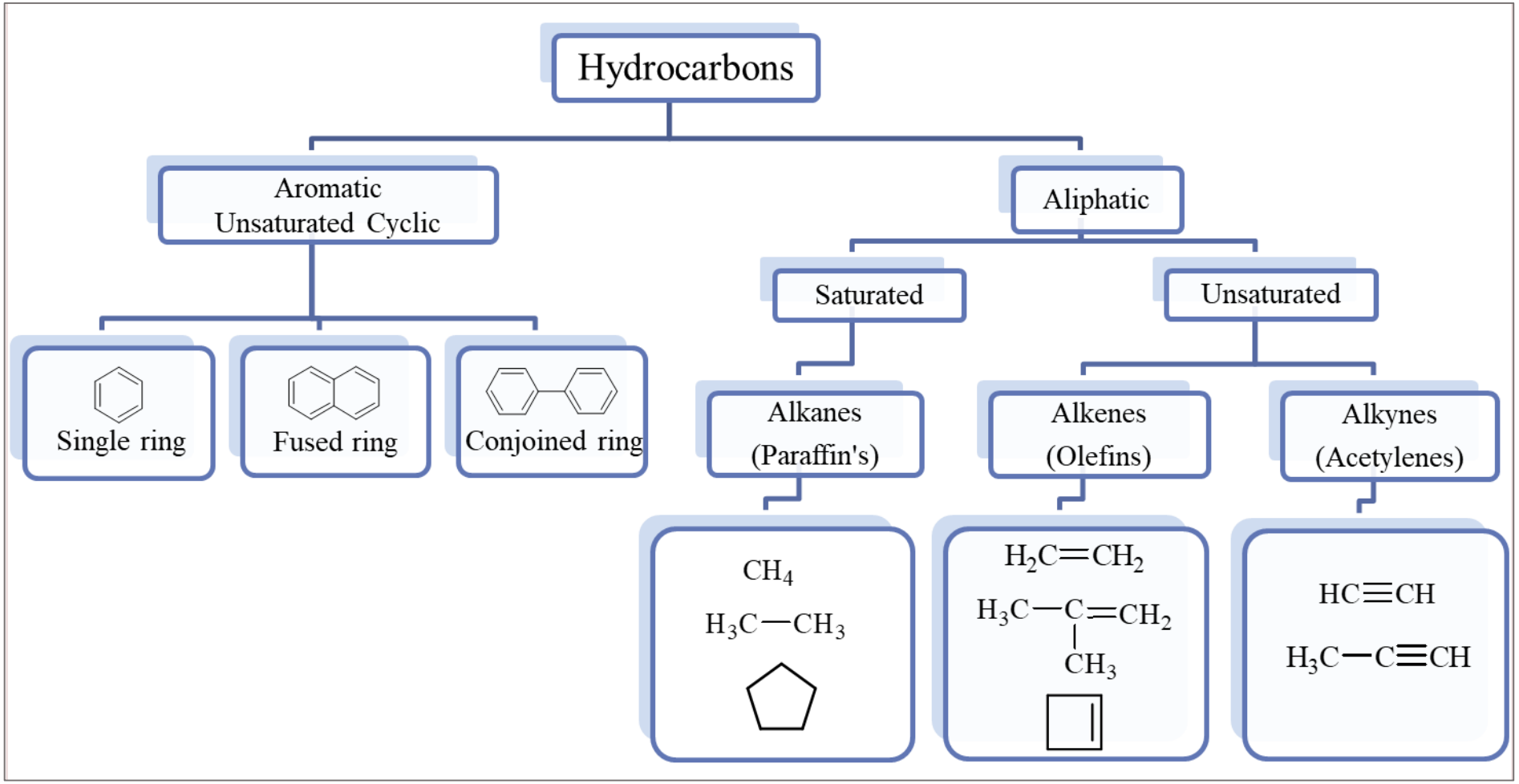
108 Chem

Chapter 2

Aliphatic Hydrocarbons

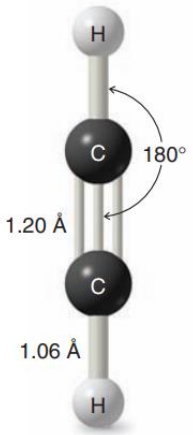
Hydrocarbons

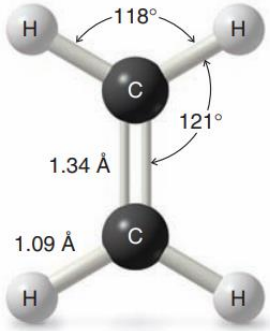
- Hydrocarbons are Organic Compounds, which contain only the two elements carbon and hydrogen.
- Aliphatic hydrocarbons are subdivided into: Saturated hydrocarbons and Unsaturated hydrocarbons.

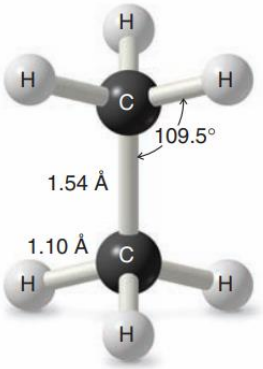


General Molecular Formula of Hydrocarbons (Homologous Series)

Alkane	C_nH_{2n+2}	Saturated
Cycloalkane	C_nH_{2n}	Containing a single ring
Alkene	C_nH_{2n}	Containing one carbon–carbon double bond
Cycloalkene	C_nH_{2n-2}	Containing a single ring with one double bond
Alkyne	C_nH_{2n-2}	Containing one carbon–carbon triple bond
Cycloalkyne	C_nH_{2n-4}	Containing a single ring with one triple bond







Alkanes

C_nH_{2n+2} Saturated

- ane

Alkanes

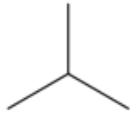
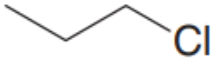
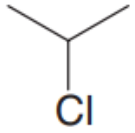
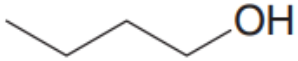
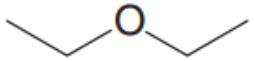
Names and Formulas of the first Ten unbranched Alkanes

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

Isomerism

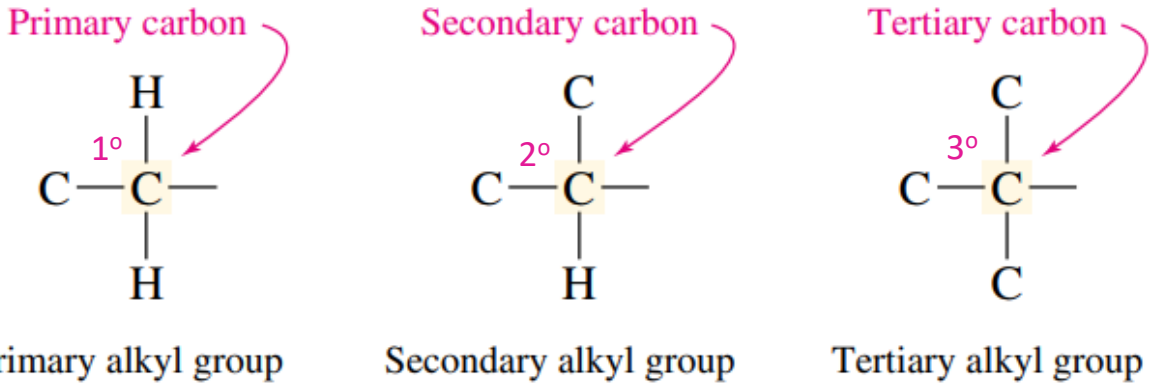
Isomers are molecules with the same number and kinds of atoms but different arrangements of the atoms.

structural (or constitutional) isomers have the same molecular formula but different structural formulas.

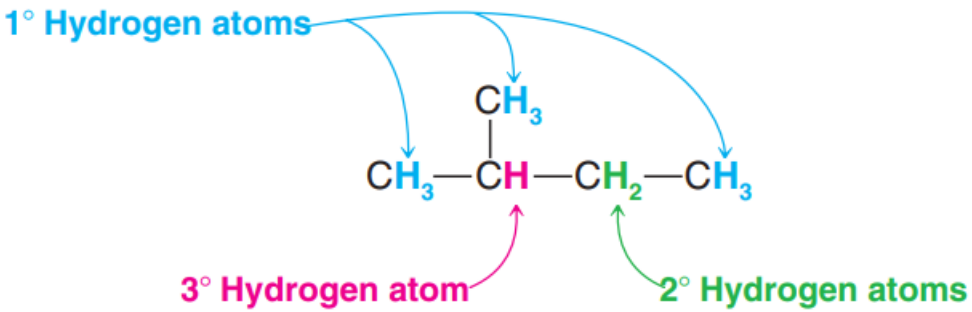
molecular formula	Structural Isomers		
C_4H_{10}	 Butane	and	 2-Methylpropane
C_3H_7Cl	 1-Chloropropane	and	 2-Chloropropane
$C_4H_{10}O$	 1-Butanol	and	 Diethyl ether

Classification of Carbon and Hydrogen Atoms

- The carbon atoms are classified according to their degree of substitution by other carbons.

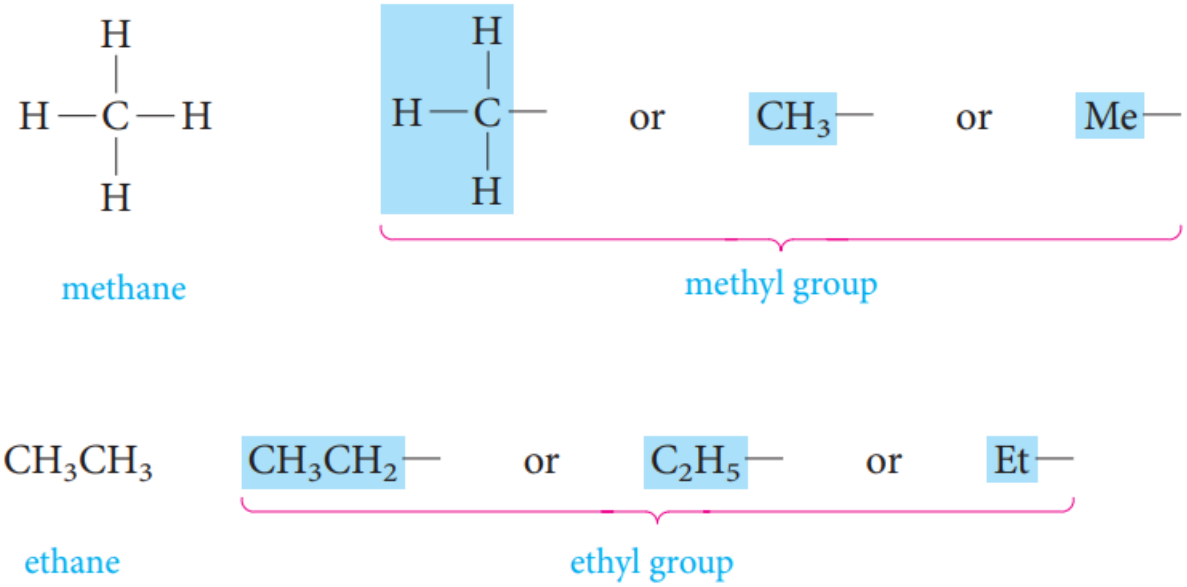


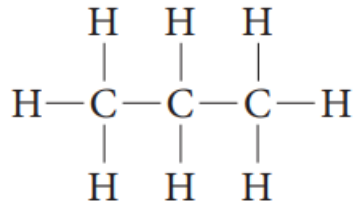
- The hydrogen atoms of an alkane are classified on the basis of the carbon atom to which they are attached. A hydrogen atom attached to a primary carbon atom is a primary (1°) hydrogen atom, and so forth.

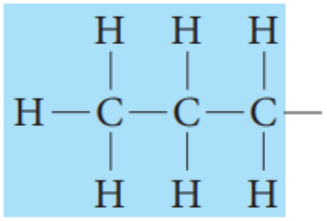


Alkyl Substituents

- An alkyl group lacks one of the hydrogen substituents of an alkane.
- An alkyl group is named by taking the name of the alkane with the same number of carbon atoms and changing the *-ane* ending to *-yl*.
- The symbol R is used as a general symbol to represent any alkyl group.

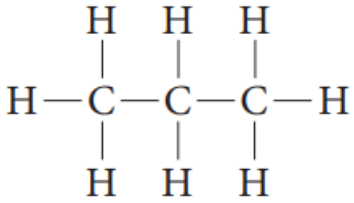




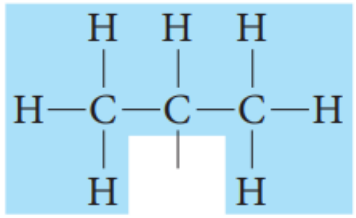


or $CH_3CH_2CH_2$— or Pr—

propyl group

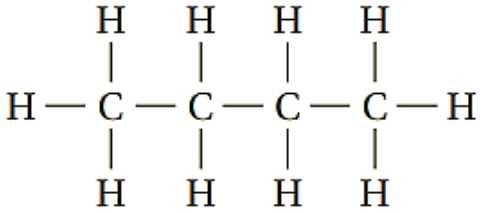


propane



or CH_3CHCH_3 or *i*-Pr—

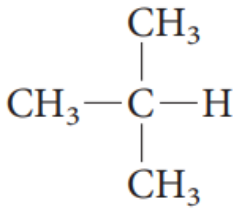
isopropyl or 1-methylethyl* group



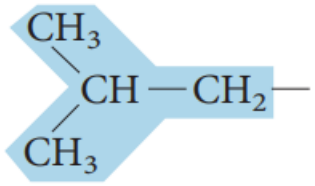
$CH_3CH_2CH_2CH_2$— and $CH_3CHCH_2CH_3$

butyl

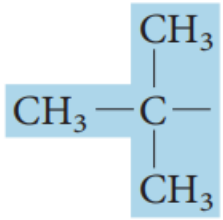
sec-butyl
(or 1-methylpropyl)



isobutane



and



isobutyl
(or 2-methylpropyl)

tert-butyl
(or 1,1-dimethylethyl)

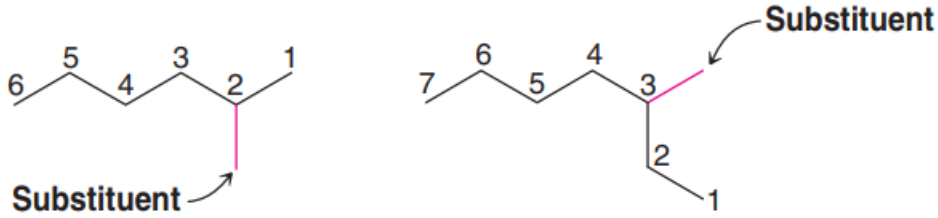
Nomenclature of Organic Compounds

- Common or trivial names: The older unsystematic names.
- Systematic names: Chemists use a systematic nomenclature developed and updated by the *International Union of Pure and Applied Chemistry* (IUPAC). Underlying the IUPAC system is a fundamental principle.

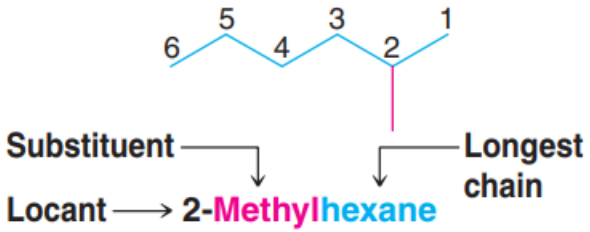
IUPAC Rules for Naming Alkanes

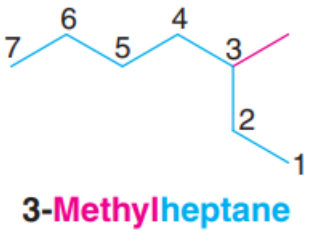
1) Locate the longest continuous carbon chain. This gives the name of the parent alkane.

2) Number the longest chain beginning with the end of the chain nearer the substituent.

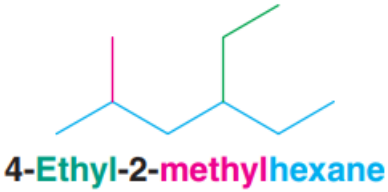


3) Use the numbers obtained by application of rule 2 to designate the location of the substituent group.

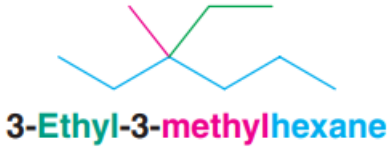




4) When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. The substituent groups should be listed alphabetically (i.e., ethyl before methyl).

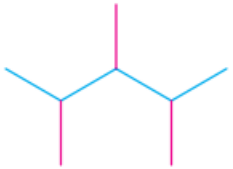


5) When two substituents are present on the same carbon atom, use that number twice.



6) When two or more substituents are identical, indicate this by the use the prefixes *di-, tri-, tetra-*, and so on.

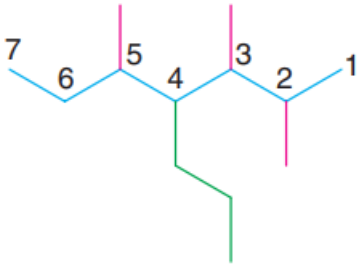
2,3-Dimethylbutane



2,3,4-Trimethylpentane

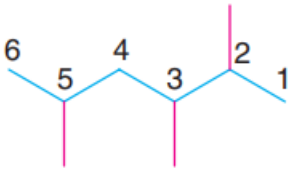
2,2,4,4-Tetramethylpentane

7) When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.

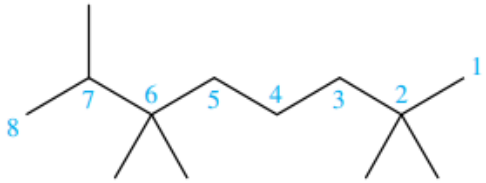


2,3,5-Trimethyl-4-propylheptane
(four substituents)

8) When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.



2,3,5-Trimethylhexane
(*not* 2,4,5-trimethylhexane)



2,2,6,6,7-Pentamethyloctane
(*not* 2,3,3,7,7-Pentamethyloctane)

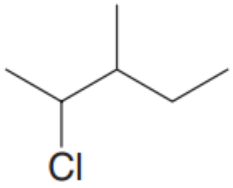
9) If substituents other than alkyl groups are also presents on the parent carbon chain, all substituents are named alphabetically.

F—	Cl—	Br—	I—	$-NO_2$	$-NH_2$	-CN
fluoro-	chloro-	bromo-	iodo-	nitro-	amino-	cyano-

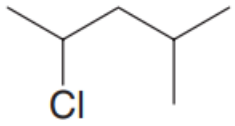
CH_3CH_2Cl
Chloroethane

$CH_3CH_2CH_2F$
1-Fluoropropane

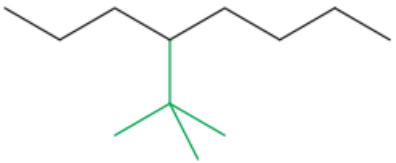
$CH_3CHBrCH_3$
2-Bromopropane



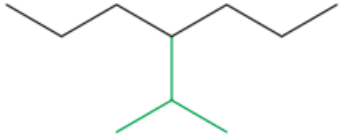
2-Chloro-3-methylpentane



2-Chloro-4-methylpentane



4-(1,1-Dimethylethyl)octane or 4-*tert*-butyloctane

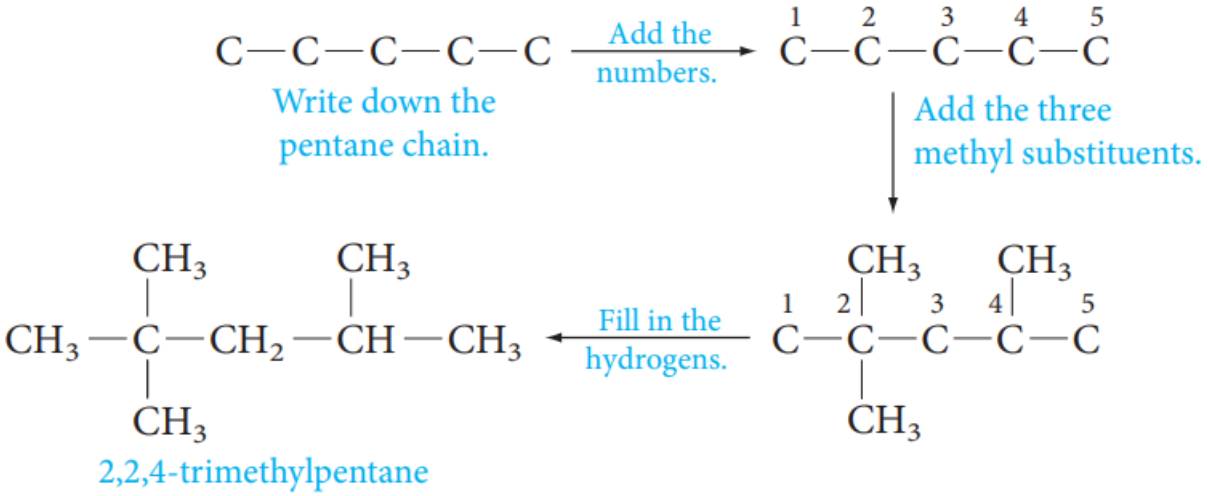


4-(1-Methylethyl)heptane or 4-isopropylheptane

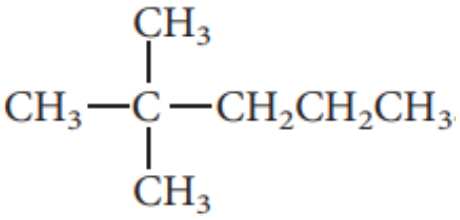
Use of the IUPAC Rules

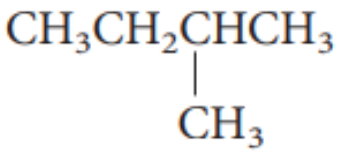
It is important not only to be able to write a correct IUPAC name for a given structure, but also to do the converse: Write the structure given the IUPAC name.

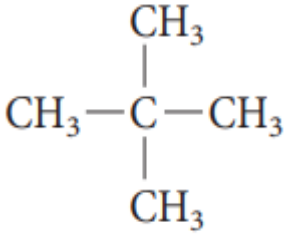
For example, to write the formula for 2,2,4-trimethylpentane :

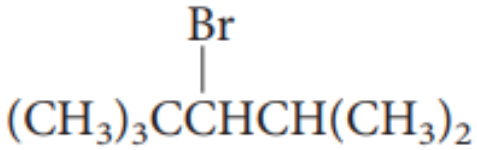


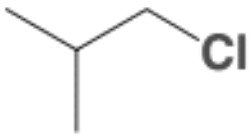
Examples

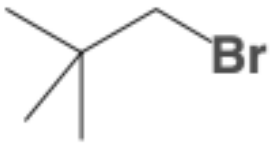


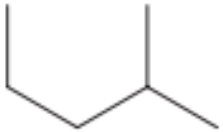


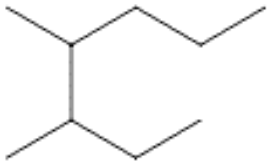


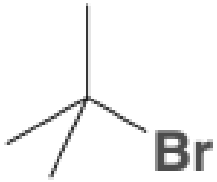


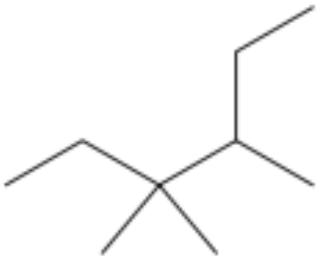


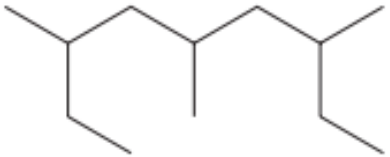


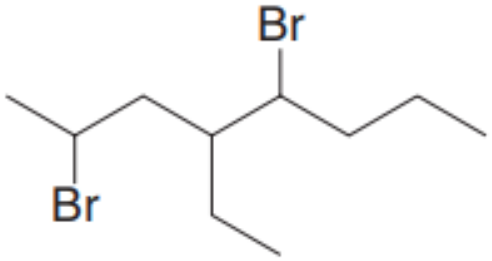












Physical properties of alkanes

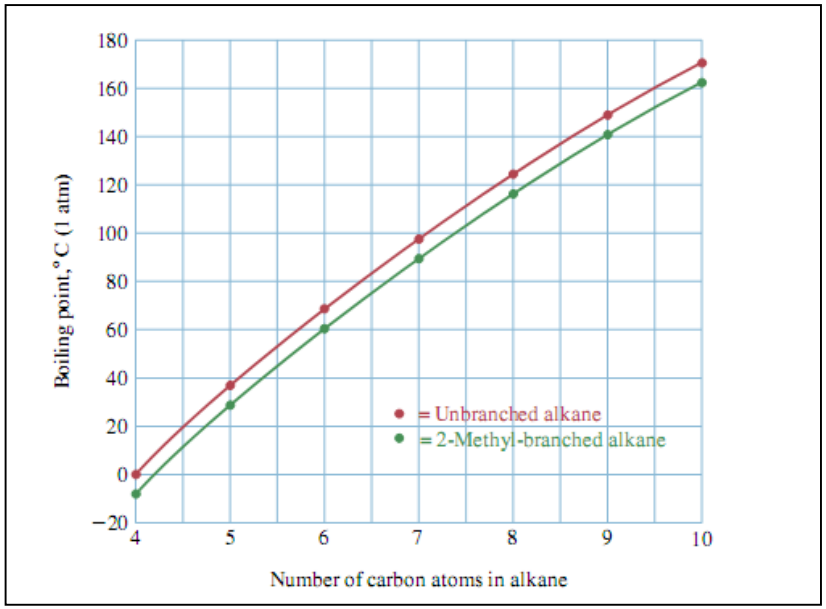
A) Physical States and Solubilities

C_1-C_4	colorless gases
C_5-C_{17}	liquids with characteristic odor
C_{20} and more	odorless waxy materials

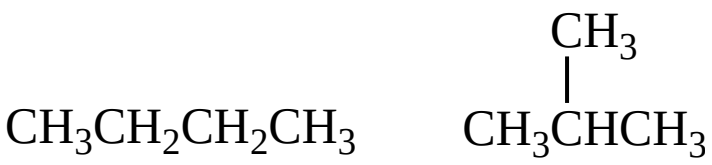
- Alkanes are nonpolar compounds. Thus alkanes are soluble in the nonpolar solvents such as carbon tetrachloride (CCl_4) and benzene (C_6H_6), but they are insoluble in polar solvents such as water.

B) Boiling Points

- The boiling points of the normal alkanes increase with increasing molecular weight.
- Branching of the alkane chain lowers the boiling point.



Example:



n-Butane (bp = 0°C)

Isobutane (bp = -12°C)

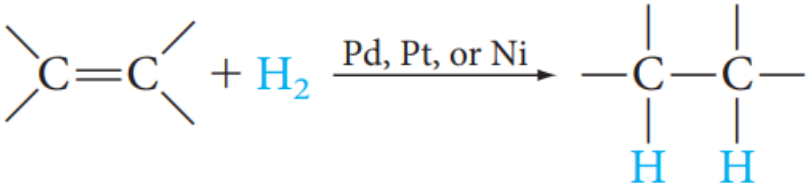
Sources of Alkanes and Cycloalkanes

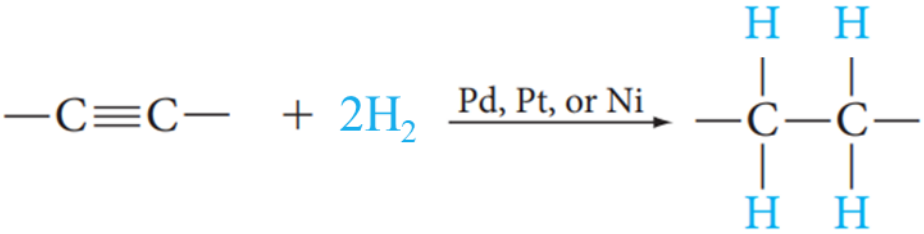
- The two most important natural sources of alkanes are petroleum and natural gas.
- Petroleum is a complex liquid mixture of organic compounds, many of which are alkanes or cycloalkanes.
- Natural gas, often found associated with petroleum deposits, consists mainly of *methane* (about 80%) and *ethane* (5% to 10%), with lesser amounts of some higher alkanes. *Propane* is the major constituent of liquefied petroleum gas (LPG), a domestic fuel used mainly in rural areas and mobile homes. *Butane* is the gas of choice in some areas. Natural gas is becoming an energy source that can compete with and possibly surpass oil.

Preparation of alkanes

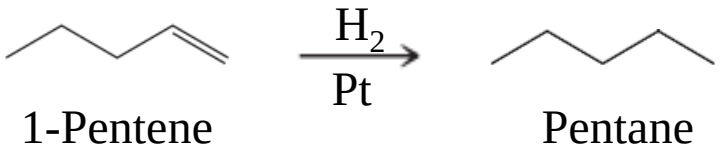
1) From Alkenes & Alkynes

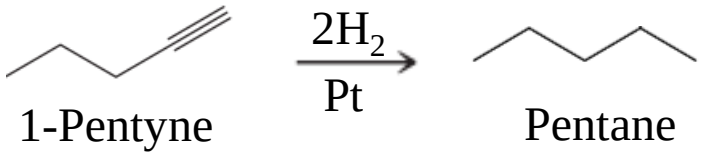
Catalytic Hydrogenation



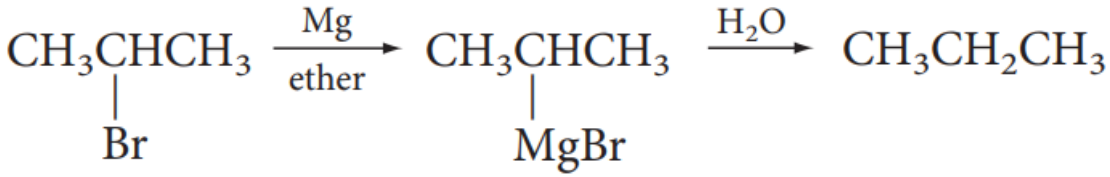


Examples





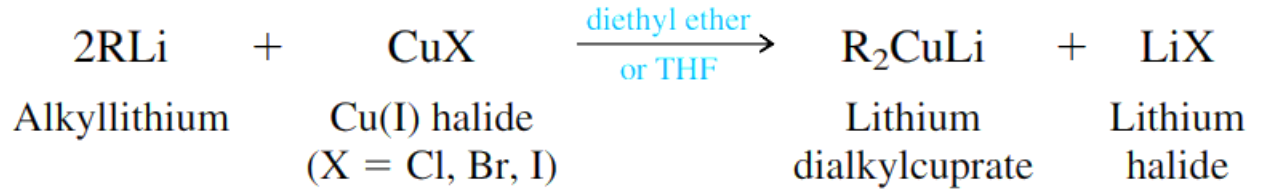
2) Hydrolysis of Grignard Reagent

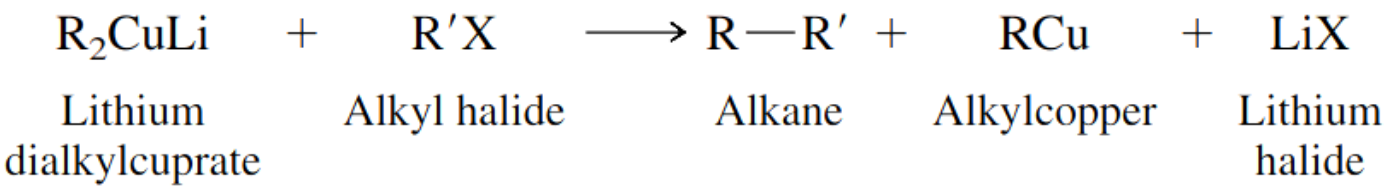


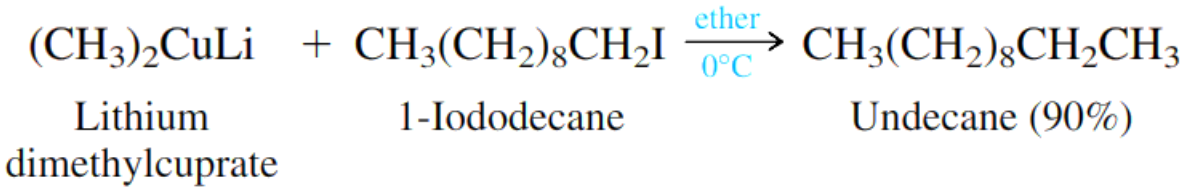
2-Bromopropane Propane

3) The Corey–Posner, Whitesides–House Reaction

Use of Lithium Dialkyl Cuprate (Gilman Reagent) in Coupling Reaction







Reactions of alkanes

1) Oxidation and Combustion; Alkanes as Fuels

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

$$\underset{\text{methane}}{CH_4} + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + \text{heat}$$

$$\underset{\text{butane}}{C_4H_{10}} + \tfrac{13}{2}\,O_2 \longrightarrow 4\,CO_2 + 5\,H_2O + \text{heat}$$

2) Halogenation

$$R{-}H + X_2 \xrightarrow[\text{or light}]{\text{heat}} R{-}X + H{-}X \quad (X = Cl, Br)$$

- Chlorination or Bromination of hydrocarbons is a substitution reaction in which a chlorine or bromine atom is substituted for a hydrogen atom.

$$R{-}H + Cl{-}Cl \xrightarrow[\text{heat}]{\text{light or}} R{-}Cl + H{-}Cl$$

$$R{-}H + Br{-}Br \xrightarrow[\text{heat}]{\text{light or}} R{-}Br + HBr$$

Free-radical reaction

$$\underset{\text{methane}}{CH_4} + Cl{-}Cl \xrightarrow[\text{or heat}]{\text{sunlight}} \underset{\text{chloromethane}}{CH_3Cl} + HCl$$

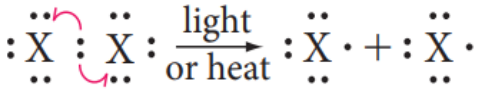
- If excess halogen is present:

$$CH_3Cl \xrightarrow{Cl_2} \underset{\text{dichloromethane}}{CH_2Cl_2} \xrightarrow{Cl_2} \underset{\text{trichloromethane}}{CHCl_3} \xrightarrow{Cl_2} \underset{\text{tetrachloromethane}}{CCl_4}$$

The Free-Radical Chain Mechanism of Halogenation

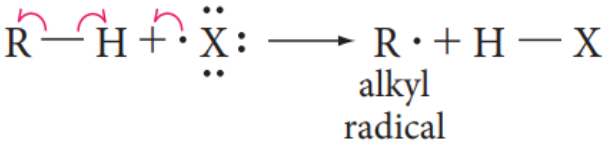
- A reaction mechanism is a step-by-step description of the bond-breaking and bond-making processes that occur when reagents react to form products.
- A free-radical chain reaction includes a chain-initiating step, chain-propagating steps, and chain-terminating steps.

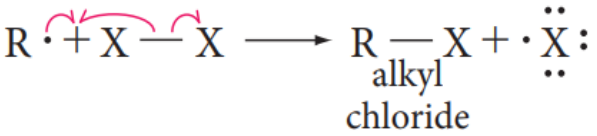
Initiation



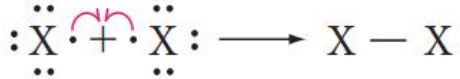
(Homolysis of a halogen molecule)

Propagation





Termination



Alkenes

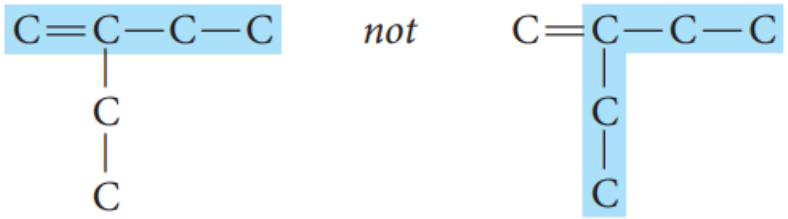
C_nH_{2n} Crabon-Carbon double bond

- ene

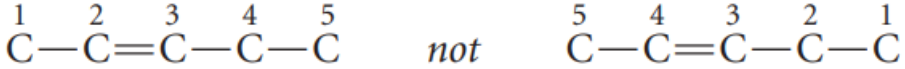
Alkenes

Nomenclature of Alkenes

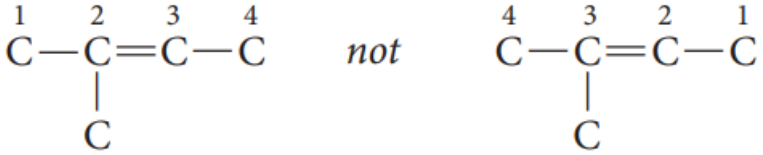
- The IUPAC rules for naming alkenes are similar to those for alkanes, but a few rules must be added for naming and locating the multiple bonds.
  1. The ending *-ene* is used to designate a carbon–carbon double bond. When more than one double bond is present, the ending is *-diene*, *-triene*, and so on.
  2. Select the longest chain that includes both carbons of the double.



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

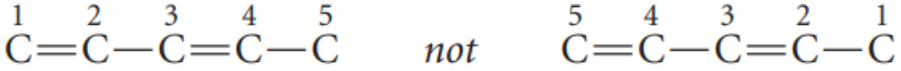


If the double bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.

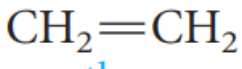


4. Indicate the position of the double bond using the lower numbered carbon atom of that bond.

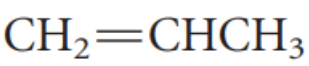
5. If more than one double bond is present, number the chain from the end nearest the first double bond.



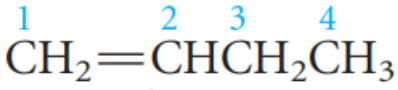
Examples



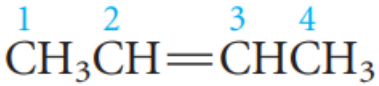
ethene



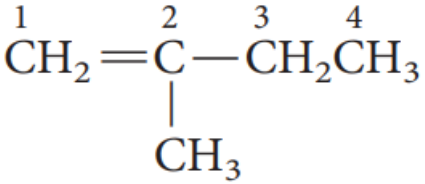
propene



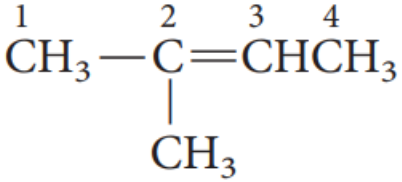
1-butene



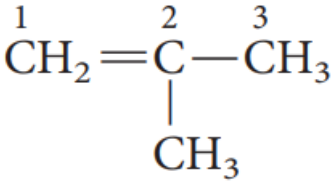
2-butene



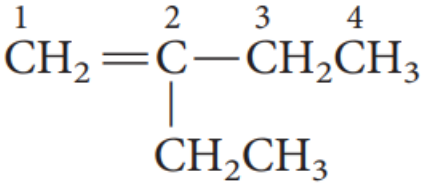
2-methyl-1-butene



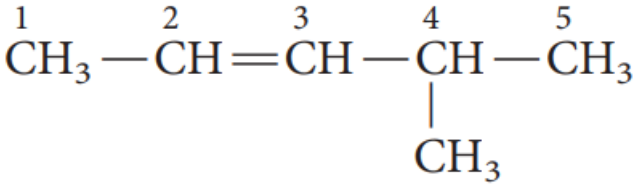
2-methyl-2-butene



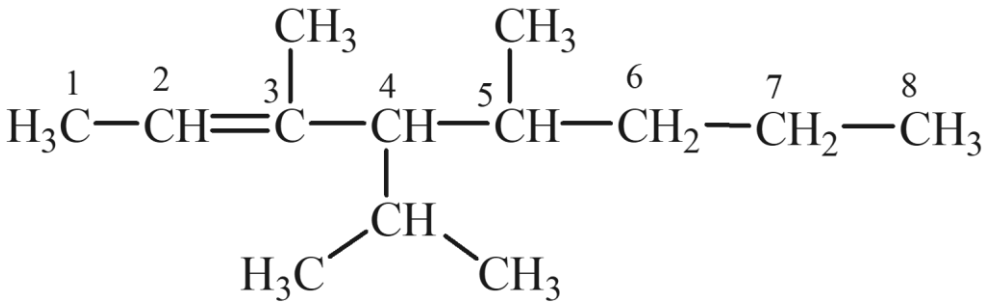
methylpropene
(isobutylene)



2-ethyl-1-butene



4-methyl-2-pentene



4-Isopropyl-3,5-dimethyl-2-octene.

Common names

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

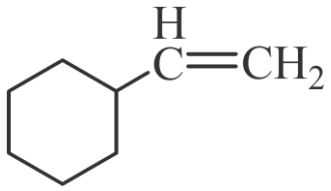
$CH_2=CH_2$
ethylene
(ethene)

$CH_3CH=CH_2$
propylene
(propene)

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

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

$CH_2=CH-$
vinyl
(ethenyl)



vinyl cyclohexane
(cyclohexylethane)

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

$CH_2=CHCl$
vinyl chloride
(chloroethene)

Cycloalkenes

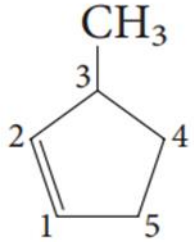
C_nH_{2n-2}

- Cycloalkenes are unsaturated hydrocarbons that have at least one ring of carbon atoms.

Nomenclature of Cycloalkenes

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

cyclopentene



3-methylcyclopentene

Physical properties of alkenes

Physical States and Solubilities

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

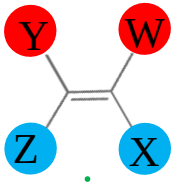
- Alkenes are nonpolar compounds. Thus alkenes are soluble in the nonpolar solvents such as carbon tetrachloride (CCl_4) and benzene (C_6H_6), but they are insoluble in polar solvents such as water.

Geometric Isomerism in Alkene

- Because rotation at carbon–carbon double bonds is restricted, geometric isomerism is possible in appropriately substituted alkenes.

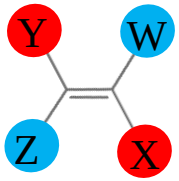
A)When W differs from X and Y from Z, Alkenes exist as geometric isomers

The *cis-trans* system



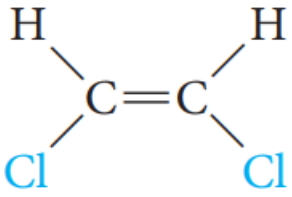
cis

(two similar groups are on the *same* side)

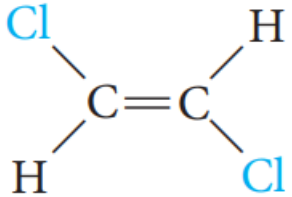


trans

(two similar groups are on the *opposite* sides)



cis-1,2-dichloroethene

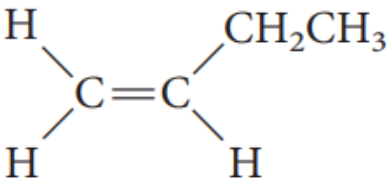


trans-1,2-dichloroethene

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

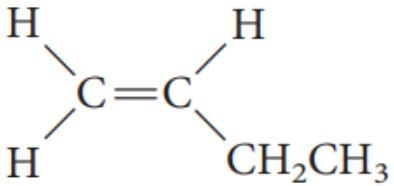
Geometric Isomerism in Alkene

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



1-butene

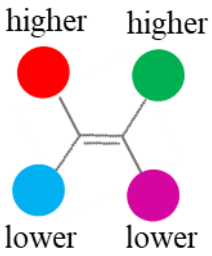
is identical to



1-butene

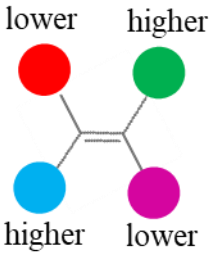
C) For alkenes with four different substituent

The *E*-*Z* System



Z : Zusammen

(two groups of higher priority are on the *same* side)



E : Entgegen

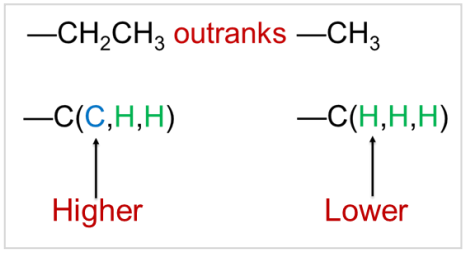
(two groups of higher priority are on the *opposite* sides)

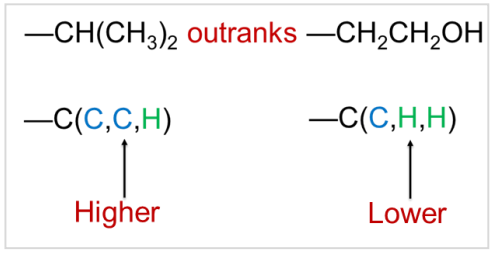
Geometric Isomerism in Alkene

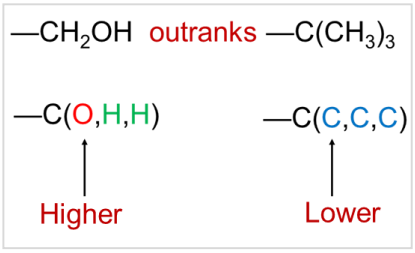
The *E*-*Z* System

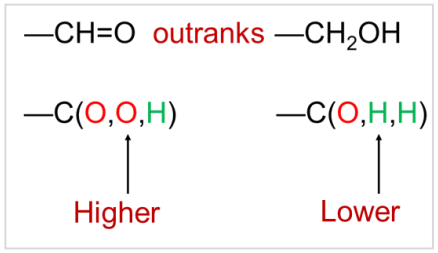
- Higher atomic number gets higher priority.

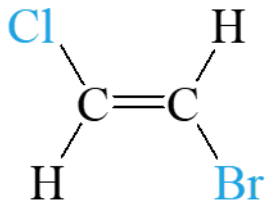
I > Br > Cl > S > P > F > O > N > C > H



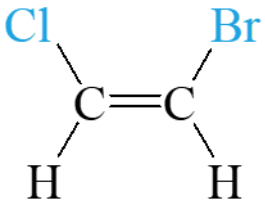








E-1-Bromo-2-chloroethene

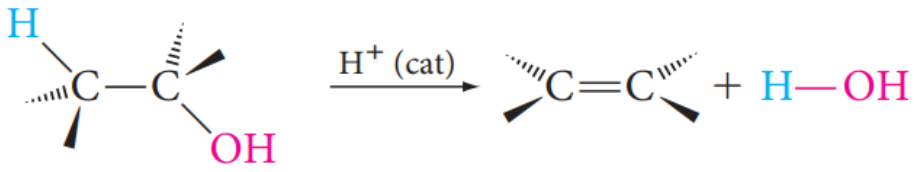


Z-1-Bromo-2-chloroethene

Preparation of alkenes

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

1- Dehydration of Alcohols



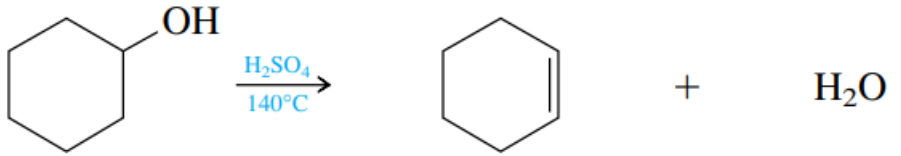
Examples:

Primary Alcohol

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

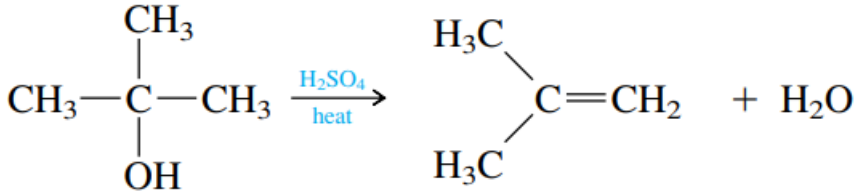
Ethyl alcohol — Ethylene — Water

Secondary Alcohol



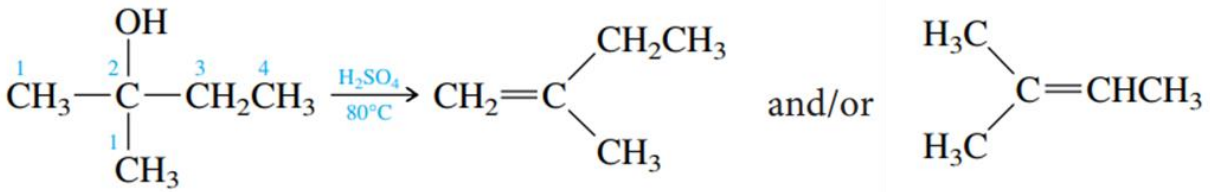
Cyclohexanol — Cyclohexene (79–87%) — Water

Tertiary Alcohol



2-Methyl-2-propanol — 2-Methylpropene (82%) — Water

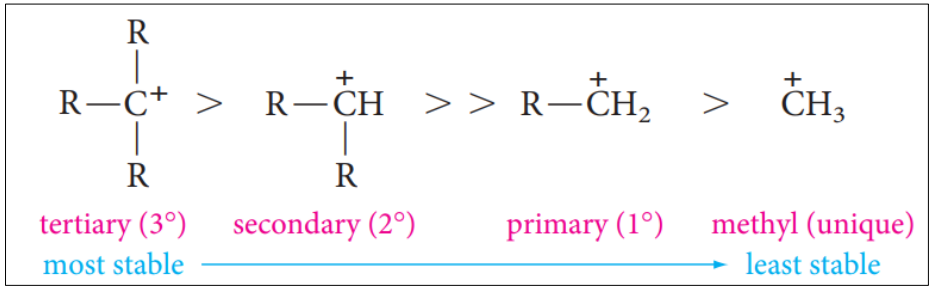
Regioselectivity in Dehydration of Alcohols: Zaitsev's Rule



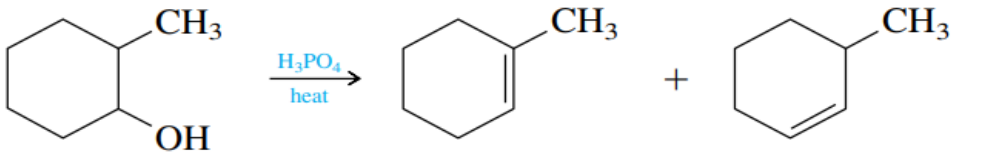
2-Methyl-2-butanol | 2-Methyl-1-butene | 2-Methyl-2-butene

Zaitsev's Rule:

- Hydrogen is preferably removed from the carbon with least no. of hydrogen since the alkene formed is more highly branched and is energetically more stable.
- The reaction proceeds *via* a carbocation intermediate, the stabilities of carbocations and the ease of dehydration of alcohols follows the order 3° > 2° > 1°.

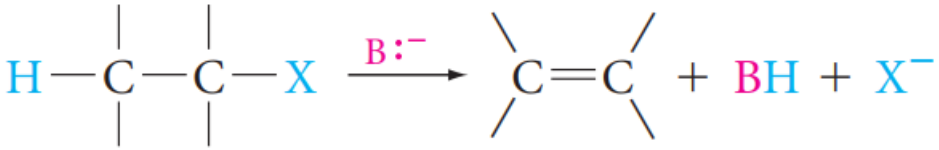


$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2$, $RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$

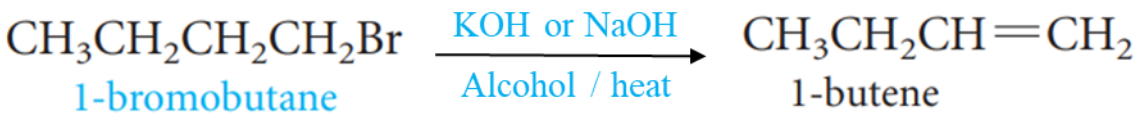


2-Methylcyclohexanol | 1-Methylcyclohexene (84%) major | 3-Methylcyclohexene (16%)

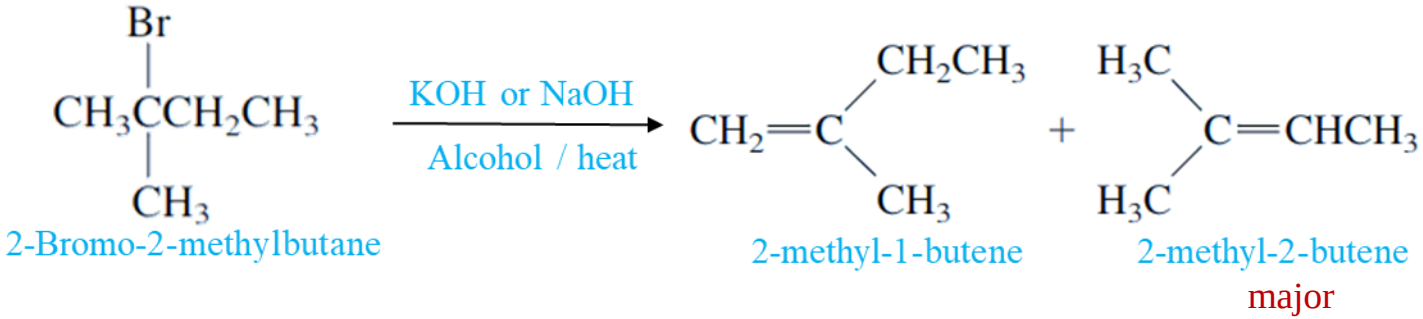
2- Dehydrohaloganation of Alkyl halides



Examples:

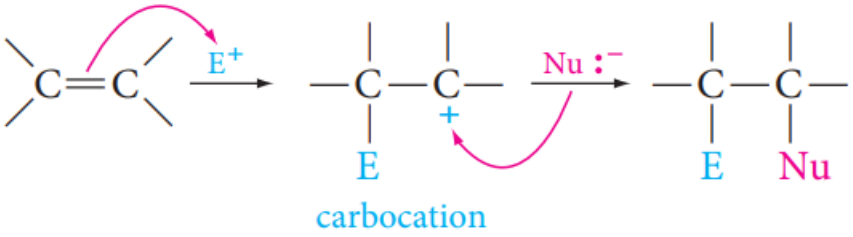


Zaitsev's Rule

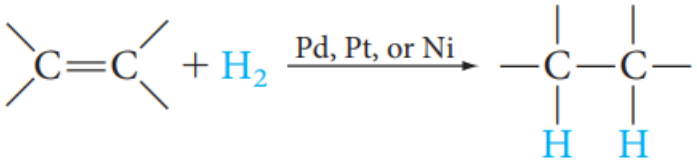


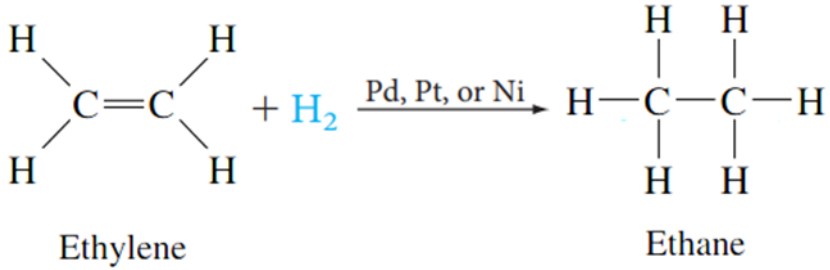
Reaction of alkenes

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



1- Addition of Hydrogen: Catalytic Hydrogenation

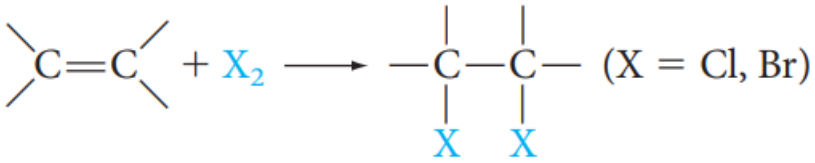


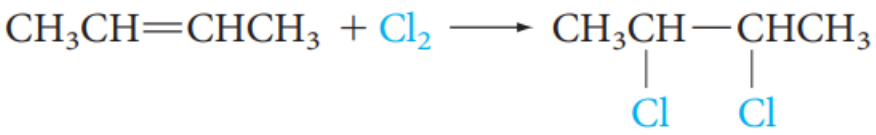


$(CH_3)_2C{=}CHCH_3 + H_2 \xrightarrow{Pt} (CH_3)_2CHCH_2CH_3$

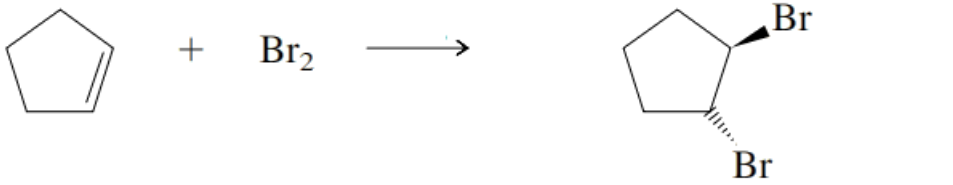
2-Methyl-2-butene → 2-Methylbutane

2- Addition of Halogens: Halogenation





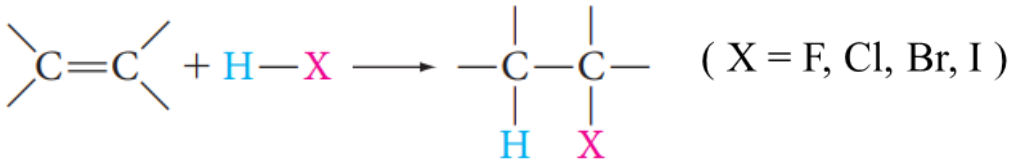
2-butene 2,3-dichlorobutane

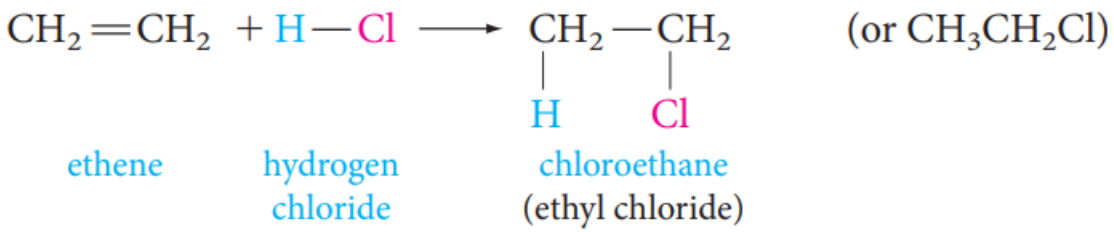


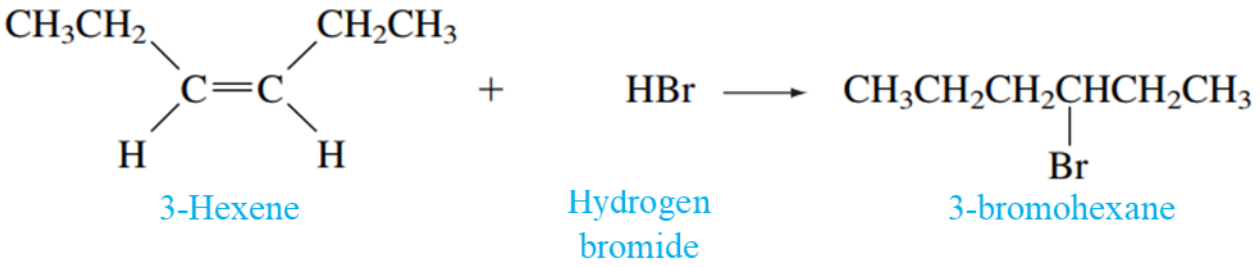
Cyclopentene *trans*-1,2-Dibromocyclopentane

3- Addition of Acids:

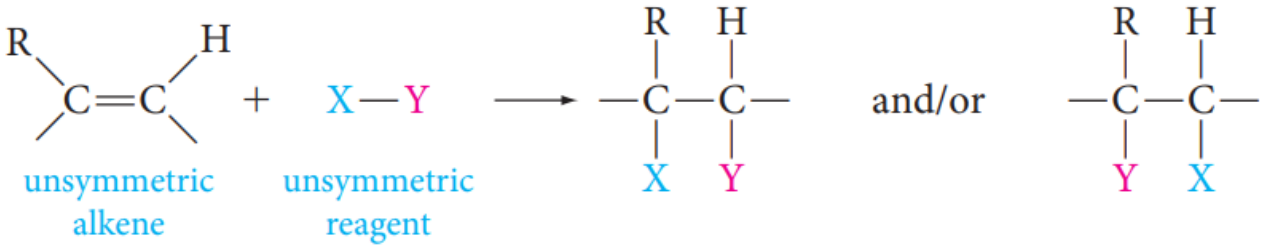
Acids that add in this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I).



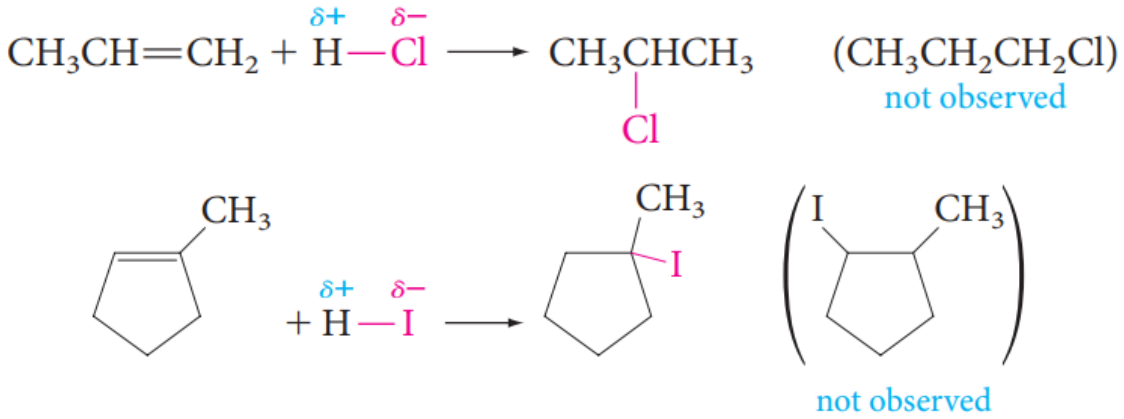


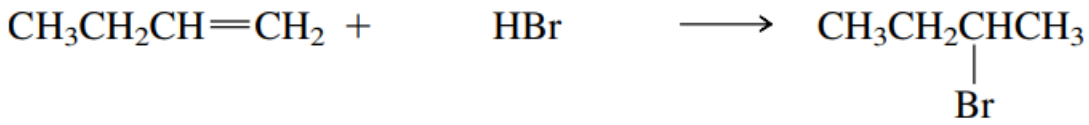


Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule

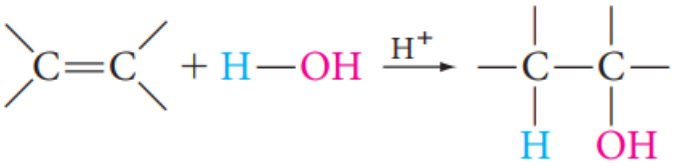


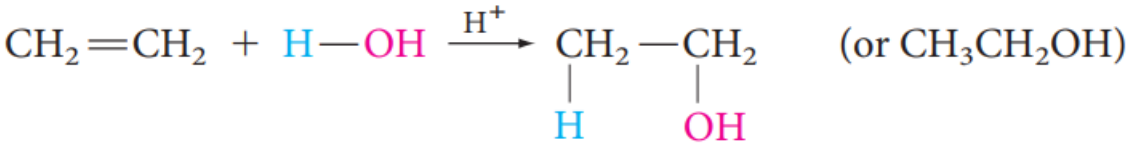
When an unsymmetric reagent adds to an unsymmetric alkene, the electropositive part of the reagent adds to the carbon of the double bond that has the greater number of hydrogen substituents .

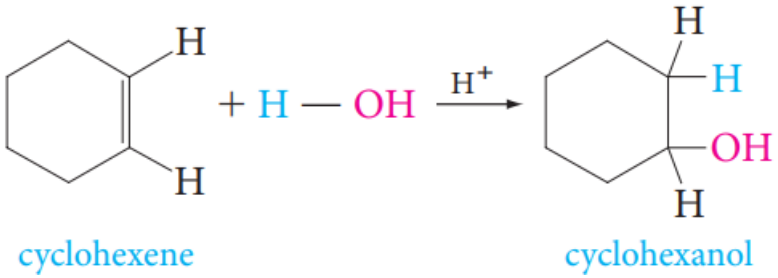




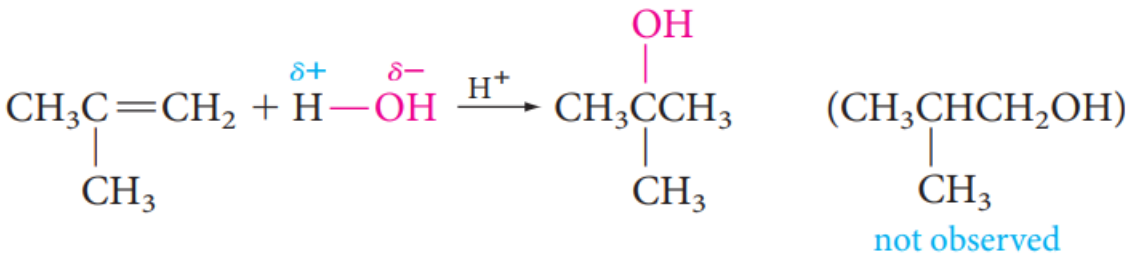
4- Addition of Water : Hydration







Markovnikov's Rule

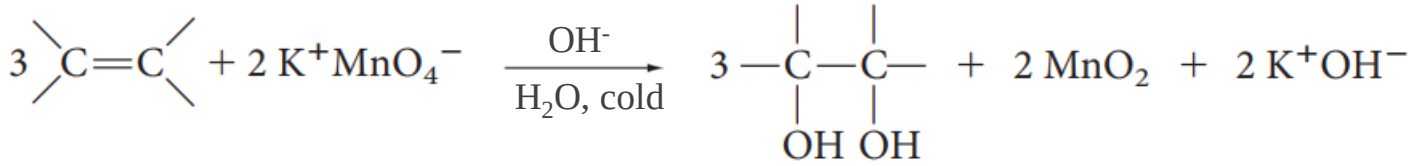


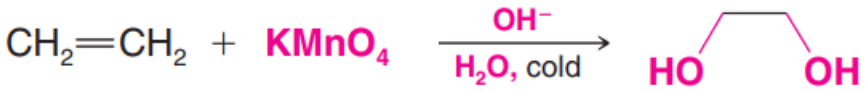
Reaction of alkenes

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

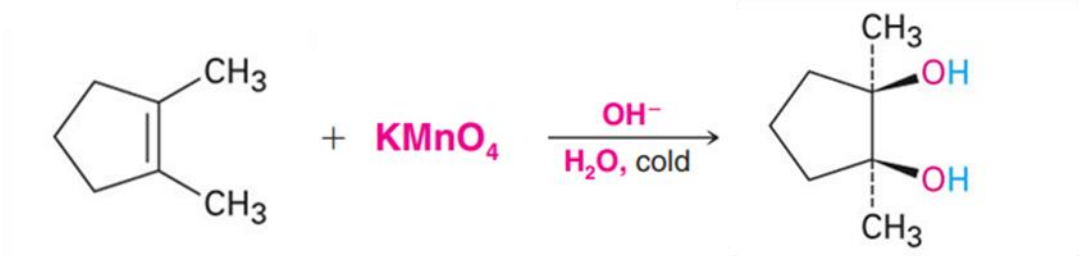
1- Oxidation of alkenes with Permanganate

syn hydroxylation





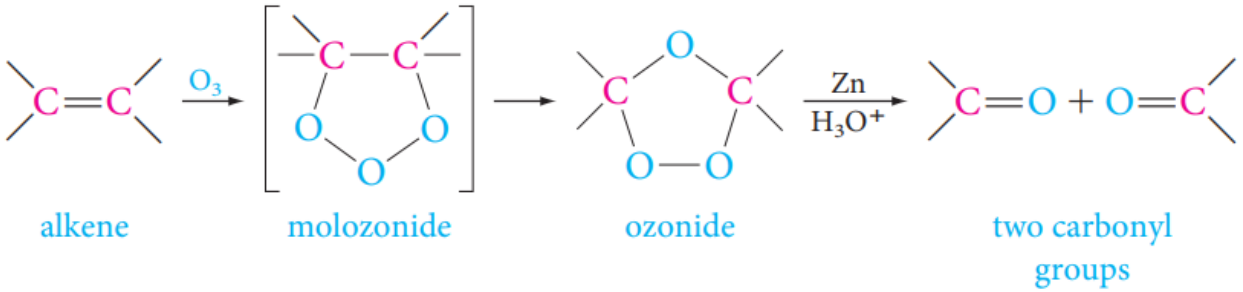
Ethene **1,2-Ethanediol**



1,2-Dimethylcyclopentene ***cis*-1,2-Dimethyl-1,2-cyclopentanediol (87%)**

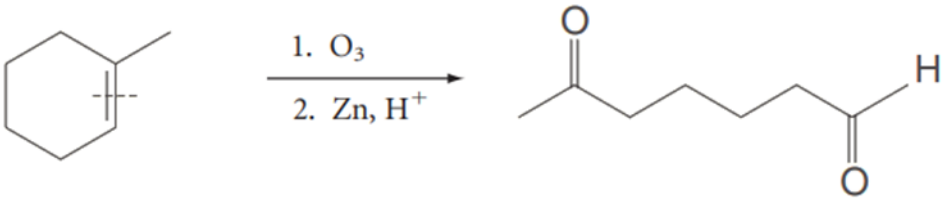
2- Ozonolysis:

Oxidation of alkenes by ozone O_3



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

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



Alkynes

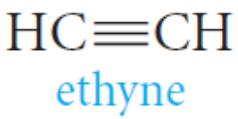
C_nH_{2n-2} Crabon-Carbon Trible bond

- yne

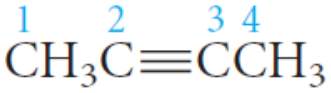
Alkynes

Nomenclature of Alkynes

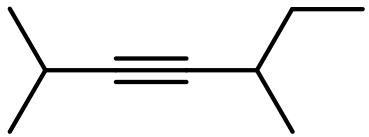
IUPAC Names: ane $\longrightarrow$ yne


ethyne


propyne


2-butyne


1-butyne


2,5-dimethyl-3-heptyne

Physical Properties

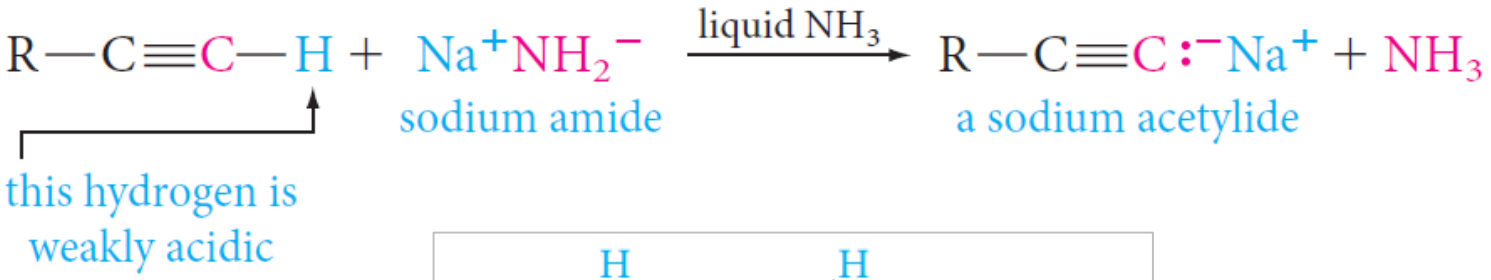
C_1-C_4 gases

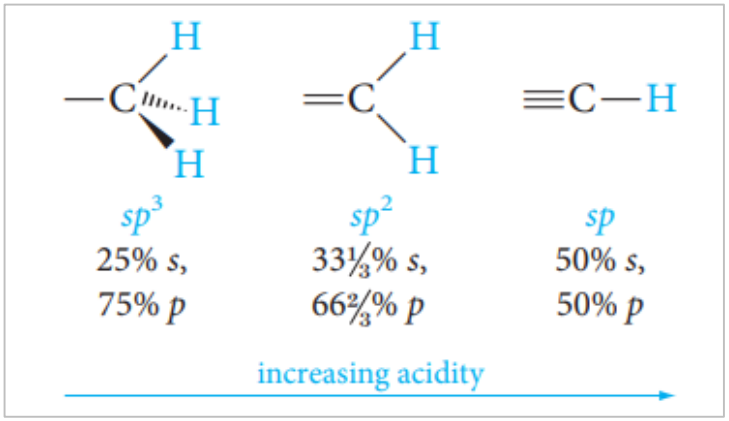
C_5-C_{18} liquid

More than C_{18} soilds

Acidity of Terminal Alkynes

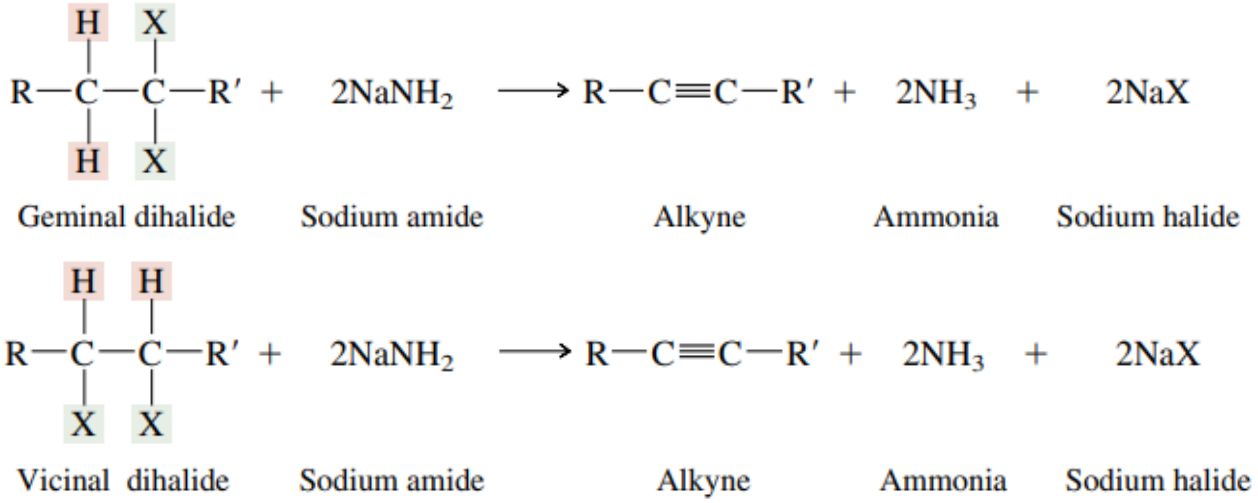
- A hydrogen atom on a triply bonded carbon is weakly acidic and can be removed by a very strong base. Sodium amide, for example, converts acetylenes to acetylides.



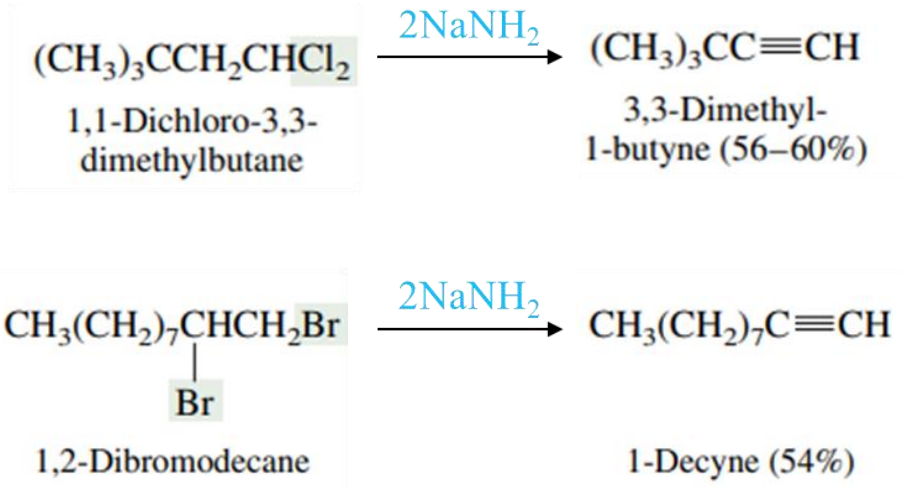


Preparation of Alkynes

1- Dehydrohalogenation of Alkyl Dihalide

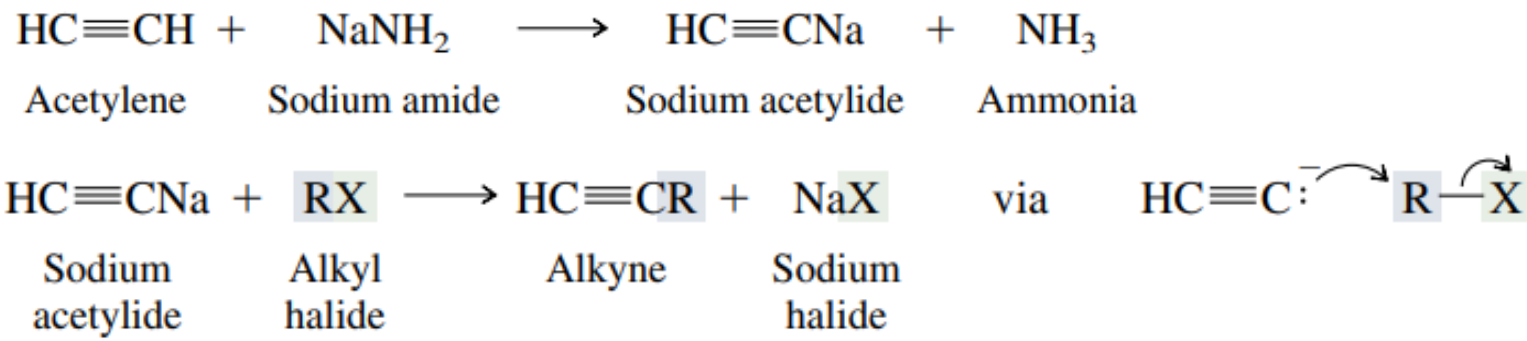


Examples:

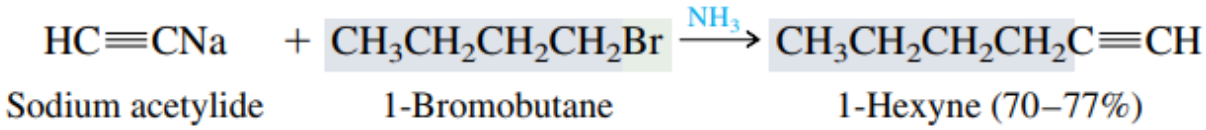


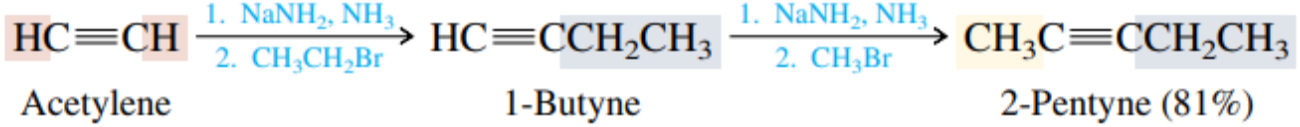
2- Alkylation of Acetylene and Terminal Acetylene

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



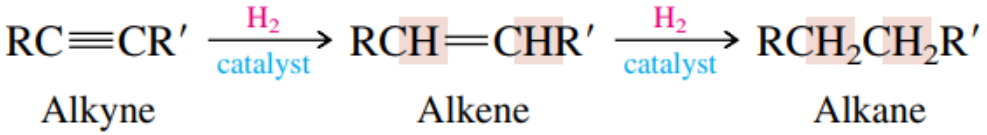
Examples:

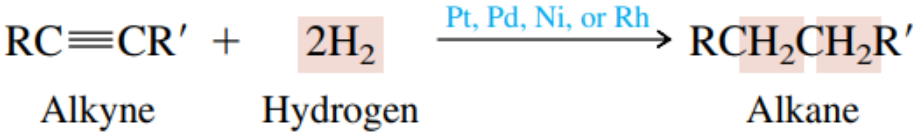


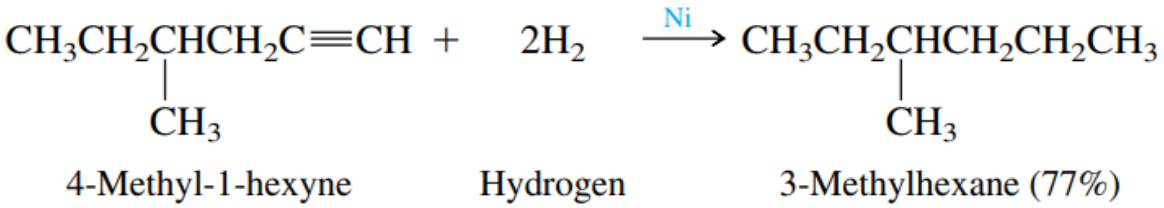


Reactions of Alkynes

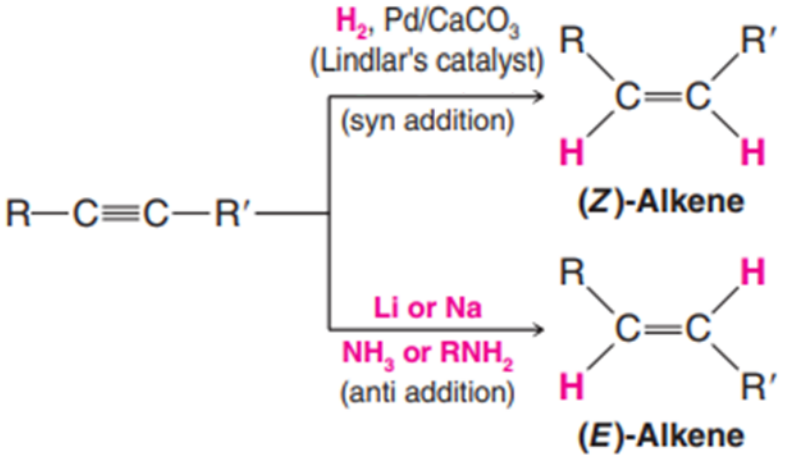
1- Addition of Hydrogen: Hydrogenation



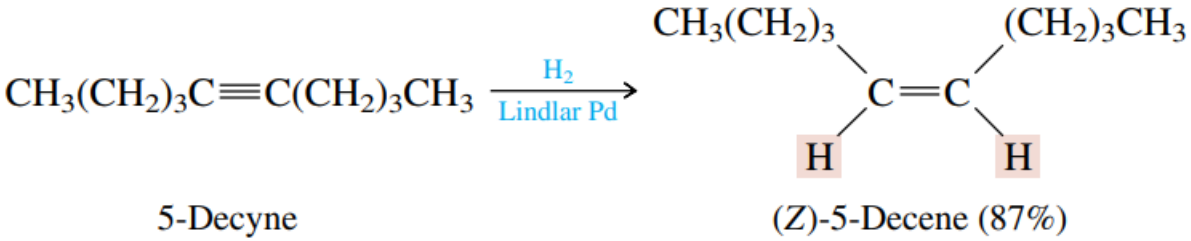


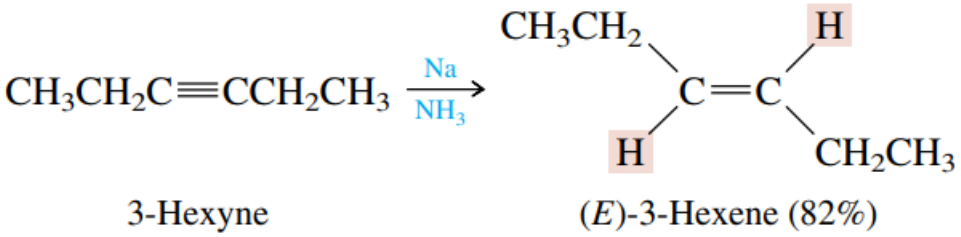


- Hydrogenation of an alkyne to an alkene can be accomplished through the use of special catalysts or reagents. Moreover, these special methods allow the preparation of either (E)- or (Z)-alkenes from disubstituted alkynes.

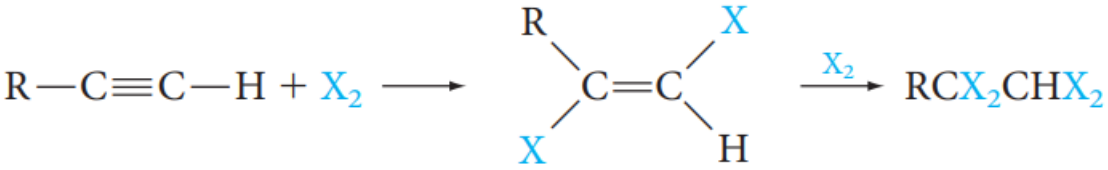


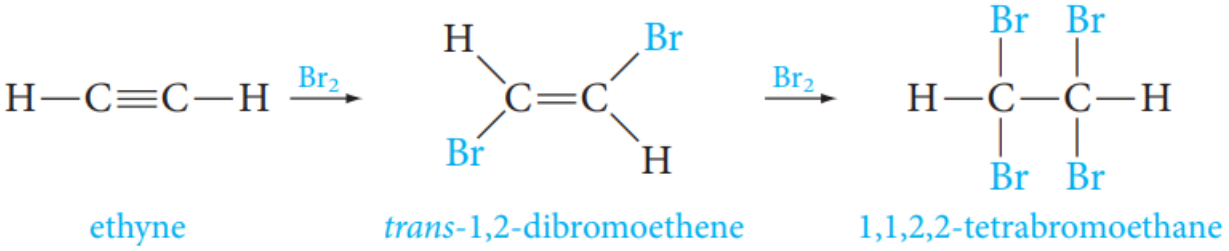
Examples:



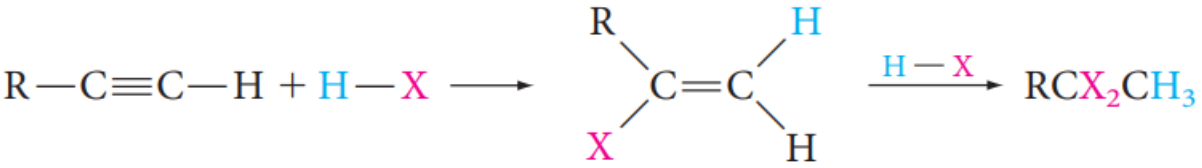


2- Addition of Halogen: Halogenation

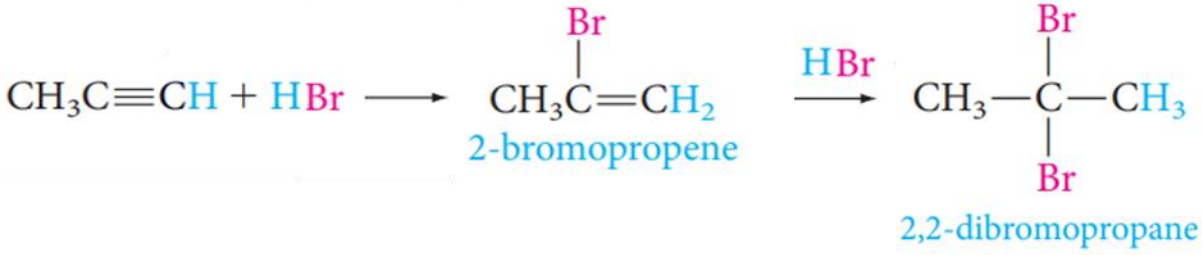




3- Addition of Hydrogen Halide: Hydrohalogenation

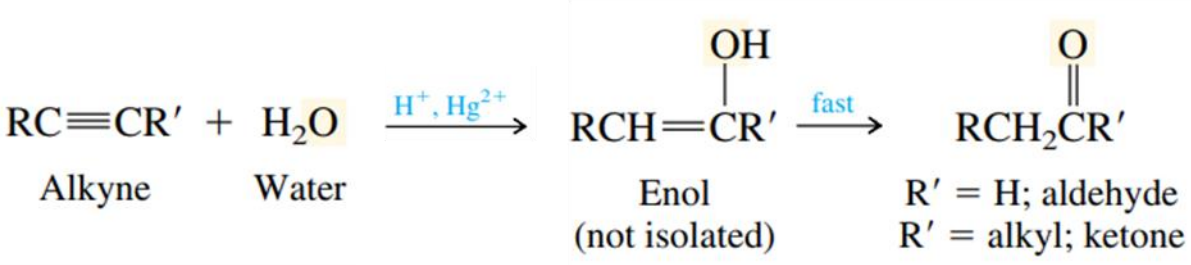


Markovnikov addition



4- Addition of Water : Hydration

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



Markovnikov addition