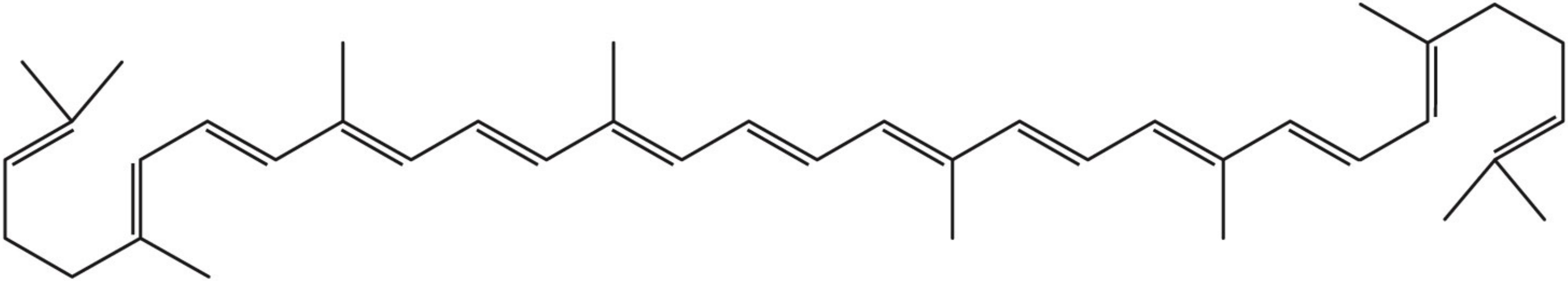
Chapter 3: Alkenes and Alkynes



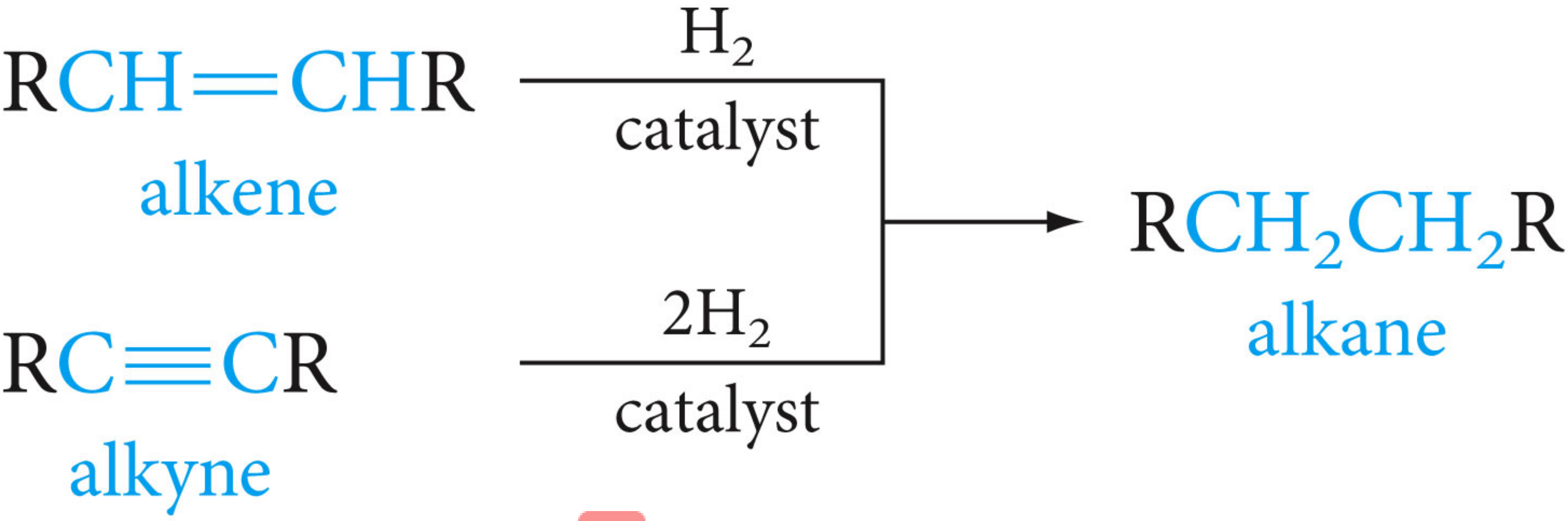
lycopene

Hydrogenation of Alkenes and Alkynes

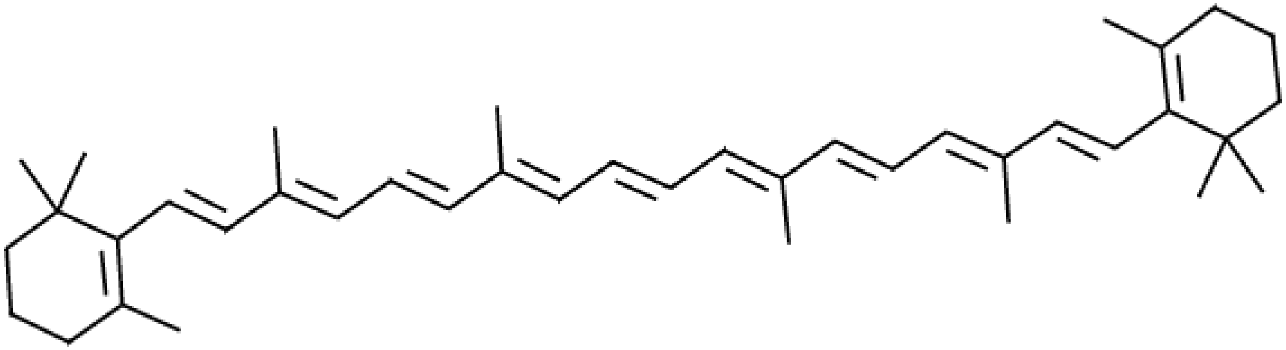
Hydrocarbons that have carbon-carbon double bond are called alkenes; those with a carbon-carbon triple bond are alkynes

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 re present in a molecule, they can be classified depending on the relative positions of the bonds

$\mathrm{C{=}C{=}C}$

$\mathrm{C{=}C{=}C{=}C}$

cumulated

$\mathrm{C{=}C{-}C{=}C}$

$\mathrm{C{=}C{-}C{\equiv}C}$

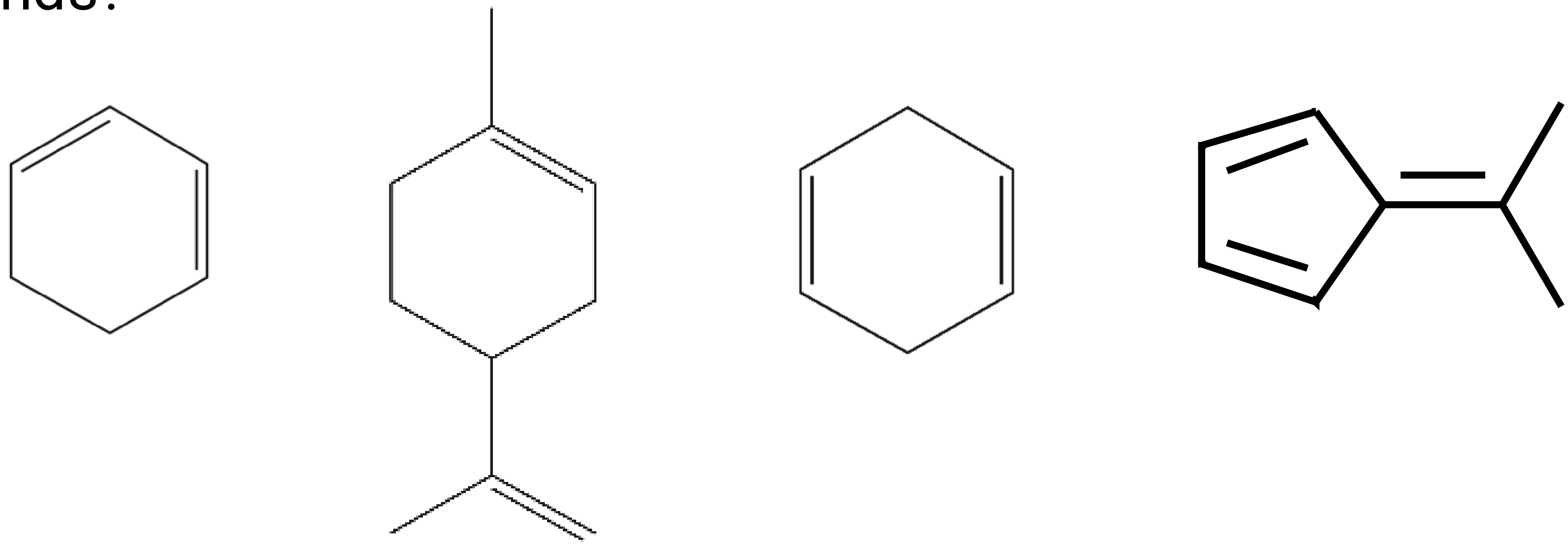
conjugated

$\mathrm{C{=}C{-}C{-}C{=}C}$

$\mathrm{C{\equiv}C{-}C{-}C{-}C{\equiv}C}$

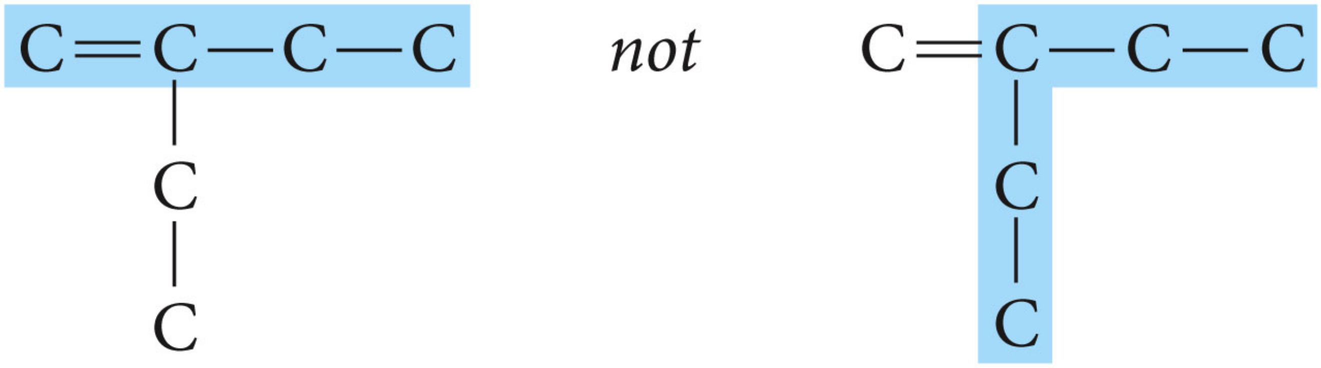
nonconjugated (isolated)

Which of the following compounds have conjugated multiple bonds?



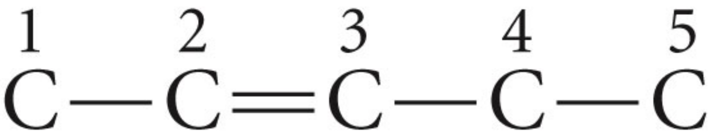
Nomenclature

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



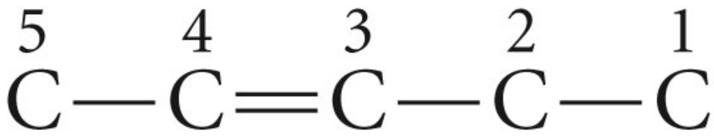
named as a butene, not as a pentene

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



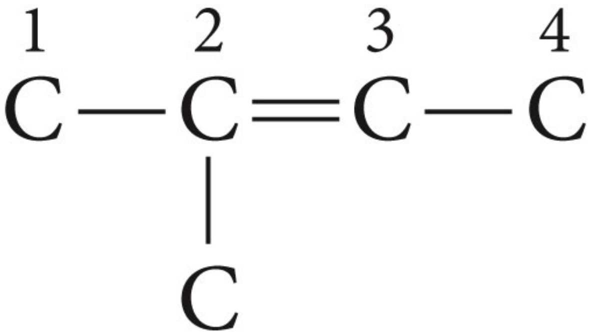
$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$

not



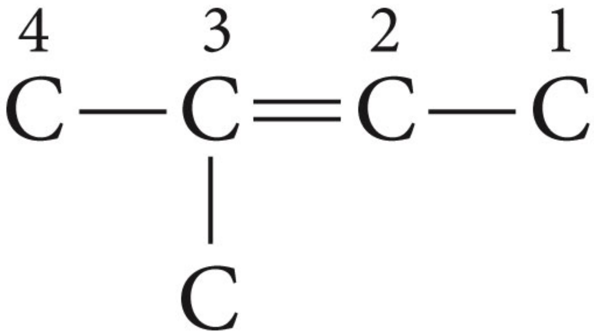
$\overset{5}{C}-\overset{4}{C}=\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$

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



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

not



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

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

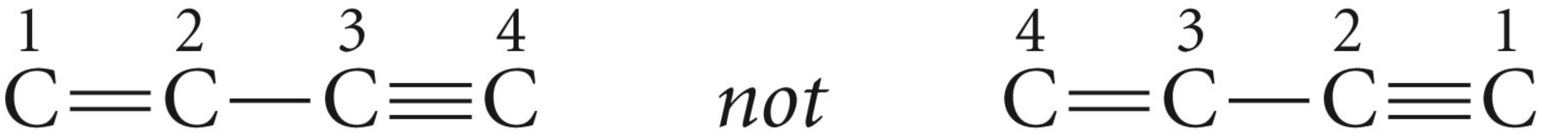
$$\overset{1}{\mathrm{C}}\mathrm{H_2}{=}\overset{2}{\mathrm{C}}\mathrm{H}\overset{3}{\mathrm{C}}\mathrm{H_2}\overset{4}{\mathrm{C}}\mathrm{H_3}$$

1-butene, *not* 2-butene

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

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

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



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

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

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

$\overset{1}{\mathrm{CH_2}}{=}\overset{2}{\mathrm{CH}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$

1-butene

$\overset{1}{\mathrm{CH_3}}\overset{2}{\mathrm{CH}}{=}\overset{3}{\mathrm{CH}}\overset{4}{\mathrm{CH_3}}$

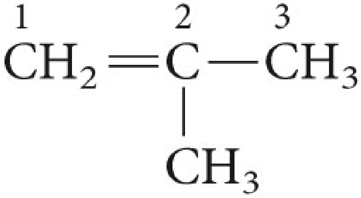
2-butene

$\overset{1}{\mathrm{HC}}{\equiv}\overset{2}{\mathrm{C}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$

1-butyne

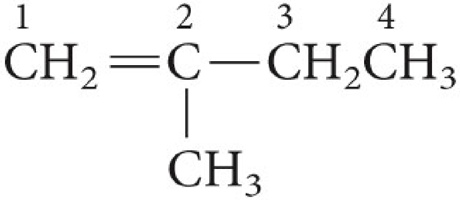
$\overset{1}{\mathrm{CH_3}}\overset{2}{\mathrm{C}}{\equiv}\overset{3}{\mathrm{C}}\overset{4}{\mathrm{CH_3}}$

2-butyne



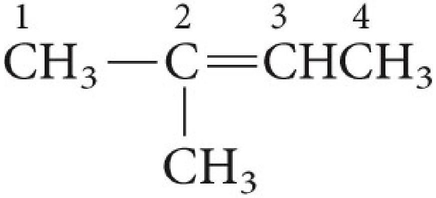
$\overset{1}{\mathrm{CH_2}}{=}\overset{2}{\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{C}}}{-}\overset{3}{\mathrm{CH_3}}$

methylpropene
(isobutylene)



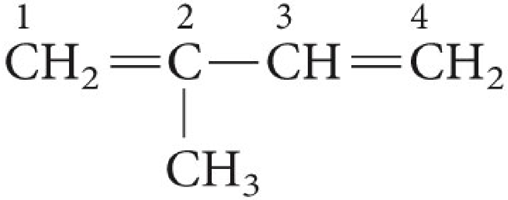
$\overset{1}{\mathrm{CH_2}}{=}\overset{2}{\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{C}}}{-}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$

2-methyl-1-butene



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

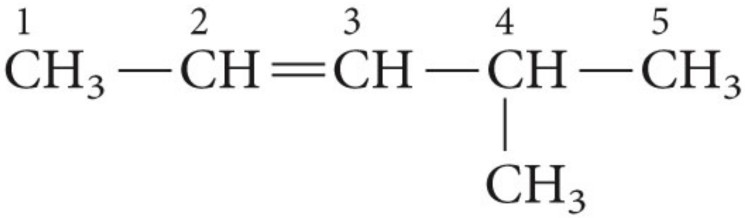
2-methyl-2-butene



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

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

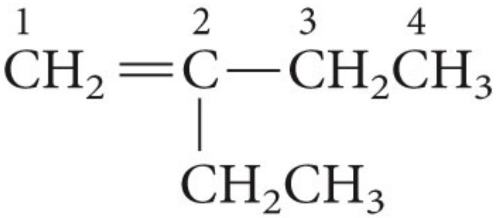
The numbering rules applied



$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\underset{\large CH_3}{\overset{4}{CH}}-\overset{5}{CH_3}$$

4-methyl-2-pentene

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



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

2-ethyl-1-butene

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

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

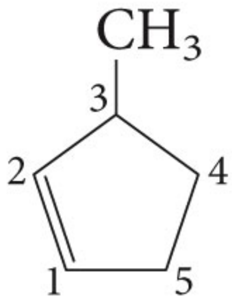
1,3-butadiene

(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.

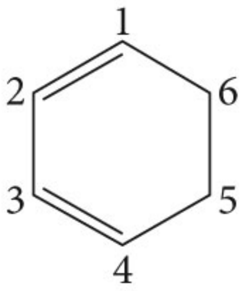
cyclopentene

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

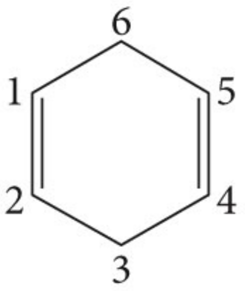


3-methylcyclopentene

(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

$CH_2{=}CH_2$

ethylene

(ethene)

$HC{\equiv}CH$

acetylene

(ethyne)

$CH_3CH{=}CH_2$

propylene

(propene)

$CH_2{=}CH{-}$

vinyl

(ethenyl)

$CH_2{=}CHCl$

vinyl chloride

(chloroethene)

$CH_2{=}CH{-}CH_2{-}$

allyl

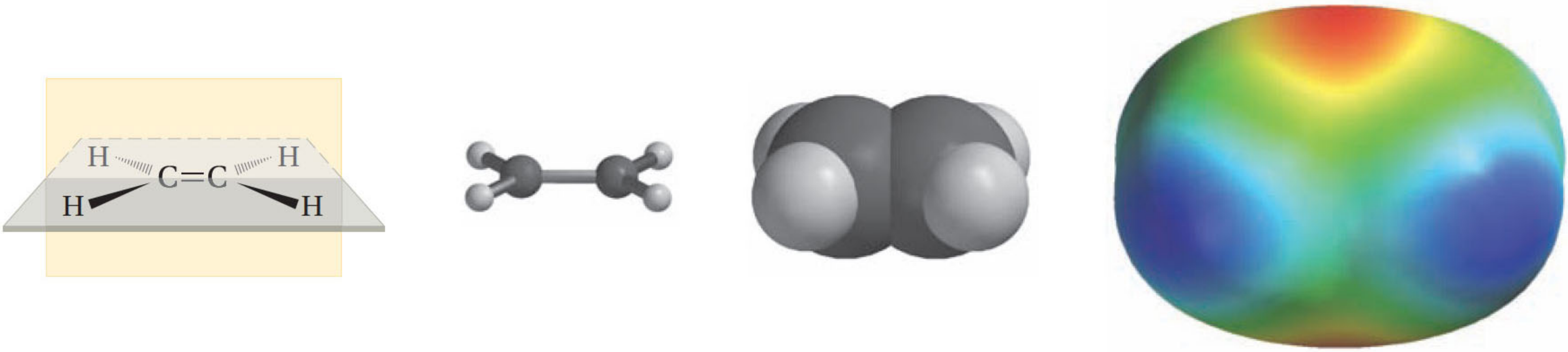
(2-propenyl)

$CH_2{=}CH{-}CH_2Cl$

allyl chloride

(3-chloropropene)

Some Facts about Double Bonds



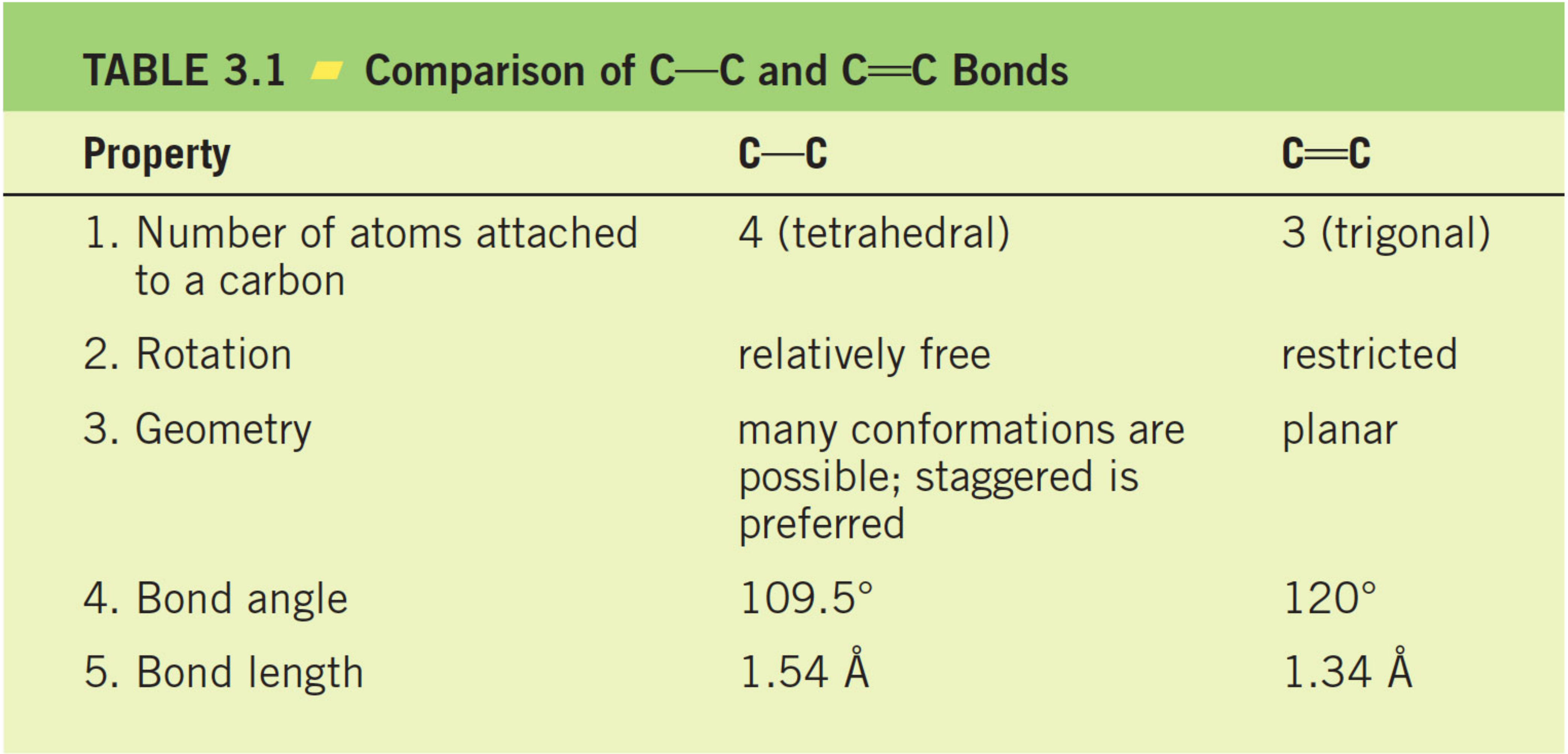
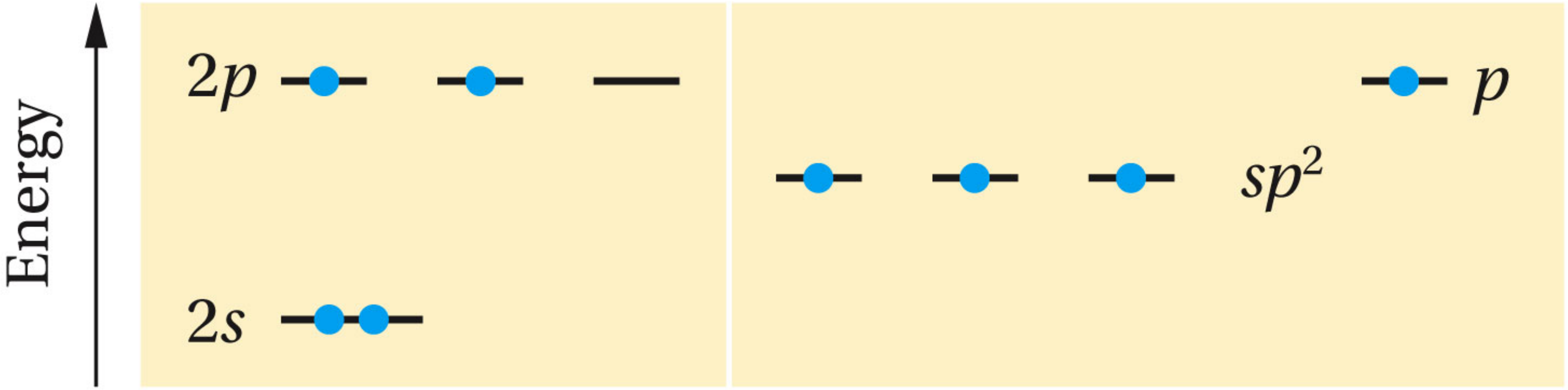


TABLE 3.1 Comparison of $\mathrm{C{-}C}$ and $\mathrm{C{=}C}$ Bonds

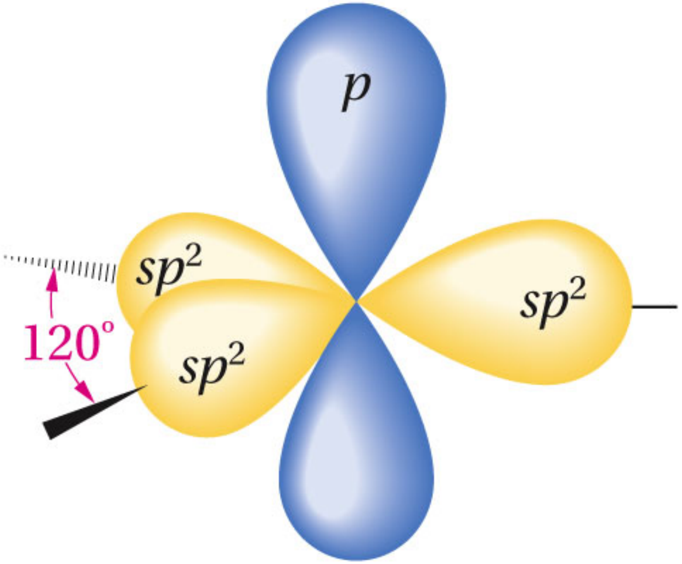
Property	$\mathrm{C{-}C}$	$\mathrm{C{=}C}$
1. Number of atoms attached to a carbon	4 (tetrahedral)	3 (trigonal)
2. Rotation	relatively free	restricted
3. Geometry	many conformations are possible; staggered is preferred	planar
4. Bond angle	109.5°	120°
5. Bond length	1.54 Å	1.34 Å

The Orbital Model of a Double Bond; the pi Bond

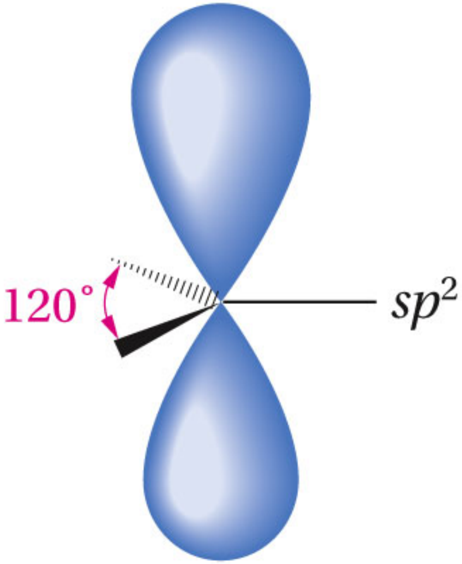


Atomic orbitals of carbon

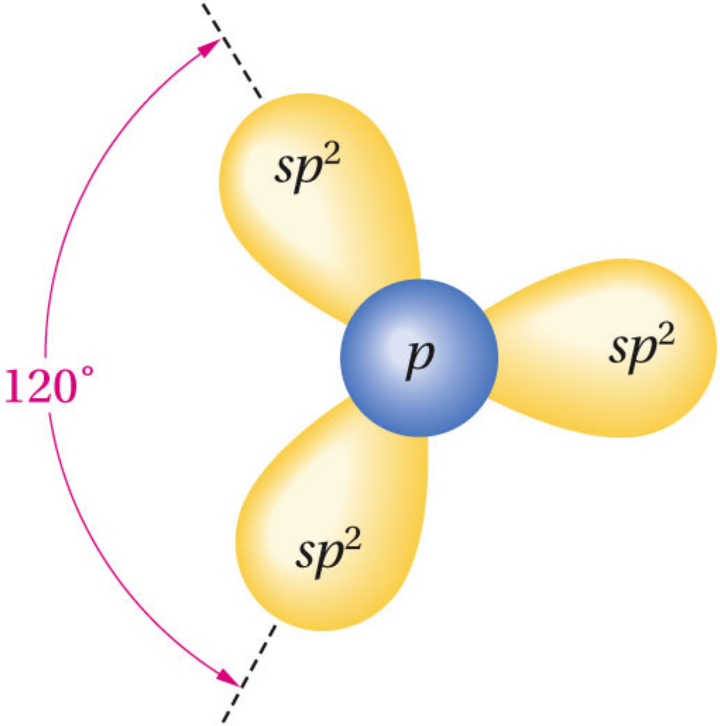
The 2*s* and two 2*p* orbitals are combined to form three hybrid sp^2 orbitals, leaving one electron still in a *p* orbital.



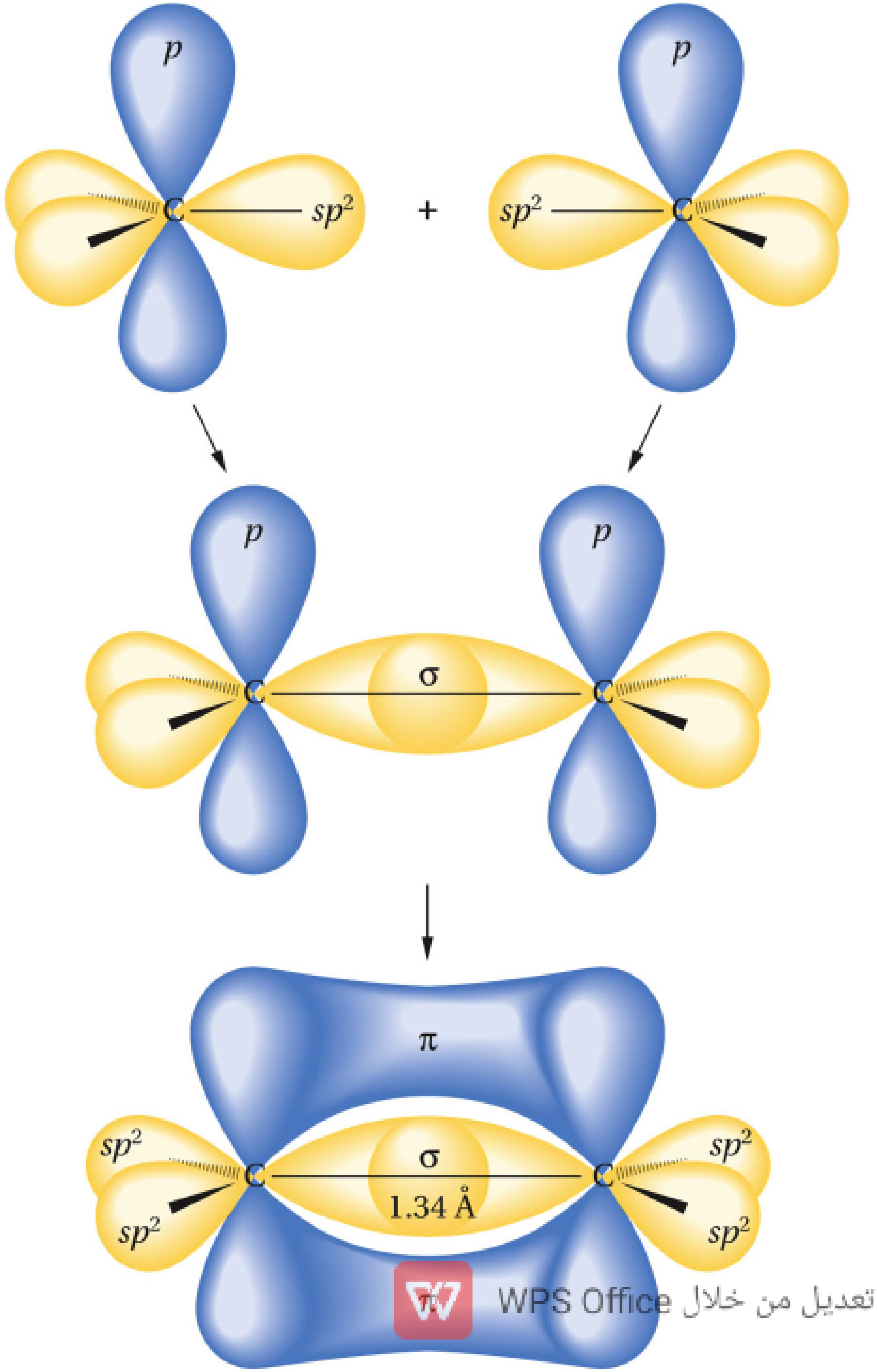
side view



side view with
the sp^2 orbitals
represented by lines



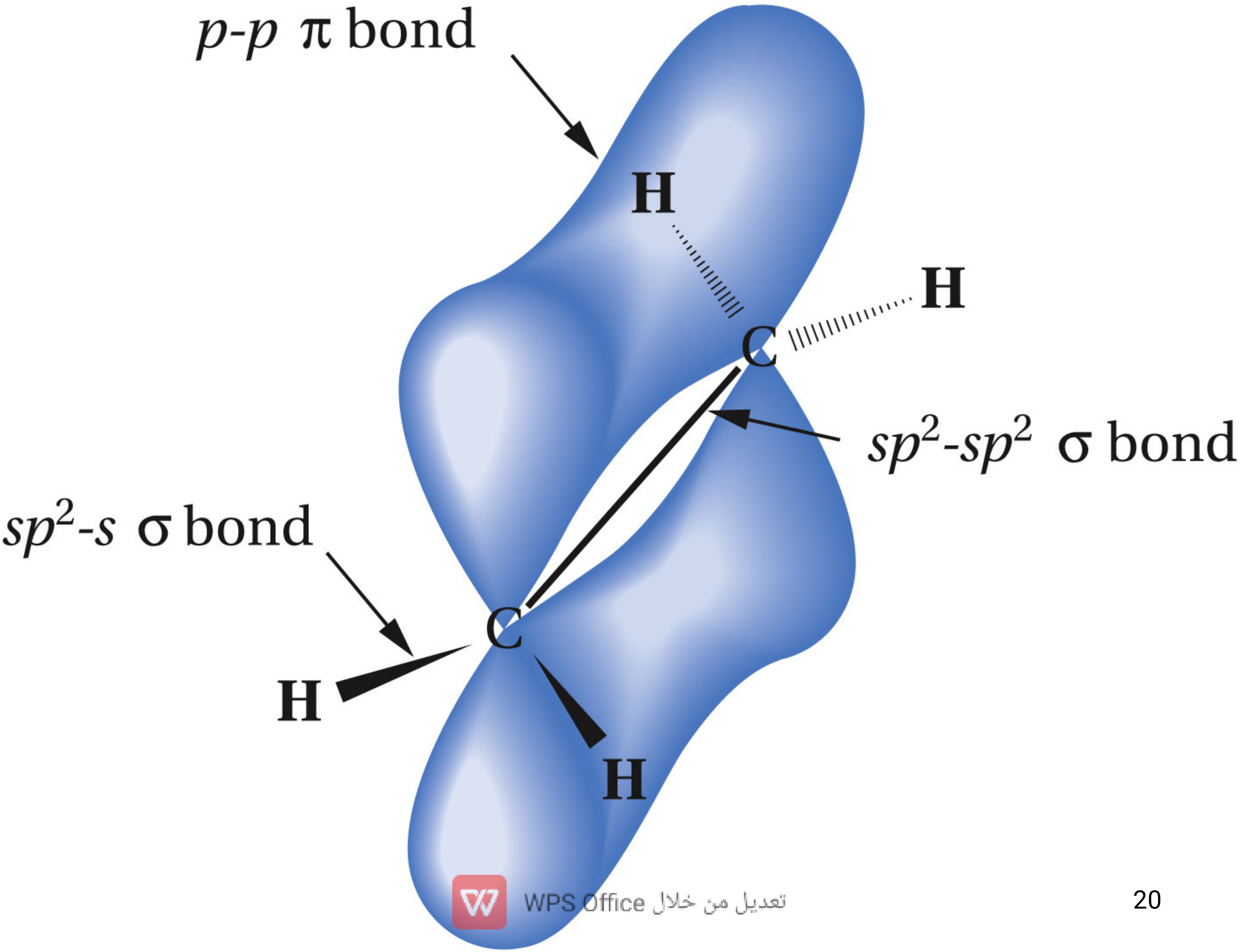
top view

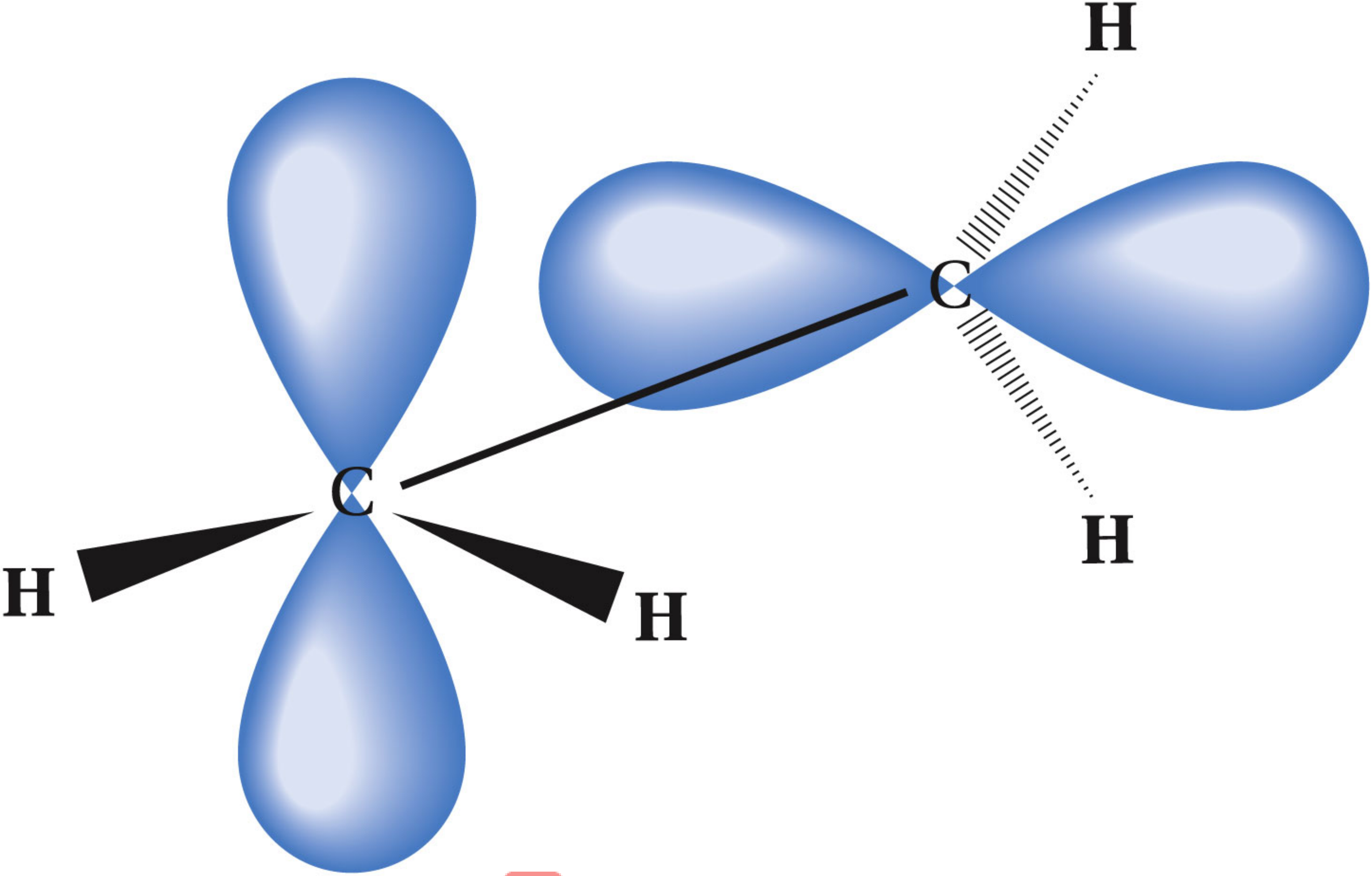


two sp^2-hybridized carbons with *p* orbitals parallel

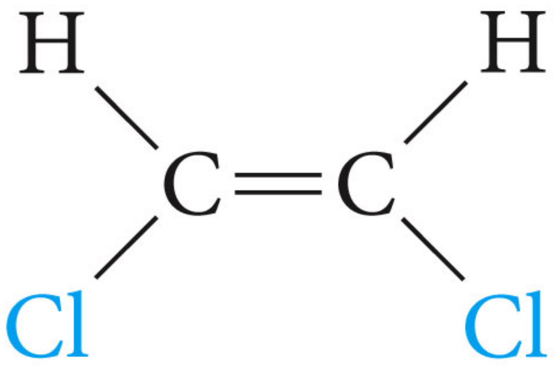
the σ bond is formed by two electrons in overlapping sp^2 orbitals

the π bond is formed by two electrons in overlapping parallel *p* orbitals

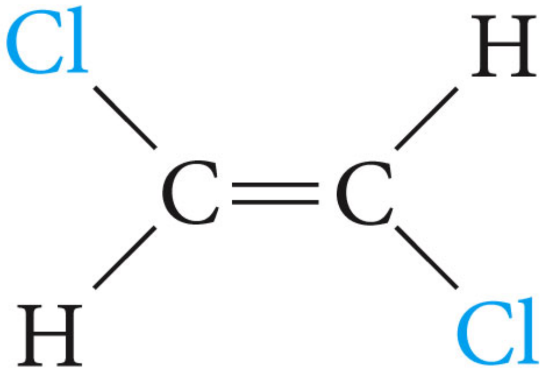

p-p π bond
H
H
C
sp^2-sp^2 σ bond
sp^2-s σ bond
C
H
H


H
C
H
H
C
H
H

Cis-Trans Isomerism in Alkenes

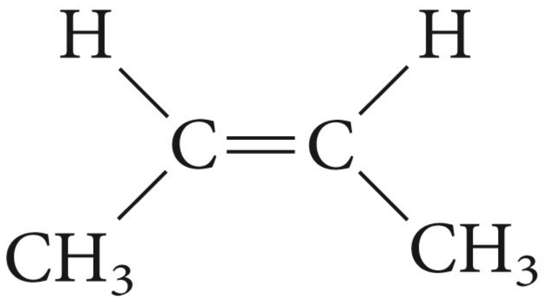


cis-1,2-dichloroethene
bp 60°C, mp −80°C



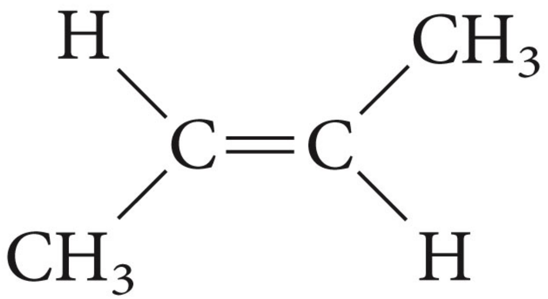
trans-1,2-dichloroethene
bp 47°C, mp −50°C

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



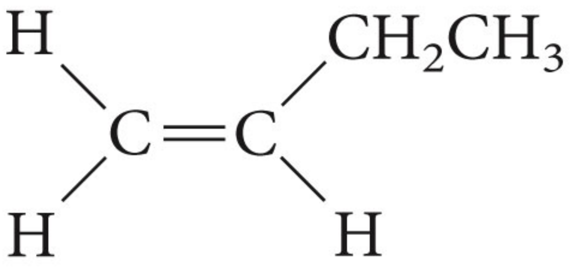
cis-2-butene

bp 3.7°C, mp −139°C



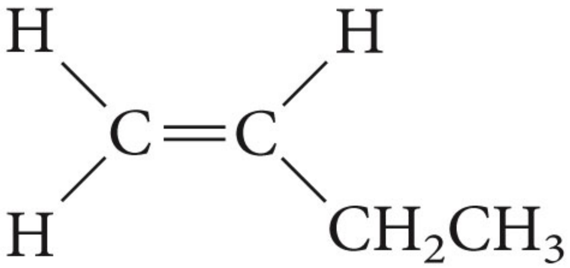
trans-2-butene

bp 0.3°C, mp −106°C



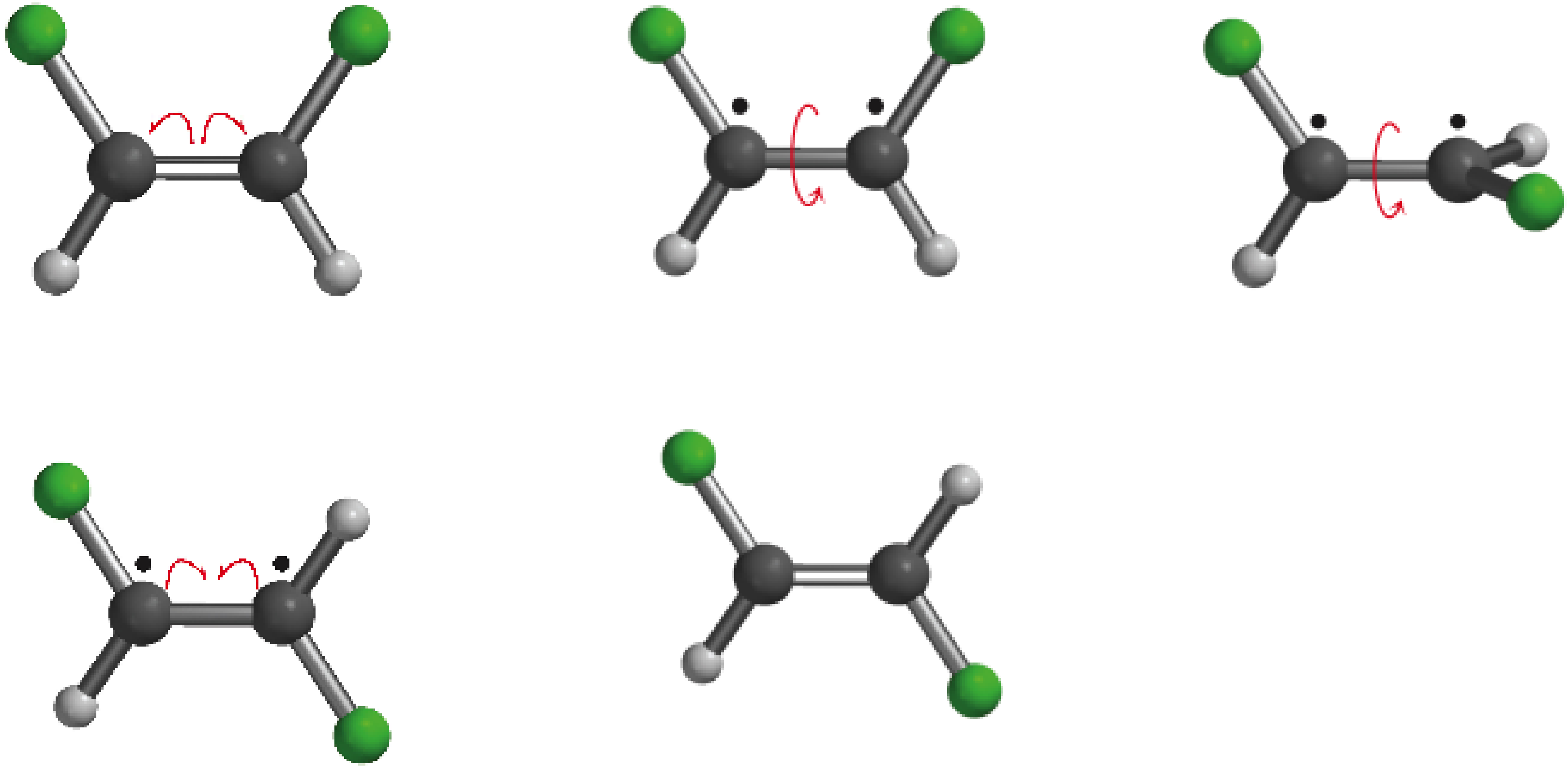
1-butene

is identical to



1-butene

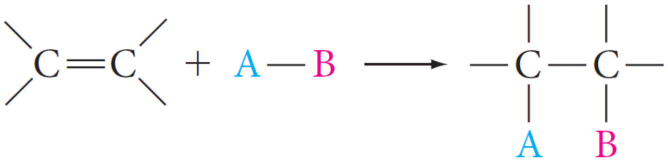
Geometric isomers of alkenes can be interconverted if sufficient energy is supplied to break the pi bond and allow rotation about the remaining sigma bond.



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

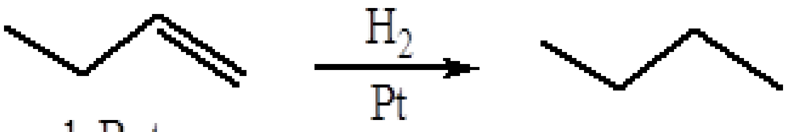
(2) Oxidation Reactions

1. Ozonolysis
2. Oxidation Using $KMnO_4$

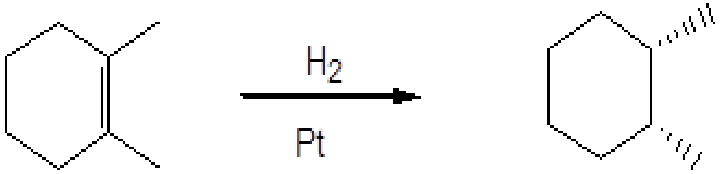
Electrophilic Addition Reactions

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.



1-Butene Butane

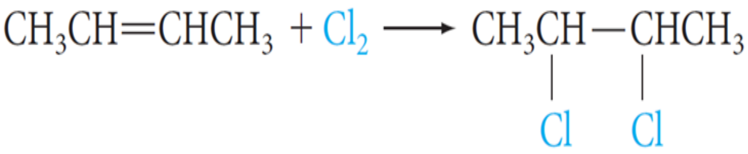


1,2-Dimethylcyclohexene *cis*-1,2-Dimethylcyclohexane

Electrophilic Addition Reactions

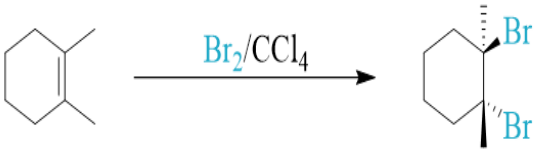
2. Addition of Halogen: Halogenation

*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)*



$$CH_3CH{=}CHCH_3 + Cl_2 \longrightarrow CH_3\underset{Cl}{\underset{|}{C}}H{-}\underset{Cl}{\underset{|}{C}}HCH_3$$

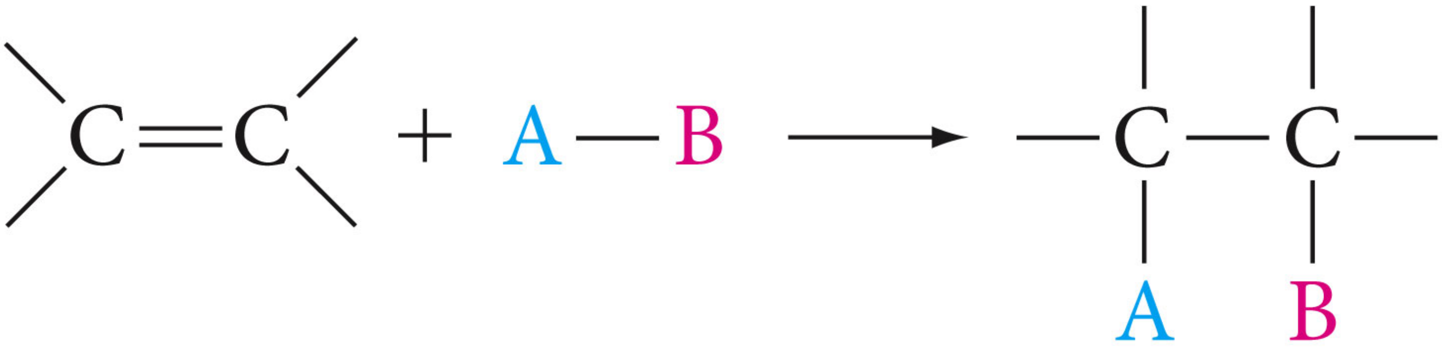
2-butene 2,3-dichlorobutane



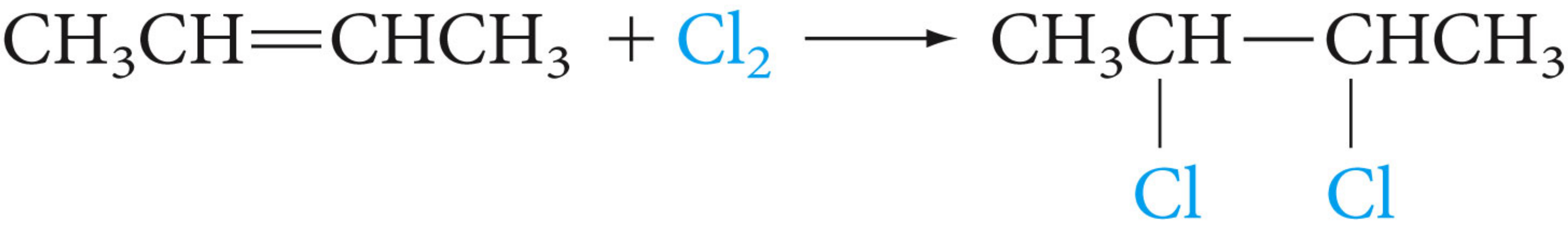
1,2-Dimethyl-cyclohexene *trans*-1,2-Dibromo-1,2-dimethyl-cyclohexane

- **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



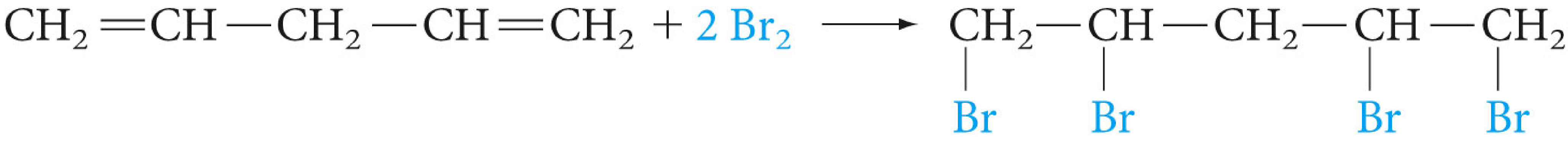
Addition of halogens X_2



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

2-butene
bp 1–4°C

2,3-dichlorobutane
bp 117–119°C

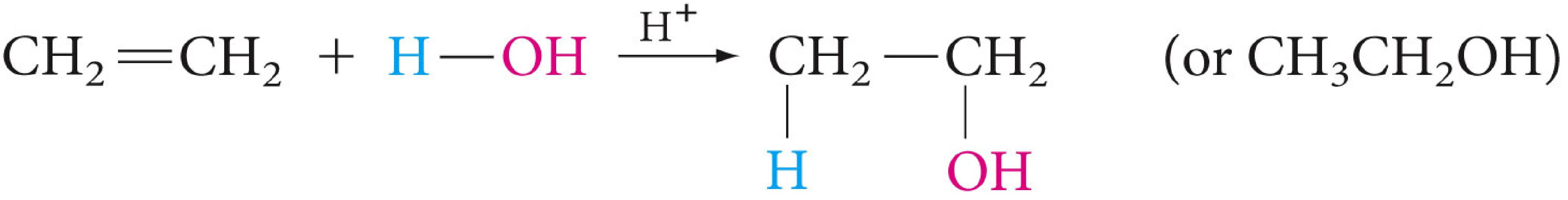


$$CH_2{=}CH{-}CH_2{-}CH{=}CH_2 + 2\,Br_2 \longrightarrow \underset{Br}{\underset{|}{CH_2}}{-}\underset{Br}{\underset{|}{CH}}{-}CH_2{-}\underset{Br}{\underset{|}{CH}}{-}\underset{Br}{\underset{|}{CH_2}}$$

1,4-pentadiene
bp 26.0°C

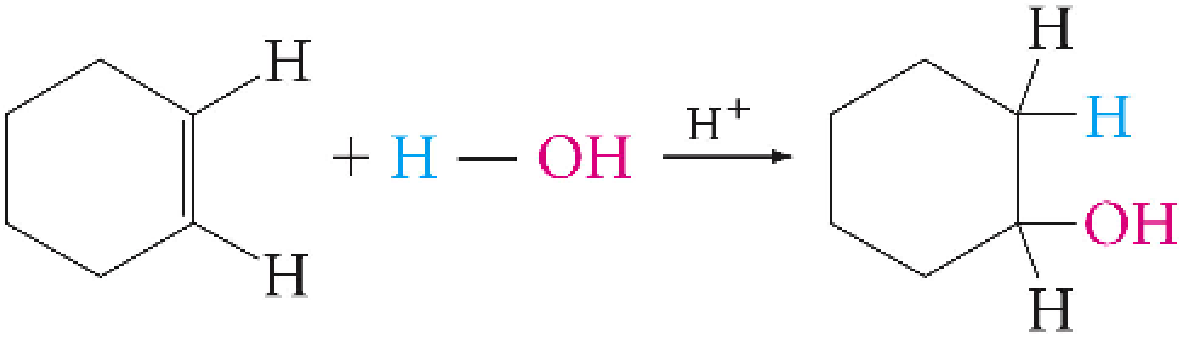
1,2,4,5-tetrabromopentane
mp 85 – 86°C

Addition of Water (Hydration)



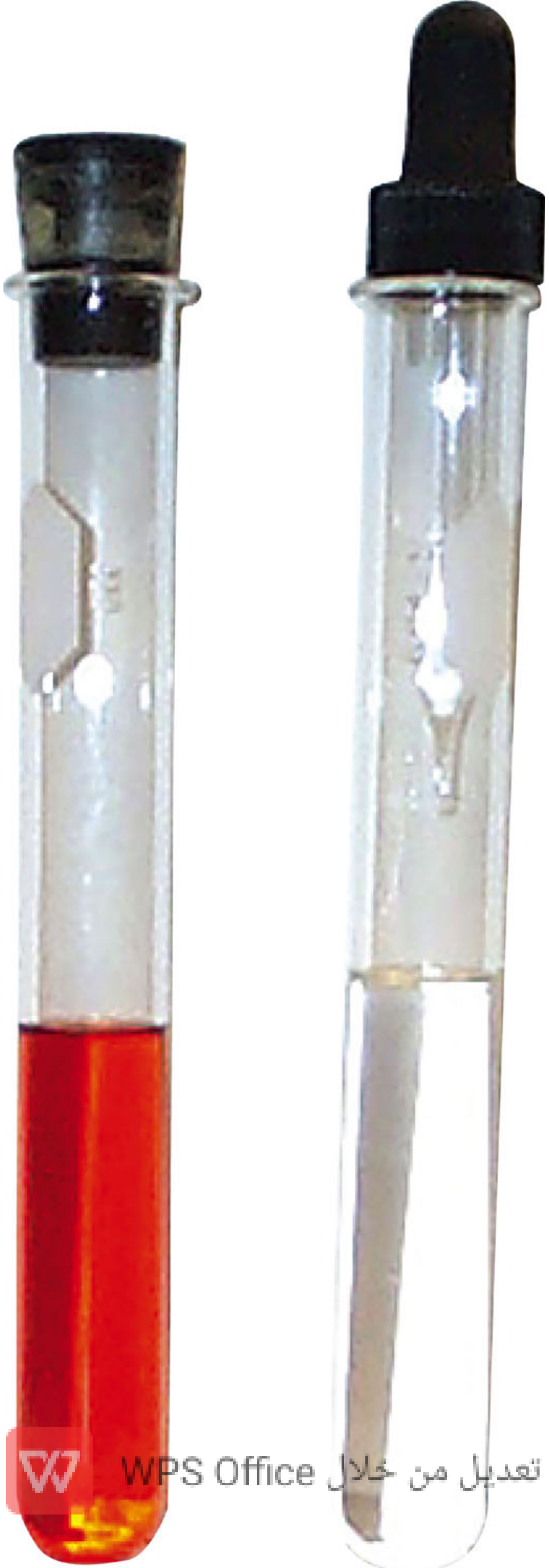
$$CH_2{=}CH_2 + H{-}OH \xrightarrow{H^+} \underset{H}{\underset{|}{CH_2}}{-}\underset{OH}{\underset{|}{CH_2}} \quad (\text{or } CH_3CH_2OH)$$

ethanol

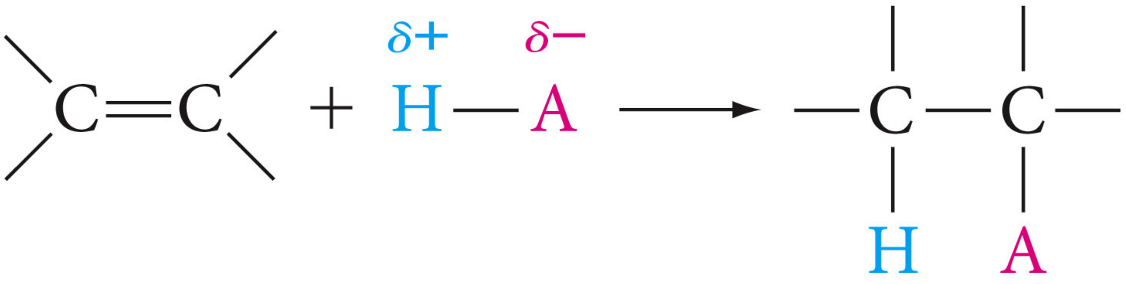


cyclohexene
bp 83.0°C

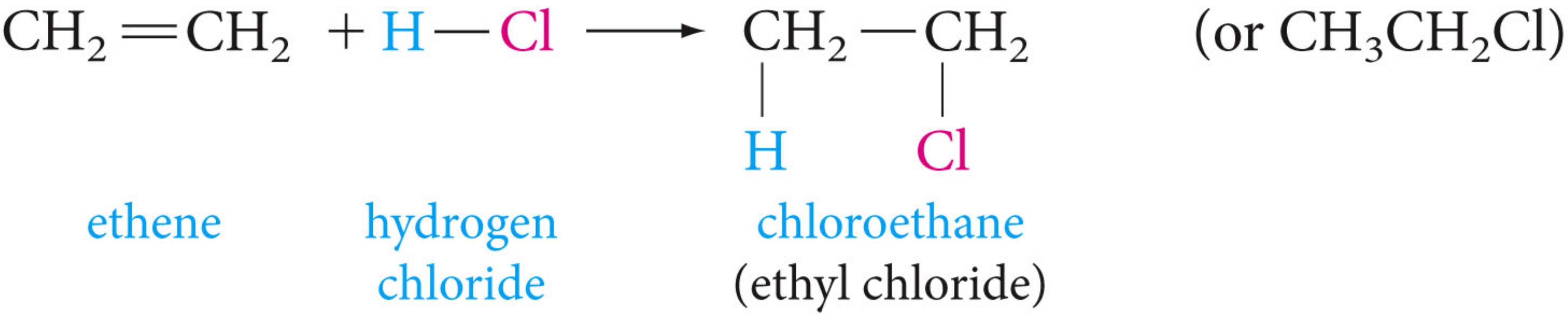
cyclohexanol
bp 161.1°C



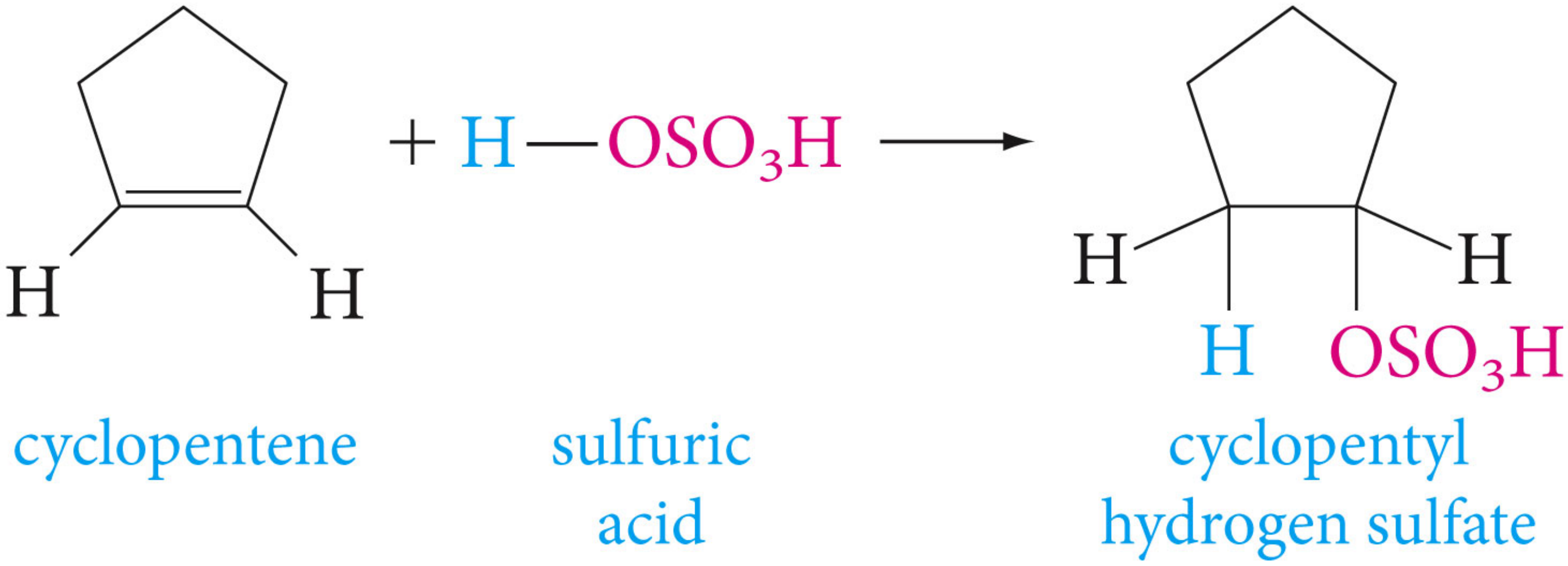
Addition of Acids



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



$$\underset{\text{ethene}}{CH_2{=}CH_2} + \underset{\text{hydrogen chloride}}{H{-}Cl} \longrightarrow \underset{\text{chloroethane (ethyl chloride)}}{\underset{H}{CH_2}{-}\underset{Cl}{CH_2}} \quad (\text{or } CH_3CH_2Cl)$$



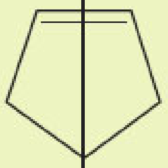
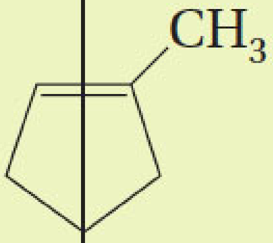
Write the equation for each of the following reactions

a)2-butene + HCl

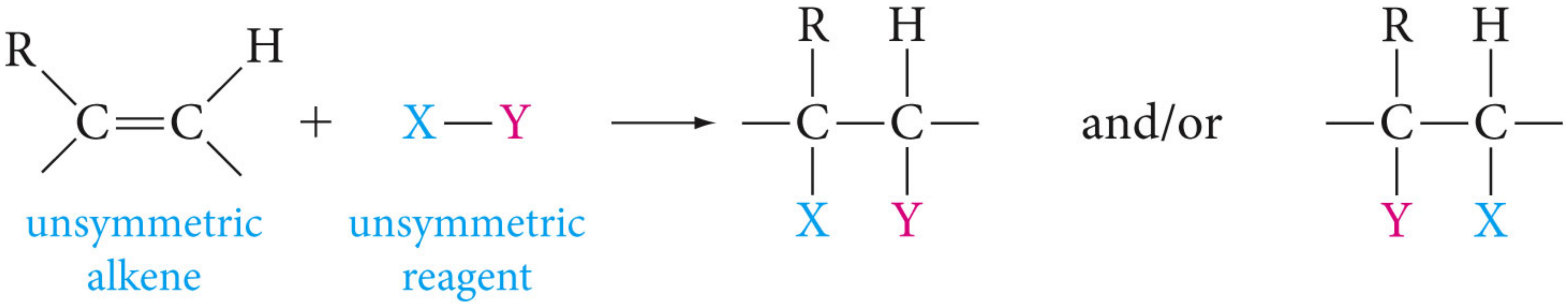
b)3-Hexene + HI

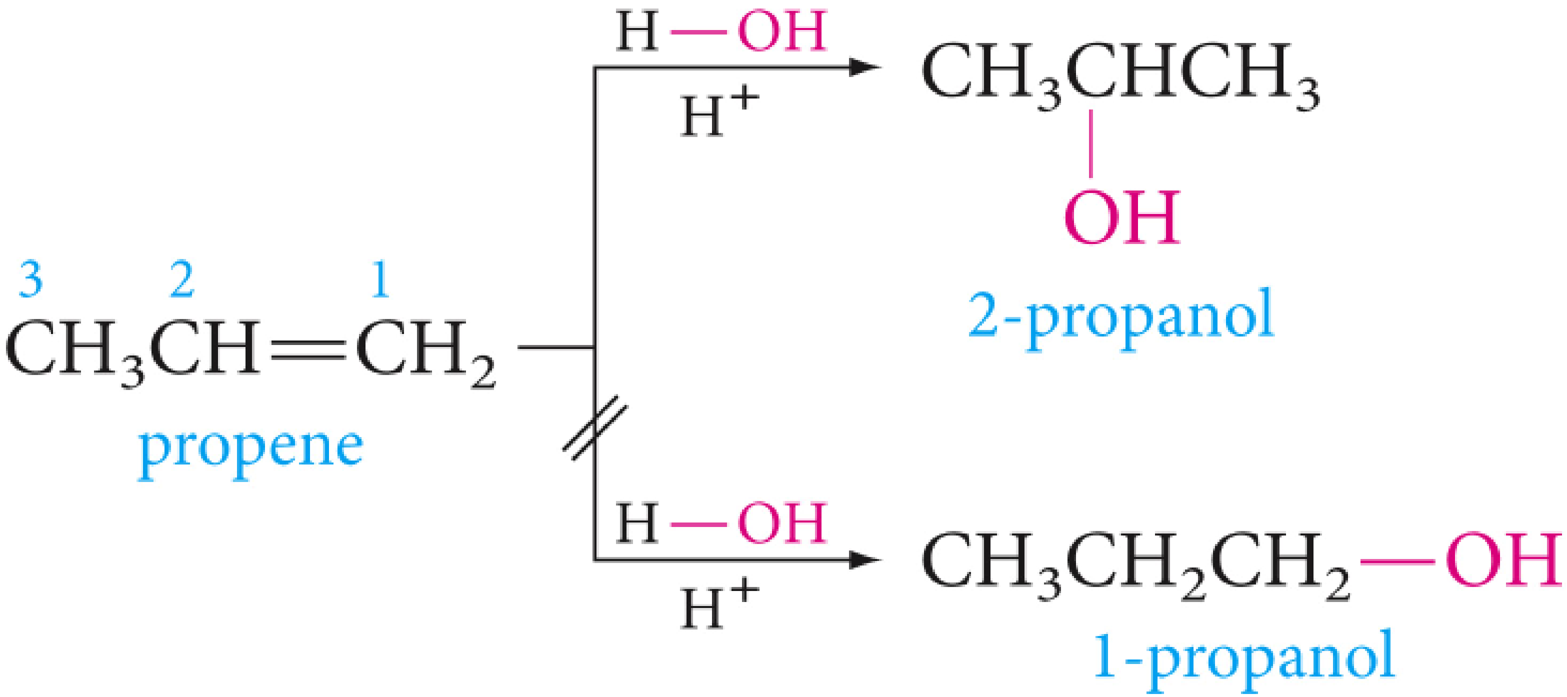
a)4-methylcyclopentene + HBr

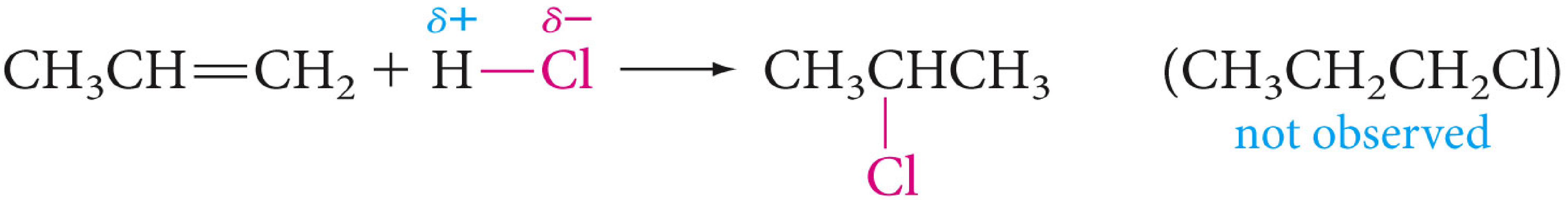
Table 3.2 Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

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

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

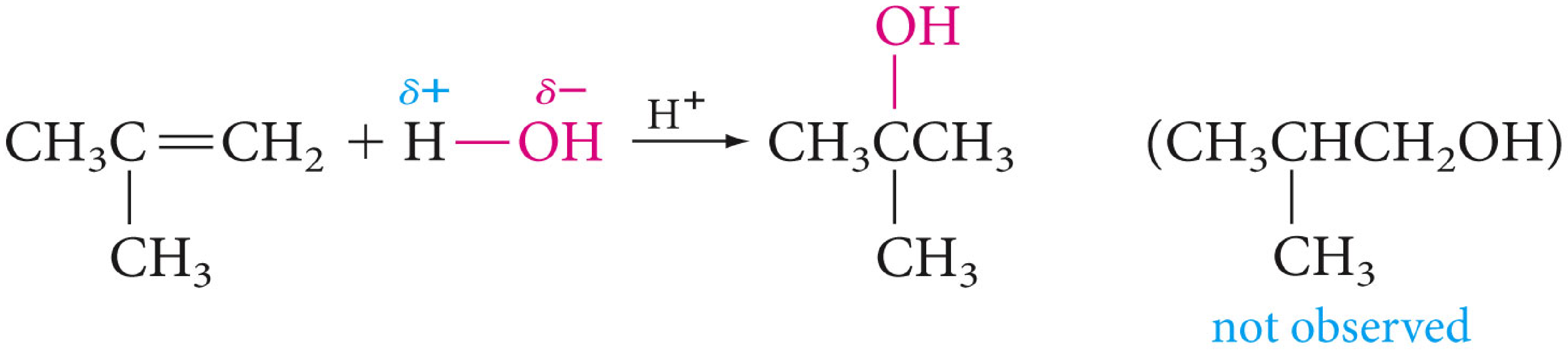



3
2
1
CH3CH=CH2
propene
H—OH
H+
CH3CHCH3
OH
2-propanol
H—OH
H+
CH3CH2CH2—OH
1-propanol



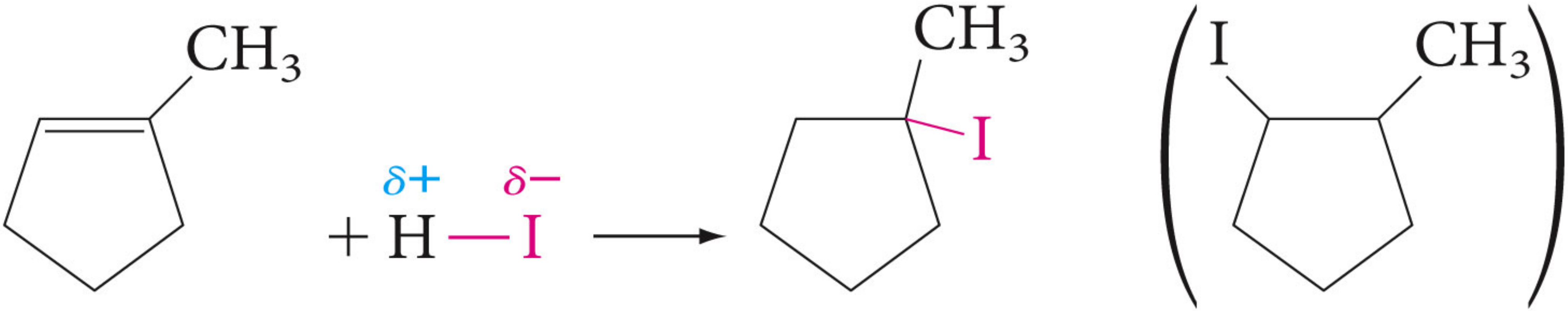
$$\mathrm{CH_3CH{=}CH_2 + \overset{\delta+}{H}{-}\overset{\delta-}{Cl} \longrightarrow CH_3\underset{\underset{\displaystyle Cl}{|}}{C}HCH_3 \qquad (CH_3CH_2CH_2Cl)}$$

not observed



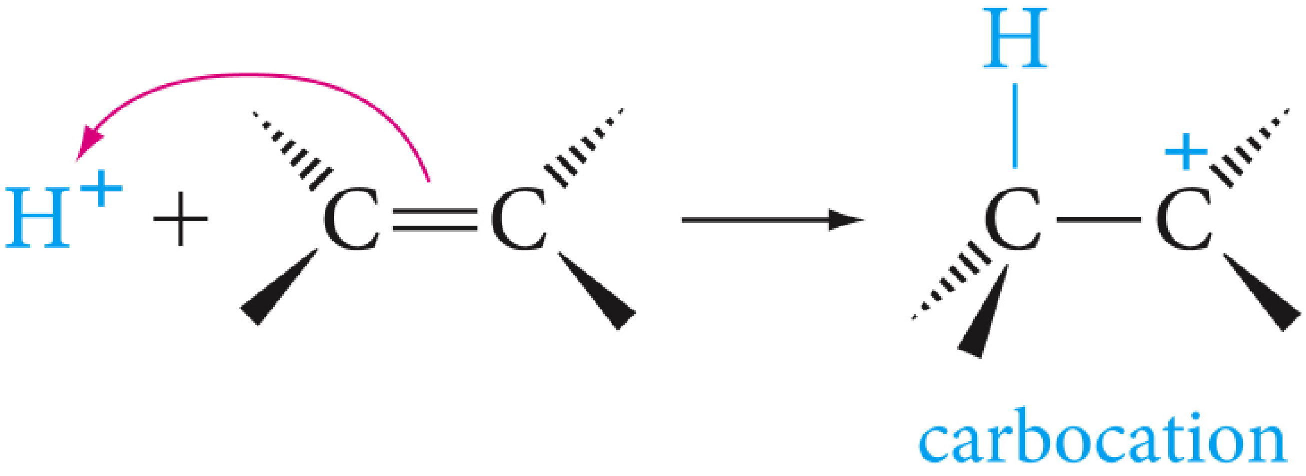
$$\mathrm{CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2 + \overset{\delta+}{H}{-}\overset{\delta-}{OH} \xrightarrow{H^+} CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3 \qquad (CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2OH)}$$

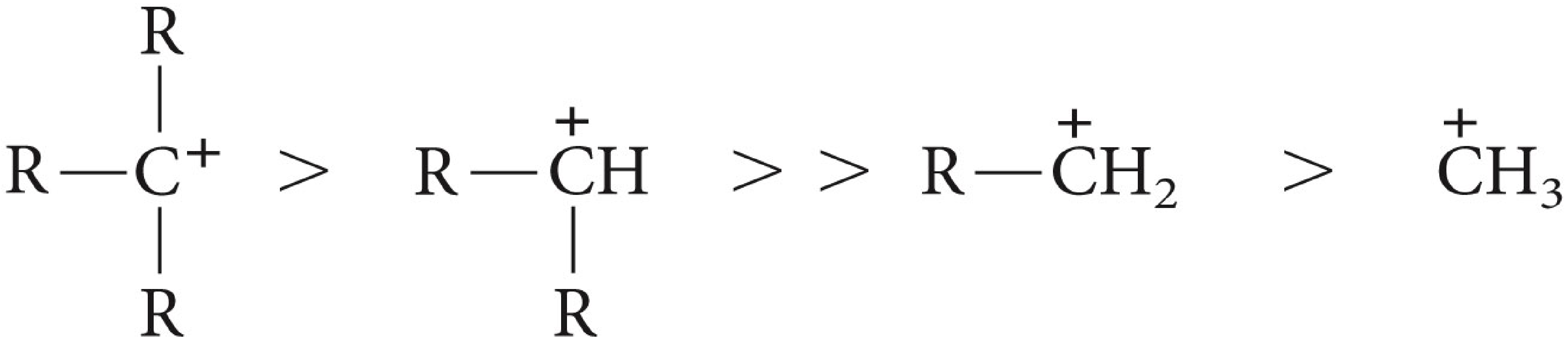
not observed



not observed

Mechanism of Electrophilic Addition to Alkenes



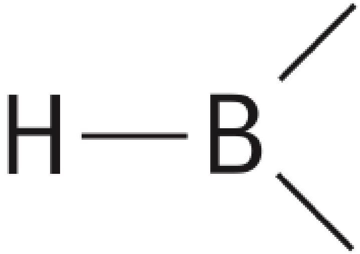


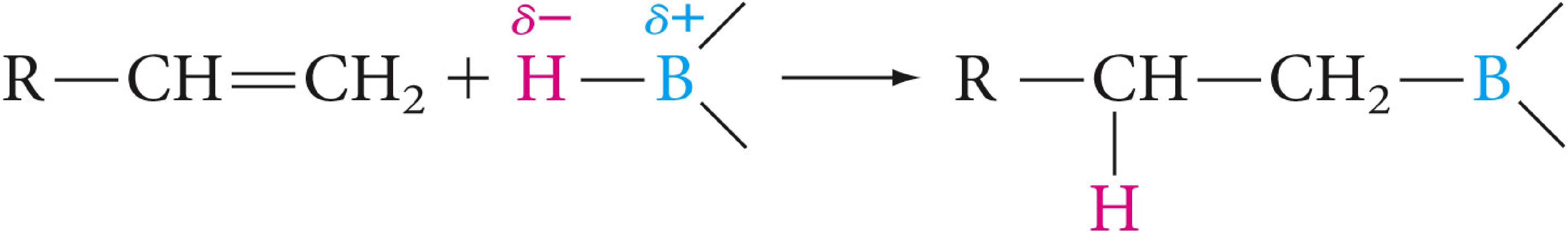
$$\mathrm{R{-}\underset{R}{\overset{R}{C^{+}}}} \; > \; \mathrm{R{-}\underset{R}{\overset{+}{C}H}} \; >> \; \mathrm{R{-}\overset{+}{C}H_2} \; > \; \mathrm{\overset{+}{C}H_3}$$

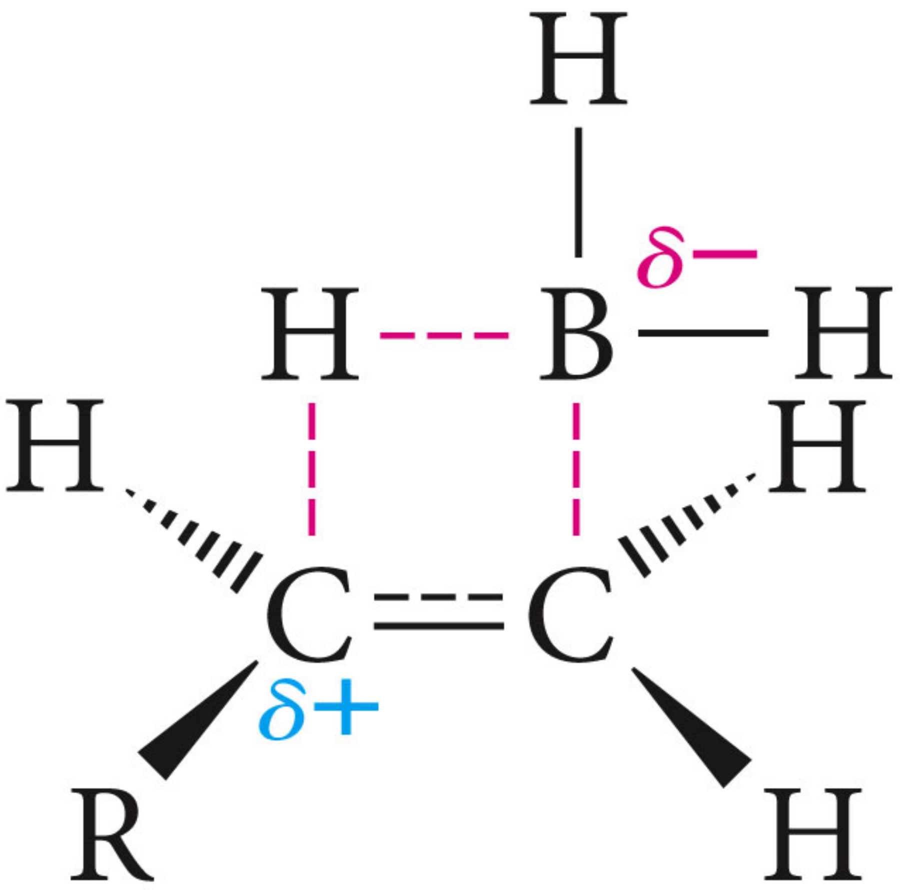
tertiary (3°) secondary (2°) primary (1°) methyl (unique)

most stable → least stable

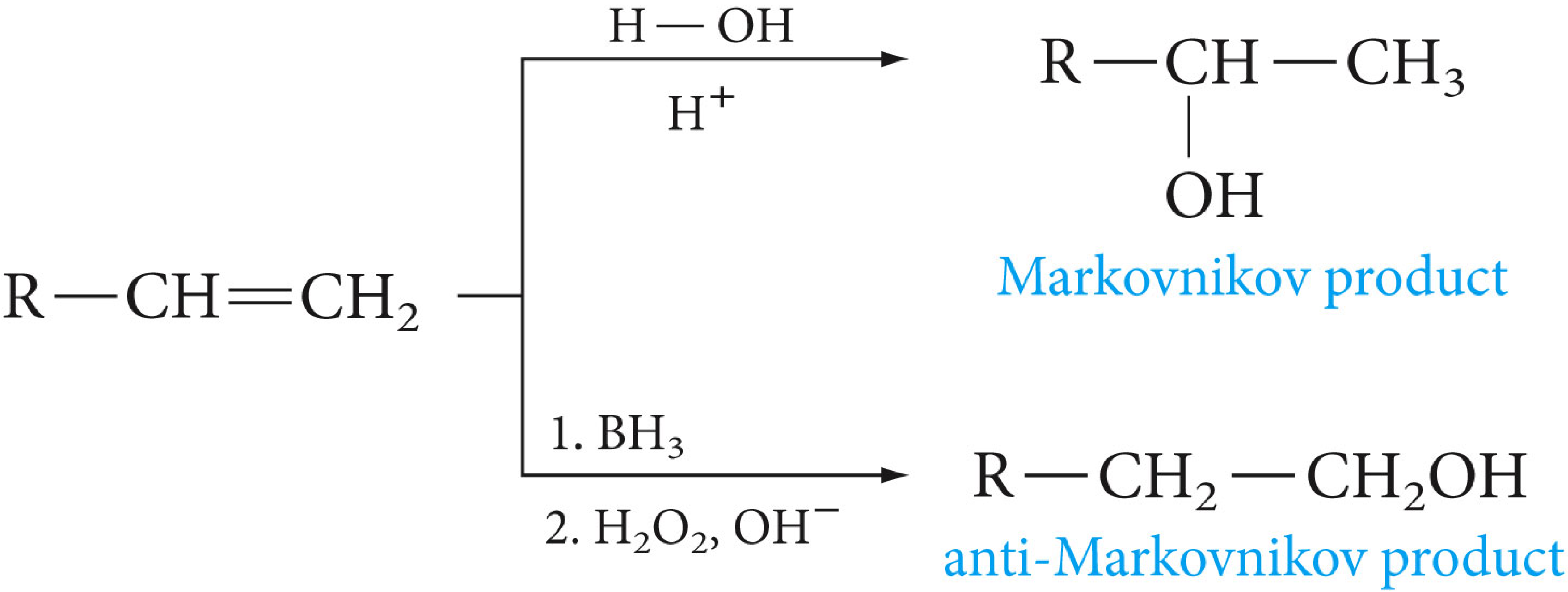
Hydroboration of Alkenes







transition state
for hydroboration

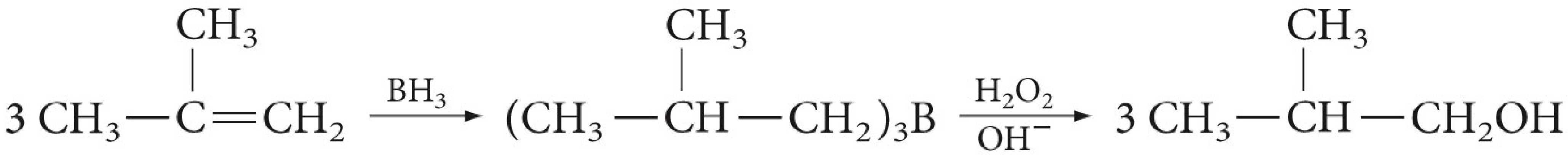


$$\mathrm{R-CH=CH_2} \xrightarrow[\mathrm{H^+}]{\mathrm{H-OH}} \mathrm{R-\underset{\underset{OH}{|}}{CH}-CH_3}$$

Markovnikov product

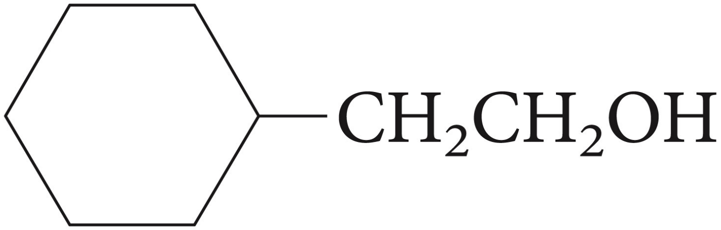
$$\mathrm{R-CH=CH_2} \xrightarrow[\mathrm{2.\ H_2O_2,\ OH^-}]{\mathrm{1.\ BH_3}} \mathrm{R-CH_2-CH_2OH}$$

anti-Markovnikov product

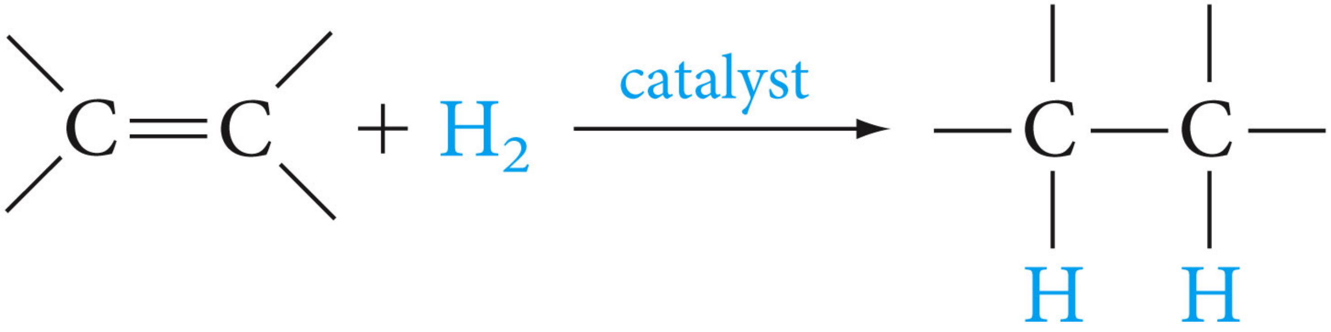


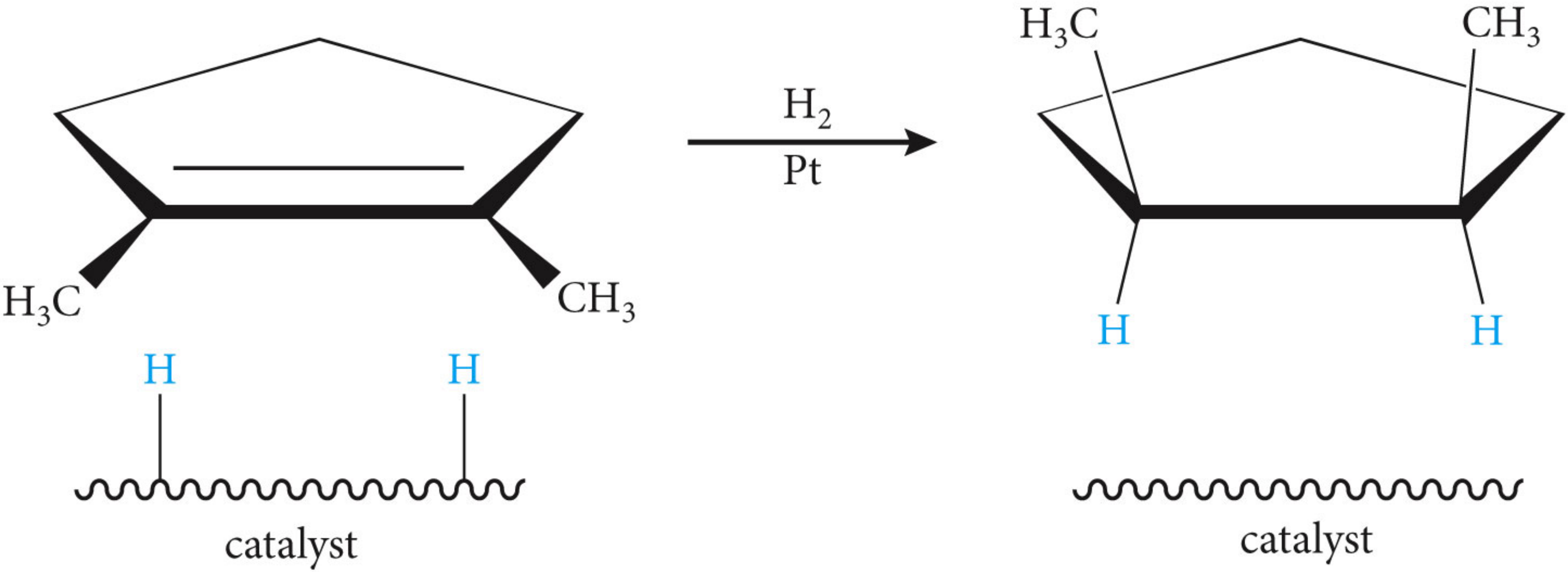
$$3\,\mathrm{CH_3}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}=\mathrm{CH_2}\xrightarrow{\mathrm{BH_3}}(\mathrm{CH_3}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2})_3\mathrm{B}\xrightarrow[\mathrm{OH^-}]{\mathrm{H_2O_2}}3\,\mathrm{CH_3}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2OH}$$

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

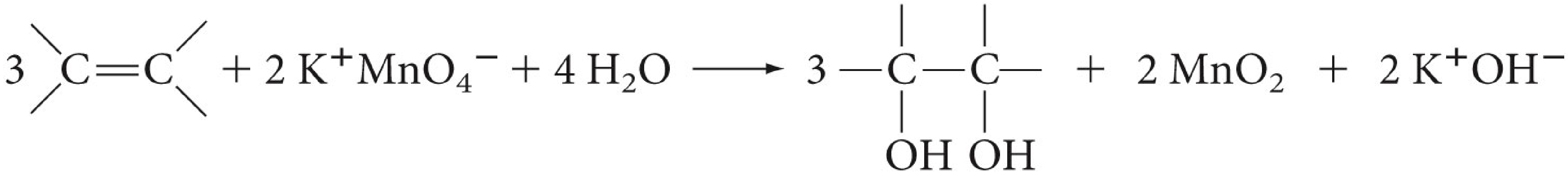


Addition of Hydrogen




H₃C
CH₃
H
H
catalyst
H₂
Pt
H₃C
CH₃
H
H
catalyst

Oxidation with permanganate; a Chemical Test



$$3\ \mathrm{C{=}C} + 2\,\mathrm{K^+MnO_4^-} + 4\,\mathrm{H_2O} \longrightarrow 3\ \mathrm{-\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-} + 2\,\mathrm{MnO_2} + 2\,\mathrm{K^+OH^-}$$

alkene

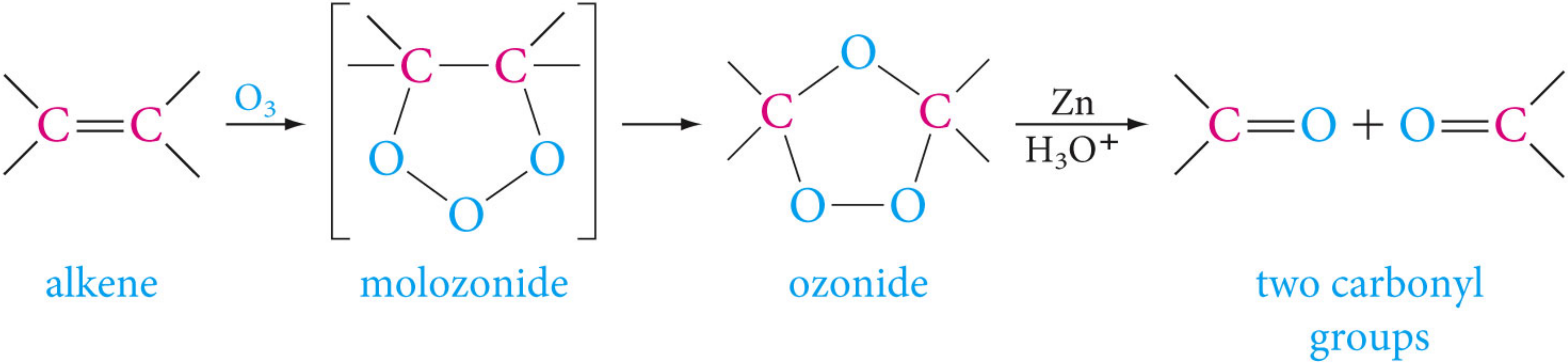
potassium
permanganate
(purple)

a glycol

manganese
dioxide
(brown-black)

Ozonolysis of Alkenes

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



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

1-butene

formaldehyde

propanal

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

2-butene

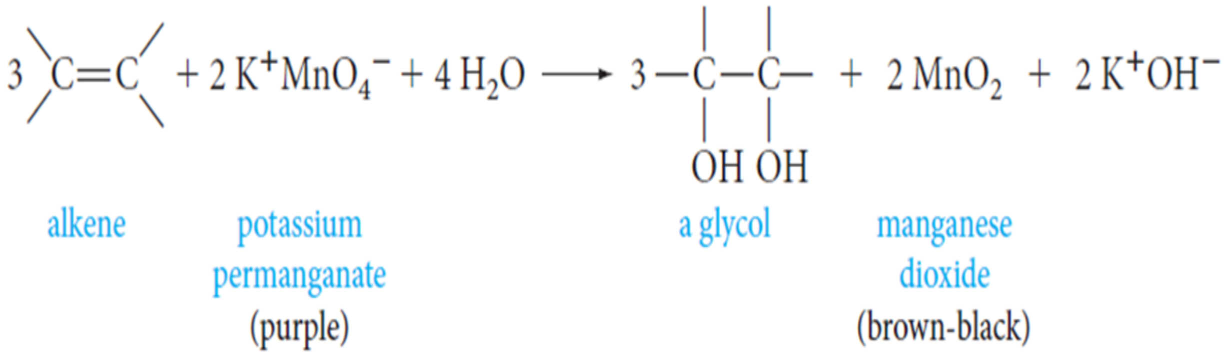
ethanal

Reactions of Alkenes

Oxidation Reactions

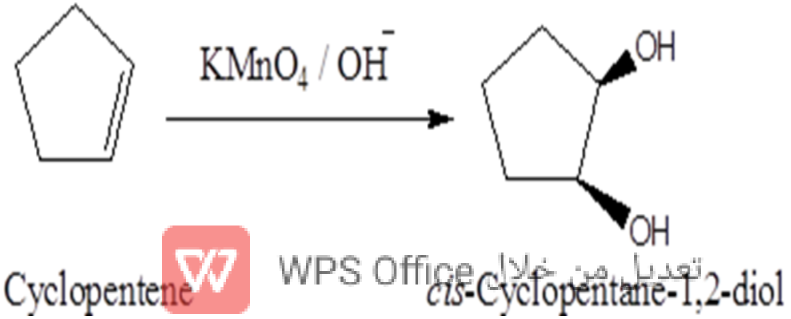
2. Oxidation Using $KMnO_4$

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



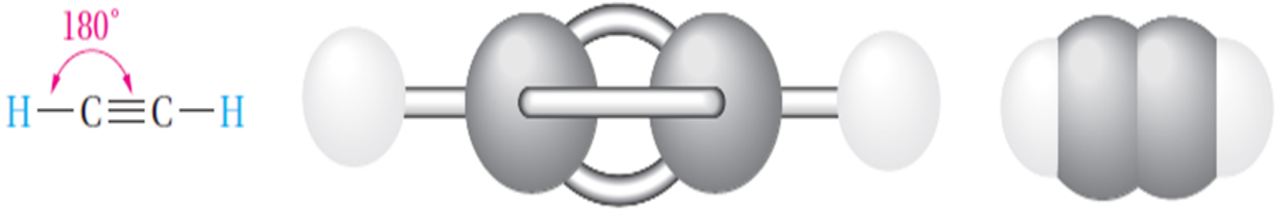
$$3\ {>}C{=}C{<} + 2\,K^+MnO_4^- + 4\,H_2O \longrightarrow 3\ -\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}-\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}- + 2\,MnO_2 + 2\,K^+OH^-$$

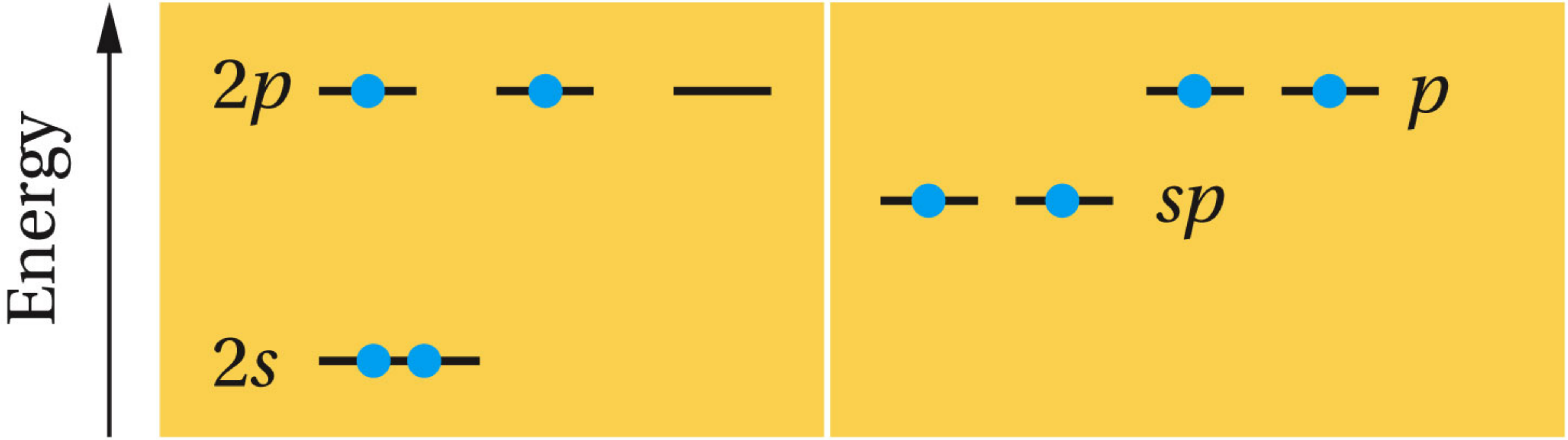
Hexane does not react with purple $KMnO_4$ (left); cyclohexene (right) reacts, producing a brown-black precipitate of MnO_2.



The Structure of Alkynes

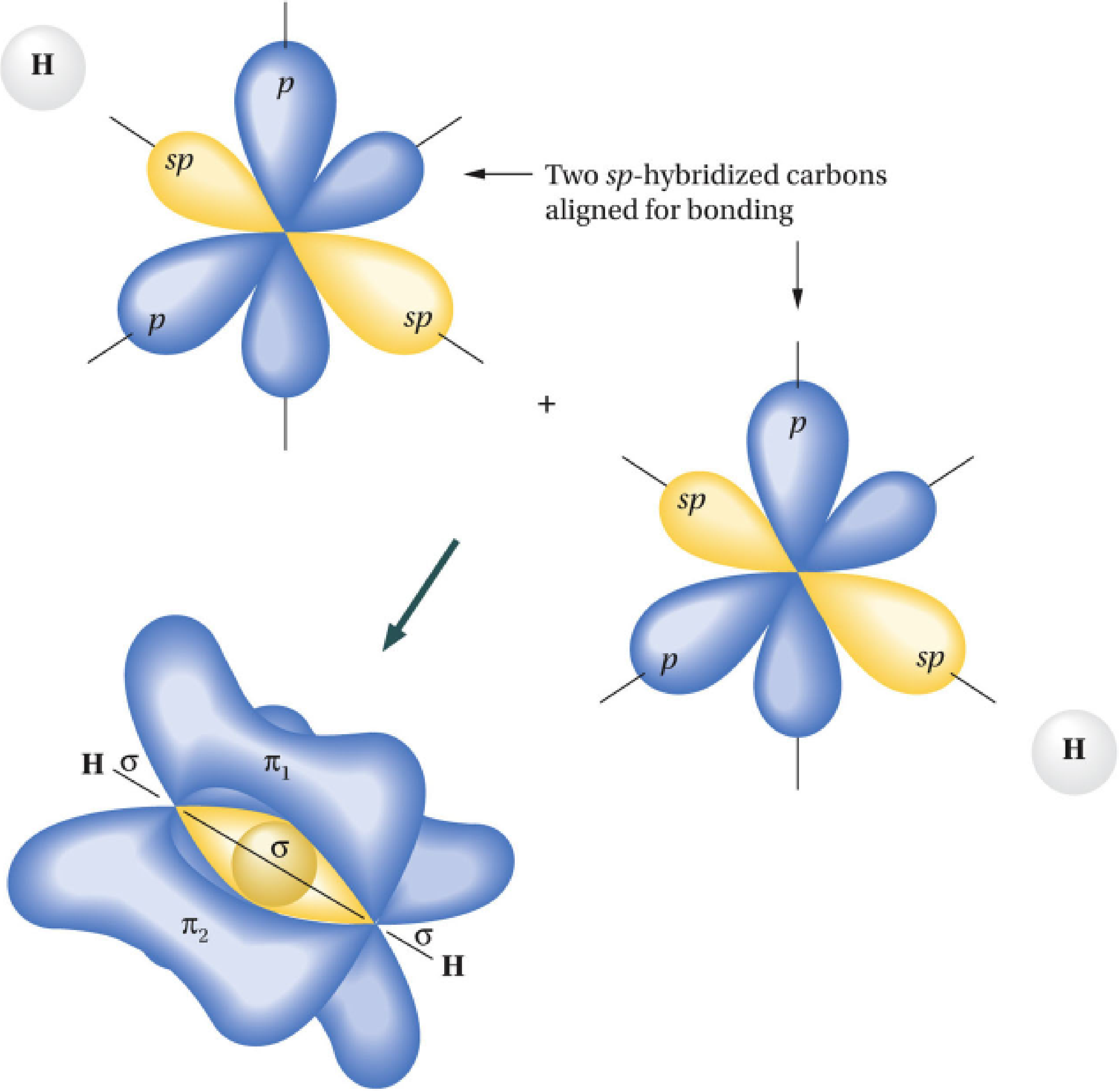
- **Alkynes** are hydrocarbons that contain a ***carbon–carbon triple bond***.
- **Alkynes** are also known as *Acetylenes*.
- General formula is C_nH_{2n-2}
- Hybridization; ***sp*-hybridized orbitals**
- The angle between them is **180°** and the bond length **1.20 A°**
- The geometry is **Linear.**





Atomic orbitals of carbon

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



Two *sp*-hybridized carbons aligned for bonding

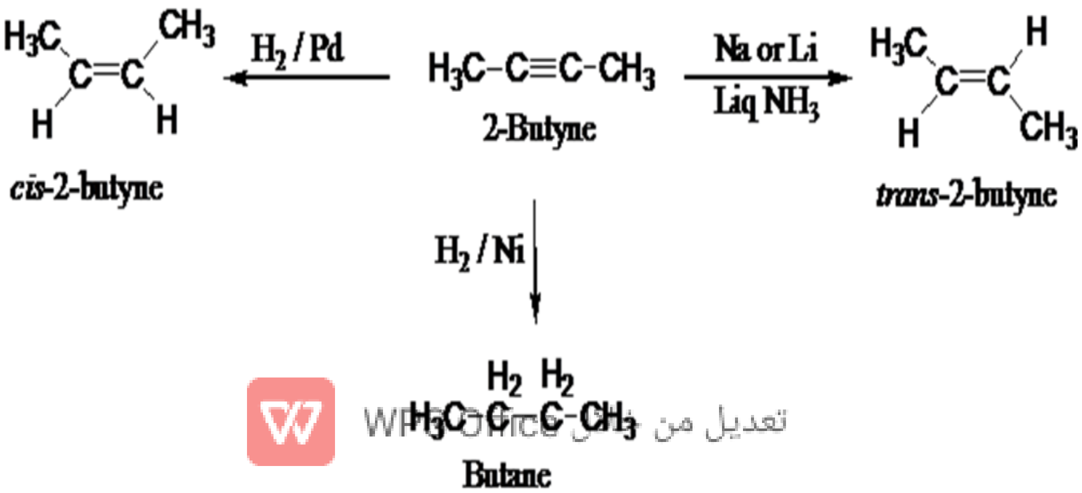
The resulting carbon–carbon triple bond, with a hydrogen atom attached to each remaining *sp* bond. (The orbitals involved in the C—H bonds are omitted for clarity.)

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 a s sodium or lithium in liquid ammonia results in formation of trans alkenes.

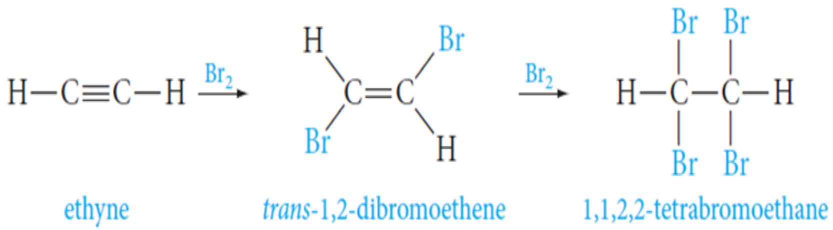


Reaction of Alkynes

Electrophilic Addition Reactions

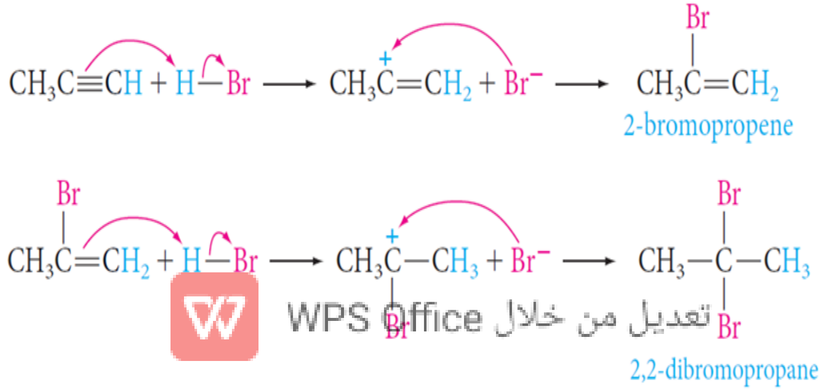
2. Addition of Halogen: Halogenation

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



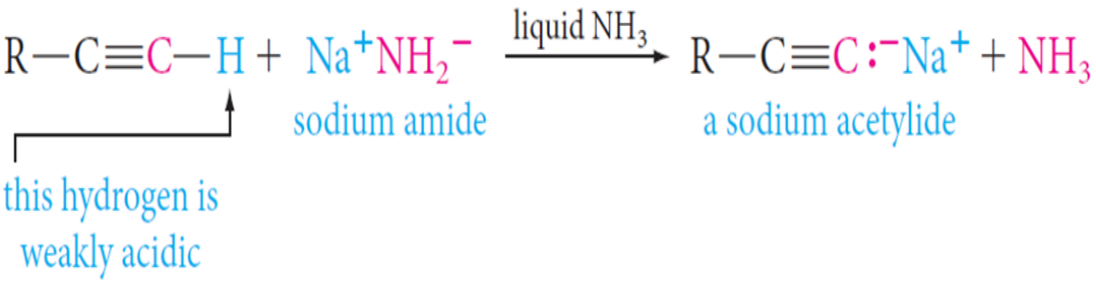
3. Addition of Hydrogen Halide

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).



$$R-C\equiv C-H + Na^+NH_2^- \xrightarrow{\text{liquid } NH_3} R-C\equiv C:^-Na^+ + NH_3$$

this hydrogen is weakly acidic

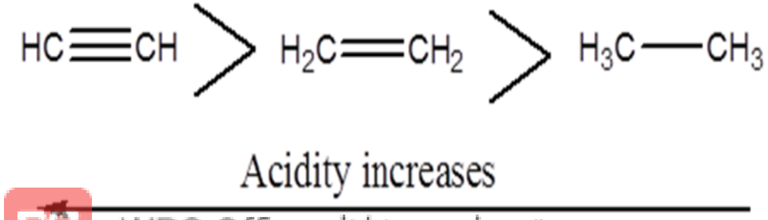
sodium amide

a sodium acetylide

- Internal alkynes (**Non-Terminal Alkyne**) have no exceptionally acidic hydrogens.

  - Relative Acidity of the Hydrocarbon.

    Terminal alkynes, are more acidic than other hydrocarbons



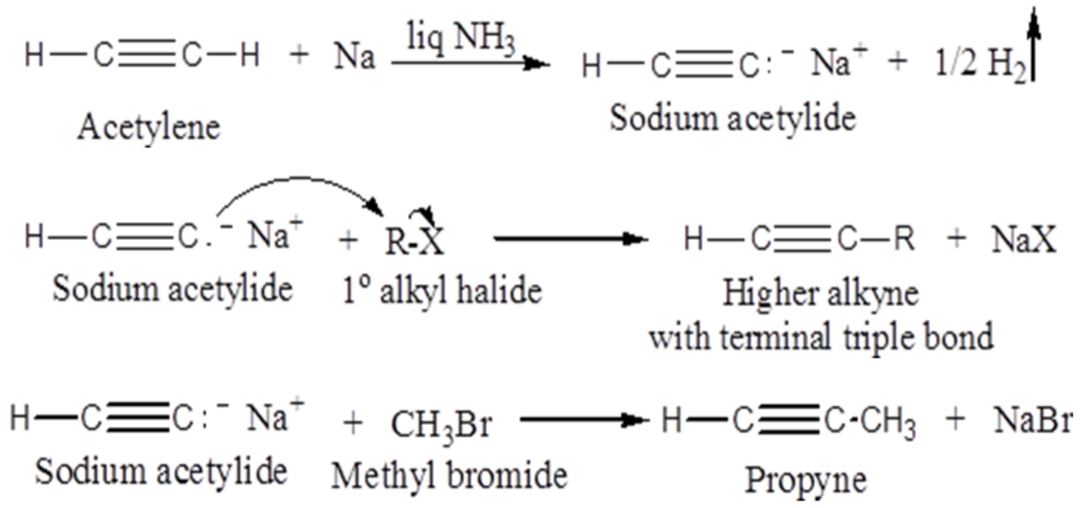
$$HC\equiv CH > H_2C=CH_2 > H_3C-CH_3$$

Acidity increases

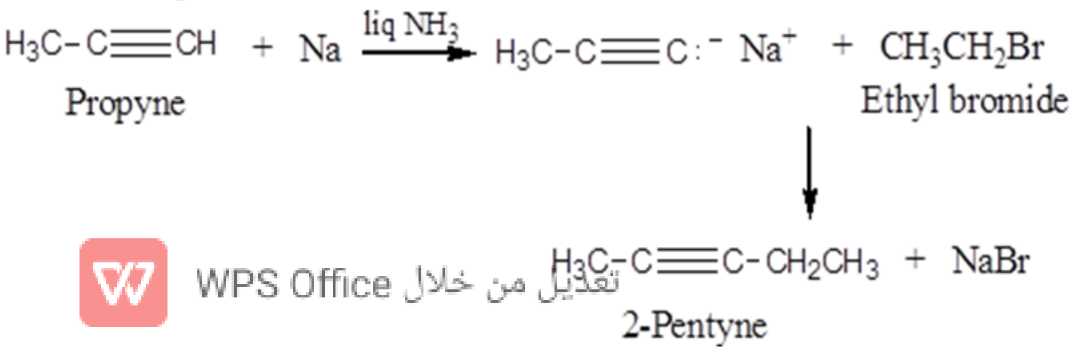
Preparation of Alkynes

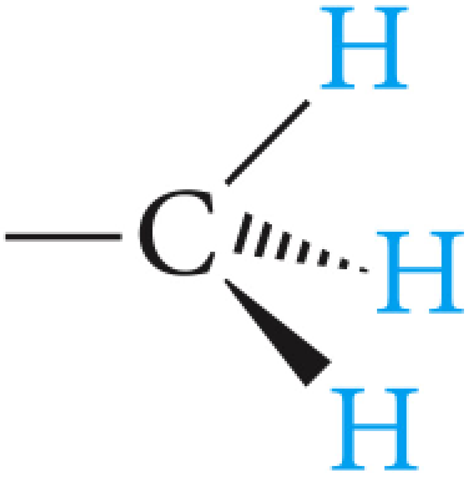
2) Reaction of Sodium Acetylide with Primary Alkyl Halides

- **Acetylene**



- **Monosubstituted Acetylenes**

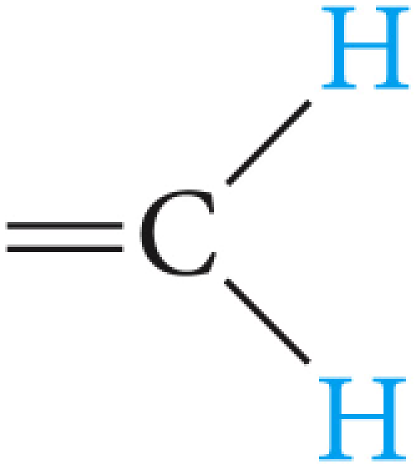




sp^3

25% *s*,

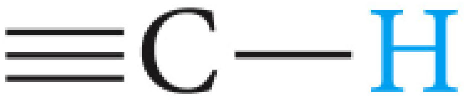
75% *p*



sp^2

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

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



sp

50% *s*,

50% *p*

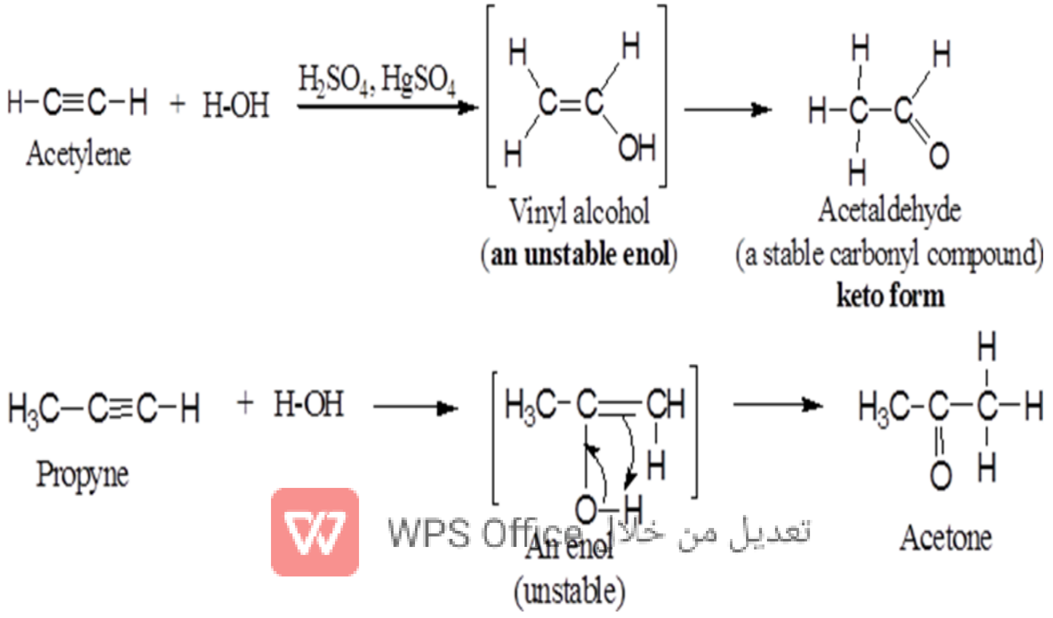
increasing acidity →

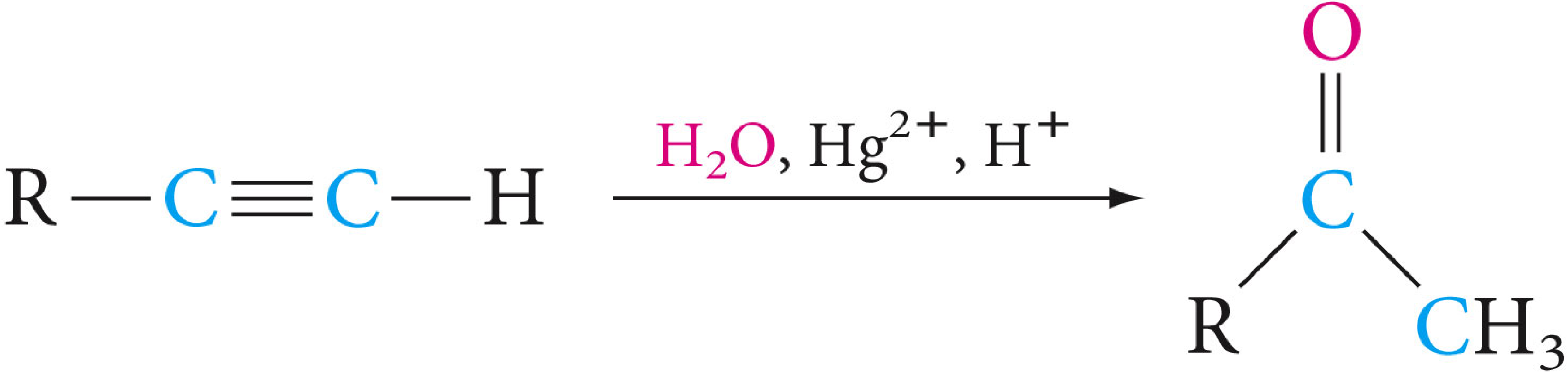
Reaction of Alkynes

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 from predominates at equilibrium for most simple aldehydes and ketones.
- The inter conversion is called **keto-enol tautomerization.**





$$\mathrm{R{-}C{\equiv}C{-}H} + \mathrm{Na^+\ NH_2^-} \xrightarrow{\mathrm{NH_3}} \mathrm{R{-}C{\equiv}C\!:^-\ Na^+} + \mathrm{NH_3}$$