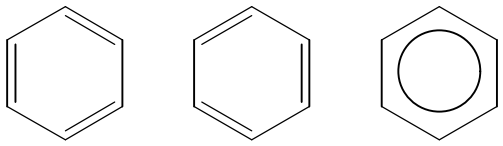
UNSATURATED HYDROCARBONS

- The ***unsaturated*** hydrocarbons consist of three families of ***homologous*** compounds that contain ***multiple bonds*** between carbon atoms.

- **Alkenes** contain carbon-carbon double bonds. Double bonded carbons possess an angle of 120° and hybridization of sp^2.

- **Alkynes** contain carbon-carbon triple bonds. Triple bonded carbons possess an angle of 180° and hybridization of sp.

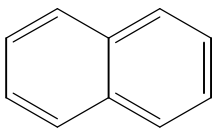
- **Aromatic compounds** contain benzene rings. Benzene rings are six membered rings that contain alternate double bonds and are represented by any of the structures shown below:



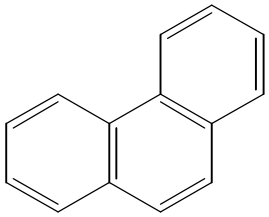
Representations of Benzene

- Benzene compounds are unlike other unsaturated compounds (alkenes and alkynes) and have their own characteristic properties and reactions.

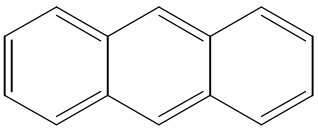
- Some organic molecules contain several benzene rings and are called polycyclic aromatic compounds. Some examples of are shown below:



naphthalene



phenanthrene



anthracene

NOMENCLATURE OF ALKENES

- Alkenes have the general formula C_nH_{2n} .

- To use the IUPAC rules for naming alkenes:

  1. Select the longest continuous carbon-carbon chain that contains the double bond.
  2. Name this parent compound as you would an alkane, but change the ***–ane*** ending to ***–ene***.
  3. Number the carbon chain of the parent compound starting with the end nearer to the double bond. Use the smaller of the two numbers on the double-bonded carbon atoms to indicate the position of the double bond. Place this number in front of the alkene name.
  4. Branch chains and other groups are treated as in naming alkanes, by numbering and assigning them to the carbon atom to which they are bonded.

$CH_3CH{=}CHCH_3$ — 2-butene

$CH_3CH_2CH_2CH{=}CH_2$ — 1-pentene

$CH_3CHCH_2CH{=}CH_2$ (CH$_3$ branch) — 4-methyl-1-pentene

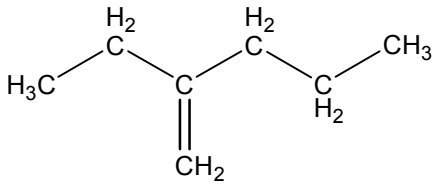
$CH_3CH_2CH_2CHCH{=}CH_2$ (CH_2CH_3 branch) — 3-ethyl-1-hexene

Examples:

1. Write a structural formula for 4-methyl-2-pentene.

2. Write a structural formula for 7-methyl-2-octene.

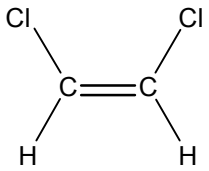
3. Name the compound shown :



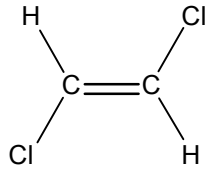
GEOMETRIC ISOMERS

- Compounds containing a carbon-carbon double bond have restricted rotation about that double bond. This restricted rotation in a molecule gives rise to a type of isomer known as ***geometric isomer***.

- Isomers that differ from each other only in the geometry of their molecules and not in the order of their atoms are known as ***geometric isomers***. They are also called ***cis-trans isomers***.

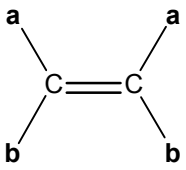


cis-1,2-dichloroethene
(bp= 60.1°C)

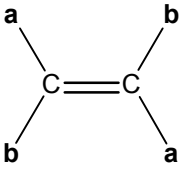


trans-1,2-dichloroethene
(bp= 48.4°C)

- An alkene shows cis-trans isomerism when each carbon atom of the double bond has two different kinds of groups attached to it.

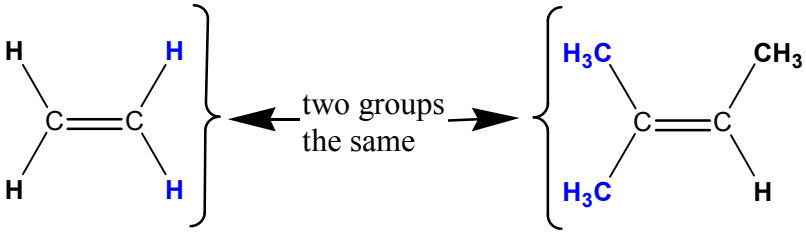


cis isomer



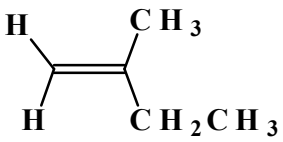
trans isomer

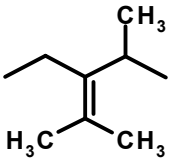
- An alkene ***does not show*** cis-trans isomerism if one carbon of the double bond has two identical groups attached to it.

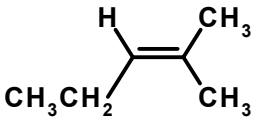


GEOMETRIC ISOMERS

- Shown below are some examples of alkenes that do not have cis/trans isomers.



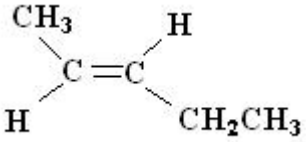




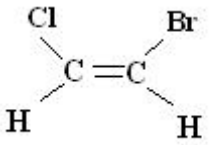
Examples:

1. Identify each of the molecules below as cis or trans isomers.

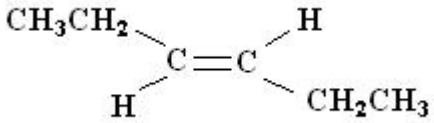
a)



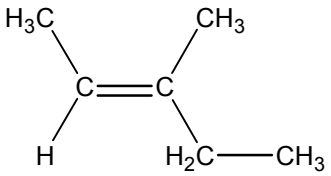
b)



2. Name the following compound:



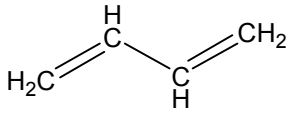
3. Is the compound shown below cis or trans isomer? Name this compound.



4. Draw structure for cis-5-chloro-2-hexene.

DIENES & TRIENES:

- Many compounds have more than one C=C. Compounds with two C=C are called ***dienes***, and are named by numbering each carbon bearing the double bond.

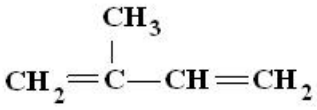


1,3-butadiene

- Compounds with three double bonds are called ***trienes*** and are named similar to other alkenes.

Examples:

1. Name the diene shown below, one of the components of natural rubber.



PREPARATION OF ALKENES

- Alkenes can be prepared by one of two methods:

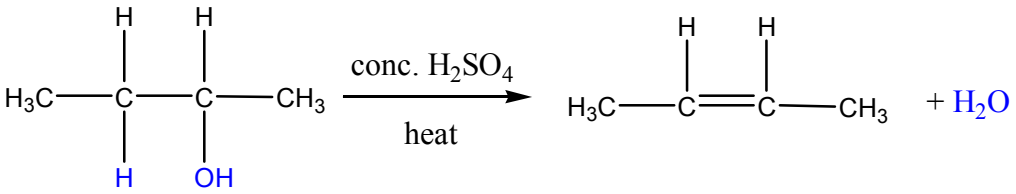
  1. Cracking of alkanes
  2. Dehydration of alcohols

- Cracking, or ***pyrolysis***, is the process in which saturated hydrocarbons are heated to very high temperatures in the presence of a catalyst (usually silica-alumina):

$$\text{Alkane } (C_nH_{2n+2}) \rightarrow \text{Mixture of alkenes} + \text{Alkanes} + H_2\,(g)$$

$$2\ CH_3CH_2CH_3 \rightarrow CH_3CH{=}CH_2 + CH_2{=}CH_2 + CH_4 + H_2$$

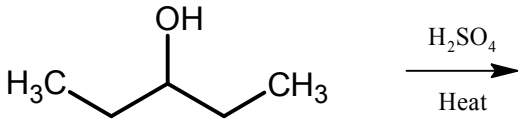
- Dehydration involves the elimination of a molecule of water from a reactant molecule.



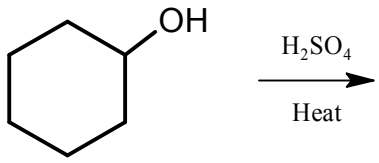
- These reactions will be further discussed in Chapter 22.

Examples:
Predict and name the alkene formed from dehydration of each alcohol shown below:

1)



2)

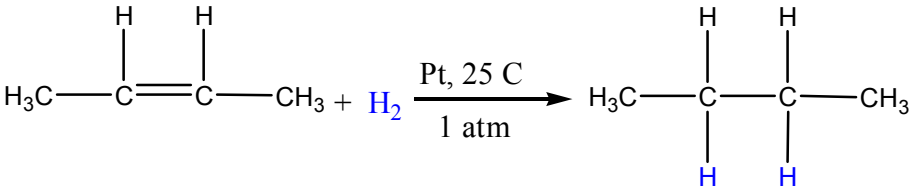


REACTIONS OF ALKENES

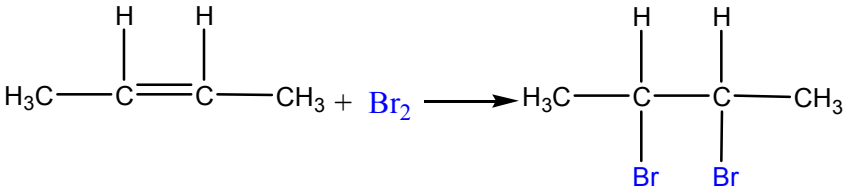
- Alkenes can undergo addition reactions of the following four types:

Addition of H_2	(hydrogenation)	Symmetrical addition
Addition of X_2	(halogenation)	
Addition of H_2O	(hydration)	Unsymmetrical addition
Addition of HX	(hydrohalogenation)	

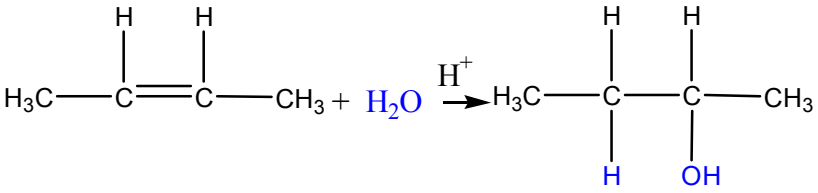
Addition of H_2



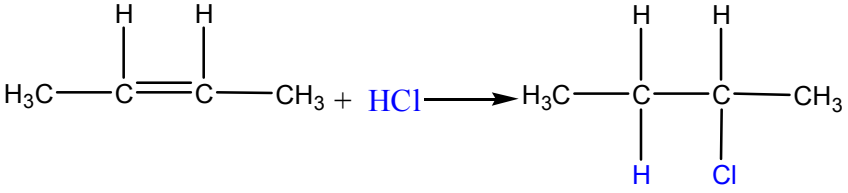
Addition of X_2



Addition of H_2O

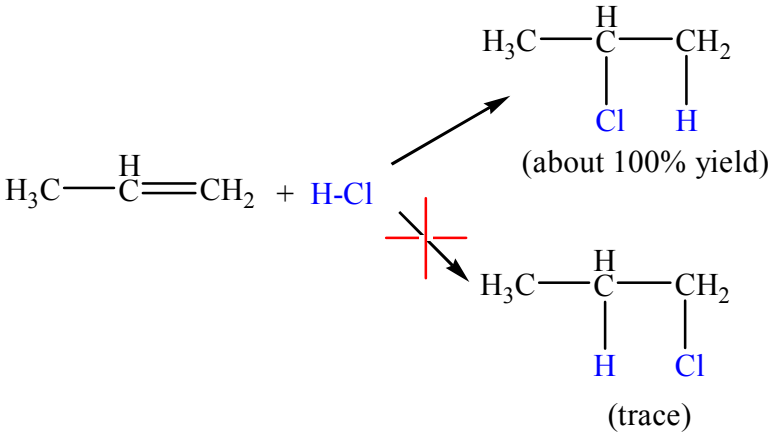


Addition of HX



MARKOVNIKOV'S RULE

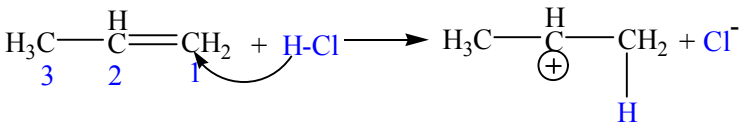
- When an unsymmetrical molecule such as HCl is added to an alkene, two products are theoretically possible. For example, when HCl adds to propene, 1-chloropropane and 2-chloropropane are possible.



- Experimentally, however, we only find one product formed (2-chloropropane).

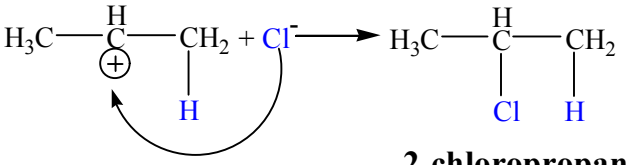
- The reason for this selectiveness lies in the ***reaction mechanism***, the pathway by which a reaction occurs. Addition of HCl to alkenes follows the following mechanism:

Step 1:



isopropyl carbocation

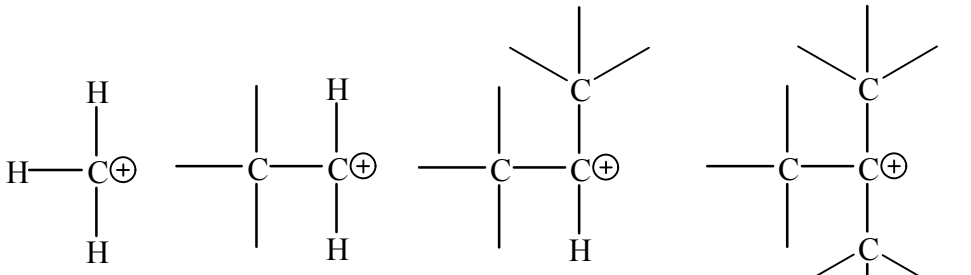
Step 2:



2-chloropropane

MARKOVNIKOV'S RULE

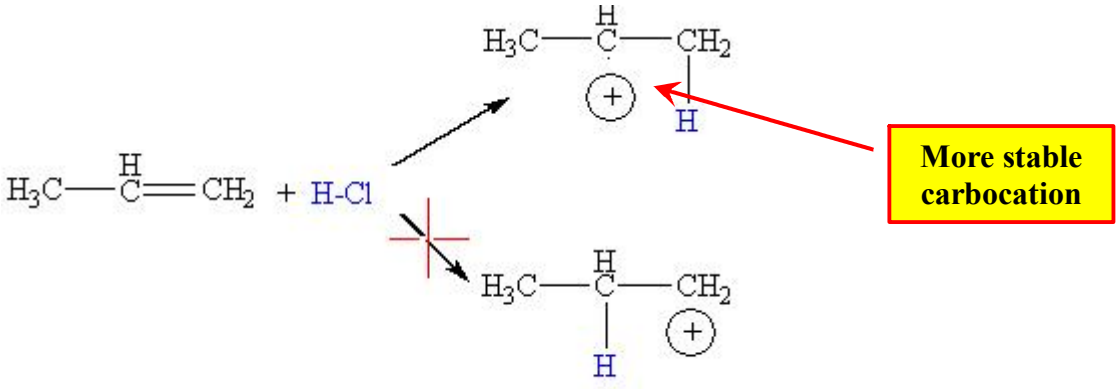
- An ion in which a carbon atom has a positive charge is known as a ***carbocation***.
- Four types of carbocations are possible:



methyl carbocation | **primary (1^o) carbocation** | **secondary (2^o) carbocation** | **tertiary (3^o) carbocation**

Stability of carbocations: $3° > 2° > 1° > C^+H_3$

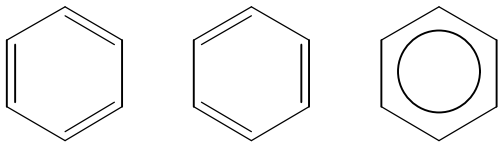
- ***Markovnikov's Rule*** states that when an unsymmetrical molecule such as HX adds to a carbon-carbon double bond, the hydrogen from HX goes to the carbon atom that has the greater number of hydrogen atoms.
- Such addition produces the more stable carbocation.



AROMATIC HYDROCARBONS

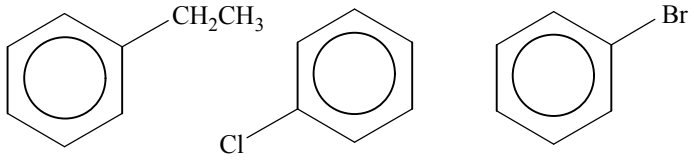
- Unsaturated hydrocarbons that contain ***benzene*** rings are called ***aromatic*** hydrocarbons.

- Benzene is a six-membered ring with molecular formula C_6H_6. It has alternating double bonds, and is represented by the following structures:



- Removal of a H from a benzene ring results in an ***aryl group*** with formula C_6H_5— called ***phenyl***.

- Some monosubstitued aromatic compounds and their names are shown below:

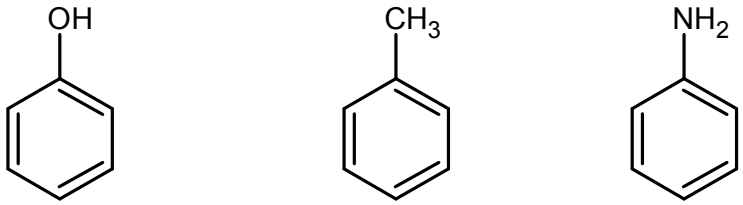


ethylbenzene **chlorobenzene** **bromobenzene**

NAMING AROMATIC COMPOUNDS

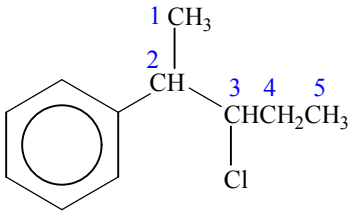
- Simple monosubstituted aromatic compounds can be named as benzene derivatives, as previously discussed.

- Some other simple aromatic compounds that have special names are shown below:



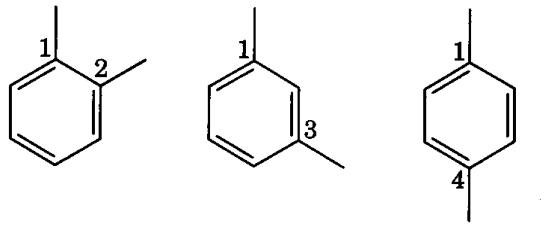
Phenol **Toluene** **Aniline**

- Compounds with benzene rings that cannot be easily named as benzene derivatives are named with phenyl groups. For example:



3-chloro-2-phenylpentane

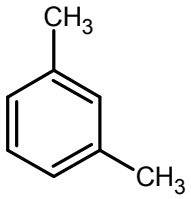
- When two substituents occur on a benzene ring, three isomers are possible. These isomers are named either by numbering of the ring atoms or the Greek prefixes ortho (o), meta (m) and para (p).

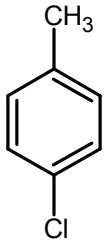


1,2- or *ortho-* 1,3- or *meta* 1,4- or *para*

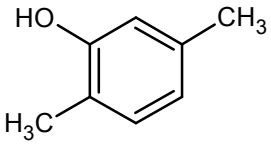
Examples:
Name the following aromatic compounds by at least 2 different names:

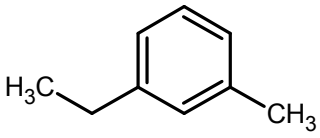
1)





2)





3. Name the following compounds: