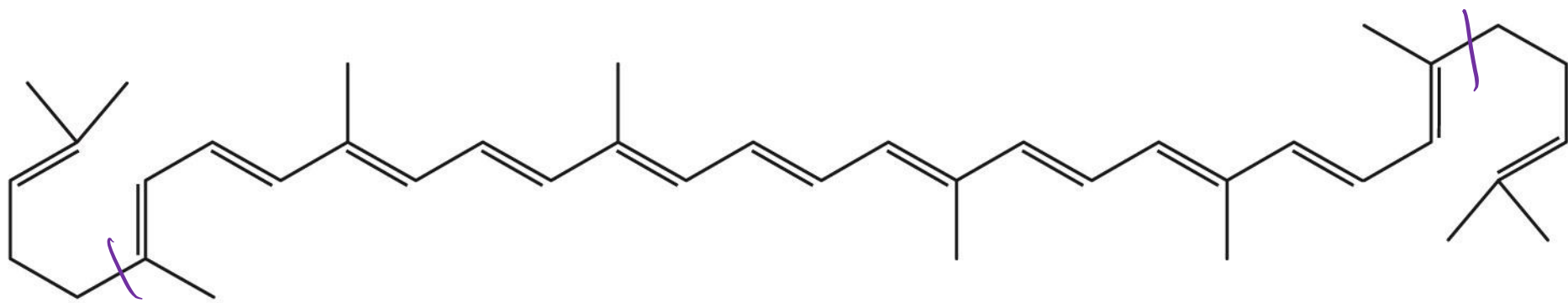


Chapter 3: Alkenes and Alkynes



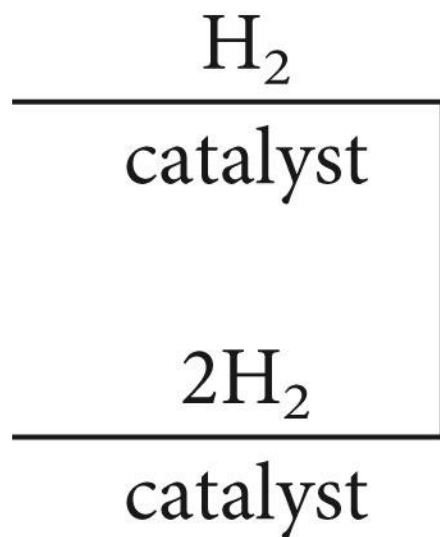
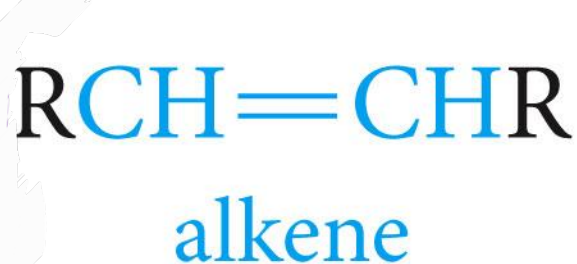
lycopene

Hydrogenation of Alkenes and Alkynes

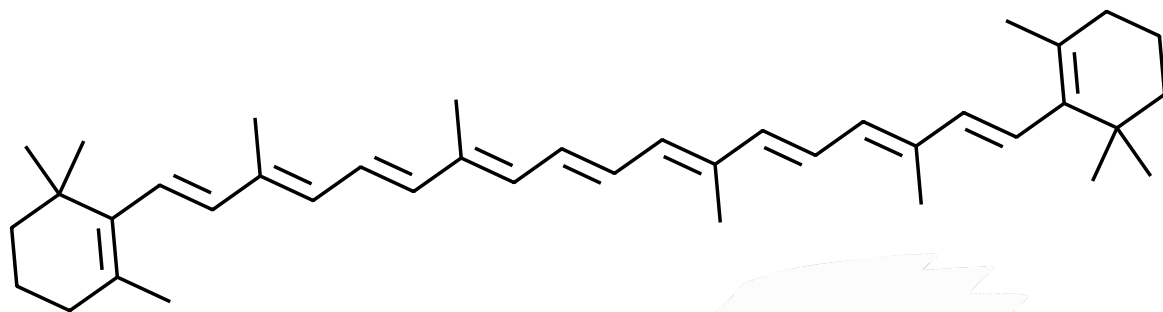
Hydrocarbons that have carbon-carbon double bond are called alkenes; those with a carbon-carbon triple bond are alkynes

Their general formulas are C_nH_{2n} alkenes and C_nH_{2n-2} alkynes

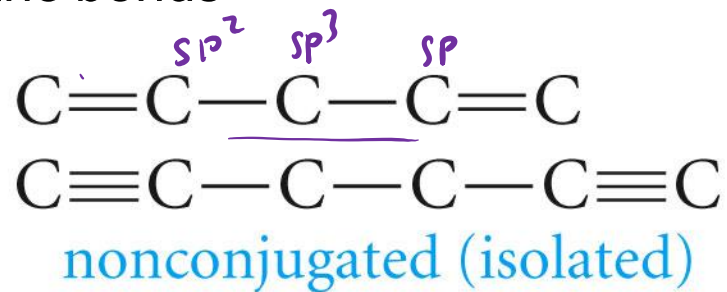
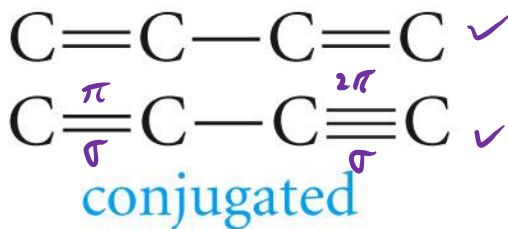
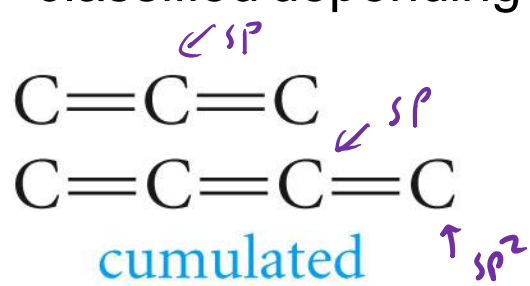
Both alkenes and alkynes are unsaturated hydrocarbons



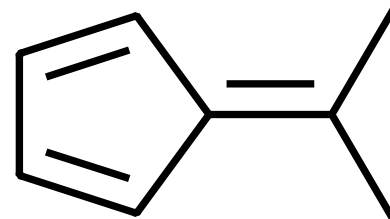
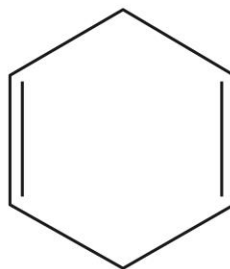
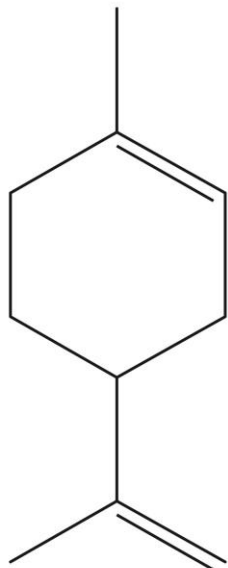
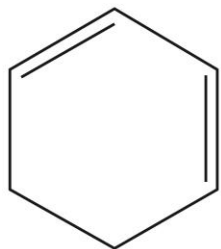
Compounds with more than one double or triple bonds exist. Multiple double bonds may lead to dienes, trienes, tetraenes and polyenes. β -carotene and lycopene are examples of polyenes



When two or more multiple bonds are present in a molecule, they can be classified depending on the relative positions of the bonds

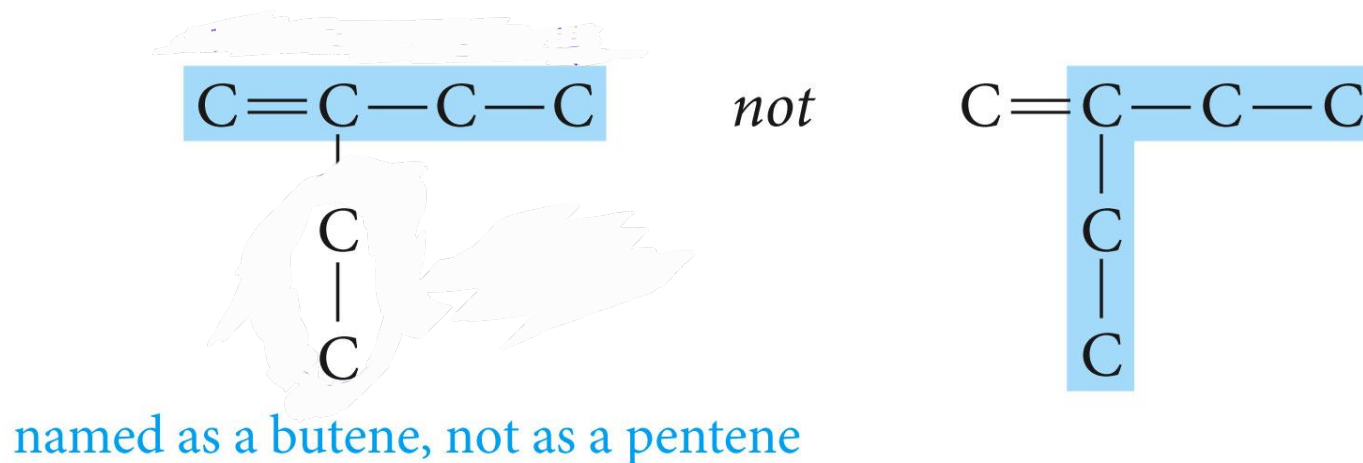


Which of the following compounds have conjugated multiple bonds?



Nomenclature

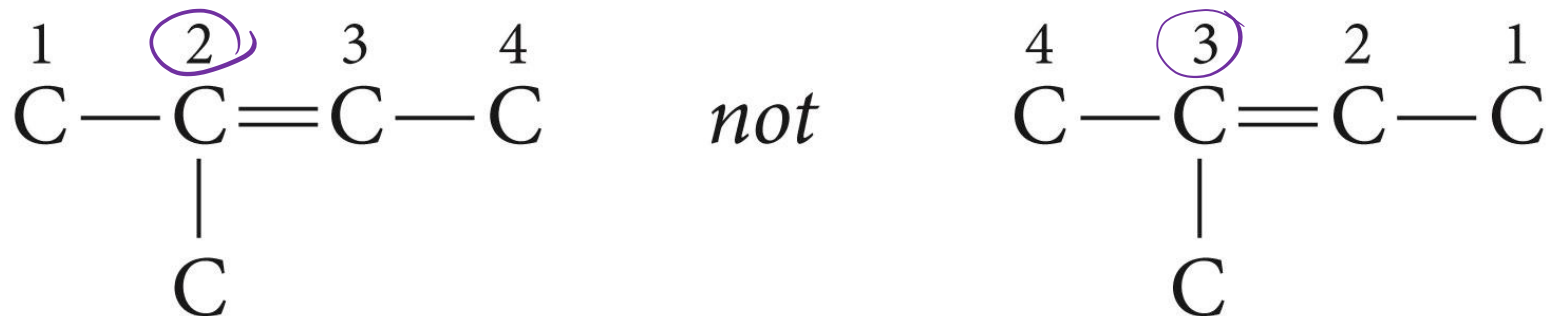
1. The ending -ene is used to designate carbon-carbon double bond. When more than one double bond is present, the ending is *-diene*, *triene*, *tetraene* and so on. The ending *-yne* is used for triple carbon-carbon bond.
2. Select the longest chain that includes both carbons of the double bond or triple bond.



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.



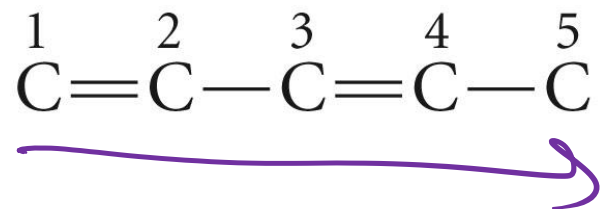
2-methyl-2-butene

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

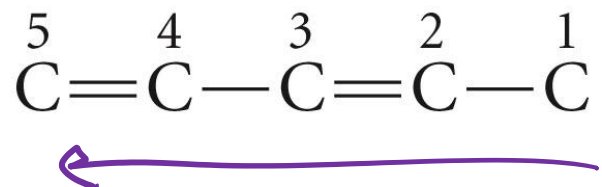


1-butene, *not* 2-butene

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



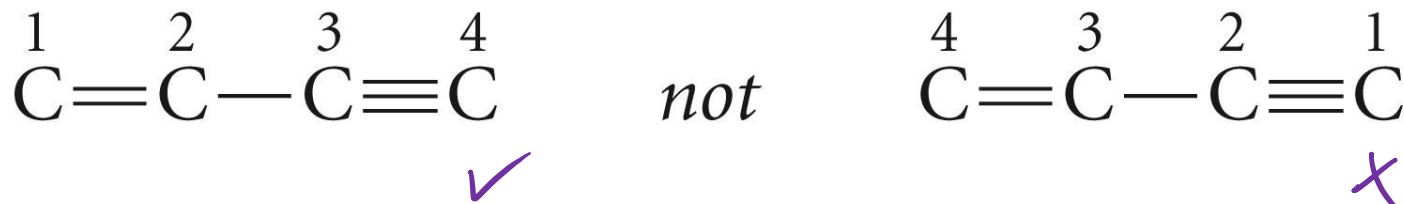
not



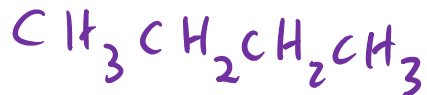
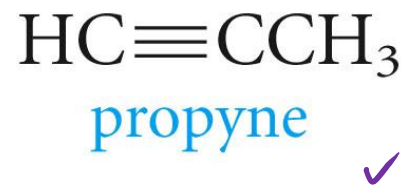
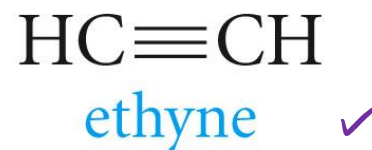
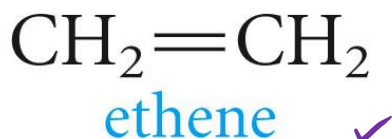
= END =

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

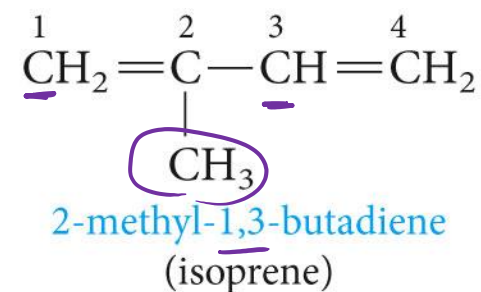
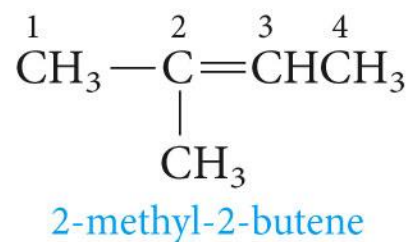
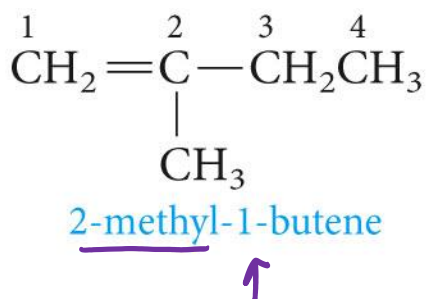
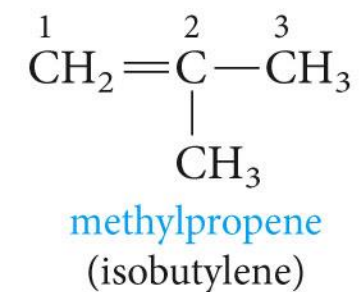
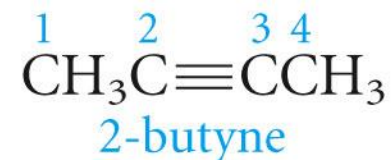
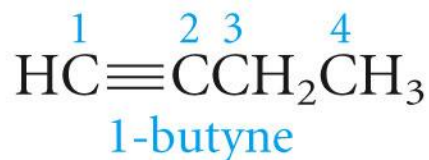
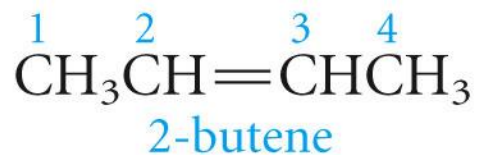
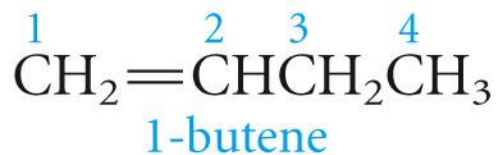
alkene takes priority over alkyne



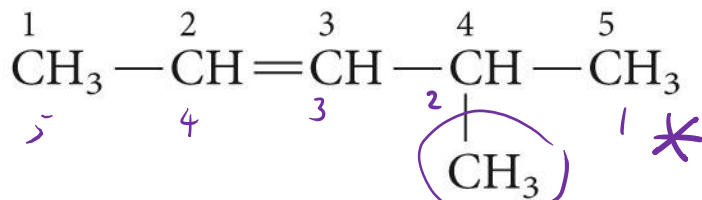
The root name is from the longest carbon chain containing the multiple bond



*So are
1-butene & 2
2-butene*

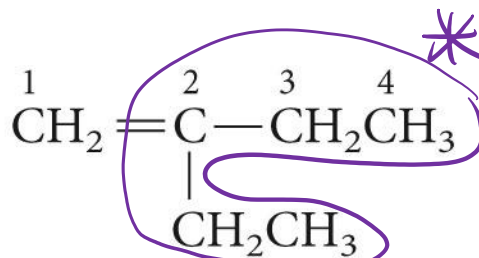


The numbering rules applied



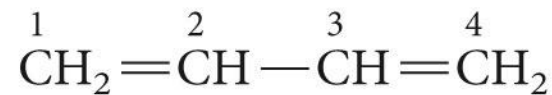
4-methyl-2-pentene ✓

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



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.)



1,3-butadiene

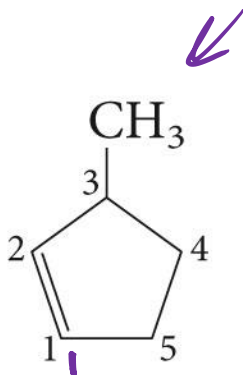
(Note the *a* inserted in the name, to help in pronunciation.)

With the cyclic hydrocarbons, we start numbering the ring with the carbons of the multiple bond.



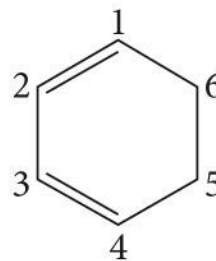
cyclopentene

(No number is necessary, because there is only one possible structure.)

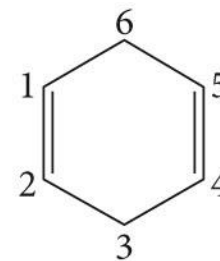


3-methylcyclopentene

(Start numbering at, and number through the double bond; 5-methylcyclopentene and 1-methyl-2-cyclopentene are incorrect names.)



1,3-cyclohexadiene



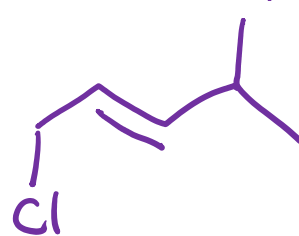
1,4-cyclohexadiene

Write the structural formula for

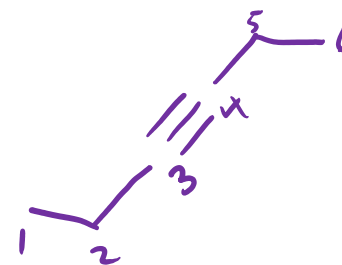
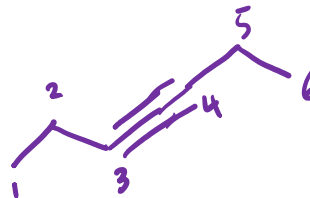
3-methyl-2-pentene



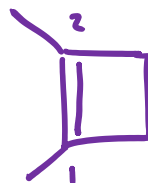
1,4-dichloro-2-pentene



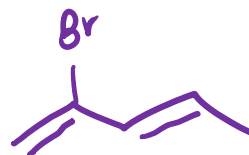
3-hexyne



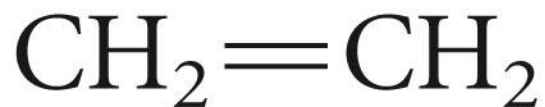
1,2-dimethylcyclobutene



2-bromo-1,3-pentadiene



Some Common names



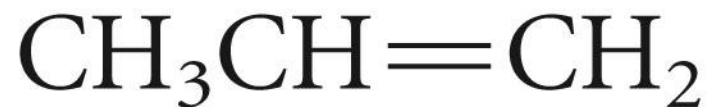
ethylene

(ethene) ✓



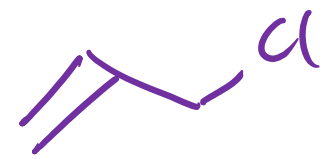
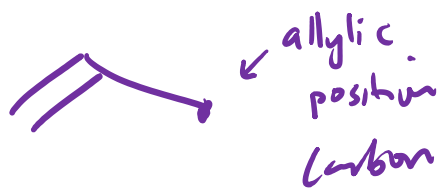
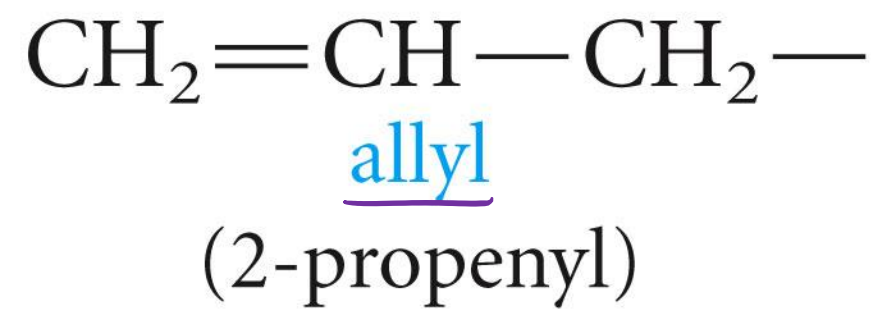
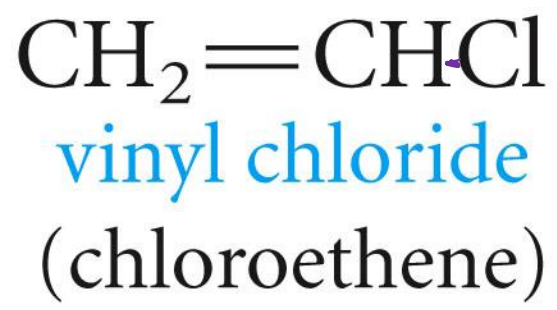
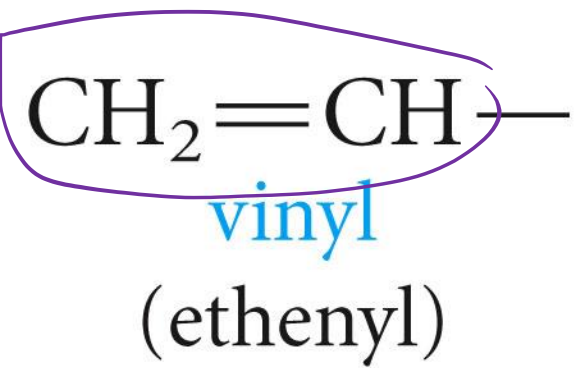
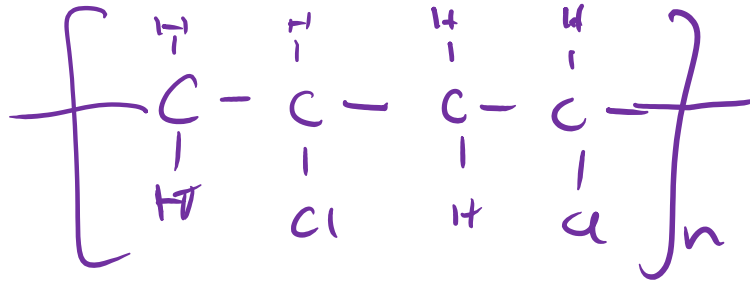
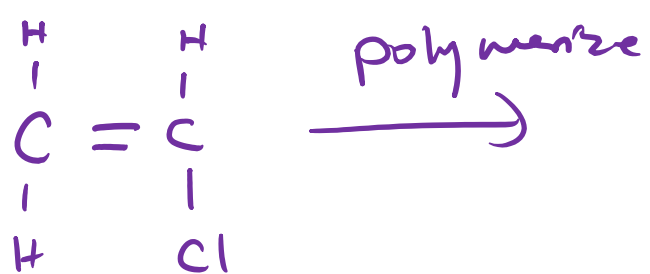
acetylene

(ethyne) ✓

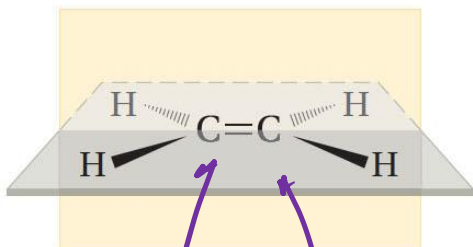


propylene

(propene) ✓



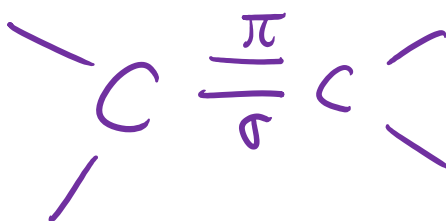
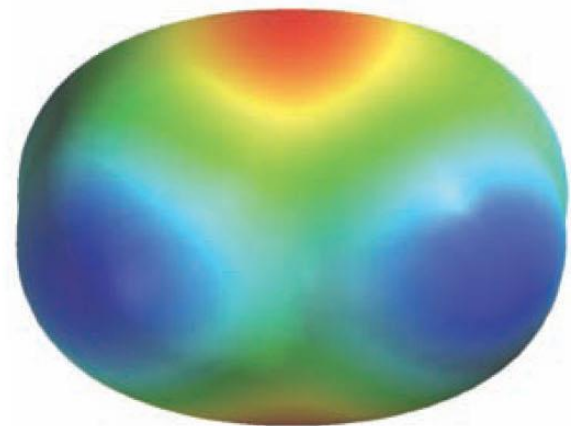
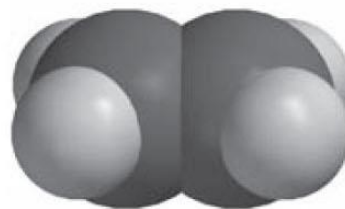
Some Facts about Double Bonds



sp^2 sp^2

trigonal planar

120°

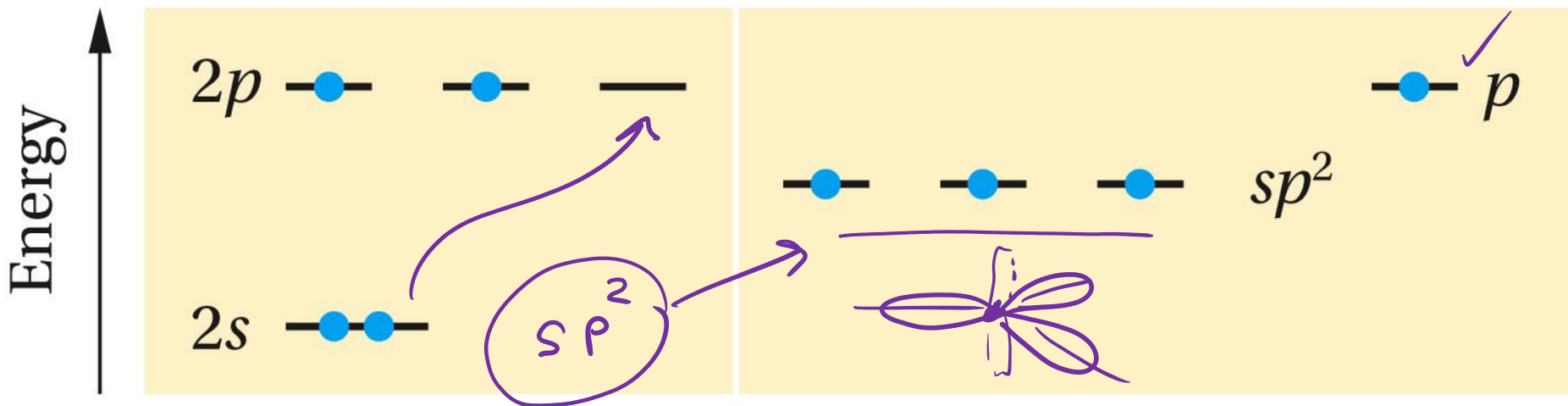


= END =

TABLE 3.1 Comparison of C—C and C=C Bonds

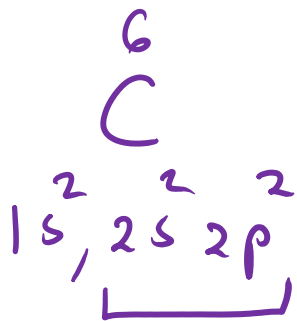
Property	C—C	C=C
1. Number of atoms attached to a carbon	<u>4</u> (tetrahedral)	<u>3</u> (trigonal)
2. Rotation	relatively <u>free</u>	<u>restricted</u>
3. Geometry	<u>many</u> conformations are possible; staggered is preferred	<u>planar</u>
4. Bond angle	109.5°	120°
5. Bond length	<u>1.54 Å</u>	<u>1.34 Å</u>

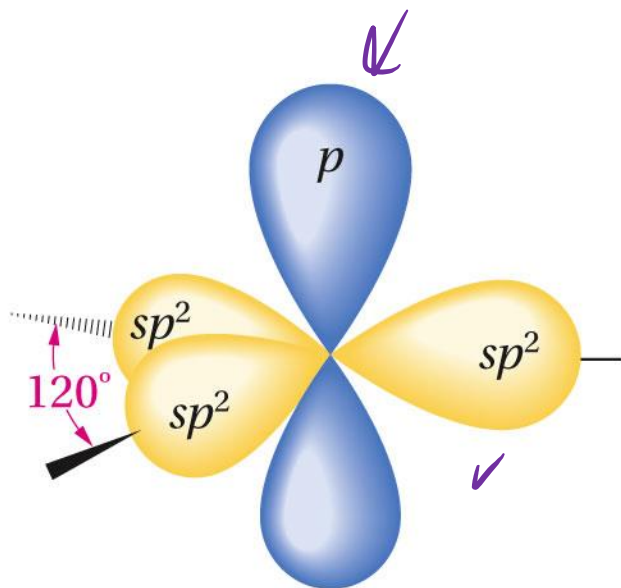
The Orbital Model of a Double Bond; the pi Bond



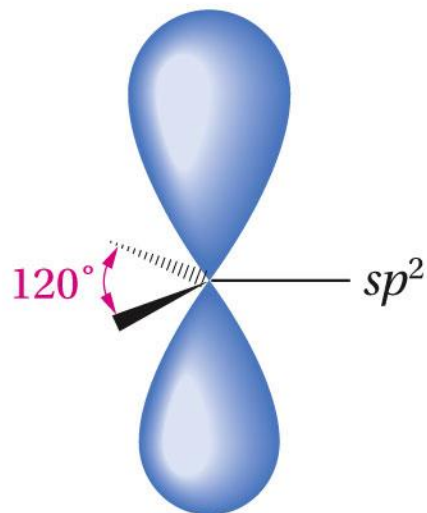
Atomic orbitals
of carbon

The 2s and two 2p orbitals are combined to form three hybrid sp^2 orbitals, leaving one electron still in a p orbital.

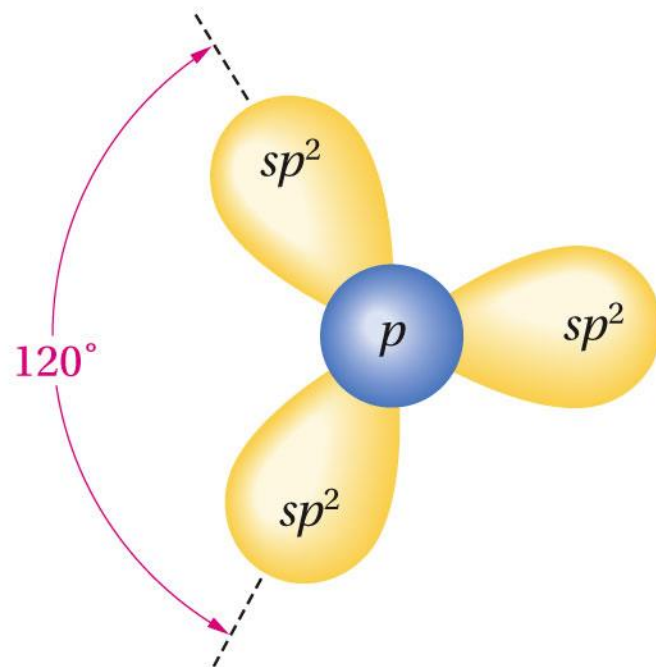




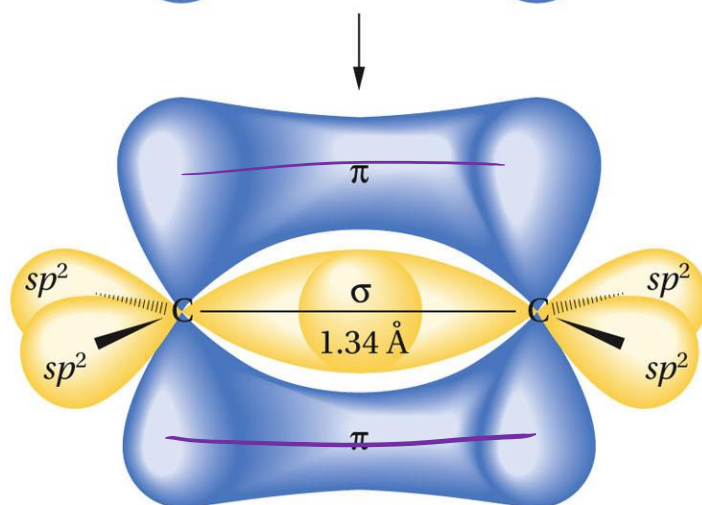
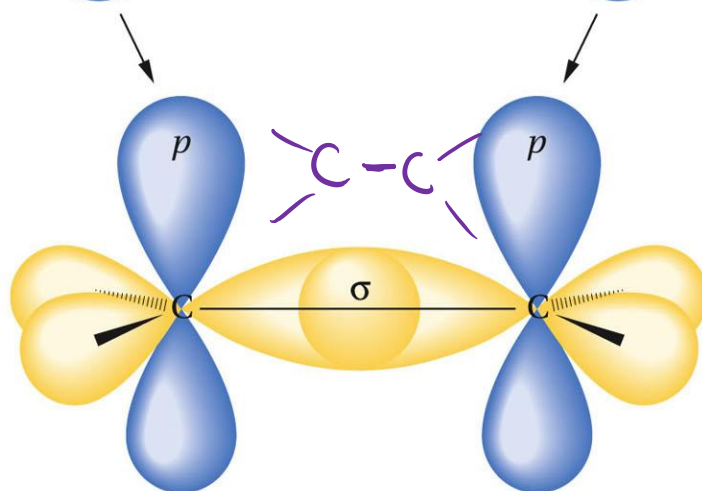
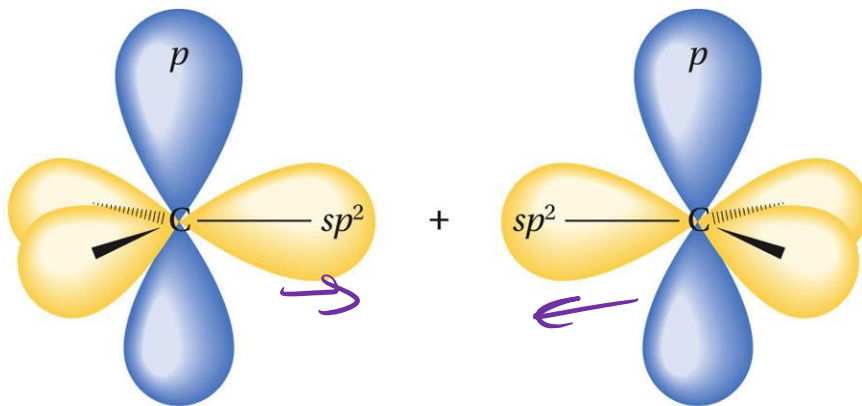
side view



side view with
the sp^2 orbitals
represented by lines



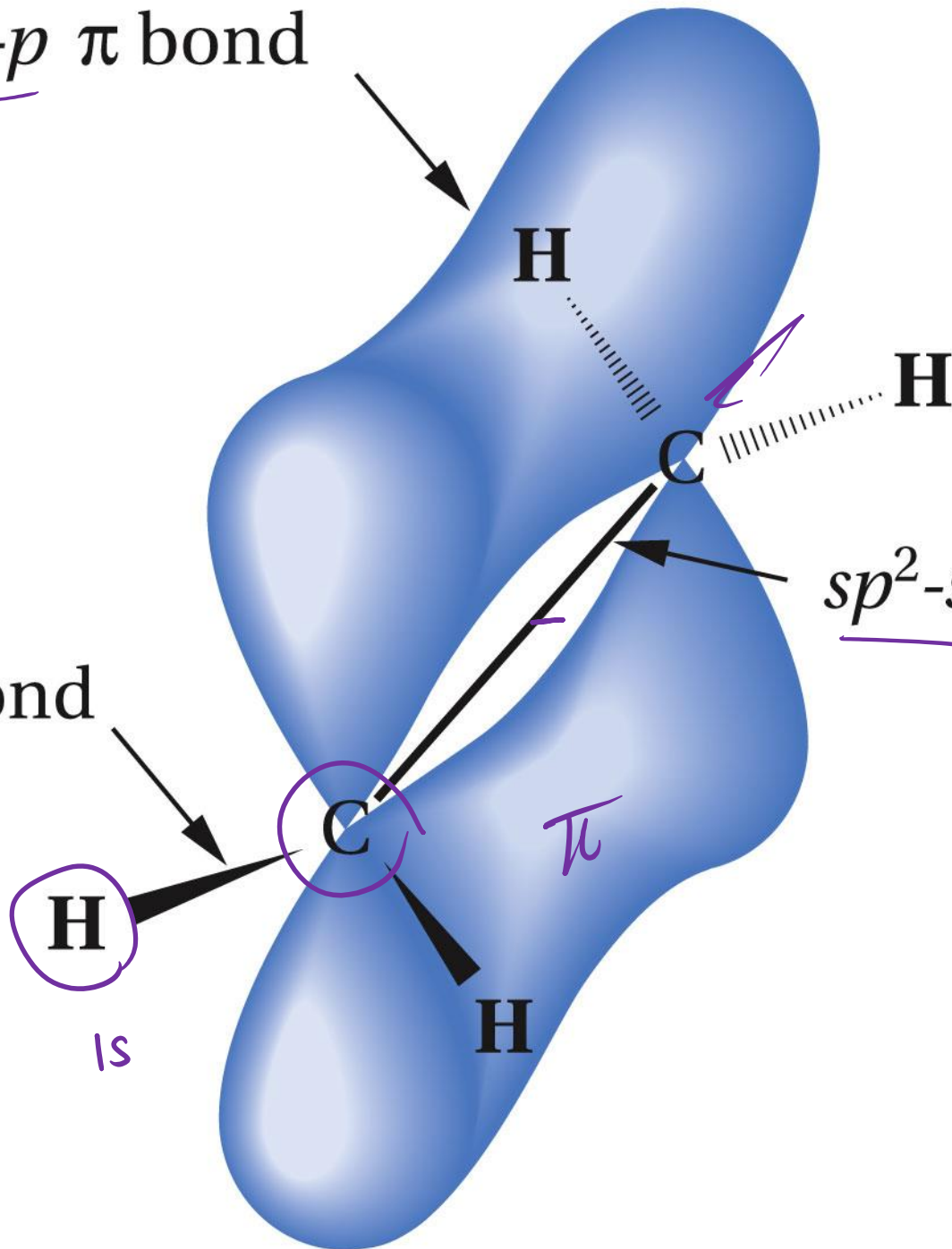
top view

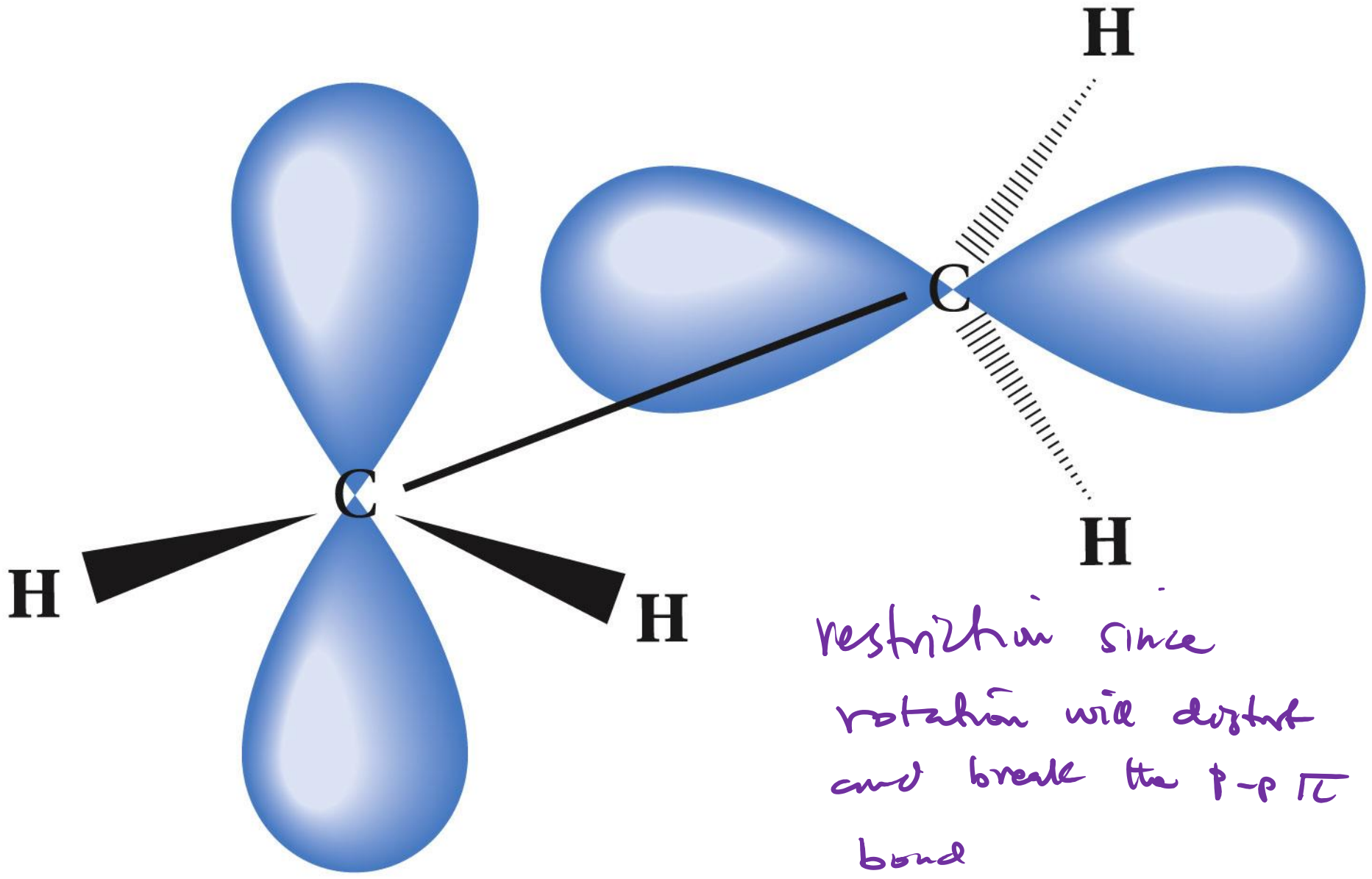


$p-p$ π bond

sp^2-s σ bond

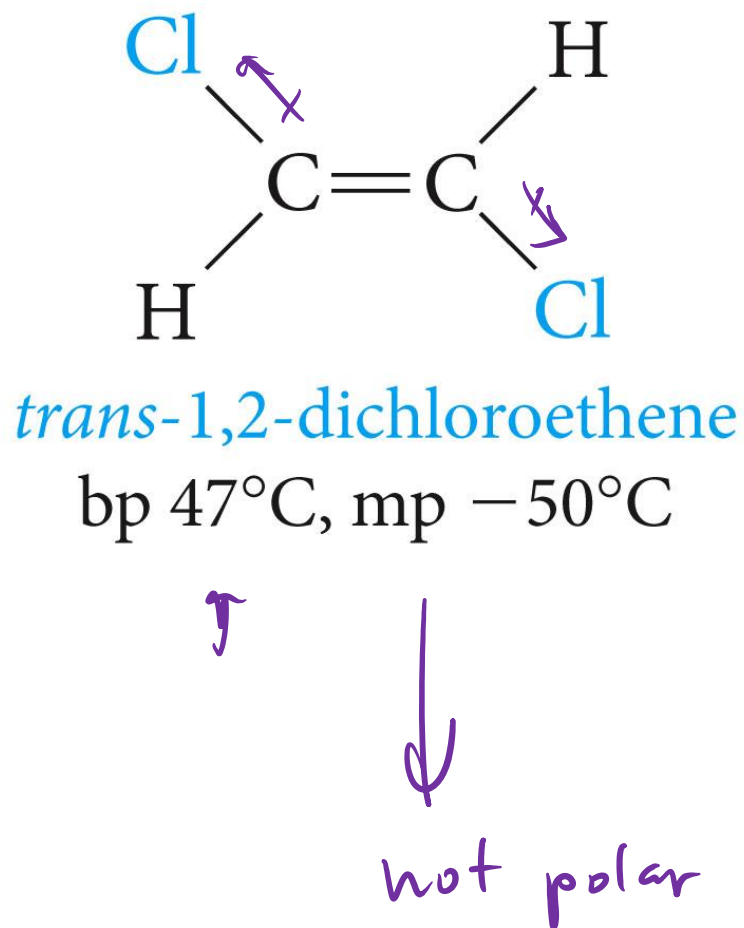
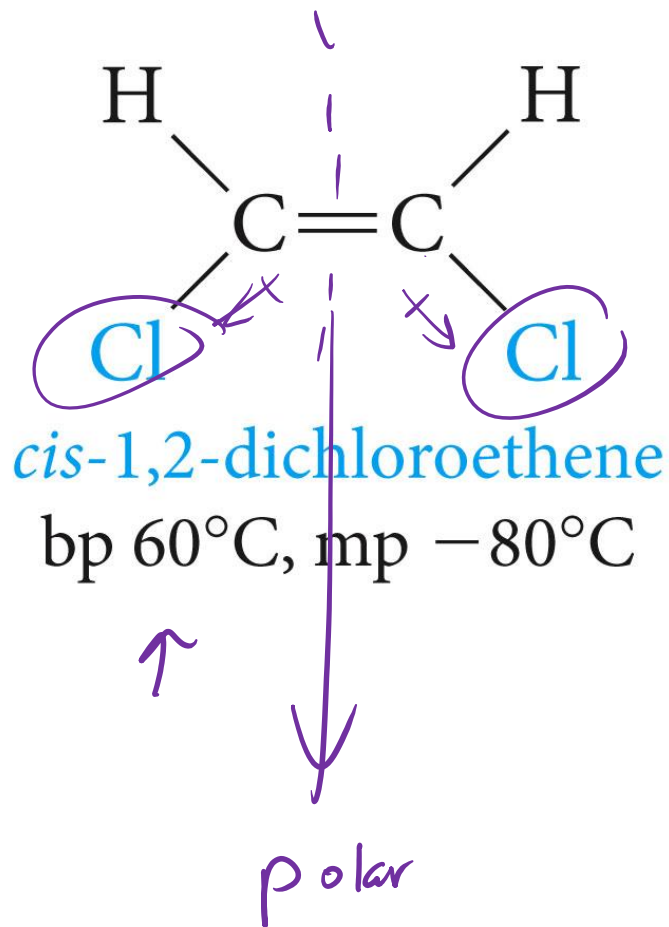
sp^2-sp^2 σ bond



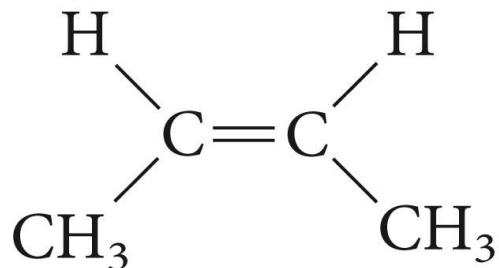


restriction since
rotation will distort
and break the p-p π
bond

Cis-Trans Isomerism in Alkenes

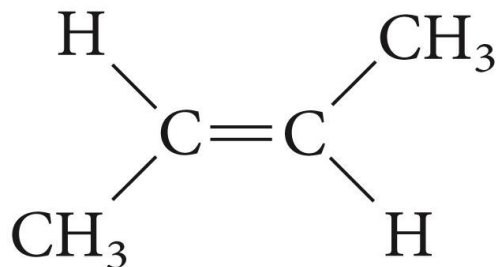


Are cis-trans isomers possible for 1-butene and 2-butene?



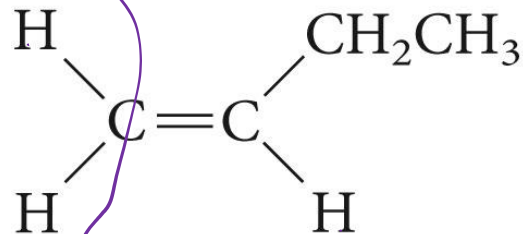
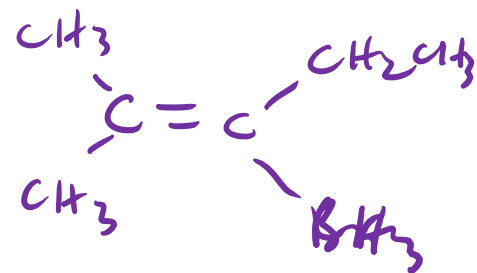
cis-2-butene

bp 3.7°C, mp -139°C



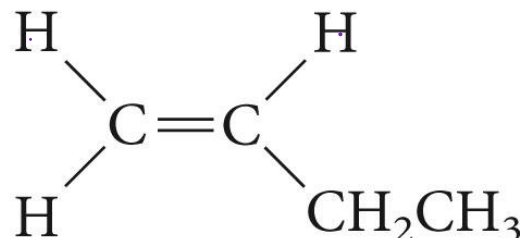
trans-2-butene

bp 0.3°C, mp -106°C



1-butene

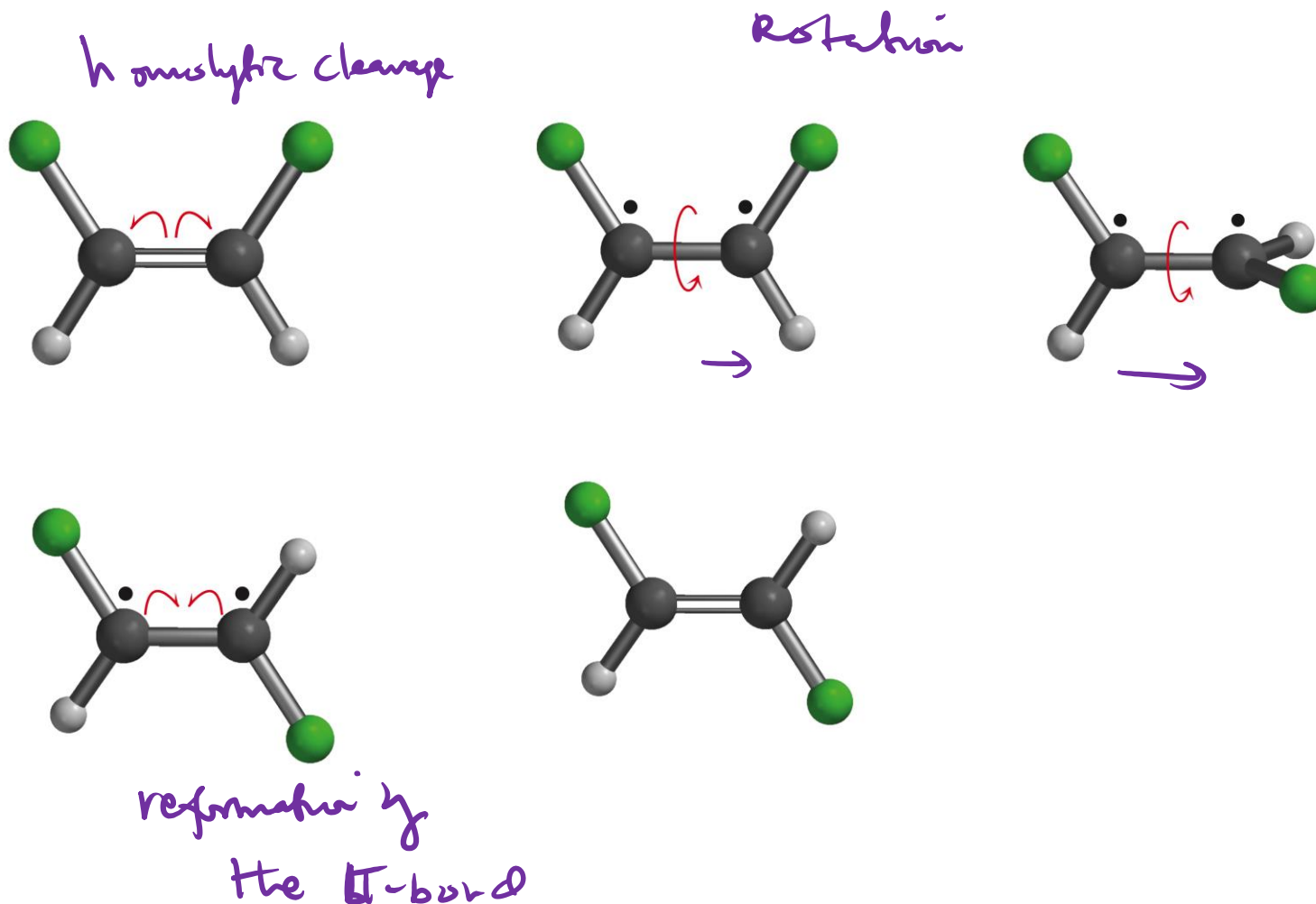
is identical to



1-butene

Whenever you have identical groups on one of the C=C bonds \Rightarrow NO ^{of cis/trans} possible

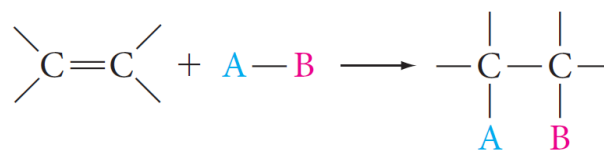
Geometric isomers of alkenes can be interconverted if sufficient energy is supplied to break the pi bond and allow rotation about the remaining sigma bond.



Reactions of Alkenes

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

(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

Reactions of Alkenes

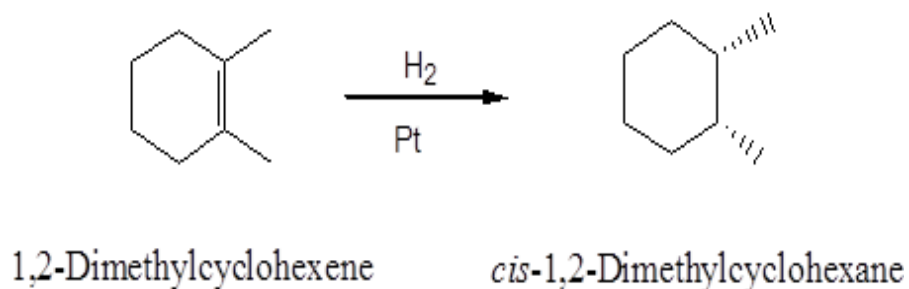
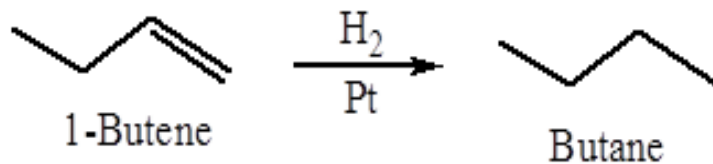
(2) Oxidation Reactions

1. Ozonolysis
2. Oxidation Using KMnO_4

Electrophilic Addition Reactions

1. Addition of Hydrogen: Hydrogenation

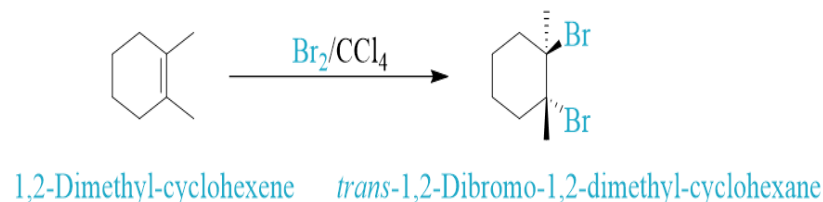
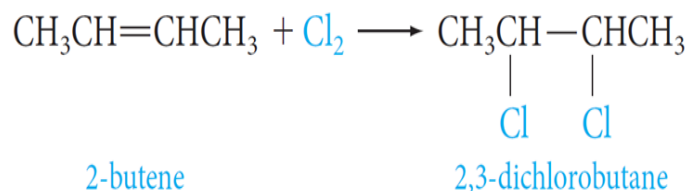
Addition of a mole of hydrogen to carbon-carbon double bond of Alkenes in the presence of suitable catalysts to give an *Alkane*.



Electrophilic Addition Reactions

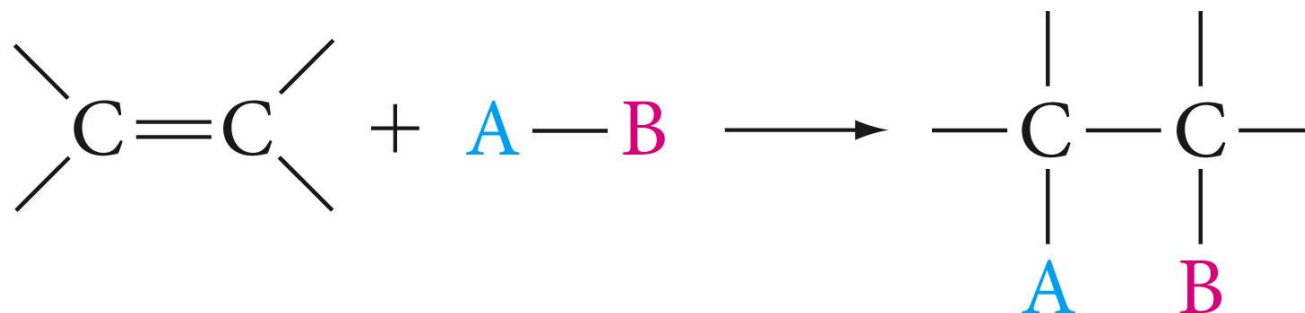
2. Addition of Halogen: Halogenation

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)

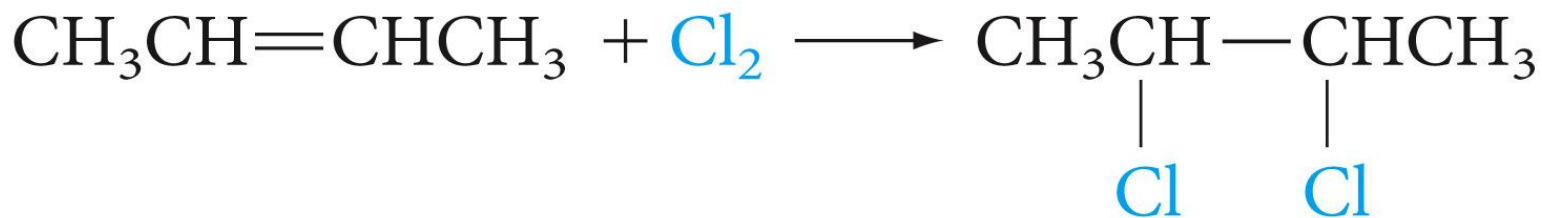


- **Iodine** is **too unreactive** and will not add to the double bond.
- **Fluorine** is **too reactive** and reacts explosively with an alkene.

Addition and Substitution Reactions Compared



Addition of halogens X_2 ($\text{Br}_2, \text{Cl}_2, \text{I}_2, \text{F}_2$)

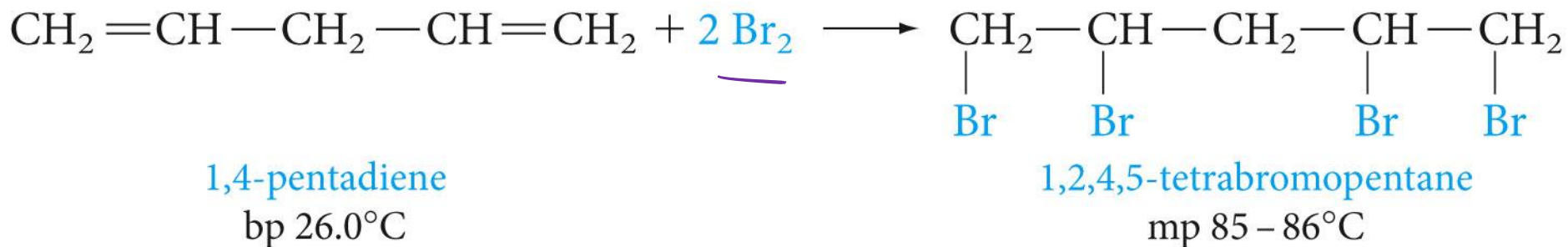
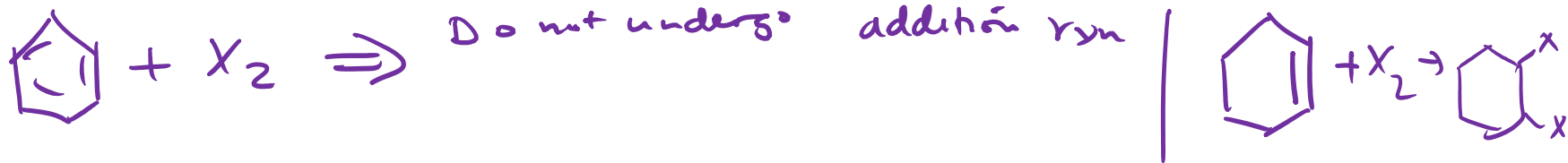


2-butene

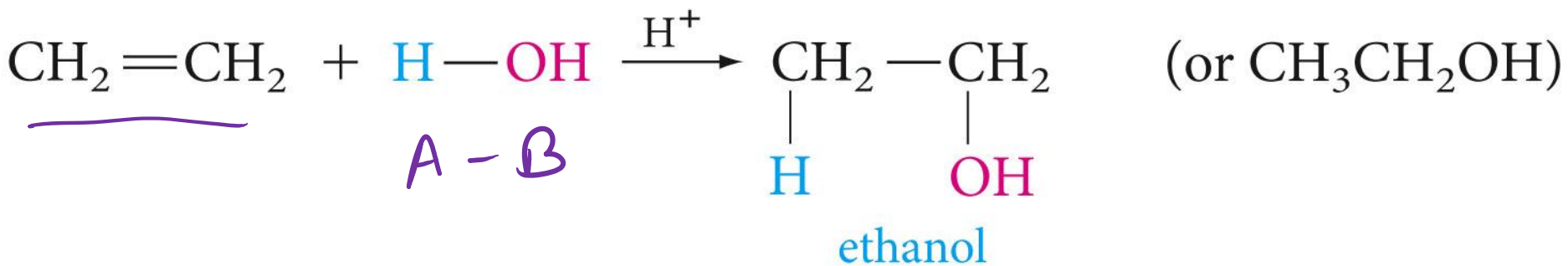
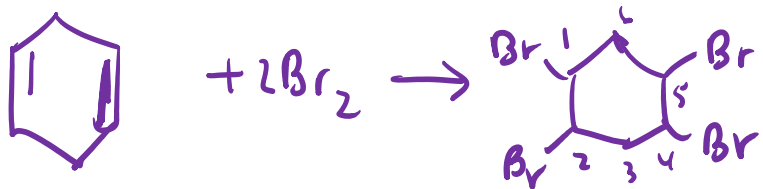
bp $1-4^\circ\text{C}$

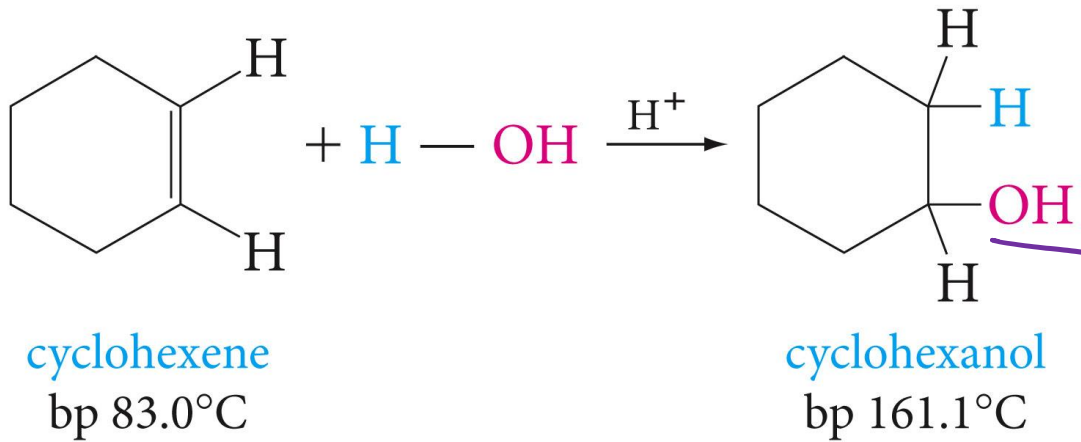
2,3-dichlorobutane

bp $117-119^\circ\text{C}$



Addition of Water (Hydration)

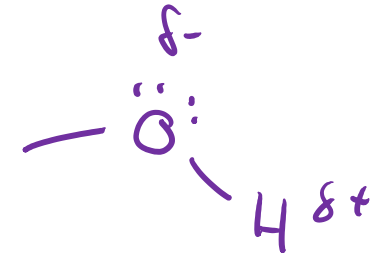




Unsaturated Cycloalkene
 non polar

alcohol
 polar

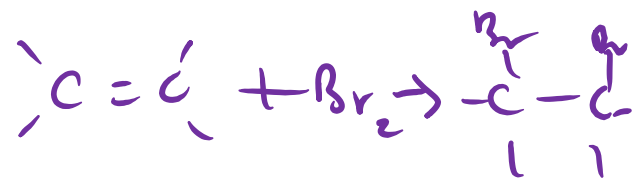
\Rightarrow hydrogen bonding



Bromine added
to →
saturated

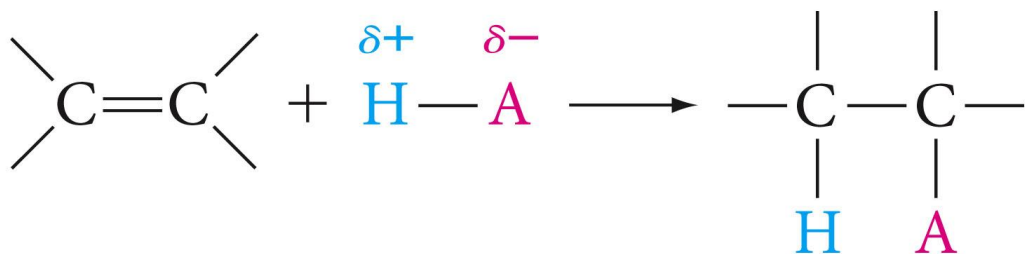


← Br₂ to
unsaturated Hydrocarbons
alkene
alkyne

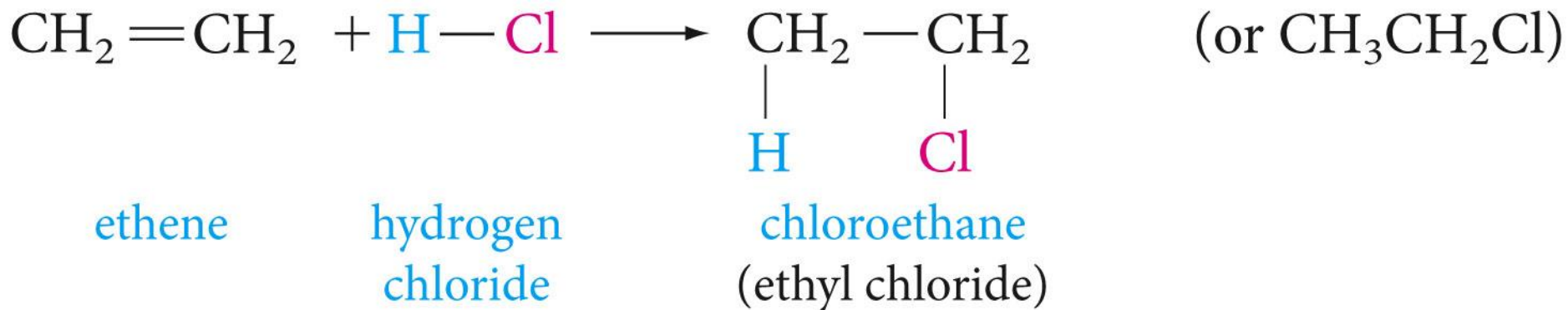


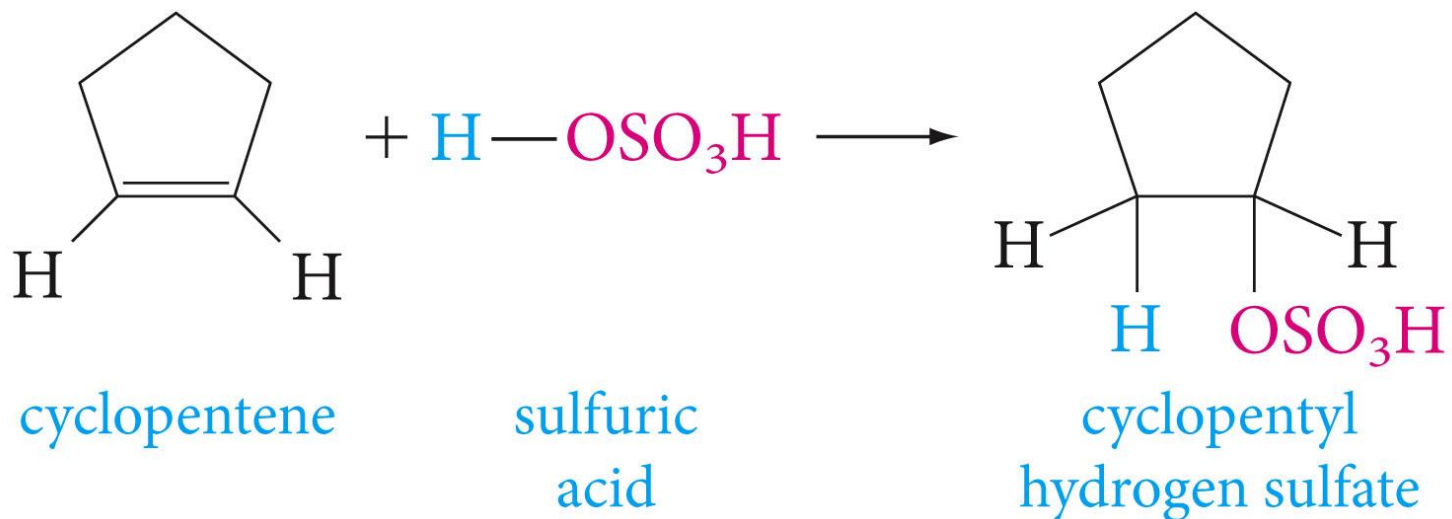
- END -

Addition of Acids



Acids that add this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I) and sulfuric acid (H-OSO₃H)





Write the equation for each of the following reactions

a) 2-butene + HCl

b) 3-Hexene + HI

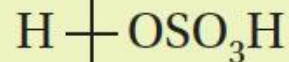
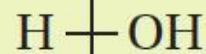
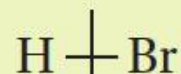
a) 4-methylcyclopentene + HBr

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

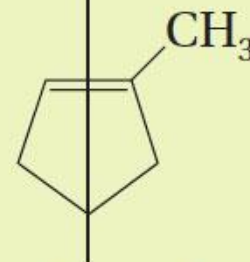
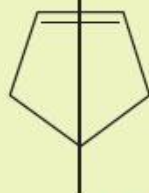
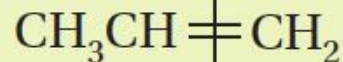
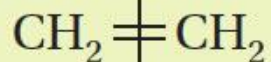
Symmetric

Unsymmetric

Reagents



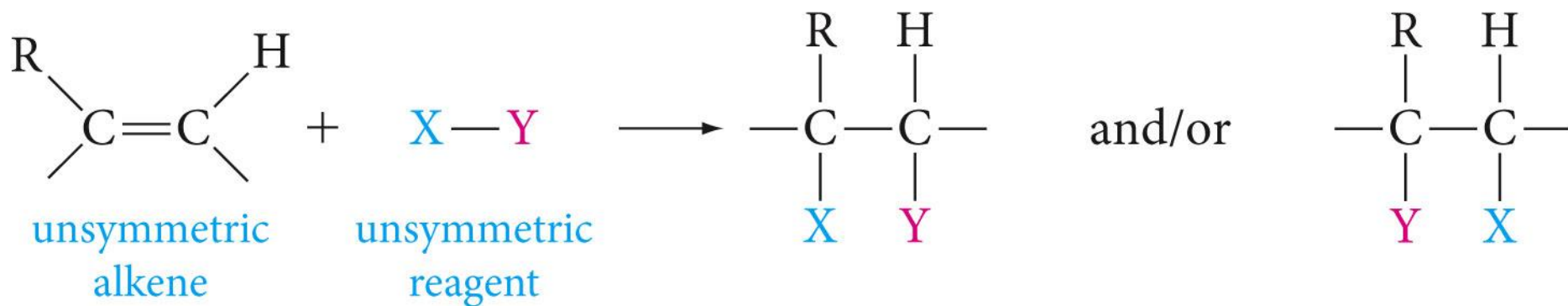
Alkenes

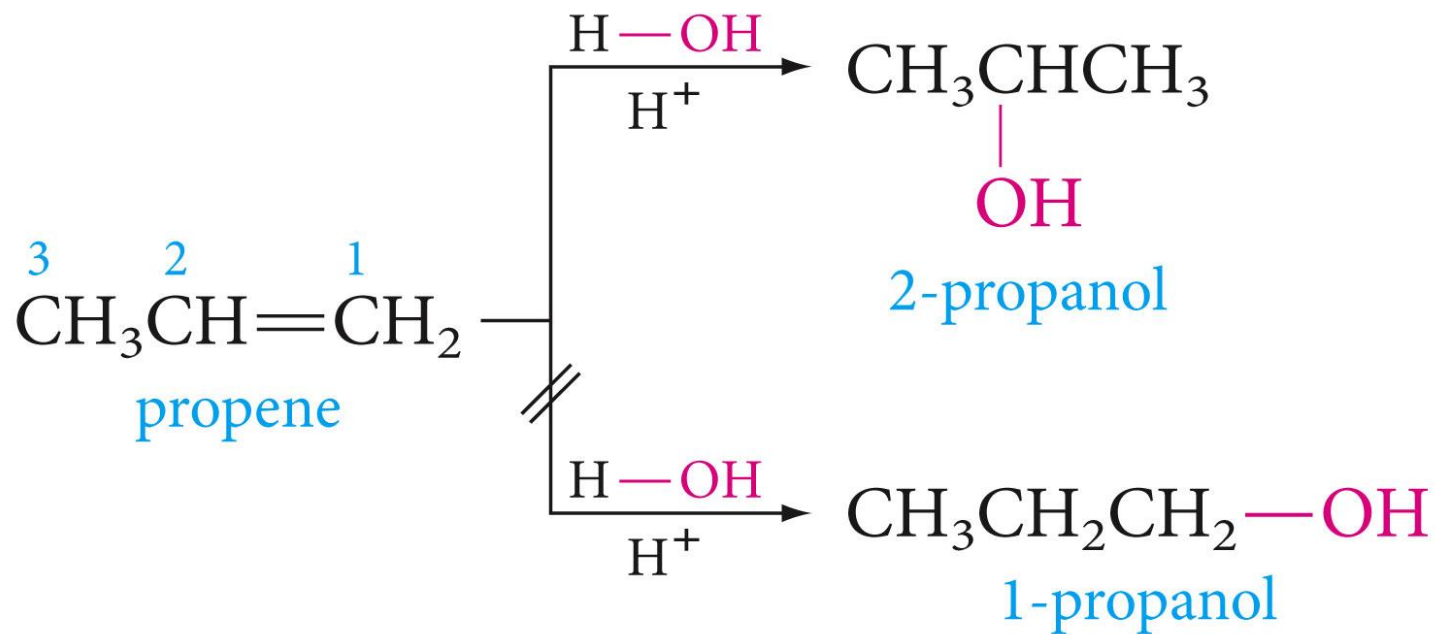


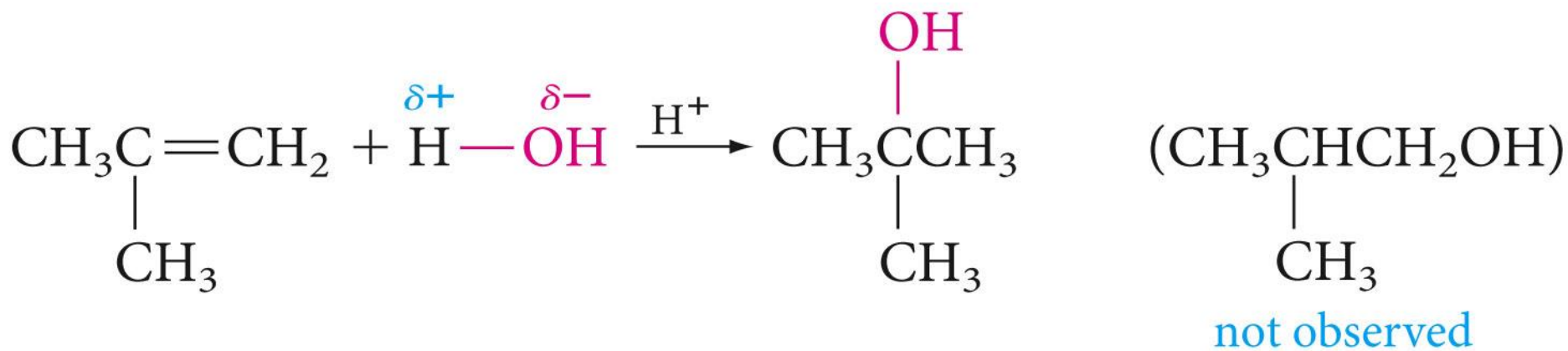
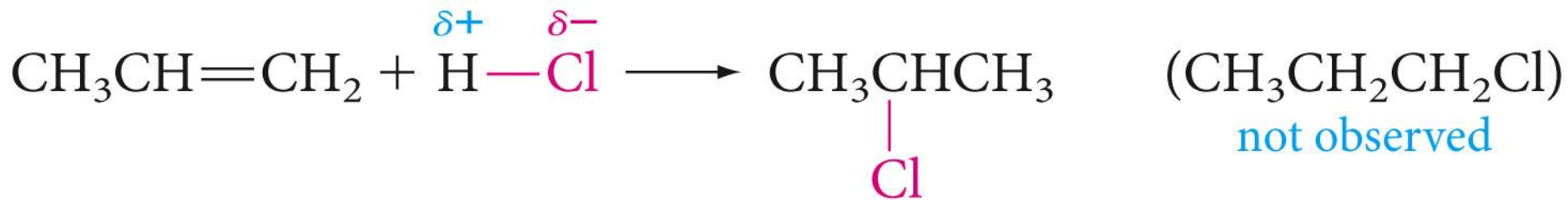
mirror plane

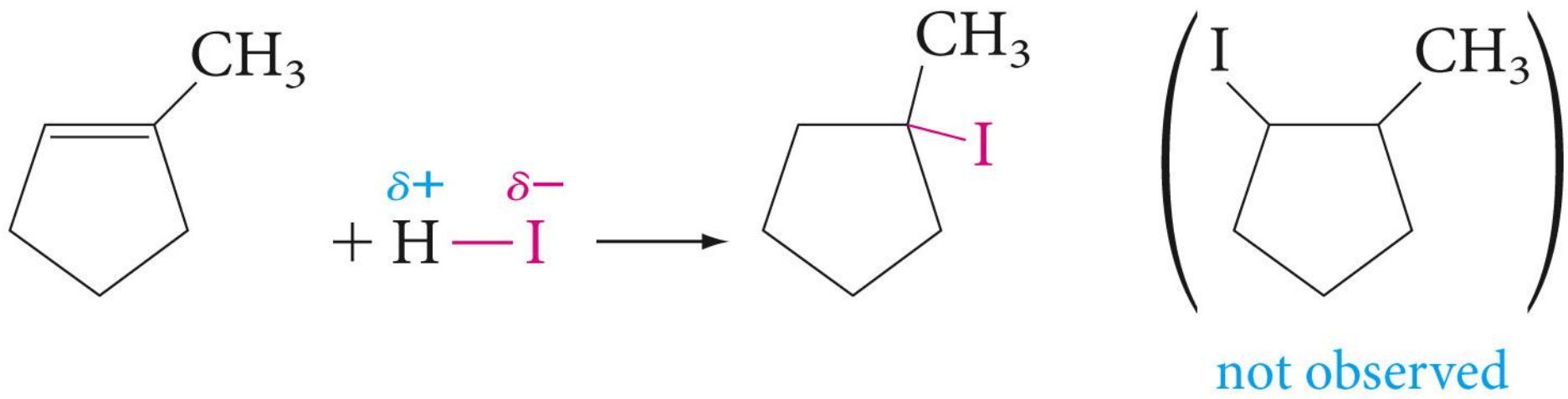
not a mirror plane

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

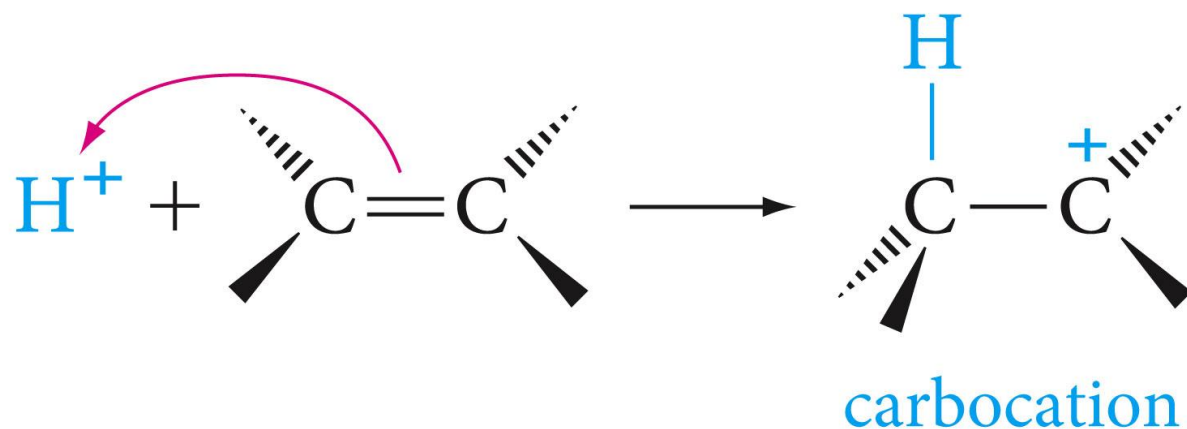


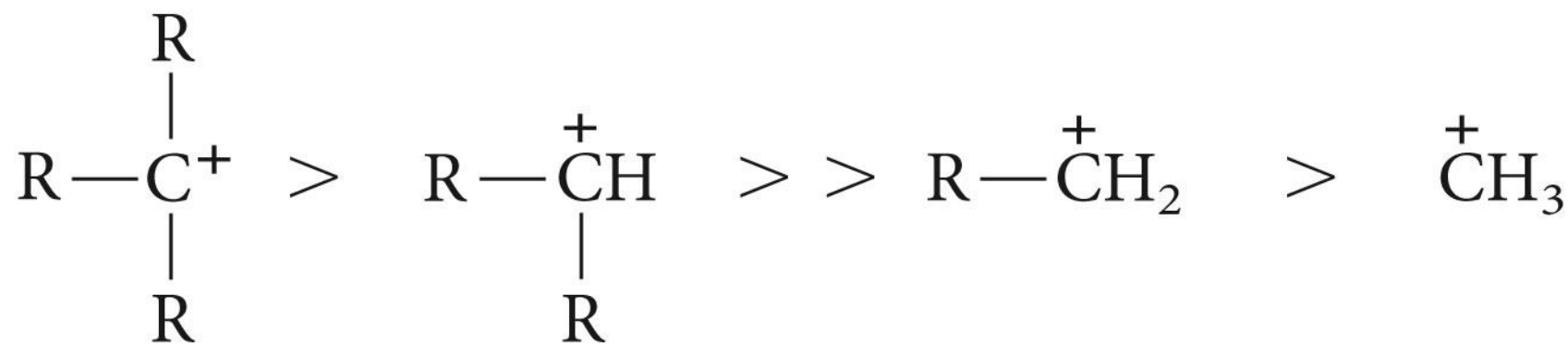






Mechanism of Electrophilic Addition to Alkenes





tertiary (3°)
most stable

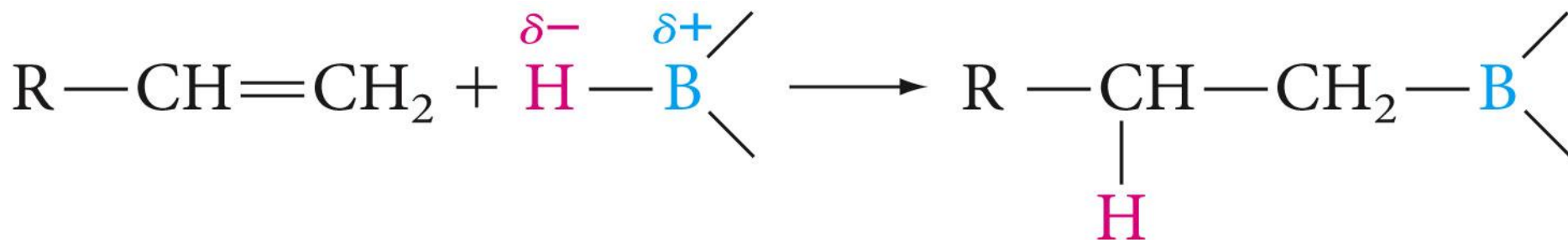
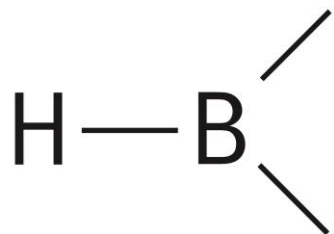
secondary (2°)

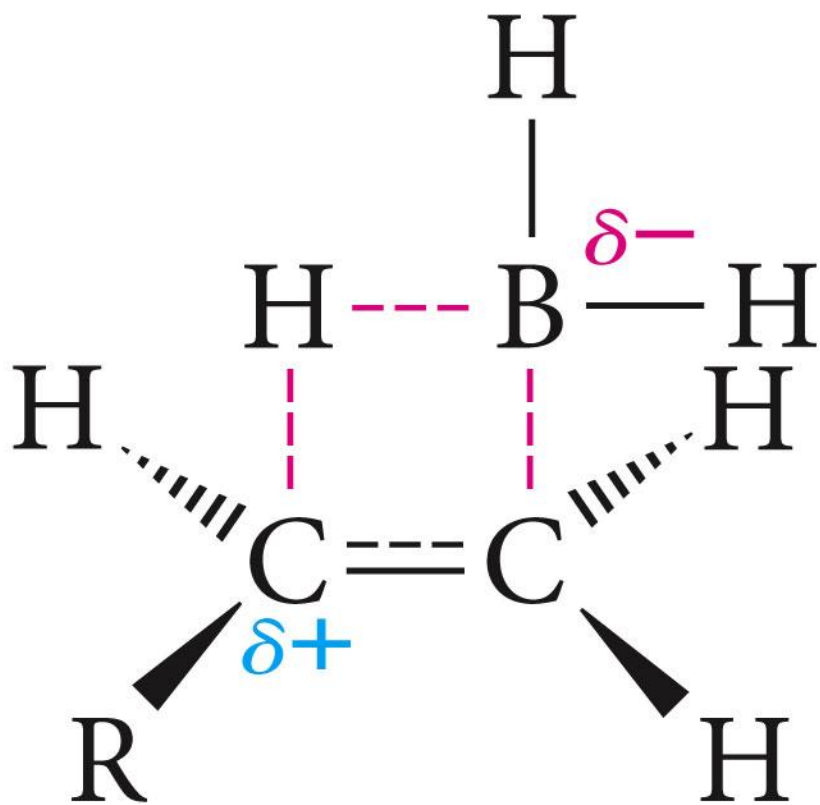
primary (1°)

methyl (unique)
least stable

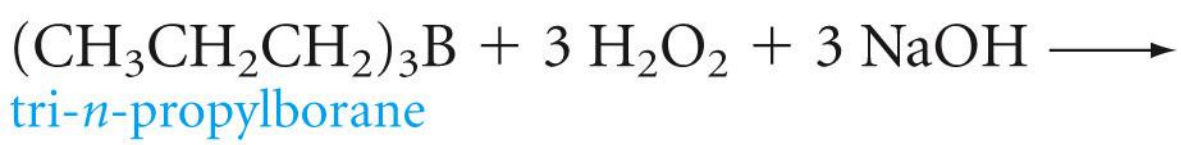
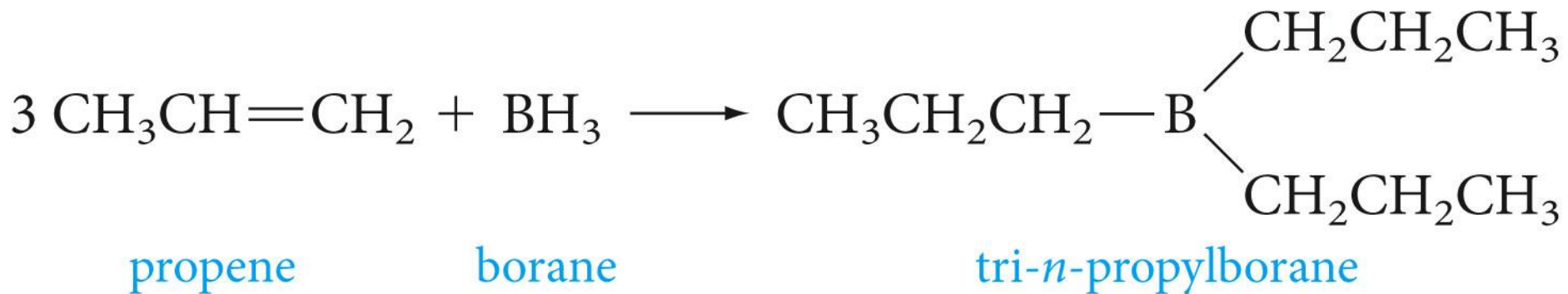


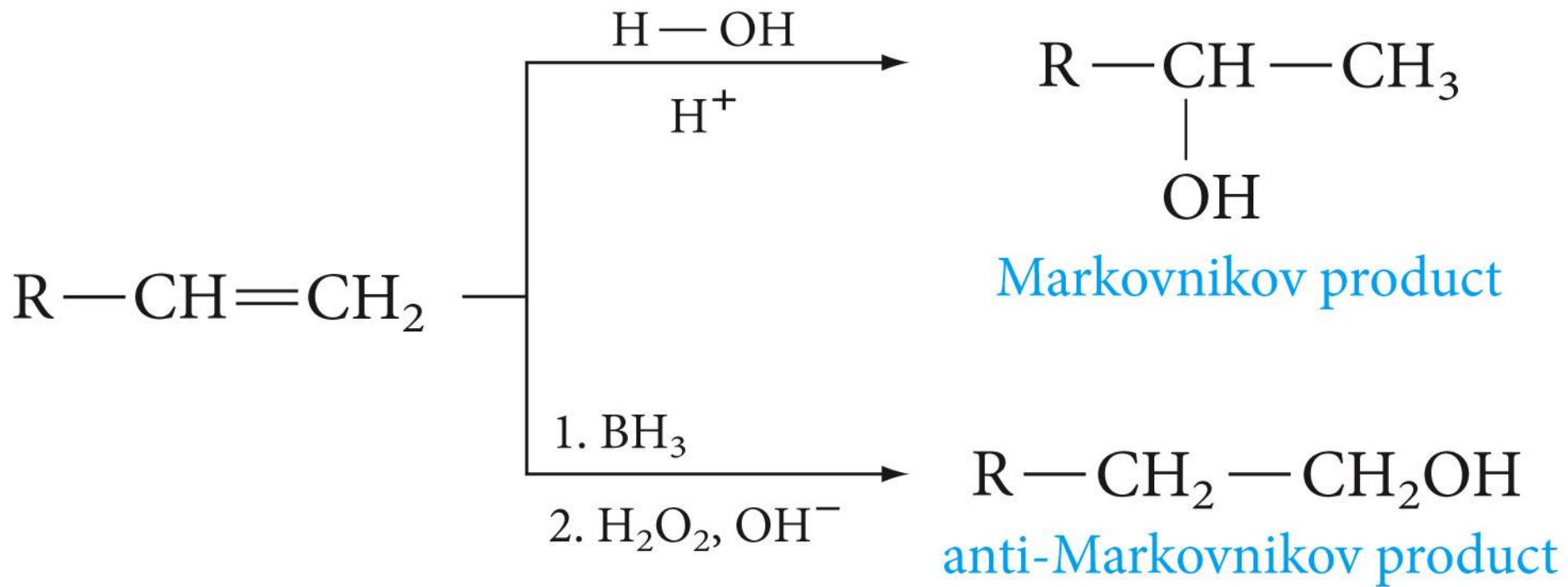
Hydroboration of Alkenes

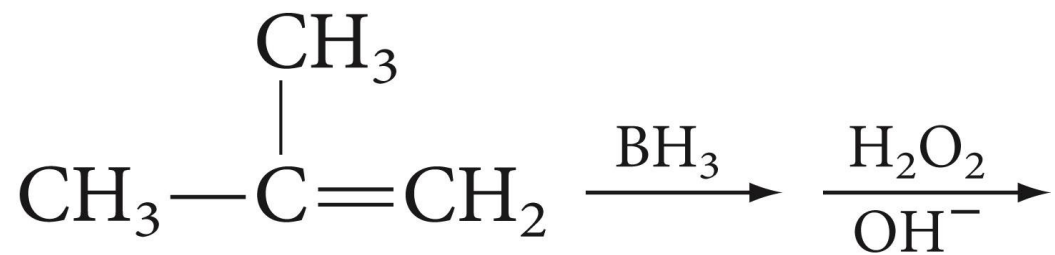


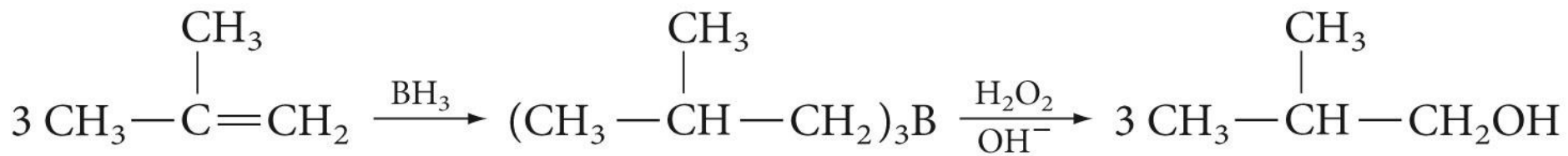


transition state
for hydroboration

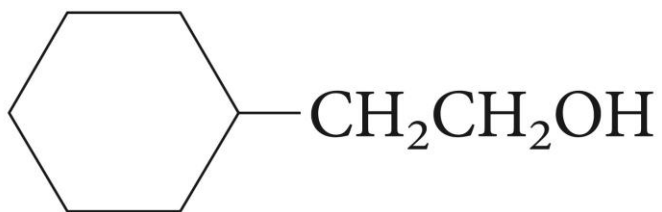




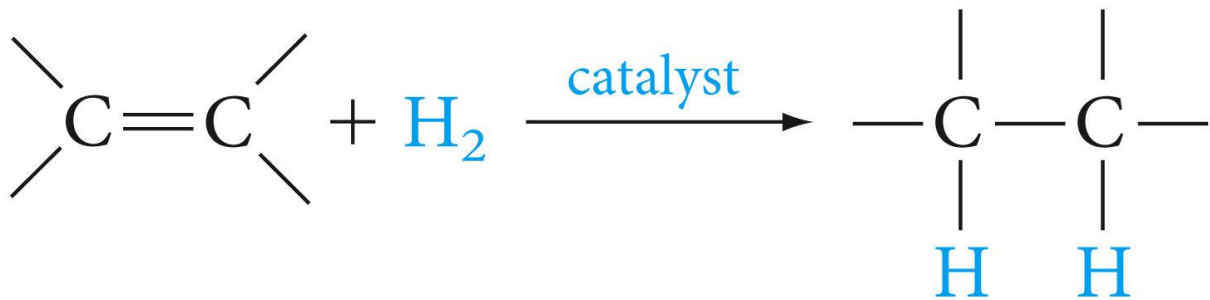


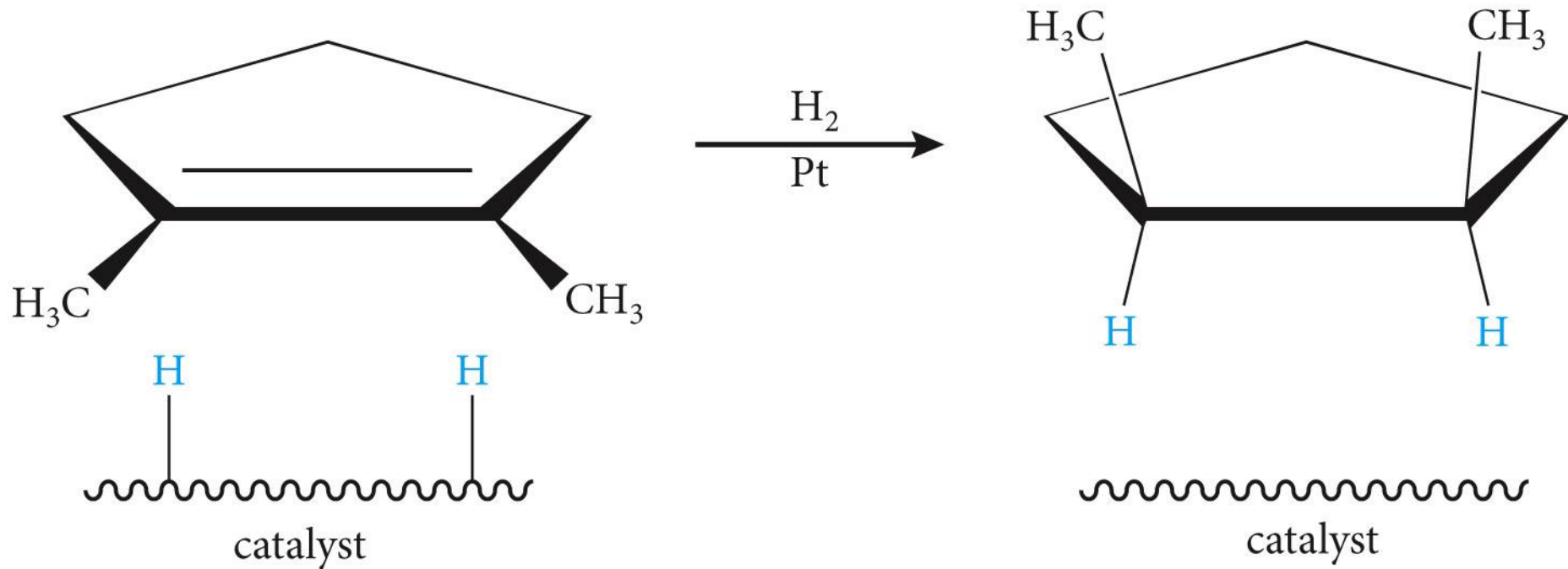


What alkene is needed to obtain the alcohol below via hydroboration-oxidation sequence, what product would this alkene give with acid-catalyzed hydration.

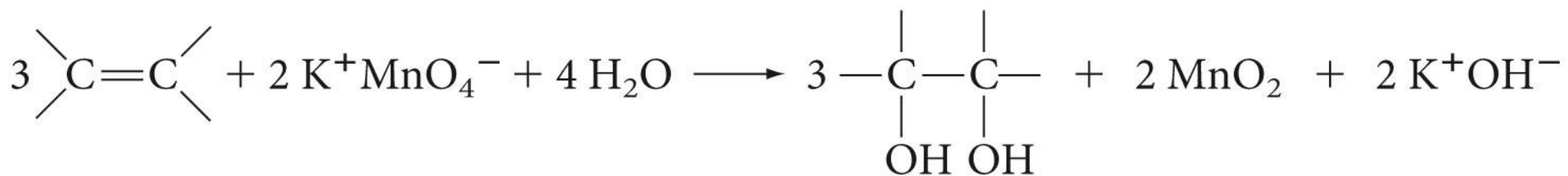


Addition of Hydrogen





Oxidation with permanganate; a Chemical Test

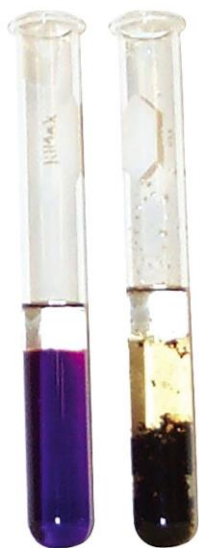


alkene

potassium
permanganate
(purple)

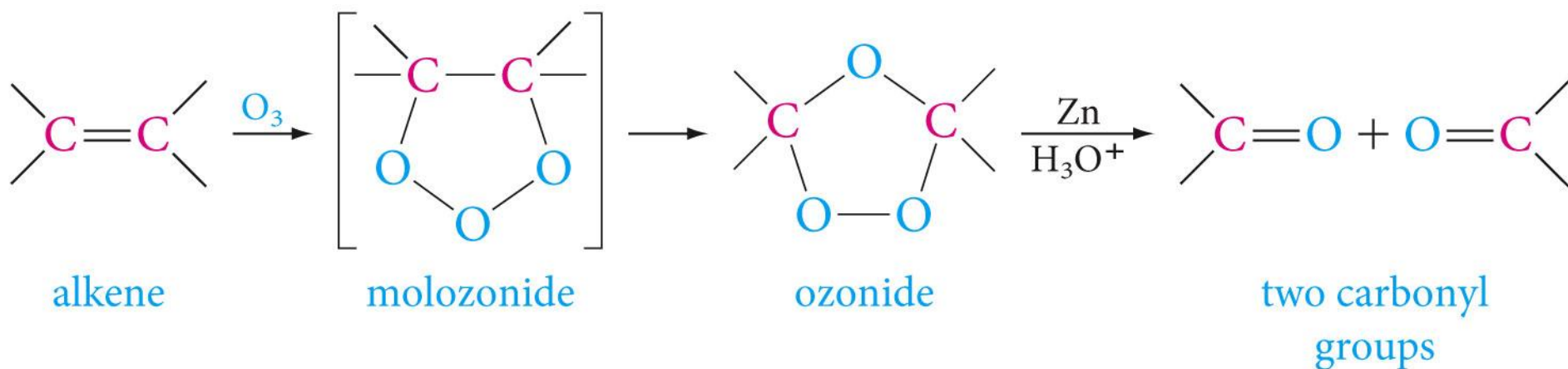
a glycol

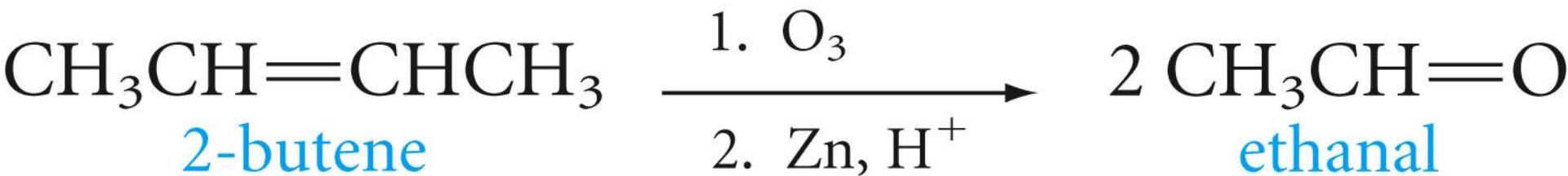
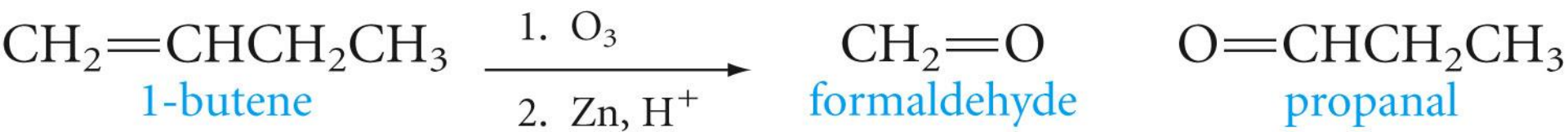
manganese
dioxide
(brown-black)



Ozonolysis of Alkenes

- The first product, a **molozone**, 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.



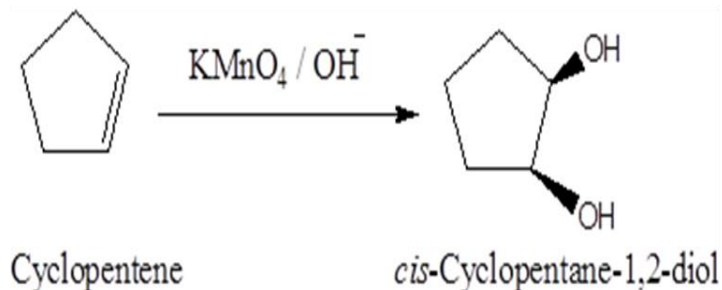
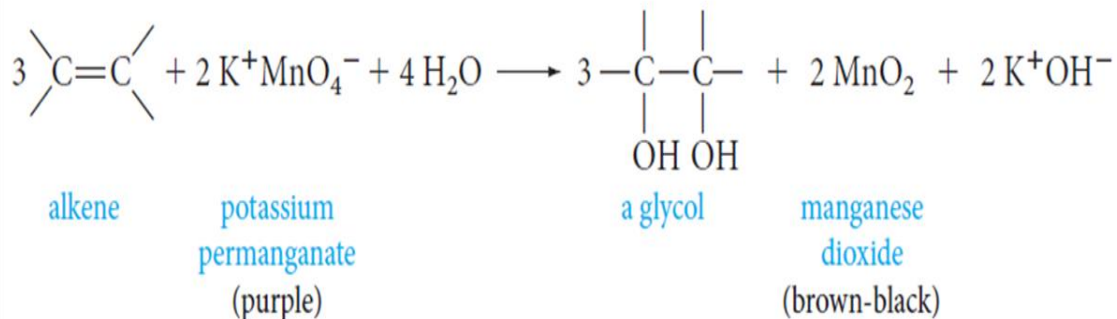


Reactions of Alkenes

Oxidation Reactions

2. Oxidation Using KMnO_4

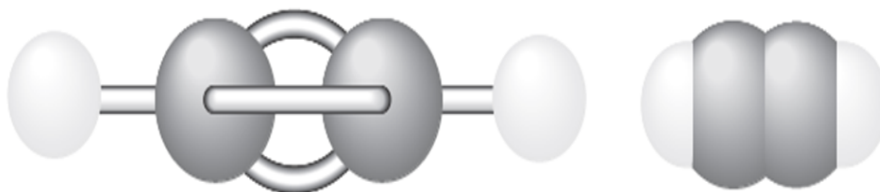
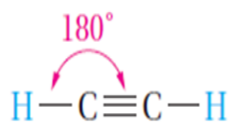
Alkenes react with alkaline potassium permanganate to form glycols (compounds with two adjacent hydroxyl groups).

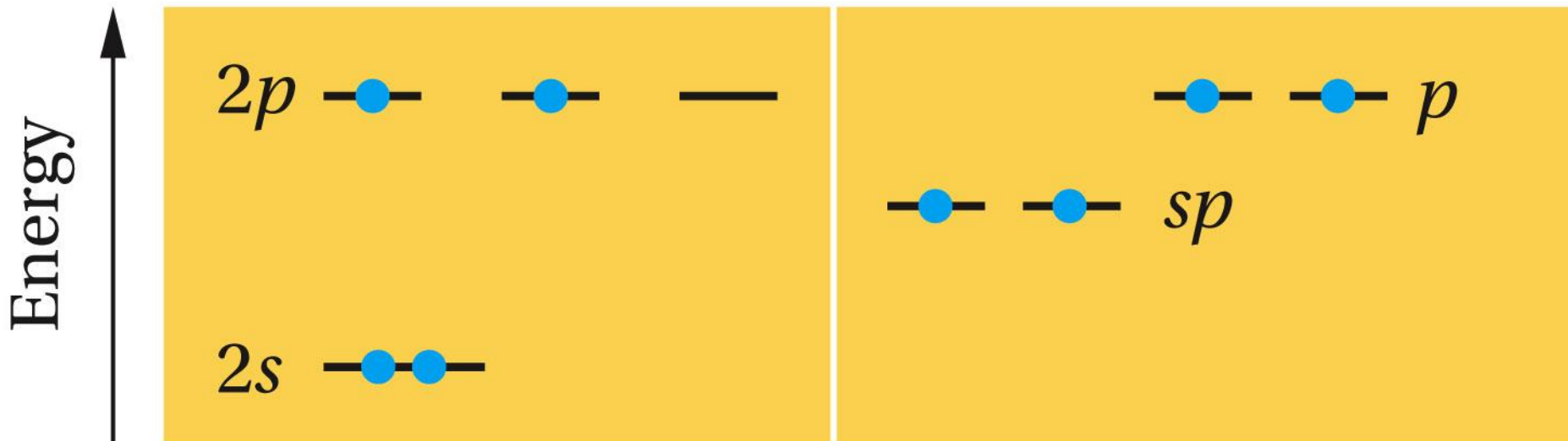


Hexane does not react with purple KMnO_4 (left); cyclohexene (right) reacts, producing a brown-black precipitate of MnO_2 .

The Structure of Alkynes

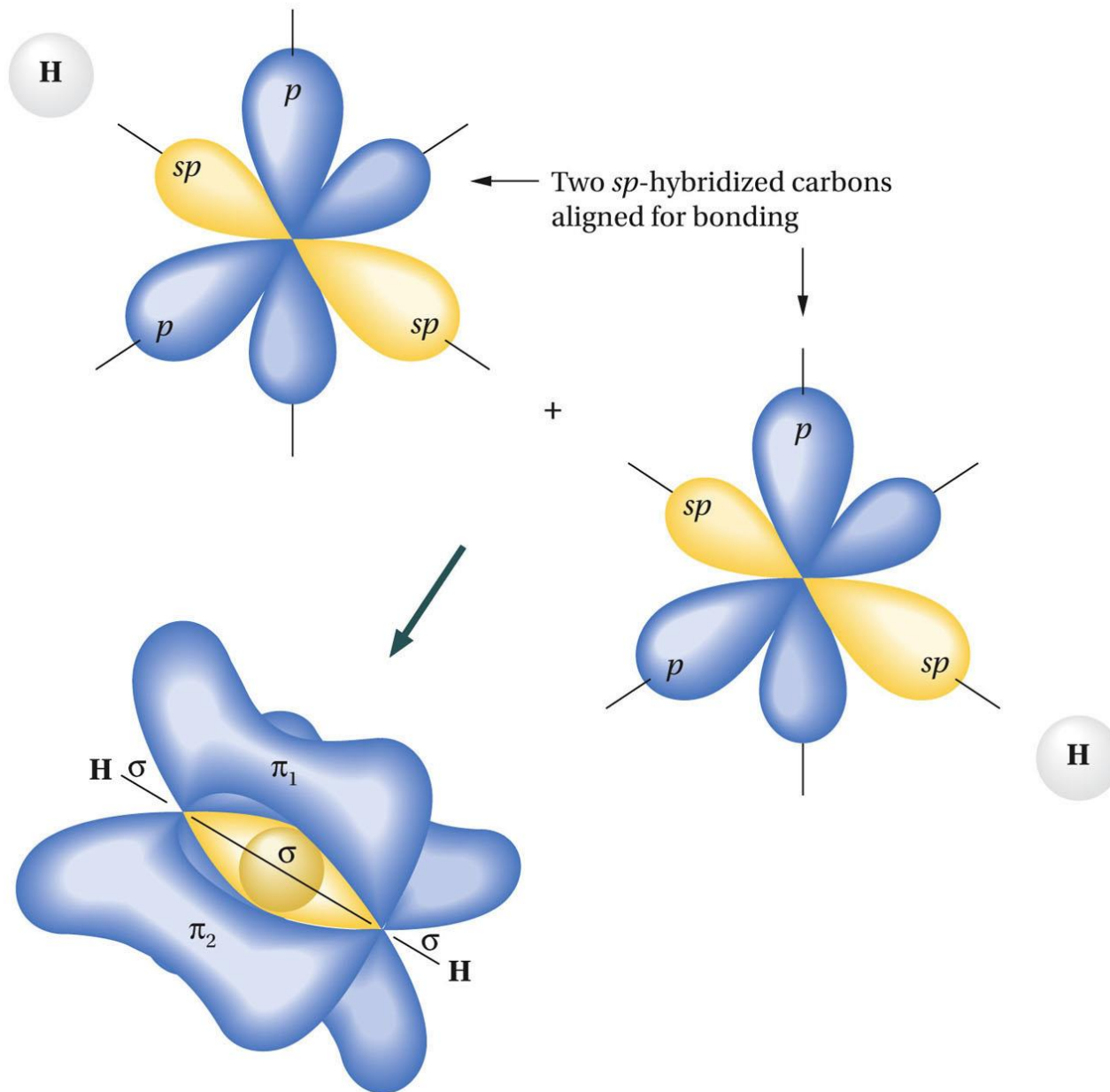
- **Alkynes** are hydrocarbons that contain a **carbon–carbon triple bond**.
- **Alkynes** are also known as **Acetylenes**.
- General formula is **C_nH_{2n-2}**
- Hybridization; **sp -hybridized orbitals**
- The angle between them is **180°** and the bond length **1.20 \AA**
- The geometry is **Linear**.





Atomic orbitals
of carbon

The 2s and one 2p orbital are combined to form two hybrid sp orbitals, leaving one electron in each of two p orbitals.



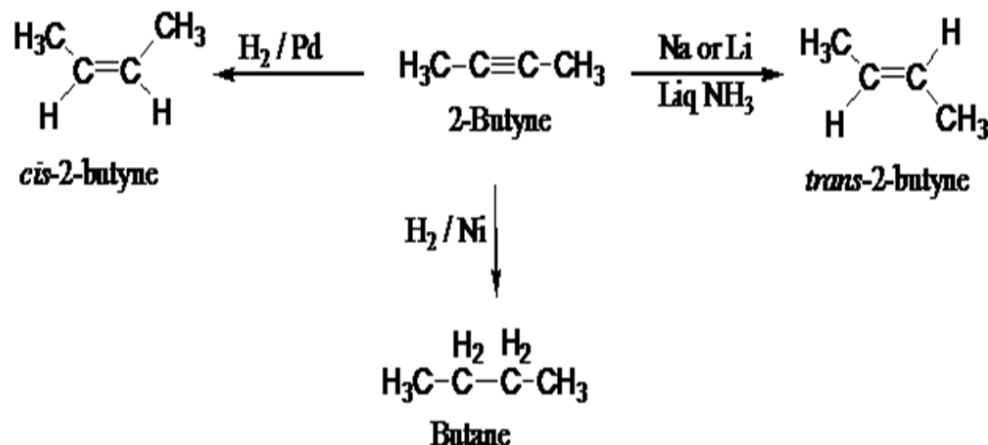
The resulting carbon–carbon triple bond, with a hydrogen atom attached to each remaining sp bond. (The orbitals involved in the C–H bonds are omitted for clarity.)

Reaction of Alkynes

Electrophilic Addition Reactions

1. Addition of Hydrogen: Hydrogenation

- With an ordinary nickel or platinum catalyst, alkynes are hydrogenated all the way to alkanes.
- However, a special palladium catalyst (called Lindlar's catalyst) can control hydrogen addition so that only one mole of hydrogen adds. In this case, the product is a **cis alkene**.
- On the other hand, reduction using metals such as sodium or lithium in liquid ammonia results in formation of **trans alkenes**.

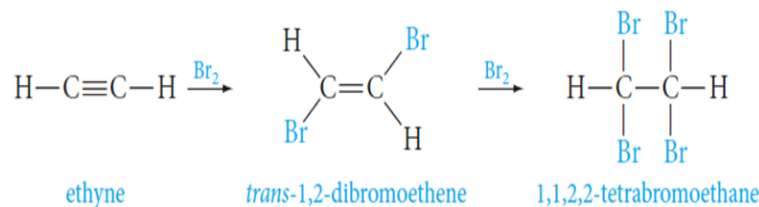


Reaction of Alkynes

Electrophilic Addition Reactions

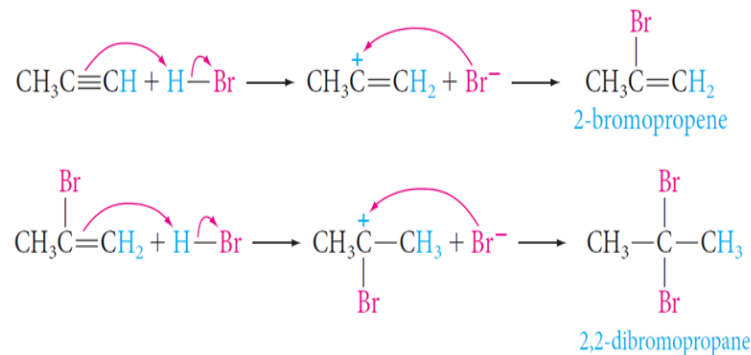
2. Addition of Halogen: Halogenation

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



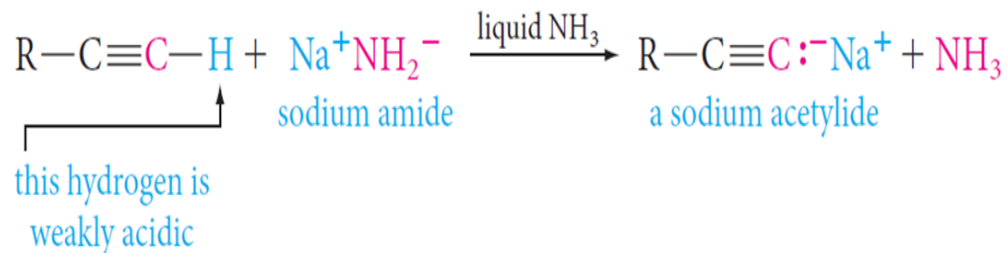
3. Addition of Hydrogen Halide

With unsymmetrical triple bonds and unsymmetrical reagents, Markovnikov's Rule is followed in each step, as shown in the following example:



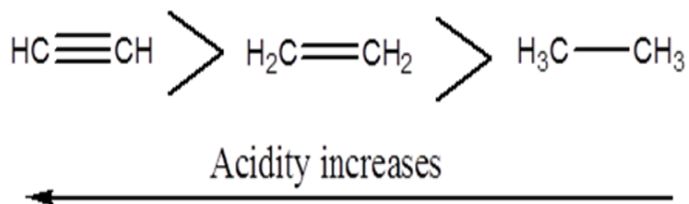
Acidity of Alkynes

- A hydrogen atom on a triply bonded carbon (**Terminal Alkyne**) is weakly acidic and can be removed by a very strong base (as Sodium amide).



- Internal alkynes (**Non-Terminal Alkyne**) have no exceptionally acidic hydrogens.
 - Relative Acidity of the Hydrocarbon.

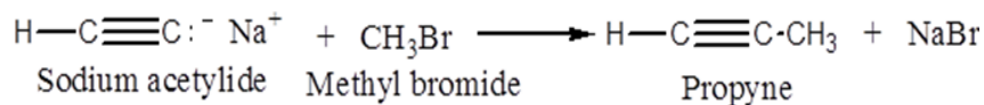
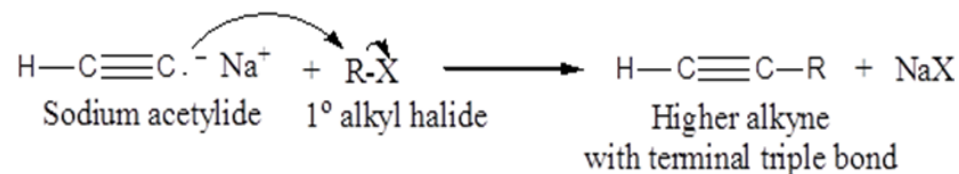
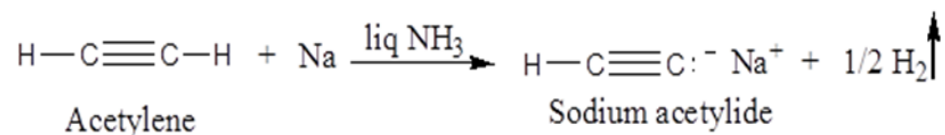
Terminal alkynes, are more acidic than other hydrocarbons



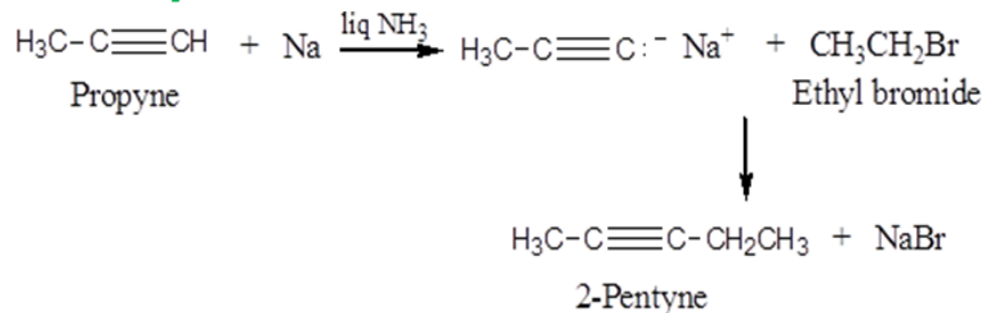
Preparation of Alkynes

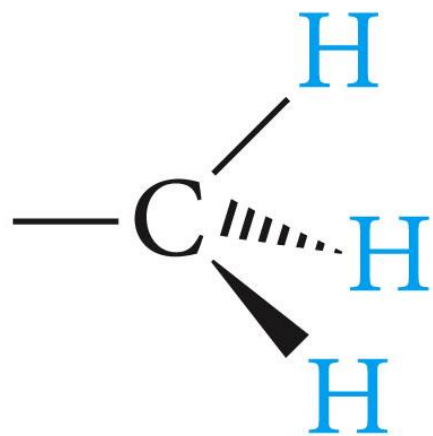
2) Reaction of Sodium Acetylide with Primary Alkyl Halides

○ Acetylene



○ Monosubstituted Acetylenes

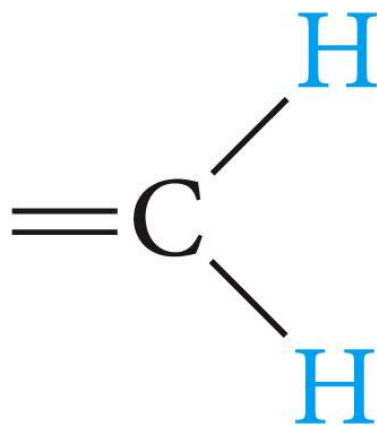




sp^3

25% s ,

75% p



sp^2

$33\frac{1}{3}\%$ s ,

$66\frac{2}{3}\%$ p



sp

50% s ,

50% p

increasing acidity



Reaction of Alkynes

Electrophilic Addition Reactions

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 (keto form).
- The keto form of aldehydes and ketones are in equilibrium with the enol form.
- The keto form predominates at equilibrium for most simple aldehydes and ketones.
- The inter conversion is called **keto-enol tautomerization**.

