ORGANIC CHEMISTRY

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First Stage
of Biology

Periodic Table of the Elements

1 IA												13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H Hydrogen 1.0079	2 IIA																2 He Helium 4.0026
3 Li Lithium 6.941	4 Be Berylium 9.0122											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22,990	12 Mg Magnesium 24.305	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.409	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xeno 131.29
55 Cs Caesium 132.91	56 Ba Barium 137.33	57 *La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 #Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Uun (281)	111 Uuu (272)	112 Uub (285)		114 Uuq (289)				

Atomic number→ 6
Symbol → C
Name (IUPAC) → Carbon
Atomic mass → 12.011

IUPAC recommendations→
Chemical Abstracts Service group notation →

*Lanthanide Series	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
# Actinide Series	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

INTRODUCATION OF ORGANIC CHEMISTRY;

A part of our lives at every moment. Organic molecules comprise the tissue of plants as mighty as the redwoods, convey signals from one neuron to the next in animals, store the genetic information of life, and are the food we eat each day. The growth of living things from microbes to elephants rests on organic reactions, and organic reactions provide the energy that drives our muscles and our thought processes. Our lives depend on organic chemistry in many other ways as well. Every article of clothing we wear is a product of organic chemistry, whether the fibers are natural or synthetic. Hardly a minute goes by when we're not using something made of organic molecules, such as a pen, a computer keyboard, a music player, or a cellular phone. We view display screens made of organic liquid crystal arrays. Natural organic polymers comprise wood and the paper we read. Natural and synthetic organic molecules enhance our health. There is not a single aspect of our lives that is not in some way dependent on organic chemistry. **But what is organic chemistry?**

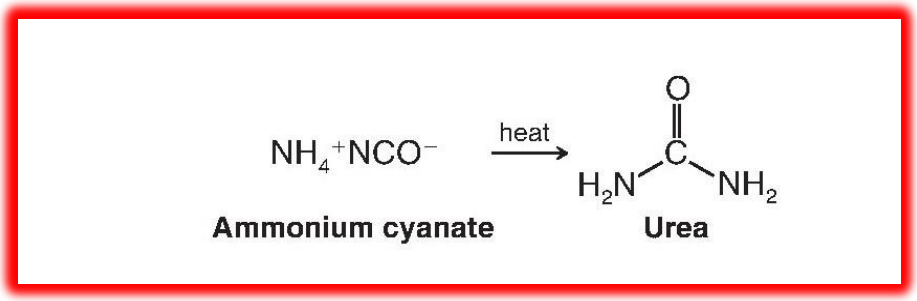
• Organic chemistry is the chemistry of compounds that contain the element carbon.

Clearly, carbon compounds are central to life on this planet. Carbon as an element, however, has its origin elsewhere.

Development of the Science of Organic Chemistry;

The science of organic chemistry began to flower with the demise of a nineteenth century theory called vitalism. According to vitalism, organic compounds were only those that came from living organisms, and only living things could synthesize organic compounds through intervention of a vital force. Inorganic compounds were

considered those compounds that came from nonliving sources. Friedrich Wohler, however, discovered in 1828 that an organic compound called urea (a constituent of urine) could be made by evaporating an aqueous solution of the inorganic compound ammonium cyanate. With this discovery, the synthesis of an organic compound, began the evolution of organic chemistry as a scientific discipline.



Despite the demise of vitalism in science, the word "organic" is still used today by some people to mean "coming from living organisms" as in the terms "organic vitamins" and "organic fertilizers." The commonly used term "organic food" means that the food was grown without the use of synthetic fertilizers and pesticides. An "organic vitamin" means to these people that the vitamin was isolated from a natural source and not synthesized by a chemist. While there are sound arguments to be made against using food contaminated with certain pesticides, while there may be environmental benefits to be obtained from organic farming, and while "natural" vitamins may contain beneficial substances not present in synthetic vitamins, it is impossible to argue that pure "natural" vitamin C, for example, is healthier than pure "synthetic" vitamin C, since the two substances are identical in all respects. In science today, the study of compounds from living organisms is called natural products chemistry.

Today, although many compounds of carbon are still most conveniently isolated from plant and animal sources, most of them are synthesized. They are sometimes synthesized from inorganic substances like carbonates or cyanides, but more often from other organic compounds. There are two large reservoirs of organic material from which simple organic compounds can be obtained ‘. petroleum and coal. (Both of these are "organic" in the old sense, being products of the decay of plants and animals.) These simple compounds are used as building blocks from which larger and more complicated compounds can be made.

Atomic Structure

Before we begin our study of the compounds of carbon we need to review some basic but familiar ideas about the chemical elements and their structure. The compounds we encounter in chemistry are made up of elements combined in different proportions. An abridged periodic table Elements are made up of atoms. An atom (Fig. 1.1) consists of a dense, positively charged nucleus containing protons and neutrons and a surrounding cloud of electrons. Each proton of the nucleus bears one positive charge; electrons bear one negative charge. Neutrons are electrically neutral; they bear no charge. Protons and neutrons have nearly equal masses (approximately 1 atomic mass unit each) and are about 1800 times as heavy as nucleus; the atomic mass contributed by the electrons is negligible. Most of the volume of an atom, however, comes from the electrons; the volume of an atom occupied by the electrons is about 10,000 times larger than that of the nucleus. **The elements commonly found in organic molecules are carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulfur, as well as the halogens: fluorine, chlorine,**

bromine, and iodine. Each element is distinguished by its **atomic number (Z),** a **number equal to the number of protons in its nucleus. Because an atom is electrically neutral, the atomic number also equals the number of electrons surrounding the nucleus.**

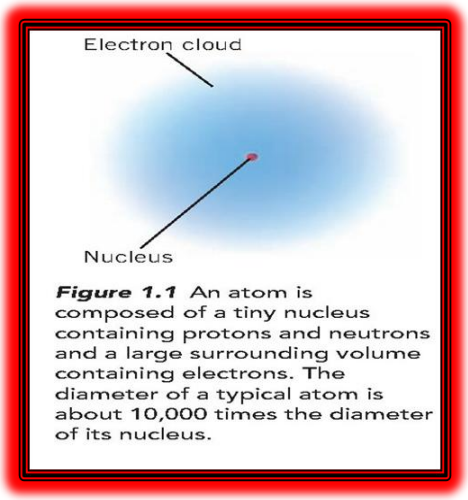
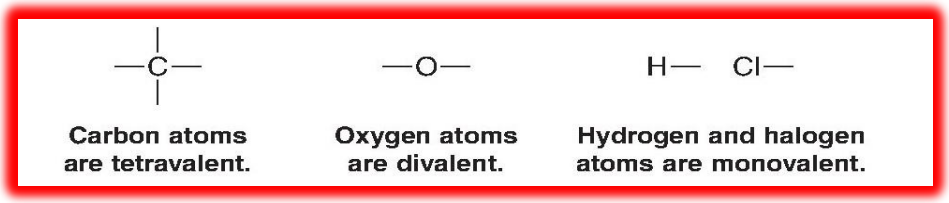


Figure 1.1 An atom is composed of a tiny nucleus containing protons and neutrons and a large surrounding volume containing electrons. The diameter of a typical atom is about 10,000 times the diameter of its nucleus.

The Structural Theory of Organic Chemistry

Between 1858 and 1861, August Kekaula, Archibald Scott Couper, and Alexander M. Butlerov, working independently, laid the basis for one of the most important theories in chemistry: the structural theory. Two central premises are fundamental:

1. The atoms in organic compounds can form a fixed number of bonds using their outermost shell (valence) electrons. Carbon is tetravalent; that is, carbon atoms have four valence electrons and can form four bonds. Oxygen is divalent, and hydrogen and(usually) the halogens are monovalent:



2. A carbon atom can use one or more of its valence electrons to form bonds to other carbon atoms .

Valence Electrons

We discuss the electron configurations of atoms in more detail . For the moment we need only to point out that the electrons that surround the nucleus exist in shell of increasing energy and at increasing distances from the nucleus. The most important shell, called the **valence shell**, is the outermost shell because the electrons of this shell are the ones that an atom uses in making chemical bonds with other atoms to form compounds.

How do we know how many electrons an atom has in its valence shell?

We look at the periodic table. The number of electrons in the valence shell **(called Valence electrons)** is equal to the group number of the atom. For example, carbon is in group IVA and carbon has four valence electrons; oxygen is in group VIA and oxygen has six valence electrons. The halogens of group VIIA all have seven electrons.

Element	*Configuration*	*Valence Electrons*
H	$1S^1$	**1**
He	$1S^2$	**2**
C	$1S^2\ 2S^2\ 2P_X^1\ 2P_y^1$	**4**
N	$1S^2\ 2S^2\ 2P_X^1\ 2P_y^1\ 2P_Z^1$	**5**
O	$1S^2\ 2S^2\ 2P_X^2\ 2P_Y^1 2P_Z^1$	**6**
F	$1S^2\ 2S^2\ 2P_X^2\ 2P_y^2\ 2P_Z^1$	**7**
Ne	$1S^2\ 2S^2\ 2P_X^2\ 2P_y^2\ 2P_Z^2$	**8**

(The electron configuration some atom represented)

Chemical Bonds

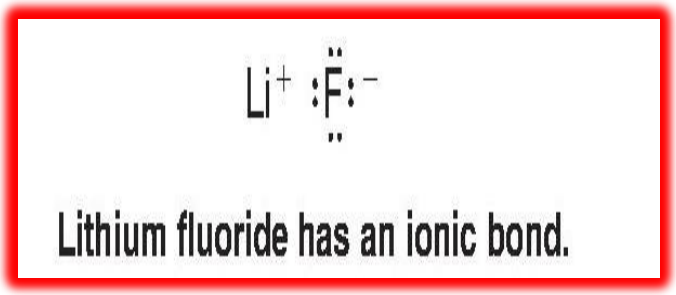
The force of attraction between any two in a compound .Interaction involving valence electrons which are responsible for the chemical bond. Two major types of chemical bonds were proposed:

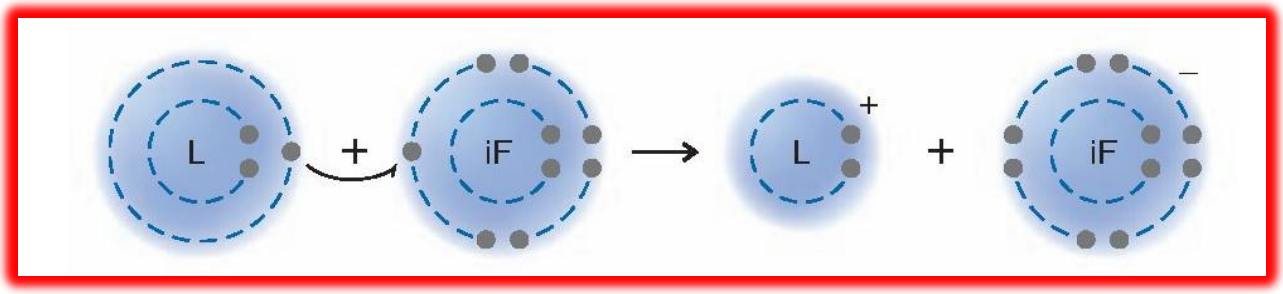
1. Ionic (or electrovalent) bonds are formed by the transfer of one or more electrons from one atom to another to create ions.
2. Covalent bonds result when atoms share electrons.

The central idea in their work on bonding is that atoms without the electronic configuration of a noble gas generally react to produce such a configuration because these configurations are known to be highly stable. For all of the noble gases except helium, this means achieving an octet of electrons in the valence shell.

Ionic Bonds

Atoms may gain or lose electrons and form charged partcles called ions. An ionic bond is an attractive force between oppositely charged ions. One source of such ions is a reaction between atoms of widely differing electronegativities .



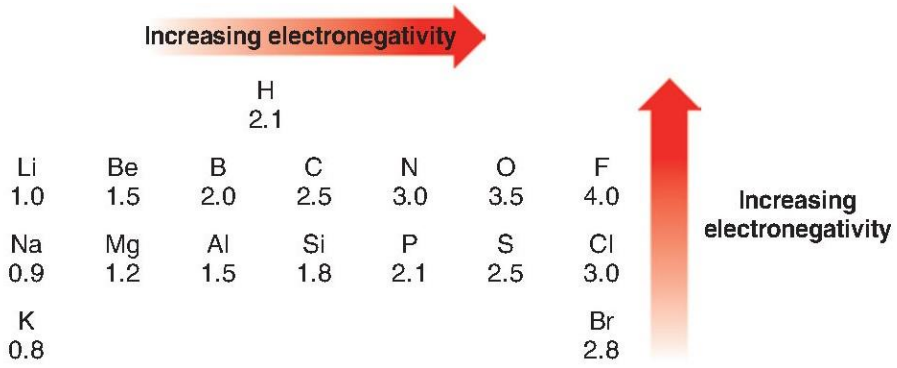


Lithium, a typical metal, has a very low electronegativity; fluorine, a nonmetal, is the most electronegative element of all. The loss of an electron (a negatively charged species)by the lithium atom leaves a lithium cation (Li^+); the gain of an electron by the fluorine atom gives a fluoride anion (F^-).

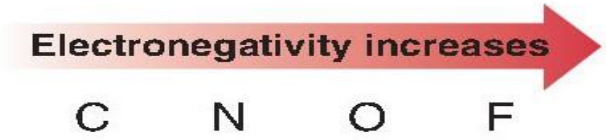
Ions form because atoms can achieve the electronic configuration of a noble gas by gaining or losing electrons. The lithium cation with two electrons in its valence shell is like an atom of the noble gas helium, and the fluoride anion with eight electrons in its valence shell is like an atom of the noble gas neon. Moreover, crystalline lithium fluoride forms from the individual lithium and fluoride ions. In this process negative fluoride ions become surrounded by positive lithium ions, and positive lithium ions by negative fluoride ions. In this crystalline state, the ions have substantially lower energies than the atoms from which they have been formed. Lithium and fluorine are thus "stabilized" when they react to form crystalline lithium fluoride. We represent the formula for lithium fluoride as LiF, because that is the simplest formula for this ionic compound.

Ionic compounds often called salts, form only when atoms of very different electronegativities transfer electrons to become ions.

Electronegativity **is a measure of the ability of an atom to attract electrons**. Electronegativity increases as we go across a horizontal row of the periodic table from left to right and it increases as we go up a vertical column. An example of the formation of an ionic bond is the reaction of lithium and fluorine atoms.



(Electronegativities of Some of the Elements)



How to Write Lewis Structures ;

Several simple rules allow us to draw proper Lewis structures:

1. Lewis structures show the connections between atoms in a molecule or ion using only the valence electrons of the atoms involved. Valence electrons are those of an atom's outermost shell.

2. For main group elements, the number of valence electrons a neutral atom brings to a Lewis structure is the same as its group number in the periodic table. Carbon, for example, is in group IVA and has four valence electrons; the halogens (e.g., fluorine) are in group VIIA and each has seven valence electrons; hydrogen is in group IA and has one valence electron.

3. If the structure we are drawing is a negative ion (an anion), we add one electron for each negative charge to the original count of valence electrons. If the structure is a positive ion (a cation), we subtract one electron for each positive charge.

4. In drawing Lewis structures we try to give each atom the electron configuration of a noble gas. To do so, we draw structures where atoms share electrons to form covalent bonds or transfer electrons to form ions.

a. Hydrogen forms one covalent bond by sharing its electron with an electron of another atom so that it can have two valence electrons, the same number as in the noble gas helium.

b. Carbon forms four covalent bonds by sharing its four valence electrons with four valence electrons from other atoms, so that it can have eight electrons (the same as the electron configuration of neon, satisfying the octet rule).

c. To achieve an octet of valence electrons, elements such as nitrogen, oxygen, and the halogens typically share only some of their valence electrons through covalent bonding, leaving others as unshared electron pairs.

Solved Problem

Write the Lewis structure for ethane (C_2H_6).

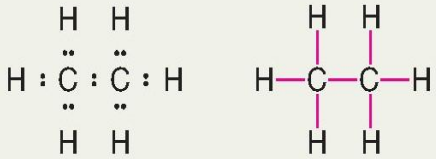
STRATEGY AND ANSWER

1. We find the total number of valence electrons of all the atoms.

$$2(4) + 6(1) = 14$$

2 C 6 H

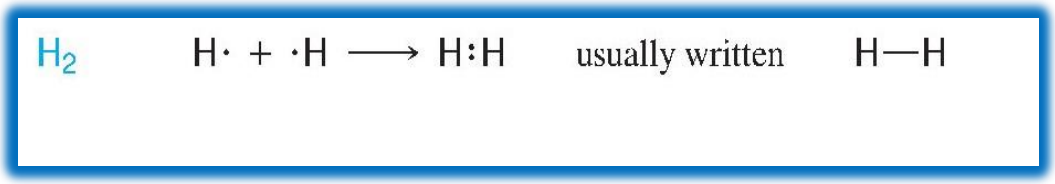
2. We use one pair of electrons to form a single bond between two carbon atoms, and six pairs of electrons to form single bonds from each carbon atom to three hydrogen atoms.



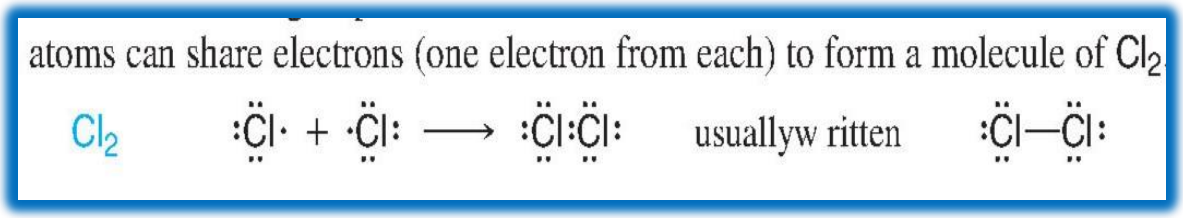
Covalent Bonds

When two or more atoms of the same or similar electronegativities react, a complete transfer of electrons does not occur. In these instances the atoms achieve noble gas configurations by sharing electrons. Covalent bonds form by sharing of electrons between atoms of similar electronegativities to achieve the configuration of a noble gas. Molecules are composed of atoms joined exclusively or predominantly by covalent bonds. Molecules may be represented by electron-dot formulas or, more conveniently, by bond formulas where each pair of electrons shared by two atoms is represented by a line. Some examples are shown here:

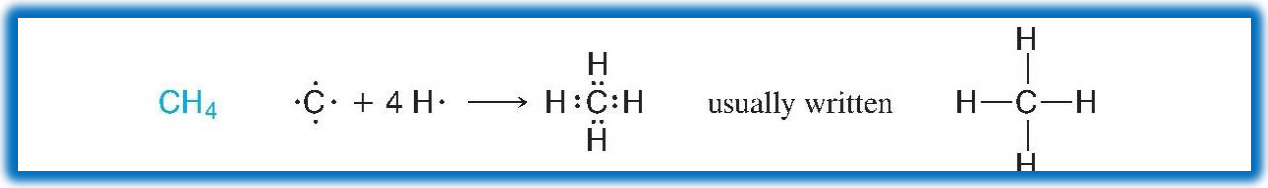
1. Hydrogen, being in group IA of the periodic table, has one valence electron. Two hydrogen atoms share electrons to form a hydrogen molecule, H_2



2. Because chlorine is in group VIIA, its atoms have seven valence electrons. Two chlorine



3. And a carbon atom (group IVA) with four valence electrons can share each of these electrons with four hydrogen atoms to form a molecule of methane, CH_4.

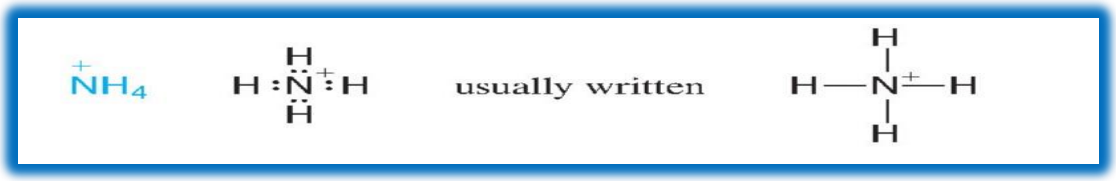


These formulas are often called Lewis structures; in writing them we show only the electrons of the valence shell

4. Atoms can share two or more pairs of electrons to form multiple covalent bonds. For example, two nitrogen atoms possessing five valence electrons each (because nitrogen is in group VA) can share electrons to form a triple bond between them.



5. Ions, themselves, may contain covalent bonds. Consider, as an example, the ammonium ion



Consider the following compounds and decide whether the bond in them would be ionic or covalent.

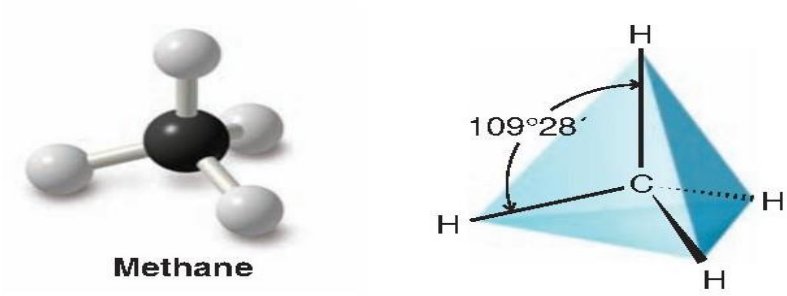


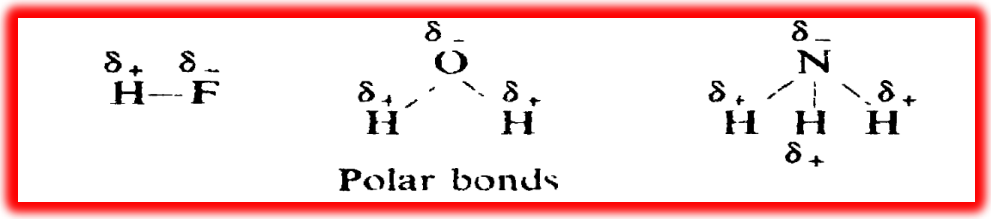
Figure 1.2 The tetrahedral structure of methane

Review Problem

(a) LiH (b) KCl (c) F_2 (d) PH_3

Polarity of bonds

Besides the properties already described^ certain covalent bonds have another property: polarity. Two atoms joined by a covalent bond share electrons; their nuclei are held by the same electron cloud. But in most cases the two nuclei do not share ihe electrons equally; the electron cloud is denser about one atom than the other. One end of the bond is thus relatively negative and the other end is relatively positive; that is, there is a negative pole and a positive pole. Such a bond is said to be a polar bond, or to possess polaritv. We can indicate polarity by using the symbols ∂ + and ∂- , which indicate partial + and - charges. For example:



Polar bonds

We can expect a covalent bond to be polar if it joins atoms that differ in their tendency to attract electrons, that is, atoms that differ in electrogenicity. Furthermore, the greater the difference in electronegativity, the more polar the bond will be.. The most electronegative elements are those located in the upper right-hand corner of the Periodic Table. Of the elements we are likely to encounter in organic chemistry, fluorine has the highest electronegativity, then oxygen, then nitrogen and chlorine, then bromine, and finally carbon. Hydrogen does not differ very much from carbon in electronegativity; it is not certain whether it is more or less electronegative.

$$F > O > Cl, N > Br > C, H$$

Polarity of molecules

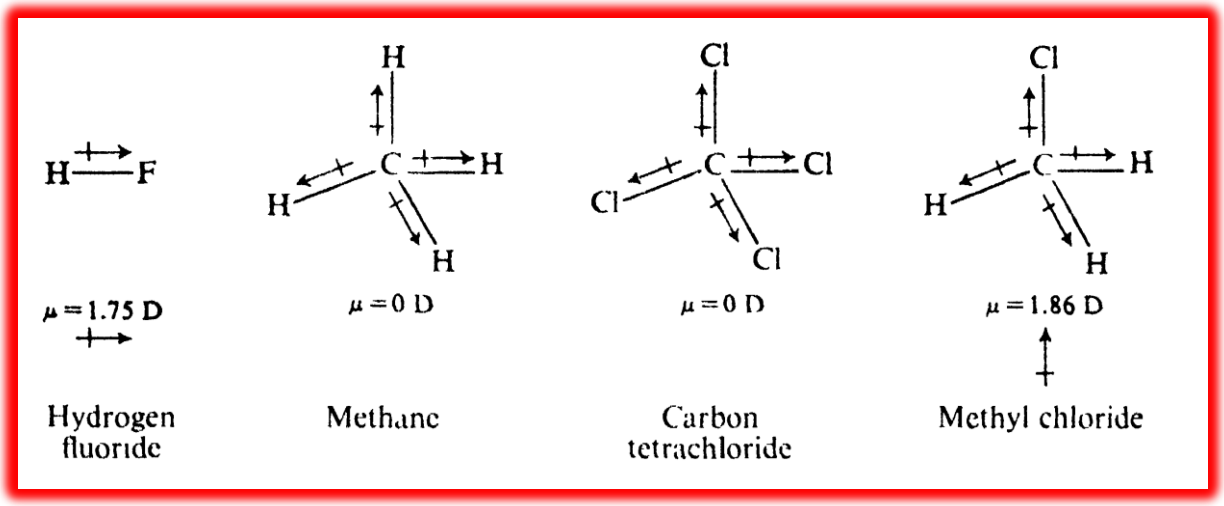
Shall be interested in the values of dipole moments as indications of the relative polarities of different molecules.

H_2	0	HF	1.75	CH_4	0
O_2	0	H_2O	1.84	CH_3Cl	1.86
N_2	0	NH_3	1.46	CCl_4	0
Cl_2	0	NF_3	0.24	CO_2	0
Br_2	0	BF_3	0		

Dipole Moments ,D

It is the fact that some molecules arc polar which has given rise to the speculation that some bonds are polar. We have taken up bond polarity first simply because it is convenient to consider that the polarity of a molecule is a composite of the polarities of the individual bonds Molecules like H_2 , O_2 , N_2 , $C1_2$, and Br_2 have zero dipole moments, that is, are non-polar. The two identical atoms of each of these molecules have, of course, the same electronegativity and share electron^ equally is zero A molecule like hydrogen fluoride has the large dipole moment of 1.75 D. Although hydrogen fluoride is a small molecule, the very high electronegative fluorine pulls the electrons strongly; Methane and carbon tetrachloride, $CC1_4$, have zero dipole moments. We certainly would expect the individual bonds of carbon tetrachloride at least to be nolar; because of the very symmetrical tetrahedral arrangement, however, they exactly cancel each other out . In methyl chloride, CH_3CL, the polarity of the carbon -chlorine bond is not canceled, however, and methyl chloride has a dipole moment of 1.86 r>. Thus the polarity of a molecule depends not only upon the

polarity of its individual bonds but also upon the way the bonds are directed, that is, upon the shape of the molecule.



Dipole moments of some molecules. Polantv of bonds and of molecules.

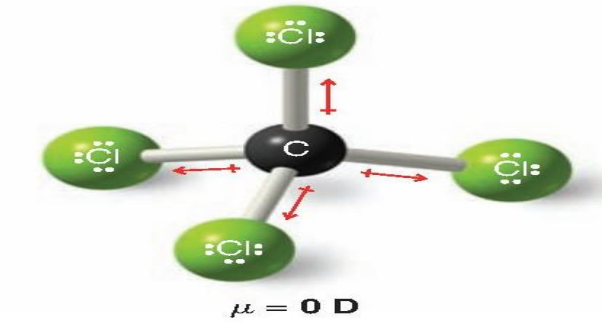
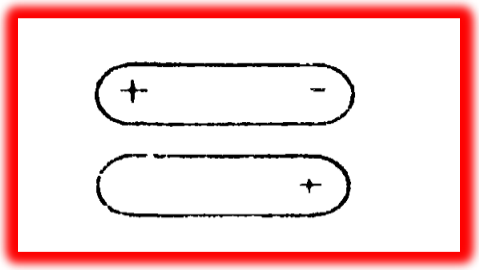


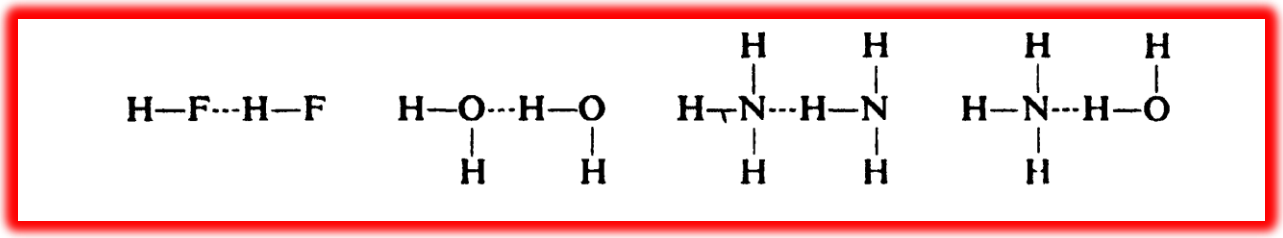
Figure 1.3 A tetrahedral orientation of equal bond moments causes their effects to cancel.

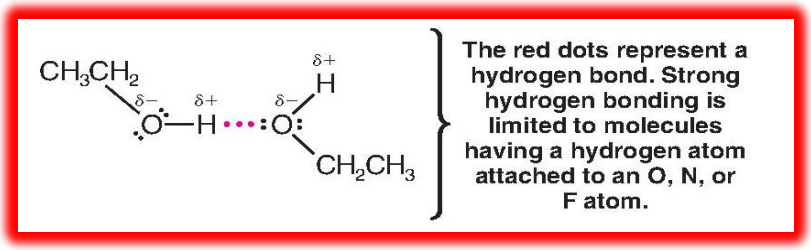
Dipole- dipolc interaction is the attraction of the positive end of one polar molecule for the negative end of another polar molecule. In hydrogen chloride, for example, the relatively positive hydrogen of one molecule is attracted to the relatively negative chlorine of another .

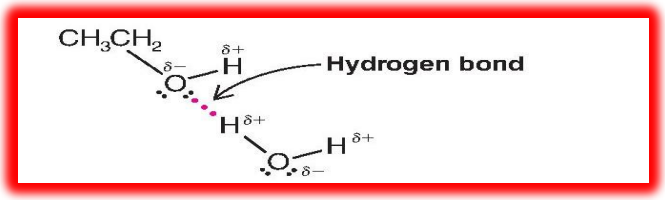


hydrogen bonding;

The strong kind of dipole- dipole attraction in which a hydrogen atom screes as a bridge between two electronegative atoms, holding one by a covalent bond and the other by purely electrostatic forces. When hydrogen is attached to a highly electronegative atom, the electron cloud is greatly distorted toward the electronegative atom, exposing the hydrogen nucleus. The strong positive charge of the thinly shielded hydrogen nucleus is strongly attracted by the negative charge of the' electronegative atom of a second molecule. For hydrogen bonding to be important, both electronegative atoms must come from the group: F, O, N. Only hydrogen bonded to one of these three elements is positive enough, and only these three elements are negative enough, for the necessary attraction to exist. These three elements owe their special effectiveness to the concentrated negative charge on their small atoms.

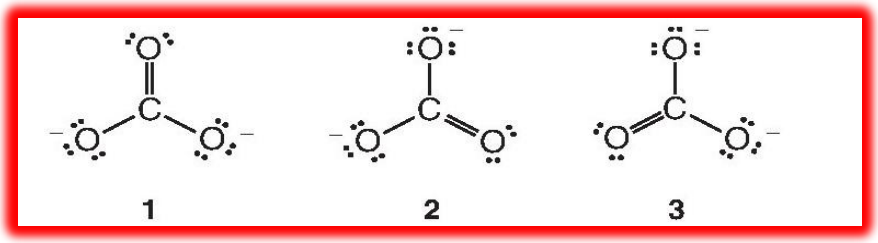




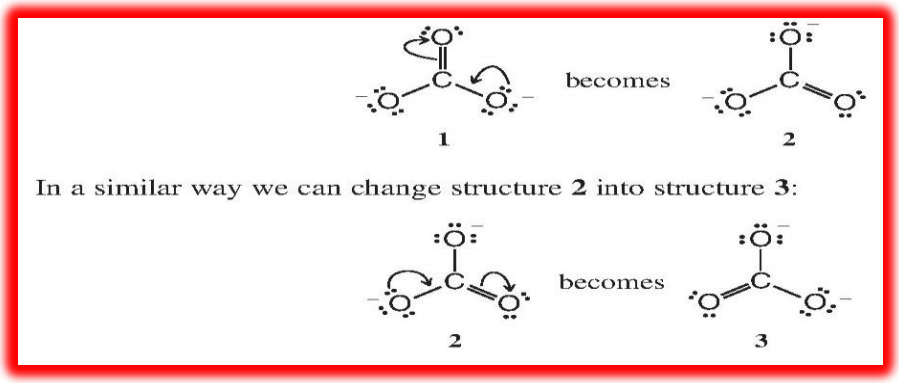


Resonance Theory

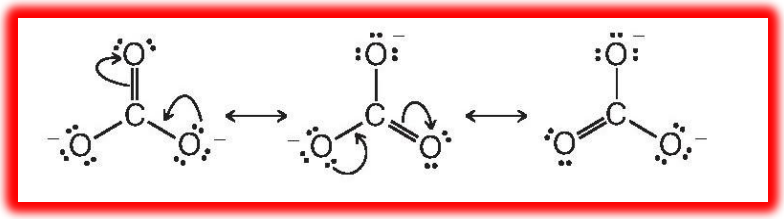
Many times more than one equivalent Lewis structure can be written for a molecule or ion. Consider, for example, the carbonate ion (CO_3^{-2}) We can write three different but equivalent structures .



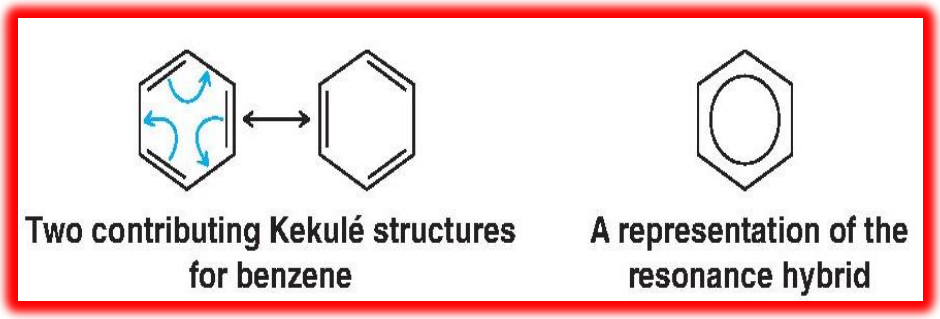
we can convert one structure into any other by changing only the positions of the electrons. We do not need to change the relative positions of the atomic nuclei. For example, if we move the electron pairs in the manner indicated by the **curved arrows** in structure 1, we change structure 1 into structure 2



One other important point: By convention, when we draw resonance structures, we connect them by double-headed arrows (⟷) to indicate clearly that they are hypothetical, not real. For the carbonate ion we write them this way:



The energy of the resonance hybrid is lower than the energy of any contributing structure. Resonance stabilizes a molecule or ion. This is especially true when the resonance structures are equivalent. Chemists call this stabilization resonance stabilization. If the resonance structures are equivalent, then the resonance stabilization is large.



Resonance theory; This theory states that whenever a molecule or ion can be represented by two or more Lewis structures that differ only inthe positions of the electrons, two things will be true. The concept of resonance stabilization is very important in organic chemistry .The hybrid is more stable than any of the individual lewis structures that may be written for it .Double headed arrows are drawn between contributing structures to describe .

Electron Configurations;

The relative energies of atomic orbitals in the first and second principal shells are as follows: ● Electrons in 1s orbitals have the lowest energy because they are closest to th positive nucleus. ● Electrons in 2S orbitals are next lowest in energy. ●Electrons of the three 2P orbitals have equal but higher energy than the 2S orbital. ● Orbitals of equal energy (such as the three 2p orbitals) are called degenerate

orbitals. We can use these relative energies to arrive at the electron configuration of any atom in the first two rows of the periodic table. We need follow only a few simple rules.

1. Aufbau principle: Orbitals are filled so that those of lowest energy are filled first. (Aufbau is German for "building up.)

2. Pauli exclusion principle: A maximum of two electrons may be placed in each orbital but only when the spins of the electrons are paired. An electron spins about its own axis. For reasons that we cannot develop here, an electron is permitted only one or the other of just two possible spin orientations. We usually show these orientations by arrows, either k or j. Thus two spin-paired electrons would be designated il. Unpaired electrons, which are not permitted in the same orbital, are designated kk (or jj).

3. Hund's rule: When we come to orbitals of equal energy (degenerate orbitals) such as the three p orbitals, we add one electron to each with their spins unpaired until each of the degenerate orbitals contains one electron. (This allows the electrons, which repel each other, to be farther apart.) Then we begin adding a second electron to each degenerate orbital so that the spins are paired. If we apply these rules to some of the second-row elements of the periodic table, we get the results shown in Fig. 1.4).

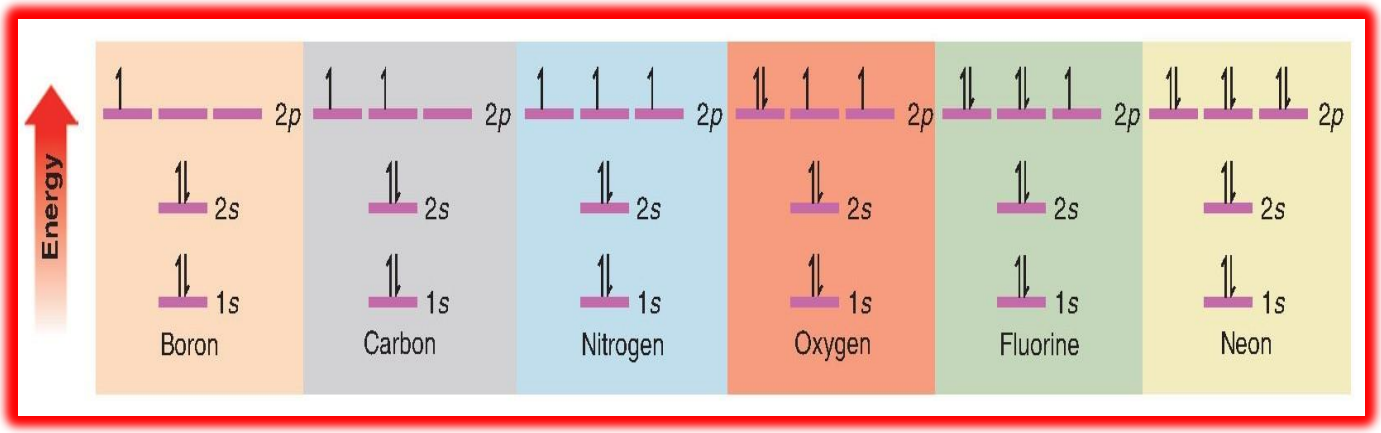


Figure 1.4 The ground state electron configurations of some second-row elements.

Hybridization

The concept of mixing atomic orbitals (with different energies , shapes) etc, and overlap to form anew hybrid orbitals with equal energies, suitable for the pairing of electrons to form **chemical bonds** in valence **bond** theory.

TYPE OF HYBRIDIZATION

SP^3 Hybridization

1 S orbital + 3P orbital ⟶ 4 SP^3 orbitals

The S and P orbitals used in the quantum mechanical description of the carbon atom, were based on calculations for hydrogen atoms. These simple s and p orbitals do not, when taken alone, provide a satisfactory model for the tetravalent– tetrahedral carbon of methane (CH_4). However, a satisfactory model of methane's structure that is based on quantum mechanics can be obtained through an approach called **orbital hybridization**. Orbital hybridization, in its simplest terms,

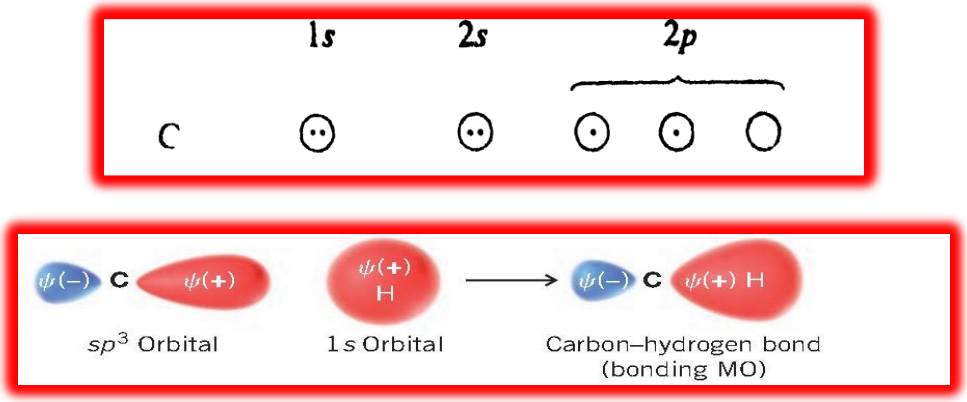
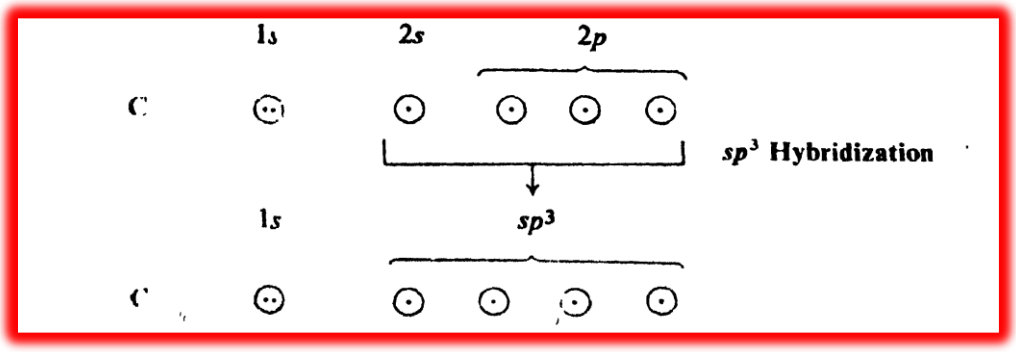
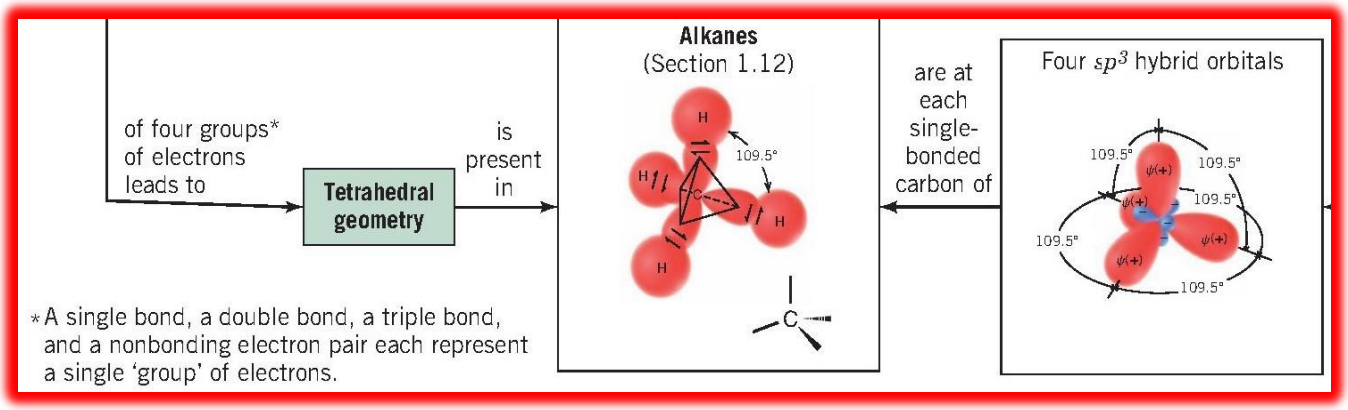


Figure 1.5 Formation of a C- H bond.

A highly reactive molecule whose properties center about the need to provide carbon with two more bonds.) Again, we see the tendency to form as many bonds as possible: in this case, to combine with four hydrogen atoms. To provide; four unpaired electrons, we promote one of the 2S electrons to the empty P orbital : Once more the most strongly directed orbitals are hybrid orbitals: this time, SP^3 orbilals, from the mixing of one S orbital and three Porbitals. Each one has the



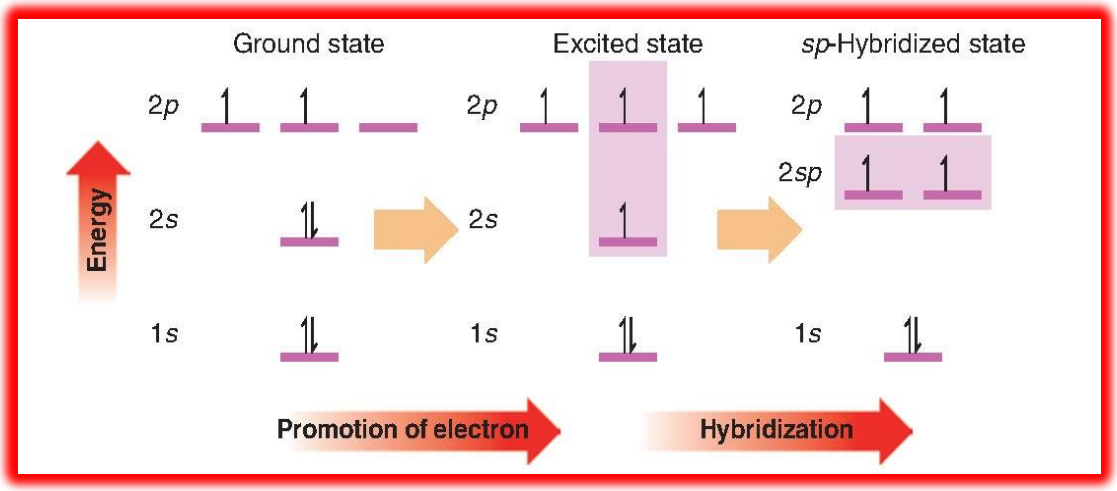
Hybridizing three P orbitals with one S orbital yields four SP^3 orbitals. Atoms that are Sp^3 hybridized direct the axes of their four Sp^3 orbitals toward the corners of a tetrahedron. The carbon of methane is SP^3 hybridized and tetrahedral.



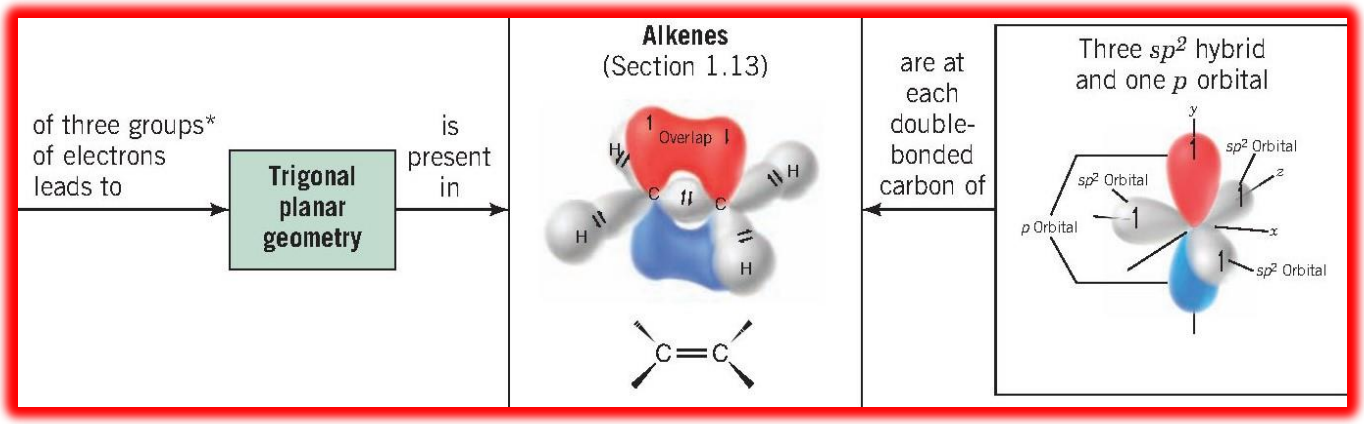
SP^2 Hybridization

1 S orbital + 2 P orbital ⟶ $3SP^2$ orbitals and 1 P orbital left over

Hybridizing two p orbitals with one s orbital yields three Sp^2 orbitals. Atoms that are Sp^2 hybridized point the axes of their three Sp^2 orbitals toward the corners of an equilateral triangle. The carbon atoms of ethene are Sp^2 hybridized and trigonal planar.

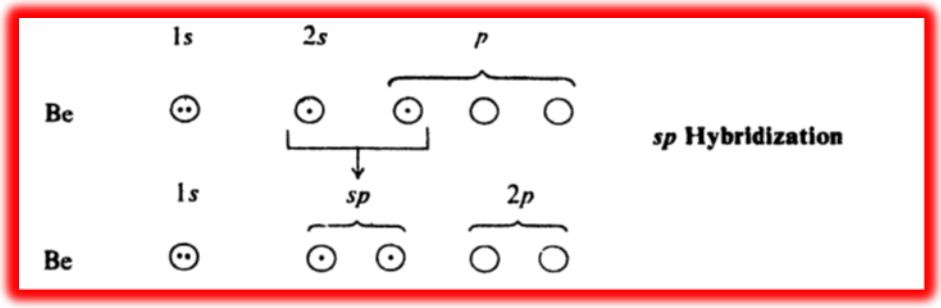


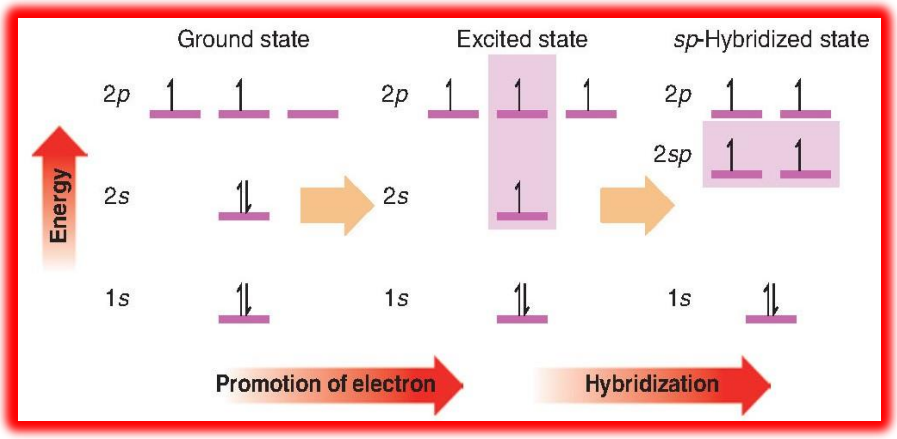
The mathematical mixing of orbitals that furnish the Sp^2 orbitals for our model can be visualized in the way. The 2S orbital is mathematically mixed (or hybridized) with two of the 2p orbitals. (The hybridization procedure applies only to the orbitals, not to the electrons.) One 2P orbital is left unhybridized. One electron is then placed in each of the sp^2 hybrid orbitals and one electron remains in the 2P orbital. The three SP^2 orbitals that result from hybridization are directed toward the corners of a regular triangle (with angles of 120° between them). The carbon p orbital that is not hybridized is perpendicular to the plane of the triangle formed by the hybrid SP^2 orbitals

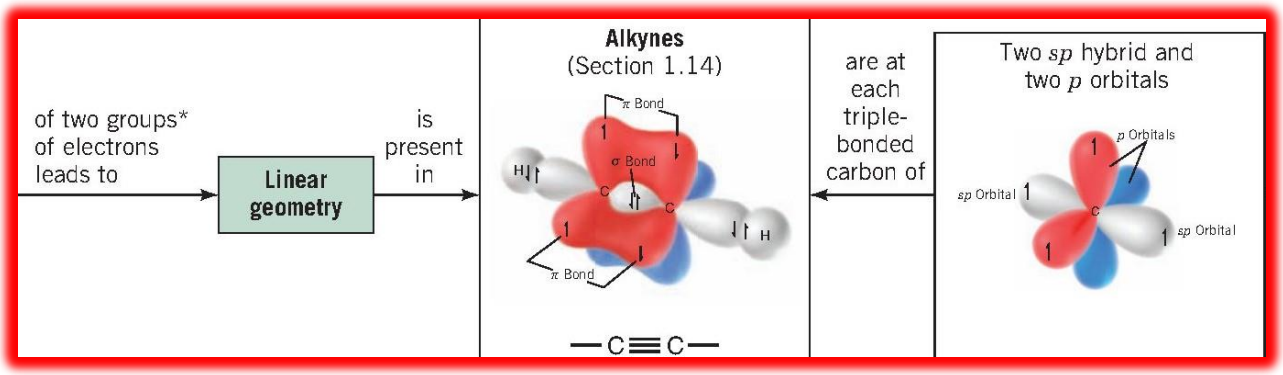


SP Hybridization

Another type of bond that carbon forms with it selfe is the triple bond found in a class of compounds called alkynes . Hybridizing one p orbital with one S orbital yields two SP orbitals. Atoms that are sp hybridized orient the axes of their two sp orbitals in opposite directions (at an angle of 180°). The carbon atoms of ethyne are SP hybridized and ethyne is a linear molecule.







Bond Lengths of Ethyne, Ethene, and Ethane

The carbon–carbon triple bond of ethyne is shorter than the carbon–carbon double bond of ethene, which in turn is shorter than the carbon–carbon single bond of ethane. The reason is that bond lengths are affected by the hybridization states of the carbon atoms involved.

1-The greater the S orbital character in one or both atoms, the shorter is the bond. This is because S orbitals are spherical and have more electron density closer to the nucleus than do P orbitals.

2- The greater the P orbital character in one or both atoms, the longer is the bond. This is because P orbitals are lobe-shaped with electron density extending away from the nucleus. In terms of hybrid orbitals, an sp hybrid orbital has 50% s character and 50% P character. An Sp^2 hybrid orbital has 33% s character and 67% P character. An SP^3 hybrid orbital has 25% s character and 75% P character. The overall trend, therefore, is as follows:

3- Bonds involving SP hybrids are shorter than those involving SP^2 hybrids, which are shorter than those involving SP^3 hybrids. This trend holds true for both C- C and C – H bonds.

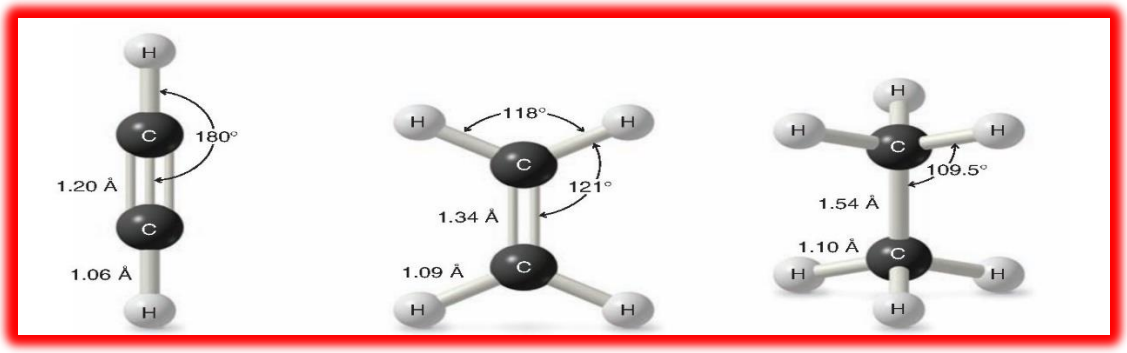


Figure 1.6 Bond angles and bond lengths of ethyne, ethene, and ethane.

Homolysis and Heterolysis of Covalent Bonds

Reactions of organic compounds always involve the making and breaking of covalent bonds. A covalent bond may break in two fundamentally different ways;

1- **Homolysis** When a bond breaks so that each fragment takes away one of the electrons of the bond, this process is called homolysis (Greek: homo, the same, +lysis). Homolysis produces fragments with unpaired electrons called radicals



2- **Heterolysis** When a bond breaks such that one fragment takes away both electrons of the bond, leaving the other fragment with an empty orbital, this kind of cleavage is called heterolysis (Greek: hetero, different, + lysis, loosening or cleavage). Heterolysis produces charged fragments or ions and is termed an ionic reaction. The broke bond is said to have cleaved heterolytically:

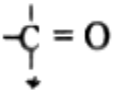
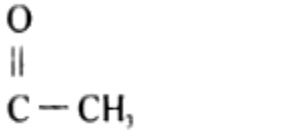


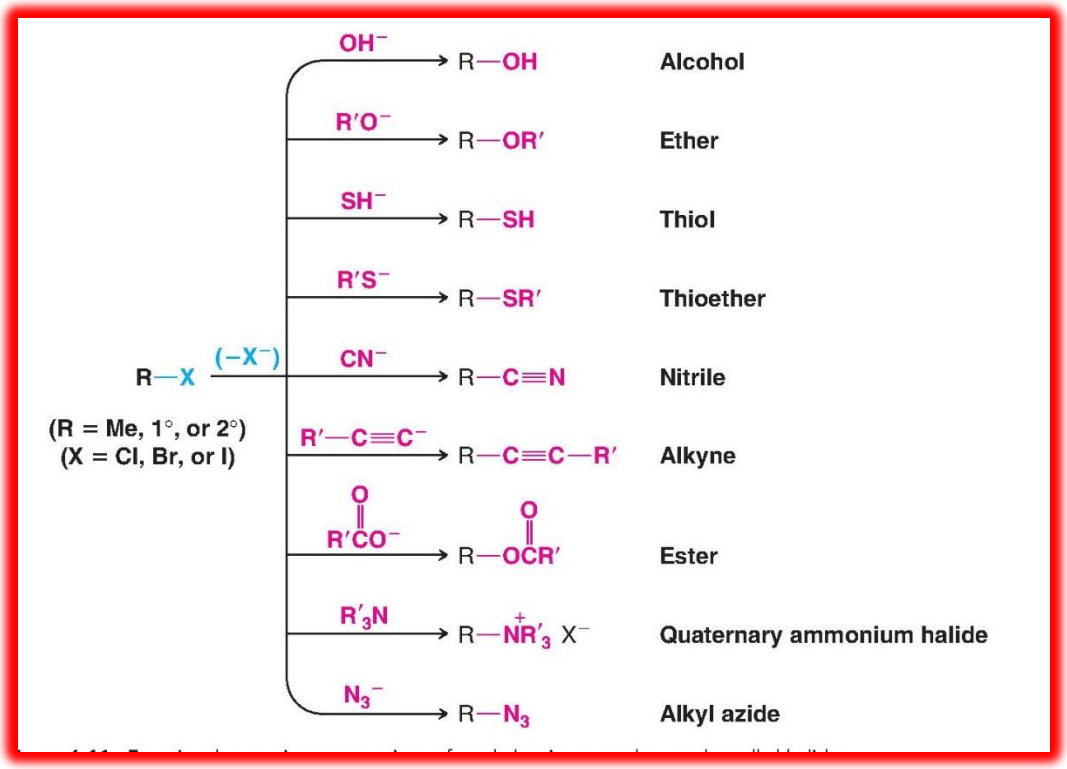
We have seen that energy is liberated when atoms combine to form a molecule. For a molecule to break into atoms, an equivalent amount of energy must be consumed. The amount of energy consumed or liberated when a bond is broken or formed is known as the bond dissociation energy, D. It is characteristic of the particular bond: Table 1 .2 lists bond dissociation energies that have been measured for a number of bonds. As can be seen, they vary widely, from weak bonds like(36 kcal/mole) to

very strong bonds like H F (136 kcal/mole). Although the accepted values may change as experimental methods improve, certain trends are clear. We must not confuse bond dissociation energy (D) with another measure of bond strength called bond energy (E). If one begins with methane, for example, and breaks, successively, four carbon-hydrogen bonds, one finds four different bond dissociation energies.

Functional Groups

Afunctional group This is atom or group of atoms that defines the structure of a particular family of organic compounds and at the same time determines their properties.;

Functional group	Name	Example
	C – C double bond	$H_2C = CH_2$ (Ethene or ethylene)
–C≡C–	C – triple bond	HC ≡ CH (Ethyne or acetylene)
–OH	Alcoholic	$H_3C - OH$ (Methanol or methylalcohol)
–CHO	Aldehyde	H – CHO (Methanal or formaldehyde)
–F	Fluoride	$H_3C - F$ (Fluoromethane or methyl flouride)
–Cl	Chloride	$H_3C - Cl$ (Chloromethane or methyl chloride)
–Br	Bromide	$H_3C - I$ (Iodomethane or methyl iodide)
	Ketone	 (Propanone or acetone)

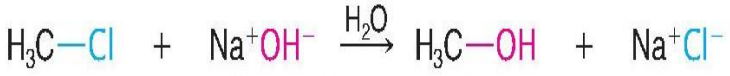


Organic Reactions

One of our goals in this course will be, in fact, to try to understand how this chemical magic takes place. We will want to be able to explain how the products of the reaction are formed. This explanation will take the form of a **reaction mechanism**—a description of the events that take place on a molecular level as reactants become products. If, as is often the case, the reaction takes place in more than one step, we will want to know what chemical species, called **intermediates**, intervene between each step along the way.

Virtually all organic reactions fall into one of four categories: **substitutions**, **additions, eliminations, or rearrangements.**

1-Substitutions reaction ; are the characteristic reactions of saturated compounds such as alkanes and alkyl halides and of aromatic compounds (even though they are unsaturated). In a substitution, one group replaces another. For example, chloromethane reacts with sodium hydroxide to produce methyl alcohol and sodium chloride:



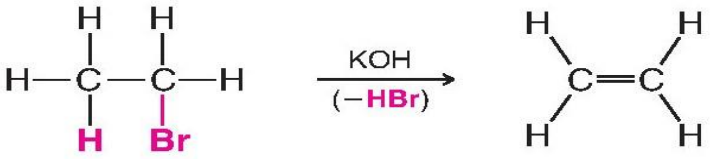
A substitution reaction

2-Additions reaction ; are characteristic of compounds with multiple bonds. Ethene, for example, reacts with bromine by an addition. In an addition all parts of the adding reagent appear in the product; two molecules become one:



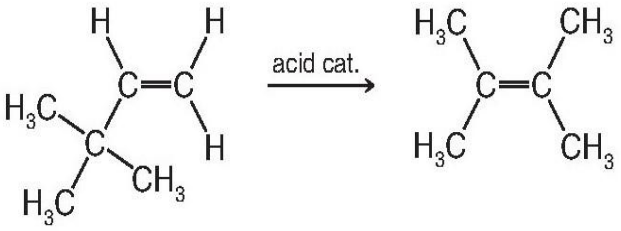
An addition reaction

3-Eliminations reaction ; are the opposite of additions. In an elimination one molecule loses the elements of another small molecule. Elimination reactions give us a method for preparing compounds with double and triple bonds.



An elimination reaction

4- Rearrangement reaction ; a molecule undergoes a reorganization of its constituent parts. For example, heating the following alkene with a strong acid causes the formation of another isomeric alkene:

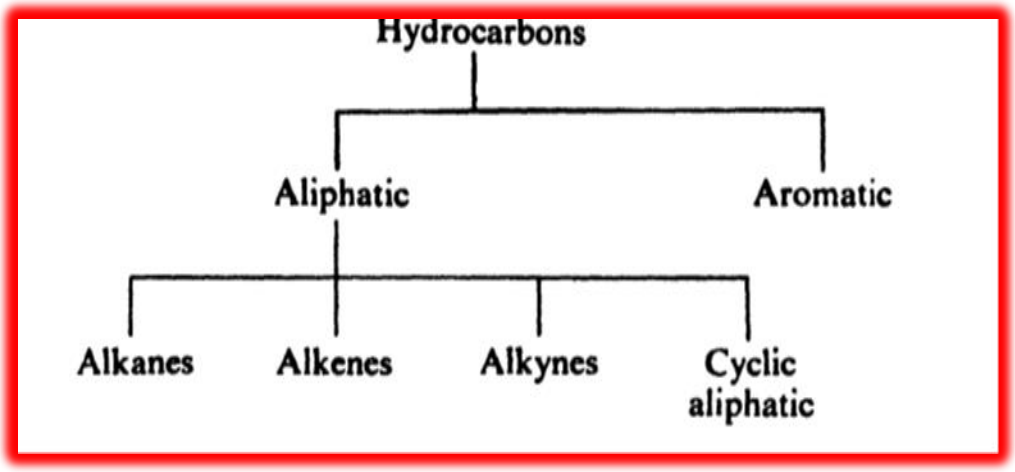


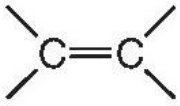
A rearrangement

In this rearrangement not only have the positions of the double bond and a hydrogen atom changed, but a methyl group has moved from one carbon to another.

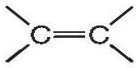
Hydrocarbons

Certain organic compounds contain only two elements, hydrogen and carbon and hence are known **as hydrocarbons**. On the basis of structure, hydrocarbons are divided into two main classes, **aliphatic** and **aromatic**. **Aliphatic hydrocarbons** are further divided into families: alkanes, alkenes, alkynes, and their cyclic ana-logs (cycloalkanes, etc.). We shall take up these families in the order given.



Alkane	Alkene	Alkyne
C—H and C—C bonds		

The simplest member of the alkane family and, indeed, one of the simplest of all organic compounds is methane, **CH_4** Alkane's have the general molecular **CnH2n+2** ,We can determine the number of hydrogen in the molecule and its molecular formula. For example, Decane ,with ten carbon atoms, must have ? Hydrogen atoms, and a molecular formula of ? We shall study this single compound at some length, since most of what we learn about it can be carried over with minor modifications to any alkane. Hydrocarbons are compounds that contain only carbon and hydrogen atoms. (CH_4) methane and ethane (C_2H_6) are hydrocarbons, for example. They also belong to a subgroup of compounds called alkanes. Alkanes are hydrocarbons that do not have multiple bonds between carbon atoms, and we can indicate this in the family name and in names for specific compounds by the -ane ending.

	Alkane	Alkene	Alkyne	Aromatic
Functional group	C—H and C—C bonds		—C≡C—	Aromatic ring
General formula	RH	$RCH{=}CH_2$ RCH=CHR $R_2C{=}CHR$ $R_2C{=}CR_2$	RC≡CH RC≡CR	ArH
Specific example	CH_3CH_3	$CH_2{=}CH_2$	HC≡CH	
IUPAC name	Ethane	Ethene	Ethyne	Benzene
Common name[a]	Ethane	Ethylene	Acetylene	Benzene

Nomenclature of Alkanes and the IUPAC System

The **IUPAC** system for naming alkanes is not difficult to learn, and the principles involved are used in naming compounds in other families as well. For these reasons we begin our study of the **IUPAC** system with the rules for naming alkanes and then study the rules for alkyl halides and alcohols. The names for several of the unbranched alkanes are listed in Table 4.3. The ending for all of the names of alkanes is -ane. The stems of the names of most of the alkanes (above C_4) are of Greek and Latin origin. Learning the stems is like learning to count in organic chemistry. Thus, one, two, three, four, and five become meth-, eth-, prop-, but-, and pentan .

Name	Number of Carbon Atoms	Structure	Name	Number of Carbon Atoms	Structure
Methane	1	CH_4	Undecane	11	$CH_3(CH_2)_9CH_3$
Ethane	2	CH_3CH_3	Dodecane	12	$CH_3(CH_2)_{10}CH_3$
Propane	3	$CH_3CH_2CH_3$	Tridecane	13	$CH_3(CH_2)_{11}CH_3$
Butane	4	$CH_3(CH_2)_2CH_3$	Tetradecane	14	$CH_3(CH_2)_{12}CH_3$
Pentane	5	$CH_3(CH_2)_3CH_3$	Pentadecane	15	$CH_3(CH_2)_{13}CH_3$
Hexane	6	$CH_3(CH_2)_4CH_3$	Hexadecane	16	$CH_3(CH_2)_{14}CH_3$
Heptane	7	$CH_3(CH_2)_5CH_3$	Heptadecane	17	$CH_3(CH_2)_{15}CH_3$
Octane	8	$CH_3(CH_2)_6CH_3$	Octadecane	18	$CH_3(CH_2)_{16}CH_3$
Nonane	9	$CH_3(CH_2)_7CH_3$	Nonadecane	19	$CH_3(CH_2)_{17}CH_3$
Decane	10	$CH_3(CH_2)_8CH_3$	Eicosane	20	$CH_3(CH_2)_{18}CH_3$

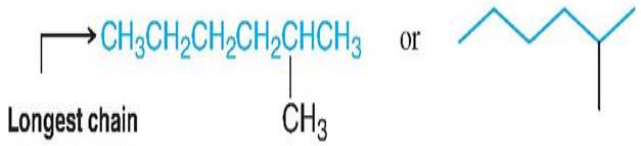
The Unbranched Alkanes

Nomenclature of Branched-Chain Alkanes

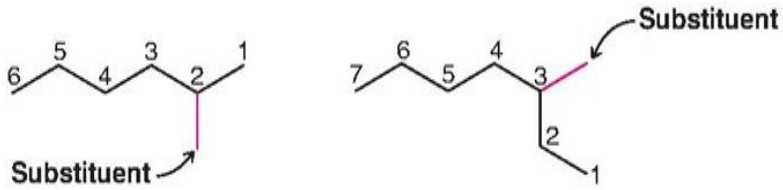
Branched-chain alkanes are named according to the following rules:

1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkane. We designate the following compound, for example, as a hexane beca

use the longest continuous chain contains six carbon atoms:



2. Number the longest chain beginning with the end of the chain nearer the substituent. Applying this rule, we number the two alkanes that we illustrated previously in the following way:



3. Use the numbers obtained by application of rule 2 to designate the location of the substituent group. The parent name is placed last, and the substituent group, preceded by the number designating its location on the chain, is placed first. Numbers are separated from words by a hyphen. Our two examples are 2-methylhexane and 3-methylheptane, respectively:



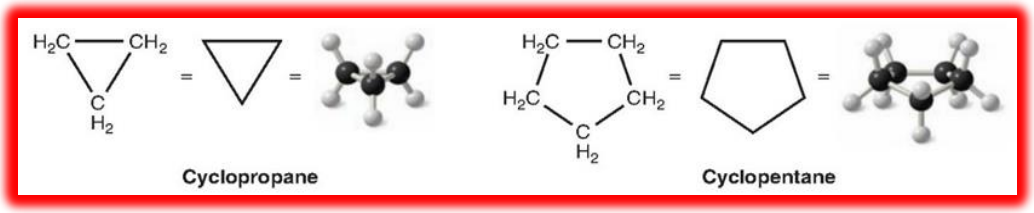
Nomenclature of Unbranched Alkyl Groups

If we remove one hydrogen atom from an alkane, we obtain what is called an alkyl group. These alkyl groups have names that end in (-yl) . When the alkane is unbranched, and the hydrogen atom that is removed is a terminal hydrogen atom, the names are straight forward:

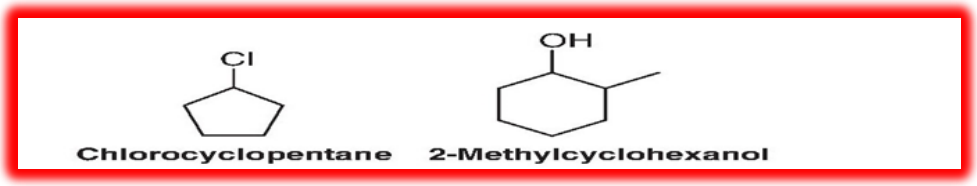
$CH_3—H$	$CH_3CH_2—H$	$CH_3CH_2CH_2—H$	$CH_3CH_2CH_2CH_2—H$
Methane	Ethane	Propane	Butane
$CH_3—$	$CH_3CH_2—$	$CH_3CH_2CH_2—$	$CH_3CH_2CH_2CH_2—$
Methyl	Ethyl	Propyl	Butyl

How to Name Cycloalkanes

Cycloalkanes with only one ring are named by attaching the prefix cyclo- to the names of the alkanes possessing the same number of carbon atoms. For example,

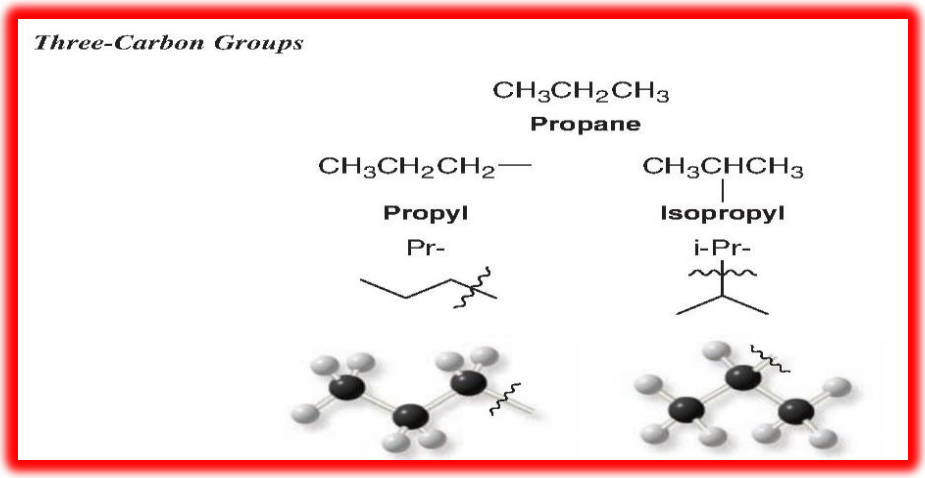


Naming substituted cycloalkanes is straightforward: We name them as alkyl cycloalkanes, halo cycloalkanes, alkyl cycloalkanols, and so on. If only one substituent is present, it is not necessary to designate its position. When two substituents are present, we number the ring beginning with the substituent first in the alphabet and number in the direction that gives the next substituent the lower number possible. When three or more substituents are present, we begin at the substituent that leads to the lowest set of locants:

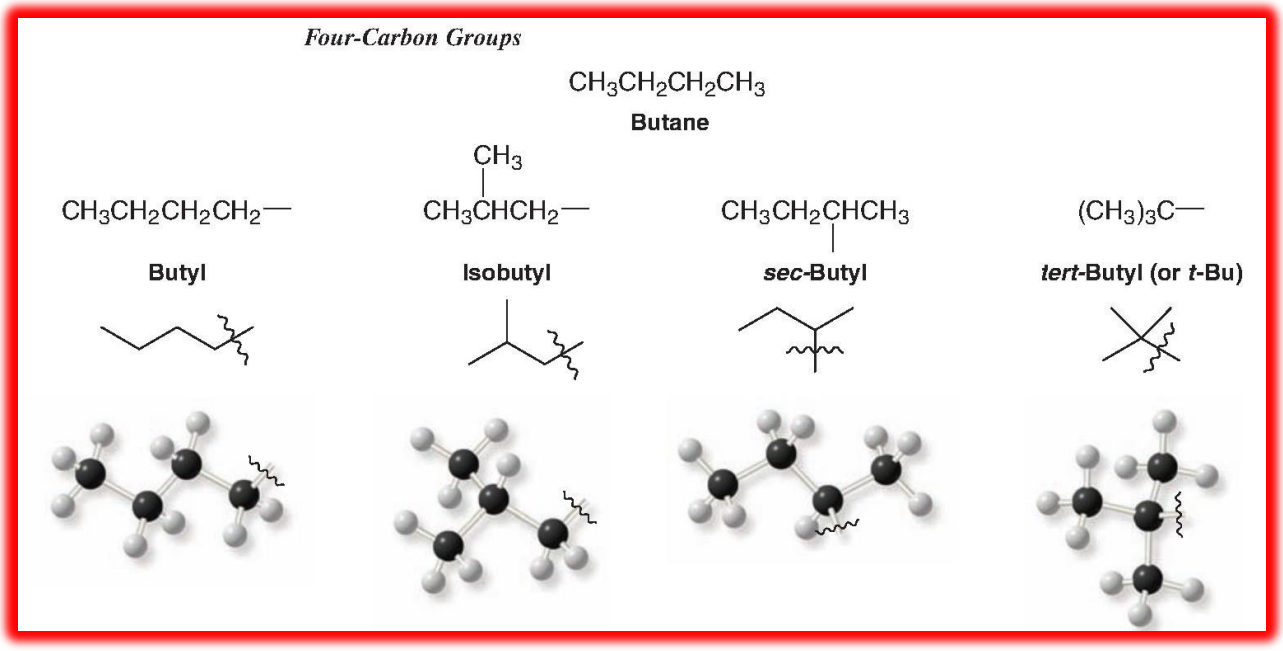


Nomenclature of Branched Alkyl Groups

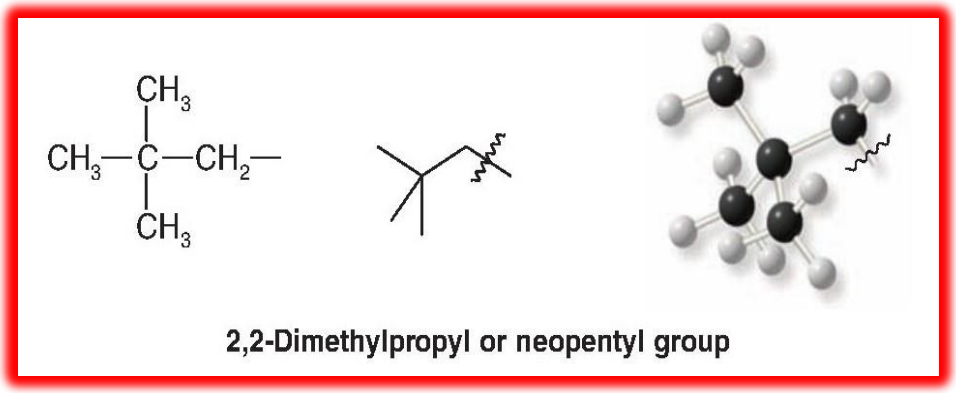
Such as methyl, you learned the names for the unbranched alkyl groups ethyl, propyl, and butyl, groups derived by removing a terminal hydrogen from an alkane. For alkanes with more than two carbon atoms, more than one derived group is possible. Two groups can be derived from propane, for example; the propyl group is derived by removal of a terminal hydrogen, and the 1-methylethyl or isopropyl group is derived by removal of a hydrogen from the central carbon:



1-Methylethyl is the systematic name for this group; isopropyl is a common name. Systematic nomenclature for alkyl groups is similar to that for branched-chain alkanes, with the provision that numbering always begins at the point where the group is attached to the main chain. There are four C4 groups.



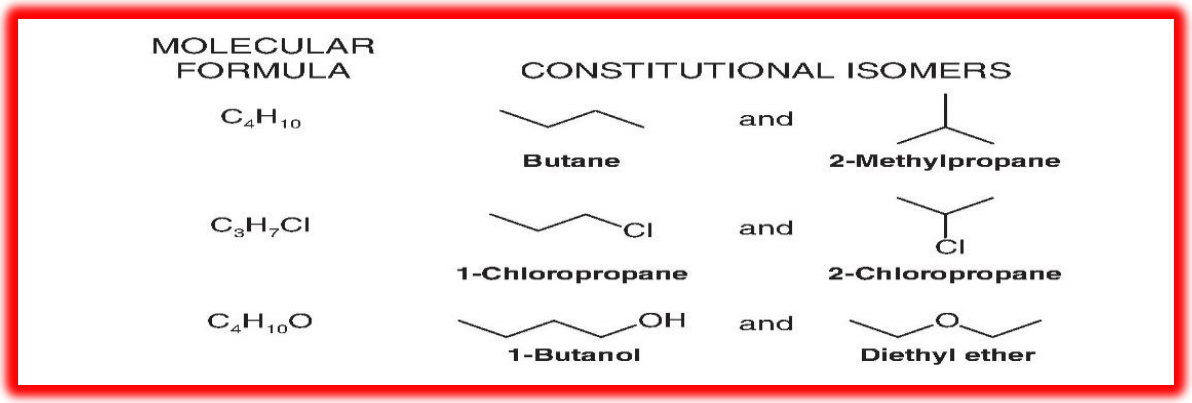
The common names isopropyl, isobutyl, sec-butyl, and tert-butyl are approved by the **IUPAC** for the unsubstituted groups, and they are still very frequently used. You should learn these groups so well that you can recognize them any way that they are written. In deciding on alphabetical order for these groups you should disregard structure-defining prefixes that are written in italics and separated from the name by a hyphen. Thus tert-butyl precedes ethyl, but ethyl precedes isobutyl.* There is one five-carbon group with an **IUPAC** approved common name that you should also know: the 2,2-dimethylpropyl group, commonly called the **neopentyl group**



2,2-Dimethylpropyl or neopentyl group

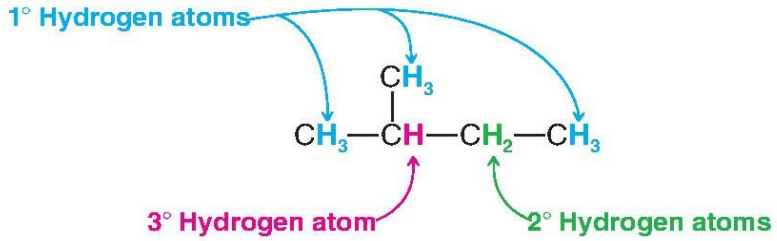
Isomers are different compounds that have the same molecular formula. In our study thus far, much of our attention has been directed toward isomers we have called constitutional **isomers.**

● Constitutional isomers have the same molecular formula but different connectivity, meaning that their atoms are connected in a different order. Examples of constitutional isomers are the following:

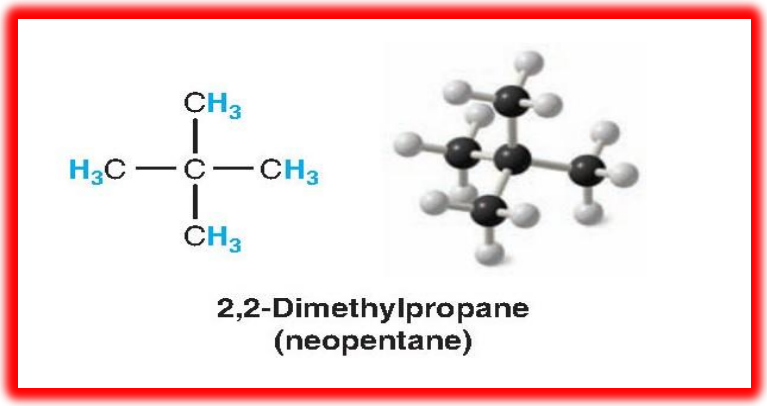


Classification of Hydrogen Atoms

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. The following compound, 2-methylbutane, has primary, secondary (2°), and tertiary (3°) hydrogen atoms:



On the other hand, 2,2-dimethylpropane, a compound that is often called neopentane, has only primary hydrogen atom



Physical Properties of Alkanes and Cycloalkanes

At room temperature (25°C) and 1 atm pressure the first four members of the homologous series of unbranched alkanes are gases , the C_5—C_{17} unbranched alkanes (pentane to hepta and decane) are liquids, and the unbranched melting point with increasing molecular weight. alkanes with 18 and more carbon atoms are solids. Boiling Points The boiling points of the unbranched alkanes show a regular increase with increasing molecular weight in the homologous series of straight-chain alkanes. Branching of the alkane chain, however, lowers the boiling point. As examples, consider the C_6H_{14} isomers in Table 4.1. Hexane boils at 68.7°C and 2-methylpentane and 3-methylpentane, each having one branch, boil lower, at 60.3 and 63.3°C, respectively. 2,3-Dimethylbutane and 2,2-dimethylbutane, each with two branches, boil lower still, at 58 and 49.7°C, respectively. Part of the explanation for these effects lies in the dispersion forces that we studied. With unbranched alkanes, as molecular weight increases, so too do molecular size and, even more importantly, molecular surface area. With increasing surface area, the dispersion forces between molecules increase; therefore, more energy (a higher temperature) is required to separate molecules from one another and produce boiling. Chain branching, on the

other hand, makes a molecule more compact, reducing its surface area and with it the strength of the dispersion forces operating between it and adjacent molecules; this has the effect of lowering the boiling point.

Melting Points ; The unbranched alkanes do not show the same smooth increase in melting points with increasing molecular weight that they show in their boiling points. There is an alternation as one progresses from an unbranched alkane with an even number of carbon atoms to the next one with an odd number of carbon atoms. For example, propane (m.p 188°C) melts lower than ethane (mp 183°C) and also lower than methane (m.p 182°C). Butane (m.p 138°C) melts 50°C higher than propane and only 8°C lower than pentane (m.p 130°C).

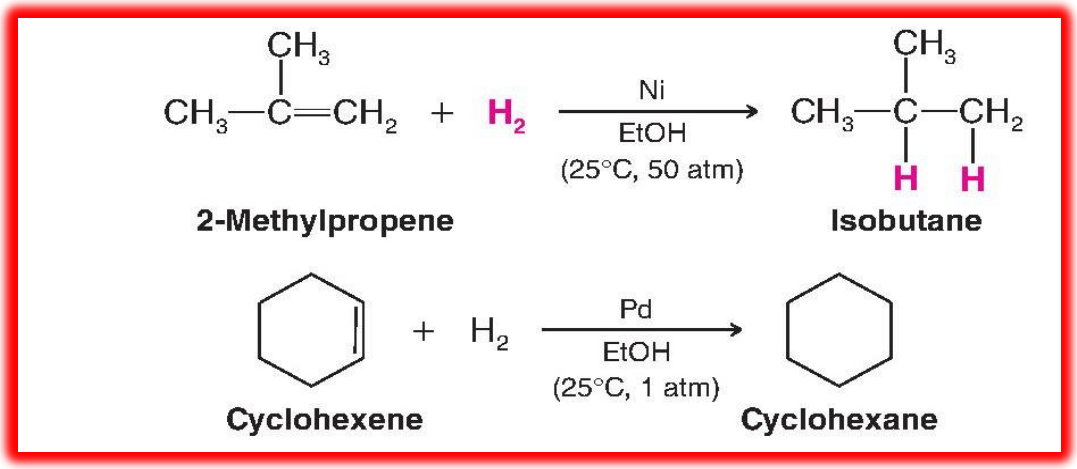
Density ; As a class, the alkanes and cycloalkanes are the least dense of all groups of organic compounds. All alkanes and cycloalkanes have densities considerably less than 1.00 g $mL^{=1}$ (the density of water at 4°C). As a result, petroleum (a mixture of hydrocarbons rich in alkanes) floats on water.

Solubility ; Alkanes and cycloalkanes are almost totally insoluble in water because of their very low polarity and their inability to form hydrogen bonds. Liquid alkanes and cycloalkanes are soluble in one another, and they generally dissolve in solvents of low polarity. Good solvents for them are benzene, carbon tetrachloride, chloroform, and other hydrocarbons.

Preparation of Alkane

1) **Hydrogenation of Alkenes;**

By far the most important of these methods is the hydrogenation of alkenes. When shaken under a slight pressure of hydrogen gas in the presence of a small amount of catalyst, alkenes are converted smoothly and quantitatively into alkanes of the same carbon skeleton. The method is limited only by the availability of the proper alkene.

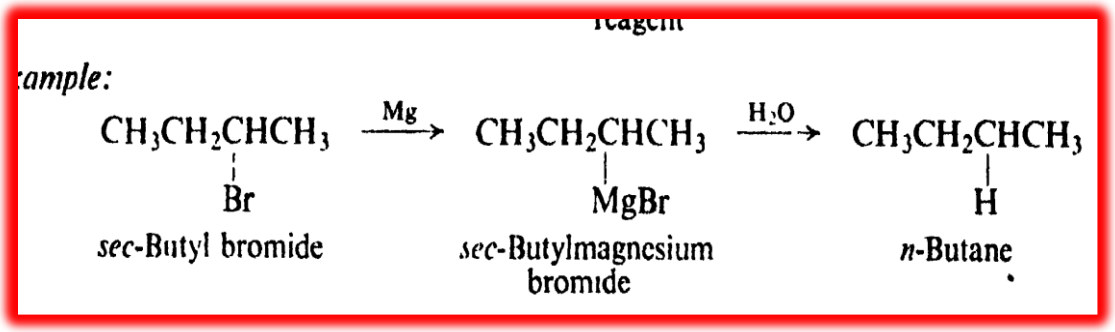


2. **Reduction of alkyl halides;**

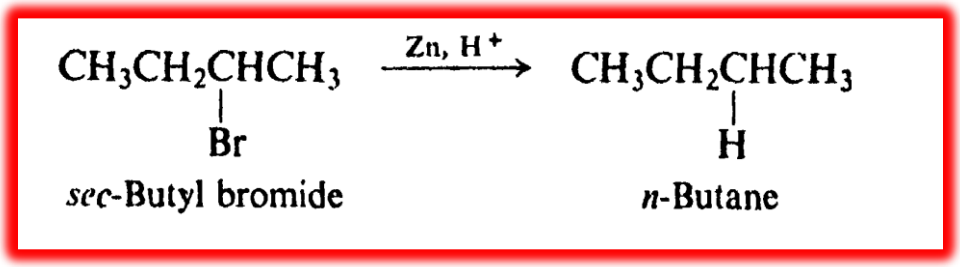
Reduction of an alkyl halide, either via the Grignard reagent or directly with metal and acid, involves simply the replacement of a halogen atom by a hydrogen atom; the carbon skeleton remains intact.

a) Hydrolysis with Grignard reagent;

The Grignard reagent has the general formula R MgX, and the general name alkyl magnesium halide. The carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium halogen bond is essentially ionic.



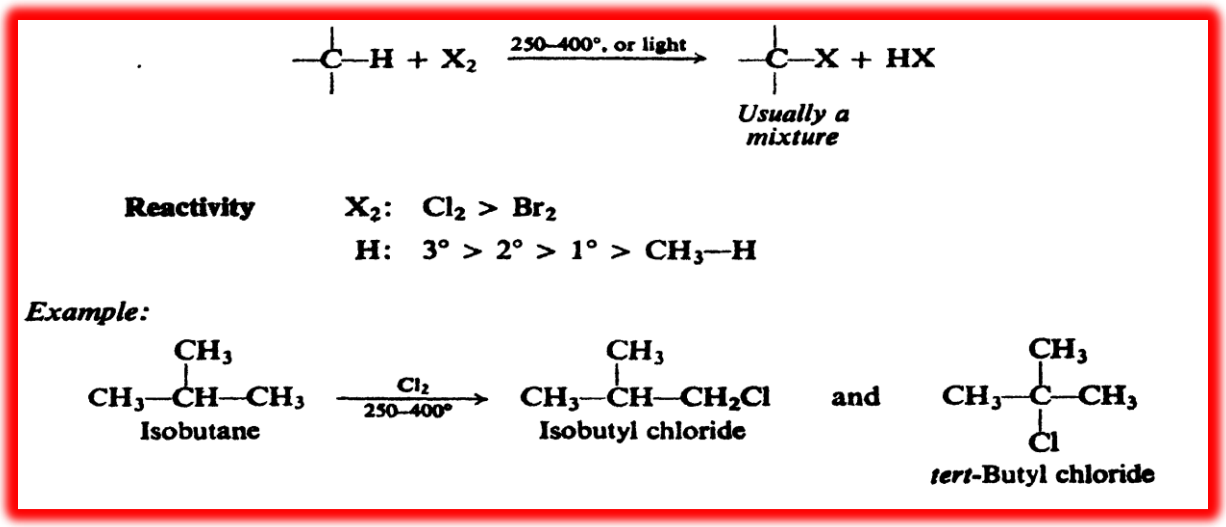
b) Reduction by metal and acid;



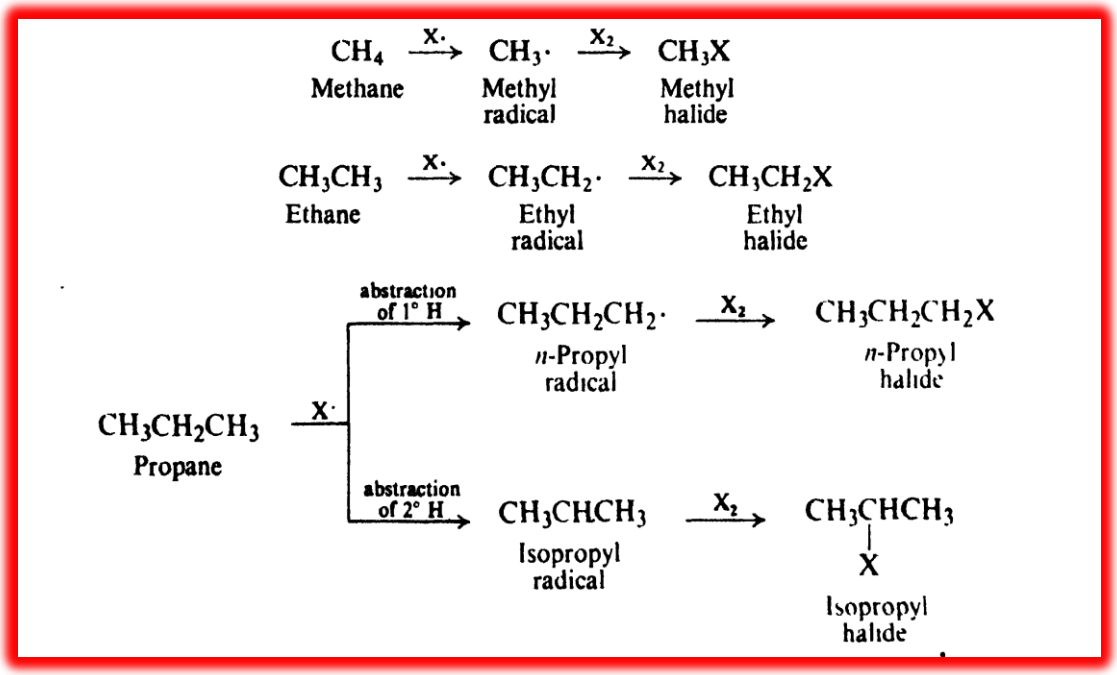
Reaction Of Alkanes

1) Halogenation

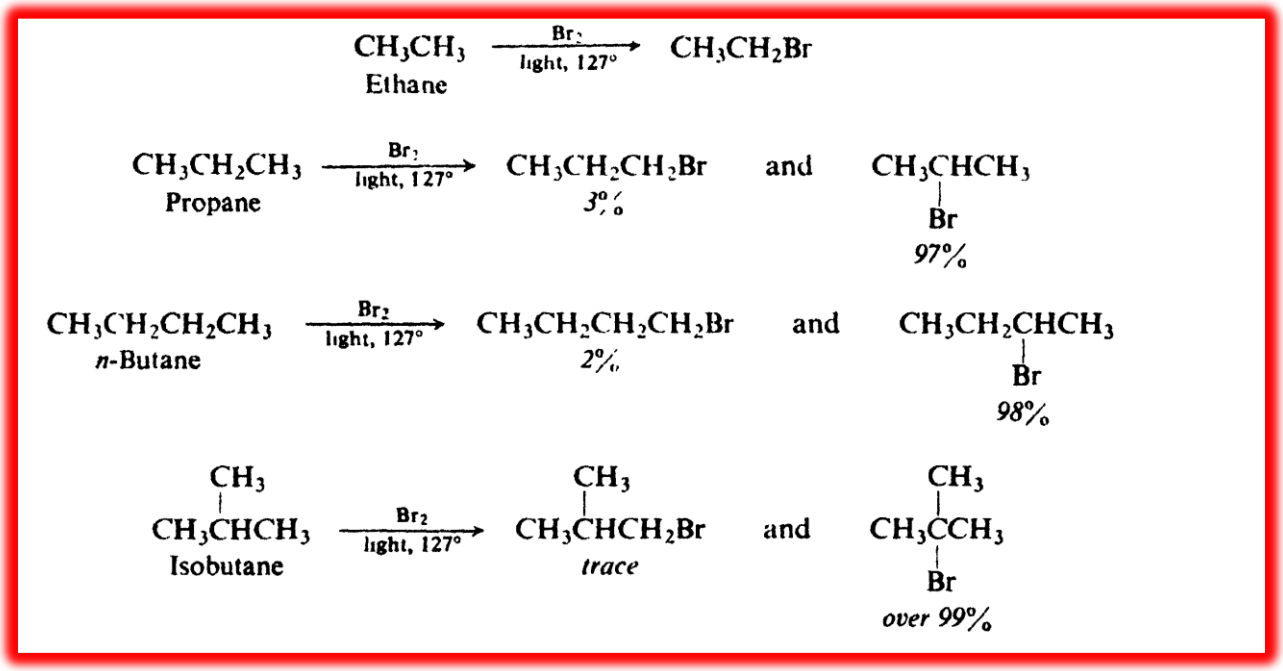
Under the influence of ultraviolet light, or at 250-400, chlorine or bromine converts alkanes into chloroalkanes (alkyl chlorides) or bromoalkenes (alkyl bromides); an equivalent amount of hydrogen chloride or hydrogen bromide is formed at the same time. When diluted with an inert gas, and in an apparatus designed to carry away the heat produced, fluorine has recently been found to give analogous results.



A halogen atom abstracts hydrogen from the alkane (RH) to form an alkyl radical (R-). The radical in turn abstracts a halogen atom from a halogen molecule to yield the alkyl halide (RX). Which alkyl halide is obtained depends upon which alkyl radical is formed.



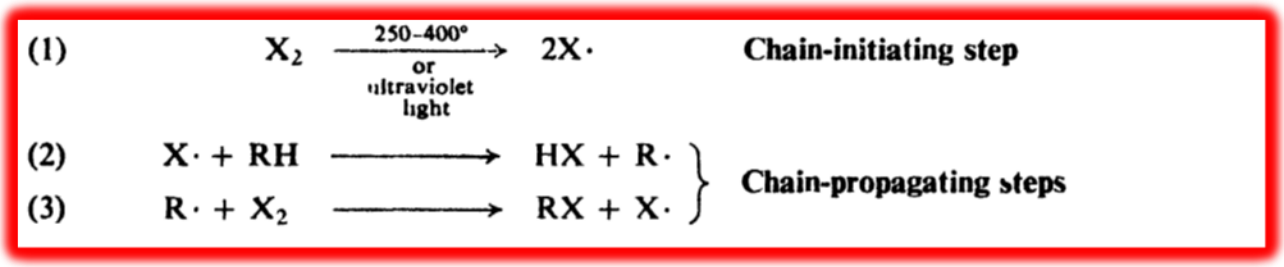
Bromination gives the corresponding bromides but in different proportions:



Stability of free radicals $3° > 2° > 1° > CH_3\cdot$

Mechanism of halogenation

Halogenation of alkanes proceeds by the same mechanism as halogenation of methane or triple bonds between their carbon atoms. Alkynes contain at least one carbon–carbon triple bond, and this is indicated in the family name and in names for specific compounds by a -yne ending .Aromatic compounds contain a special type of ring, the most common example of which is a benzene ring. There is no special ending for the general family of aromatic compounds. We shall introduce representative examples of each of these classes of hydrocarbons in the following sections. Generally speaking, compounds such as the alkanes, whose molecules contain only single bonds, are referred to as saturated compounds because these compounds contain the maximum number of hydrogen atoms that the carbon compound can possess. Compounds with multiple bonds, such as alkenes, alkynes, and aromatic hydrocarbons, are called unsaturated compounds because they possess fewer than the maximum number of hydrogen atoms, and they are capable of reacting with hydrogen under the proper conditions.



Reaction with Oxygen Combustion;

alkanes are a type of hydrocarbon, which means they are made up of hydrogen and carbon atoms. When they react with oxygen, this is known as a combustion reaction. Combustion reactions are exothermic, meaning they

release energy in the form of heat and light. This is why alkanes are often used as fuels.

The general equation for the combustion of an alkane is: alkane + oxygen → carbon dioxide + water. For example, the combustion of methane (CH4), the simplest alkane, can be represented as:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

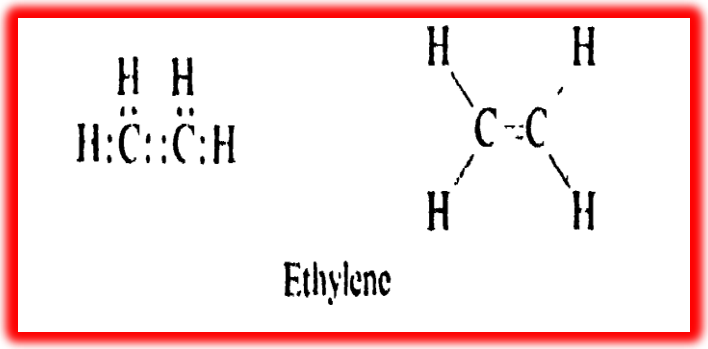
$$CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

This equation shows that one molecule of methane reacts with two molecules of oxygen to produce one molecule of carbon dioxide and two molecules of water.

Alkenes

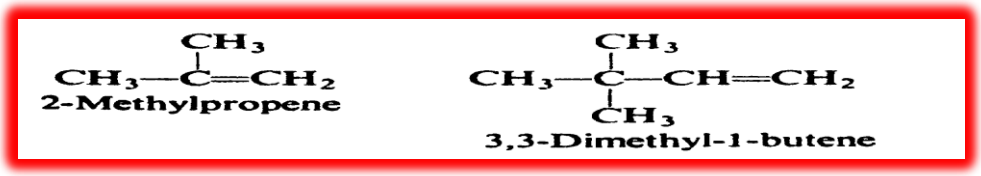
Other hydrocarbons may contain double bonds , alkenes contain at least one carbon–carbon double bond, and this is indicated in the family name and in names for specific compounds by an -ene ending. The simplest member of the alkene family is ethylene, C_2H_4 . have the general molecular **CnH2.** In view of the ready conversion of ethylene into ethane, we can reasonably expect certain structural similarities between the two compounds. To start, then, we connect the carbon atoms by a covalent bond, and then attach two hydrogen atoms to each carbon atom. At this stage we find that each carbon atom possesses only six electrons in its valence shell, instead of the required eight, and the entire molecule needs an additional pair, of electrons if it is to be neutral. We can solve both these problems by assuming that the carbon atoms can share two pairs of electrons. To describe this sharing of two pairs of electrons, we say that the carbon atoms are joined by a double bond. The

carbon-carbon double bond is the distinguishing feature of the alkene structure.



The rules IUPAC of the system are:

1) Select as the parent structure the longest continuous chain that contains the carbon-carbon double bond; then consider the compound to have been derived from this structure by replacement of hydrogen by various alkyl groups. The parent structure is known as ethene<propene,butene,pentene, and so on, depending upon the number of carbon atoms; each name is derived by changing the ending -ane of the corresponding alkane name to -ene:



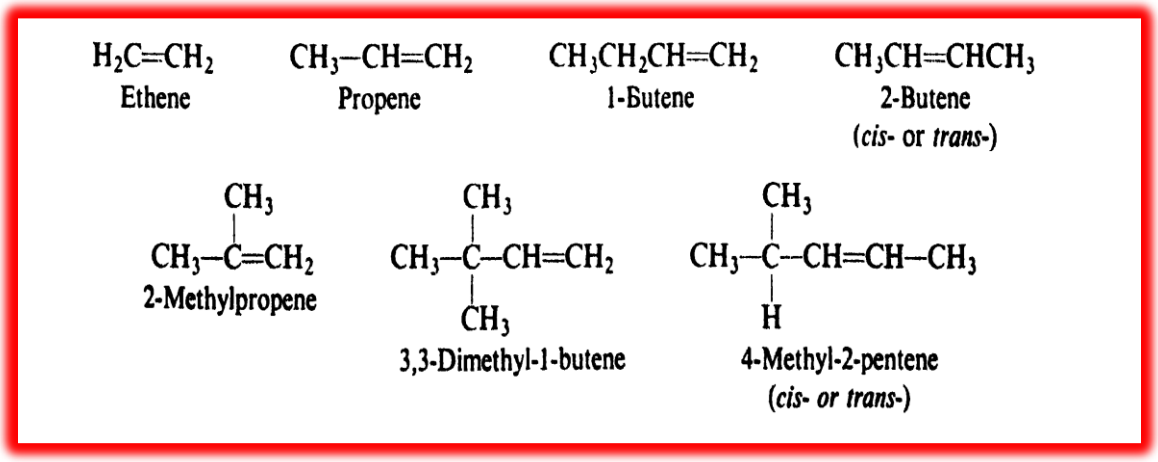
2) Indicate by a number the position of the double bond in the parent chain. Although the double bond involves two carbon atoms, designate its position by the number of the first doubly-bonded carbon encountered when

numbering from the end of the chain nearest the double bond; thus J-butene and 2-butene.

3) Indicate by numbers the positions of the alkyl groups attached to the parent chain.

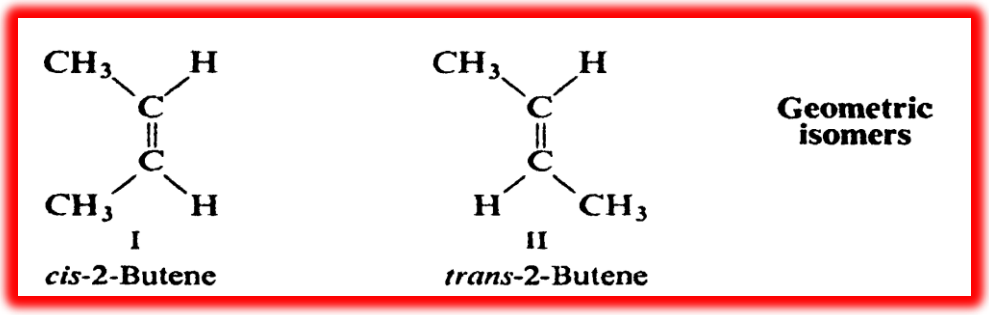
Common Names;

Used except for three simple alkenes: ethylene ,propylene, and isobutylene. The various alkenes of a given carbon number are ,however, sometimes referred to collectively as the pentylenes (amylenes), hexylenes, heptylenes, and so on. (One sometimes encounters the naming of alkenes as derivatives of ethylene: as, for example, tetramethyl ethylene for $(CH_3)_2C\ C(CH_3)_2$).



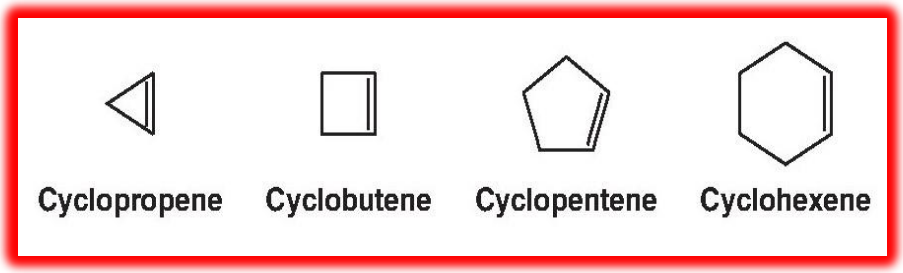
The Cis - Trans System (Geometric isomerism) (Stereochemistry)

We recall that the arrangement of atoms that characterizes a particular stereoisomer is called its configuration. The configurations of the isomeric2-butenes are the structures I and II. These configurations are differentiated intheir names by the prefixes cis- (Latin: on this side) and trans- (Latin: across),which indicate that the methyl groups are on the same side or on opposite sides of the molecule.



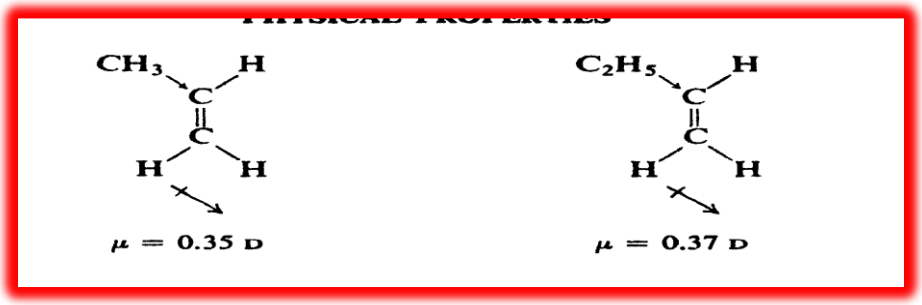
In the **Cis** example, carbon atoms of the main chain (carbons1 and 4)are on the same side of the double bond, In the **trans** example, the same carbon atoms of the main chain are on opposite sides of the double bond. Rotation around the double bond is restricted because the bond would have to be broken to allow rotation .Thus ,the double bond is rigid geometric isomers are formed.

Naming Cycloalkenes



Physical properties

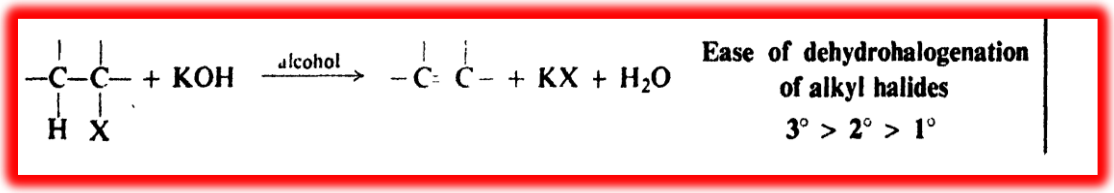
As a class, the alkenes possess physical properties that are essentially the same as those of the alkanes. They are insoluble in water, but quite soluble in nonpolar solvents like benzene, ether, chloroform, or ligroin. They are less dense than water. Like alkanes, alkenes are at most only weakly polar. Since the loosely held electrons of the double bond are easily pulled or pushed, dipole moments are larger than for alkanes. They are still small, however: compare the dipole moments shown for propylene and 1-butene, for example, with the moment of 1.83 r> for methyl chloride. The bond joining the alkyl group to the doubly-bonded carbon has a small polarity, which is believed to be in the direction shown, that is, with the alkyl group releasing electrons to the doubly-bonded carbon. Since this polarity is not canceled by a corresponding polarity in the opposite direction, it gives a net dipole moment to the molecule.



Prparation of Alkenes

1. Dehydrohalogenation of alkyl halides.

Alkyl halides are converted into alkenes by dehydrohalogenation: elimination of the elements of hydrogen halide. Dehydrohalogenation involves removal of the halogen atom together with a hydrogen atom from a carbon adjacent to the one.



Examples:

$CH_3CH_2CH_2CH_2Cl \xrightarrow{KOH\ (alc)} CH_3CH_2CH{=}CH_2$

n-Butyl chloride — 1-Butene

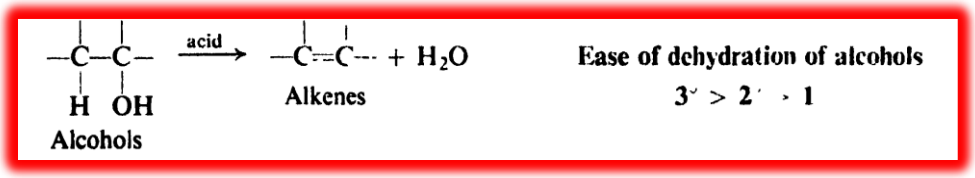
$CH_3CH_2CHClCH_3 \xrightarrow{KOH\ (alc)} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$

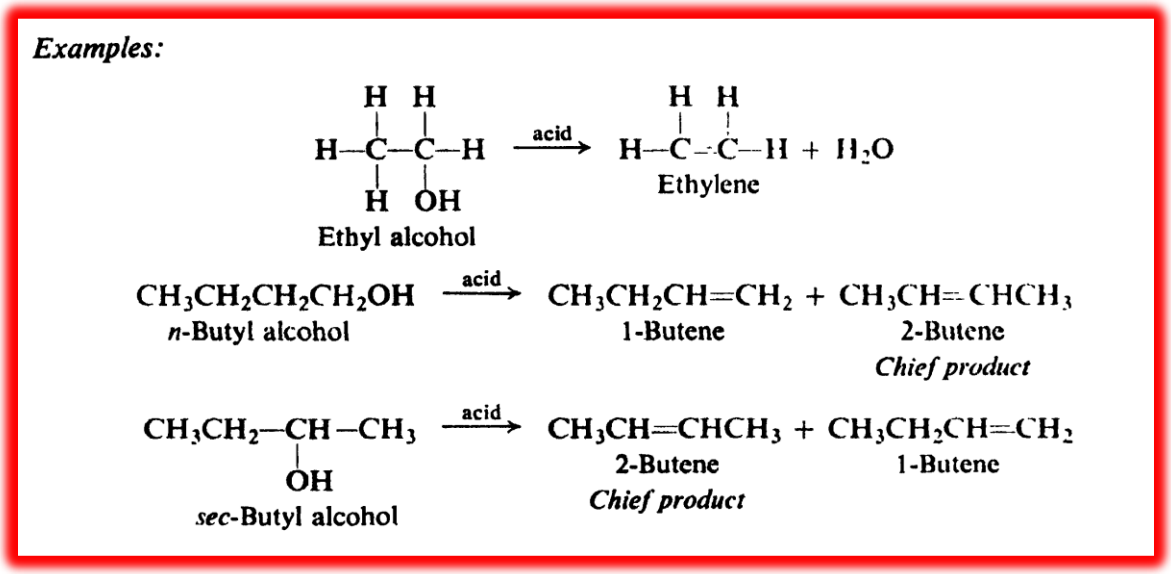
sec-Butyl chloride — 2-Butene *80%* — 1-Butene *20%*

2. Dehydration of alcohols;

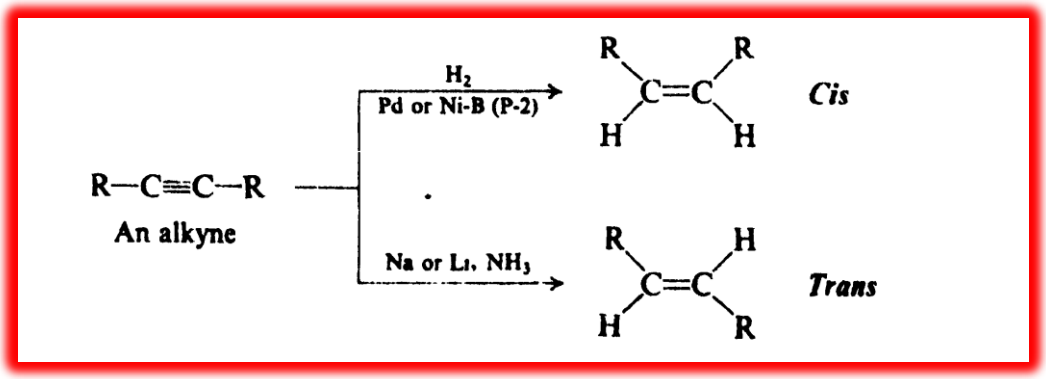
An alcohol is converted into an alkene by dehydration: elimination of a molecule of water. Dehydration requires the presence of an acid and the application of heat. It is generally carried out in either of two ways: (a)

heating the alcohol with sulfuric or phosphoric acid to temperatures as high as 200, or (b) passing the alcohol vapor over alumina, $A1_2O_3$, at 350-400, alumina here serving as a Lewis acid.



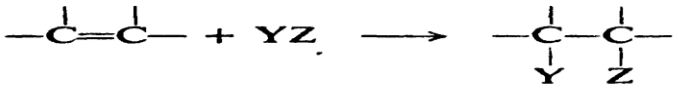


3- Reduction of alkynes.



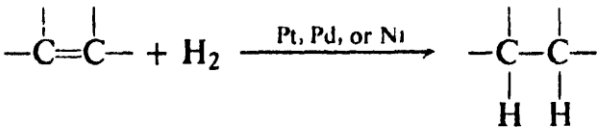
REACTIONS OF ALKENES

Addition Reactions

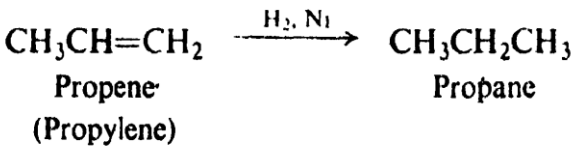


1. Addition of hydrogen. Catalytic hydrogenation;

We have already encountered hydrogenation as the most useful method for preparing alkanes . It is not limited to the synthesis of alkanes, but is a general method for the conversion of a carbon-carbon double bond into a carbon carbon single bond: using the same apparatus, the same catalyst, and very nearly the same conditions,

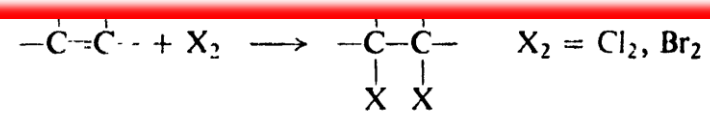


Example:



2-Addition of halogens;

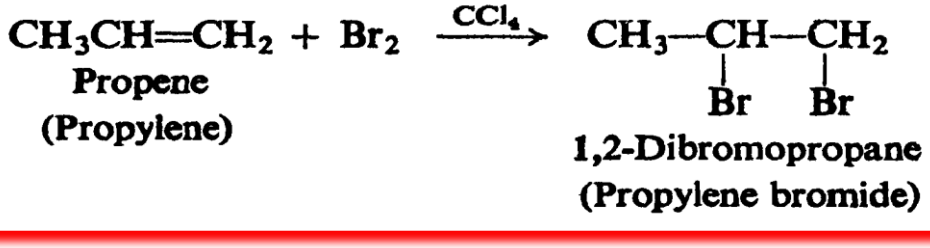
Alkenes are readily converted by chlorine or bromine into saturated compounds that contain two atoms of halogen attached to adjacent carbons; iodine generally fails to react.



$X_2 = Cl_2, Br_2$

Example:

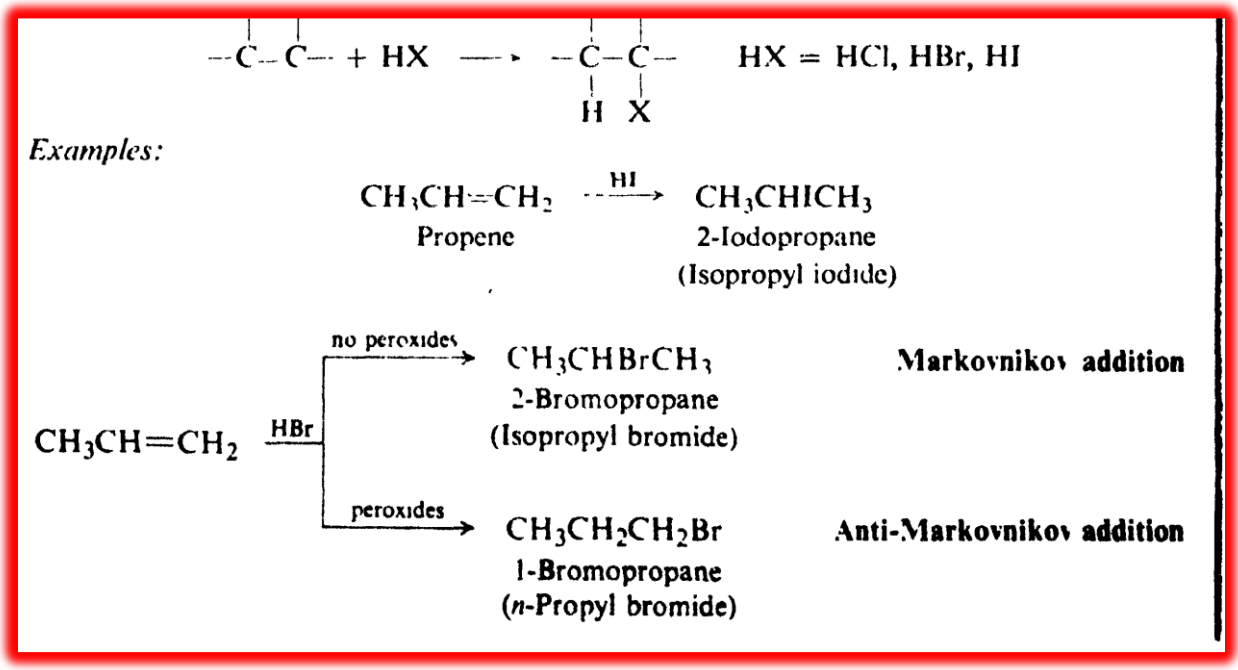
$CH_3CH{=}CH_2$ (Propene, Propylene) $\xrightarrow{Br_2 \text{ in } CCl_4}$ $CH_3CHBrCH_2Br$ (1,2-Dibromopropane, Propylene bromide)



Propene (Propylene) $\xrightarrow{CCl_4}$ **1,2-Dibromopropane (Propylene bromide)**

Addition of hydrogen halides. Markovnikov's rule;

An alkene is converted by hydrogen chloride, hydrogen bromide, or hydrogen iodide into the corresponding alkyl halide.



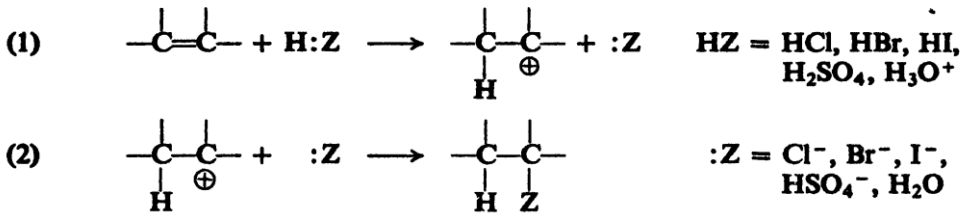
Addition of hydrogen halides. Markovnikov's rule;

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Mechanism of addion reaction (Markonlkove)

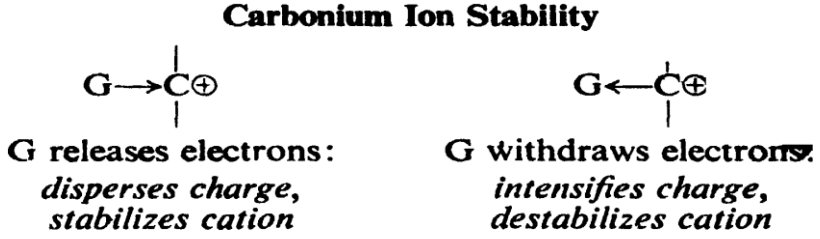
Addition of the acidic reagent, HZ, is believed to proceed by two steps:



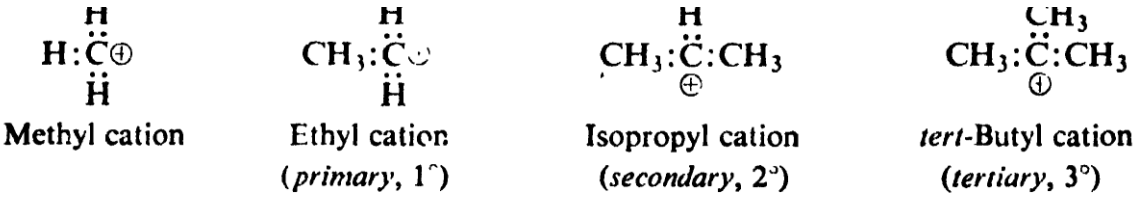
Step (1) involves transfer of hydrogen ion from : Z to the alkene to form a carbonium ion; this is a transfer of a proton from one base to another.

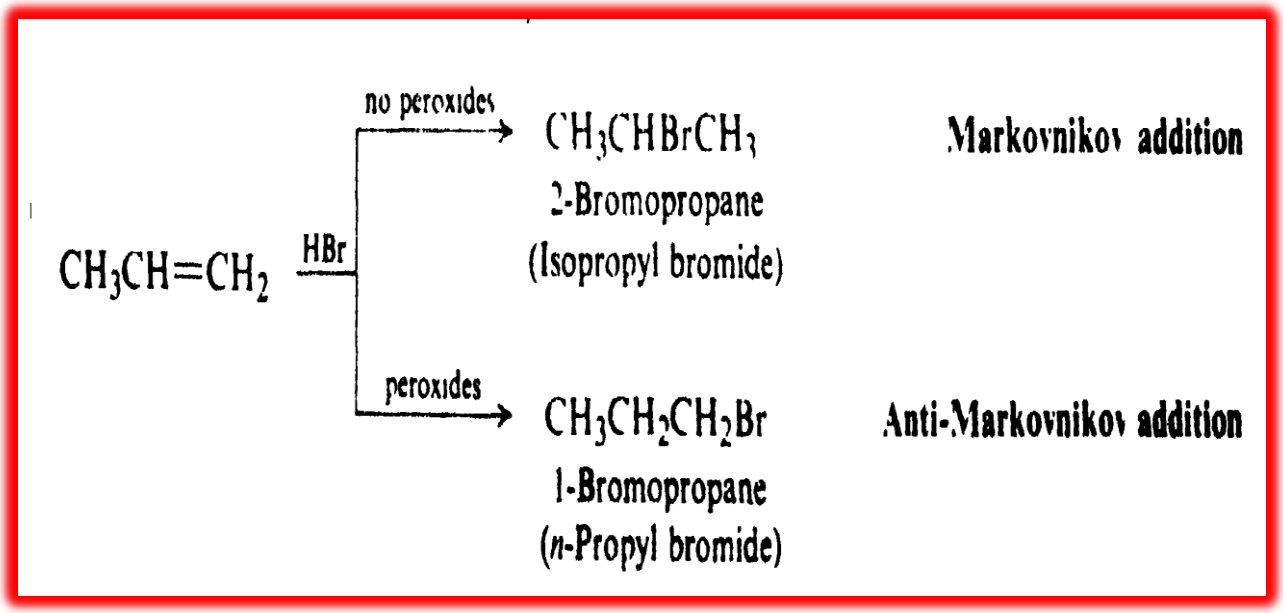
Carbonium ions

the carbonium ion, a group of atoms that contains a carbon atom bearing only six electrons Carbonium ions are classified as primary, secondary, or tertiary after the carbon bearing the positive charge. They are named by use of the word cation. For example;



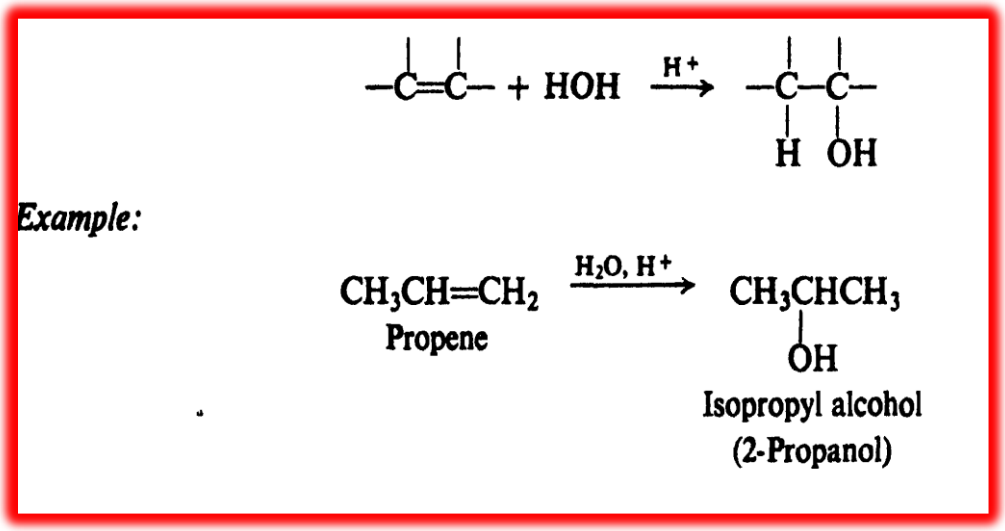
The facts are. Then. that the greater the number of alkyl groups. The more stable the carbonium ion



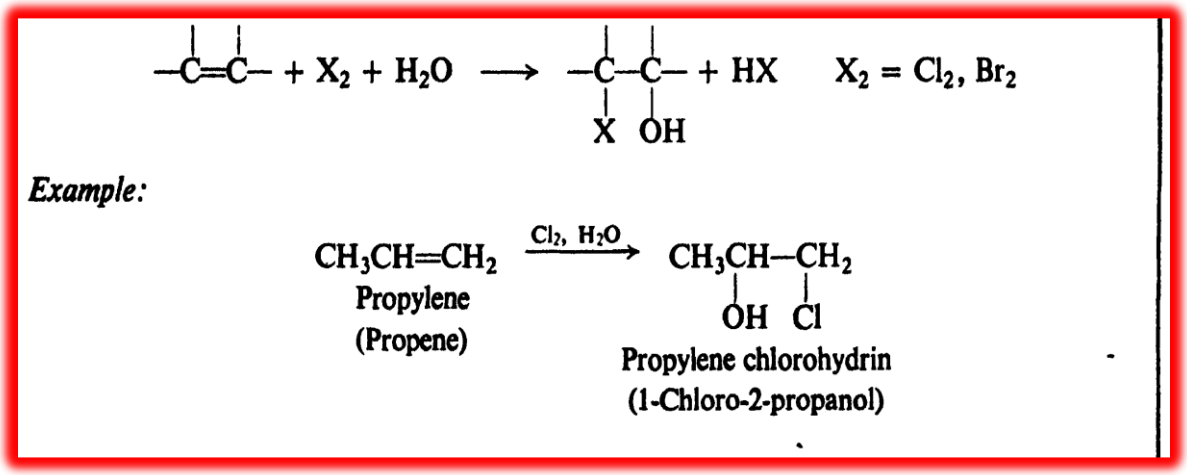


4 -Addition of water. Hydration.

Water adds to the more reactive alkenes in the presence of acids to yield alcohols. Since this addition, too, follows Markovnikov's rule, the alcohols are the same as those obtained by the two-step synthesis just described; this direct hydration is, of course, the simpler and cheaper of the two processes. Hydration of alkenes is the principal industrial source of those lower alcohols whose formation is consistent with Markovnikov's rule.



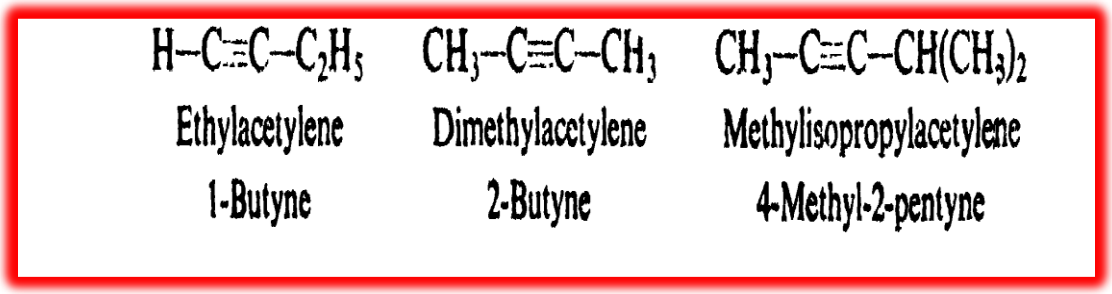
5. Halohydrin formation



Alkyne

Nomenclature;

The alkynes are named according to two systems. In one, they are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl groups**,** have the general molecular **CnH2n-2**

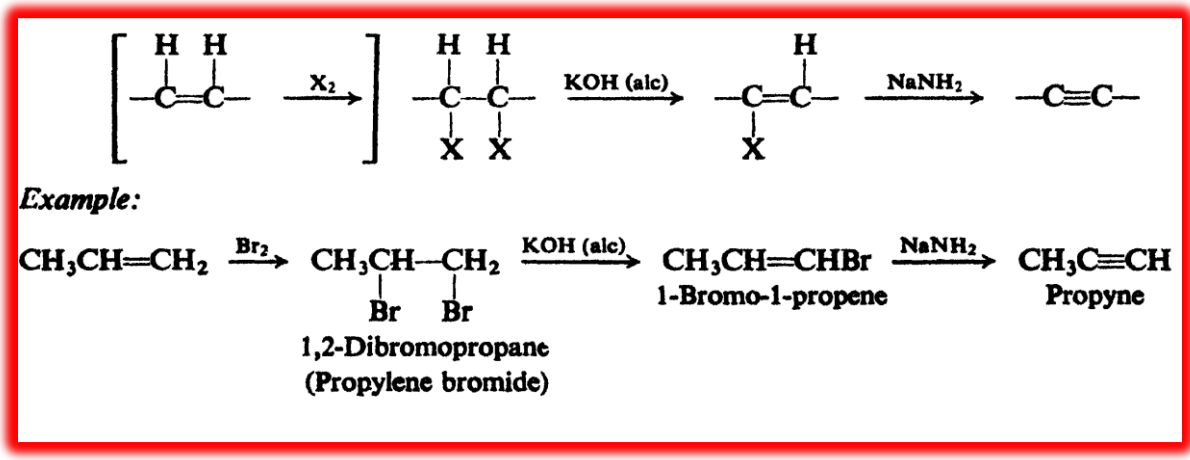


For more complicated alkynes the **IUPAC** names are used. The rules areexactly the same as for the naming of alkenes, except that the ending -yne replaces.

Name	Formula
Acetylene	$HC{\equiv}CH$
Propyne	$HC{\equiv}CCH_3$
1-Butyne	$HC{\equiv}CCH_2CH_3$
1-Pentyne	$HC{\equiv}C(CH_2)_2CH_3$
2-Butyne	$CH_3C{\equiv}CCH_3$
2-Pentyne	$CH_3C{\equiv}CCH_2CH_3$
3-Methyl-1-butyne	$HC{\equiv}CCH(CH_3)_2$
2-Hexyne	$CH_3C{\equiv}C(CH_2)_2CH_3$
3-Hexyne	$CH_3CH_2C{\equiv}CCH_2CH_3$

PREPRATION OF ALKYNES

1. Dehydrohalogenation of alkyl dihalides



Example:

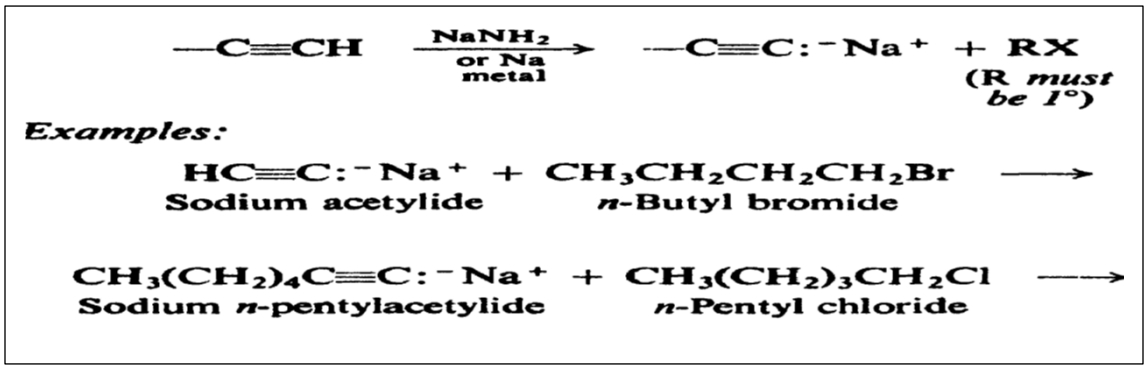
$CH_3CH{=}CH_2 \xrightarrow{Br_2} CH_3CHBrCH_2Br \xrightarrow{KOH\ (alc)} CH_3CH{=}CHBr \xrightarrow{NaNH_2} CH_3C{\equiv}CH$

1,2-Dibromopropane (Propylene bromide)

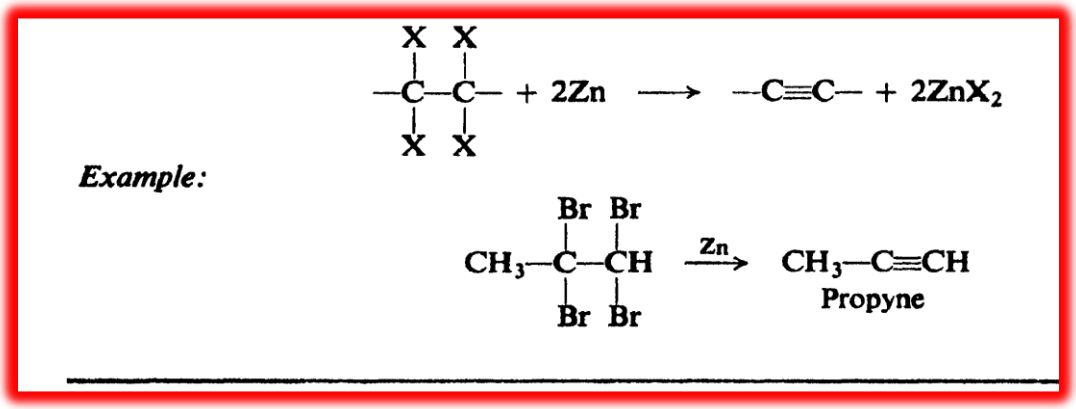
1-Bromo-1-propene

Propyne

2. Reaction of sodium acetylides with primary alkyl halides

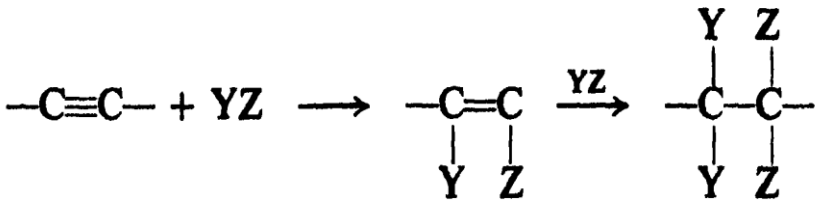


3. Dehalogenation of tetrahalides.

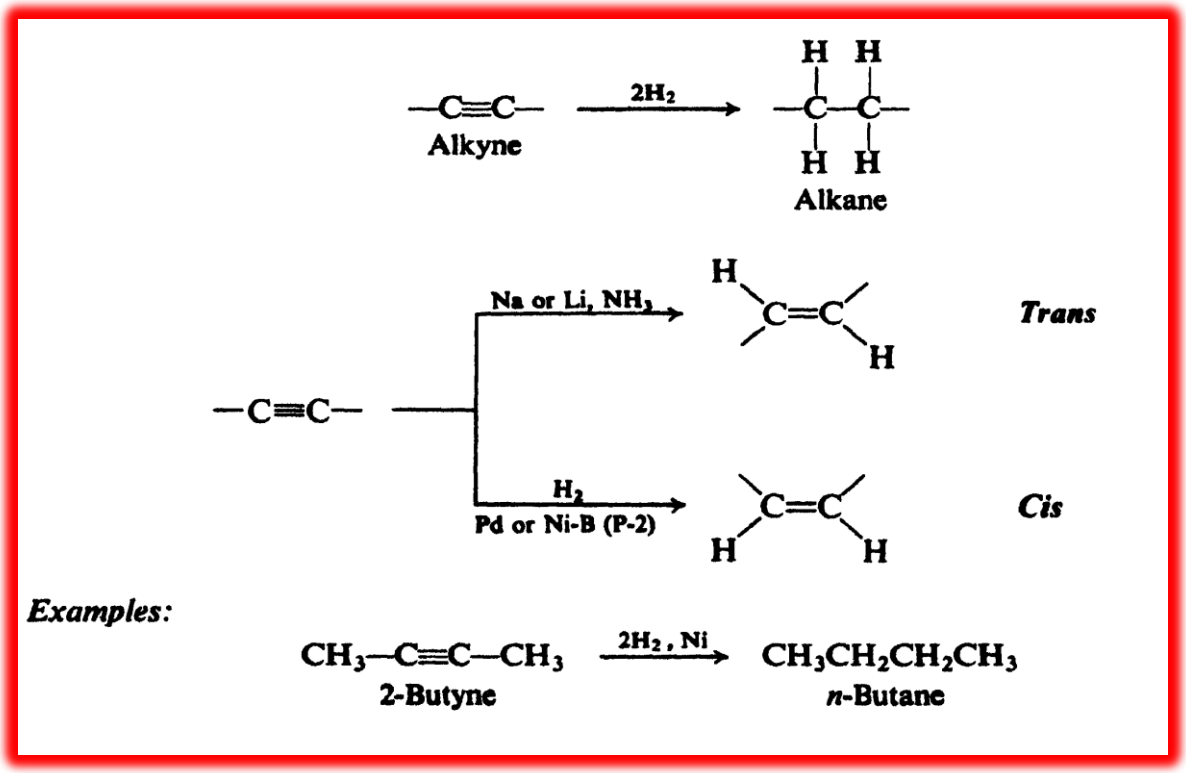


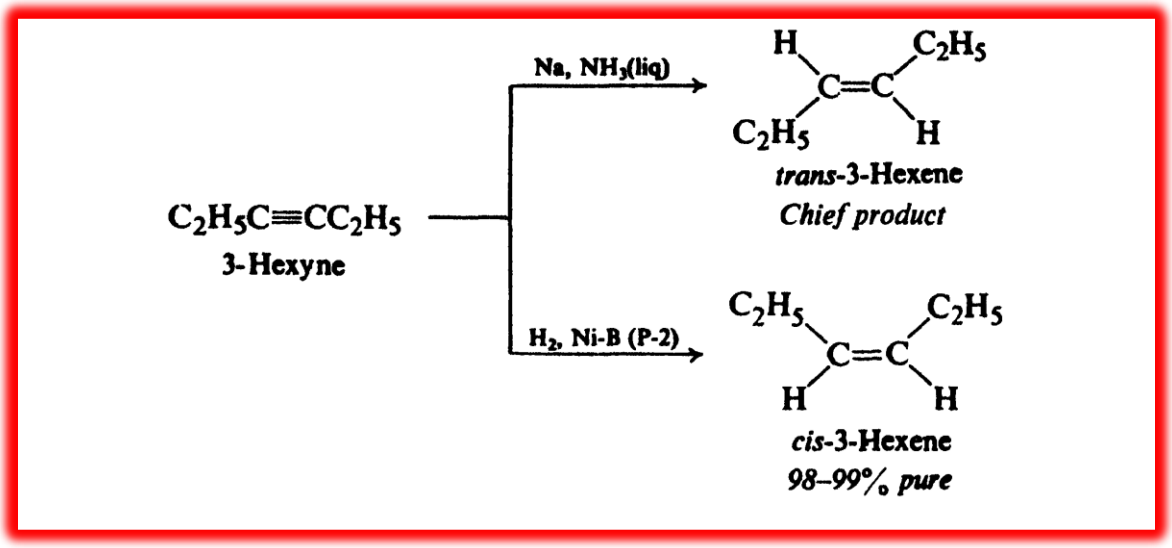
REACTION OF ALKYNES

Addition Reactions

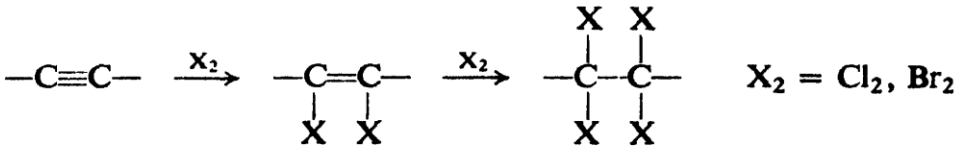


1. **Addition of hydrogen.**

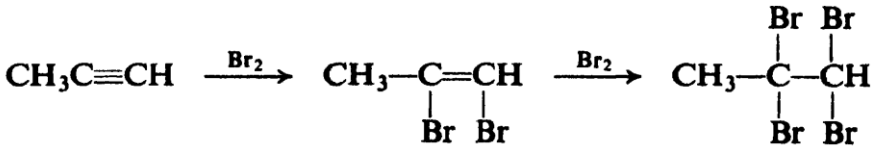




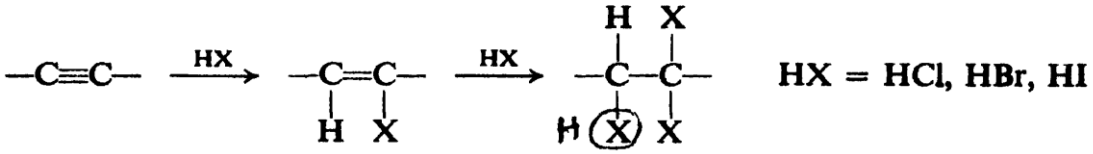
2-Addition of halogens



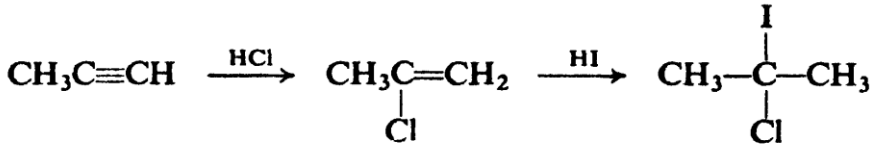
Example:



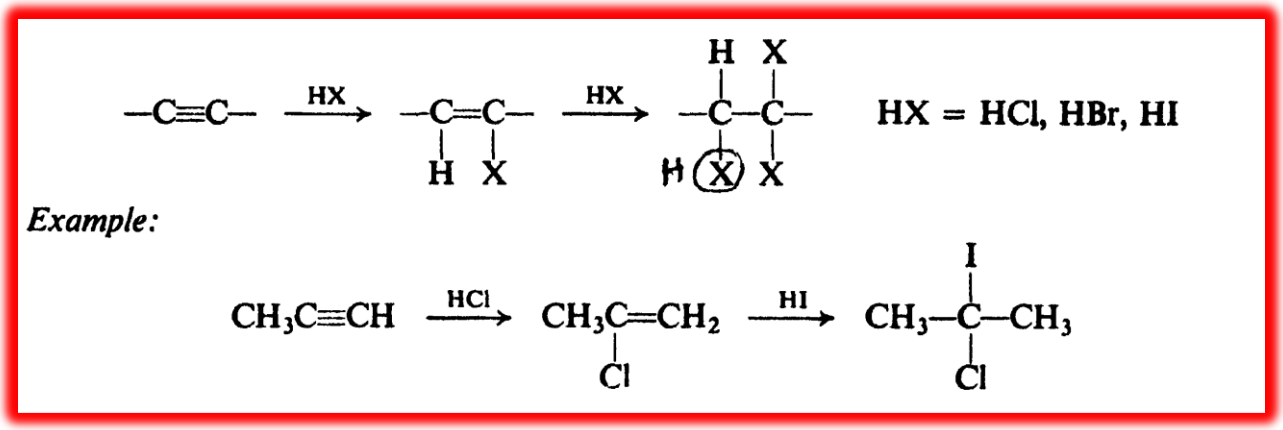
3. Addition of hydrogen halides. Discussed in Sec. 8.8.



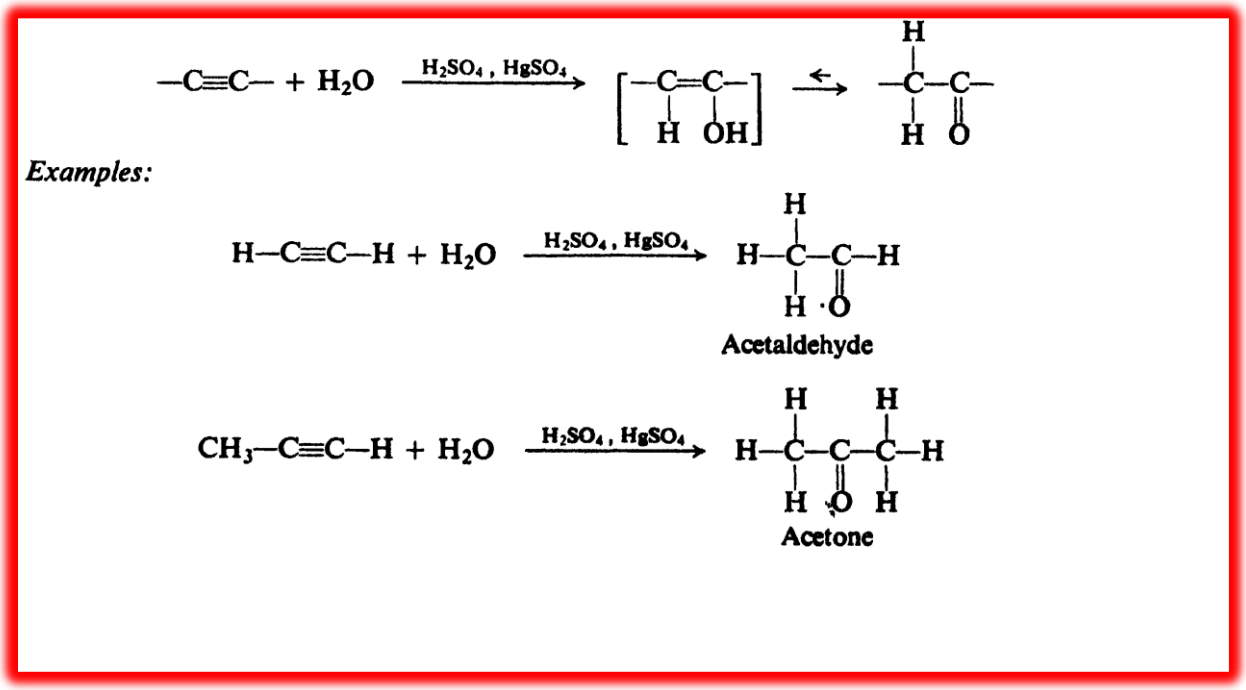
Example:



4- Addition of hydrogen halides.



5- Addition of water. Hydration



Reactions as Acids

6- Formation of heavy metal acetylides

$$-C\equiv C-H + M^+ \longrightarrow -C\equiv C-M + H^+$$

Examples:

$$H-C\equiv C-H + 2Ag^+ \xrightarrow{\text{alcohol}} Ag-C\equiv C-Ag + 2H^+$$

Silver acetylide

Identification of terminal alkynes

$$CH_3C\equiv C-H + Cu(NH_3)_2^+ \longrightarrow CH_3C\equiv C-Cu + NH_4^+ + NH_3$$

Cuprous methylacetylide

7- Formation of alkali metal acetylides.

Examples:

$$H-C\equiv C-H + Na \xrightarrow{\text{liq } NH_3} H-C\equiv C:^-Na^+ + \tfrac{1}{2}H_2$$

Sodium acetylide

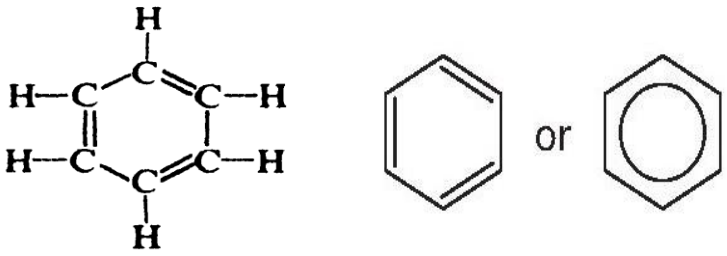
$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv C-H + NaNH_2 \xrightarrow{\text{ether}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv C:^-Na^+ + NH_3$$

Sodium isopropylacetylide

Aromatic compounds

Benzene has the molecular formula C_6H_6. From its elemental composition and molecular weight, benzene was known to contain six carbon atoms and six hydrogen atoms. In 1858, August Kekaula (of the University of Bonn) had proposed that carbon atoms can join to one another to form chains. Then, in 1865, he offered an answer to the question of benzene: these carbon chains can. sometimes be close

Kekune's structure of benzene was one that we would represent today as ;



I

Kekulé formula

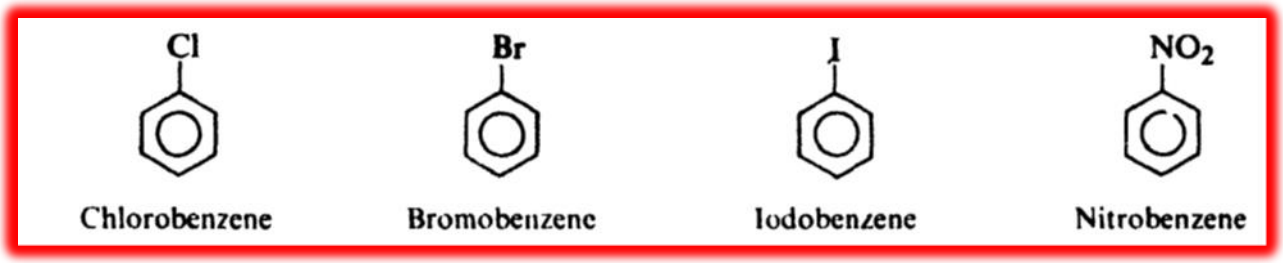
Benzene

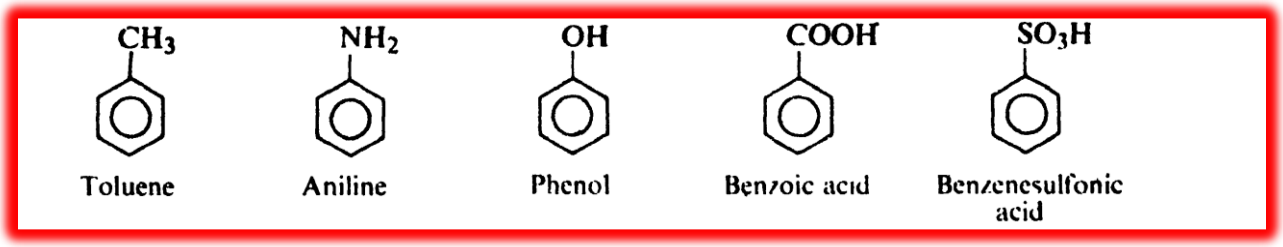
Aromaticity and the Hückel's Rule: 4n + 2 Rule

In 1931 the German physicist Erich Hückel carried out a series of mathematical calculations based on the kind of theory that we have just described. Hückel's rule is concerned with compounds containing one planar ring in which each atom has a p orbital as in benzene. His calculations show that planar monocyclic rings containing **4n + 2** p electrons, where **n**= 0, 1, 2, 3, and so on (i.e., rings containing 2, 6, 10, 14, . . . , etc., p electrons), have closed shells of delocalized electrons like benzene and should have substantial.

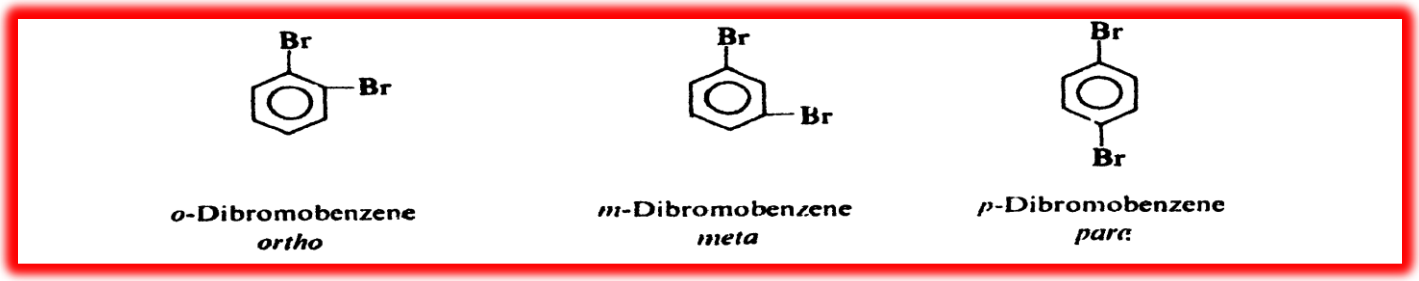
Nomenclature of benzene derivative

For many of these derivatives we simply prefix the name of the substituent group to the word -benzene, as, for example, in the other derivatives have special names which may show no resemblance to the name of the attached substituent group. For example methylbenzene is always known as toluene, aminobenzene as aniline hydroxybenzenes phenol, and so on. The most important of these special compounds are:

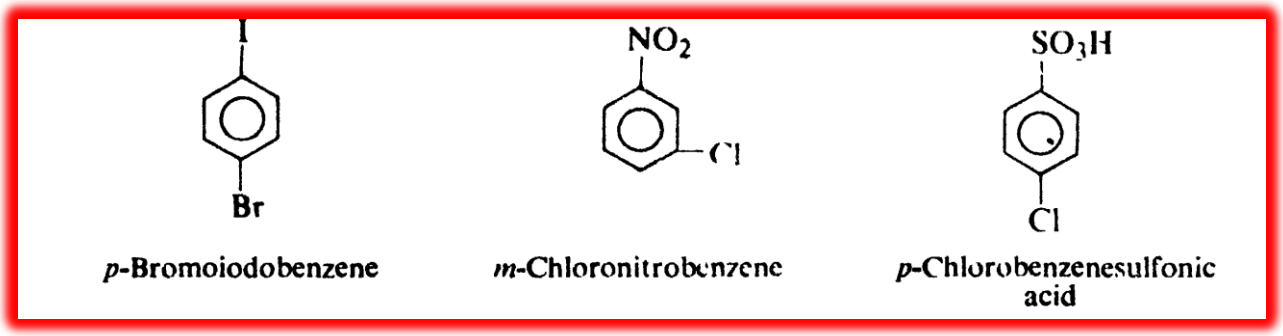




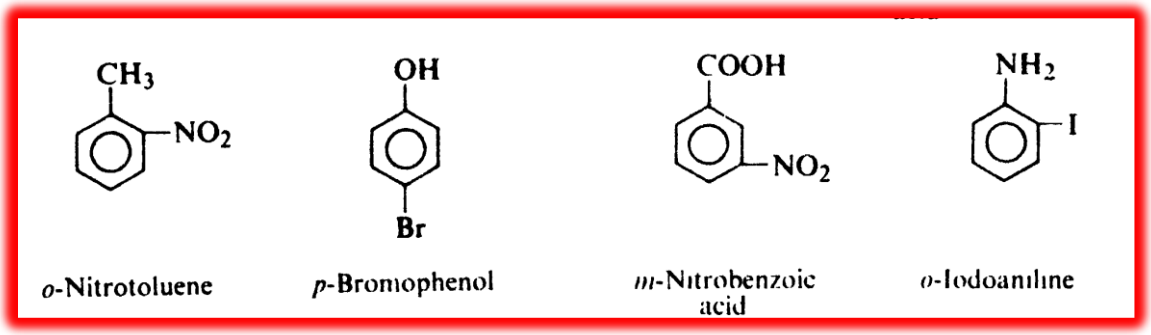
If several groups are attached to the benzene ring, we must not only tell what they are, but also indicate their relative positions. The three possible isomers of a disubstituted benzene are differentiated by the use of the names ortho, meta, and para. For example**:**



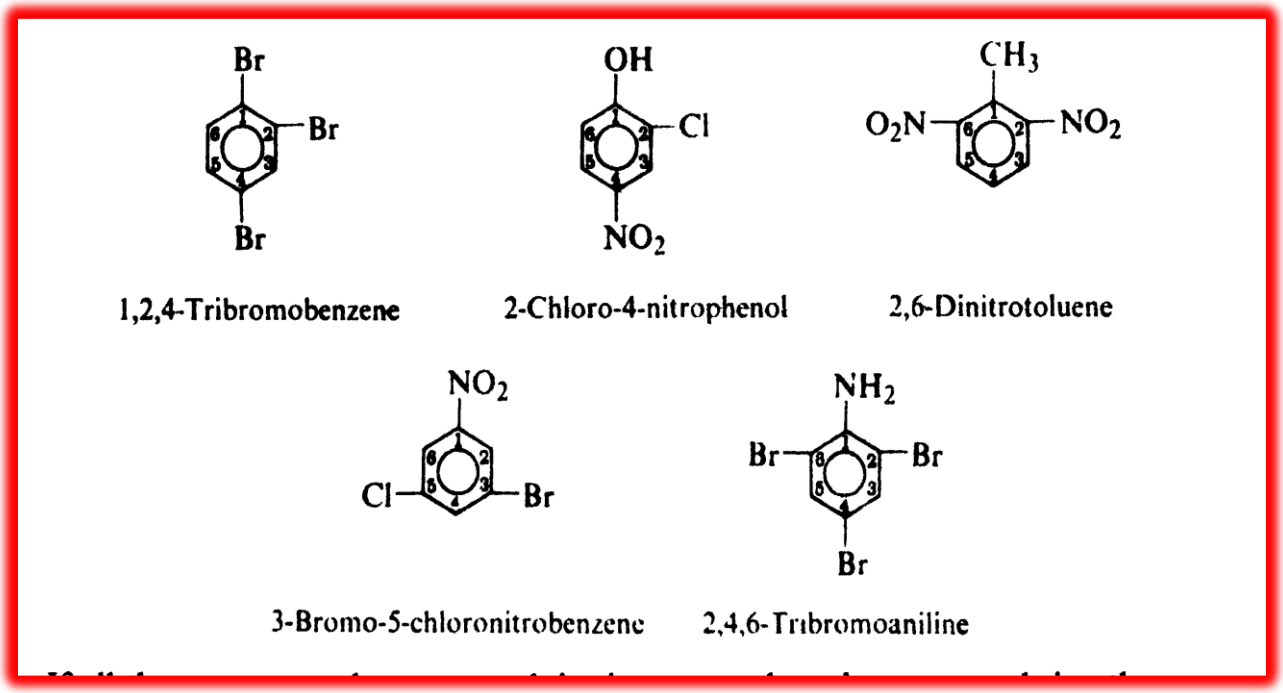
If the two groups are different, and neither is a group that gives a special narne to the molecule, we simply name the two groups successively and end the word with-benzene, as, for example, chloronitrobenzene, bromo iodo benzene, etc.



If one of the two groups is the kind that gives a special name to the molecule, then the compound is named as a derivative of that special compound, as, for example, nitrotoluene, bromophenol, etc.



If more than two groups are attached to the benzene ring, numbers are used to indicate their relative positions with the lowest possible value and list the substituent alphabetically with hyphenated number. For example :

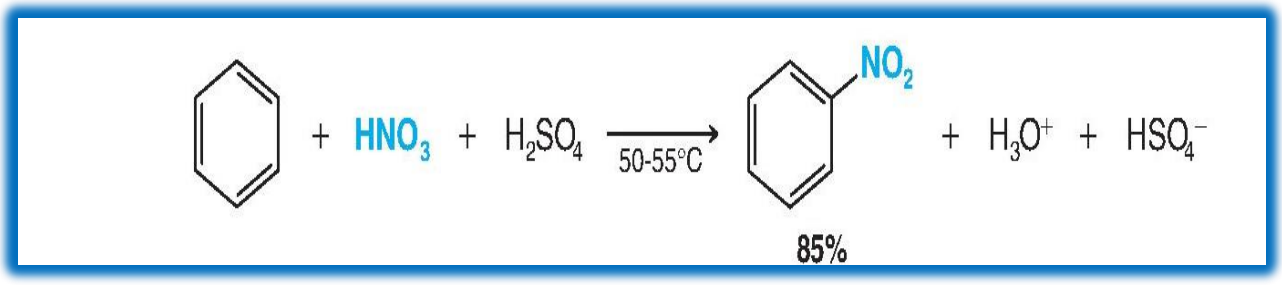


ELECTROPHILIC AROMATIC SUBSTITUTION

Electrophilic aromatic substitution includes a wide variety of reactions: nitration, halogenation, sulfonation, and Friedel-Crafts reactions, undergone by nearly all aromatic rings; reactions like nitridation and diazo coupling, undergone only by rings of high reactivity; and reactions like dislocation, isotopic exchange, and many ring closures which, although apparently unrelated, are found on closer examination to be properly and profitably viewed as reactions of this kind. In synthetic importance electrophilic aromatic substitution is probably unequaled by any other class of organic reactions. It is the initial route of access to nearly all aromatic compounds: it permits the direct introduction of certain substituent groups which can then be converted, by replacement or by transformation, into other substituents, **including even additional aromatic rings.**

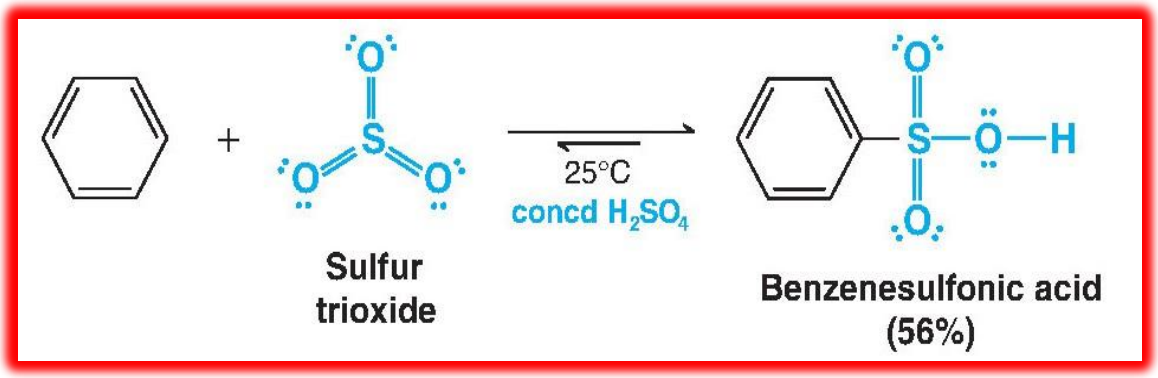
1- Nitration;

Benzene undergoes nitration on reaction with a mixture of concentrated nitric acid and concentrated sulfuric acid. Concentrated sulfuric acid increases the rate of the reaction by increasing the concentration of the electrophile, the nitronium ion (NO_2^+).



2. Sulfonation;

Benzene reacts with fuming sulfuric acid at room temperature to produce benzenesulfonic acid. Fuming sulfuric acid is sulfuric acid that contains added sulfur trioxide (SO_3). Sulfonation also takes place in concentrated sulfuric acid alone, but more slowly. Under either condition, the electrophile appears to be sulfur trioxide

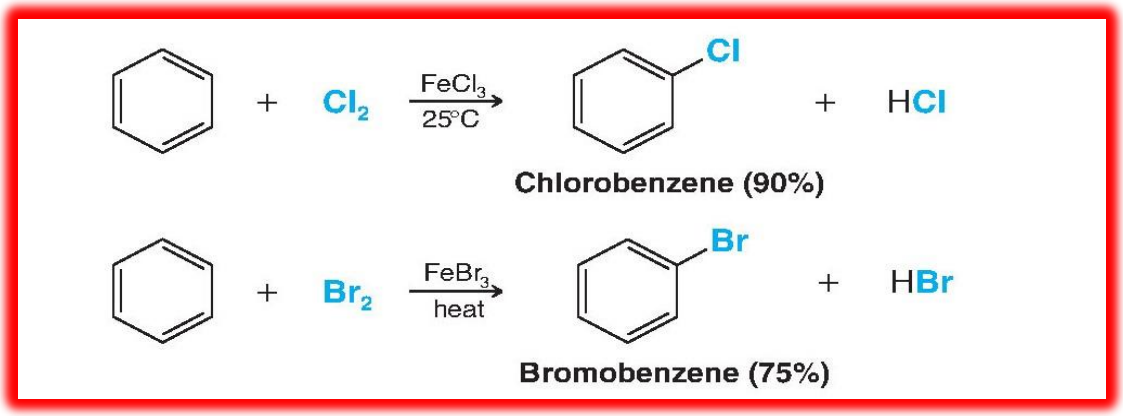


In concentrated sulfuric acid, sulfur trioxide is produced in an equilibrium in which H_2SO_4 acts as both an acid and a base.

3. Halogenation ;

Aromatic halogenation, illustrated for chlorination, involves , the attachment of positive chlorine to the aromatic ring. The less reactive benzene molecule needs the assistance of a Lewis acid; reaction occurs with the loss of the better leaving group $FeCl_4$

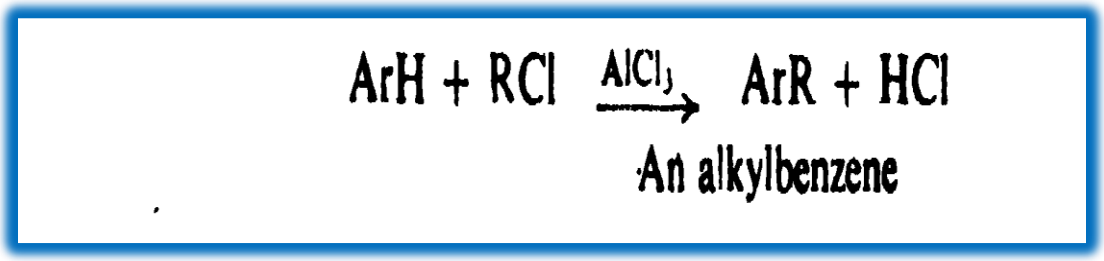
Ar = aryl, any aromatic group with attachment directly to ring carbon



The Lewis acids typically used are aluminum chloride ($AlCl_3$) and iron chloride ($FeCl_3$) for chlorination, and iron bromide ($FeBr_3$) for bromination. The purpose of the Lewis acid is to make the halogen a stronger electrophile. A mechanism for electrophilic aromatic bromination is shown here.

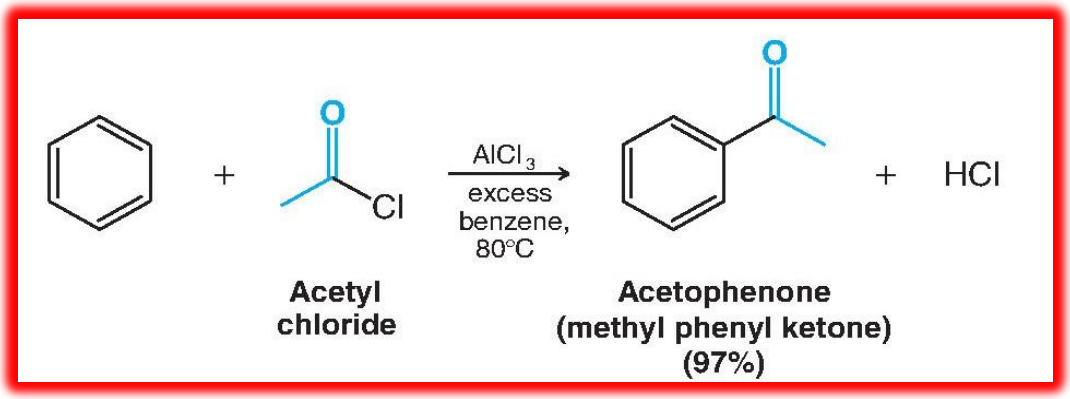
4 . Friedel-Crafts alkylation;

This reaction involves nucleophilic attack by the aromatic ring on the alkyl group of complex .The $A1C1_4^-$ ion is a better leaving group than Cl^- would be. the Friedel-Crafts reaction in its widest sense involves reactants other than alkyl halides and Lewis acids other than aluminum chloride: BF_3, $SnCl_4$, HF, and even H+.



5 .Friedel-Crafts acylation;

Acylation of benzene refers to the substitution of an acyl group (RCO-) on to a benzene ring. In order to be substituted onto the ring, the acyl group must be an electrophile. Acyl chlorides provide an easy way to form an acyl group with a positive charge on the carbon atom.

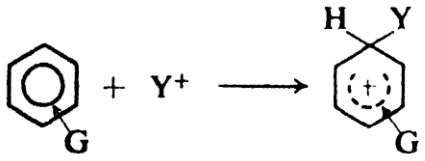


Orientation in monostituted benzenes

Effect of substituent groups

Any group attached to a benzene ring affects the reactivity of the ring and determines the orientation of the next substitution . when an electrophilic reagent attacks an aromatic ring .A group that makes the ring more reactive than benzene is called an activating group ,and causes attack to occur chiefly at positions ortyo and para to it is called an ortho , para director.

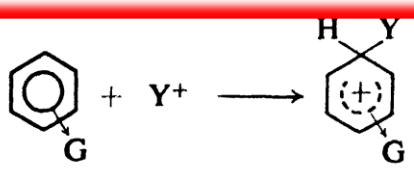
Electrophilic Aromatic Substitution



G releases electrons, stabilizes carbonium ion, activates

G = $-NH_2$
$-OH$
$-OCH_3$
$-NHCOCH_3$
$-C_6H_5$
$-CH_3$

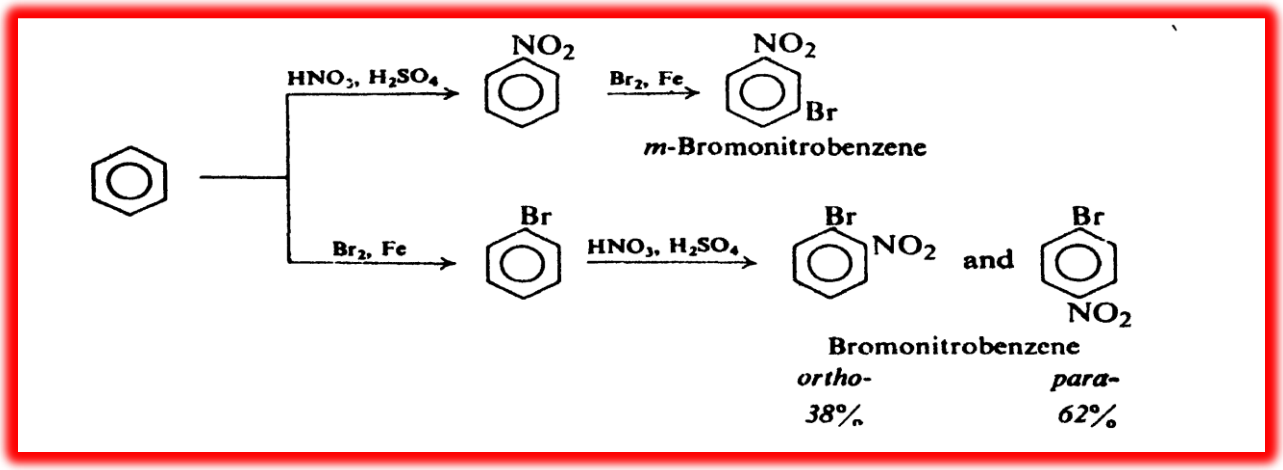
A group that makes the ring less reactive than benzene is called a deactivating group .and causes attack to occur chiefly at positions meta to it is called a meta director.

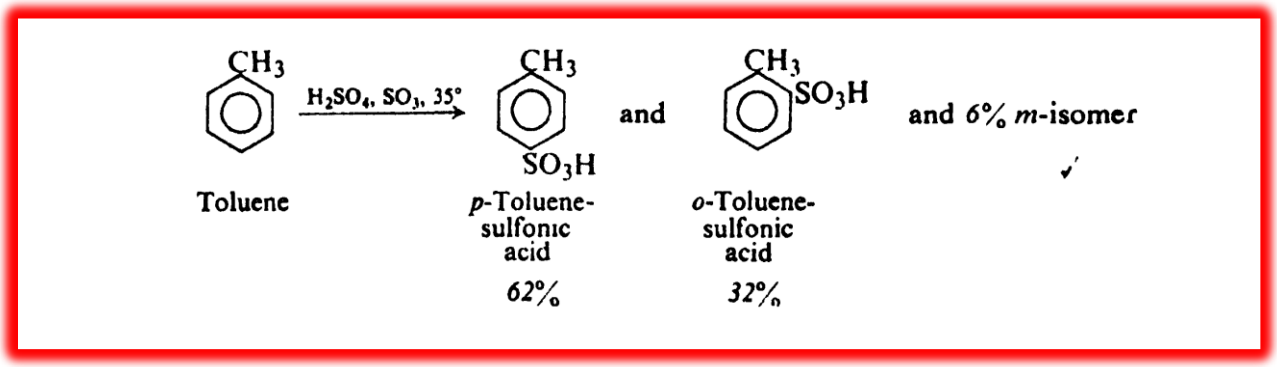


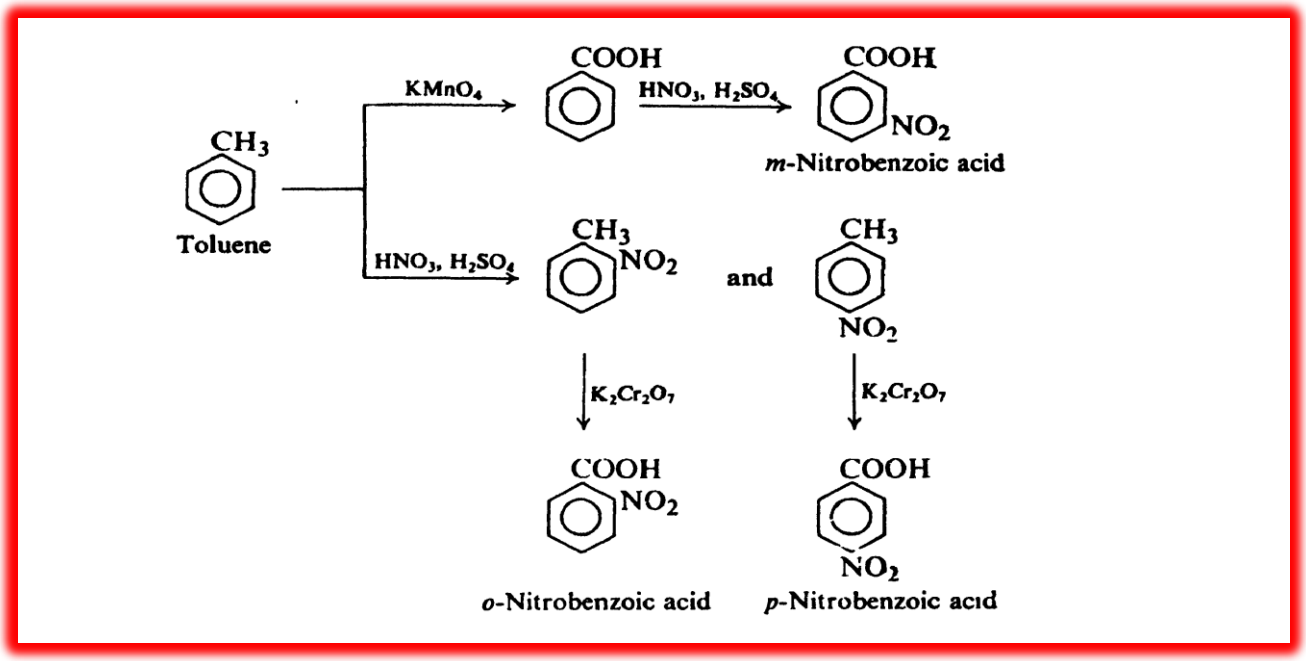
G withdraws electrons · destabilizes carbonium ion, deactivates

G = $-N(CH_3)_3^+$
$-NO_2$
$-CN$
$-SO_3H$
$-COOH$
$-CHO$
$-COR$
$-X$

Examples on orientation in monostituted benzene







References:

1-**Organic Chemistry William H.Brown ,Brent L.Iverson, Eric V.Anslyn Christopher S.Foote, 7th 2014,2012.**

2-R. T.Morrison and R .N. Boyd " organic chemistry " 6th Prentice Hall P , 1205 (1990).

3-T. W. GRAHAM S OLOMONS CRAIG B. FRYHLE \ Organic Chemistry 10th (2011).