

# **Organic Chemistry I**

## **Chem.2042**

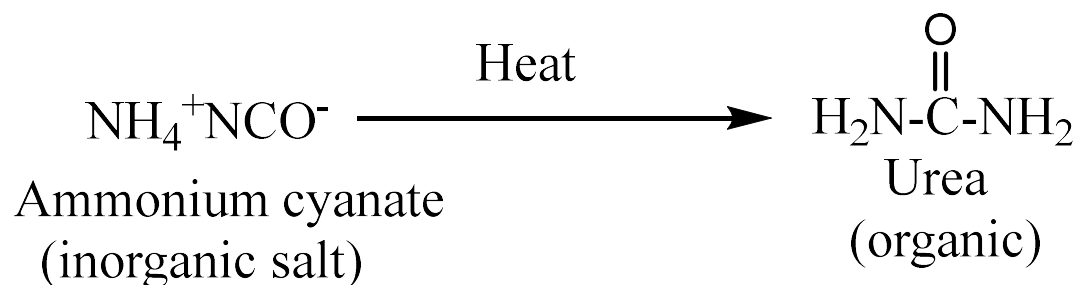
Instructor: *Dr. Kibrom G.Hiwot Bedane*

2022

# 1. Introduction

## 1.1 Historical Background of Organic Chemistry

- In 1780s, scientists distinguished between organic compounds and inorganic compounds (Swedish chemist Torbern Bergman). Organic compounds: as compounds derived from living organisms (vegetables and animals).
- **Vitalism theory** - organic compounds couldn't be synthesized in the laboratory. Because of the vital force requirement.
- In 1828 Friedrich Wöhler synthesized urea from inorganic compound.



After the synthesis of urea in laboratory, theory of Vitalism has been rejected. No special force is required to synthesis organic compounds.

What is organic chemistry?

**Organic chemistry** is the study of carbon containing compounds.

- Why carbon special?
- There are more than 30 million known chemical compounds, of these more than 99% of them contain carbon.
  - Carbon's electron structure and its position in the periodic table.
  - Group IVA element,
  - Carbon can share four valence electrons and form four strong covalent bonds.
  - Carbon atom can bond to one another, forming long chains and rings.



# Organic chemistry

**What:** The study of carbon-containing compounds.

**Why:** Spreading widely in nature.

Chemical foundation of biology.

Improve standard of living (medicines, plastics, pesticides . . .)

**How:** Examine structure and analyse how it governs reactivity

How do you differentiate organic compounds from inorganic compounds?

- Compounds containing carbon may or may not be organic.  
 $\text{NH}_4\text{NCO}$  (ammonium cyanate) is not organic. It is an inorganic salt.
- Organic compounds distinguish from inorganic compounds in that they contain a characteristic functional group (unit 2).

Classify the following compounds as organic or inorganic.

a.  $\text{CO}_2$

d.  $\text{CS}_2$

g.  $\text{HC}\equiv\text{CH}$

b.  $\text{CH}_4$

e.  $\text{CH}_3\text{COOH}$

h.  $\text{Ln}_4(\text{C}_2)_3$

c.  $\text{C}_2\text{H}_5\text{OH}$

f.  $\text{CaC}_2$

i.  $\text{CO}_3^-$

What atoms (besides carbon) are important?

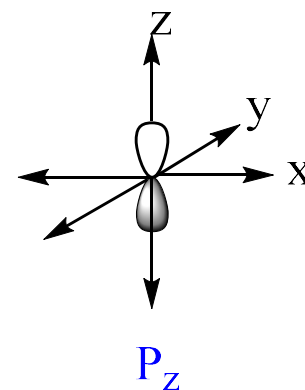
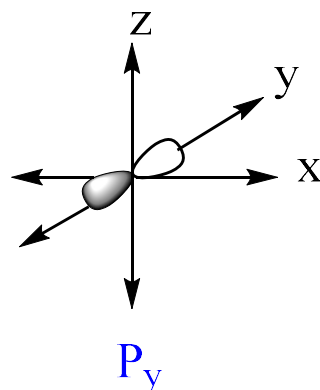
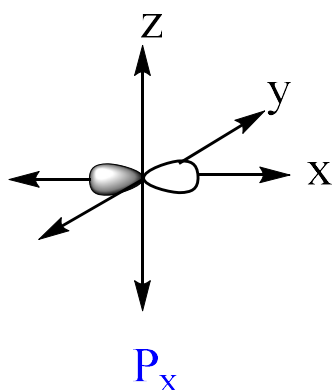
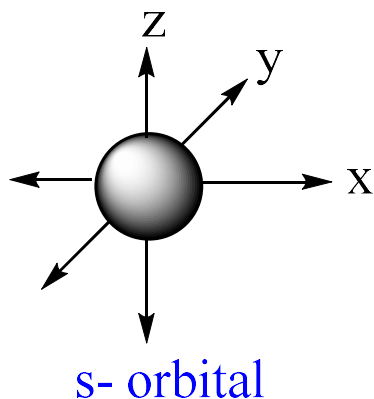
Main Atoms in Organic Chemistry																	
<b>H</b>																	He
Li	Be											<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	Ne
Na	Mg											<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	<b>Br</b>	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	<b>I</b>	Xe

## 1.2 Atomic structure of carbon, covalent bond and hybridization

**Atomic orbitals** - the region in which there is high probability of finding an electron in space.

**Shape of Orbitals** –s, p, d, and f.

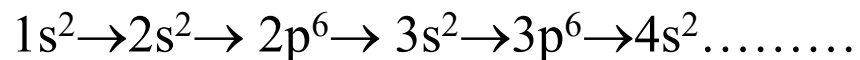
- s and p orbitals most commonly found in organic compounds



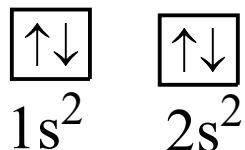
An atomic orbital contain at most two electrons.

## Electron Configuration

i. **The Aufbau principle:-** Electrons enter orbitals of lowest energy first.



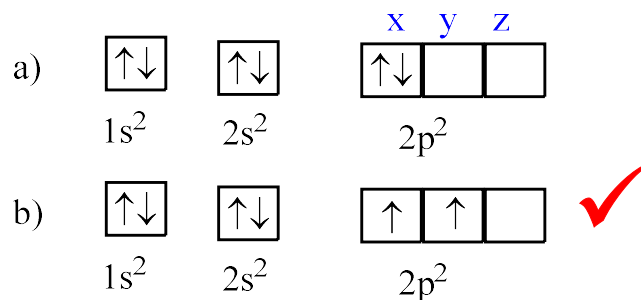
ii. **The Pauli Exclusion Principle:** To occupy the same orbital, two electrons must have opposite spins.



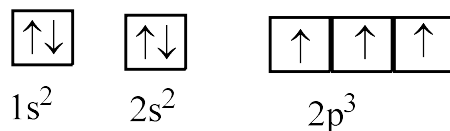
iii. **Hund's rule:** When electrons occupy orbitals of equal energy, one electron enters each orbital unit all the orbitals contain one electron with spins parallel.

**Carbon** (Z=6):  $1s^2, 2s^2, 2p^2$

Two configurations possible



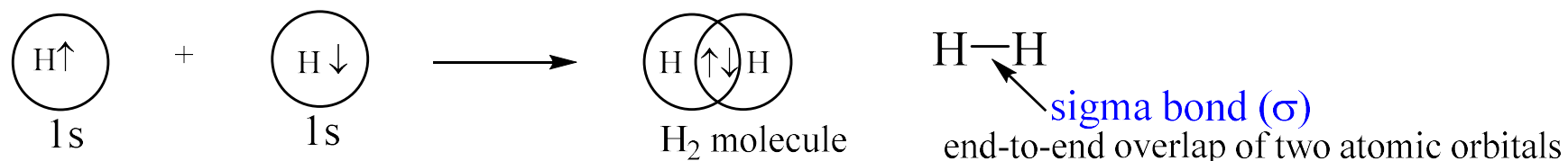
**Nitrogen** (Z=7):  $1s^2, 2s^2, 2p^3$



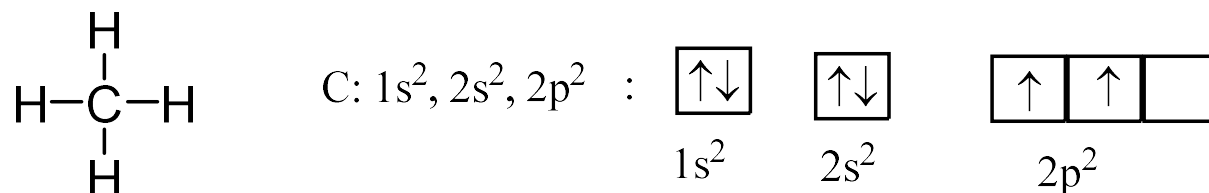
## Bonding in Carbon Compounds

Two models to describe covalent bonding: **valence-bond theory** and **molecular orbital theory**.

- **valence-bond theory:** a half-filled orbital of one atom overlaps with a half-filled orbital of the other atom to form a covalent bond.



\* In order to overlap during covalent bond formation, the two overlapping orbitals must be half-filled.



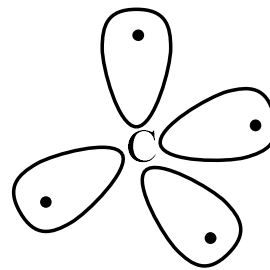
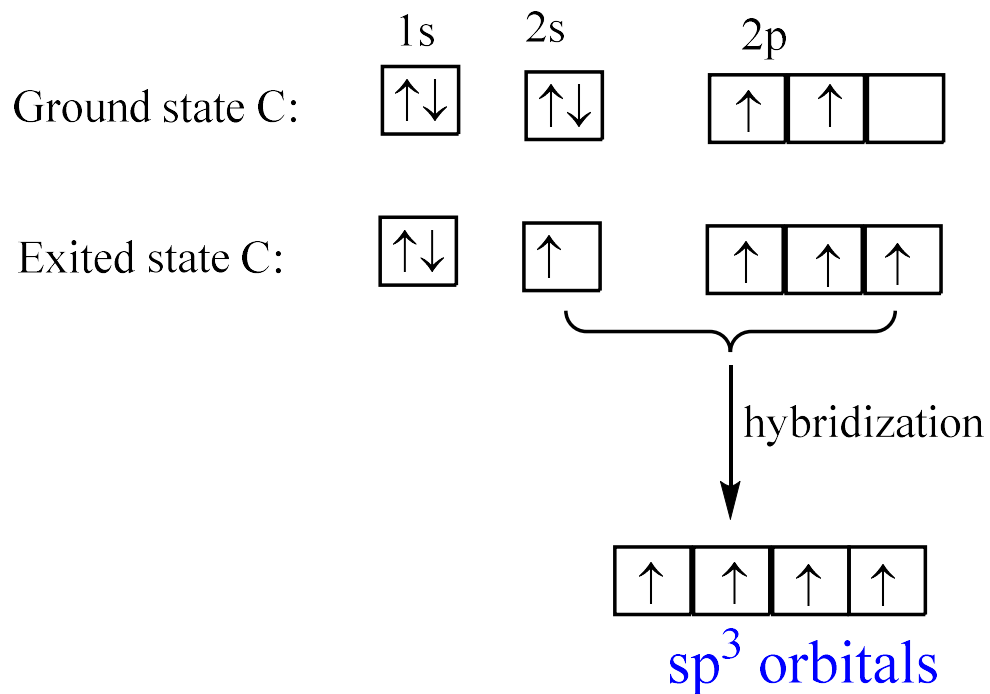
- Only two half-filled orbitals exist in carbon for bond formation according to VB theory.

But in methane there are four bonds (four overlapping) exist. How do we explain this?

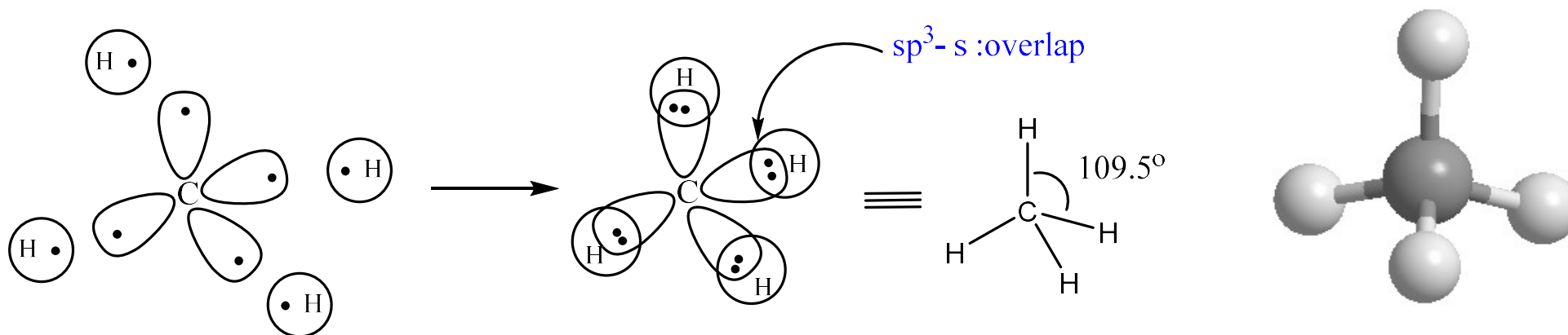
This can be explained by the concept of hybridization



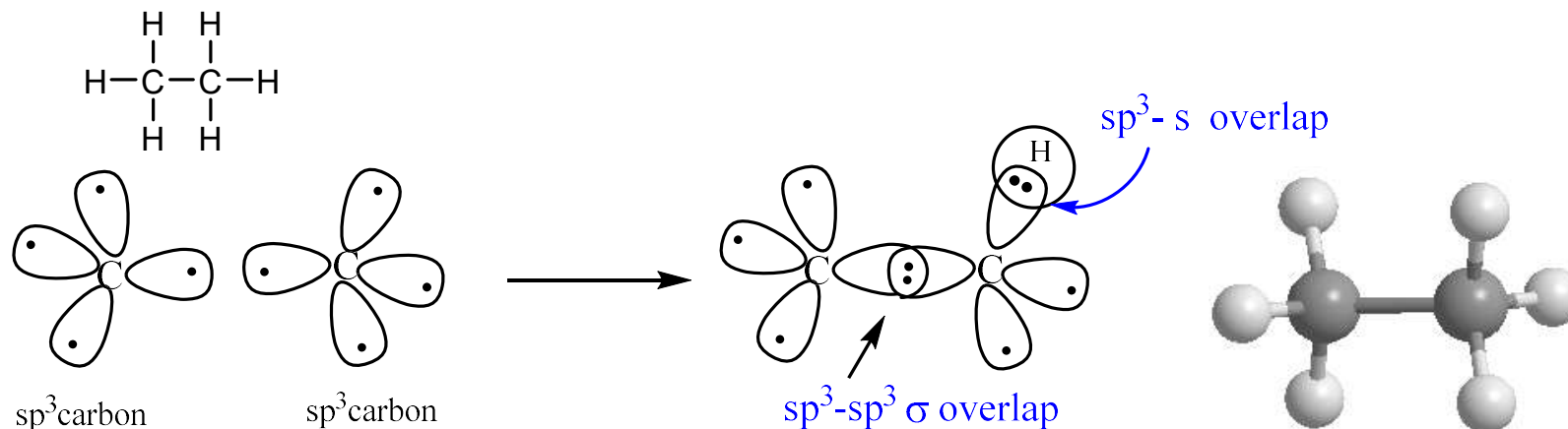
# $sp^3$ Hybridization



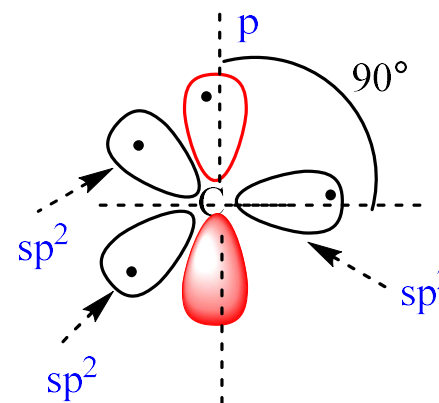
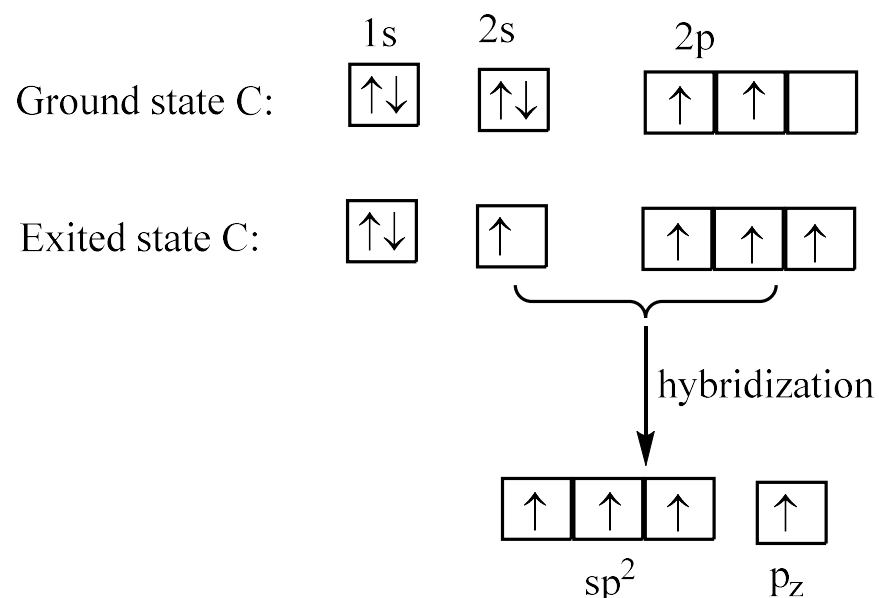
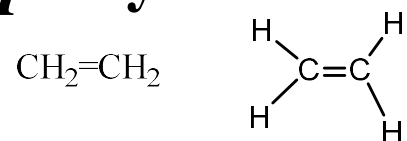
- By mixing ("hybridizing") the  $2s$ ,  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals, four new orbitals obtained ( $sp^3$ ).
- Each  $sp^3$  hybrid orbital has 25% s character and 75% p character.



## Ethane

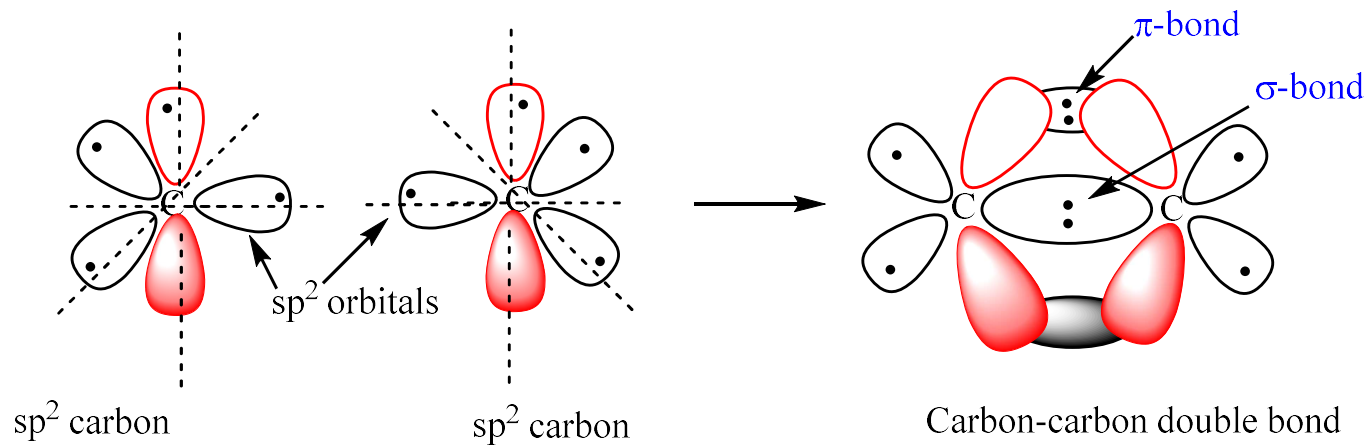


## $\text{sp}^2$ Hybridization



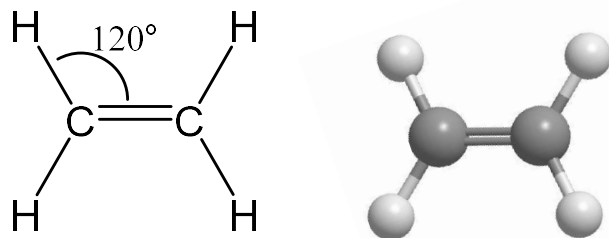
The three  $\text{sp}^2$  orbitals lie in a plane at angle of  $120^\circ$ .  
The remaining  $p$  orbital perpendicular to the  $\text{sp}^2$  plane.

$2s$  orbital combines with only two of three available  $2p$  orbitals.  
One of the  $2p$  orbitals is left unhybridized.

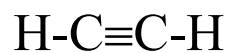


Sigma bond ( $\sigma$ ) resulted due to end- to-end overlap of orbitals

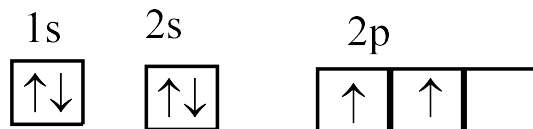
Pi bond ( $\pi$ ) resulted due to side-to-side overlap of p orbitals



# *sp* Hybridization



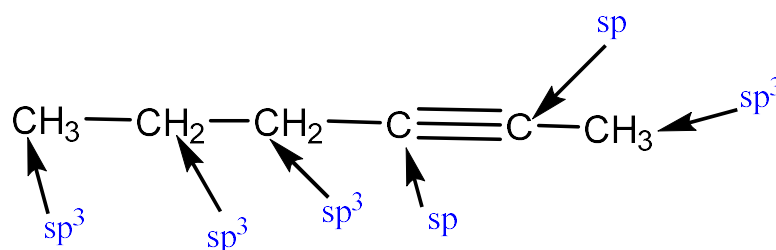
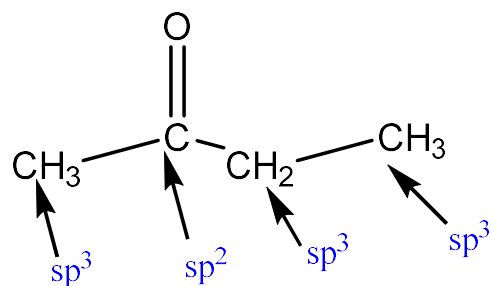
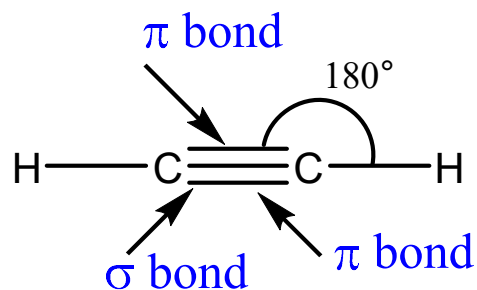
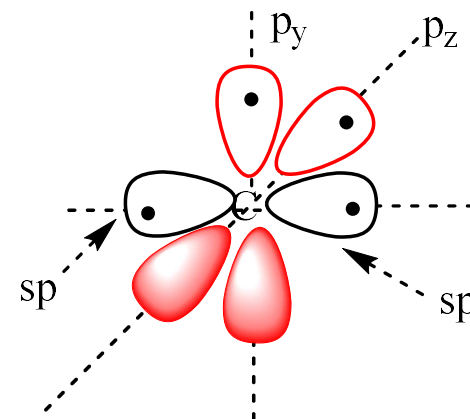
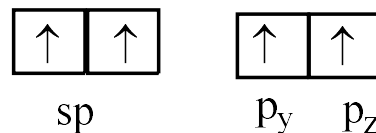
Ground state C:



Excited state C:



hybridization



Ex. What is the hybridization of N in ammonia  $\text{NH}_3$ ? The bond angle?

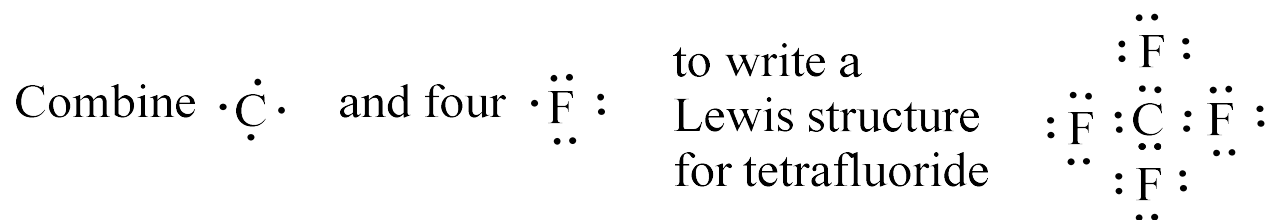
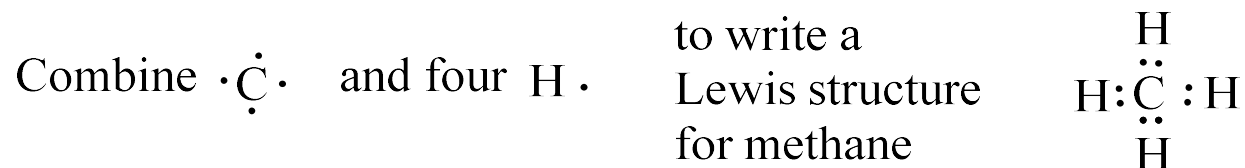
# 1.4 Lewis structure and Resonance

## Lewis structure

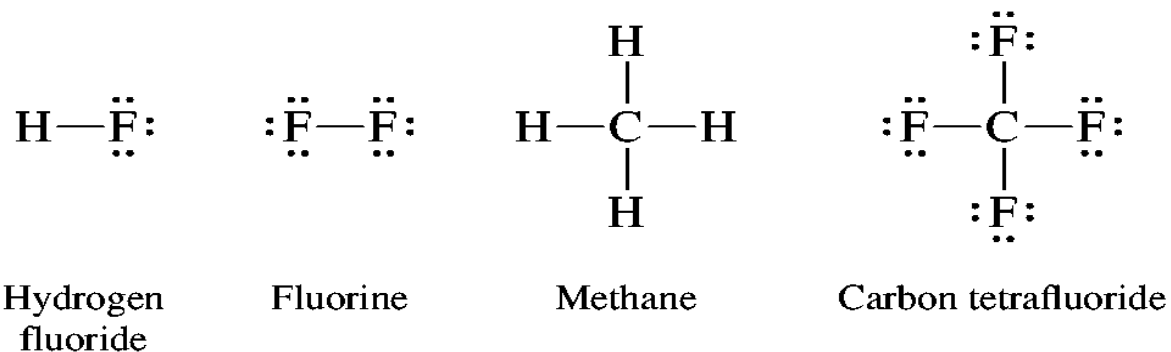
Structural formulas in which electrons are represented as dots are called **Lewis structures**.



Covalent bonding in  $\text{F}_2$  gives each fluorine eight electrons in its valence shell and a stable electron configuration equivalent to that of the noble gas neon.



Representing a two-electron covalent bond by a dash (-)



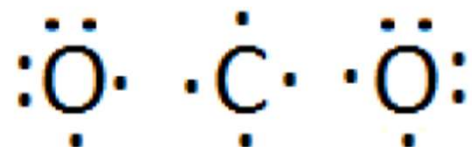
## Rules for drawing Lewis structures

1. Identify the central atom of the molecule (the first atom written, the least electronegative atom) Place all terminal atoms around the central atom.
2. Count the total number of valence electrons
3. Complete the octet for all atoms in the structure with lone pairs of electrons
4. Lone electrons (not lone pairs) indicate an ability to form more covalent bonds, resulting in either **double or triple bonds**. Make double bond or triple bond by rearrange the lone electrons.
5. Check the structure by counting the number of valence electrons used  
Lewis structure should have the same total between all its bonds and lone pairs.

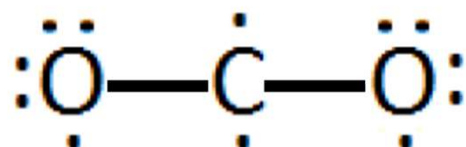
E. g Carbon Dioxide, CO<sub>2</sub>

1.) Carbon is the least electronegative atom, hence the central.

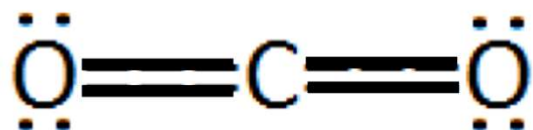
2.) Carbon has 4 valence electrons, each oxygen atom has 6.



3.) Single Bonded.



4.) Double bonded to remove lone electrons.



5.) Total valence electrons = 4 + 2(6) = **16** electrons

2 double bonds = 2 x 4 electrons = 8 electrons

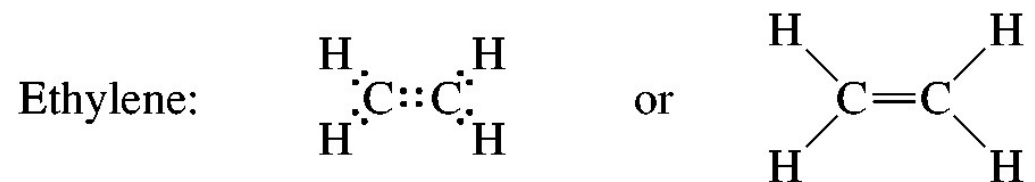
4 lone pairs = 2 x 4 electrons = 8 electrons

8 + 8 = **16** electrons CHECK

## HCN

Hydrogen cyanide      $\text{H}:\text{C}:::\text{N}:$      or      $\text{H}-\text{C}\equiv\text{N}:$

Multiple bonds are very common in organic chemistry



Ex. Write the most stable Lewis structure for

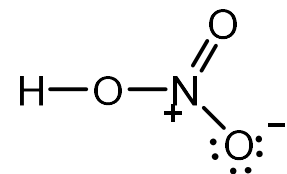
- a) Formaldehyde,  $\text{CH}_2\text{O}$
- b) Tetrafluoroethylene,  $\text{C}_2\text{F}_4$
- c) Acrylonitrile,  $\text{C}_3\text{H}_3\text{N}$ .



## FORMAL CHARGE

Lewis structures frequently contain atoms that bear a positive or negative charge. If the molecule as a whole is neutral, the sum of its positive charges must equal the sum of its negative charges.

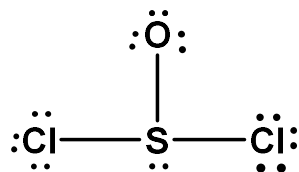
e.g  $\text{HNO}_3$ :



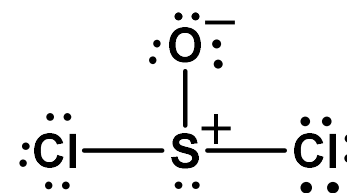
The positive and negative charges on each atom in a compound or an ion are called **formal charges**.

**Formal charge** = **no. of valence  $e^-$**  — **Number of bonds** — **Number of unshared electrons**

e.g thionyl chloride,  $\text{SOCl}_2$ :



	Valence $e^-$	Formal charge
Sulfur	6	$6-3-2= +1$
Oxygen	6	$6-1-6= -1$
Chlorine	7	$7-1-6= 0$



The formal charge in thionyl chloride 17

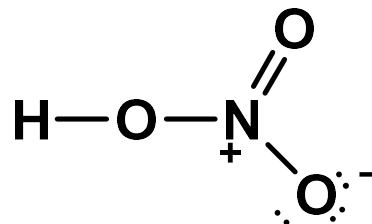
**Example:** Calculate the formal charge on each of the atoms in  $\text{HNO}_3$

Formal charge of N = +1

Formal charge of double bonded O = 0

Formal charge of single bonded O = -1

Formal charge of single bonded O (bonded to H) = 0



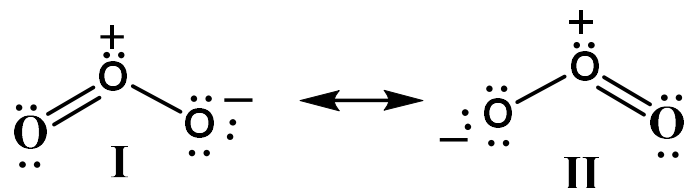
Ex. Calculate the formal charge on atoms in

a)  $\text{POCl}_3$    b)  $\text{H}_2\text{SO}_4$

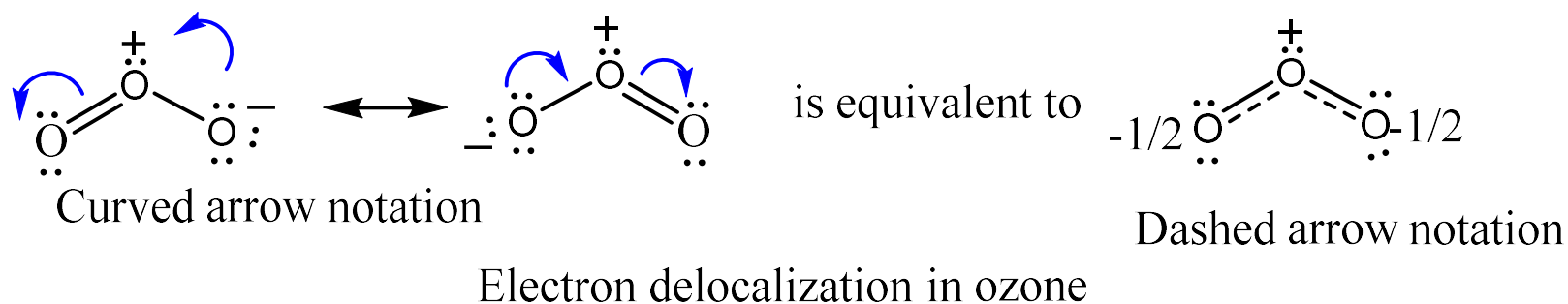
## RESONANCE

**Resonance structures** are sets of Lewis structures that describe the delocalization of electrons in a molecule or a polyatomic ion.

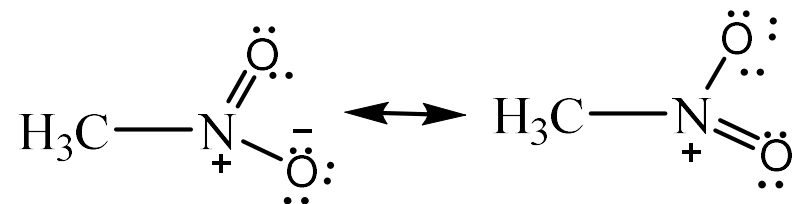
For  $O_3$ , two equivalent Lewis structures may be written



- Structure I and II are resonance structure of ozone.
- We use a double-headed arrow ( $\longleftrightarrow$ ) to represent resonance between these two Lewis structures.
- curved arrows are used to show this electron delocalization

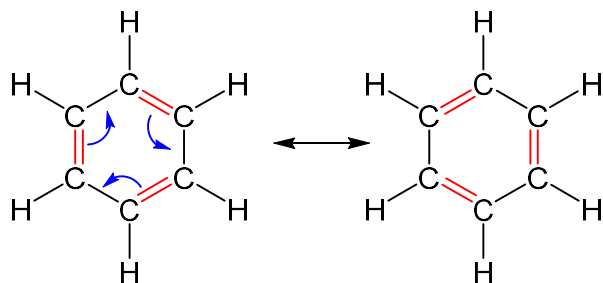


Two resonance structures are possible for  $\text{CH}_3\text{NO}_2$

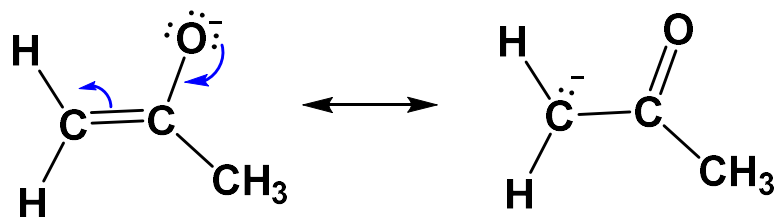


## Rules for resonance

1. Individual resonance forms are imaginary, not real.
2. Resonance forms differ only in the placement of their  $\pi$  or non bonding  $e^-$



3. Different resonance forms of a substance don't have to be equivalent.



4. The resonance hybrid is more stable than any individual resonance forms.

## 1.4 Formula of organic compounds

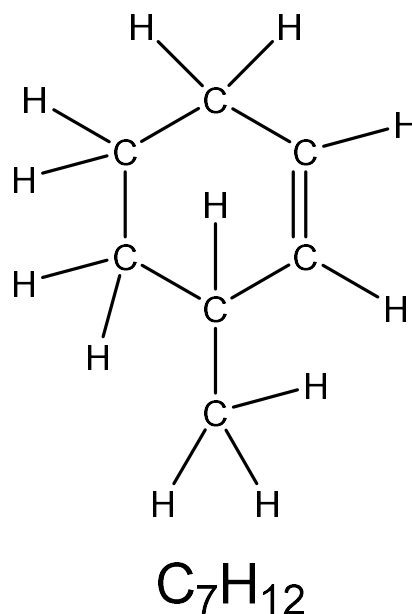
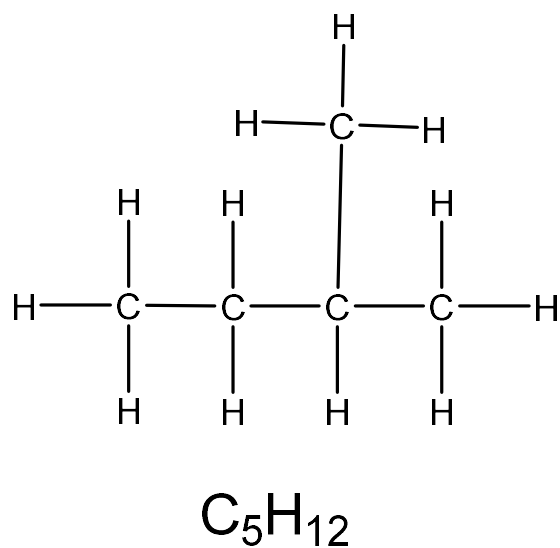
### A) Molecular Formula

This indicates the total number of atoms present a molecule.

Example:  $\text{C}_6\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_{20}\text{H}_{42}$

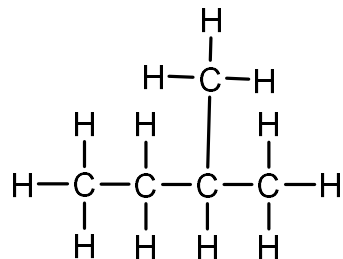
### B) Structural formula

All bonds present in the molecule should be shown.

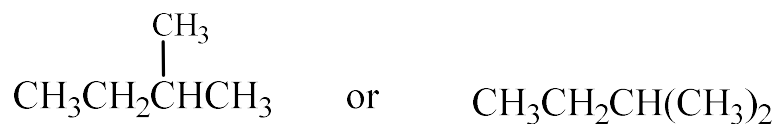


## C) Condensed structural formula

We leave out some, many, or all of the covalent bonds and use sub-scripts to indicate the number of identical groups attached to a particular atom.



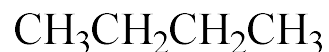
Structural formula



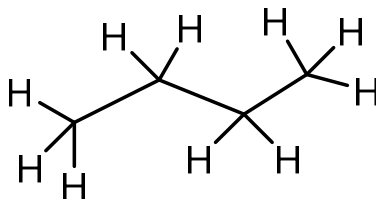
Condensed structural formula

## D) Bond-line formulas or carbon skeletal structure

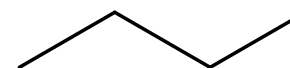
- a carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line.
- The hydrogen atoms are not shown. Since carbon always has a valance of 4, we mentally supply the correct number of hydrogen atoms for each carbon.
- Atoms other than carbon and hydrogen should be written.



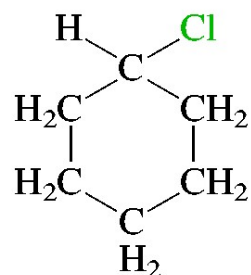
becomes



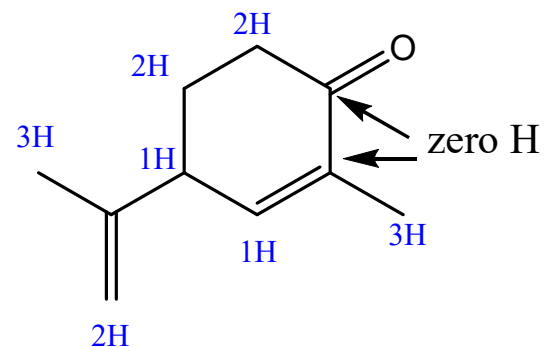
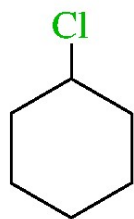
simplified to



Bond line formula

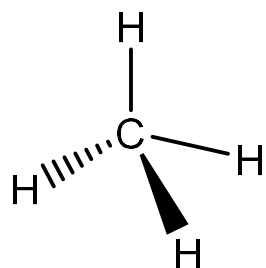



becomes




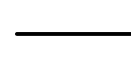
molecular formula,  $\text{C}_{10}\text{H}_{14}\text{O}$

### E) Wedge- line formula (three-dimensional formula)

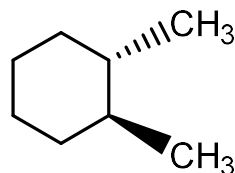
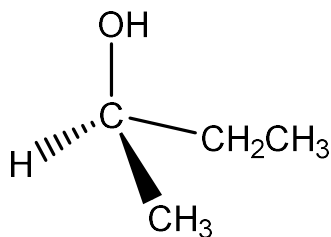


 (wedge): a bond projecting from the plane.

 (dash): a bond projecting in to the plane.

 (line): a bond that lies on the plane.

Is useful to show the stereochemistry of a molecule.

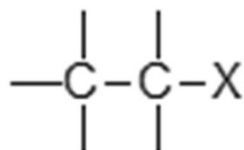


## 1.6 Factors influencing electron availability and reactivity of organic compounds

- Inductive effect
- Resonance effect
- Steric effect

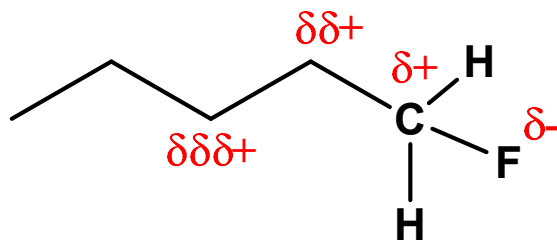
**Inductive Effect-** the shifting of electrons in a  $\sigma$ -bond in response to the electronegativity of a nearby atoms.

F, Cl, Br, I, O, N are more electronegative than carbon, and thus exert electron withdrawing inductive effects.



X = F, Cl, Br, I, O, N


- the carbon where X is attached feels positive. Moreover,
- the electro withdrawing effect of X is also transmitted through the sigma bond and carbon-2 will also be positive even though it is less positive than carbon-1.



Inductive effects rationalize reactivities of organic compounds




## Examples: Inductive Effect And Relative Strength Of Carboxylic acids

	Ka	
$\text{CH}_3-\text{C}(=\text{O})-\text{OH}$	$1.75 \times 10^{-5}$	 acidity
$\text{ClCH}_2-\text{C}(=\text{O})-\text{OH}$	$1.86 \times 10^{-5}$	
$\text{Cl}_2\text{HC}-\text{C}(=\text{O})-\text{OH}$	$5530 \times 10^{-5}$	
$\text{Cl}_3\text{C}-\text{C}(=\text{O})-\text{OH}$	$23,200 \times 10^{-5}$	

- As more chlorine groups which exert electron withdrawing inductive effect exist, the acidity strength increases (bigger Ka Value)

The electron withdrawing inductive effect of groups reduces as the group exists far from the reaction center.

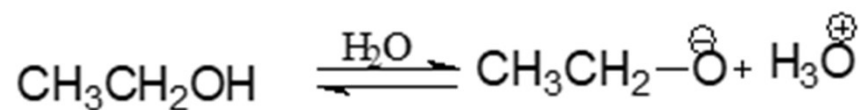
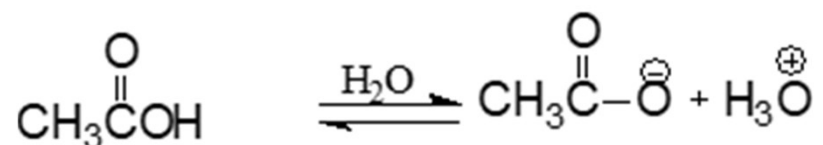
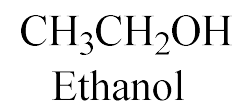
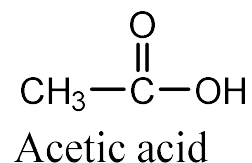
	PKa	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	4.82	 acidity
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$	4.52	
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{COOH} \\   \\ \text{Cl} \end{array}$	4.05	
$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCOOH} \\   \\ \text{Cl} \end{array}$	2.86	

- The last compound is strong acid than the rest of the compounds because chlorine is closest to the reaction center.

## Resonance Effect

- This involves delocalization  $\pi$ (pi) electrons and non-bonded electrons. It also has effects on the reactivity of compounds.
- Charge produced in a reaction can be stabilize by resonance (distributed in a molecule).

E.g acidity of acetic acid and ethanol.



The conjugate base of acetic acid (acetate ion) is resonance stabilized while the conjugate base of ethanol (ethoxide) is not.

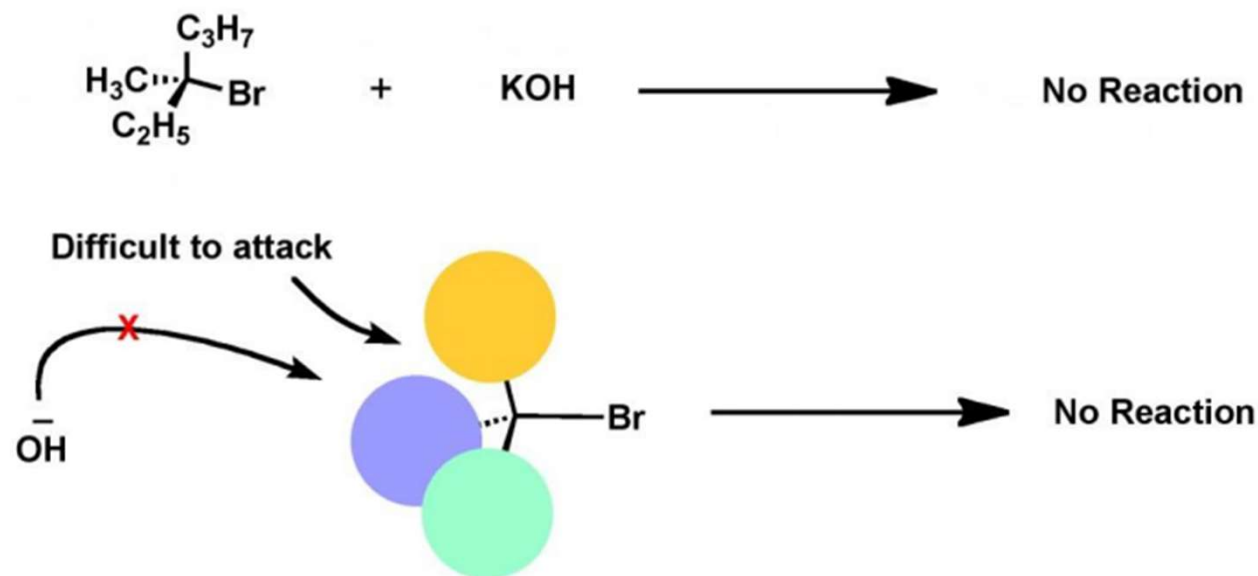


➤ acetic acid is stronger acid than ethanol

## Steric effect

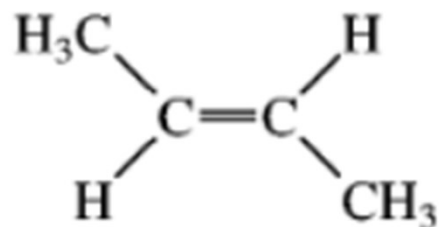
- The word steric is derived from 'stereos' meaning space.
- This effect is manifested when two or more groups or atoms come in close proximity to each other.
- It is the influence of the spatial configuration of reacting substances upon the rate, stability, and extent of reaction.

E.g substitution reaction



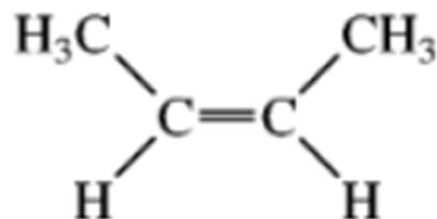
A substitution reaction on a halide by a hydroxide does not work in this case because of steric hindrance.

stability between isomeric alkenes affected by steric effect



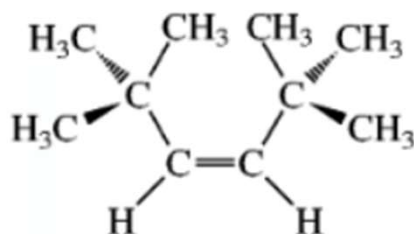
*trans*-2-Butene

more stable



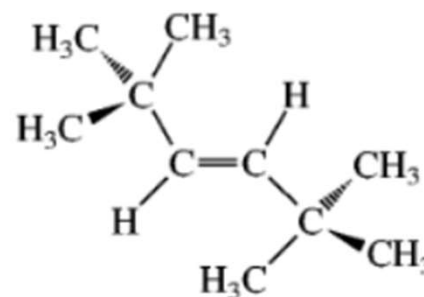
*cis*-2-Butene

less stable



*cis*-2,2,5,5-Tetramethyl-3-hexene  
(less stable)

Energy difference =  
44 kJ/mol  
(10.5 kcal/mol)



*trans*-2,2,5,5-Tetramethyl-3-hexene  
(more stable)