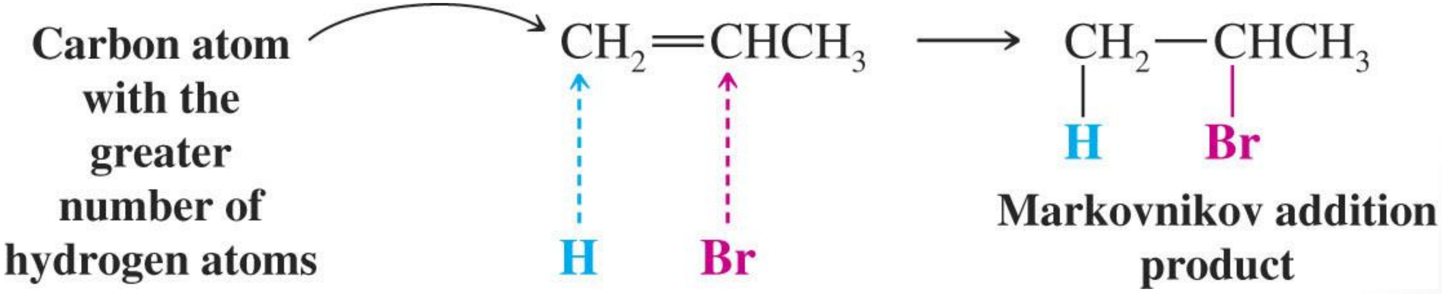
$$\underset{Cl\text{-}H}{CH_3\text{-}CH{=}CH_2} \longrightarrow CH_3\text{-}\underset{\underset{\displaystyle Cl}{|}}{CH}\text{-}CH_3$$

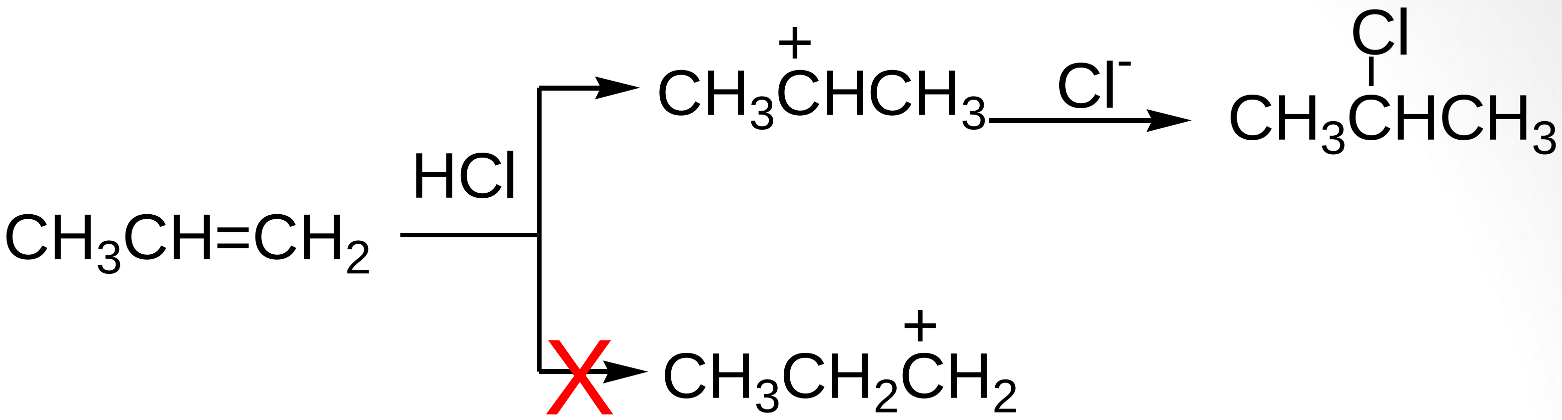
Only 2-chloropropane is formed

Markovnikov’s rule



In 1869, *Markovnikov* proposed that : addition of HX to an alkene proceeds so that the hydrogen atom adds to the carbon that already has the most hydrogen atoms

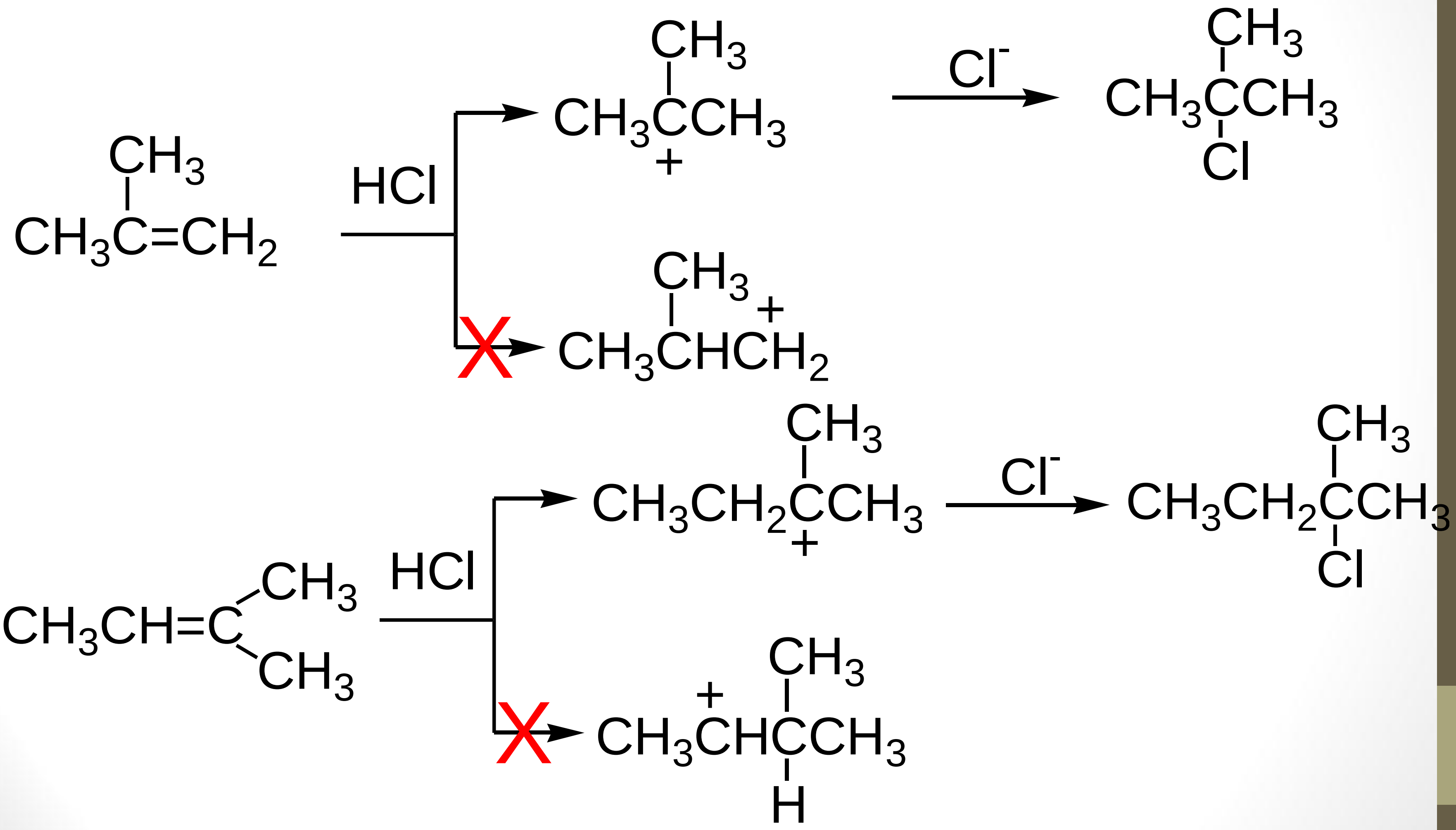




$$CH_3CH{=}CH_2 \xrightarrow{HCl} CH_3\overset{+}{C}HCH_3 \xrightarrow{Cl^-} CH_3\overset{\overset{Cl}{|}}{C}HCH_3$$

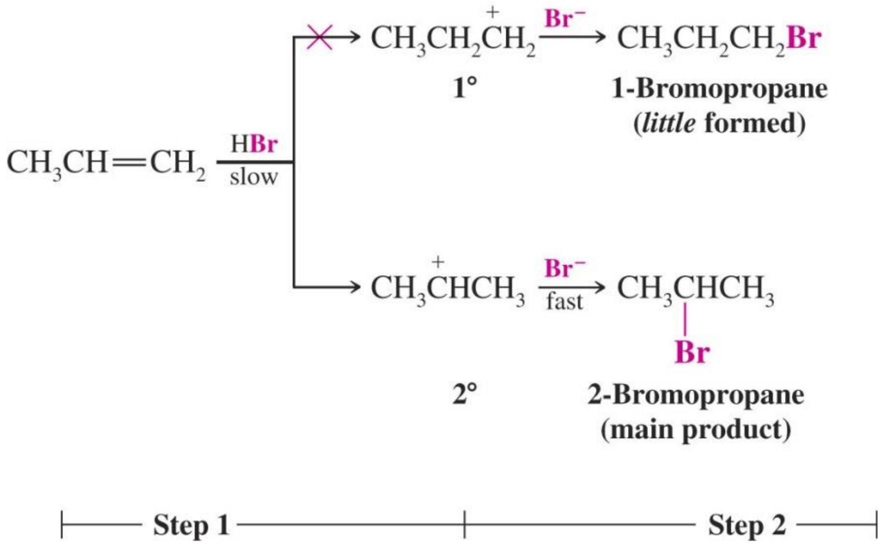
$$CH_3CH{=}CH_2 \xrightarrow{HCl} \cancel{\rightarrow}\ CH_3CH_2\overset{+}{C}H_2$$

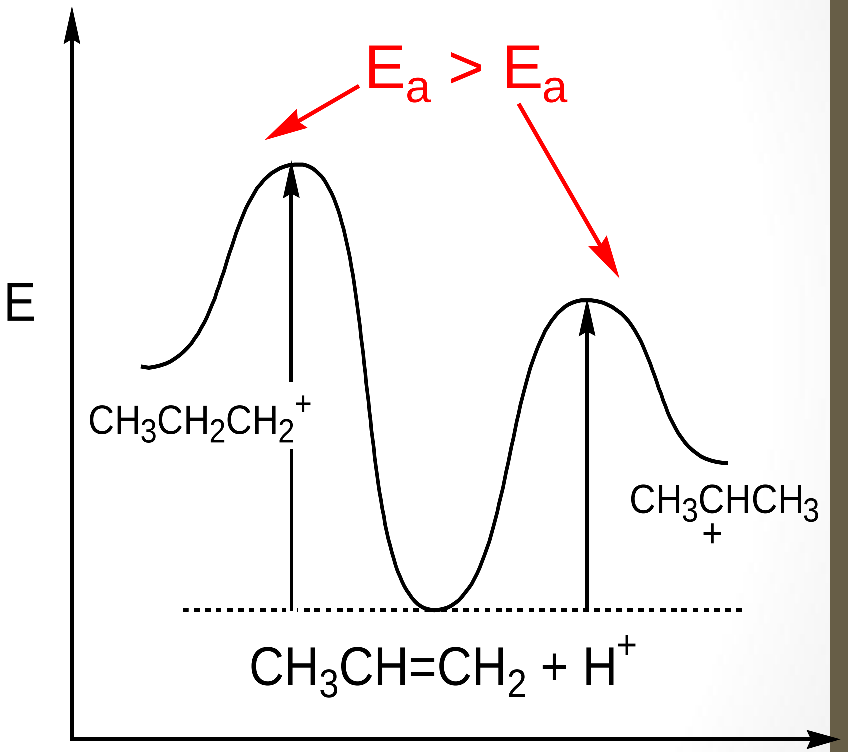
Orientation



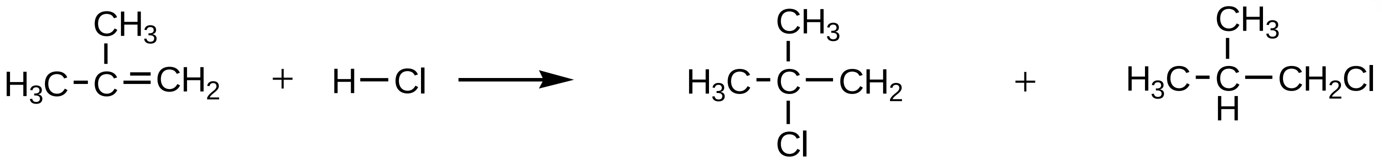
Theoretical Explanation of Markovnikov's Rule

The product with the more stable carbocation intermediate predominates





Addition of HCl to 2-methylpropene



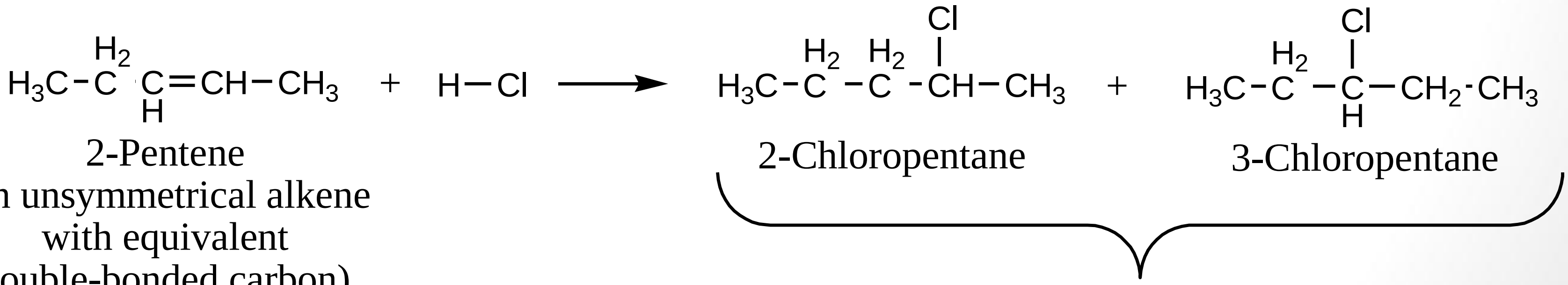
$$H_3C-\overset{CH_3}{\overset{|}{C}}=CH_2 + H-Cl \longrightarrow H_3C-\overset{CH_3}{\underset{Cl}{C}}-CH_2 + H_3C-\overset{CH_3}{\underset{H}{C}}-CH_2Cl$$

2-Chloro-2-methylpropane (major product)

1-Chloro-2-methylpropane (minor product)

- **In some *unsymmetrical alkenes* the two double-bonded carbons may be equivalent**

  Equimolar mixture of the two possible addition products is obtained.



$$H_3C-\overset{H_2}{C}-\underset{H}{C}=CH-CH_3 + H-Cl \longrightarrow \underbrace{H_3C-\overset{H_2}{C}-\overset{H_2}{C}-\overset{Cl}{CH}-CH_3 + H_3C-\overset{H_2}{C}-\overset{Cl}{\underset{H}{C}}-CH_2-CH_3}_{\text{Equimolar mixtures}}$$

2-Pentene
(an unsymmetrical alkene
with equivalent
double-bonded carbon)

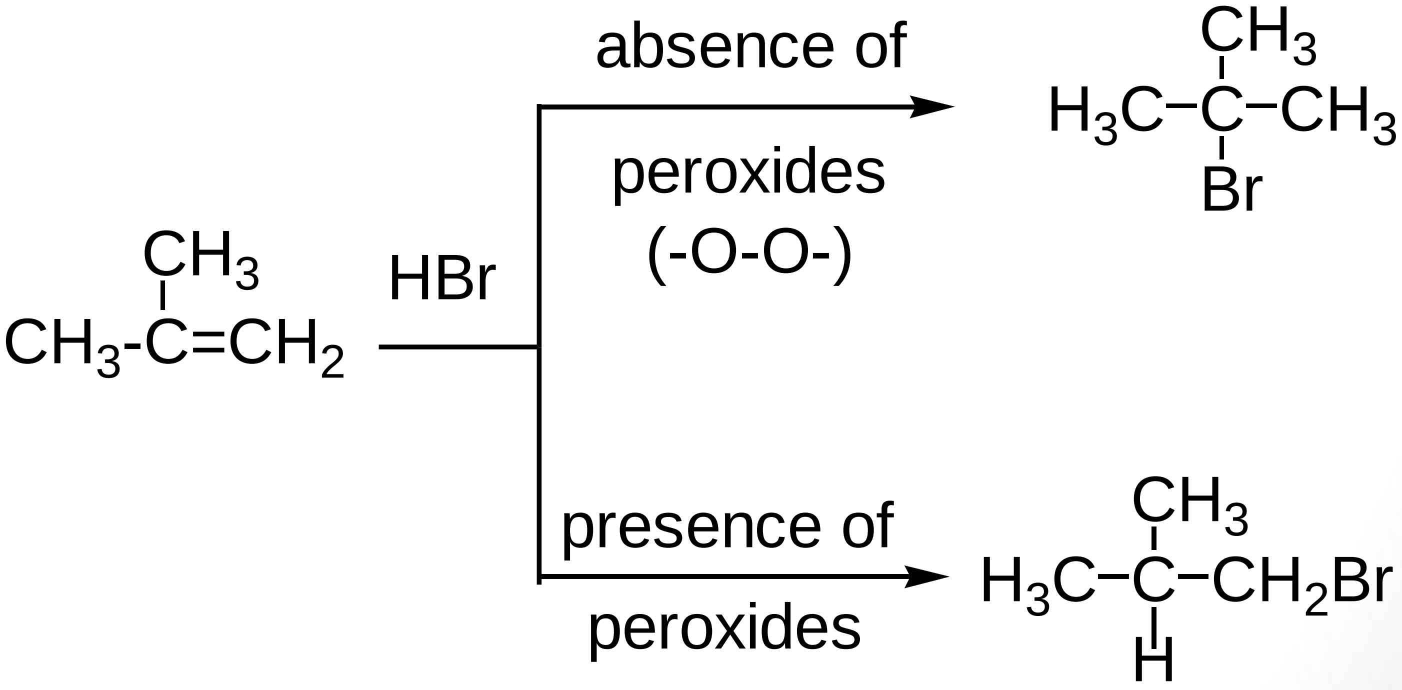
2-Chloropentane

3-Chloropentane

Equimolar mixtures

HBr - the peroxide effect

1933, Kharasch and Mayo found that:



$$CH_3\text{-}\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{HBr}$$

absence of peroxides (-O-O-)

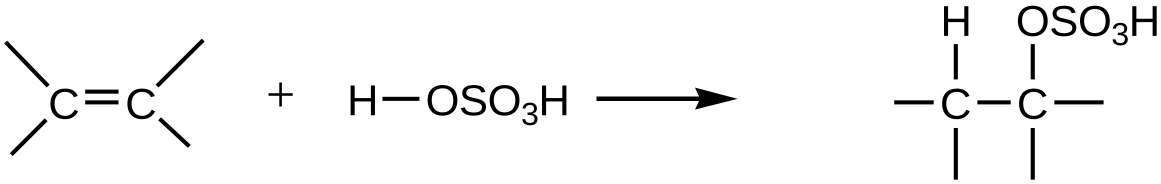
$$H_3C-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

presence of peroxides

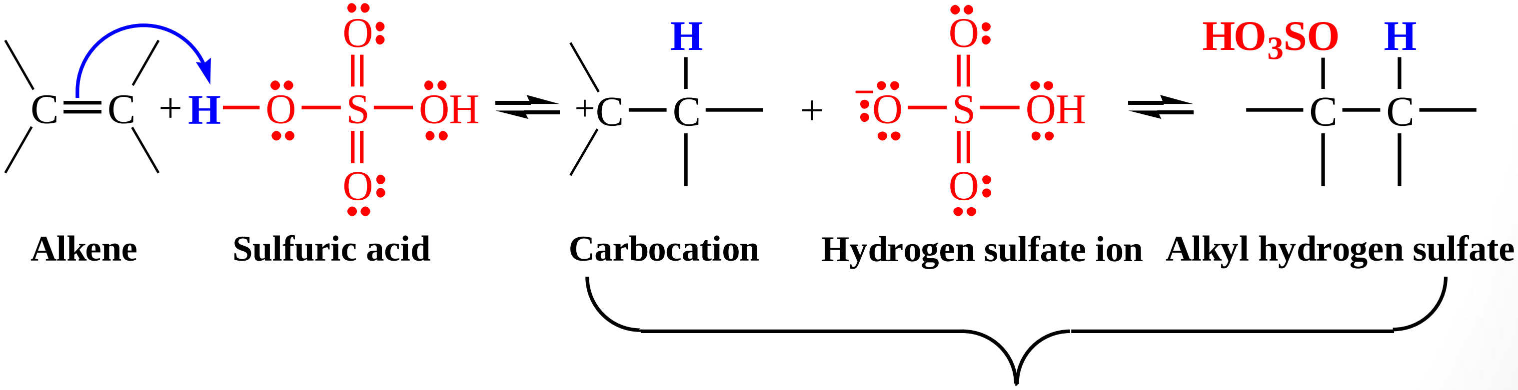
$$H_3C-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2Br$$

Addition of sulfuric acid

General equation for this reaction is

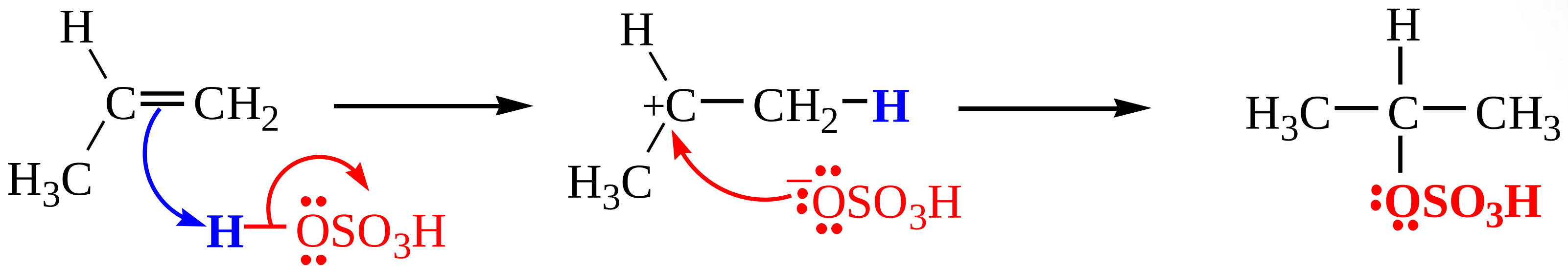


An alkyl hydrogen sulfate



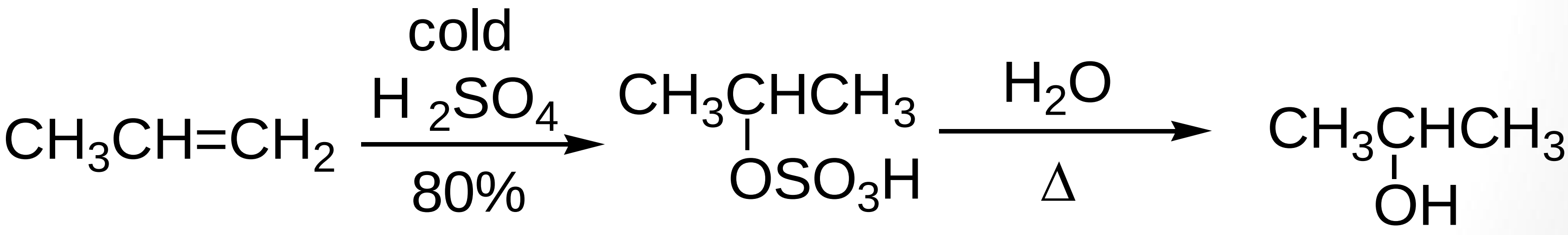
Soluble in sulfuric acid

The addition of H_2SO_4 follows Markovnikov's rule:



2^{o} Carbocaion
(more stable carbocation)

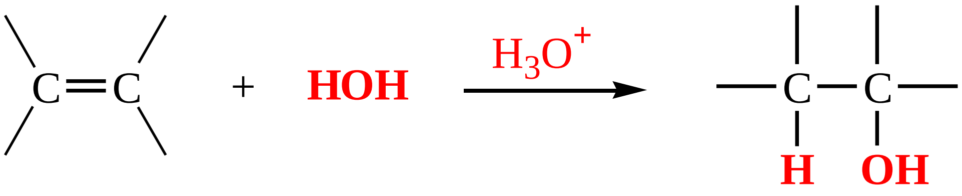
Isopropyl hydrogen sulfate

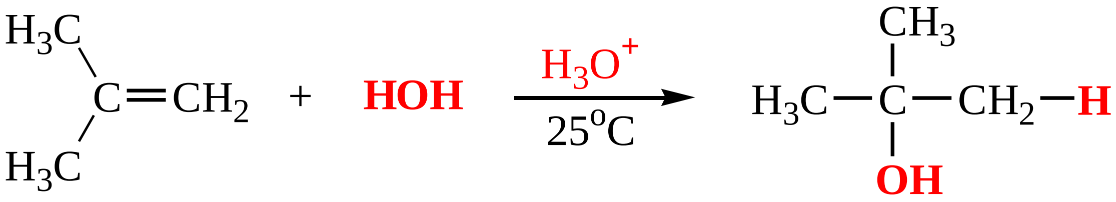


$$CH_3CH{=}CH_2 \xrightarrow[80\%]{\text{cold } H_2SO_4} \underset{OSO_3H}{CH_3CHCH_3} \xrightarrow[\Delta]{H_2O} \underset{OH}{CH_3CHCH_3}$$

ADDITION OF WATER TO ALKENES:
ACID-CATALYZED HYDRATION

1. The acid-catalyzed addition of water to the double bond of an alkene is a method for the preparation of low molecular weight alcohols.
   - a)The acids most commonly used to catalyze the hydration of alkenes are dilute solutions of sulfuric acid and phosphoric acid.
   - b)The addition of water to a double bond is usually regioselective and follows Markovnikov's rule.





2-Methylpropene
(isobutylene)

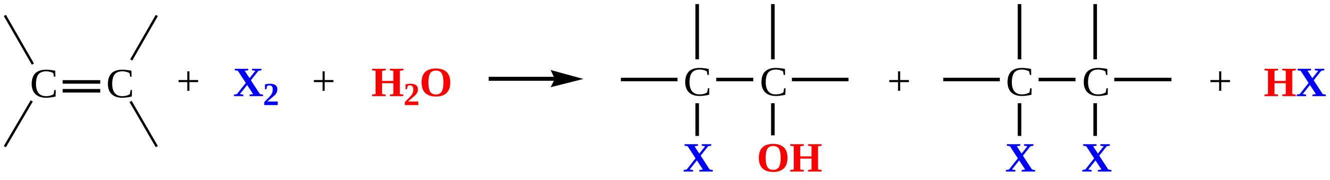
***tert*-Butyl alcohol**

2. The acid-catalyzed hydration of alkenes follows Markovnikov’s rule
   ⇒ the reaction does not yield 1° alcohols except in the special case of the hydration of ethene.

$$H_2C{=}CH_2 \; + \; \mathbf{HOH} \xrightarrow[300^{o}C]{H_3PO_4} CH_3CH_2OH$$

Addition of HOX: Halohydrin Formation

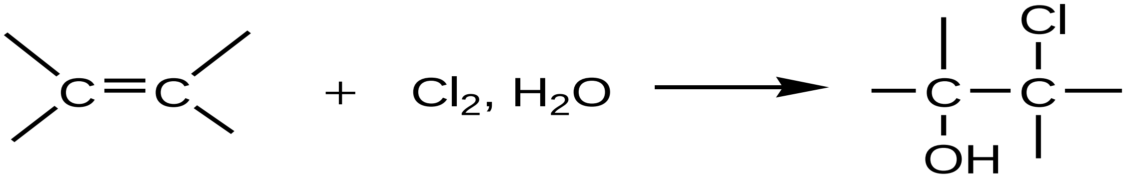
When an alkene is reacted bromine in aqueous solution (rather than CCl_4), the major product is a **halohydrin** (**halo alcohol**).



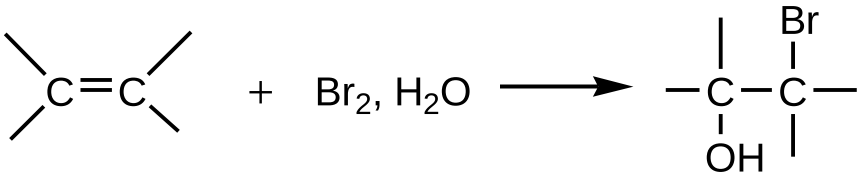
X = Cl or Br

Halohydrin (major)

***vic*-Dihalide (minor)**



A chlorohydrin



A bromohydrin

The reaction proceeds as if hypochlorous acid, HO—Cl, or hypobromous acid, HO—Br, were the adding reagent.

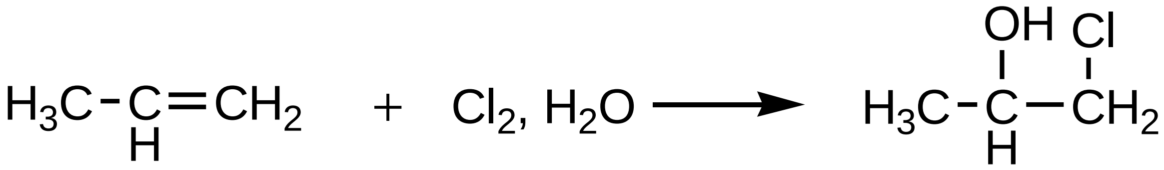
- The electrophile is

  chloronium ion, Cl^+, or bromonium ion, Br^+.

- The nucleopbile is

  hydroxide ion, OH^-.

- Addition of HOX also follows Markovnikov's rule.



$$H_3C-CH=CH_2 + Cl_2, H_2O \longrightarrow H_3C-CH(OH)-CH_2Cl$$

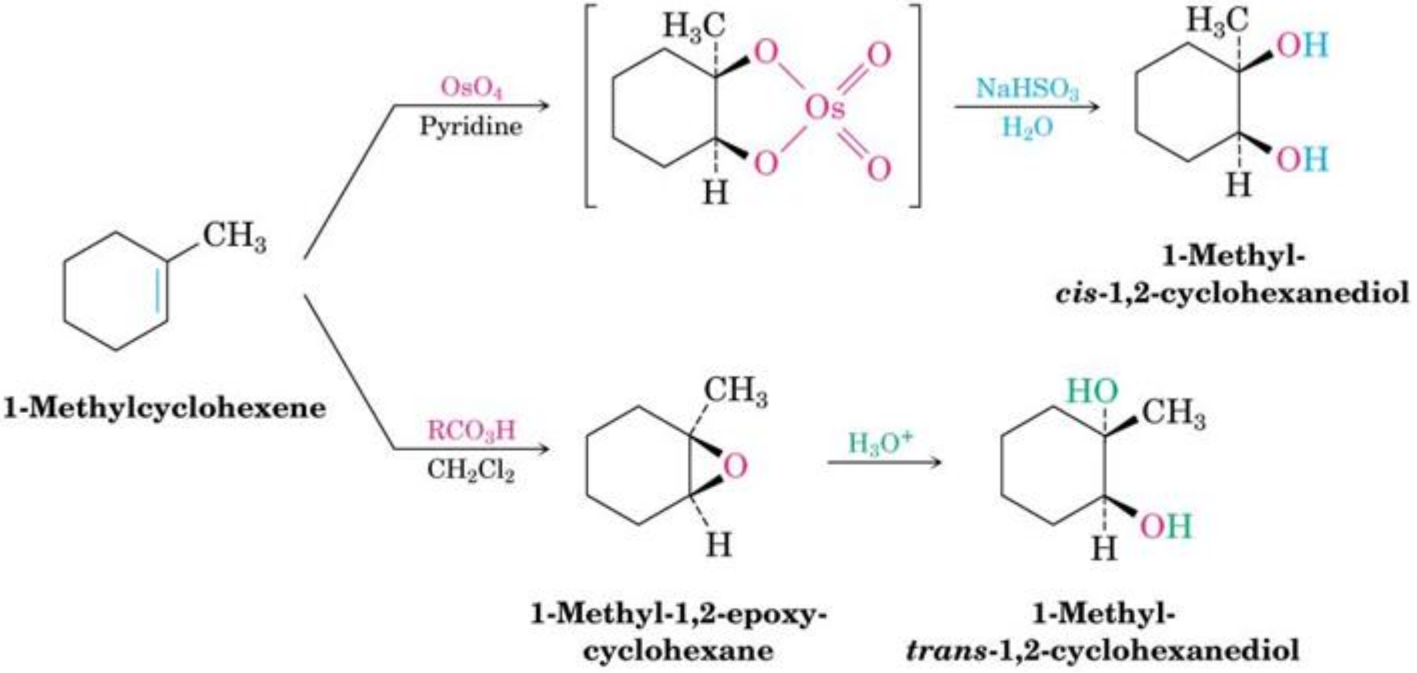
Propene

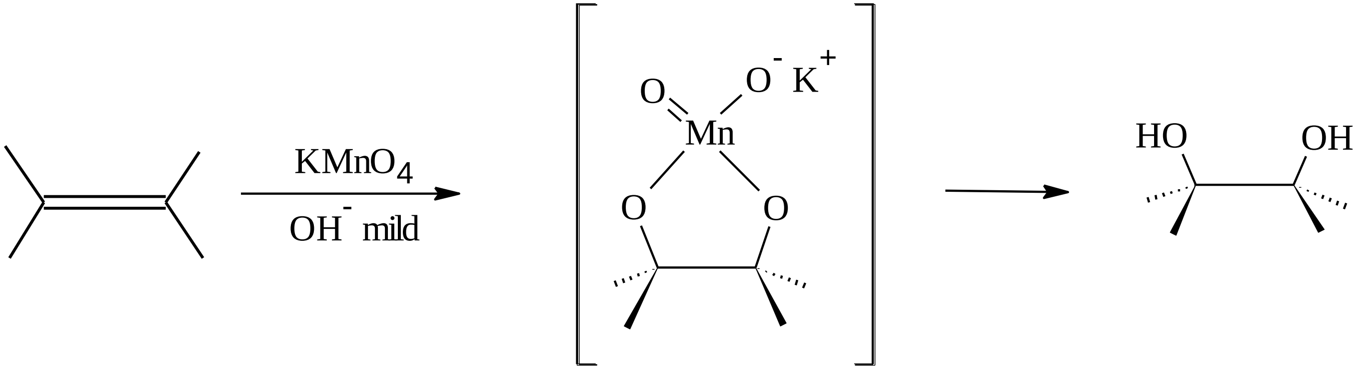
Propane chlorohydrin
(1-Chloro-2-propanol)

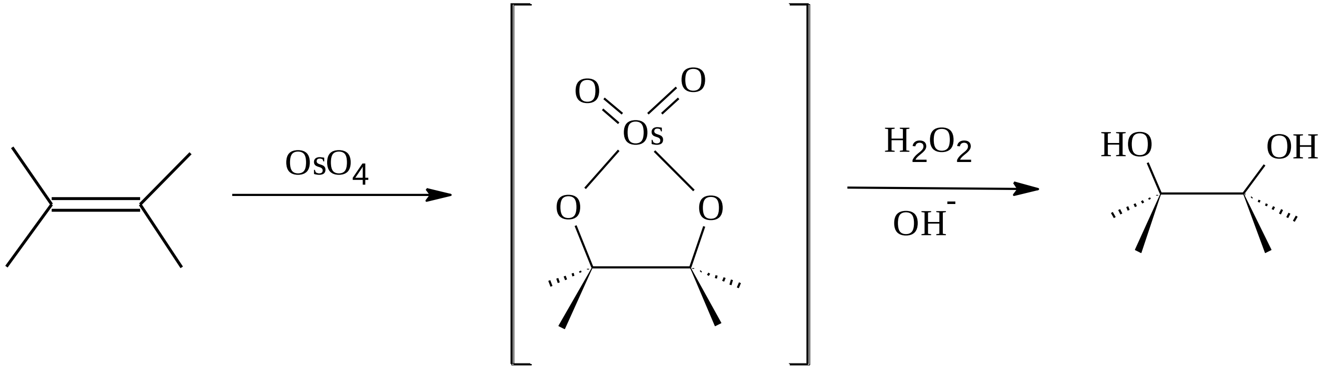
OXIDATION: **Preparation of 1,2-Diols**

Formation of *cis* 1,2-diols can be done by hydroxylation of an alkene with OsO_4 followed by reduction with $NaHSO_3$

Formation of : *Trans*-1,2-diols can be done by acid-catalyzed hydrolysis of *epoxides*



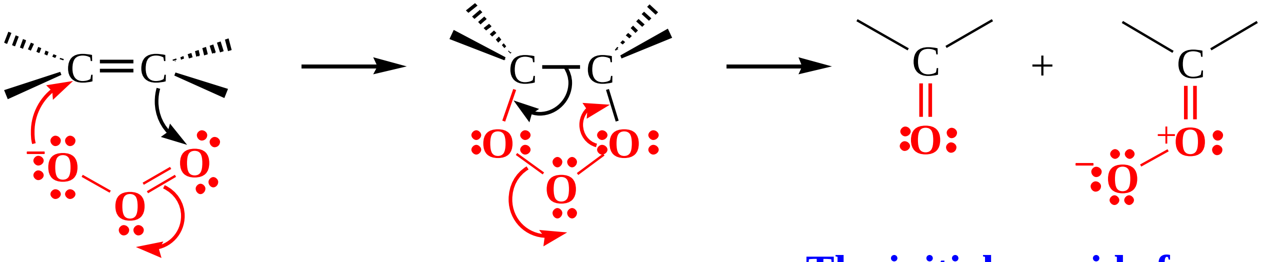

KMnO$_4$
OH$^-$ mild
O
O$^-$ K$^+$
Mn
O
O
HO
OH


OsO$_4$
O
O
Os
O
O
H$_2$O$_2$
OH$^-$
HO
OH

Ozonolysis of Alkenes

1. Ozone reacts vigorously with alkenes to form unstable ***initial ozonides*** (***molozonides***) which rearrange spontaneously to form **ozonides**.

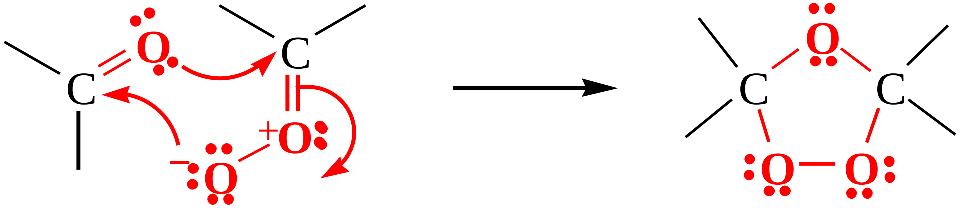
   a)The rearrangement is thought to go through dissociation of the initial ozonide into reactive fragments that recombine to give the ozonide.



Ozone adds to the alkene to form an initial ozonide.

Initial ozonide

The initial ozonide fragments.



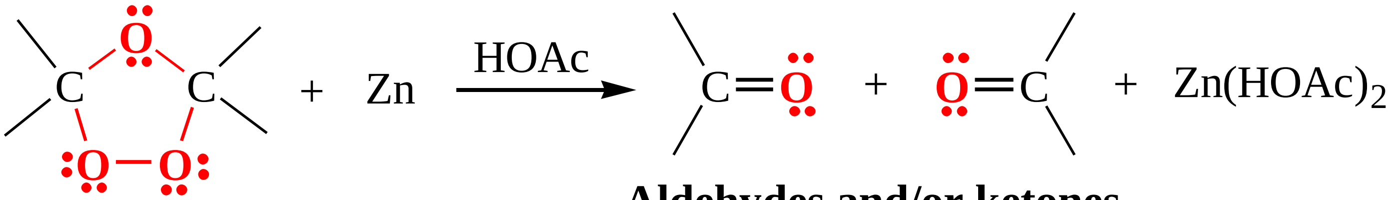
The fragments recombine to form the ozonide.

Ozonide

2.Ozonides are very unstable compounds and low molecular weight ononides often explode violently.

a) Ozonides are not usually isolated but are reduced directly by treatment with znic and acetic acid (HOAc).

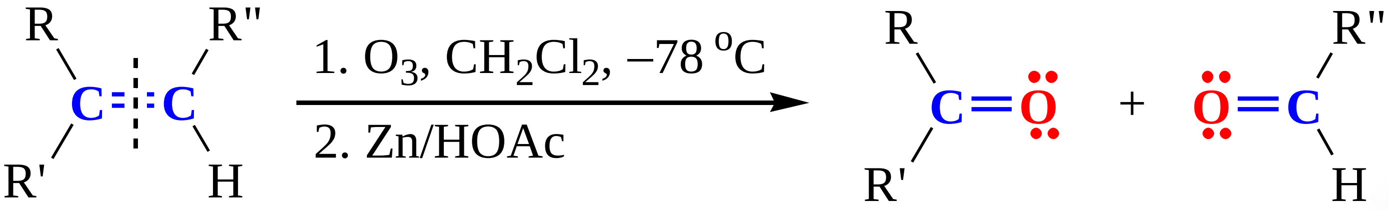
b) The reduction produces carbonyl compounds (aldehydes or ketones) that can be safely isolated and identified.



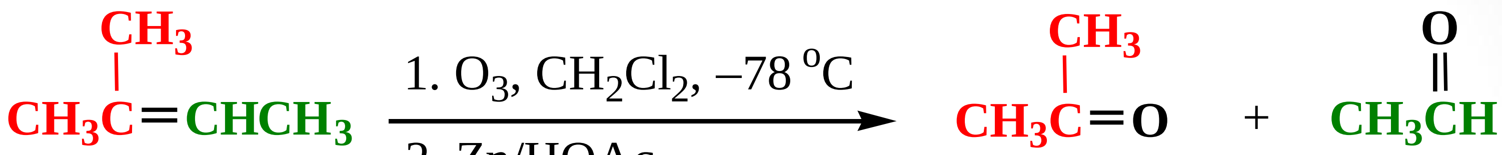
Ozonide

Aldehydes and/or ketones

The overall process of onzonolysis is:

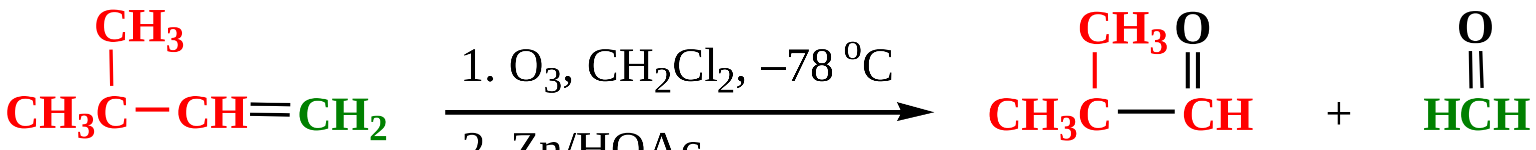


Examples :



$$CH_3\overset{\overset{CH_3}{|}}{C}=CHCH_3 \xrightarrow[\text{2. Zn/HOAc}]{\text{1. }O_3,\ CH_2Cl_2,\ -78\ ^{o}C} CH_3\overset{\overset{CH_3}{|}}{C}=O + CH_3\overset{\overset{O}{\|}}{C}H$$

2-Methyl-2-butene **Acetone** **Acetaldehyde**

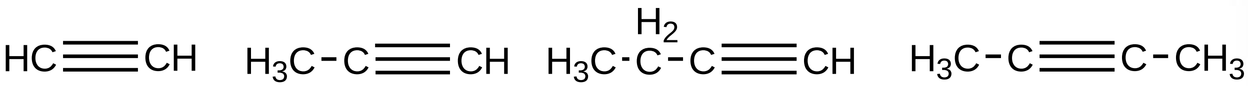


$$CH_3\overset{\overset{CH_3}{|}}{C}-CH=CH_2 \xrightarrow[\text{2. Zn/HOAc}]{\text{1. }O_3,\ CH_2Cl_2,\ -78\ ^{o}C} CH_3\overset{\overset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}H + H\overset{\overset{O}{\|}}{C}H$$

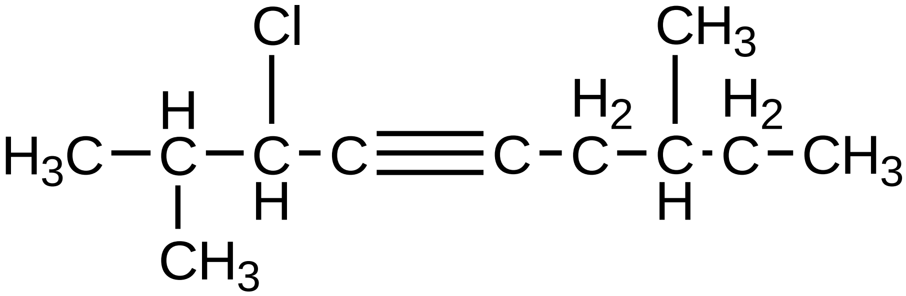
3-Methyl-1-butene **Isobutyraldehyde** **Formaldehyed**

Nomenclature of Alkynes

- **The simplest members of the alkynes series (C_2 & C_3) derived from the corresponding alkanes by replacing the –ane ending by –yne.**



	$HC\equiv CH$	$H_3C-C\equiv CH$	$H_3C-\overset{H_2}{C}-C\equiv CH$	$H_3C-C\equiv C-CH_3$
IUPAC name:	Ethyne	Propyne	1-Butyne	2-Butyne
Common name:	Acetylene			



$$H_3C-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-C\equiv C-\overset{H_2}{C}-\underset{H}{\overset{CH_3}{C}}-\overset{H_2}{C}-CH_3$$

3-Chloro-2,7-dimethyl-4-nonyne

Physical Properties of Alkynes

- The physical properties of alkynes are much the same as those of corresponding alkanes.

C_2 to C_4 alkenes are gases

C_5 to C_{18} alkenes are liquids

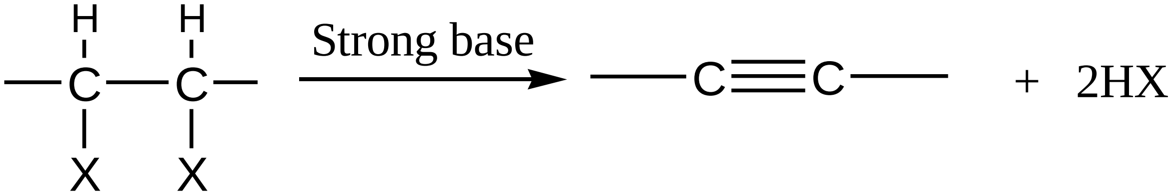
above C_{18} are solids.

- Alkynes are insoluble in water and soluble in nonpolar organic solvents such as benzene or in carbon tetrachloride.

Preparation of Alkynes

Dehydrohalogenation of Alkyl dihalides

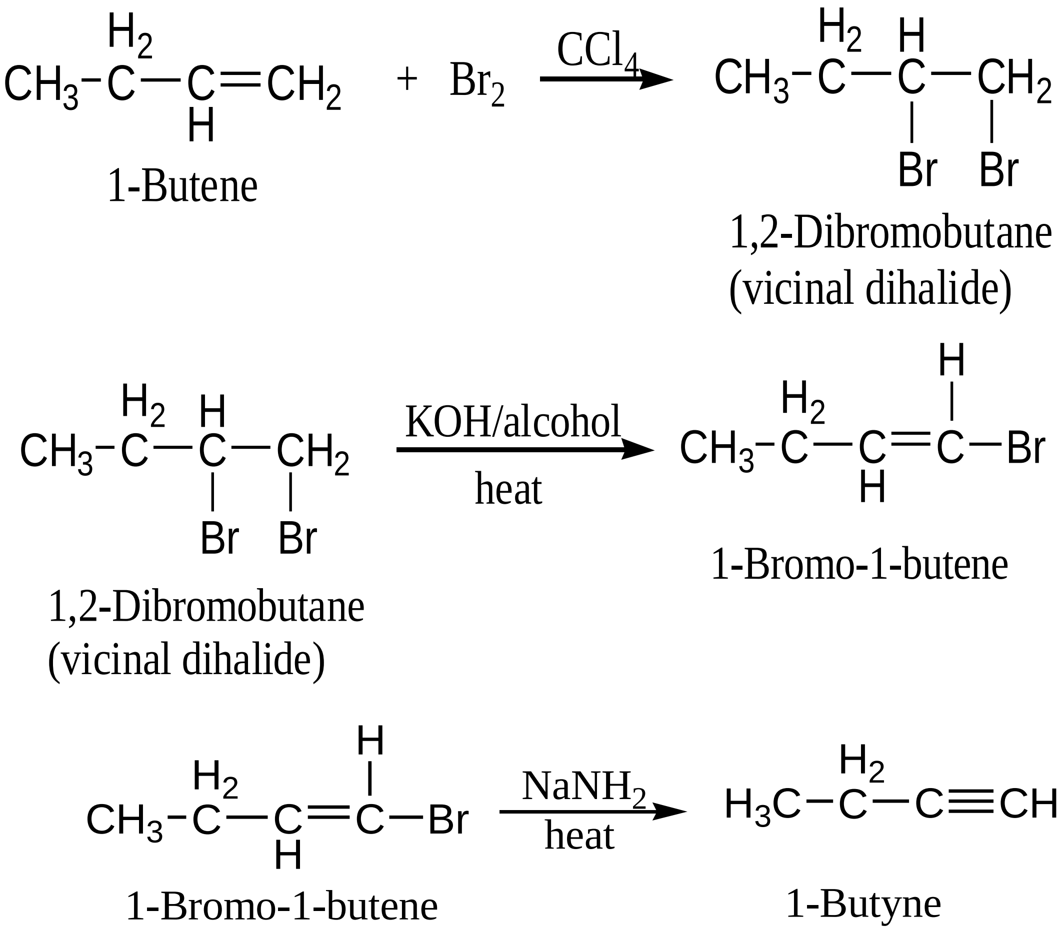
- Treatment of vicinal dihalides with strong base followed by sodium amide.



- Vicinal diahalides are obtained by addition of halogen to alkenes.
- This general method for the conversion of alkenes to alkynes.

Preparation of Alkynes

Dehydrohalogenation of Alkyl dihalides



$$CH_3-\overset{H_2}{C}-\underset{H}{C}=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3-\overset{H_2}{C}-\underset{Br}{\overset{H}{C}}-\underset{Br}{CH_2}$$

1-Butene

1,2-Dibromobutane
(vicinal dihalide)

$$CH_3-\overset{H_2}{C}-\underset{Br}{\overset{H}{C}}-\underset{Br}{CH_2} \xrightarrow[\text{heat}]{\text{KOH/alcohol}} CH_3-\overset{H_2}{C}-\underset{H}{C}=\overset{H}{C}-Br$$

1,2-Dibromobutane
(vicinal dihalide)

1-Bromo-1-butene

$$CH_3-\overset{H_2}{C}-\underset{H}{C}=\overset{H}{C}-Br \xrightarrow[\text{heat}]{NaNH_2} H_3C-\overset{H_2}{C}-C\equiv CH$$

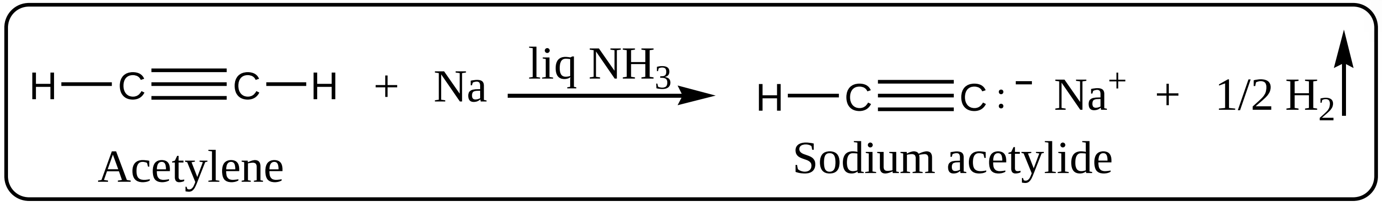
1-Bromo-1-butene

1-Butyne

Preparation of Alkynes

Reaction of Sodium Acetylide with Primary Alkyl Halides

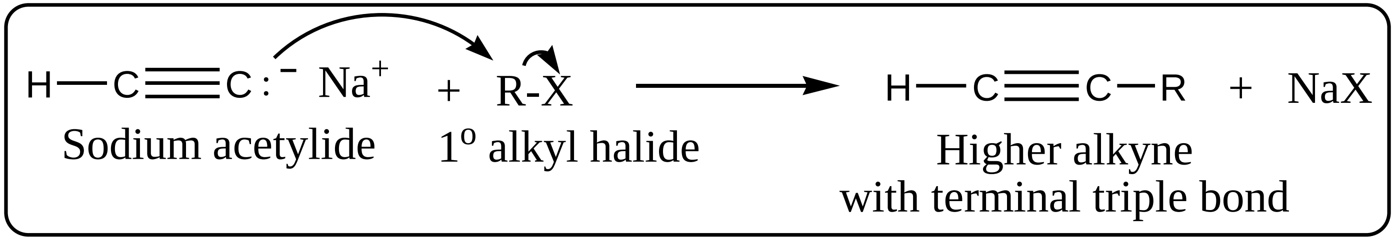
Acetylenes



$$H-C\equiv C-H + Na \xrightarrow{\text{liq } NH_3} H-C\equiv C:^{-}\ Na^{+} + 1/2\ H_2\uparrow$$

Acetylene

Sodium acetylide



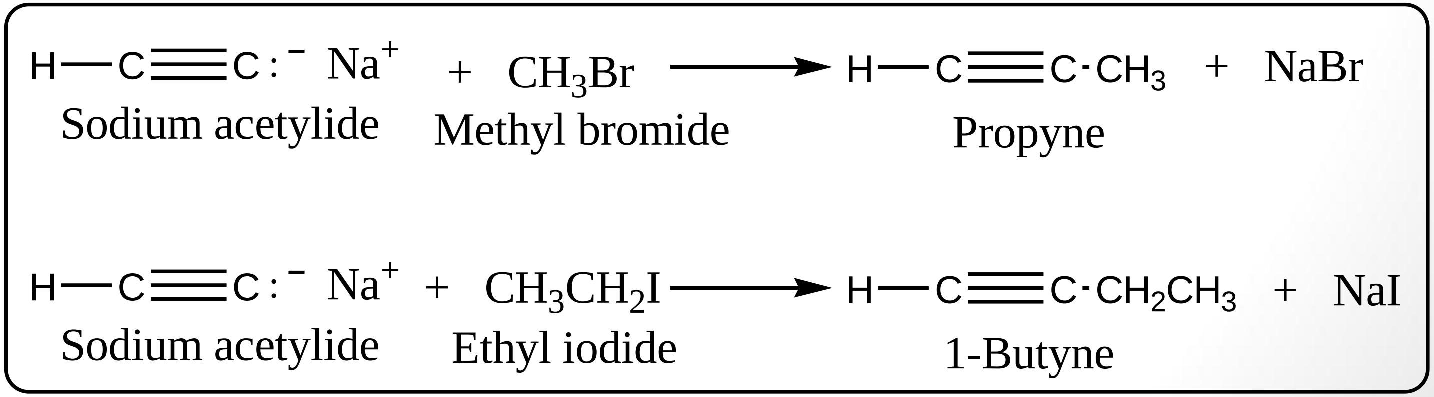
$$H-C\equiv C:^{-}\ Na^{+} + R\text{-}X \longrightarrow H-C\equiv C-R + NaX$$

Sodium acetylide

1^{o} alkyl halide

Higher alkyne
with terminal triple bond

Example



$$H-C\equiv C:^{-}\ Na^{+} + CH_3Br \longrightarrow H-C\equiv C\cdot CH_3 + NaBr$$

Sodium acetylide

Methyl bromide

Propyne

$$H-C\equiv C:^{-}\ Na^{+} + CH_3CH_2I \longrightarrow H-C\equiv C\cdot CH_2CH_3 + NaI$$

Sodium acetylide

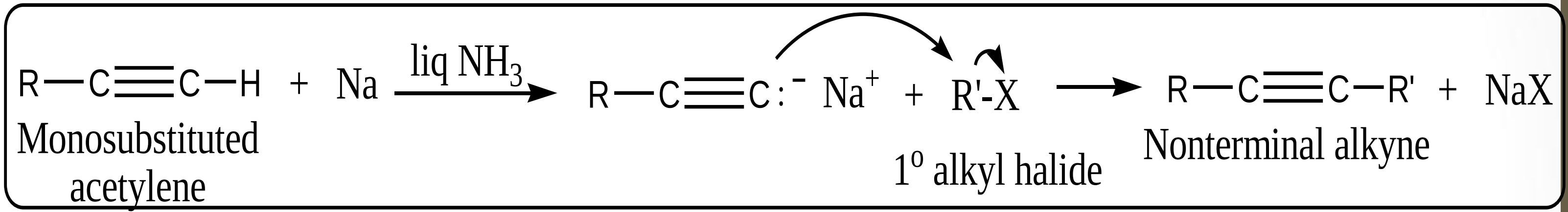
Ethyl iodide

1-Butyne

Preparation of Alkynes

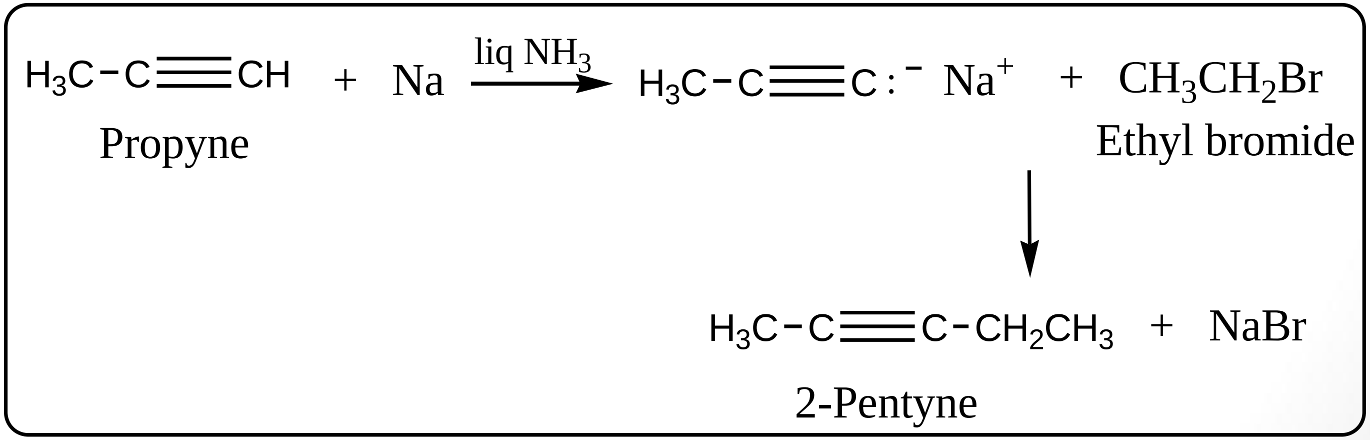
Reaction of Sodium Acetylide with Primary Alkyl Halides

Monosubstituted Acetylenes



$$R{-}C{\equiv}C{-}H + Na \xrightarrow{\text{liq } NH_3} R{-}C{\equiv}C{:}^{-}\ Na^{+} + R'{-}X \longrightarrow R{-}C{\equiv}C{-}R' + NaX$$

Example



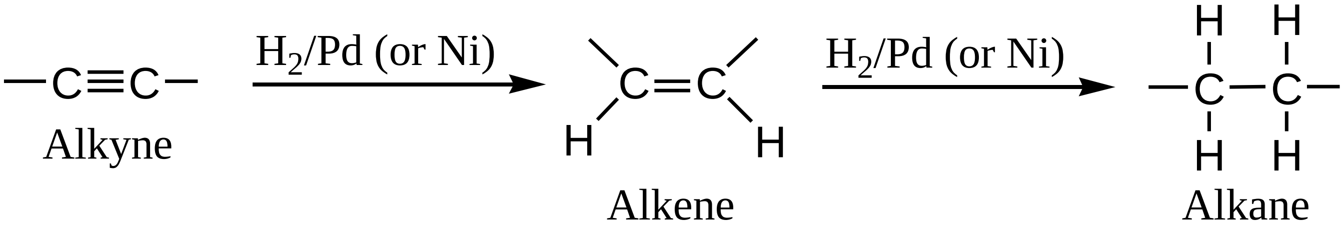
$$H_3C{-}C{\equiv}CH + Na \xrightarrow{\text{liq } NH_3} H_3C{-}C{\equiv}C{:}^{-}\ Na^{+} + CH_3CH_2Br$$

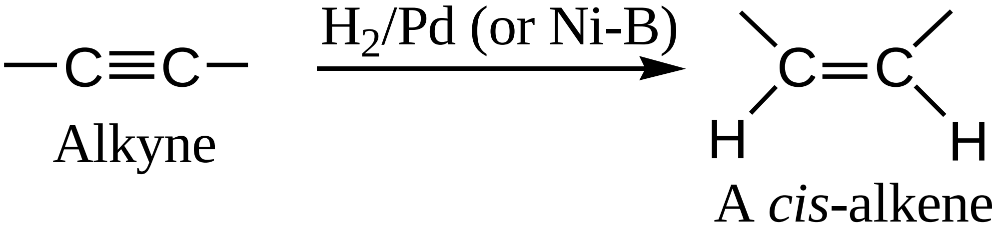
$$\downarrow$$

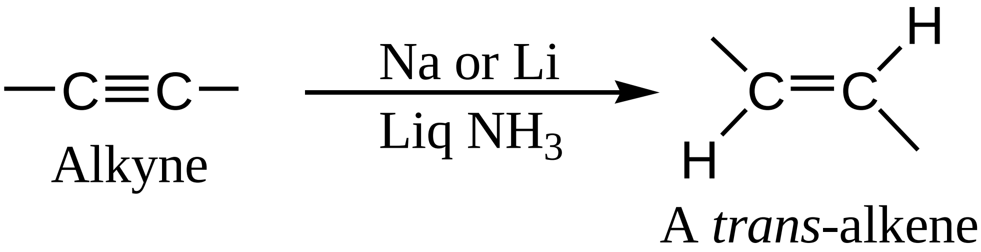
$$H_3C{-}C{\equiv}C{-}CH_2CH_3 + NaBr$$

Reactions of Alkynes

1. Addition of Hydrogen: Catalytic Hydrogenation

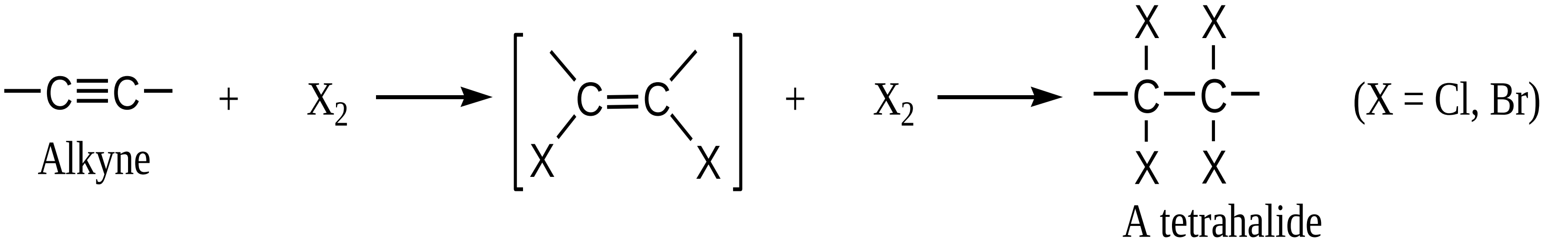






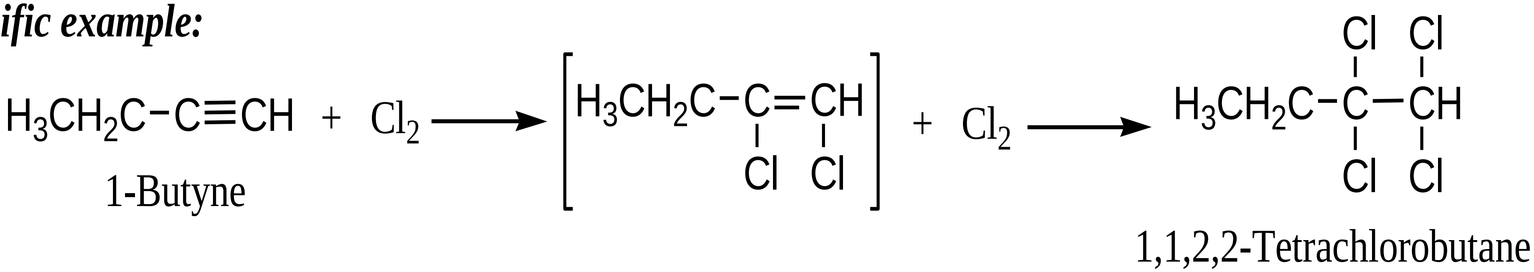
Reactions of Alkynes

2. Addition of Halogens: Halogenation



$$-C\equiv C- \;+\; X_2 \longrightarrow \left[\underset{X}{\diagup}\!\overset{\diagdown}{C}{=}\overset{\diagup}{C}\!\underset{X}{\diagdown} \right] \;+\; X_2 \longrightarrow -\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}- \qquad (X = Cl, Br)$$

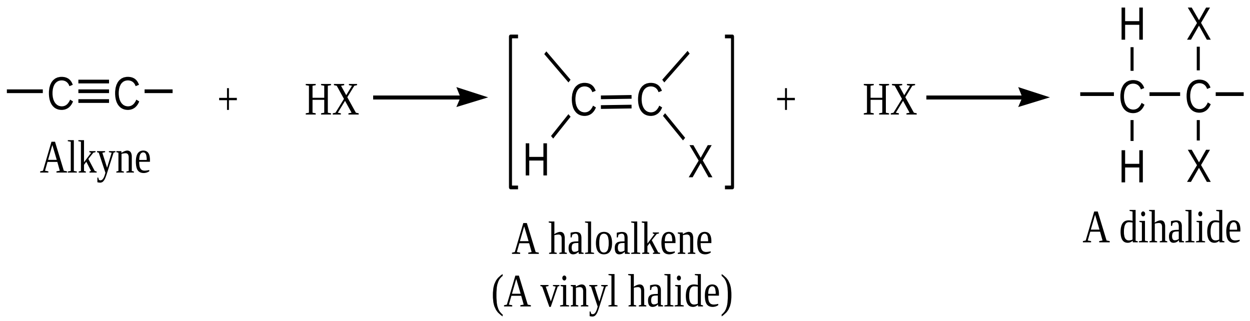
Specific example:



$$H_3CH_2C-C\equiv CH \;+\; Cl_2 \longrightarrow \left[H_3CH_2C-\underset{Cl}{C}{=}\underset{Cl}{CH} \right] \;+\; Cl_2 \longrightarrow H_3CH_2C-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{CH}}$$

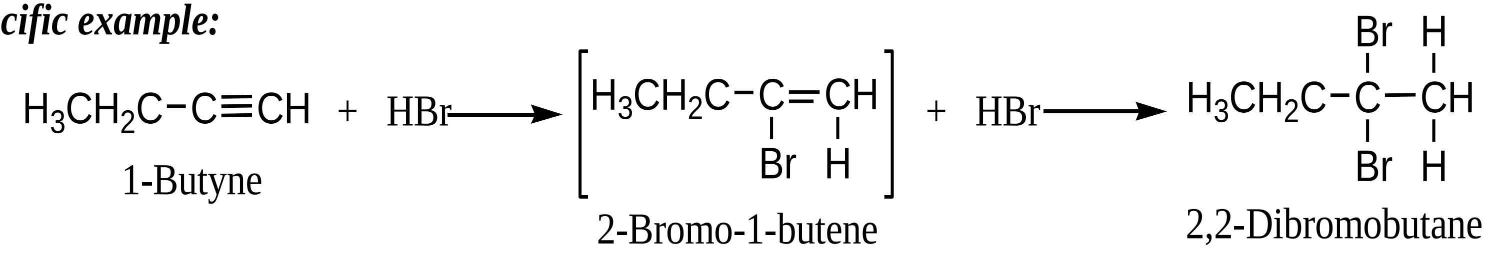
Reactions of Alkynes

3. Addition of Hydrogen Halide



$$-C\equiv C- + HX \longrightarrow \left[\begin{array}{c} C=C \\ H \quad\; X \end{array}\right] + HX \longrightarrow -\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-$$

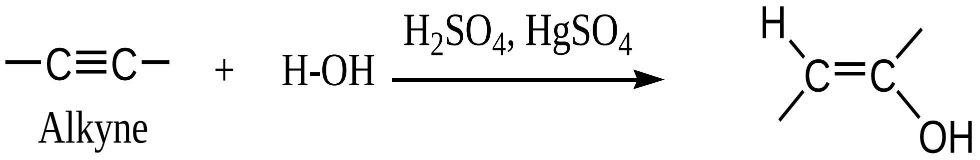
Specific example:



$$H_3CH_2C-C\equiv CH + HBr \longrightarrow \left[H_3CH_2C-\underset{Br}{C}=\underset{H}{CH}\right] + HBr \longrightarrow H_3CH_2C-\overset{Br}{\underset{Br}{C}}-\overset{H}{\underset{H}{CH}}$$

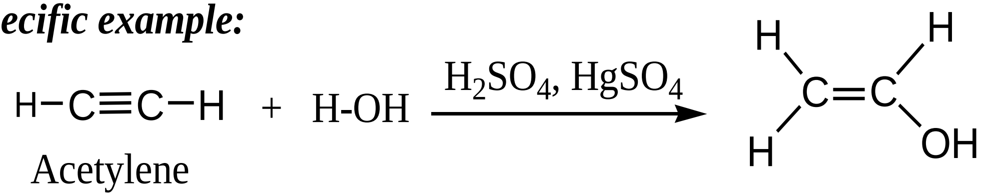
Reactions of Alkynes

4. Addition of Water: Hydration

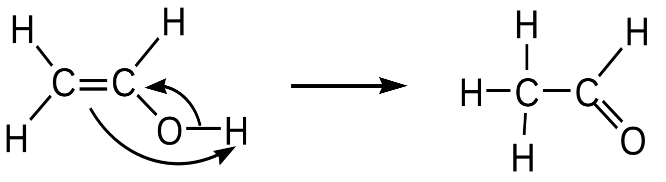


Initial adduct: an enol
(unstable)

Specific example:



Vinyl alcohol
(an unstable enol)



Vinyl alcohol
(an unstable enol)

Acetaldehyde
(a stable carbonyl compound)