Aliphatic Organic chemistry

4022132-3

Course Outline

- Shapes of organic molecules
- Chemical bonding
- Functional groups
- Hybridization
- Stereochemistry
- Hydrocarbons (alkanes; alkenes; alkynes)
- Alkyl halides
- Alcohols
- Ethers and thioethers
- Carbonyl compounds (aldehydes and ketones)
- Carboxylic acids and their derivatives
- Amines

References

Required Reference

Organic Chemistry – Structure and Function, K. Peter C. Vollhardt, Neil E. Schore, (4th edition), W. H. Freeman & Co., New York, USA

Organic Chemistry, Paula Yurkanis Bruice, (4th edition – International edition), Pearson Education, Inc., Upper Saddle River, NJ, USA

Organic chemistry, T.W. Graham Solomons and Craig Fryhle, 9th ed., Wiley, 2007.

Essential Reference

Organic Chemistry, Jonathan Clayden, Nick Greeves, Stuart Warren, Peter Wothers, OUP Oxford, 2001.

Recommended Reference

Organic Chemistry, Jonathan Clayden, Nick Greeves, Stuart Warren, Peter Wothers, OUP Oxford, 2001.

Electronic Materials, Web Sites etc

Scopus ,Science direct , Reaxys, Science finder.

Review on Atomic structure and Electronic configuration

Atomic structure

- **Electrons and energy levels:**

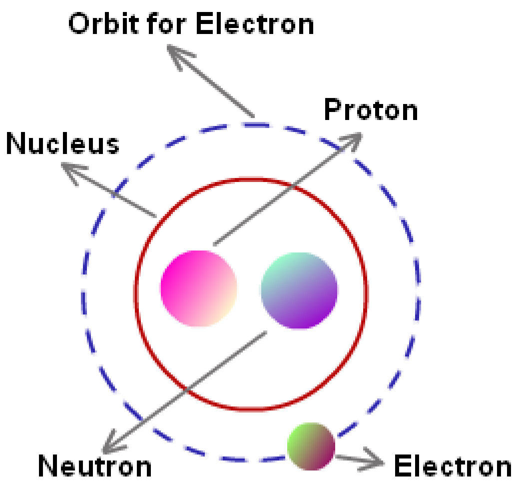
1. Atoms consist of three particles: neutrons, protons and electrons.

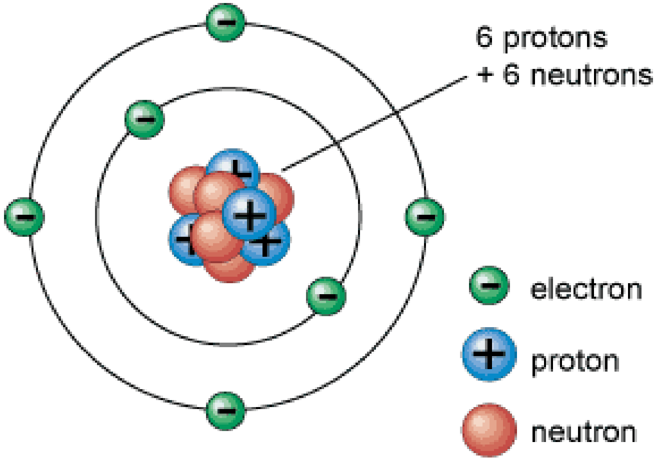
2. Neutrons and protons are found in the nucleus; electrons are outside the nucleus.

3. Neutrons are particles that have no charge, protons are positively charged particles and electrons are negatively charged particles.

4. The atomic number of an element indicates the number of protons.

5. Electrons are distributed around the nucleus in successive shells or principle energy levels of increasing radius.



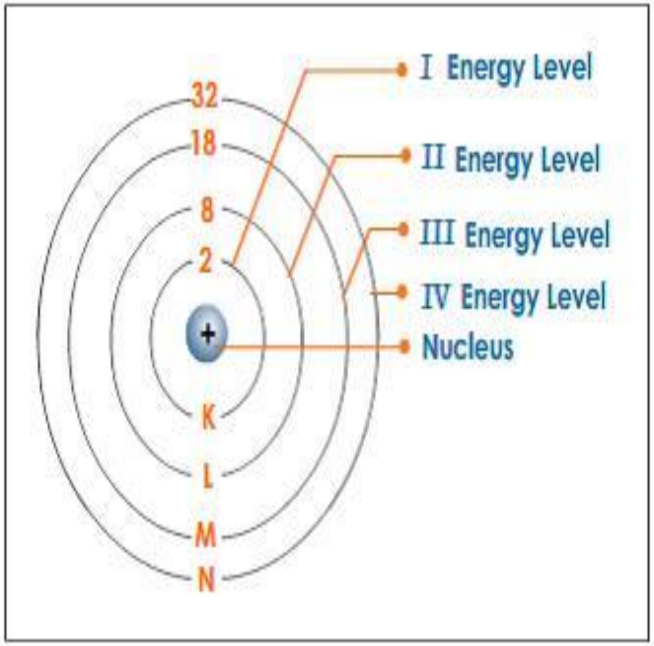


Carbon atom

Atomic structure

6. The electrons in levels close to the nucleus have lower energy than do electrons in levels farther from the nucleus.
7. The various energy levels are designated by capital letters or whole numbers (n)=the number of the energy level (shell)= quantum number.
8. The first energy level, the one closest to the nucleus and therefore the one having the lowest energy, is called the *K* level and corresponds to n=1.
9. The second energy level, farther from the nucleus and with a higher energy content than the *K* level , is called the *L* level and corresponds to n=2.
10. The third energy level, the *M* level, corresponds to n=3; the fourth energy level, the *N* level, corresponds to n=4 and so on.
11. Each energy level has a given capacity for electrons. The *K* level may contain a maximum of 2 electrons and never more . The *L* energy level for 8 electrons the M level for 18 electrons and the N level for 32 electrons.
12. The maximum capacity of a shell is equal to $2n^2$ electrons, where n is the number of the energy level.

The number of electrons in the shell= $2n^2$



Atomic structure

- **Arrangement of electrons in energy levels (shell):**

How many electrons are needed to fill a particular shell?

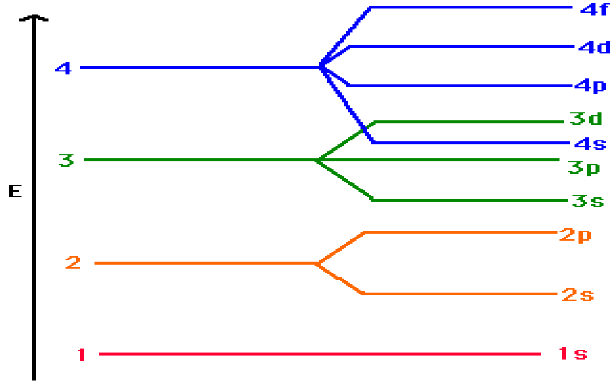
1. The first 2 electrons enter the *K* shell. The next 8 electrons enter the *L* shell.

2. After the *L* energy level is filled, electrons do not fill the third energy level *M* before the fourth energy level *N* is started.

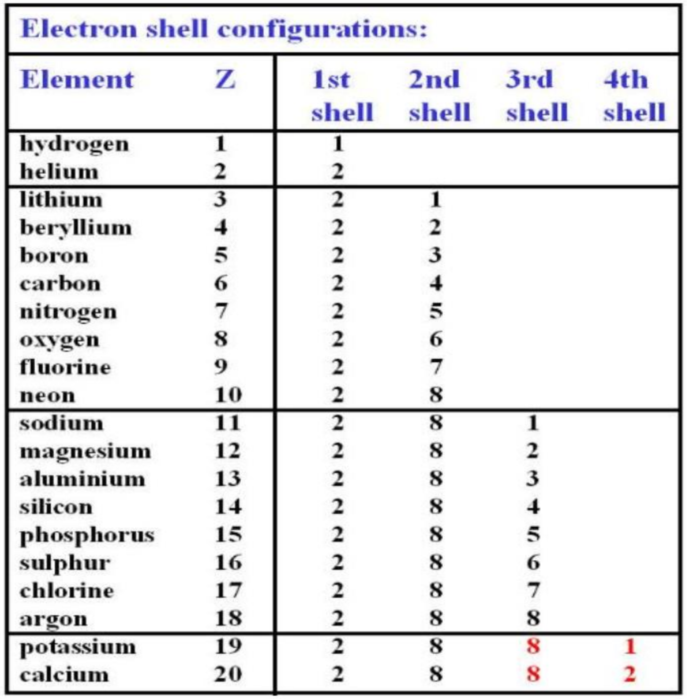
3. In fact, there are never more than 8 electrons in the outermost energy level of an atom. The reason is that 8 electrons in the outermost shell give atoms their greatest stability (noble gas configuration).

   (Valence shell=outer shell)

4. Electrons within each energy level (shell) are located in orbitals.



The table below lists the electron shell arrangements for the first 20 elements.



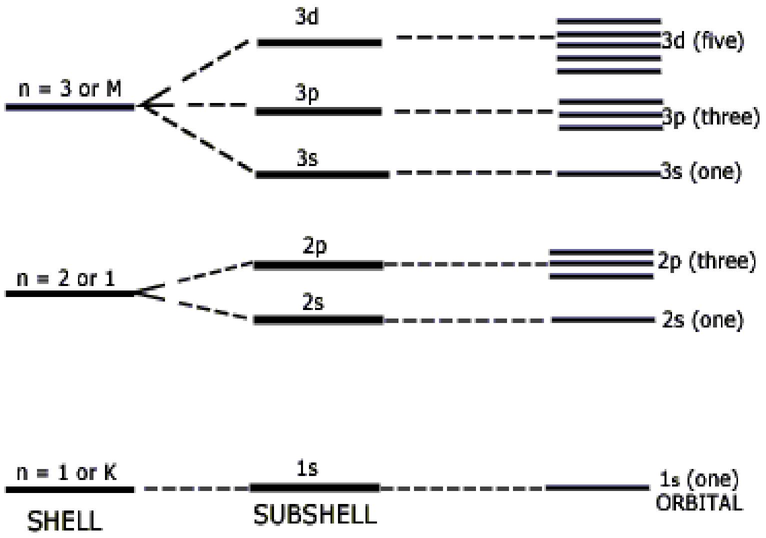
Electron shell configurations:

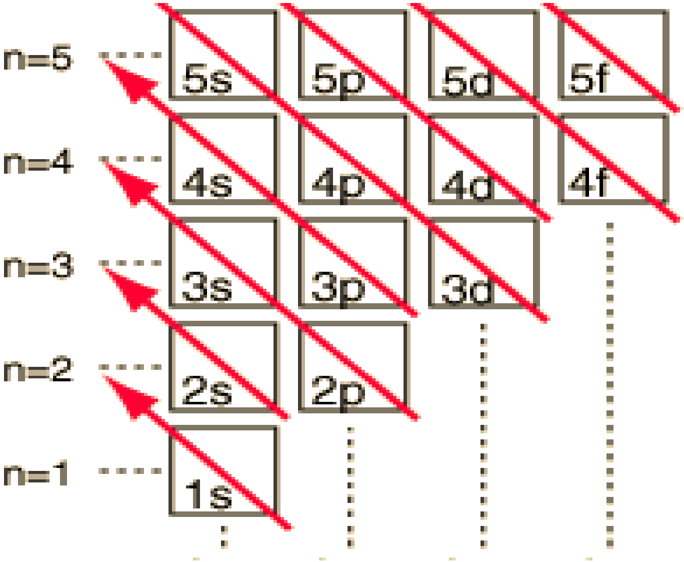
Element	Z	1st shell	2nd shell	3rd shell	4th shell
hydrogen	1	1			
helium	2	2			
lithium	3	2	1		
beryllium	4	2	2		
boron	5	2	3		
carbon	6	2	4		
nitrogen	7	2	5		
oxygen	8	2	6		
fluorine	9	2	7		
neon	10	2	8		
sodium	11	2	8	1	
magnesium	12	2	8	2	
aluminium	13	2	8	3	
silicon	14	2	8	4	
phosphorus	15	2	8	5	
sulphur	16	2	8	6	
chlorine	17	2	8	7	
argon	18	2	8	8	
potassium	19	2	8	8	1
calcium	20	2	8	8	2

Atomic structure

- **Atomic subshells and orbitals:**

1. Represented a specific region in space in which an electron is most likely to be found.
2. Designated by the letters *s, p, d* and *f*.
3. The number of orbitals in the shell=n^2
4. The first energy level (*K* shell) has only one orbital, the 1*s*.
5. The second energy level (*L* shell) has four orbitals: one 2*s* and three 2*p* orbitals.
6. The third energy level (*M* shell) has nine orbitals: one 3*s* and three 3*p* and five 3*d* orbitals.
7. The fourth energy level (*N* shell) has 16 orbitals: one 4*s* and three 4*p*, five 4*d* orbitals and seven 4*f*.

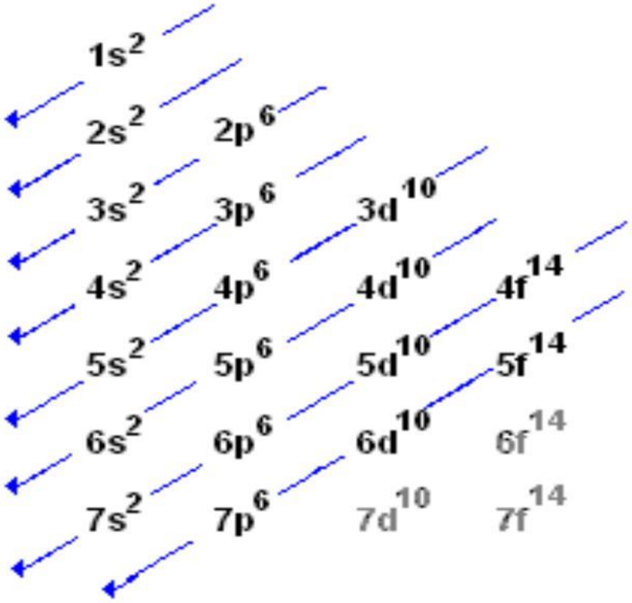


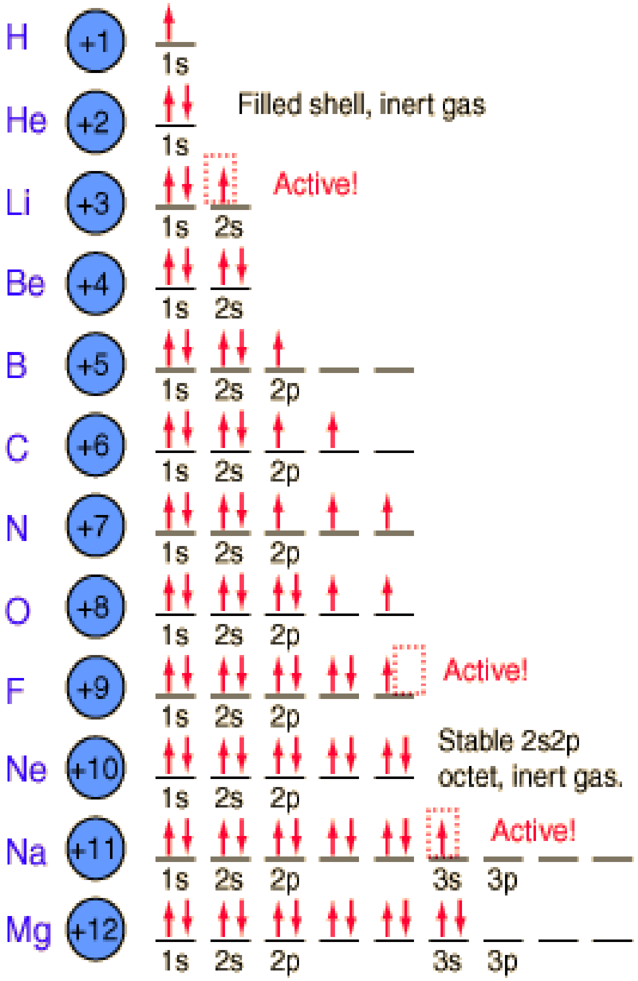


Electronic configuration

Note that when filling the atomic orbitals:

1. An atomic orbital can contain no more than two electrons.
2. Electrons fill orbitals of lower energy first.
3. No orbital is filled by two electrons until all the orbitals of equal energy have at least one electron.





Review

Energy	Shells	Quantum Number n	Subshells	Number Of Orbitals n^2	Orbitals & Drawing Levels Boxes	Number Of Electrons $2n^2$	Orbitals & Electronic coding
Increase ↓	*K*	1	*s*	1	■ 1	2	*1s*
	L	2	*s,p*	4	☐ 1 ☐☐☐ 3	8	*2s,* *2p2p2p*
	M	3	*s,p,d*	9	☐ 1 ☐☐☐ 3 ☐☐☐☐☐ 5	18	*3s,* *3p3p3p,* *3d3d3d3d3d*
	N	4	*s,p,d,f*	16	☐ 1 ☐☐☐ 3 ☐☐☐☐☐ 5 ☐☐☐☐☐☐☐ 7	32	*4s,* *4p4p4p,* *4d4d4d4d4d,* *4f4f4f4f4f4f4f*
	O	5		25		50	
	P	6		36		72	
	Q	7		49		98	

Periodic table

Increasing electronegativity

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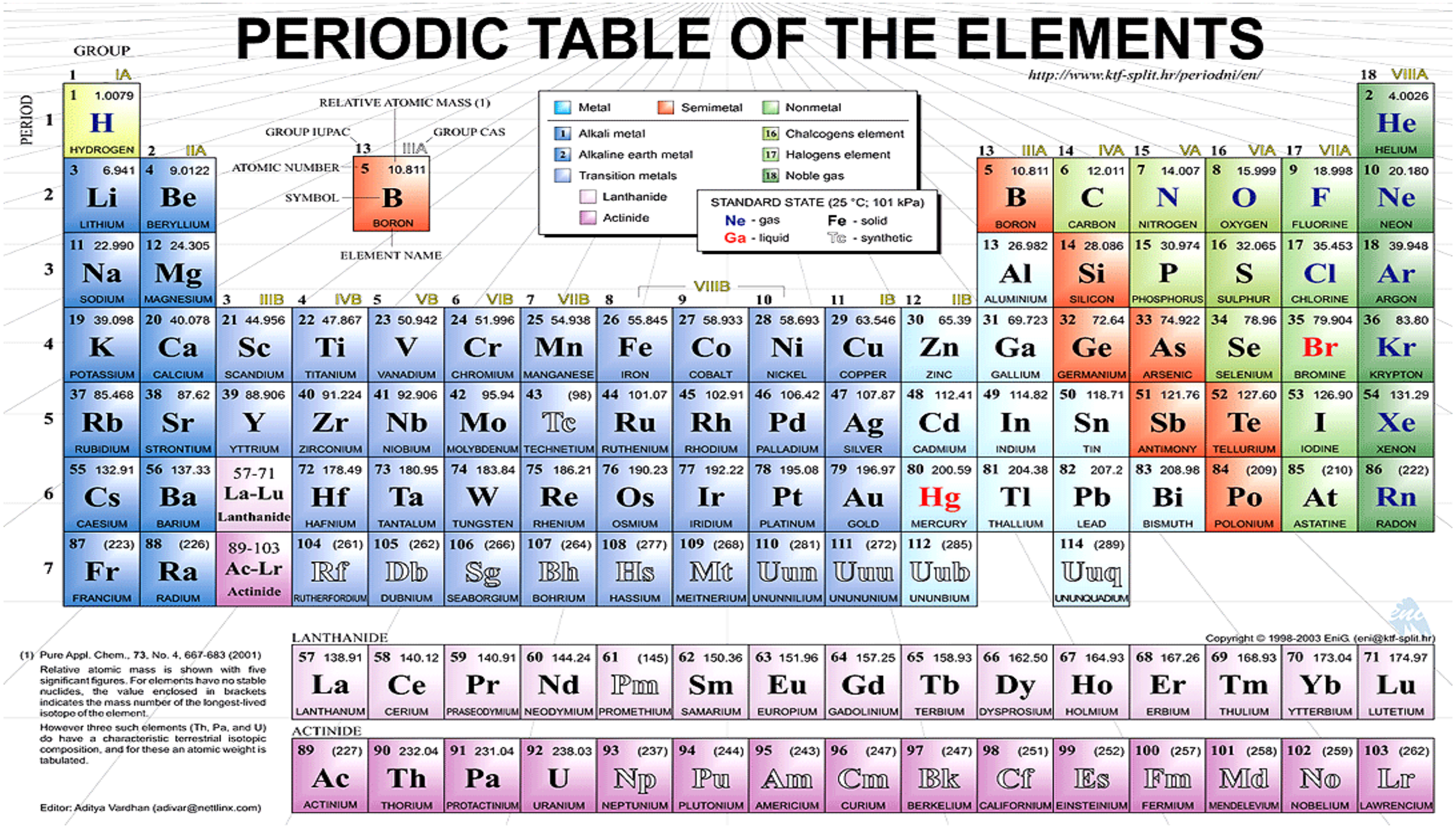


PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

RELATIVE ATOMIC MASS (1)
GROUP IUPAC
GROUP CAS
ATOMIC NUMBER
SYMBOL
ELEMENT NAME
13 IIIA
5 10.811
B
BORON

🟦 Metal 🟥 Semimetal 🟩 Nonmetal
1 Alkali metal
2 Alkaline earth metal
🟦 Transition metals
☐ Lanthanide
☐ Actinide
16 Chalcogens element
17 Halogens element
18 Noble gas

STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Fe - solid
Ga - liquid
Tc - synthetic

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.96 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., **73**, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netlinx.com)

Increasing electronegativity

Organic chemistry

Introduction about organic chemistry

- **Definition:**

The branch of chemistry that deals with carbon/hydrogen-containing compounds and their derivatives.

- **Organic compounds:**

Compounds based on carbon and hydrogen (hydrocarbons). Also carbon compounds containing other elements, especially oxygen, nitrogen, sulfur, phosphorus.

- **The uniqueness of carbon:**

The number of known organic compounds are several millions, and thousands of new ones are synthesized and described each year.

Carbon form so many compounds ,that’s due to the structure of carbon atom and the position of carbon in the periodic table, which enable it to form strong bonds with other carbon atoms and with other elements.

- **Inorganic compounds:**

Compounds formed from elements other than carbon. There are only 100,000 known inorganic compounds.

Introduction about organic chemistry

- **Sources of organic compounds:**

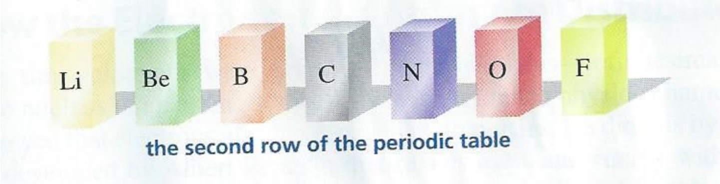
Petroleum, coal and natural gas are natural reservoirs from which many organic materials are extracted.

All were formed over long periods of time, from decay of plants and materials.

- **Importance:**

1. Organic compounds form the basis important constituents of, many commercial products including pharmaceuticals; petrochemicals and products made from them (including lubricants, solvents, etc.); plastics; fuels and explosives; etc.
2. As indicated, the study of organic chemistry overlaps with organometallic chemistry and biochemistry, but also with medicinal chemistry, polymer chemistry, as well as many aspects of materials science.

Carbon

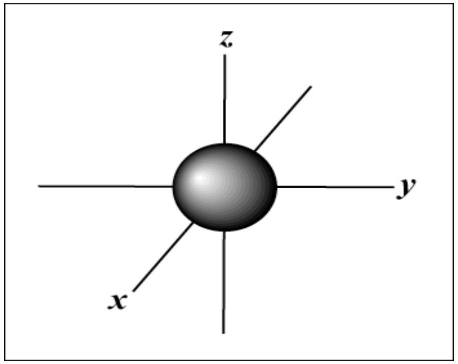


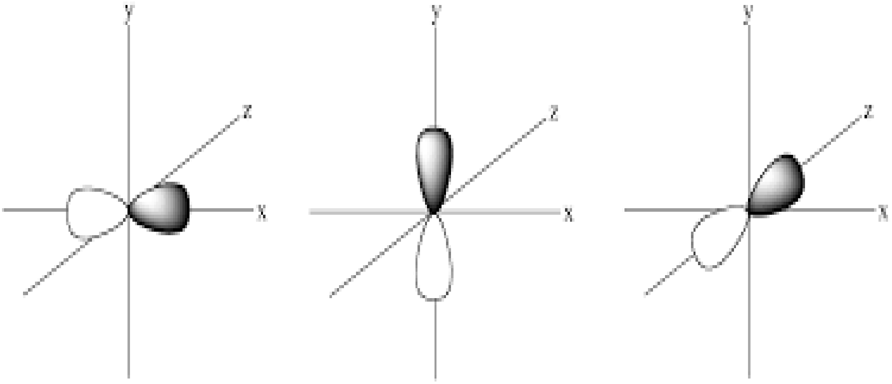
- The existence of carbon in the middle of the second row of periodic table, makes it special.
- The atoms to the left of carbon have a tendency to give up electrons
- The atoms to the right of carbon have a tendency to accept electrons
- **Carbon** neither readily gives up nor readily accepts electrons.
- Instead, it can **shares** electrons with several different kinds of atoms and also with other carbon atoms.

Shapes of organic molecules

Shapes of organic molecules

1. Most of organic compounds have only *s* and *p* orbitals.
2. An *s* orbital is a spherically electron cloud with the atom’s nucleus at its center.
3. A *p* orbital is a dumbbell-shaped electron cloud with nucleus between the two lobes.
4. Each *p* orbital is oriented along one of three perpendicular coordinate axes, that is, in the *x, y* or *z* direction.
5. The *p* orbitals are designated as $2p_x$, $2p_y$ and $2p_z$ if they are located in the L shell and so on.
6. Note that the three 2*p* orbitals are of equal energy and so on.

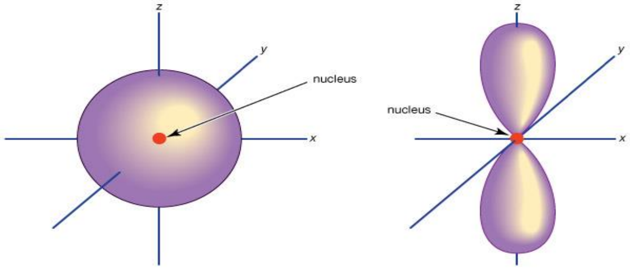




$2p_x$ orbital

$2p_y$ orbital

$2p_z$ orbital



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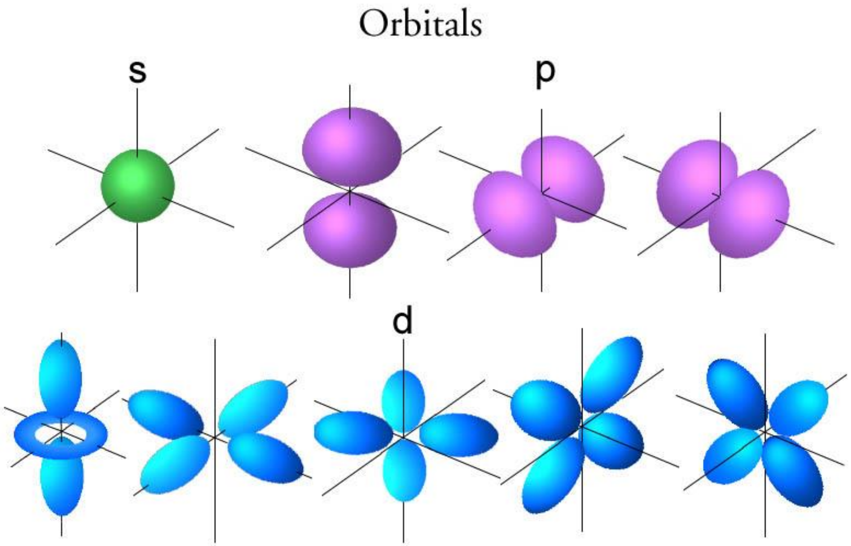
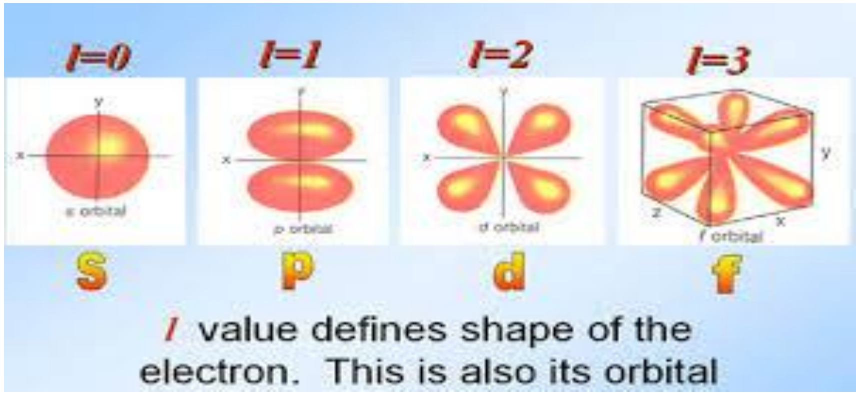
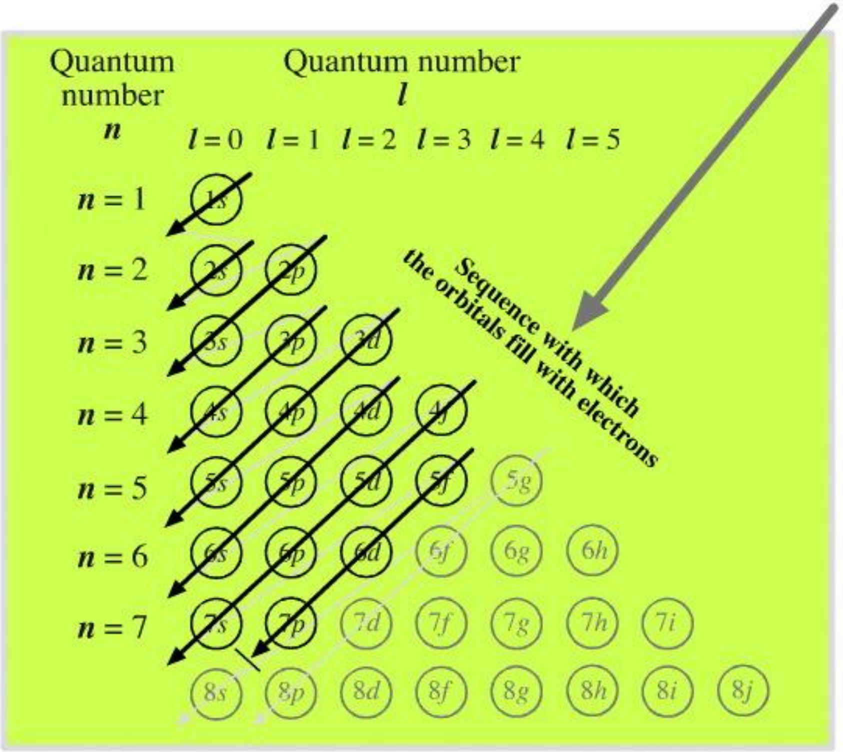
Shapes of organic molecules





l value defines shape of the electron. This is also its orbital

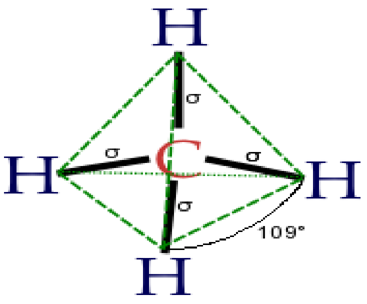


Hybridization

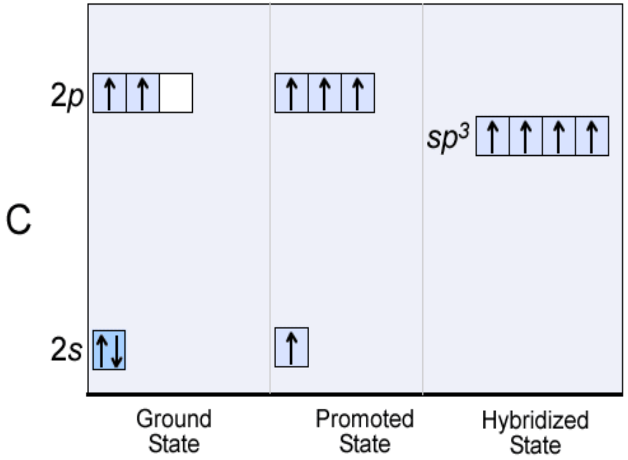
Hybridization

sp3 Hybridization: the tetrahedral carbon:

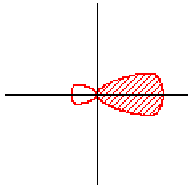
- The simplest organic molecule is methane.
- Methane is known to consist of a carbon atom bonded covalently to four hydrogen atoms, thus having the molecular formula CH_4.
- Each of the four carbon-hydrogen bonds is identical and directed toward the corners of a regular tetrahedron with all H-C-H bond angles equal to 109.5°.
- The tetrahedron is pyramid-like structure with the carbon atom at the center and each of the four attached hydrogen atoms at the corner.
- The electron configuration for C's ground state is $1s^2\,2s^2\,2p^1_x\,2p^1_y\,2p^0_z$.
- In order for C to be able to form 4 bonds, one electron from the *2s* orbital is promoted to the empty *2pz* orbital - this is referred to as the promoted state; or excited or activated state; this leads to the formation of hybrid orbitals - one *s* orbital mixes with the three *p* orbitals to form four *sp3* hybrid orbitals (each having 25% *s* and 75% *p* character), thus called hybridized state. Once the hybrid orbitals are formed, no longer refer to any of the three *p* orbitals.
- The four *sp3* orbitals now form *sigma* bonds with four H atoms to produce the tetrahedral-shaped methane molecule.

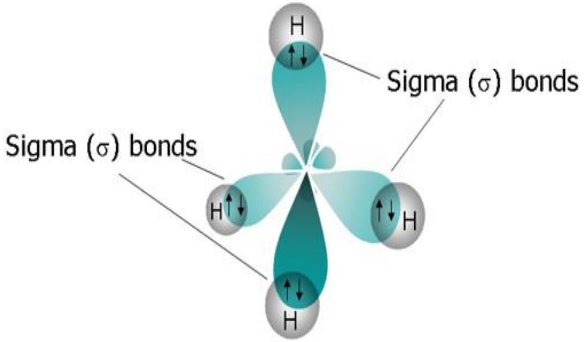


sp^3 Hybridization



Sp3 shape

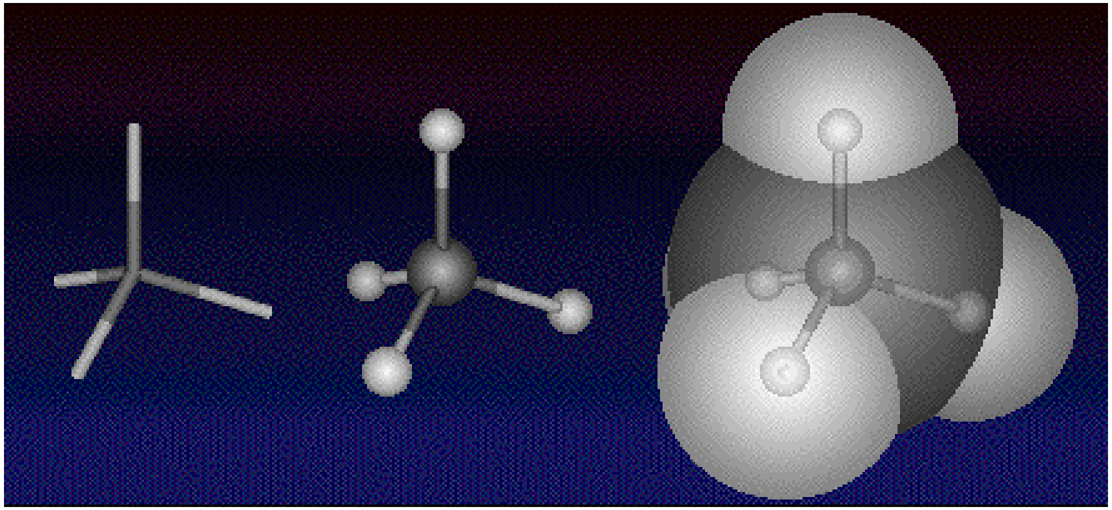




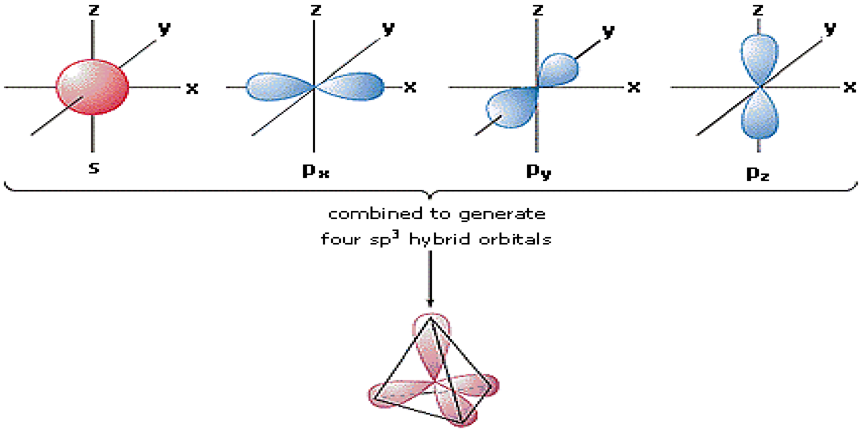
Carbon is sp^3 hybridized

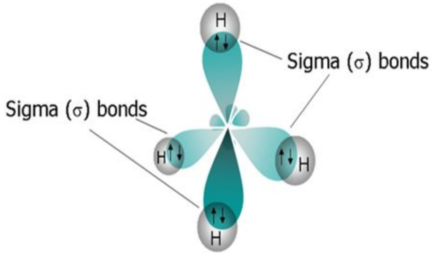
tetraedral arrangement of 4 equivalent orbitals can form C-C bonds and produce a huge number of different compounds.

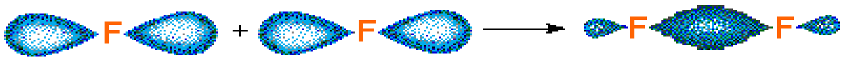
Carbon and Hydrogen have similar electronegativity (C: 2.5, H: 2.1). C-H bond is not very reactive, ‘saturation‘ of free valences of C with H results in stable molecules.



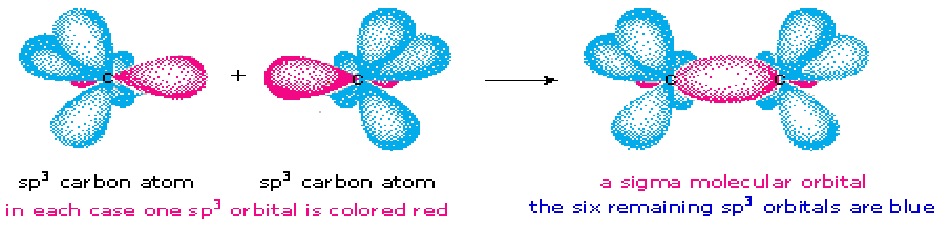
- In the case of bonds between second period elements, *p*-orbitals or hybrid atomic orbitals having *p*-orbital character are used to form molecular orbitals.
- For example, the *sigma* molecular orbital that serves to bond two fluorine atoms together is generated by the overlap of *p*-orbitals.
- Another example, two *sp³* hybrid orbitals of carbon may combine to give a similar sigma orbital.
- When these bonding orbitals are occupied by a pair of electrons, a covalent bond, the *sigma* bond results.
- Although the remaining *p*-orbitals were ignored and dose not lead to any additional bonding, as shown by activating the fluorine.







A σ-orbital formation from two p-orbitals



B σ-orbital formation from two sp^3 orbitals

Hybridization

Hybridization involving multiple bonds:

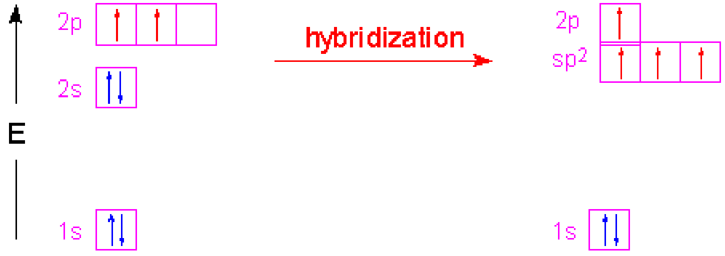
- Only a maximum of two electrons can occupy any orbital whether it is an atomic orbital or a molecular orbital due to electron-electron repulsion.
- When drawing a double or a triple-bond between two atoms, thus either four or six electrons are directly between these two atoms. Since this is impossible, so must have these extra electrons off to the side in what refer to as *pi* bonds.
- Therefore, all multiple bonds are composed of two different kinds of molecular bonds called *pi*-bonds and *sigma*-bonds.
- The *sigma*-bond is defined as the linear overlap of atomic orbitals (hybrids except for hydrogen) in which two electrons are directly between the two bonded nuclei.
- *Pi*-bonds are defined as the parallel overlap of *p*-orbitals. A double bond has one *sigma*-bond and one *pi*-bond. A triple bond thus consists of a *sigma*-bond and two *pi*-bonds with the *pi*-bonds in different planes.

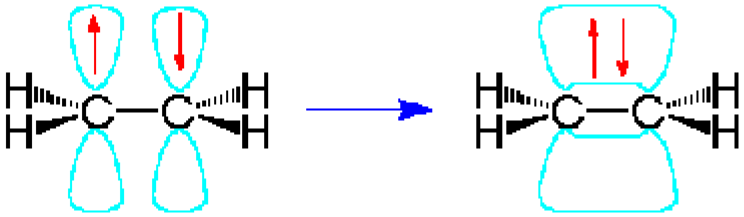
Hybridization

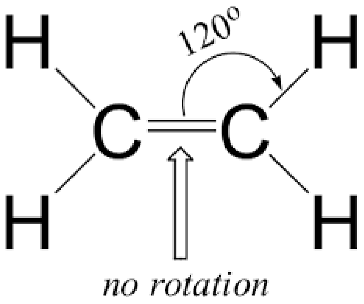
sp2 Hybridization:

In the molecule C_2H_4, ethene=ethylene, both carbon atoms will be *sp*^{2} hybridized and have one unpaired electron in a non-hybridized *p* orbital.

- These *p*-orbitals will undergo parallel overlap and form one *pi* bond with bean-shaped probability areas above and below the plane of the six atoms. This pair of bean-shaped probability areas constitutes one *pi*-bond and the pair of electrons in this bond can be found in either bean-shaped area.
- The 3-dimensional model of ethene is therefore trigonal planar with H-C-H and H-C-C bond angles of 120º.







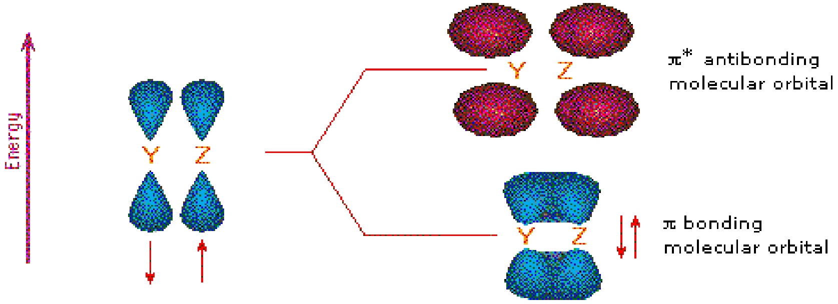
Hybridization

- The π orbital is formed from two *p*-orbitals by a lateral overlap.

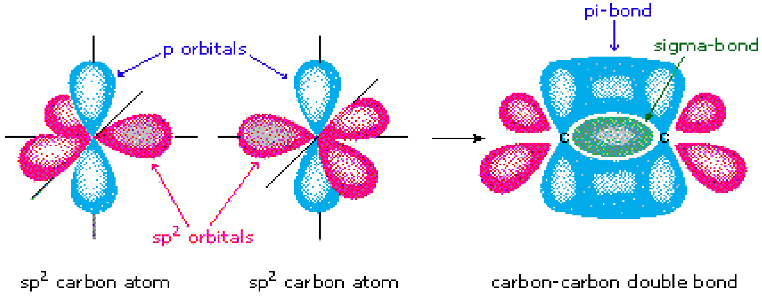
- π-orbitals (*pi*-bonds) are weaker than *sigma* bonds. Thus, *pi*-bonding between two atoms occurs only when a *sigma* bond has already been established.

- *pi*-Bonding is generally found only as a component of double and triple covalent bonds.

- Since carbon atoms involved in double bonds have only three bonding partners, they require only three hybrid orbitals to contribute to three sigma bonds. A mixing of the 2*s*-orbital with two of the 2*p* orbitals gives three sp^2 hybrid orbitals, leaving one of the *p*-orbitals unused. Two sp^2 hybridized carbon atoms are then joined together by *sigma* and two *p*-orbitals overlap to give *pi*-bonds (a double bond).

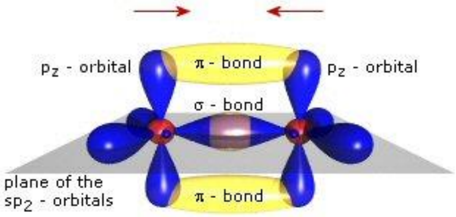


A π-orbital formation from two p-orbitals



sp^2 carbon atom
sp^2 carbon atom
carbon-carbon double bond

B Formation of σ- and π- molecular orbitals from two sp^2 hybridized carbon atoms



Hybridization

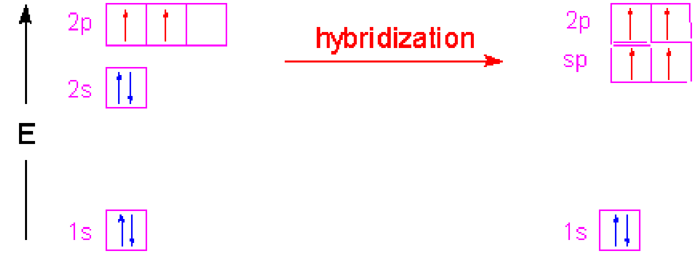
sp Hybridization:

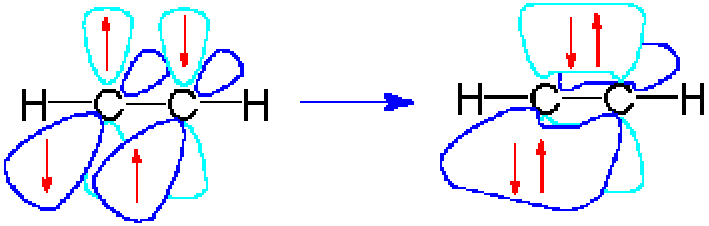
- At H_2C_2 ethyne=acetylene, both carbon atoms will be *sp* hybridized and have one electron in each of two unhybridized *p* orbitals.

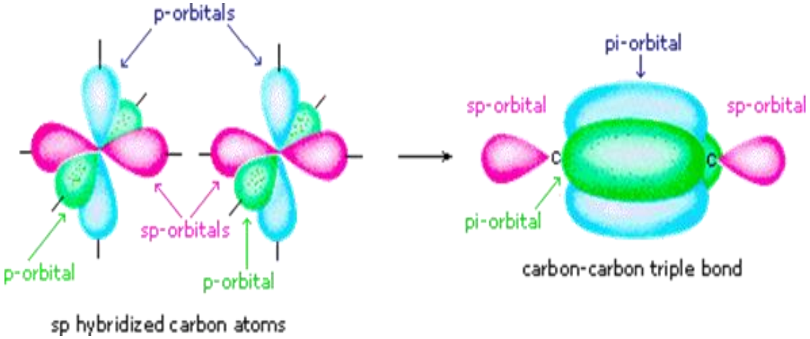
- These *p* orbitals will undergo parallel overlap to form two *pi*-bonds at right angles to each other.

- The 3-dimensional model of acetylene is therefore linear with H-C-C bond angles of 180º.

- In the case of carbon atoms with only two bonding partners only two hybrid orbitals are needed for the sigma bonds, and these *sp* hybrid orbitals are directed 180º from each other. Two *p*-orbitals remain unused on each *sp* hybridized atom, and these overlap to give two *pi*-bonds following the formation of a *sigma* bond (a triple bond).



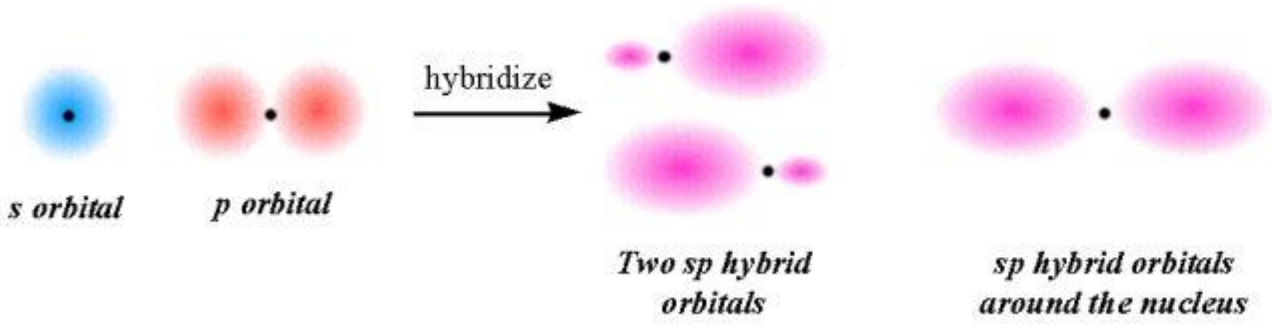




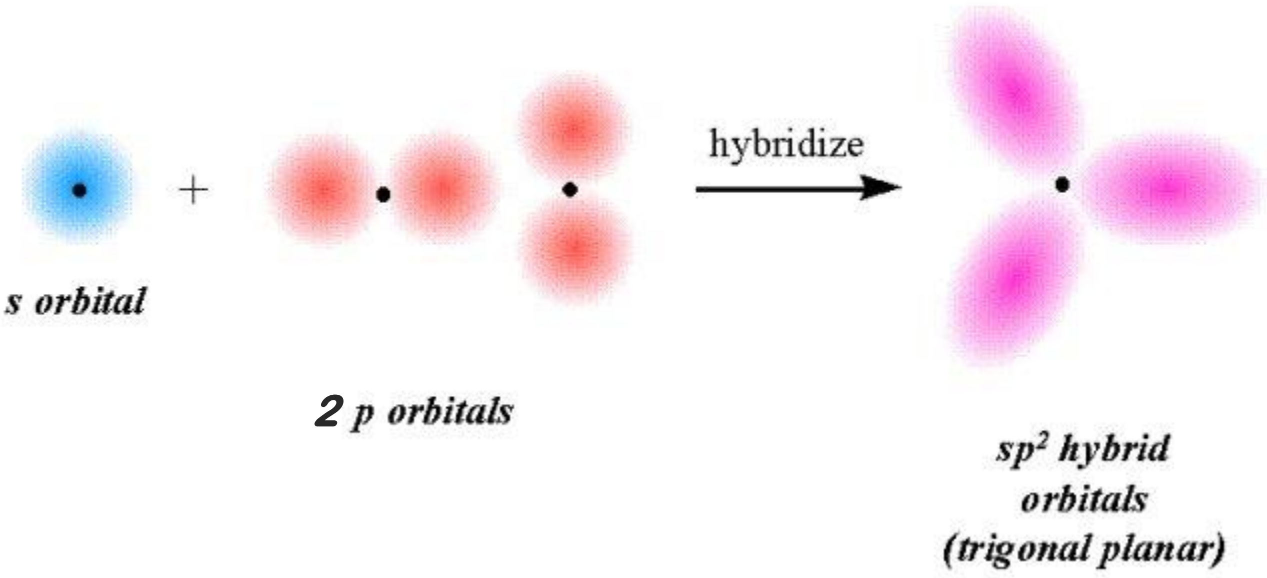
Hybridization of Atomic Orbitals

Orbitals of one atom can be 'mixed' – hybridization leads to 'new' orbitals

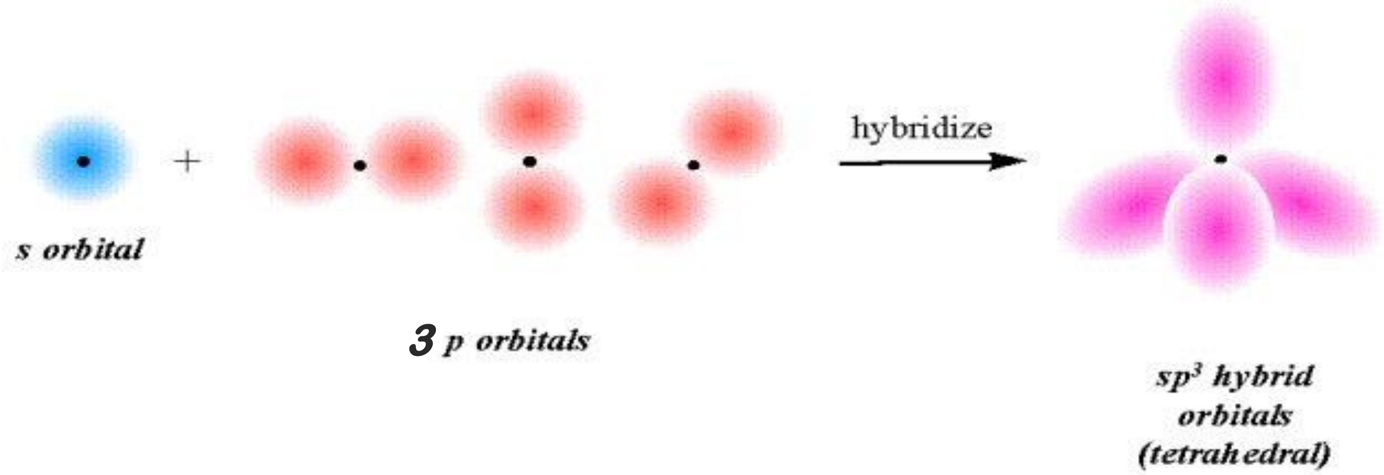
SP-Hybridization

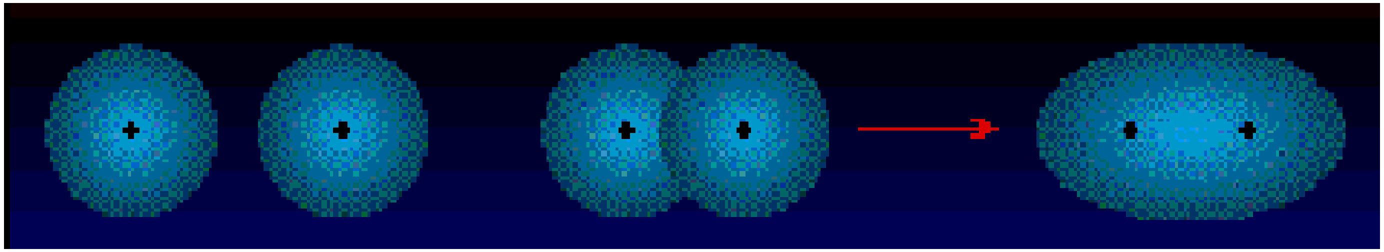


SP^2-Hybridization

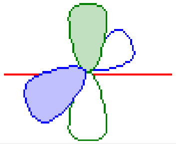
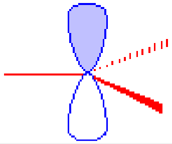
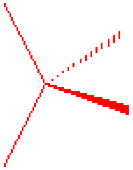


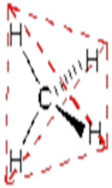
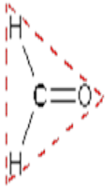
SP^3-Hybridization





Electron-Pair Geometry and Molecular Geometry

Number of Groups Attached to a Central Atom	Description and 3-Dimensional Shape
Two Groups...sp	2 groups = sp hybridization 180 degree bond angle linear electron-pair geometry 
Three Groups...sp^2	3 groups = sp^2 hybridization 120 degree bond angles trigonal planar electron-pair geometry 
Four Groups...sp^3	4 groups = sp^3 hybridization 109.5 degree bond angles tetrahedral electron-pair geometry 

Configuration	Bonding Partners	Bond Angles	Example
Tetrahedral	4	109.5°	
Trigonal	3	120°	
Linear	2	180°	

Stereochemistry

Stereochemistry

Introduction:

Stereochemistry is a branch of chemistry that deals with the:

- Description of the arrangements of atoms in molecules.
- Molecular shape depending on the physical and chemical properties of molecules.

Definition:

The study of the three-dimensional orientations of the atoms in molecules as they undergo a chemical reaction.

Classification:

1. Constitutional isomers.
2. Stereoisomerism.

STRUCTURE AND ISOMERISM

Isomers are compounds have identical molecular formulas but different structural formulas (different atom arrangements).

If the compounds with the same molecular formulas have their atoms bonded in different orders, they have different structure and are said to be structural isomers of each other.

- **Isomers (same molecular formula, non-identical molecules)**
  - **Constitutional Isomers** (different C – C connectivity)
    - **Skeletal Isomers**
    - **Positional Isomers**
    - **Functional group Isomers**
  - **Stereoisomers** (same C – C connectivity, different arrangement of atoms in space)
    - **Geometrical Isomers**
    - **Conformational Isomers**
    - **Optical Isomers**

Stereochemistry

1. Constitutional isomers:

Two compounds that have the same molecular formulas but different structural formulas.

Classification:

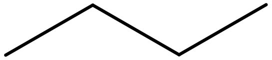
a) **Structural:** are different in the number of carbon atoms that form the carbon chain. Such as alkanes (methane CH_4, ethane CH_3CH_3, ….).

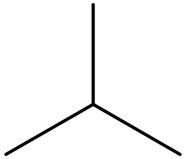
b) **Positional:** are different in the position of the functional group. Such as 2-pentanol $CH_3CH_2CH_2CHOHCH_3$ and 3-pentanol $CH_3CH_2CHOHCH_2CH_3$.

c) **Functional:** are different in the types of the functional group. Such as ethanoic acid CH_3COOH and ethylamine $CH_3CH_2NH_2$.

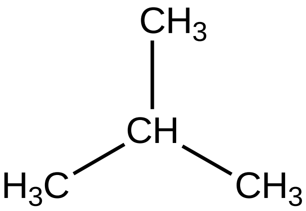
Skeletal Isomerism

Skeletal isomerism differ in the arrangement of the carbon atoms that is the arrangement of the carbon skeleton. Alkanes demonstrate best skeletal isomerism. In the first three members of the class CH_4, CH_3CH_3 and $CH_3CH_2CH_3$ Only one structural formula can be drawn so, they do not exhibit this kind of isomerism. Starting from C_4H_{10}, It has two structures or isomers that can be drawn for the same chemical formula as follows





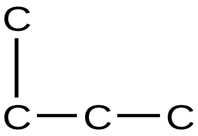
$H_3C-CH_2-CH_2-CH_3$



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ & CH & \\ H_3C & & CH_3 \end{array}$$

n-Butane isobutane n-Butane isobutane

Students must be cautious while determining the straight continuous chain. For example, the carbon chain:



$$\begin{array}{l} C \\ | \\ C-C-C \end{array}$$

(a)

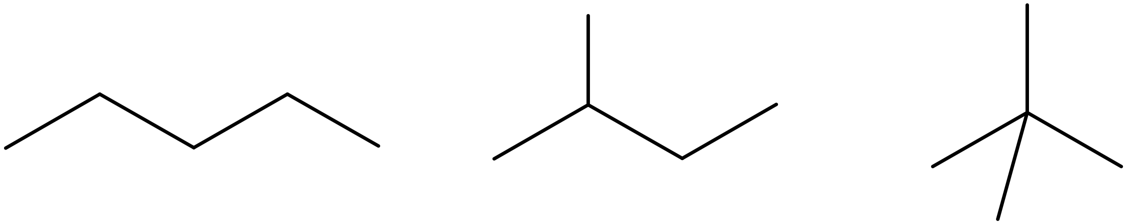
$C-C-C-C$

(b)

or

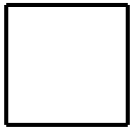
Skeleton in both (a) and (b) is the same and straight continuous chain does not mean that they are linear since the carbon atoms are free to rotate (move) in any directions without breaking the C-C bond. Both (a) and (b) structures represent the compound butane and the 4 carbon atoms making the molecular skeleton are in a straight chain.

Let us try to find out the numbers of skeletal isomers of the next alkane C_5H_{12}

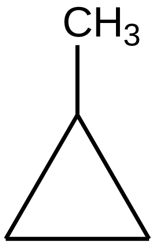


Students should notice that there is only three skeletal isomers of the C_5 alkane and any other structure will be repetition of one of the three.

Skeletal isomerism in cycloalkanes also can be explained by the same principle. For example the following cycloalkane skeletal isomers can be formed for the molecular formulaC_4H_8.



Cyclobutane



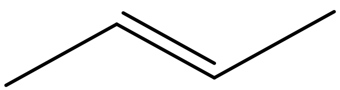
methylcyclopropane

It should be noted that the alkene with the same molecular formula is not a skeletal isomer of cyclobutane and meth , since it belongs to a different family of hydrocarbons

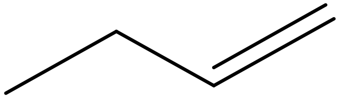
Exercise: Draw all possible isomers of cycloalkanes with molecular formula C_5H_{10}

2-Positional Isomerism

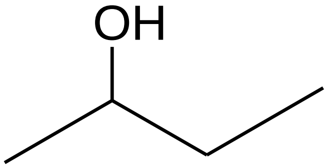
Positional isomers have the same carbon skeleton but differ in the position of a non-carbon group (or the functional group), for example the following two compounds:



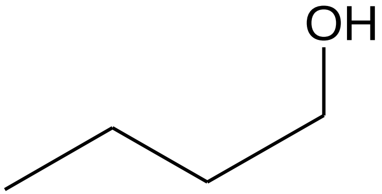
2-Butene



1-Butene



2-Butanol



1-Butanol

Positional isomer have the same carbon skeleton but differ only in the position of the OH group.

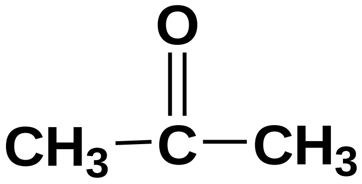
Positional isomers can also exist in alkenes and alkynes: (The same skeleton but different positions of the double bond)

3-Functional Isomerism

Compounds that have the same molecular formulas but belong to the different classes of organic compounds are called functional isomers. There are two functional isomers for the molecular formulas C_2H_6O

CH_3-CH_2-CHO

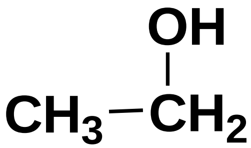
Aldehyde



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Ketone

Another example the following isomers are functional isomers with molecular formulas C_3H_6O



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH_2}$$

Alcohol

CH_3-O-CH_3

Ether

Stereochemistry

2. Stereoisomerism:

One aspect of stereochemistry that relates to biological processes.

Two compounds that have not only the same molecular formulas but also the identical sequence of bonding of the atoms in the molecule.

They differ in one respect only the spatial orientation or configuration of their constituent atoms.

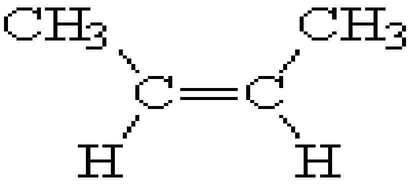
Classification:

a) Geometric isomers:

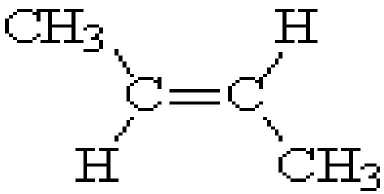
Geometric isomers differ from one another only in the spatial orientation of the groups attached to the C=C bond.

Certain alkenes can exist as *cis* or *trans* isomers, such as 2-butene can exist as *cis*-2-butene and *trans* -2-butene.

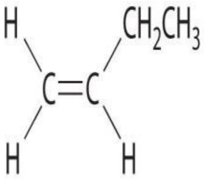
When two similar or large groups are on the same side of the double bond, the compound is called the *Cis* isomer; when they are on the opposite side of the double bond, the compound is called the *trans* isomer.



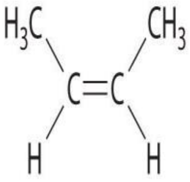
cis-2-Butene



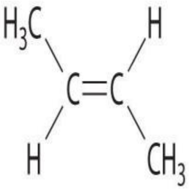
trans -2-Butene



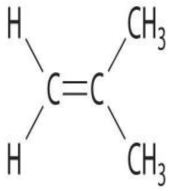
1-Butene
bp 26.2C
mp 2185.3C



Cis-2-butene
bp 3.7C
mp 2138.9C



Trans-2-butene
bp 0.8C
mp 2105.5C



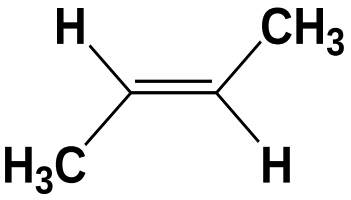
2-Methyl-1-propene
bp 26.9C
mp 2140.4C

Geometric Isomerism

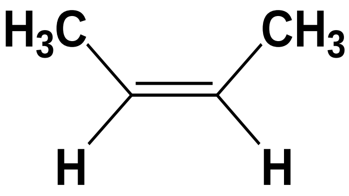
- A type of stereoisomerism is geometric isomerism, which occurs in alkenes and cyclic compounds.
- Geometric isomers are compounds that have different configurations because of the presence of rigid structure in the molecule. For alkenes there are only two geometric isomers that correspond to each double bond (cis and trans).
- If the two identical groups are on the same side of a double bond or ring, the isomer is cis, and if they occur on opposite sides, trans.
- This method is not convenient when there are no identical groups.
- The configuration of these can be specified using the letters Z and E, (Z) Zusammen means together and (E) entgegen means apposite. For example if the two high-priority groups are together on the same side, the configuration is Z. If they are on opposite side, the configuration is E.

- The priority sequence depends on atomic number, the highest atomic number getting the highest priority. The priority order of some atoms commonly found in organic compounds is:
    - High Priority I > Br > Cl > S > F > O > N > C > H Low Priority

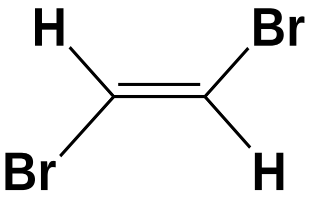
For example



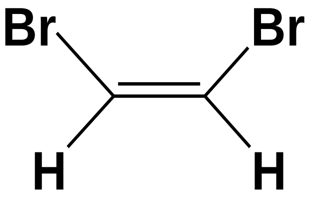
Trans or E



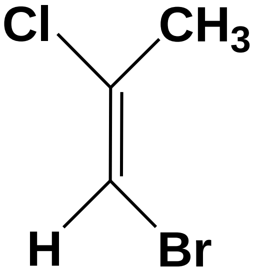
Cis or Z



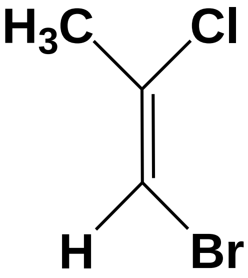
Trans or E



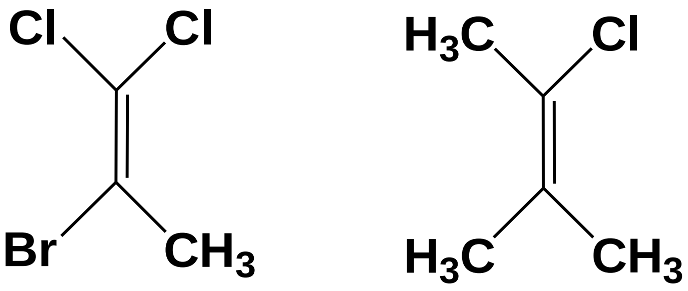
Cis or Z



E



Z



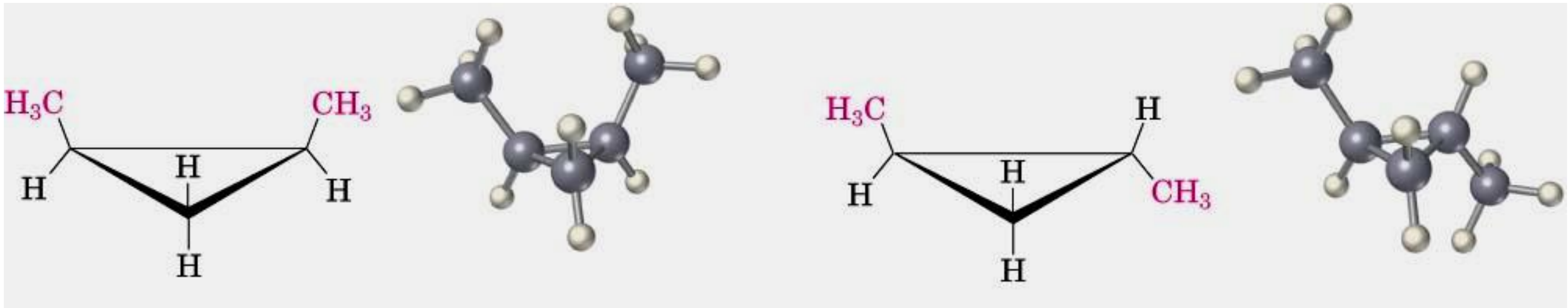
No geometric isomerism

Stereoisomerism in cycloalkanes

For cycloalkanes, cis-trans isomers have to be considered:

Cis: both substituents (functional groups of interest) on the same side of the ring

Trans: substituents (functional groups of interest) on different sides of the ring



Stereochemistry

b) Optical isomerism:

In optical isomerism, the optically active compound differ from another in its effect on plane-polarized light.

- Plane-polarized light

A light vibrates in one plane only.

- Ordinary white light

A bundle of rays of different wavelength vibrating in all possible planes.

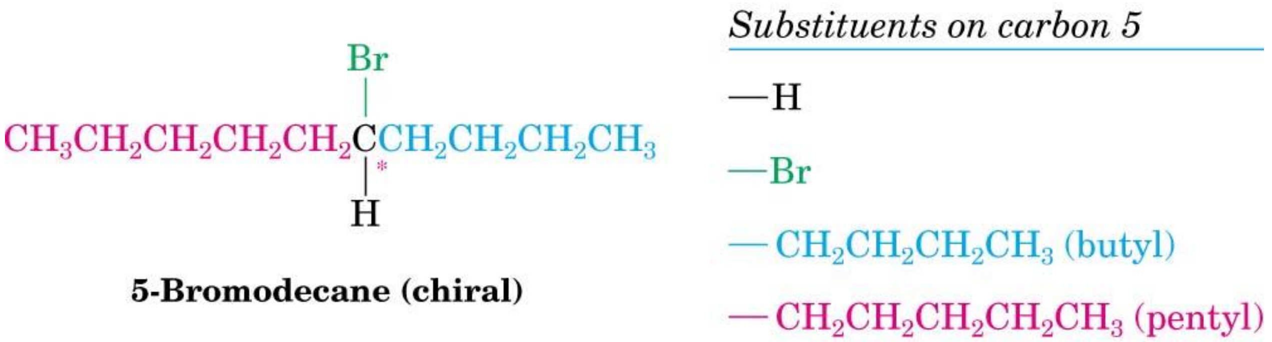
- Optically active compound (chiral compound)

Compound has the ability to change the direction of plane-polarized light or to rotate it.

Also it is called chiral compound, because it has at least one chiral carbon atom (chirality center).

- Chiral carbon atom (chirality center)

A point in a molecule where four different groups (or atoms) are attached to carbon.



$CH_3CH_2CH_2CH_2CH_2\overset{Br}{\underset{H}{C^*}}CH_2CH_2CH_2CH_3$

5-Bromodecane (chiral)

Substituents on carbon 5

—H

—Br

—$CH_2CH_2CH_2CH_3$ (butyl)

—$CH_2CH_2CH_2CH_2CH_3$ (pentyl)

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Stereochemistry

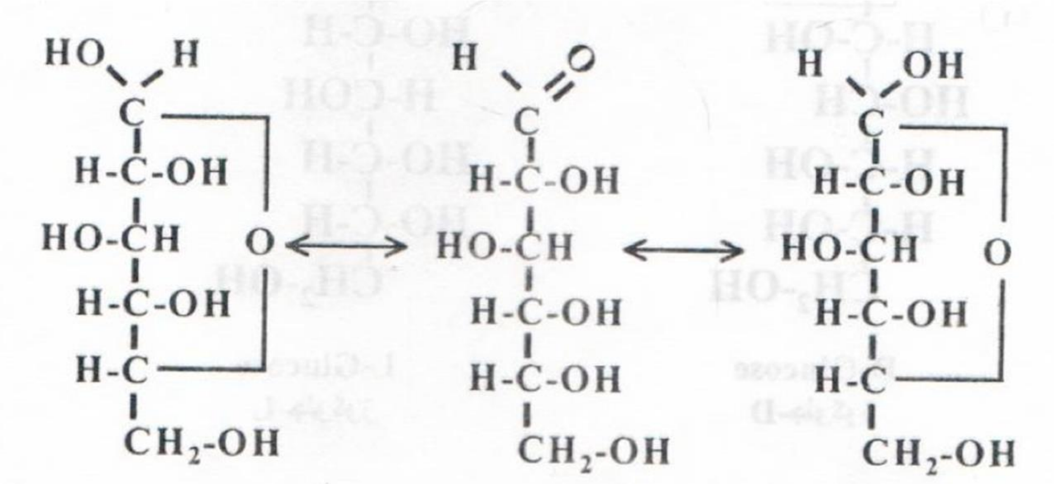
- Optical activity:

The rotation itself is called optical activity.

- Rotational change (mutarotation), optical rotation:

The change in the degree of deviation of polarized light while passing the solution of optically active compound in the polarimeter as a result of the transformation of alpha (when the hydroxyl group of carbon atom 1 is on the right in the D isomer) to beta (when the hydroxyl group of carbon atom 1 is on the left in the D isomer) and vice versa, while breaking of hemiacetal bond in one configuration and re-association to form the other until the solution reaches equilibrium.

Fisher project

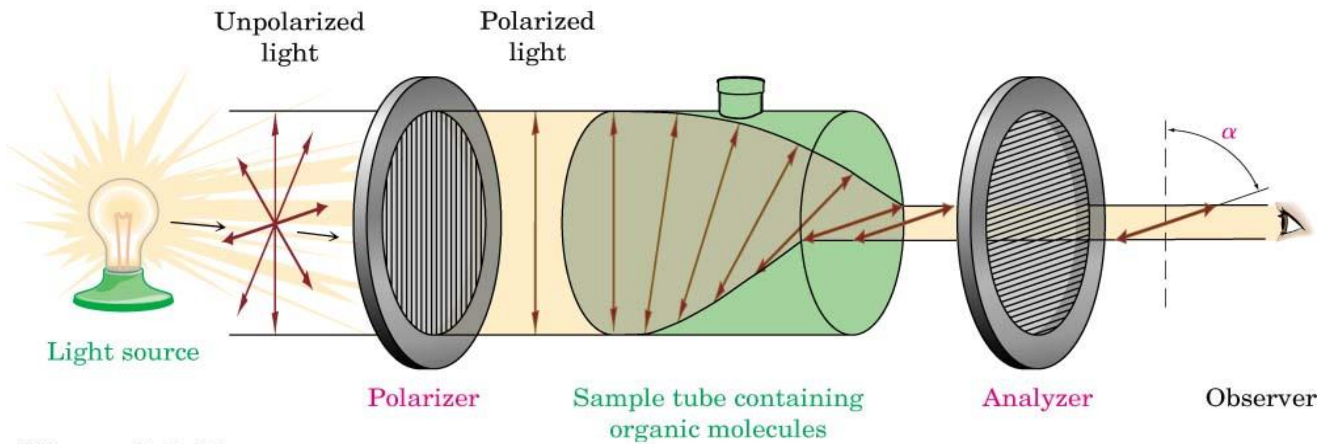


β,D-Glucose (63%) D-Glucose (1%) α,D-Glucose (36%)

Stereochemistry

- *Polarimeter:*

1. The optical activity of the compound can be measured *by polarimeter.*
2. A *polarimeter* measures the rotation of plane-polarized light that has passed through a solution.
3. Plane polarized light is rotated in solutions of optically active compounds.
4. The light source passes through a *polarizer* and then is detected at an analyzer (a second *polarizer).*
5. The angle between the entrance and exit planes is the optical rotation.
6. Rotation, in degrees, is [α].
7. Clockwise rotation is called **dextrorotatory.**
8. Anti-clockwise is **levorotatory.**



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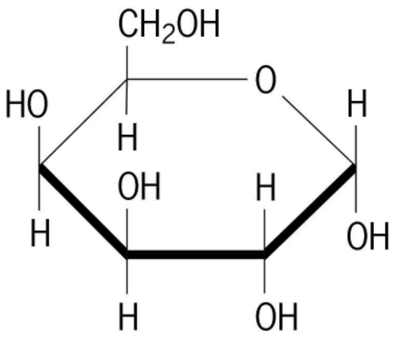
Stereochemistry
Optical isomerism

- **Classification:**

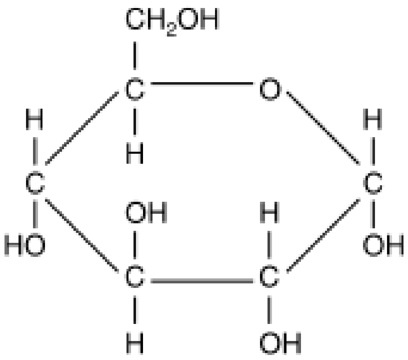
1. **Epimers:**

- Sugars have different names but have the same number of carbon, oxygen and hydrogen atoms and differ in the configuration of only one chirality center (stereogenic center) = asymmetric carbon atom other than the anomeric carbon atom (chiral carbon atom #1= hemiacetal or hemiketal carbon).
- All other stereogenic centers in the molecules, if any, are the same in each.

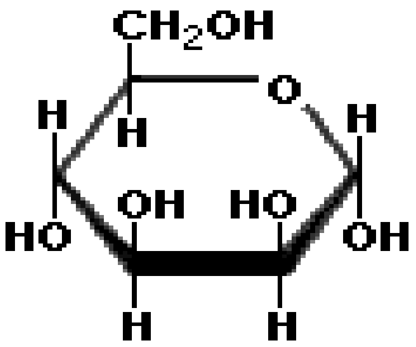
Haworth project



α,D-Galactose



α,D-Glucose

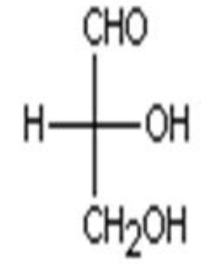


α,D-Manose

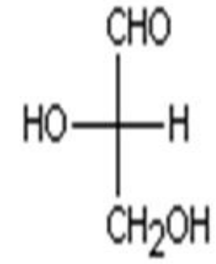
Stereochemistry
Optical isomerism

2. Enantiomers:

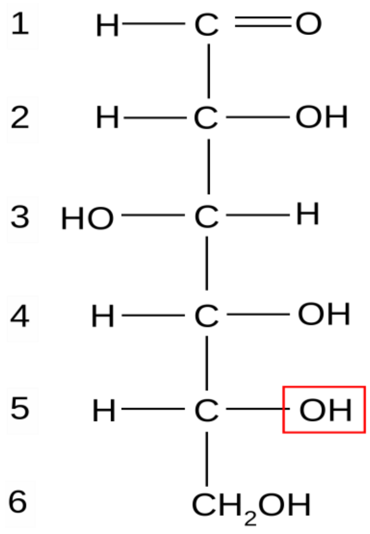
- Sugars have the same name but they are mirror images of one another.
- Form D and L isomers.
- D and L isomers are based on the configuration of the single asymmetric carbon (sugars with one chirality center) in glyceraldehyde the simplest sugar with 3 carbon atoms.
- For sugars with more than one chiral center, the D or L isomers refers to the asymmetric carbon furthest from the aldehyde or ketone group.
- D isomers is formed when the hydroxyl group of this carbon atom is on the right and L isomers is formed when the hydroxyl group of this carbon atom is on the left.
- Most naturally occurring sugars are D isomers.



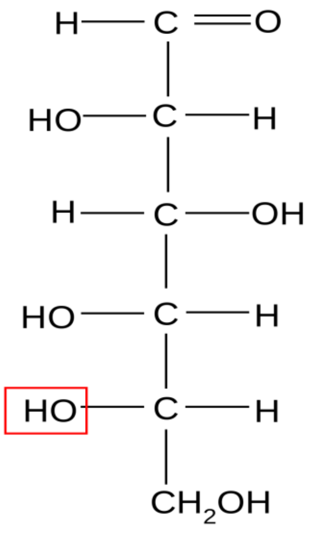
D-glyceraldehyd



L-glyceraldehyd



D-glucose



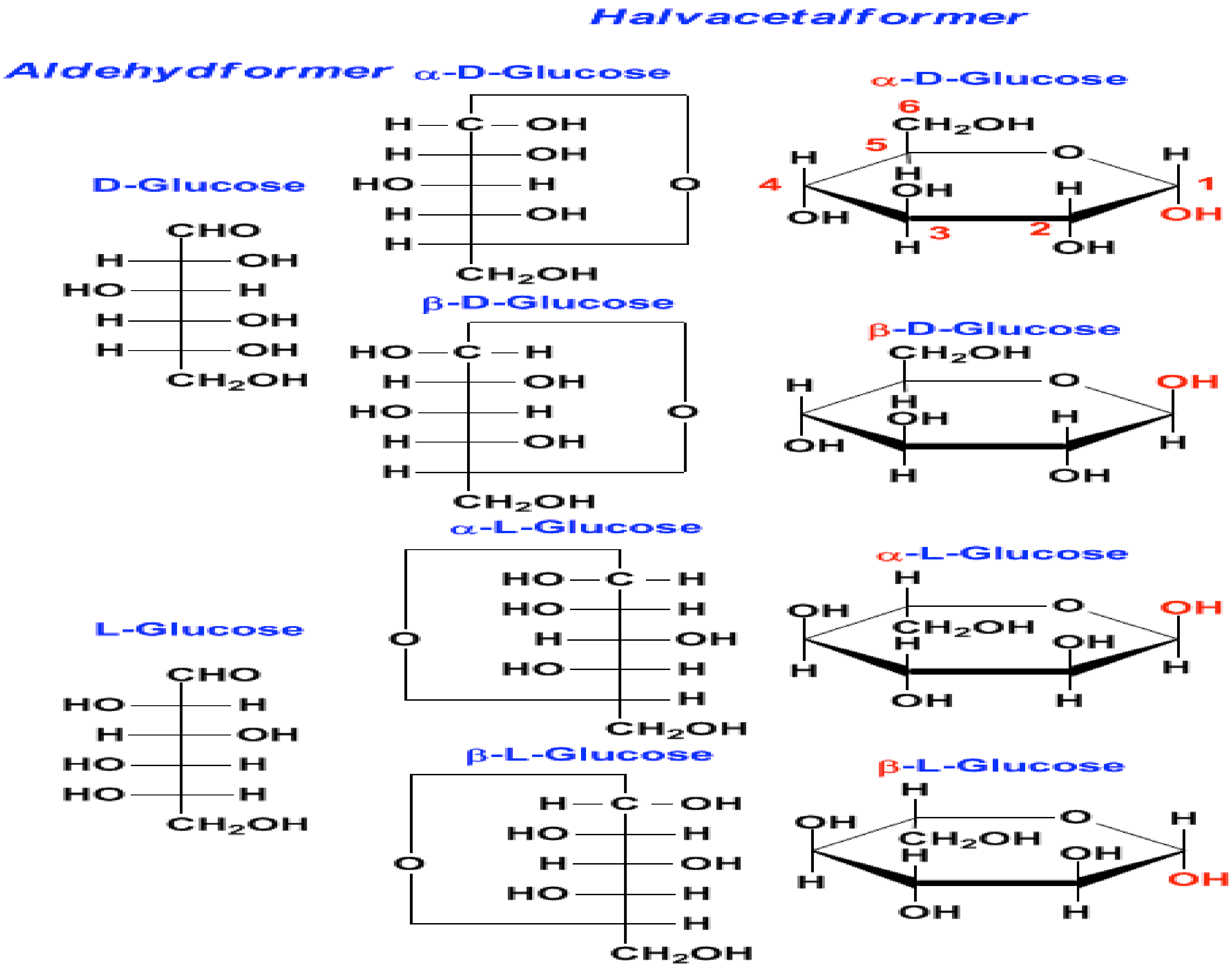
L-glucose

Stereochemistry
Optical isomerism

3. Anomer:

- It is a special type of epimers. It is stereoisomers of a cyclic saccharide that differs only in its configuration at the anomeric carbon atom (chiral carbon atom #1= hemiacetal or hemiketal carbon).
- Formation of a new configuration at the anomeric carbon depends on the orientation of the hydroxyl group (-OH) and hydrogen atom on this carbon.
- In the form of D isomers it is called alpha when the hydroxyl group of carbon atom 1 is on the right (Fisher) or down (Haworth), and the beta on the left or up.

Stereochemistry
Optical isomerism

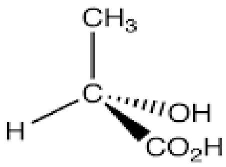


www.biosite.dk 230299; rettet 060302, 171011

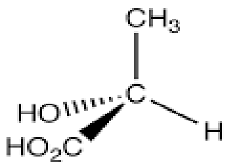
Stereochemistry
Optical isomerism

- Racemic mixture:

Racemic mixture is an equal mixture of enantiomers. It is optically inactive. This is not due to the absence of chiral center but it is due to the optical rotation caused by one enantiomer is exactly canceled by the optical rotation in the opposite direction of the other enantiomer.



(*R*)–lactic acid

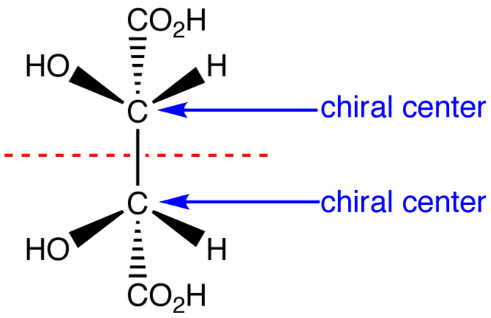


(*S*)–lactic acid

- Meso compound:

Meso compound is a compound possesses more than one chiral center but an optically inactive compound because the molecule possesses a plane of symmetry.

Meso tartaric acid

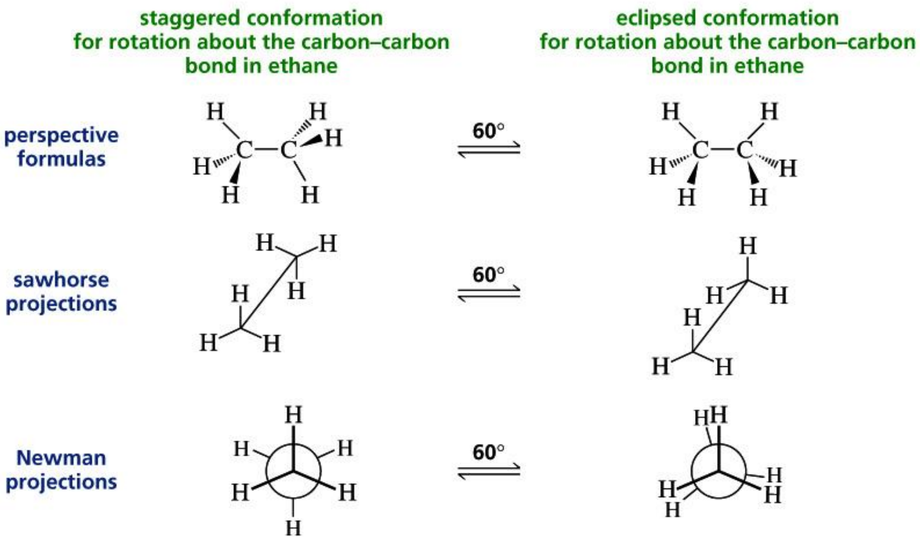


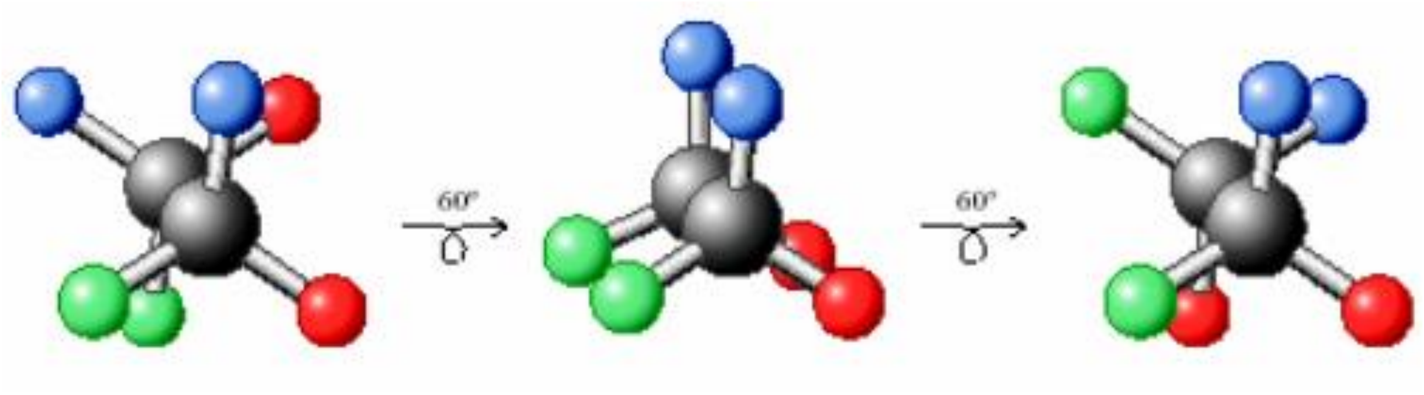
C) Conformational Isomerism

This type of stereoisomerism exists in compounds with C-C sigma bonds which has unrestricted rotation of atoms attached to each carbon making the sigma bond For example ethane

This unrestricted rotation can produce an infinite number of atomic arrangements called conformations.

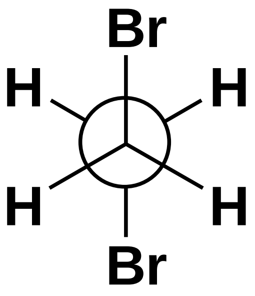
There are two extreme forms the staggered conformation which is the most stable and most abundant and the eclipsed which is the least stable and least abundant, the two extreme forms are interconvertaible merely by rotation around the carbon-carbon single bond. They can be represented by Newman projections or sawhorse diagrams.



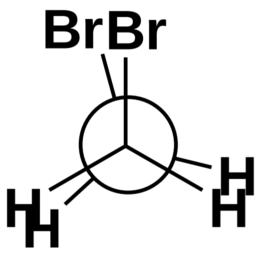


staggered eclipsed staggered

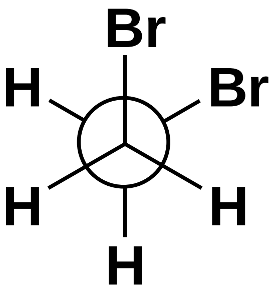
The conformational isomer or conformers of 1,2- dibromoethane are shown as follows, with three conformations, one eclipsed and two staggered (one with the two bromine atoms next to each other 60° apart (Gauche) and the other is staggered with the two bromine atoms 180° apart (Anti).



Staggered (Anti)



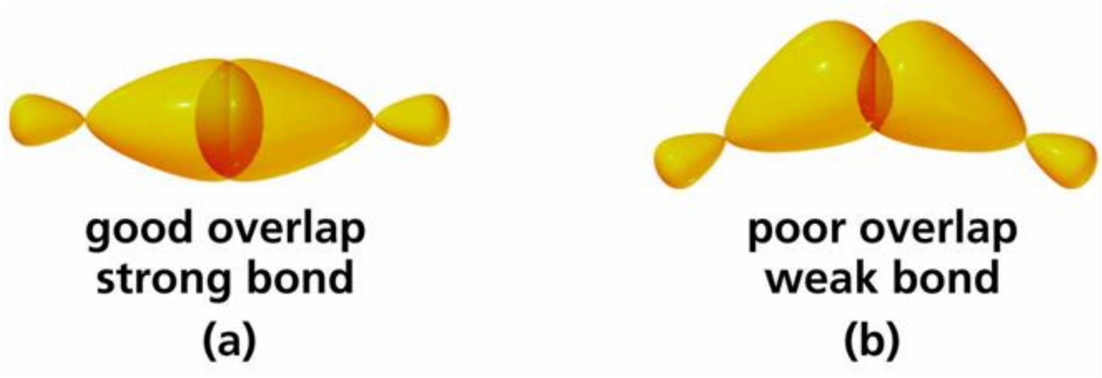
Eclipsed



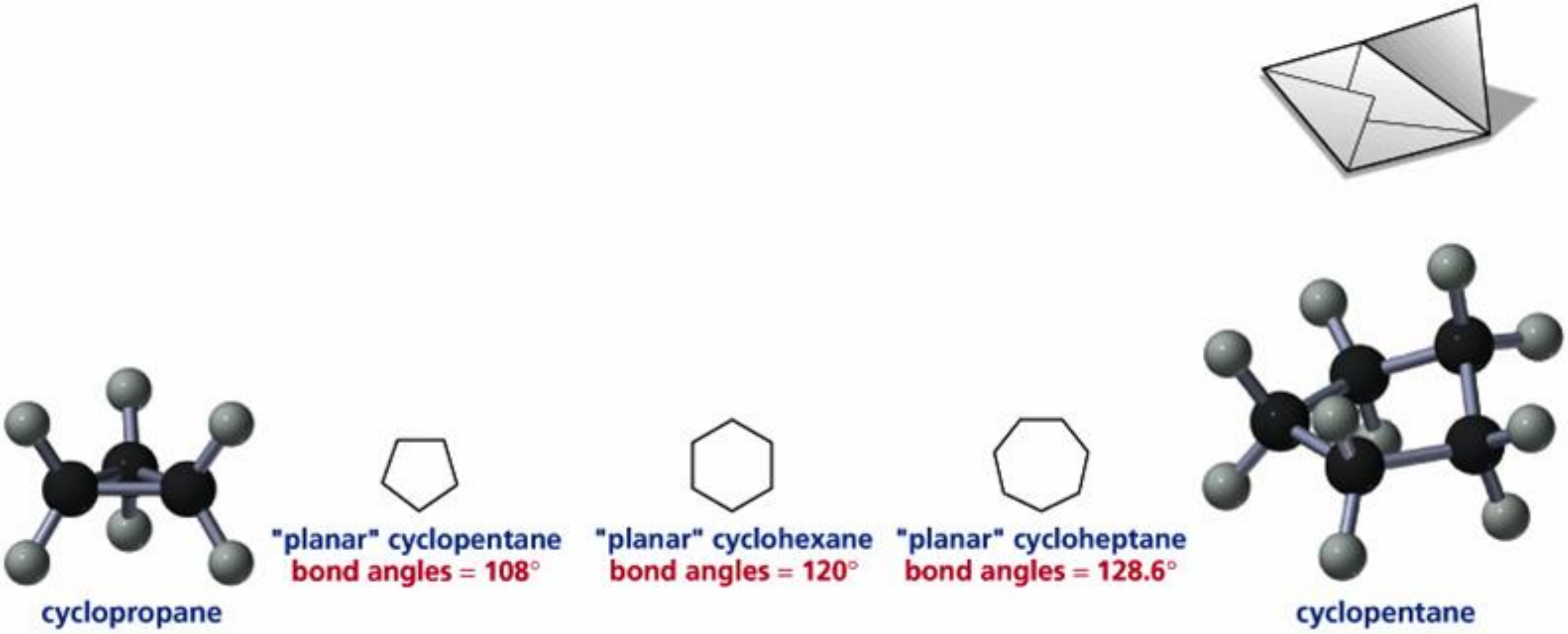
Staggered (Gauche)

Conformations of Cycloalkanes
Cycloalkanes – Ring Strain
Angle Strain:

The ideal tetrahedral angle is 109.5°. In open-chain molecules, sp3 orbitals have ideal overlap (a). In small ring molecules, the angle between carbons has to be much smaller, this is only possible when sp3 orbitals overlap at an angle (b). This angular orientation results in non-ideal overlap, i.e. a weaker bond.



Angle strain is strongest in cyclopropane (angle C-C-C = 60 °), pronounced in cyclobutane (angle C-C-C = 90 °), already from cyclopentane on other forms of strain become relevant. In large rings, there is more conformational flexibility.

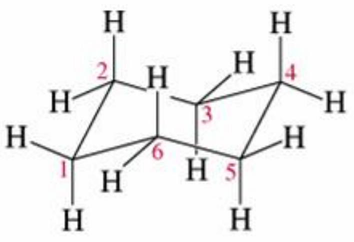


Torsional Strain:

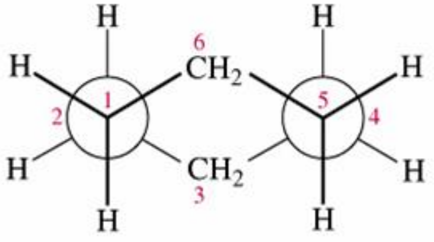
If all cycloalkane rings were planar, hydrogen atoms (and substituents) would be in a perfectly ecliptic orientation. Since three points define a plane, cyclopropane is planar and has the additional torsional strain from ecliptic hydrogens.

Cyclohexane

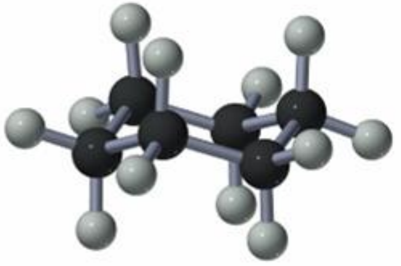
In planar cyclohexane, the C-C-C angles would be 120°; however, cyclohexane can adopt a conformation, where unstrained tetrahedral bonds are almost perfectly realized (C-C-C angles of 111°), and there is no torsional strain (all-staggered conformation); this is the chair conformation. Deviations from the chair conformation will still have no, or little, angle strain, but torsional and steric strain will increase.



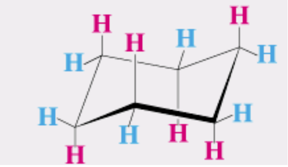
chair conformer of cyclohexane

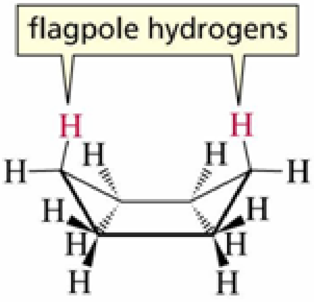


Newman projection of the chair conformer

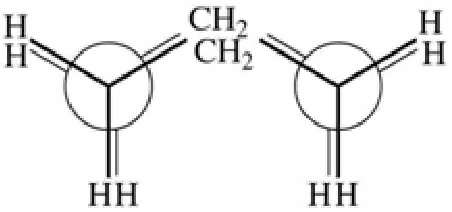


ball-and-stick model of the chair conformer of cyclohexane

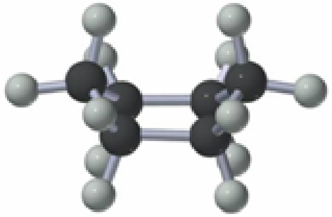




boat conformer of cyclohexane



Newman projection of the boat conformer



ball-and-stick model of the boat conformer of cyclohexane

Non-ring bonds can be equatorial, eq (in the ring plane), or axial, ax (perpendicular to the ring plane). Ring flip will exchange axial and equatorial positions.

Chemical bonding

Chemical bonding

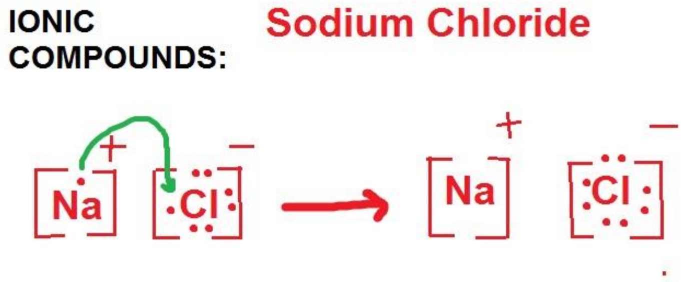
A- Ionic bonding:

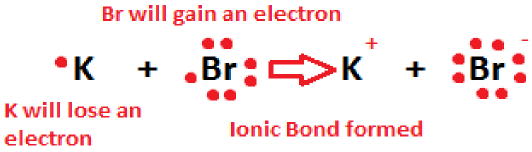
1. Elements at opposite ends of the periodic table attain the noble gas configuration by transferring electrons to one another.
2. In the electron-transfer process:

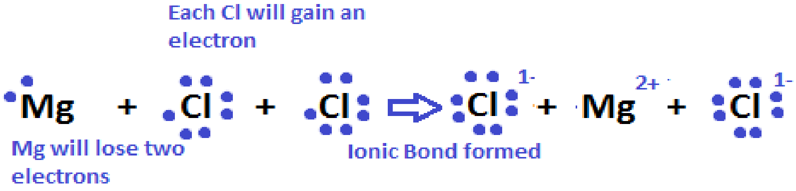
a) elements at the left of the periodic table transfer their valence electrons and become positively charged ions (cations +).

b) Elements at the right gain the electrons, thus becoming negatively charged ions (anions -).

3. The ionic bond is constitutes due to the electrostatic force of attraction between oppositely charged ions.
4. The majority of ionic compounds are inorganic substances, they exist in solid and liquids states.

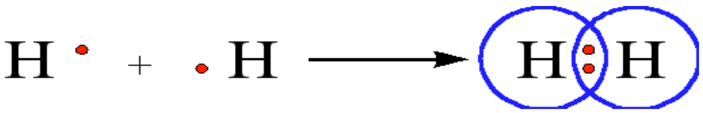






Chemical bonding

B- Covalent bonding:



1. Elements that are close to each other in the periodic table attain the stable noble gas configuration, not through a transfer of electrons **but by sharing valence electrons between them.**
2. Covalent bond is the chemical bond formed when two atoms share one pair of electrons.
3. Atoms in most substances are held together by covalent bonds.

Chemical bonding

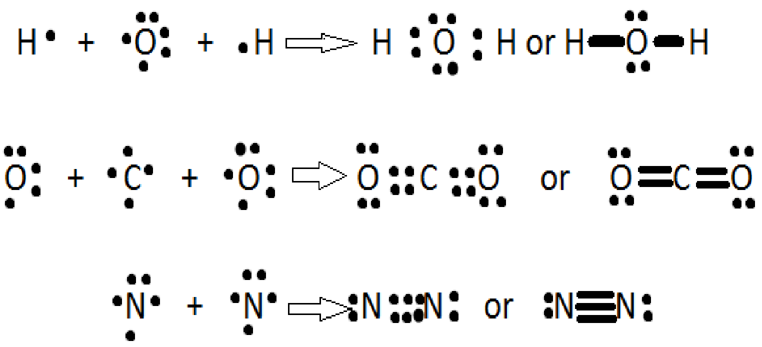
4. How many bonds to an atoms? =Covalence number

a) The number of covalent bonds an atom can form with other atoms is called its covalence number.

b) Note that the covalence number for an element is equal to the number of electrons needed to fill its valence shell.

c) Element satisfies its covalence number by sharing one electron pair-forming a single bond with another atom connected to it. If two pairs of electrons are shared, a double bond is formed; if three pairs of electrons are shared, a triple bond is formed. A single bond is represented by a dash (-), a double bond by two dashes (=) and a triple bond by three dashes (≡).

Element	Number of valence electrons	Number of electrons in filled valence shell	Covalence number
H	1	2	1
C	4	8	4
N	5	8	3
O	6	8	2
F,Cl,Br,I	7	8	1



All these diagrams show the formation of covalent bonds as electrons from elements are shared to form single, double, and triple bonds

Chemical bonding

5. Types of covalent bonding:

1) Nonpolar covalent bonding is:

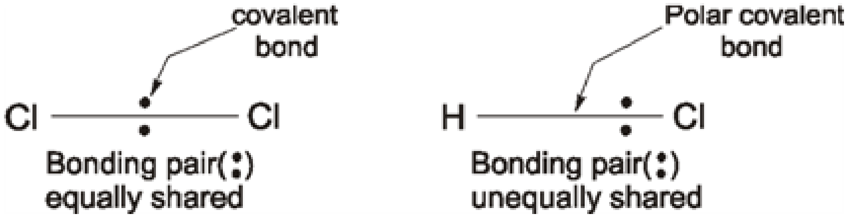
Bond between two like atoms or between two unlike atoms have the same electronegativity. Thus, the electron pair is shared equally

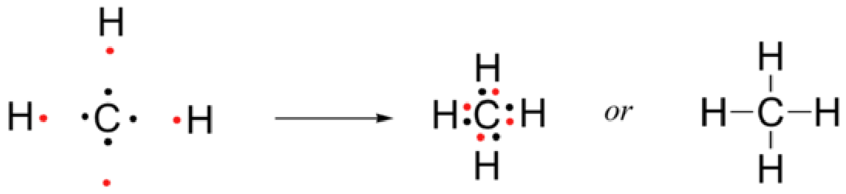
2) Polar covalent bonding is:

Bond between two unlike atoms and the electron pair is shared unequally. The greater electronegativity of one atoms causes the electron pair to be closer to this atom. Thus, assumes a partial negative charge δ^- and the less electronegative atom assumes a partial positive charge δ^+

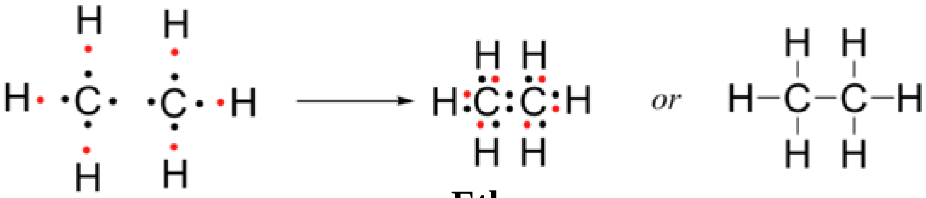
3) Coordinate covalent bonding:

One atom supplies both electrons to another atom in the formation of a covalent bond in a molecules.

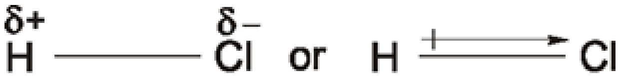


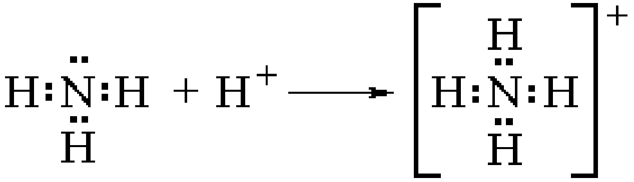


methane



Ethane

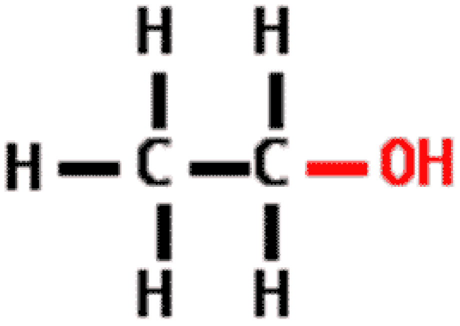




Functional groups

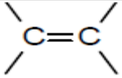
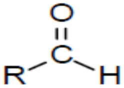
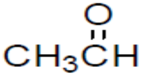
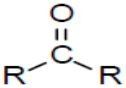
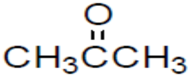
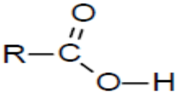
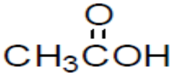
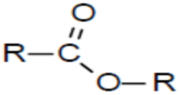
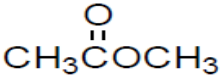
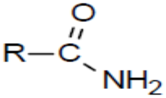
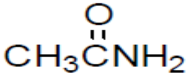
Functional groups

- There are several million organic compounds. Thus, study their chemistry is possible only when classified them depending on the functional groups present.
- A functional group is a reactive portion of an organic molecule, an atom or a group of atoms that confers on the whole molecule its characteristic properties.
- All compounds with the same functional groups belong to one family.
- An example: an alcohol, indicated by hydroxyl group, OH, attached to carbon atom.



Ethanol

Organic Functional Group List

Functional Group	Compound	Prefix/Suffix	Example	IUPAC Name (Common Name)
R-H	alkane	-ane	CH_3CH_3	ethane
	alkene	-ene	$H_2C{=}CH_2$	ethene (ethylene)
$-C\equiv C-$	alkyne	-yne	$HC\equiv CH$	ethyne (acetylene)
R-X	haloalkane	halo-	CH_3Cl	chloromethane
R-OH	alcohol	-ol (hydroxy-)	CH_3OH	methanol
$R-NH_2$	amine	-amine (amino-)	$CH_3CH_2NH_2$	ethylamine aminoethane
R-O-R	ether	ether (alkoxy-)	CH_3OCH_3	dimethyl ether
	aldehyde	-al	 $CH_3\overset{O}{\overset{\|}{C}}H$	ethanal (acetaldeyde)
	ketone	-one	 $CH_3\overset{O}{\overset{\|}{C}}CH_3$	propanone (acetone)
	carboxylic acid	-oic acid	 $CH_3\overset{O}{\overset{\|}{C}}OH$	ethanoic acid (acetic acid)
	ester	-oate	 $CH_3\overset{O}{\overset{\|}{C}}OCH_3$	methyl ethanoate (methyl acetate)
	amide	-amide	 $CH_3\overset{O}{\overset{\|}{C}}NH_2$	ethanamide (acetamide)

R = alkyl group, an unfunctionalized saturated chain; X = halogen

Hydrocarbons

Hydrocarbons

Introduction:

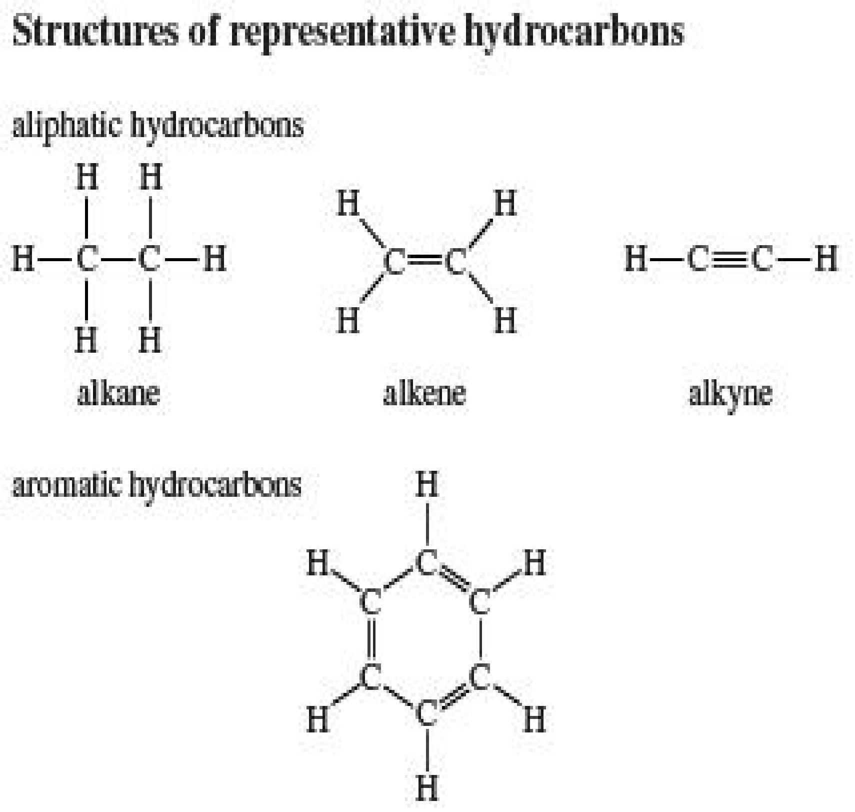
- A large group of organic compounds, known as hydrocarbons, contain only the two elements: carbon and hydrogen. Based on their structural features.

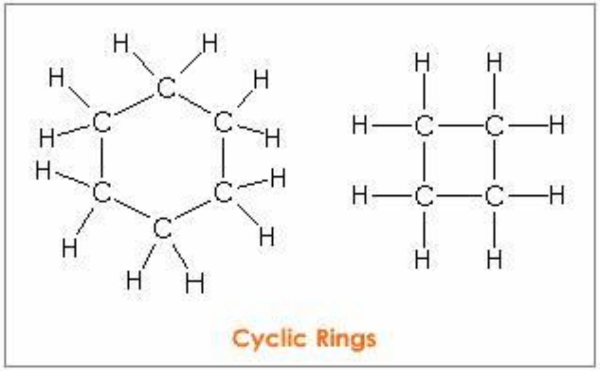
- They are divided into two main classes: aliphatics and aromatics.

- Aliphatic hydrocarbons are subdivided into three families:

alkanes (open chain and cycloalkanes), (saturated hydrocarbons),

alkenes and alkynes (unsaturated hydrocarbons).





Definitions, classification, characterizations and general formula

- **Hydrocarbons:** are compounds that contain only carbon and hydrogen atoms.

- **Aliphatic:**

a) Saturated hydrocarbons:

➢ **Alkanes:** are hydrocarbons that characterized by single bond.
They are divided into:

1. Open chain saturated hydrocarbons (acyclic-alkanes) with general formula (C_nH_{2n+2}).
2. Cyclic saturated hydrocarbons (cycloalkanes) with general formula (C_nH_{2n}).

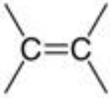
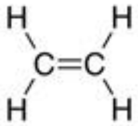
b) Unsaturated hydrocarbons:

➢ **Alkenes** (C_nH_{2n}) contain at least one carbon–carbon double bond. They formed in open chain with general formula C_nH_{2n}. Also formed in cyclic chain with general formula $C_nH_{2n-2.}$

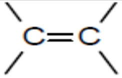
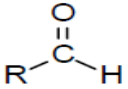
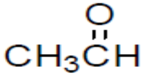
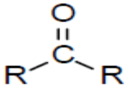
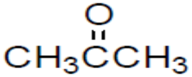
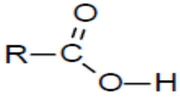
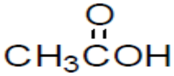
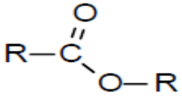
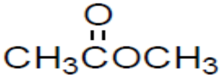
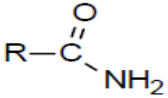
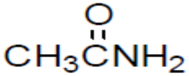
➢ **Alkynes** (C_nH_{2n-2}) contain at least one carbon–carbon triple bond. They formed in open chain with general formula C_nH_{2n-2}. Also formed in cyclic chain with general formula C_nH_{2n-4}

- **Aromatic compounds:** mean benzene (C_6H_6) and derivatives of benzene, which contain a special type of ring, characterized by alternate double bonds.

General structure of hydrocarbons

Type of compound	General structure	Example	Functional group
Alkane	R—H	CH_3CH_3	—
Alkene			double bond
Alkyne	—C≡C—	H—C≡C—H	triple bond
Aromatic compound			phenyl group

Organic Functional Group List

Functional Group	Compound	Prefix/Suffix	Example	IUPAC Name (Common Name)
R-H	alkane	-ane	CH_3CH_3	ethane
	alkene	-ene	$H_2C{=}CH_2$	ethene (ethylene)
$-C\equiv C-$	alkyne	-yne	$HC\equiv CH$	ethyne (acetylene)
R-X	haloalkane	halo-	CH_3Cl	chloromethane
R-OH	alcohol	-ol (hydroxy-)	CH_3OH	methanol
$R\text{-}NH_2$	amine	-amine (amino-)	$CH_3CH_2NH_2$	ethylamine aminoethane
R-O-R	ether	ether (alkoxy-)	CH_3OCH_3	dimethyl ether
	aldehyde	-al	 $CH_3\overset{\overset{O}{\|}}{C}H$	ethanal (acetaldeyde)
	ketone	-one	 $CH_3\overset{\overset{O}{\|}}{C}CH_3$	propanone (acetone)
	carboxylic acid	-oic acid	 $CH_3\overset{\overset{O}{\|}}{C}OH$	ethanoic acid (acetic acid)
	ester	-oate	 $CH_3\overset{\overset{O}{\|}}{C}OCH_3$	methyl ethanoate (methyl acetate)
	amide	-amide	 $CH_3\overset{\overset{O}{\|}}{C}NH_2$	ethanamide (acetamide)

R = alkyl group, an unfunctionalized saturated chain; X = halogen

Alkanes

Alkanes and Cycloalkanes

Alkanes: are aliphatic hydrocarbons characterized by single bond having only C–C and C–H σ bonds. Each carbon is bonded to four other atoms and do not have multiple bonds between carbon atoms.

Other hydrocarbons may contain double or triple bonds between their carbon atoms.

They are also called saturated hydrocarbons because they have the maximum number of hydrogen atoms per carbon.

Alkanes lack of chemical activity and extremely flammable. Thus they are constitute the fuels that used in heating and in machine.

They are categorized as acyclic or cyclic.

Acyclic alkanes have the molecular formula C_nH_{2n+2} and contain only linear and branched chains of carbon atoms.

Cycloalkanes their general formula is C_nH_{2n} and contain carbons joined in one or more rings. They have two fewer H atoms than an acyclic alkane with the same number of carbons.

Aliphatics

Saturated hydrocarbons: Alkanes

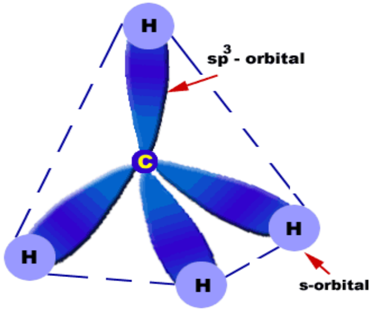
Saturated hydrocarbons (alkanes=paraffins):

The three simplest alkanes (Methane, ethane and propane):

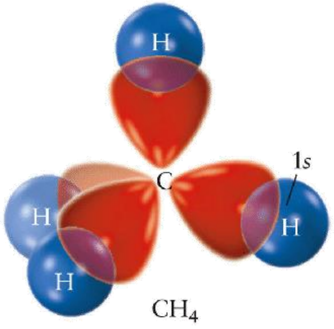
1- Methane CH_4 has the shape of a tetrahedron with an *sp*^{3}-hybridized orbitals, carbon at the center. All four C-H bonds in the molecule are equivalent.

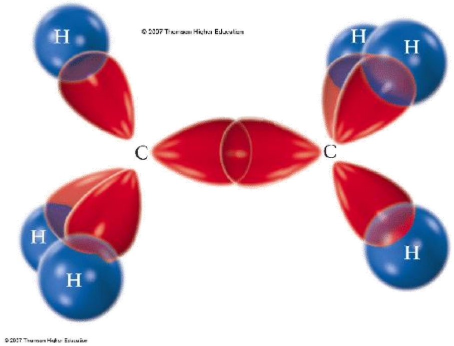
2- Ethane C_2H_6 is more than methane with alkyl group (CH_2). Each carbon in ethane is *sp3* hybridized orbitals and the bond joining the two carbons is called an *sp3-sp3* molecular orbital.

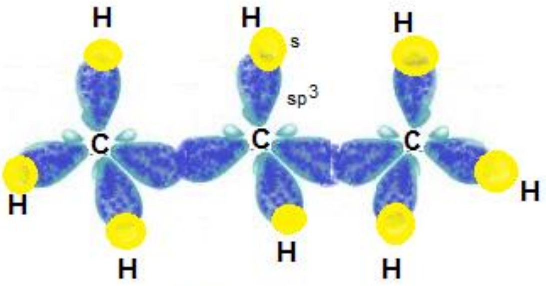
3- Propane C_3H_8 is more than ethane with alkyl group (CH_2) . Also, each carbon in propane is *sp*^{3} hybridized orbitals.



Orbital structure of methane



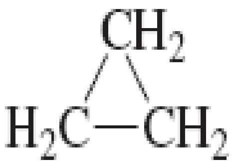




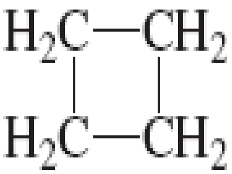
Propane

Structure of Cycloalkanes

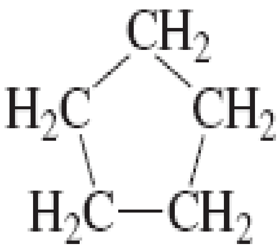
Cycloalkanes are hydrocarbons in which all Carbon atoms form the cycle and are in the state of sp3 hybridization. Cycloalkanes are saturated hydrocarbons. Cycloalkanes have the general molecular formula C_nH_{2n}.



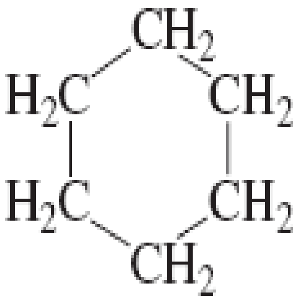
cyclopropane



cyclobutane



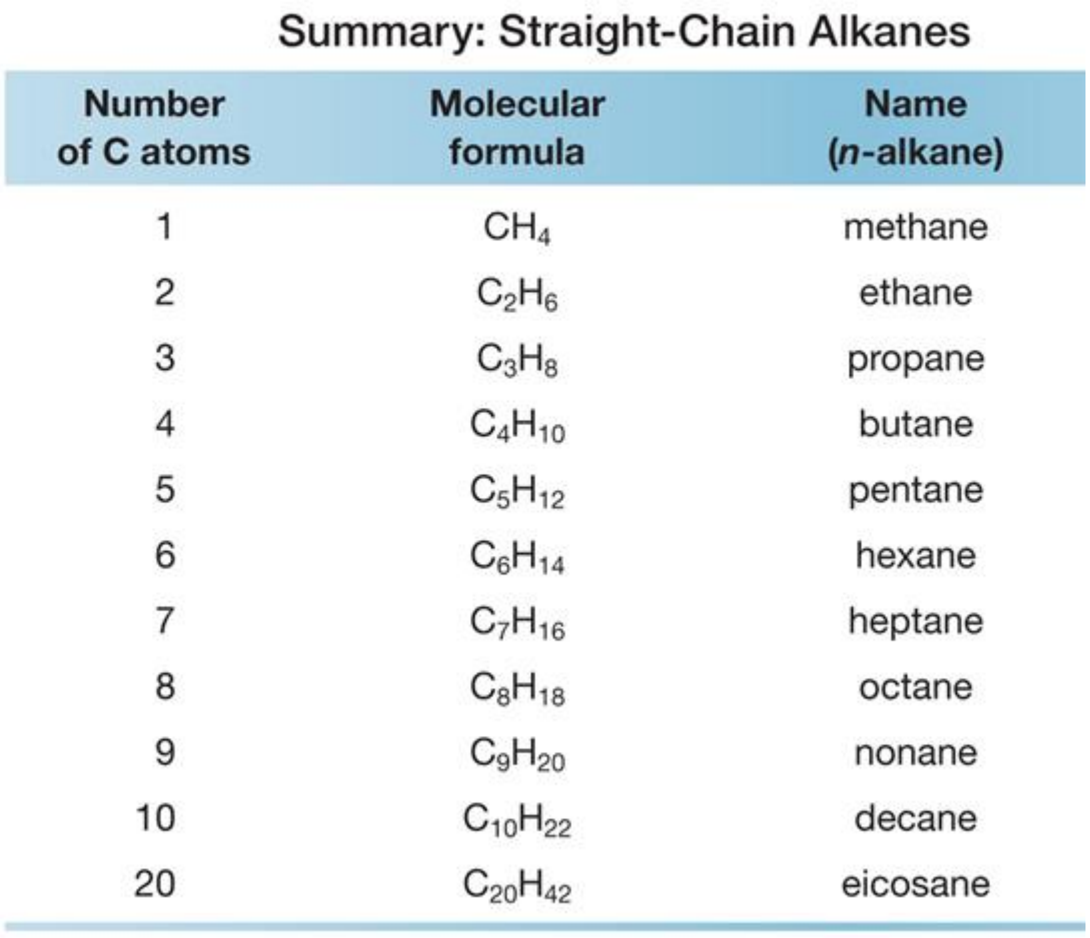
cyclopentane



cyclohexane

Naming Alkanes

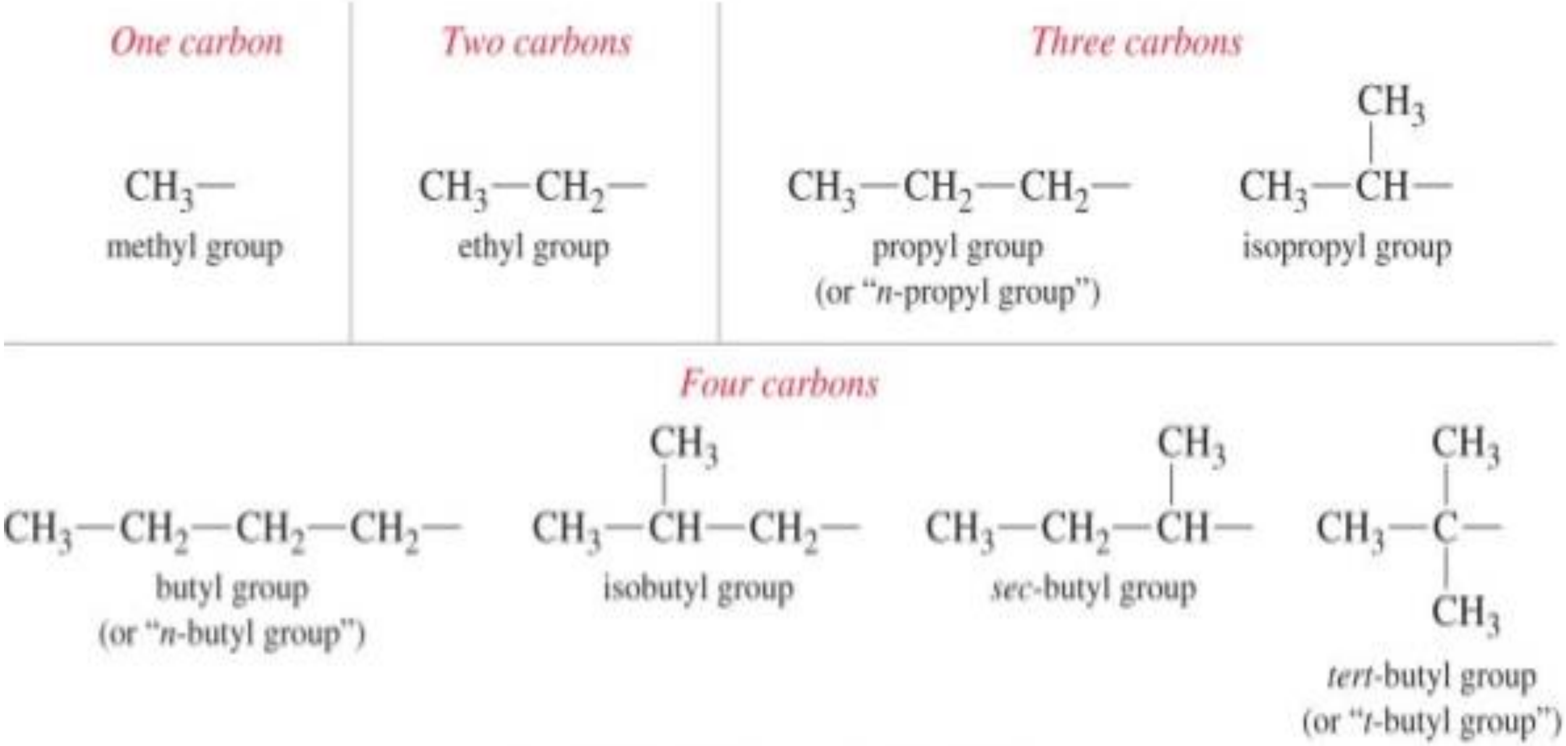
The suffix “-ane” identifies a molecule as an alkane.



Summary: Straight-Chain Alkanes

Number of C atoms	Molecular formula	Name (*n*-alkane)
1	CH_4	methane
2	C_2H_6	ethane
3	C_3H_8	propane
4	C_4H_{10}	butane
5	C_5H_{12}	pentane
6	C_6H_{14}	hexane
7	C_7H_{16}	heptane
8	C_8H_{18}	octane
9	C_9H_{20}	nonane
10	$C_{10}H_{22}$	decane
20	$C_{20}H_{42}$	eicosane

Common Alkyl Groups



One carbon

$\mathrm{CH_3-}$
methyl group

Two carbons

$\mathrm{CH_3-CH_2-}$
ethyl group

Three carbons

$\mathrm{CH_3-CH_2-CH_2-}$
propyl group
(or "*n*-propyl group")

$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}H-}$
isopropyl group

Four carbons

$\mathrm{CH_3-CH_2-CH_2-CH_2-}$
butyl group
(or "*n*-butyl group")

$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-}$
isobutyl group

$\mathrm{CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-}$
sec-butyl group

$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-}$
tert-butyl group
(or "*t*-butyl group")

Sources of alkanes

- Petroleum and natural gas.
- Both are products of the decay of animal, vegetable and marine matter.
- A great number of alkanes can be obtained in pure form most economically by fractional distillation of crude petroleum.
- Also, they are prepared at laboratory using methods.

Physical Properties of Alkanes

1- Solubility:

- Alkanes occur at room temperature as gases, liquids and solids.
- Alkanes from C_1 to C_4 are gases; most C_5 to C_{17} alkanes are liquids and the C_{18} and larger alkanes are wax-like solid. (The first four alkanes in homological row are gaseous at room temperature. The unbranched alkanes pentane (C_5H_{12}) through heptadecane ($C_{17}H_{36}$) are liquids, whereas higher homologs are solids).
- Gaseous and solid alkanes odorless. But liquids have “benzene” smell.

- Alkanes are nonpolar, so they dissolve in nonpolar or organic solvents.
- Alkanes are said to be **hydrophobic** (“water hating”) because they do not dissolve in water.
- Their insolubility increases with increasing molecular weight.

Physical Properties of Alkanes

2- Boiling point:

The straight–chain compound has the highest boiling point. The greater the number of branches, the lower the boiling point.

$CH_3CH_2CH_2CH_2CH_3$

Pentane
(bp 36°C)

$$\begin{array}{l} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3 \end{array}$$

2-Methylbutane
(bp 28°C)

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_3$$

2,2-Dimethylpropane
(bp 9°C)

3- Melting point:

Like their boiling points, the melting points increase with increasing molecular weight. Alkanes with even numbers of carbon atoms pack better into a solid structure, so that higher temperatures are needed to melt them.

4- Density:

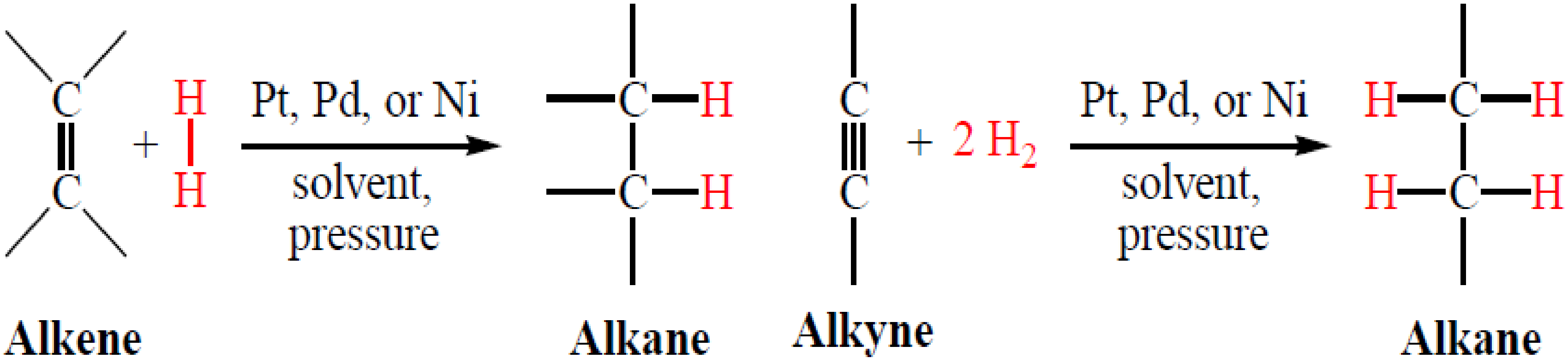
The alkanes are the least dense of all groups of organic compounds.

Preparation of Alkanes and Cycloalkanes

1- Hydrogenation of alkenes and alkynes (Sabatier and senderen's method):

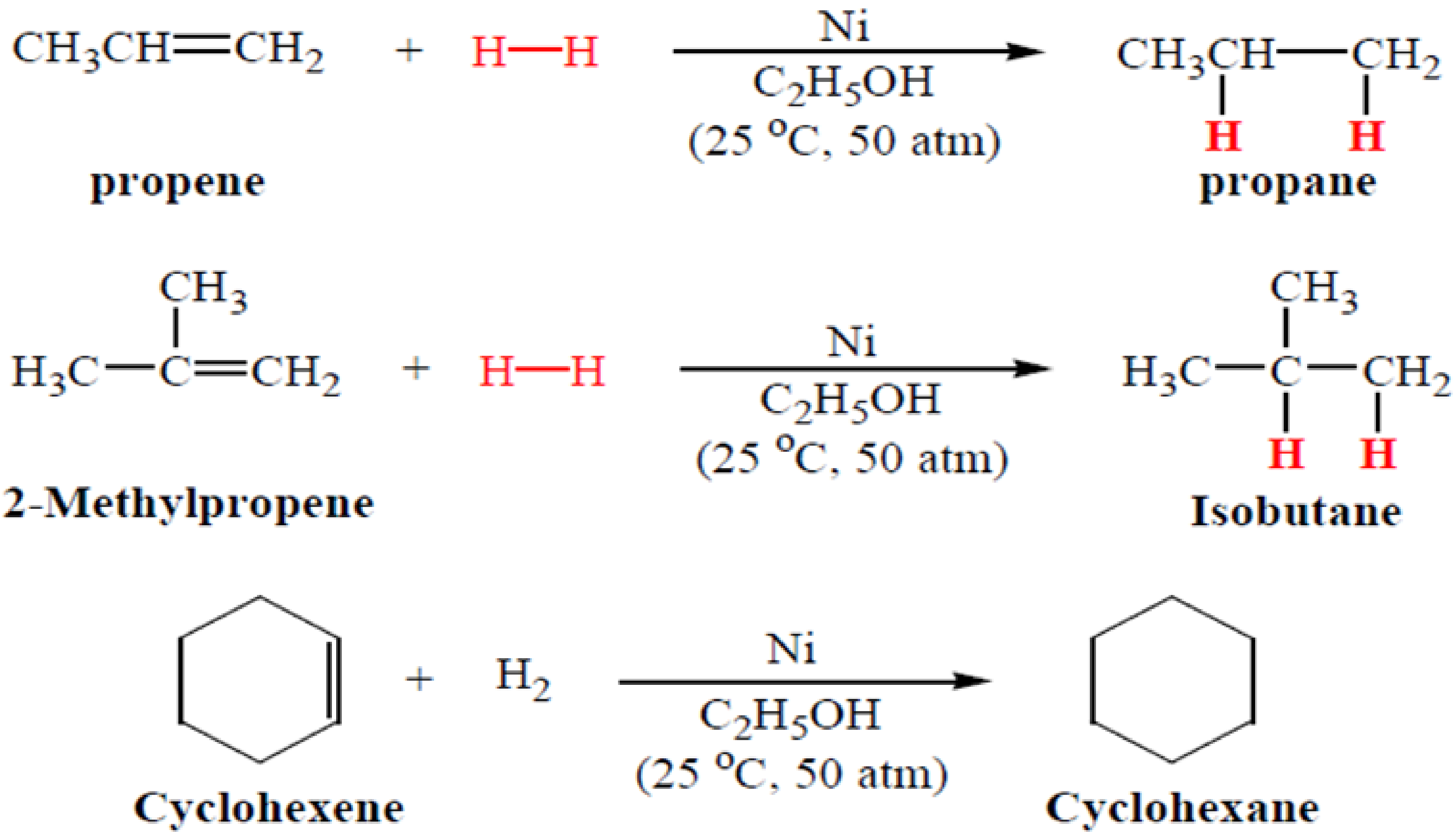
Alkenes and alkynes react with hydrogen in the presence of metal catalysts such as nickel, palladium, and platinum to produce alkanes.

General Reaction:



Preparation of Alkanes and Cycloalkanes

Examples:



$$CH_3CH{=}CH_2 + H{-}H \xrightarrow[\text{(25 °C, 50 atm)}]{\text{Ni}\quad C_2H_5OH} CH_3CH(H){-}CH_2(H)$$

$$H_3C{-}C(CH_3){=}CH_2 + H{-}H \xrightarrow[\text{(25 °C, 50 atm)}]{\text{Ni}\quad C_2H_5OH} H_3C{-}C(CH_3)(H){-}CH_2(H)$$

Preparation of Alkanes and Cycloalkanes

2- Reduction of alkyl halides:

Most alkyl halides react with zinc and aqueous acid to produce an alkane.

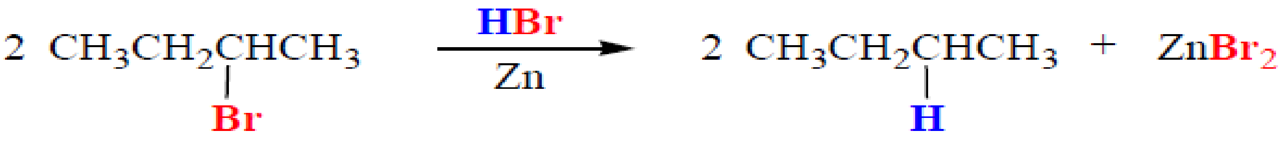
General Reaction:

$$\underset{\text{Alkyl halide}}{R{-}X} + Zn + HX \longrightarrow \underset{\text{Alkane}}{R{-}H} + ZnX_2$$

or*

$$R{-}X \xrightarrow[(-ZnX_2)]{Zn,\ HX} \underset{\text{Alkane}}{R{-}H}$$

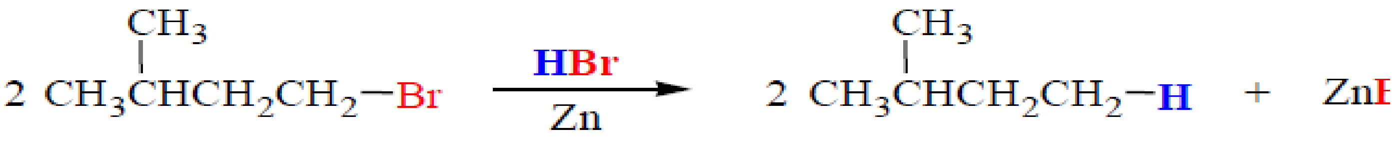
Example:



$$2\ CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[Zn]{HBr} 2\ CH_3CH_2\underset{\displaystyle H}{\underset{|}{C}}HCH_3 + ZnBr_2$$

***sec*-Butyl bromide**
(2-bromobutane)

Butane



$$2\ CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2{-}Br \xrightarrow[Zn]{HBr} 2\ CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2{-}H + Zn$$

Isopentyl bromide
(1-bromo-3-methylbutane)

Isopentane
(2-methylbutane)

Preparation of Alkanes and Cycloalkanes

3- Wurtz reaction (Alkyl halides via coupling):

- A solution of alkyl halide in ether on heating with sodium gives alkane.
- Two R groups can be coupled by reacting RBr, RCl or RI with Na or K.

General Reaction:

$$2\text{R-X} + 2\text{Na} \xrightarrow{\text{Dry ether}} \text{R-R} + 2\text{NaX}$$

Alkane

Example:

$$2CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl + 2Na \xrightarrow{\text{Dry ether}} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 + 2NaCl$$

n-Propylchloride n-Hexane

- An alkyl halide on Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms.
- Two different alkyl halides, on Wurtz reaction give all possible alkanes.

Preparation of Alkanes and Cycloalkanes

4- Alkyl halides via Grignard reagent:

(a) Formation of alkyl magnesium halide (R-MgX), which is called Grignard reagent or organometallic compound.

$$R{-}X + Mg \xrightarrow[\text{Dry ether}]{CH_3CH_2OCH_2CH_3} \overset{\delta-}{R}{-}\overset{\delta+}{Mg}{-}X$$

(X = Cl, Br, or I)

Alkyl halide

organomagnesium halide

(Grignard reagent)

(b) Grignard reagent on double decomposition with water give alkane.

$$R\text{-}MgX \xrightarrow{H_2O} R\text{-}H + Mg(OH)X$$

Alkane

General reaction:

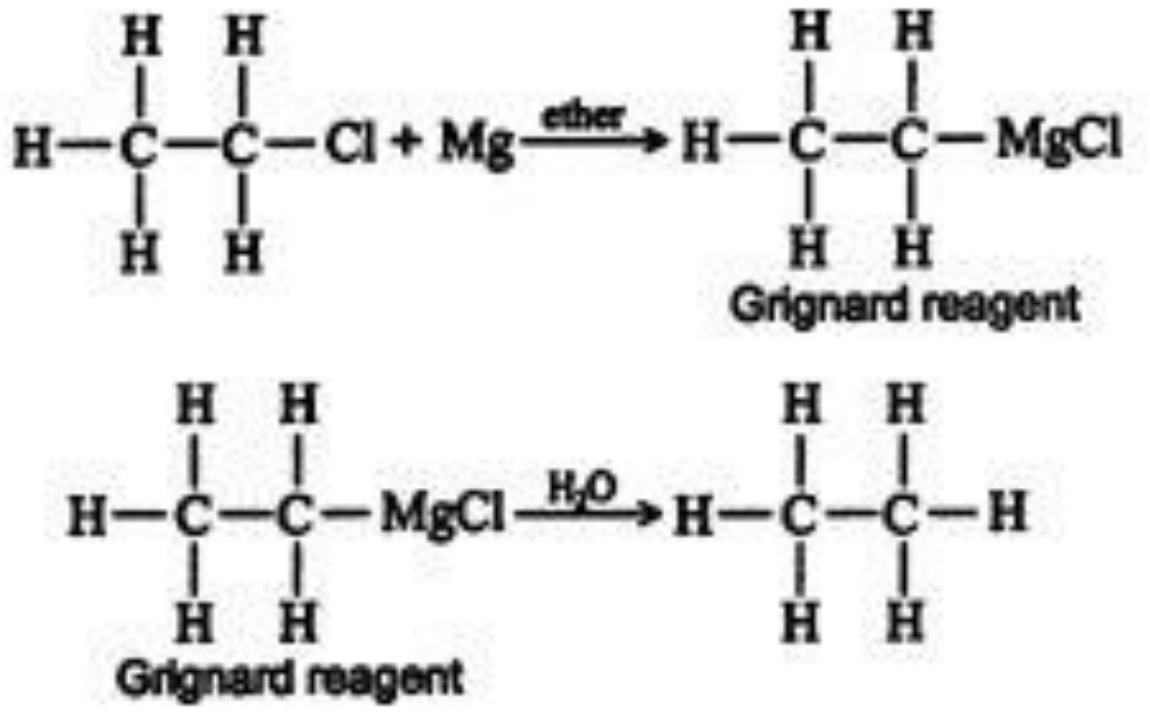
$$R{-}X + Mg \xrightarrow[\text{ether}]{} R{-}MgX \xrightarrow{H_2O} R{-}H + XMgOH$$

Alkyl halide

Alkane

Preparation of Alkanes and Cycloalkanes

Example:



Ethane

Preparation of Alkanes and Cycloalkanes

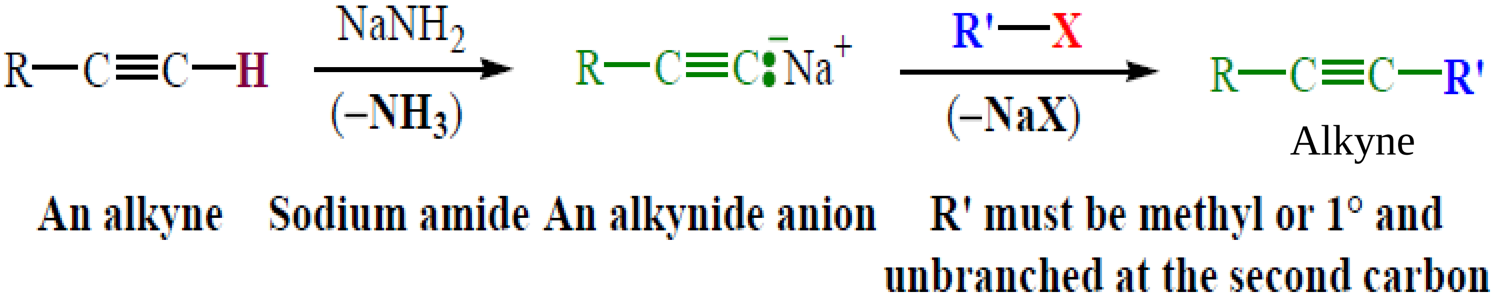
5- Alkylation of terminal alkynes:

1. Terminal alkyne: an alkyne with a hydrogen attached to a triply bonded carbon.

The **acetylenic hydrogen** is weakly acidic and can be removed with a strong base (e.g. $NaNH_2$) to give an anion (called **acetylide ion**).

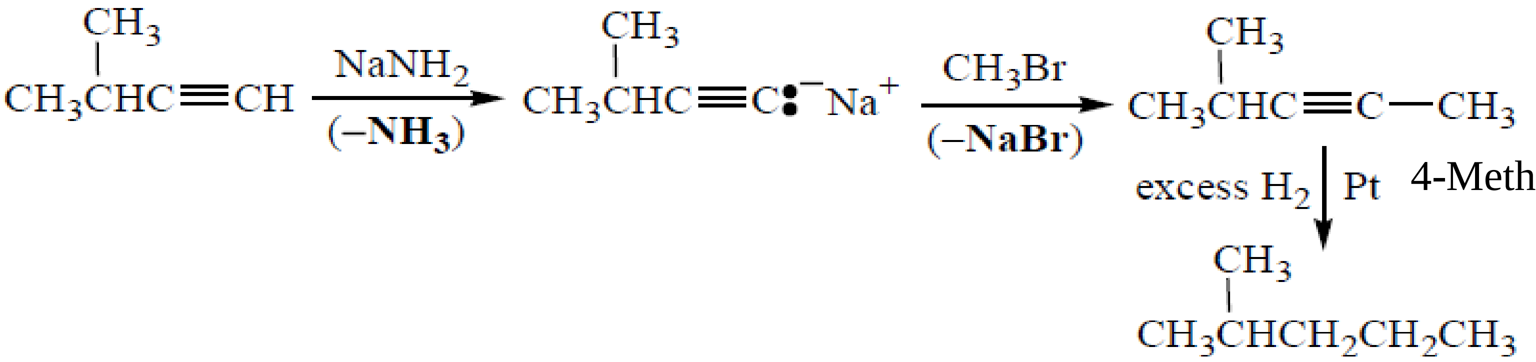
2. Alkylation: the **formation of a new C—C bond** by replacing a **leaving group** on an **electrophile** with a **nucleophile**.

General Reaction:



Preparation of Alkanes and Cycloalkanes

Example:

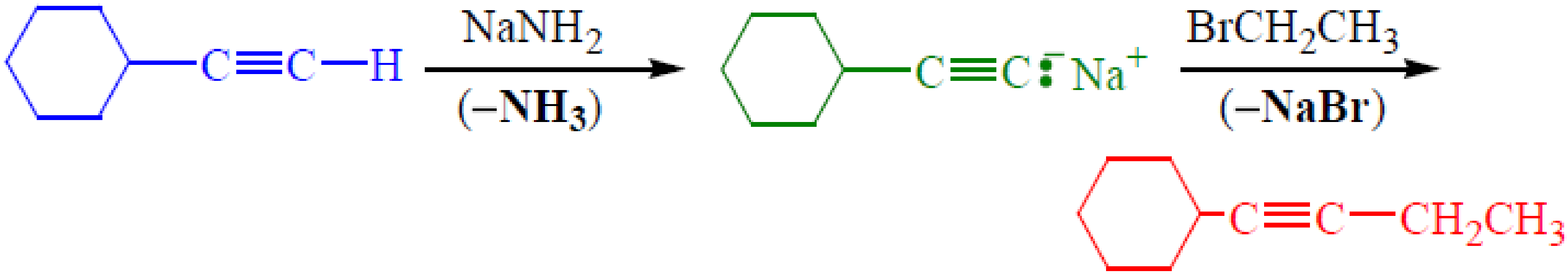


$$CH_3\overset{\overset{CH_3}{|}}{C}HC\equiv CH \xrightarrow[(-NH_3)]{NaNH_2} CH_3\overset{\overset{CH_3}{|}}{C}HC\equiv C:^-Na^+ \xrightarrow[(-NaBr)]{CH_3Br} CH_3\overset{\overset{CH_3}{|}}{C}HC\equiv C-CH_3$$

4-Methyl,2-pentyne

$$CH_3\overset{\overset{CH_3}{|}}{C}HC\equiv C-CH_3 \xrightarrow[Pt]{\text{excess } H_2} CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3$$

2-Methylpentane
Isohexane



1-Cyclohexyl,1-butyne

Chemical properties of Alkanes

In normal conditions alkanes do not react with acids and alkalis because σ-bonds in their molecules are very strong. Alkanes take part in such reactions as:

- *-reactions of the substitution;*
- *-reactions of the oxidation;*
- *-reactions of the destruction.*

Reaction of alkanes

1- Halogenation:

- Halogenation is the replacement of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine except iodine).
- Unlike the complex transformations of combustion, the halogenation of an alkane appears to be a simple **substitution reaction** in which a C-H bond is broken and a new C-X bond is formed.
- The chlorination of methane, shown below, provides a simple example of this reaction.

$$CH_4 + Cl_2 + \text{energy} \longrightarrow CH_3Cl + HCl$$

Methane

methyl chloride

- Since only two covalent bonds are broken (C-H & Cl-Cl) and two covalent bonds are formed (C-Cl & H-Cl).
- In the case of methane, a large excess of the hydrocarbon favors formation of methyl chloride as the chief product; whereas, an excess of chlorine favors formation of chloroform and carbon tetrachloride.

$$CH_4 + Cl_2 + \text{energy} \longrightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$$

Methane

methyl chloride dichloromethane chloroform carbon tetrachloride

- The reactivity of the halogens decreases in the following order: $F_2 > Cl_2 > Br_2 > I_2$.

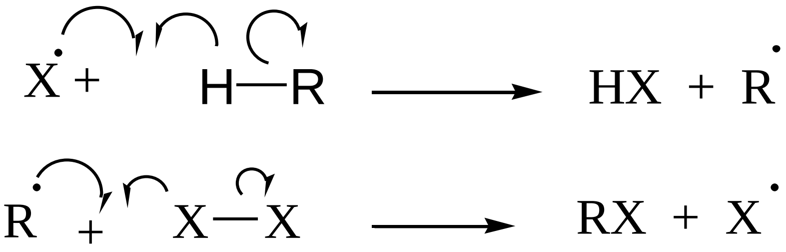
Mechanism of Halogenation

This is a Free Radical Substituted Reaction, including 3 steps:

Initiation:

$$X_2 \xrightarrow{hv} 2X^{\bullet}$$

Propagation:



$$X^{\bullet} + H—R \longrightarrow HX + R^{\bullet}$$

$$R^{\bullet} + X—X \longrightarrow RX + X^{\bullet}$$

Termination:

$$X^{\bullet} + X^{\bullet} \longrightarrow X_2$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R—R$$

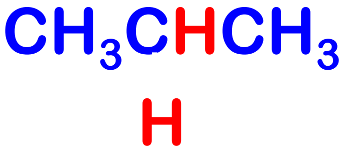
$$R^{\bullet} + X^{\bullet} \longrightarrow RX$$

Notes:

- Order of Free adicals' Stability:

$$R_3\dot{C} > R_2\dot{C}H > R\dot{C}H_2 > \dot{C}H_3$$

- Order of Reactivity of hydrogens attached to
  3° carbon > 2° carbon > 1° primary > CH_4



$$\underset{H}{CH_3CHCH_3}$$

Secondary Hydrogens
(in red)

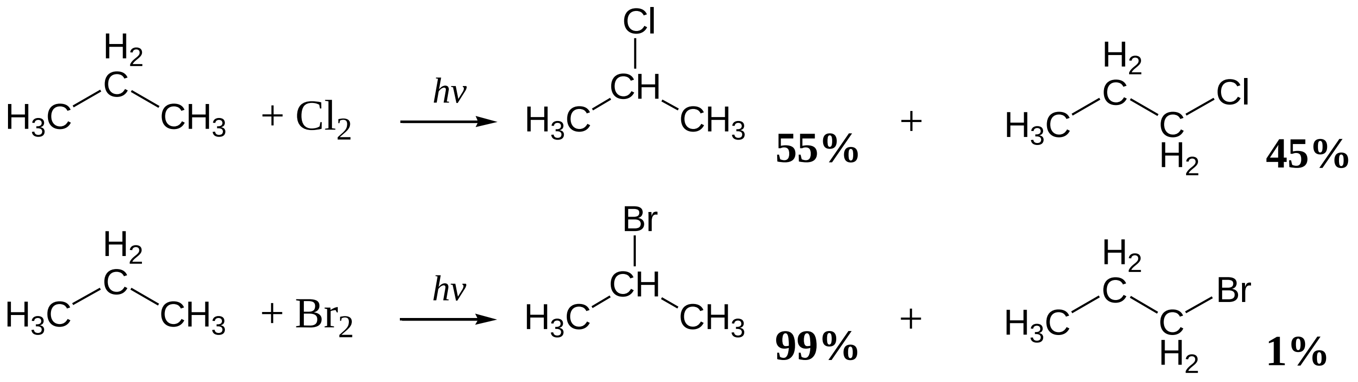
$CH_3CH_2CH_3$

Primary Hydrogens
(in red)

- Order of Reactivity and selectivity of Halides:
  Cl_2 is highly reactive & less selective.
  Br_2 is less reactive & highly selective.

$$CH_3CH_2CH_3 + Cl_2 \qquad CH_3\underset{Cl}{C}HCH_3 + CH_3CH_2CH_2\text{-}Cl + HCl$$

Tertiary hydrogens react faster than secondary hydrogens and secondary hydrogens react faster than primary hydrogens.



? ? ?

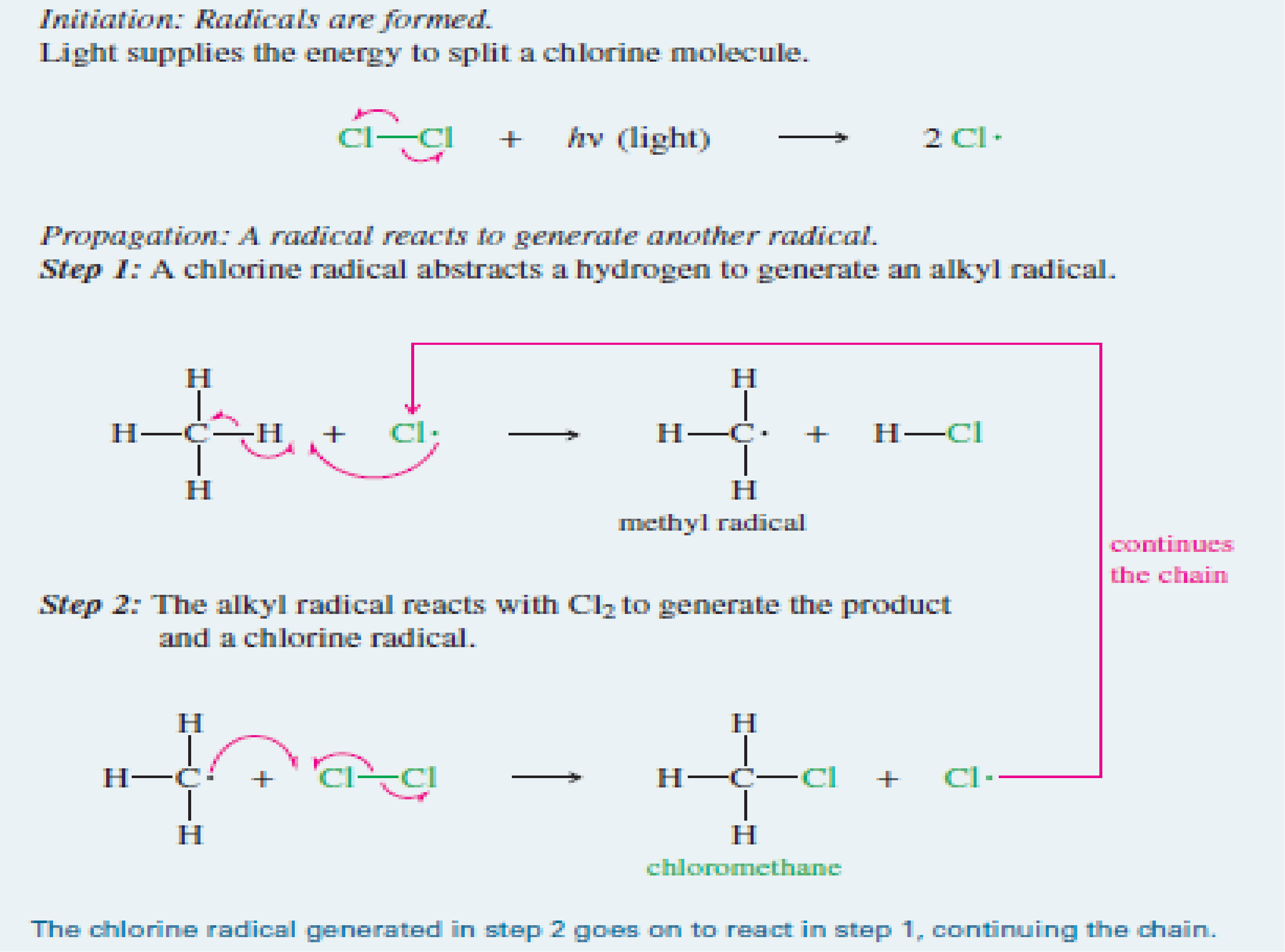
F2

What about OTHER HALOGENS?

I2

will react like chlorine, however, the F-F bond is stronger and harder to breakreaction is more exothermic (C-F bonds are stronger) and is difficult to control (gets out of hand).

is not reactive, even though the I-I bond is the easiest halogen bond to break. The reaction is not very exothermic and the C-I bonds in the products are not stable.



Initiation: Radicals are formed.

Light supplies the energy to split a chlorine molecule.

$$\mathrm{Cl{-}Cl} + h\nu\ (\text{light}) \longrightarrow 2\ \mathrm{Cl}\cdot$$

Propagation: A radical reacts to generate another radical.

Step 1: A chlorine radical abstracts a hydrogen to generate an alkyl radical.

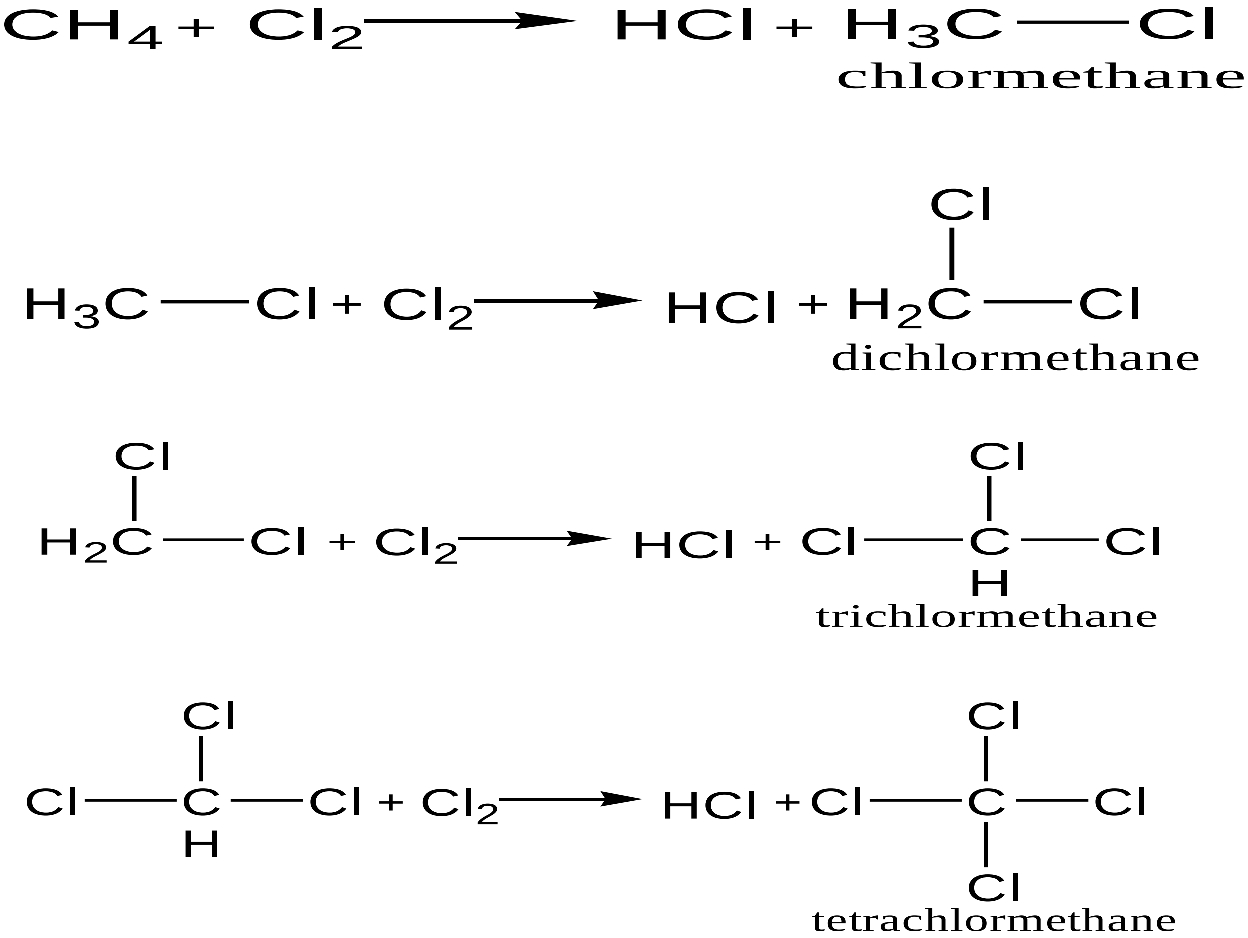
Step 2: The alkyl radical reacts with Cl_2 to generate the product and a chlorine radical.

The chlorine radical generated in step 2 goes on to react in step 1, continuing the chain.

Write the propagation steps leading to the formation of dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$) and tetrachloromethane (CCl_4)?

Steps of Halogenation:

$$RH + X2 \xrightarrow[\Delta]{uv} RX + HX$$



$$CH_4 + Cl_2 \longrightarrow HCl + H_3C\text{—}Cl$$

chlormethane

$$H_3C\text{—}Cl + Cl_2 \longrightarrow HCl + H_2C(Cl)\text{—}Cl$$

dichlormethane

$$H_2C(Cl)\text{—}Cl + Cl_2 \longrightarrow HCl + Cl\text{—}CH(Cl)\text{—}Cl$$

trichlormethane

$$Cl\text{—}CH(Cl)\text{—}Cl + Cl_2 \longrightarrow HCl + Cl\text{—}C(Cl)(Cl)\text{—}Cl$$

tetrachlormethane

Reaction of alkanes

2- Combustion:

- The combustion of carbon compounds, especially hydrocarbons, has been the most important source of heat energy for human civilizations throughout recorded history.
- General formula for combustion reaction:

$$\underset{\text{Alkane}}{C_nH_{2n+2}} + 3n+1/2\ O_2 \longrightarrow \underset{\text{Carbondioxide}}{n\ CO_2} + \underset{\text{Water}}{(n+1)\ H_2O} + \text{heat}$$

- Using the combustion of propane as an example, as in the following equation that every covalent bond in the reactants has been broken and an entirely new set of covalent bonds have formed in the products.

$$CH_3\text{-}CH_2\text{-}CH_3 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O + \text{heat}$$

- The mechanism of combustion is so complex that chemists are just beginning to explore and understand some of its elementary features.
- If insufficient oxygen is supplied some of the products will consist of carbon monoxide, a highly toxic gas.

$$\underset{\text{Propane}}{CH_3\text{-}CH_2\text{-}CH_3} + 4\ O_2 \longrightarrow CO_2 + \underset{\text{Carbonmonoxide}}{2\ CO} + 4\ H_2O + \text{heat}$$

Reaction of alkanes

3- Nitration of alkanes:

The alkanes can be converted to the nitro Alkanes by treating them with nitric acid at very high temperatures.

$$R\text{-}H + HNO_3 \xrightarrow{400^\circ} R\text{-}NO_2 + H_2O$$

Alkane Nitroalkane

$$H_3C-CH_2-CH_3 + HNO_3 \xrightarrow{t,\,p} H_3C-CH_2-CH_2-NO_2 + H_2O$$

Propane Nitropropane

4- Cracking of alkanes:

Cracking is the destroying of some $-C-C-$ and $-C-H$ bonds in the molecule of alkanes at high temperature.

$$CH_3-CH_3 \rightarrow CH_2=CH_2 + H_2$$

Ethane Ethene

$$2\,CH_3-CH_2-CH_2-CH_3 \rightarrow CH_4 + CH_2=CH-CH_3 + CH_3-CH_3 + CH_2=CH_2$$

Butane Methane Propene Ethane Ethene

Alkenes

Aliphatics

Unsaturated hydrocarbons: Alkenes

- Unsaturated hydrocarbons (Alkenes):

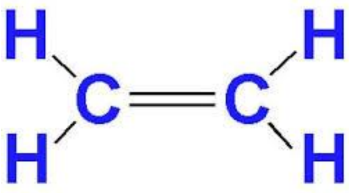
1- They are hydrocarbons contain fewer hydrogens than do alkanes having the same number of carbon atoms.

2-These compounds are deficient in hydrogen that why called unsaturated.

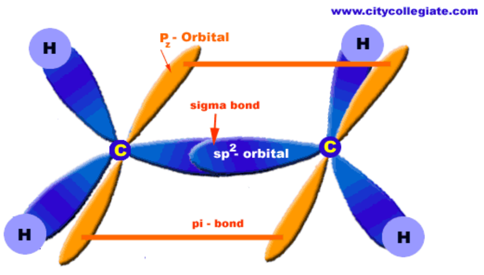
3- Characterized by: the presence of a carbon-carbon double bonds is called the alkenes and has the general formula C_nH_{2n}

4- They are also formed in open chain and cyclic chain with general formula C_nH_{2n-2}

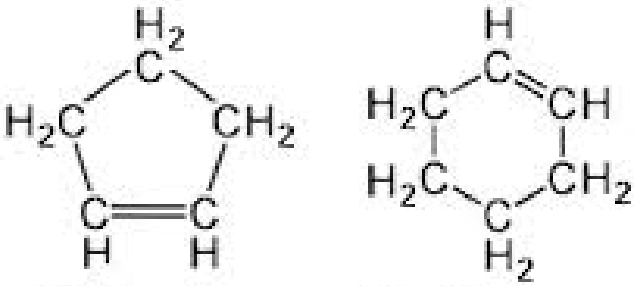
5- In alkenes carbon atoms will have three *sp*^{2} hybridized orbitals and have one non-hybridized *p* orbital.



Ethylene



Orbital structure of ethene



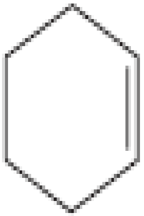
Cyclopentene Cyclohexene

(PD) Image: Milton Beychok

Example cycloalkenes.

Alkene

Simple alkenes are named much like alkanes, using the root name of the longest chain containing the double bond. The ending is changed from -*ane* to -*ene*. For example, “ethane” becomes “ethene,” “propane” becomes “propene,” and “cyclohexane” becomes “cyclohexene.”

	$CH_2{=}CH_2$	$CH_2{=}CH{-}CH_3$	
IUPAC names:	ethene	propene	cyclohexene
Common names:	ethylene	propylene	

Physical properties of alkenes

Most physical properties of alkenes are similar to those of the corresponding alkanes.

1. Solubility & Polarity:

- At room temperature the C_2 to C_4 alkenes are gases; the C_5 to C_{17} alkenes are liquids and those above C_{18} are solids.
- Like alkanes, alkenes are relatively nonpolar. Alkenes tend to be slightly more polar than alkanes, Alkyl groups are slightly electron-donating toward a double bond, helping to stabilize it.
- Like alkanes, alkenes are insoluble in water and soluble in nonpolar organic solvents such as gasoline, halogenated solvents, ethers, benzene C_6H_6 , chloroform $CHCl_3$ or in carbon tetrachloride CCl_4.

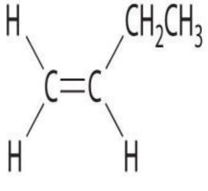
2. Boiling point:

The boiling points of alkenes increase smoothly with molecular weight. As with alkanes, increased branching leads to greater volatility and lower boiling points.

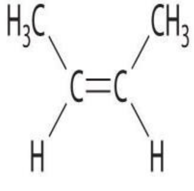
Physical properties of alkenes

3. Geometric isomerism in alkenes:

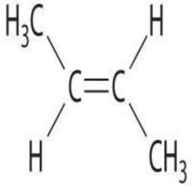
- When two similar groups are on the same side of the double bond, the compound is called the *Cis* isomer; when they are on the opposite side of the double bond, the compound is called the *trans* isomer.
- In *Cis* isomer, the vector sum of the two dipole moments is directed perpendicular to the double bond.
- In *trans* isomer, the two dipole moments tend to cancel out. If an alkene is symmetrically *trans* isomer, the dipole moment is zero.
- For example, cis-but-2-ene has a nonzero dipole moment, but trans-but-2-ene has no measurable dipole moment.



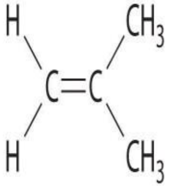
1-Butene
bp 26.2C
mp 2185.3C



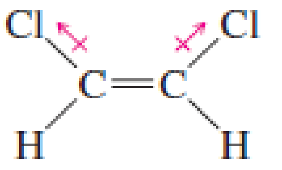
Cis-2-butene
bp 3.7C
mp 2138.9C



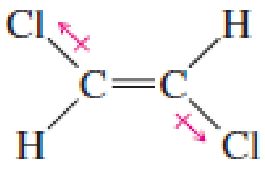
Trans-2-butene
bp 0.8C
mp 2105.5C



2-Methyl-1-propene
bp 26.9C
mp 2140.4C



cis
vector sum = $\uparrow$
μ = 2.4 D
bp = 60 °C

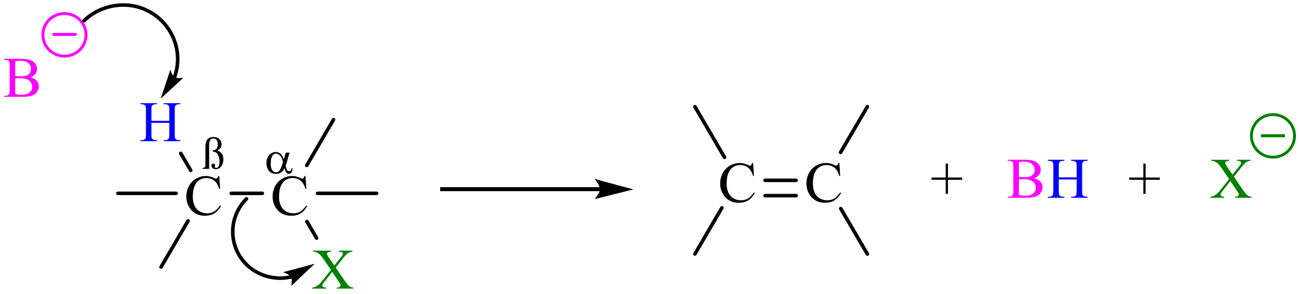


trans
vector sum = 0
μ = 0
bp = 48 °C

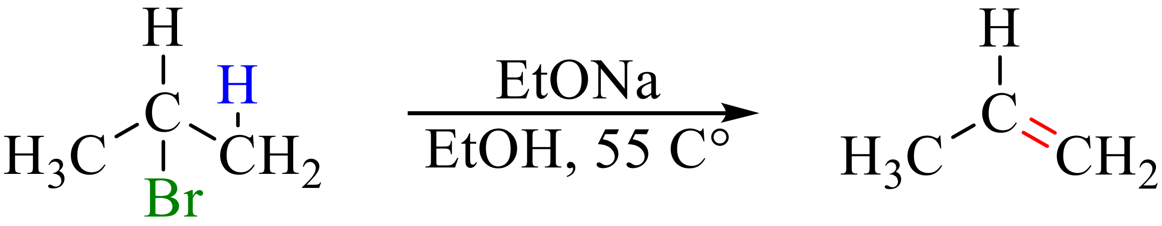
Preparation of Alkenes

1. Dehydrohalogenation of alkyl halides

Dehydrohalogenation occurs when a strong base removes a β hydrogen from the β carbon, and a leaving group (halogen) departs from the α carbon to form a double bond.



Examples:

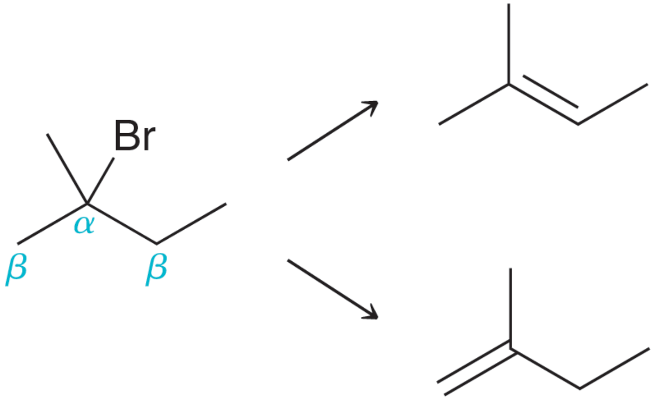


2-bromopropane

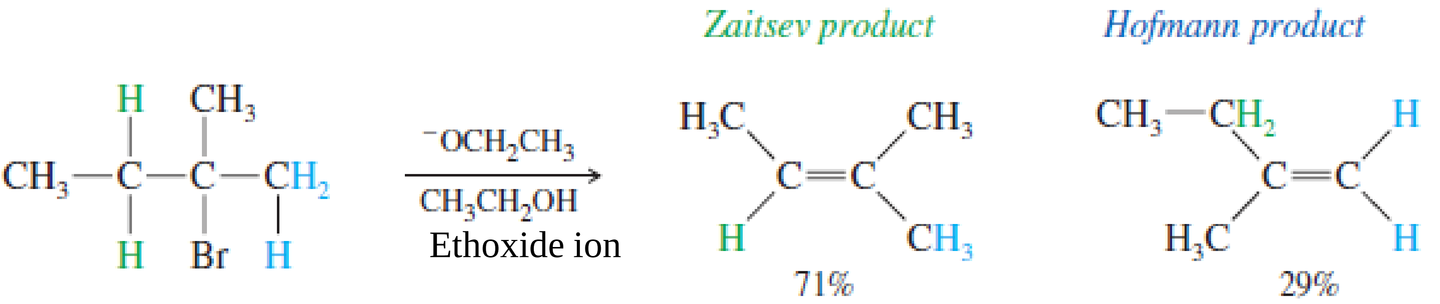
prop-1-ene

Preparation of Alkenes

In many cases, the dehydrohalogenation of alkyl halides can produce two products. In this example, the β positions are not identical, so the double bond can form in two different regions of the molecule.



If we use a **small base** such as **ethoxide or hydroxide**, the major product of the reaction will be the **highly substituted alkene** and it is called **Zaitsev product**. While the less substituted alkene is the minor product and it is called **Hofmann product**.



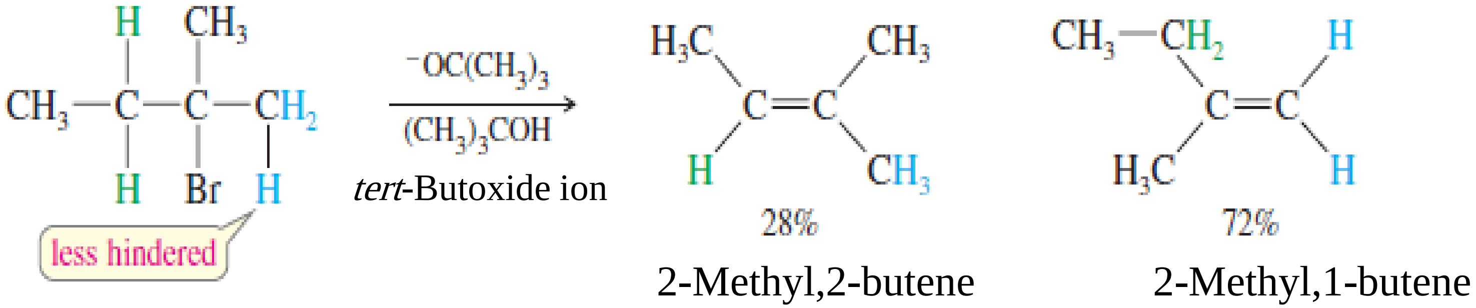
2-Bromo,2-methylbutane

2-Methyl,2-butene

2-Methyl,1-butene

Preparation of Alkenes

If a bulky base was used in the dehydrohalogenation such as potassium *tert*-butoxide (*t*-BuOK) in *tert*-butyl alcohol (*t*-BuOH), **Hofmann product** (less substituted alkene) will be **the major product** whereas **Zaitsev product** (more substituted alkene) is **the minor**. It is difficult to remove the internal protons by the bulky base due to the steric hindrance of the base (*t*-BuOK) and the crowding around the internal (2°) hydrogen.



tert-Butoxide ion

2-Methyl,2-butene

2-Methyl,1-butene

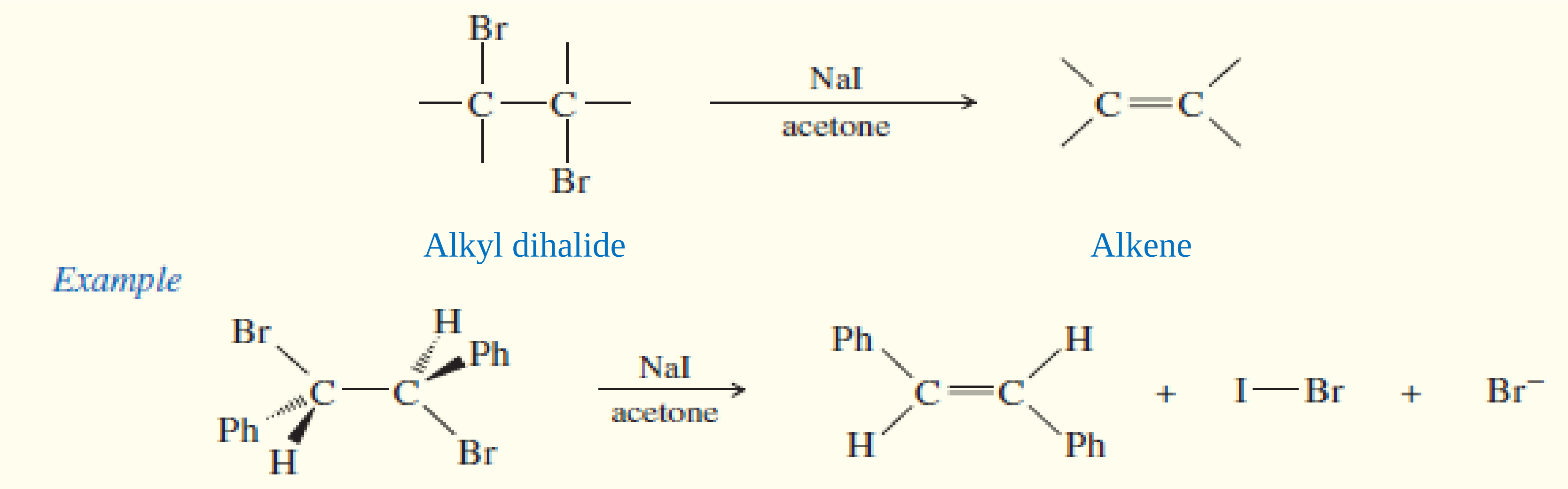
Zaitsev's Rule: The formation of the more substituted alkene is favoured with small bases.

Hofmann's Rule: The formation of the less substituted alkene is favoured with large bulky bases.

Preparation of alkenes

2. Dehalogenation of vicinal dibromides:

Vicinal dibromides (two bromines on adjacent carbon atoms) are converted to alkenes by reduction with iodide ion in acetone.

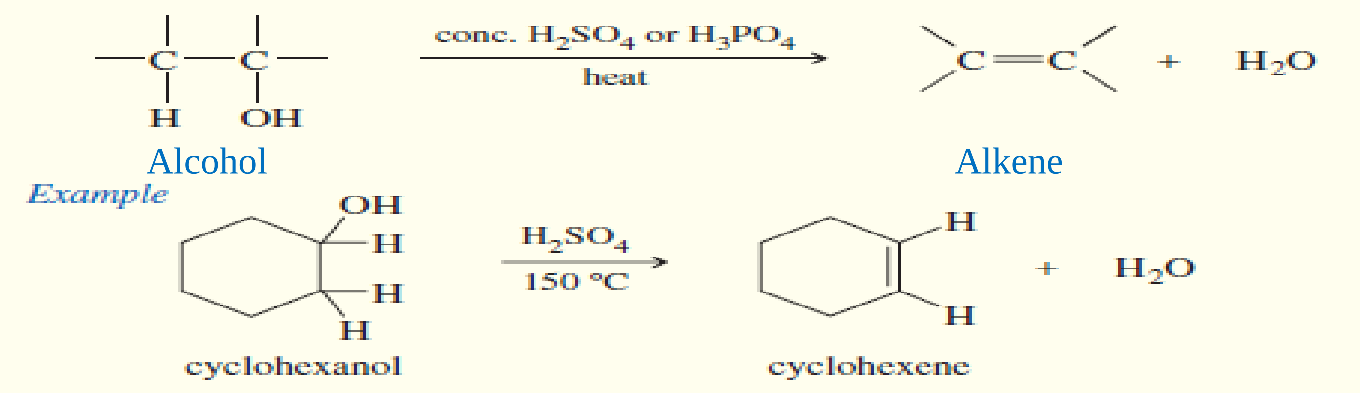


1,2-Dibromo,1,2-diphenyl,ethane trans-1,2 diphenylethene

Preparation of Alkenes

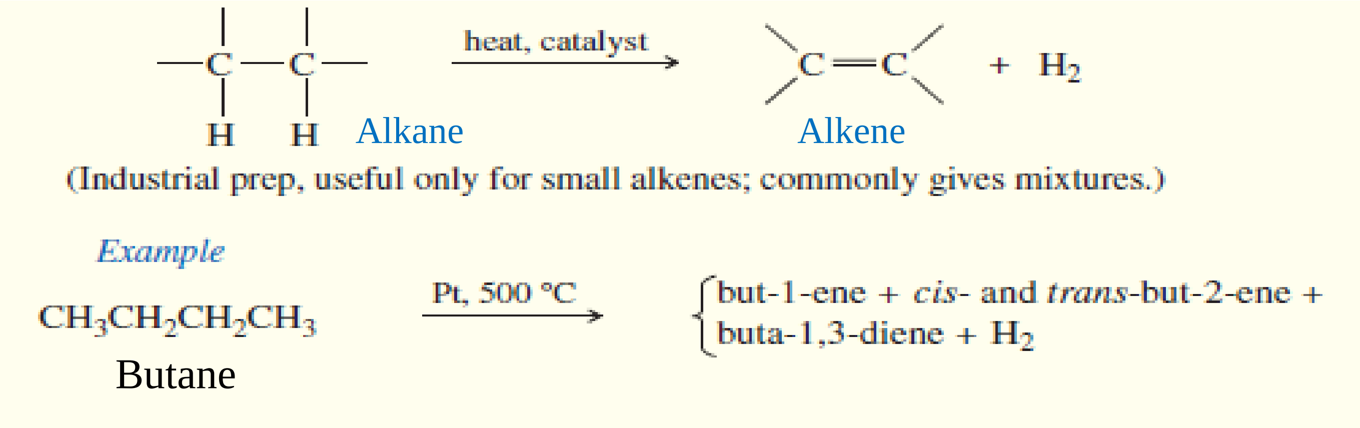
3. Dehydration of alcohols:

Dehydration of alcohols is a common method for making alkenes. The word *dehydration* literally means “removal of water.”



4. Dehydrogenation of alkanes:

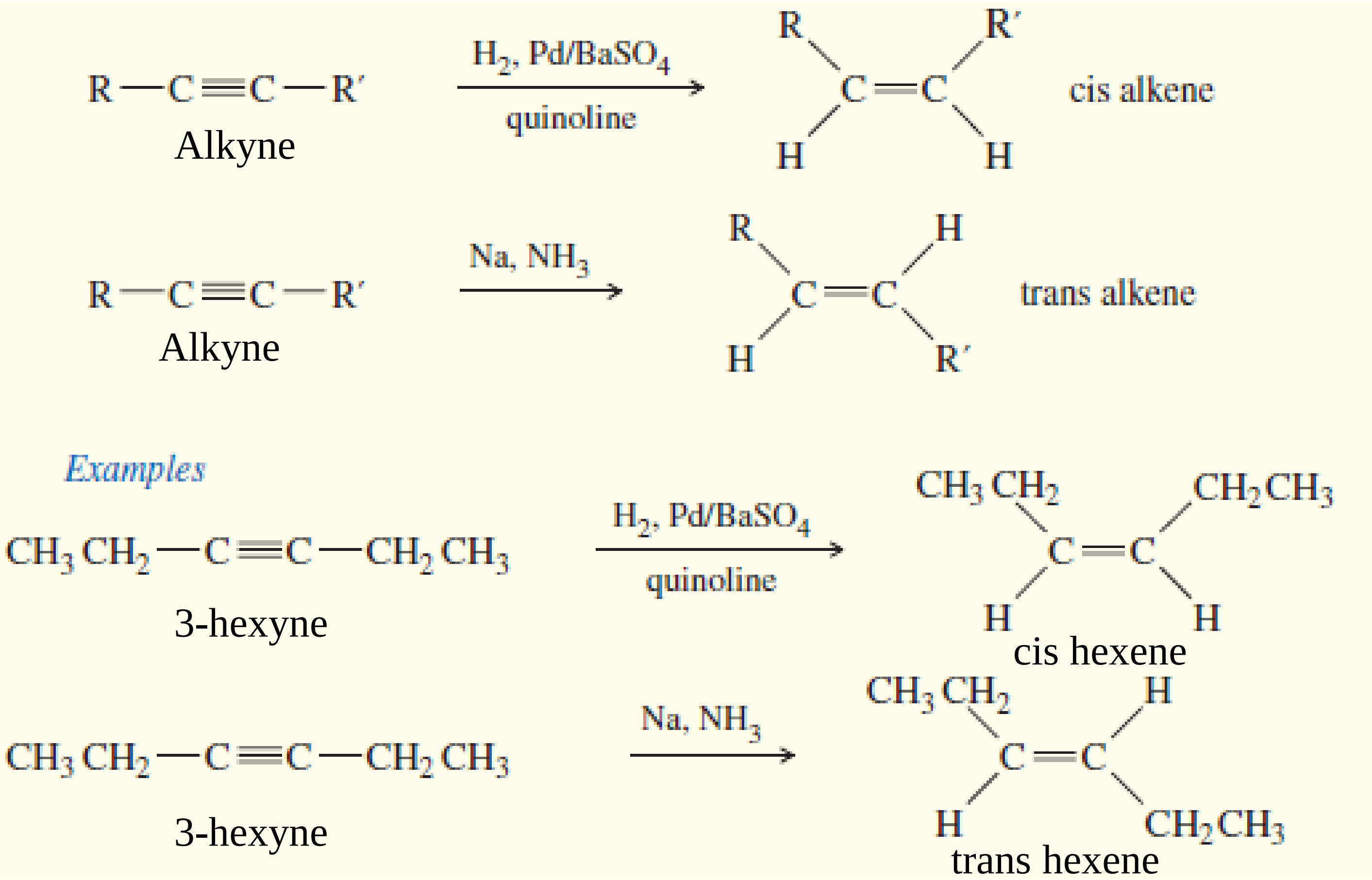
Dehydrogenation is the removal of H_2 from a molecule.



(Industrial prep, useful only for small alkenes; commonly gives mixtures.)

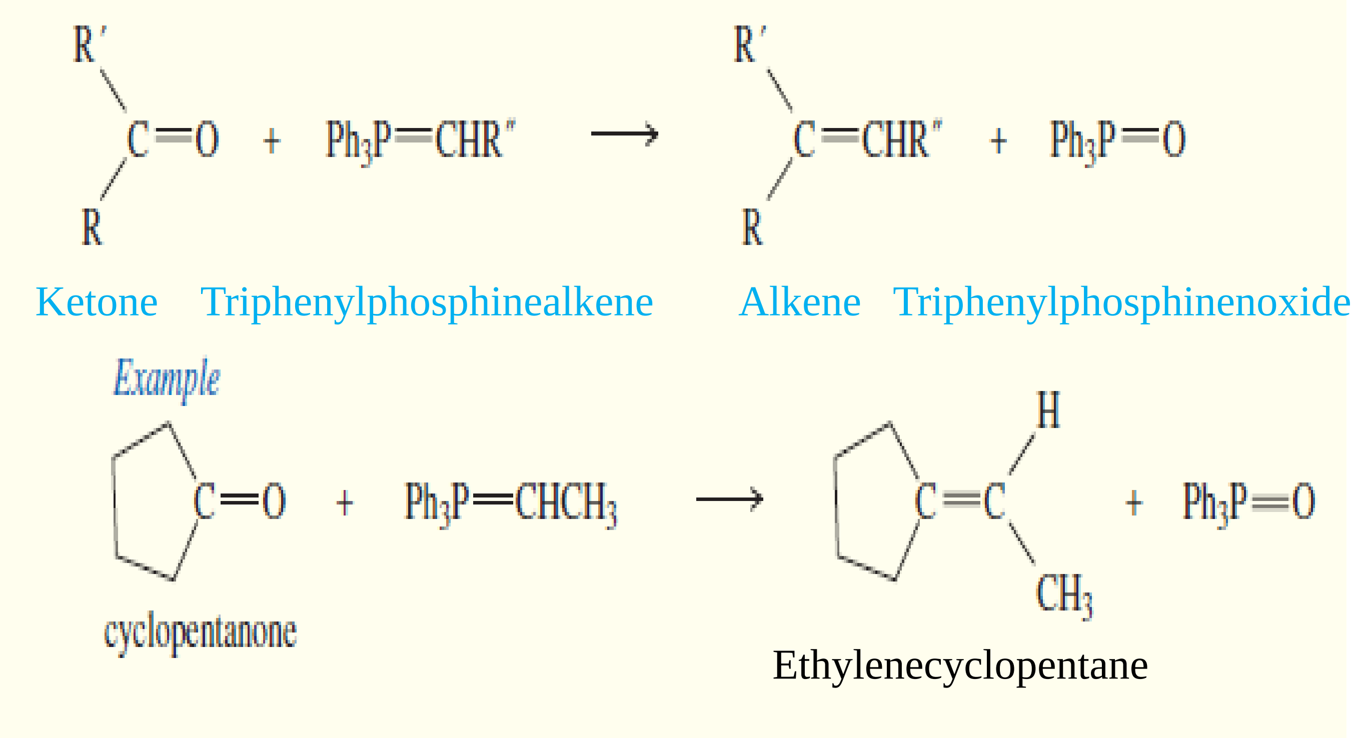
Preparation of Alkenes

5-Reduction of alkynes:



Preparation of Alkenes

6-Wittig reaction:

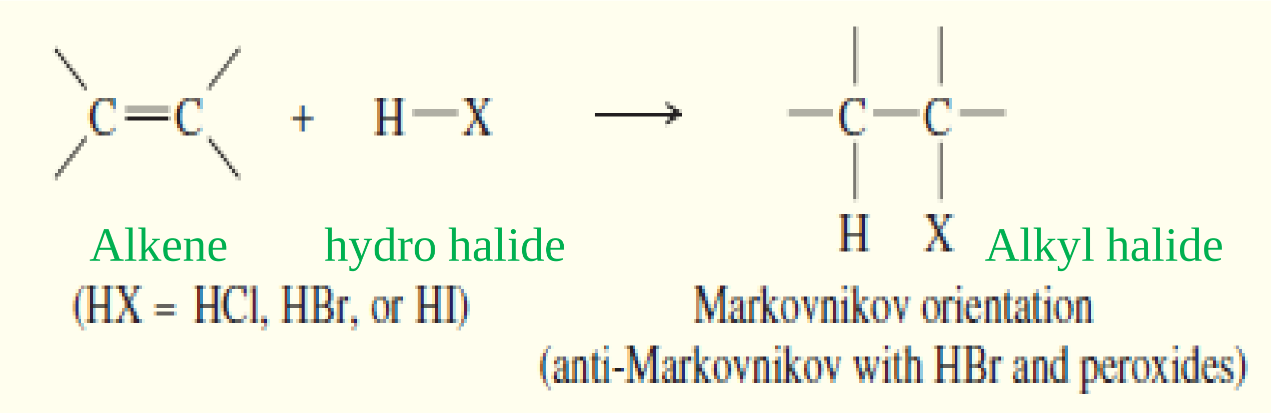


Ketone Triphenylphosphinealkene Alkene Triphenylphosphinenoxide

Ethylenecyclopentane

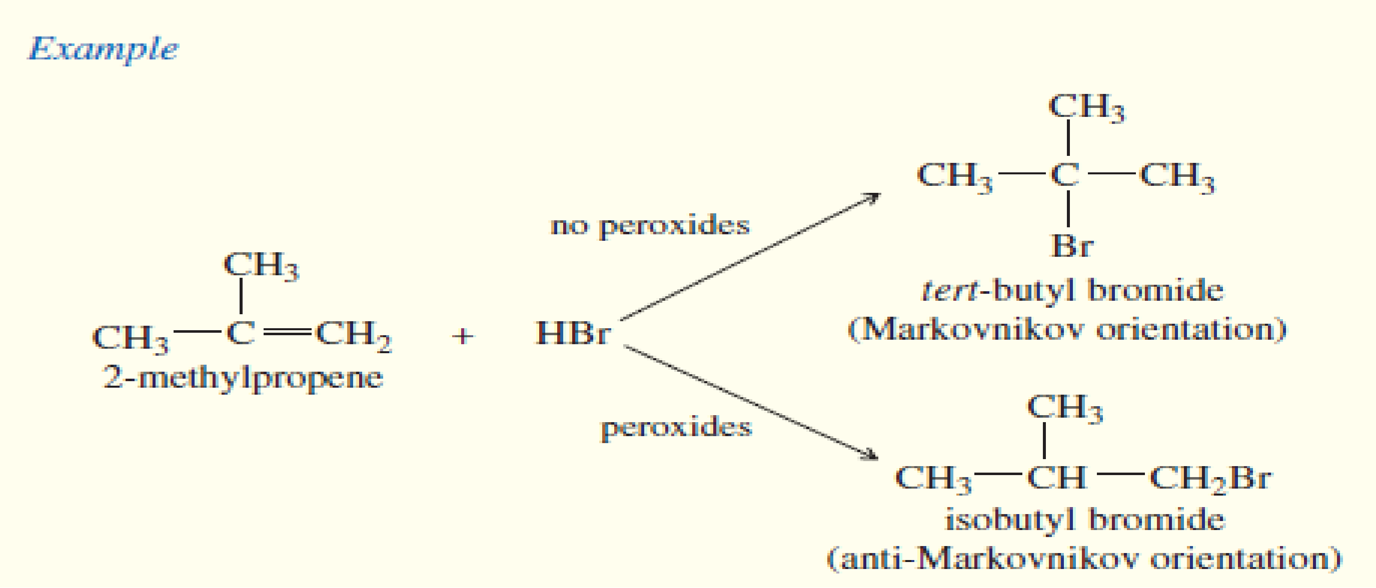
Reaction of Alkenes

1- Addition of hydrogen halides:



(HX = HCl, HBr, or HI)

Markovnikov orientation
(anti-Markovnikov with HBr and peroxides)

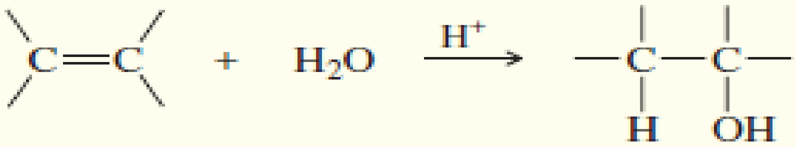


tert-butyl bromide
(Markovnikov orientation)

isobutyl bromide
(anti-Markovnikov orientation)

Reaction of Alkenes

2- Acid-catalyzed hydration: the reaction requires a catalyst—usually a strong acid, such as sulfuric acid (H_2SO_4):

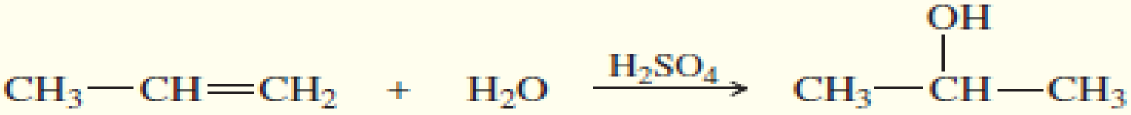


Alkene

Alcohol

(Markovnikov orientation)

Example

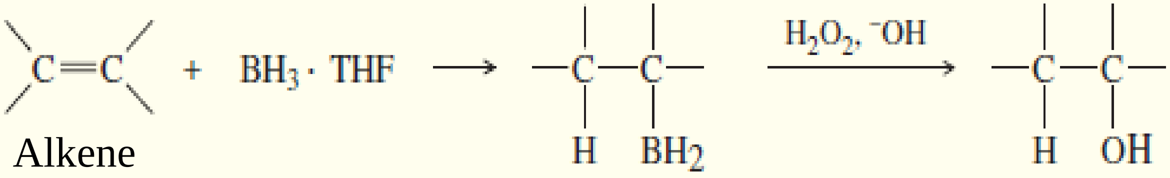


$$CH_3{-}CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3{-}\overset{OH}{CH}{-}CH_3$$

propene

propan-2-ol

3-Hydroboration–oxidation:



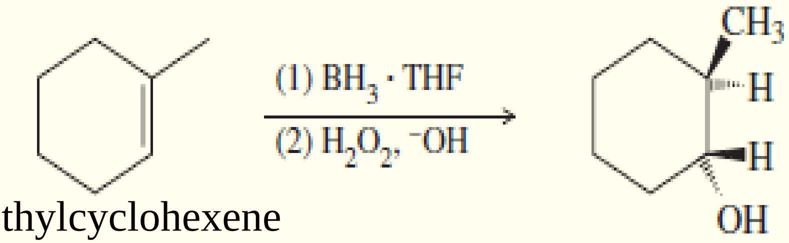
Alkene

Alcohol

1-Hydroborationaklane

anti-Markovnikov orientation
(syn addition)

Example

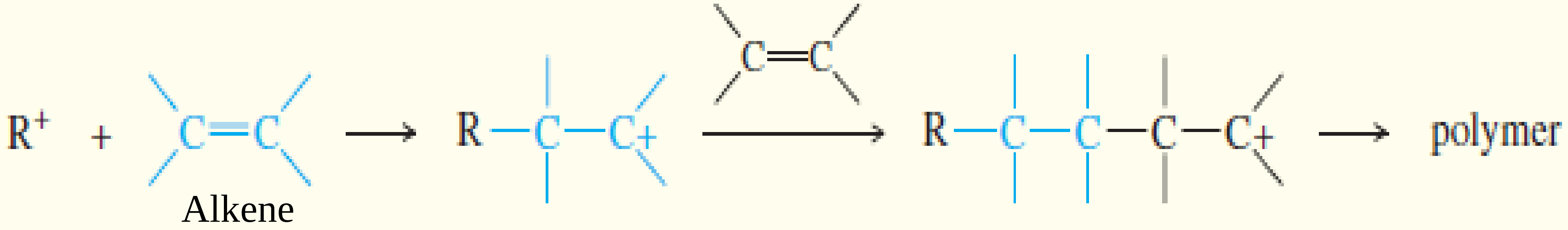


1-methylcyclohexene

2-methylcyclohexanol

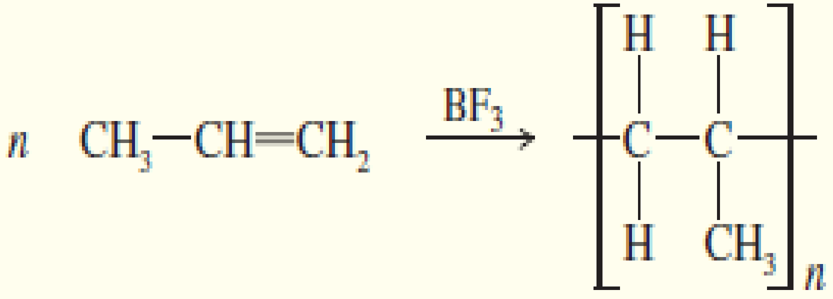
Reaction of Alkenes

4- Polymerization:



(also radical and anionic polymerization)

Example

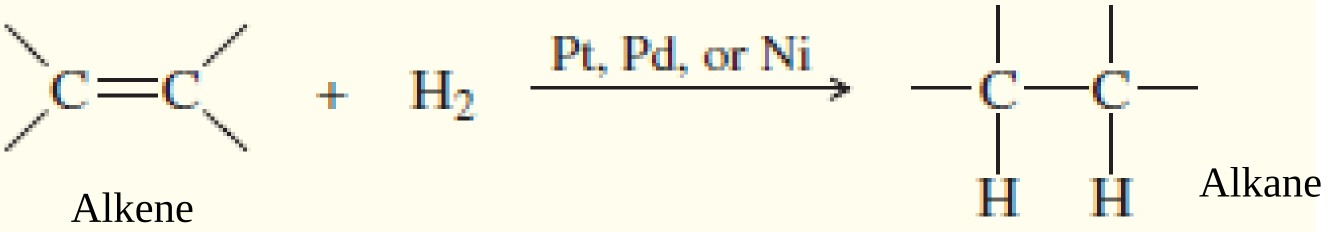


$$n\ CH_3-CH=CH_2 \xrightarrow{BF_3} \left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}- \right]_n$$

propylene polypropylene

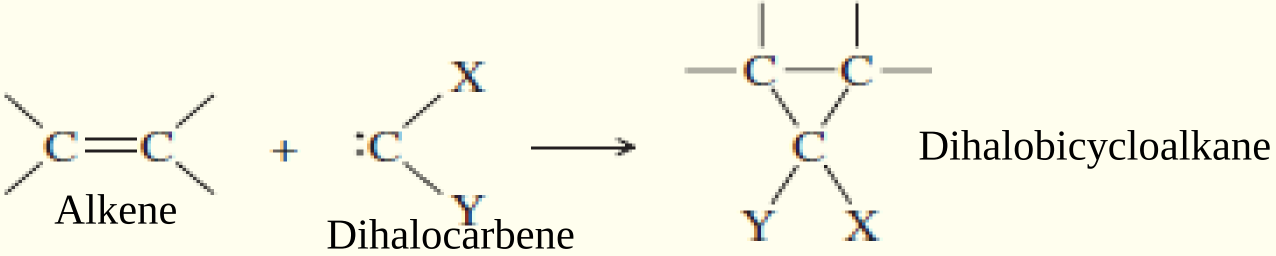
Reaction of Alkenes

5- Reduction: catalytic hydrogenation:



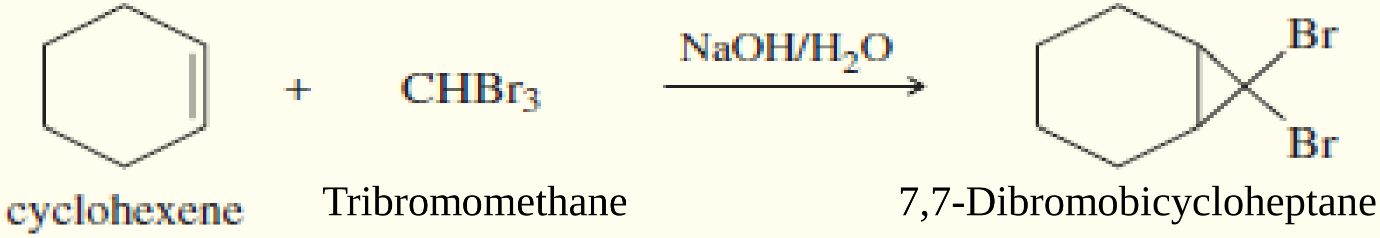
(syn addition)

6- Addition of carbenes: cyclopropanation:



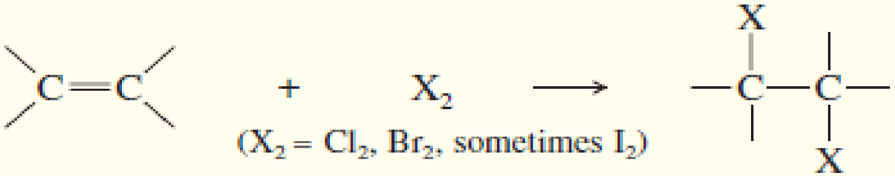
(X,Y = H, Cl, Br, I, or —COOEt)

Example



Reaction of Alkenes

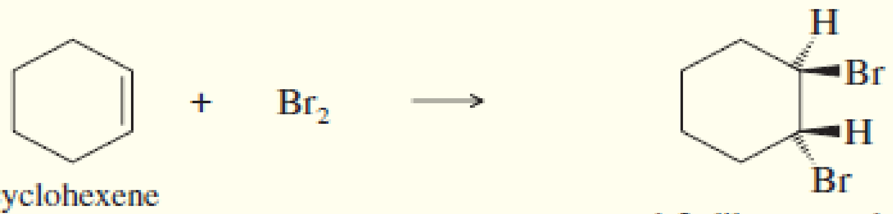
7- Addition of halogens:



($X_2 = Cl_2$, Br_2, sometimes I_2)

(anti addition)

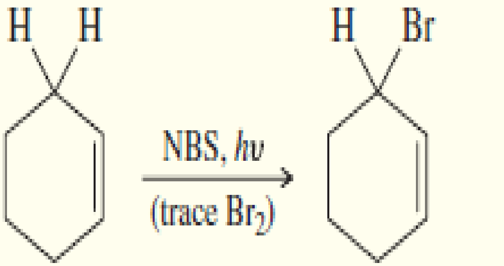
Example



cyclohexene

trans-1,2-dibromocyclohexane

(or substitution)



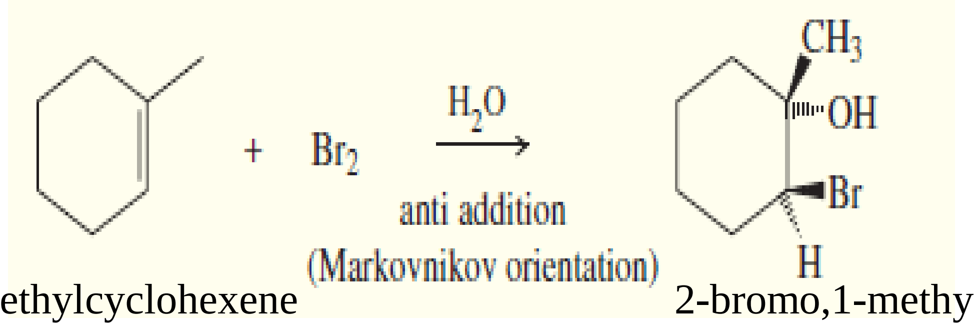
cyclohexene

3-bromocyclohexene

At low concentrations of Br_2, an allylic substitution may be observed. NBS provides a trace of Br_2 that (with light as initiator) allows radical substitution to proceed faster than the ionic addition. (Section 6-6B)

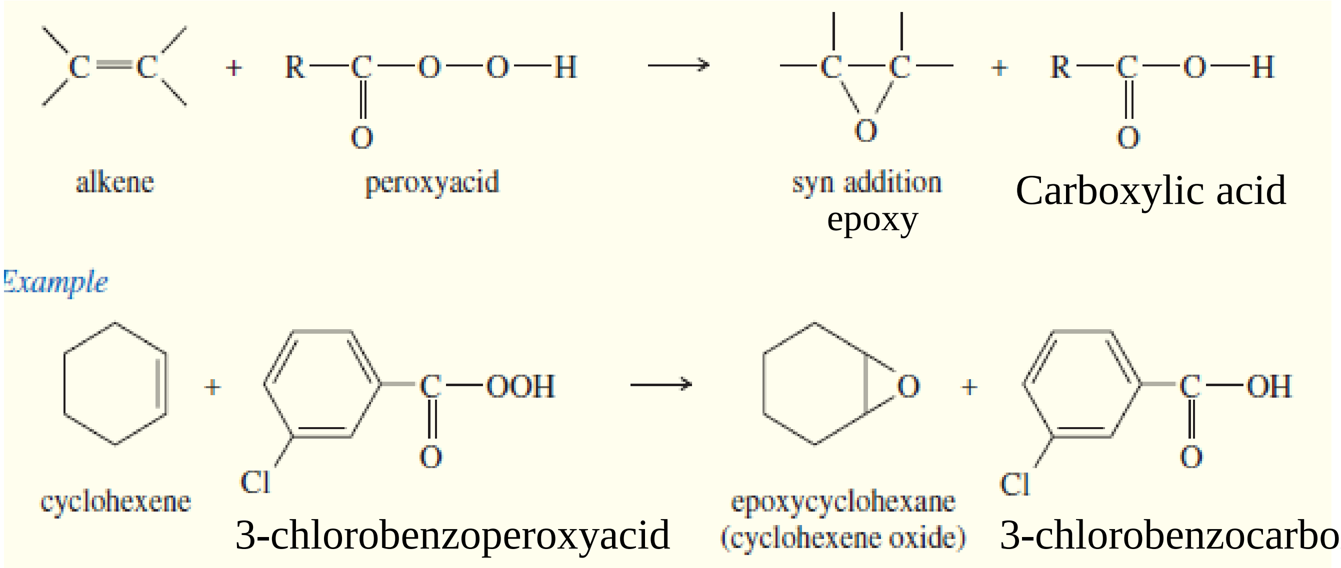
Reaction of Alkenes

8-Halohydrin formation:



1-methylcyclohexene 2-bromo,1-methylcyclohexanol

9- Epoxidation:



epoxy

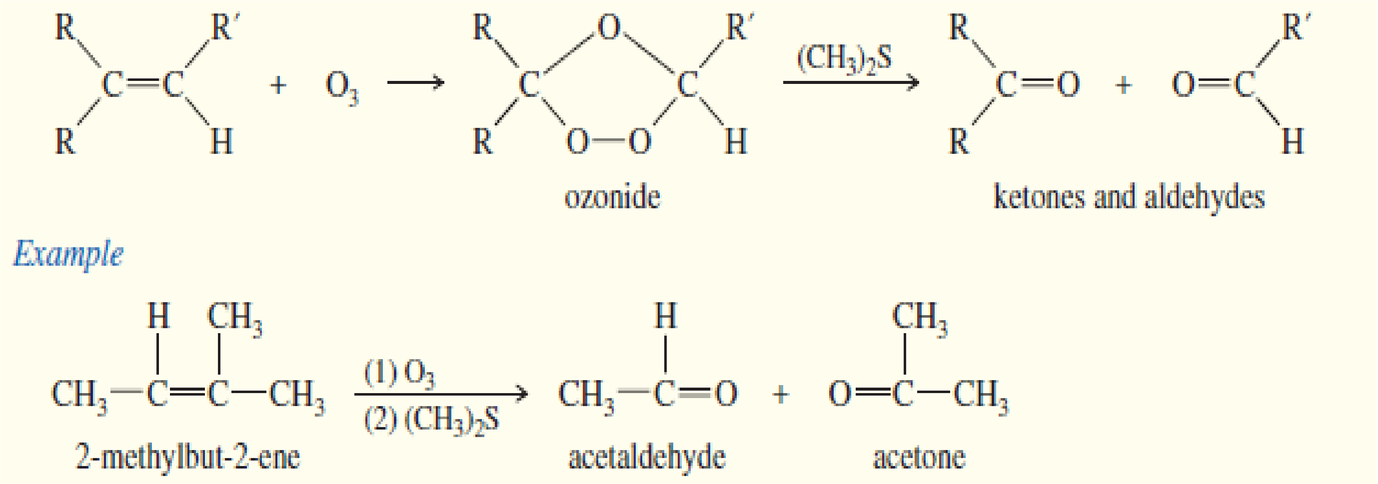
Carboxylic acid

3-chlorobenzoperoxyacid

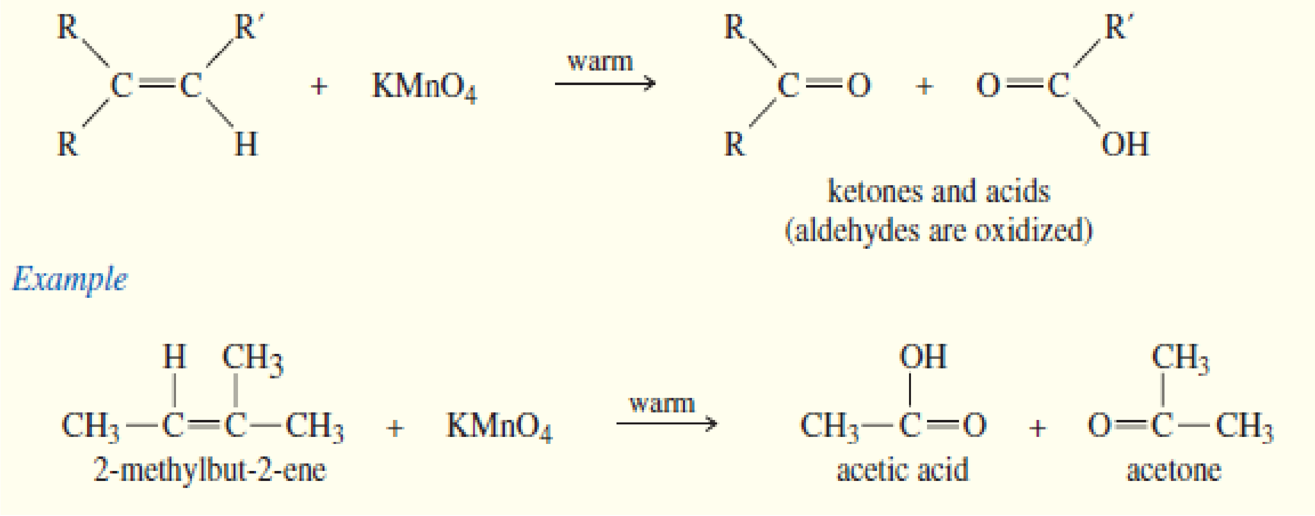
3-chlorobenzocarboxylicacid

Reaction of Alkenes

10- Ozonolysis:



11- Potassium permanganate:



Alkynes

Aliphatics

Unsaturated hydrocarbons: Alkynes

- Unsaturated hydrocarbons (Alkynes):

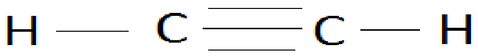
1- They are hydrocarbons contain fewer hydrogens than do alkanes having the same number of carbon atoms.

2-These compounds are deficient in hydrogen that why called unsaturated.

3- Characterized by: the presence of a carbon-carbon triple bonds is called the alkynes and has the general formula C_nH_{2n-2}.

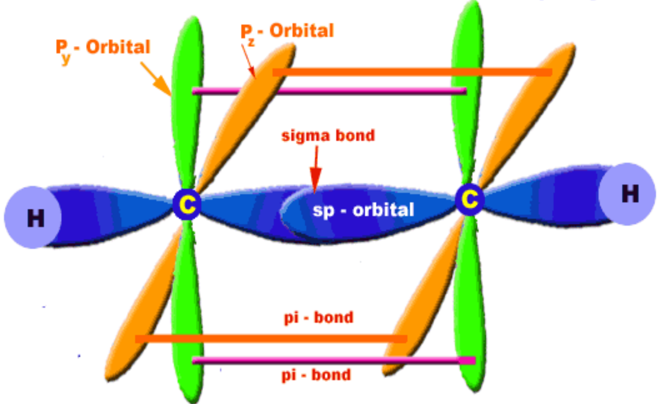
4-They are formed in open chain with general formula C_nH_{2n-2} and cyclic chain with general formula C_nH_{2n-4}

5- In alkynes carbon atoms will have two *sp* hybridized orbitals and have two non-hybridized *p* orbitals.

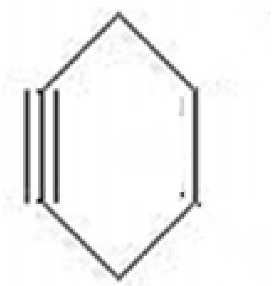


ethyne

www.citycollegiate.com



Orbital structure of ethyne



Alkynes

Alkynes are hydrocarbons that contain carbon–carbon triple bonds. Alkynes are also called **acetylenes** because they are derivatives of acetylene, the simplest alkyne.

$H-C\equiv C-H$	$CH_3CH_2-C\equiv C-H$	$CH_3-C\equiv C-CH_3$
acetylene	ethylacetylene	dimethylacetylene
ethyne	but-1-yne	but-2-yne

Physical Properties of Alkynes

In general, the physical properties of alkynes are much the same as those of corresponding alkanes and alkene.

1- Solubility:

Alkynes are relatively nonpolar, nearly insoluble in water and soluble in nonpolar organic solvents.

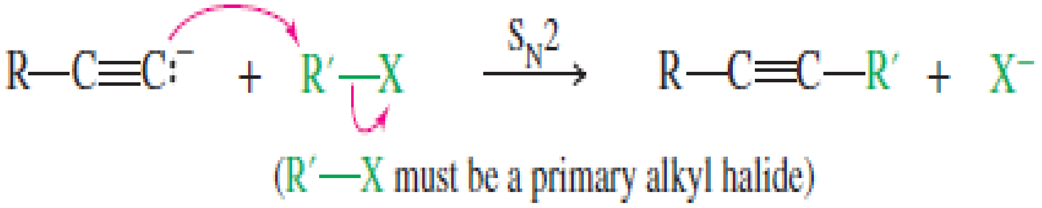
2- Boiling point:

It is increasing with increasing molecular weight. In fact, the boiling points of alkynes are nearly the same as those of alkanes and alkenes with similar carbon skeletons.

Preparation of Alkynes

1. Alkylation of acetylide ions:

An acetylide ion is a strong base and a powerful nucleophile. It can displace a halid ion from a suitable substrate, giving a substituted acetylene.

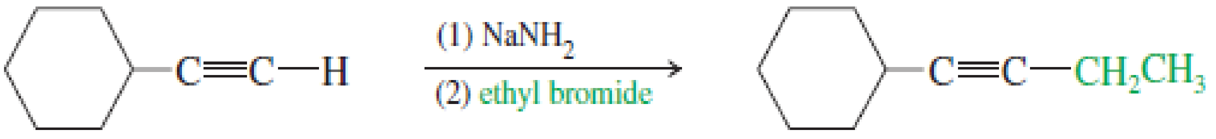


$$R{-}C{\equiv}C{:}^{-} + R'{-}X \xrightarrow{S_N2} R{-}C{\equiv}C{-}R' + X^{-}$$

(R′—X must be a primary alkyl halide)

$$H{-}C{\equiv}C{:}^{-}\ Na^{+} + CH_3CH_2CH_2CH_2{-}Br \longrightarrow H{-}C{\equiv}C{-}CH_2CH_2CH_2CH_3 + NaBr$$

sodium acetylide; 1-bromobutane; hex-1-yne (butylacetylene) (75%)



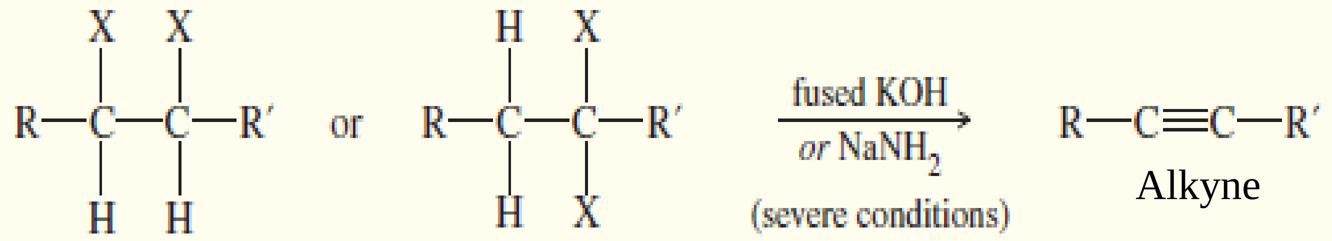
ethynylcyclohexane
(cyclohexylacetylene)

1-cyclohexylbut-1-yne
(ethylcyclohexylacetylene)
(70%)

Preparation of Alkynes

2- Double dehydrohalogenation of alkyl dihalides:

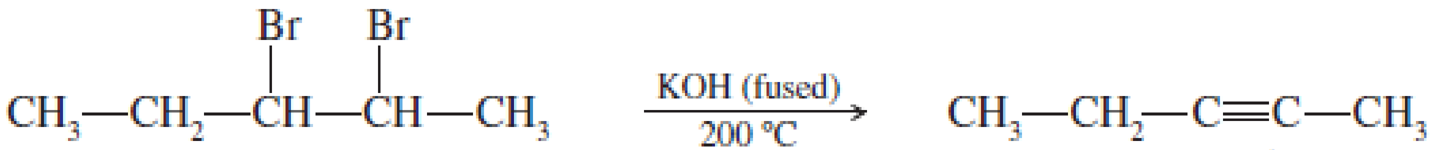
In some cases, we can generate a carbon–carbon triple bond by eliminating two molecules of HX from a dihalide. Dehydrohalogenation of a vicinal or geminal dihalide gives a vinyl halide. Under strongly basic conditions, a second dehydrohalogenation may occur to form an alkyne.



$$R-\underset{H}{\overset{X}{C}}-\underset{H}{\overset{X}{C}}-R' \quad \text{or} \quad R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-R' \xrightarrow[\text{or } NaNH_2 \text{ (severe conditions)}]{\text{fused KOH}} \underset{\text{Alkyne}}{R-C\equiv C-R'}$$

(KOH forms internal alkynes; $NaNH_2$ forms terminal alkynes.)

Example:

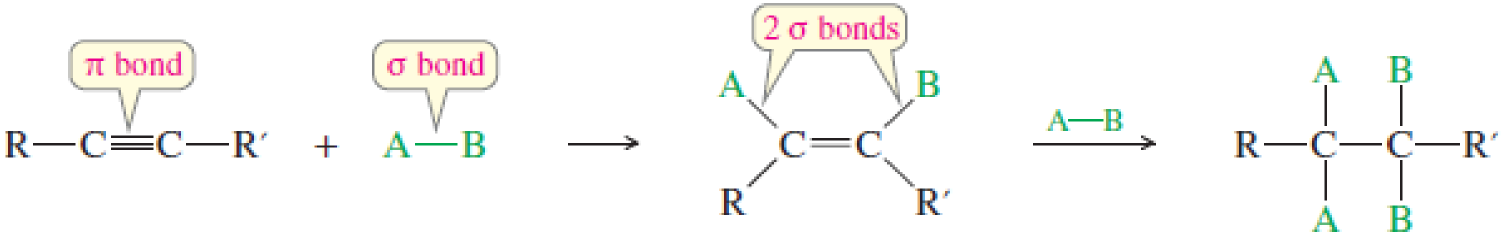


$$\underset{\text{2,3-dibromopentane}}{CH_3-CH_2-\overset{Br}{CH}-\overset{Br}{CH}-CH_3} \xrightarrow[200\ ^\circ C]{\text{KOH (fused)}} \underset{\text{pent-2-yne (45\%)}}{CH_3-CH_2-C\equiv C-CH_3}$$

$$\underset{\text{1,1-dichloropentane}}{CH_3CH_2CH_2CH_2-CHCl_2} \xrightarrow[150\ ^\circ C]{NaNH_2} CH_3CH_2CH_2C\equiv C:^- \quad Na^+ \xrightarrow{H_2O} \underset{\text{pent-1-yne (55\%)}}{CH_3CH_2CH_2C\equiv CH}$$

Reaction of alkynes

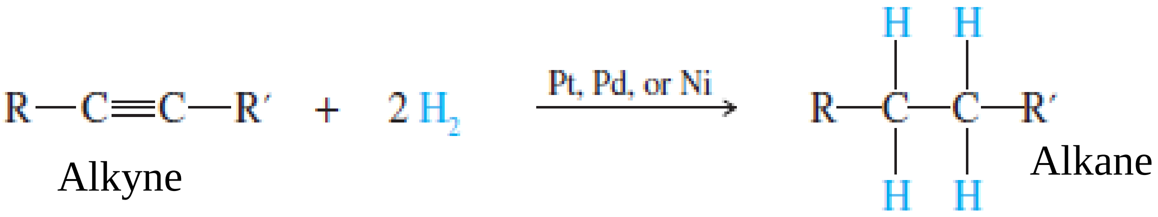
1-Addition reactions of alkynes:



a-Catalytic hydrogenation to alkanes:

In the presence of a suitable catalyst, hydrogen adds to an alkyne, reducing it to an alkane. For example, when either of the butyne isomers reacts with hydrogen and a platinum catalyst, the product is *n*-butane. Platinum, palladium, and nickel catalysts are commonly used in this reduction.

Examples:



$$R-C\equiv C-R' + 2\,H_2 \xrightarrow{\text{Pt, Pd, or Ni}} R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-R'$$

Alkyne

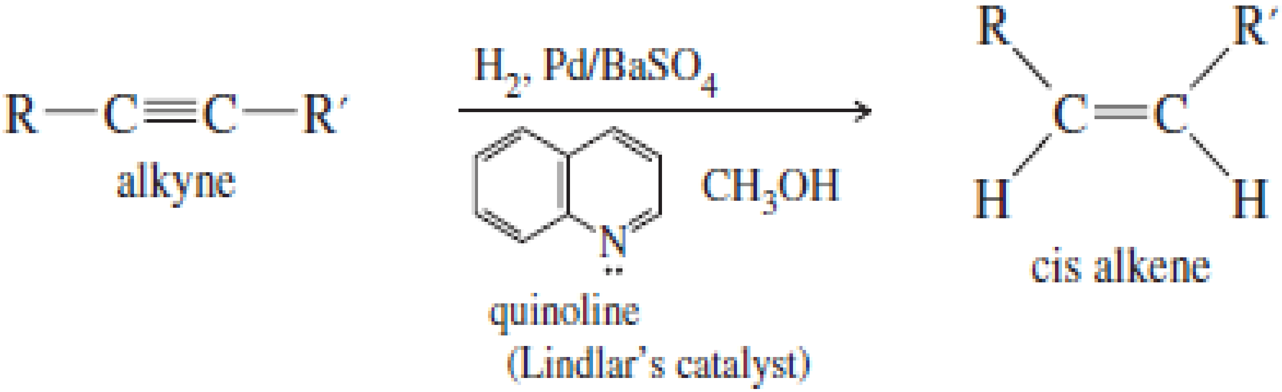
Alkane

$$\underset{\text{but-1-yne}}{H-C\equiv C-CH_2CH_3} + 2\,H_2 \xrightarrow{Pt} \underset{\text{butane (100\%)}}{H-CH_2-CH_2-CH_2CH_3}$$

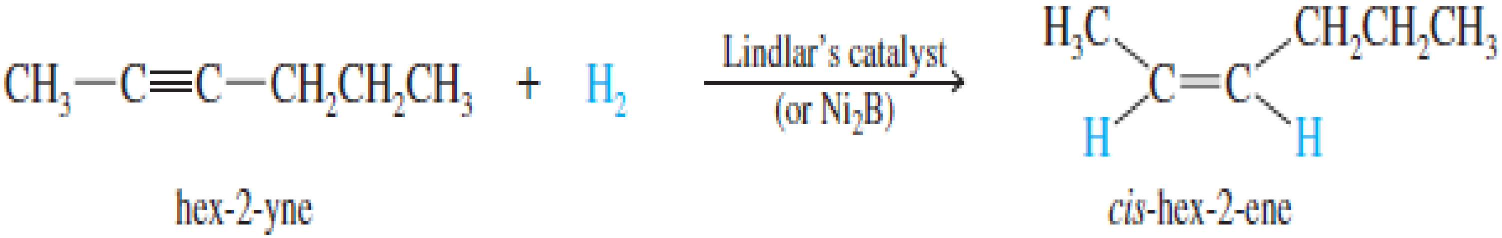
$$\underset{\text{but-2-yne}}{CH_3-C\equiv C-CH_3} + 2\,H_2 \xrightarrow{Pt} \underset{\text{butane (100\%)}}{CH_3-CH_2-CH_2-CH_3}$$

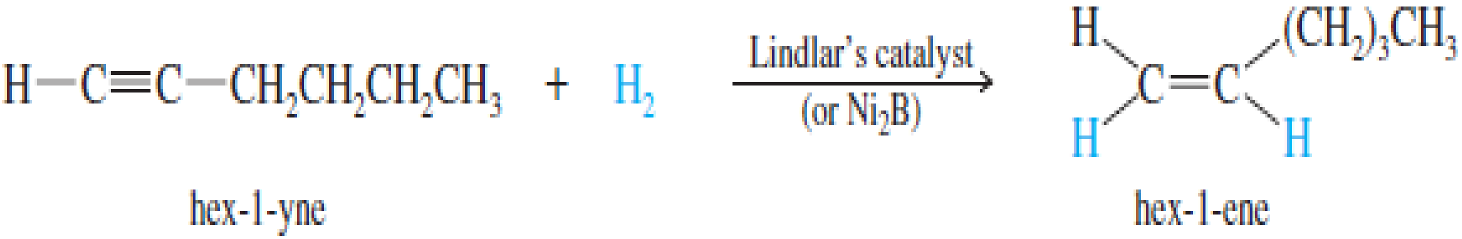
Reaction of alkynes

b- Catalytic hydrogenation to cis alkenes:



Example:

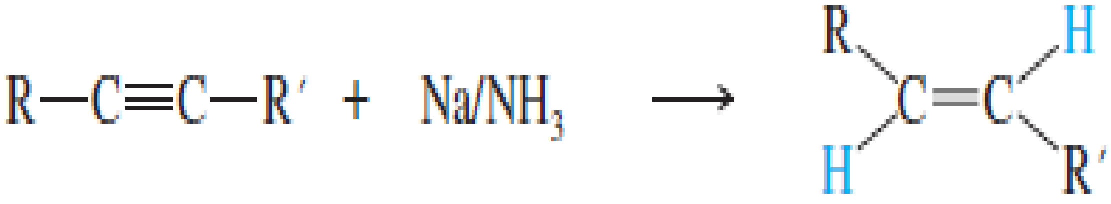




Reaction of alkynes

c-Metal–ammonia reduction to trans alkenes:

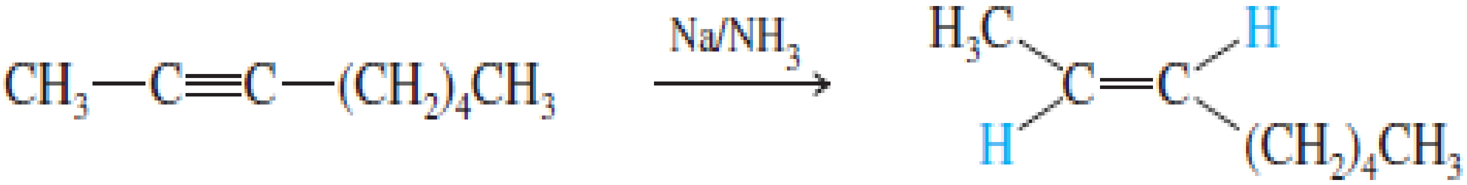
Sodium metal in liquid ammonia reduces alkynes with anti stereochemistry, so this reduction is used to convert alkynes to trans alkenes.



alkyne

trans alkene

Example:



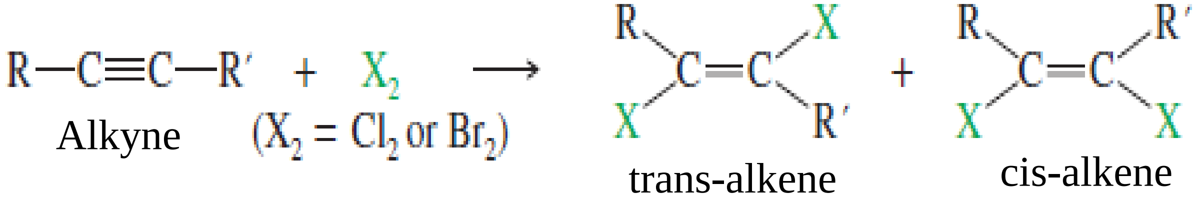
oct-2-yne

trans-oct-2-ene
(80%)

Reaction of alkynes

2- Addition of Halogens:

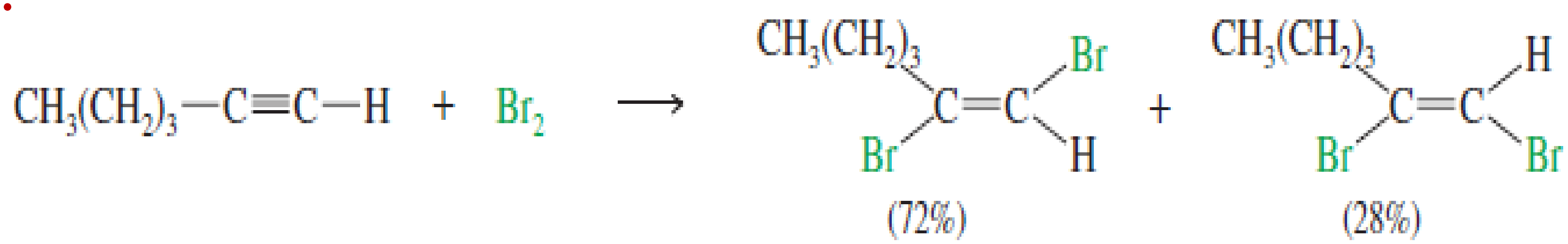
Bromine and chlorine add to alkynes just as they add to alkenes. If 1 mole of halogen adds to 1 mole of an alkyne, the product is a dihaloalkene. The stereochemistry of addition may be either syn or anti, and the products are often mixtures of cis and trans isomers.


Alkyne $(X_2 = Cl_2 \text{ or } Br_2)$

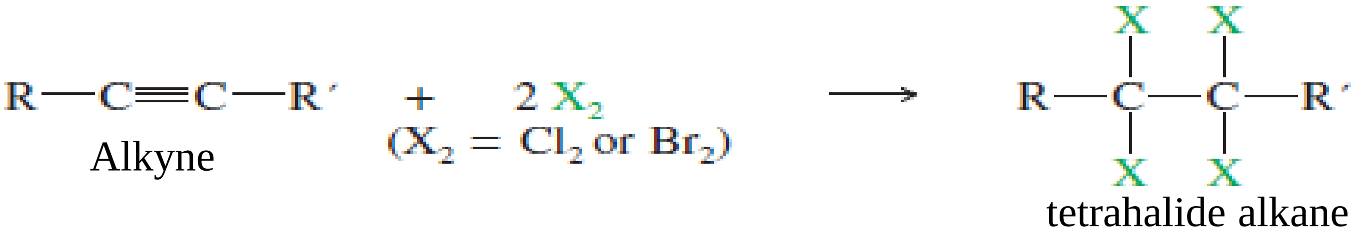
trans-alkene

cis-alkene

Example:


(72%) (28%)

If 2 moles of halogen add to 1 mole of an alkyne, a tetrahalide results.

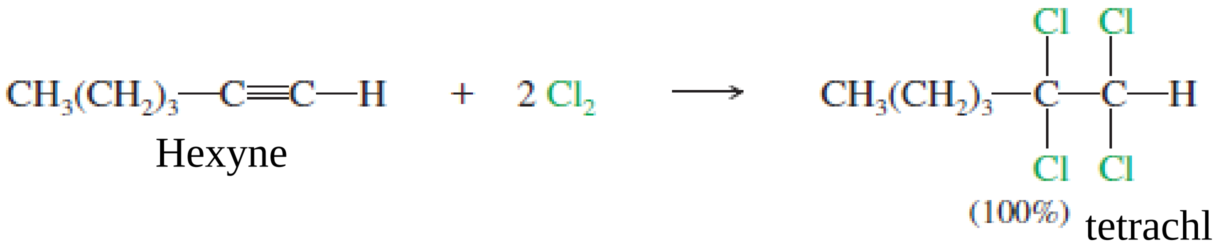


$$R-C\equiv C-R' + 2X_2 \longrightarrow R-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-R'$$

Alkyne $(X_2 = Cl_2 \text{ or } Br_2)$

tetrahalide alkane

Example:



$$CH_3(CH_2)_3-C\equiv C-H + 2Cl_2 \longrightarrow CH_3(CH_2)_3-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{C}}-H$$

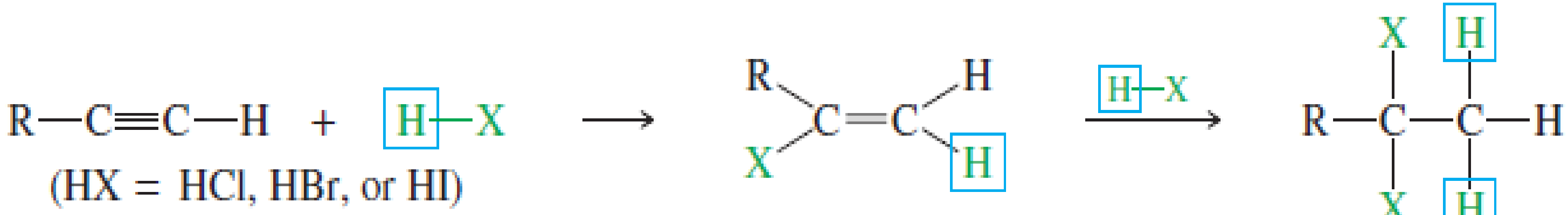
Hexyne

(100%) tetrachlorohexane

Reaction of alkynes

3- Addition of hydrogen halides:

Hydrogen halides add across the triple bond of an alkyne in much the same way they add across the alkene double bond. The initial product is a vinyl halide. When a hydrogen halide adds to a terminal alkyne, the product has the orientation predicted by Markovnikov's rule. A second molecule of HX can add, usually with the same orientation as the first.

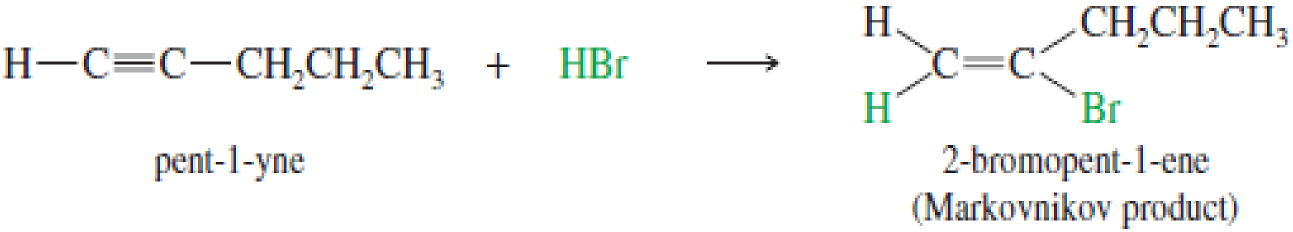


Alkyne

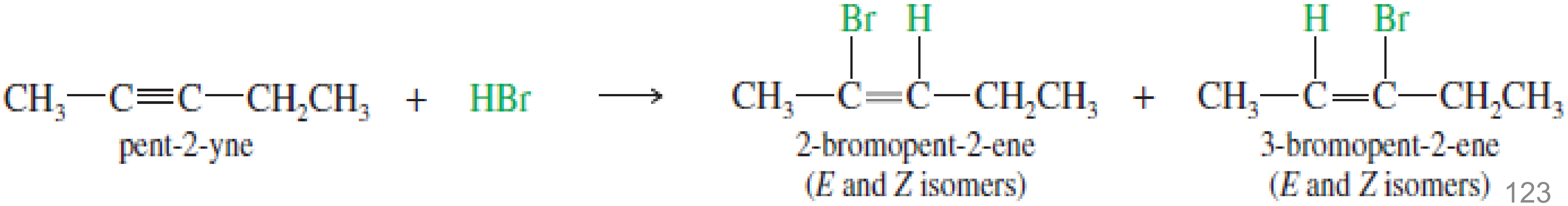
Halide alkene

Dihalide alkane

Example:


pent-1-yne

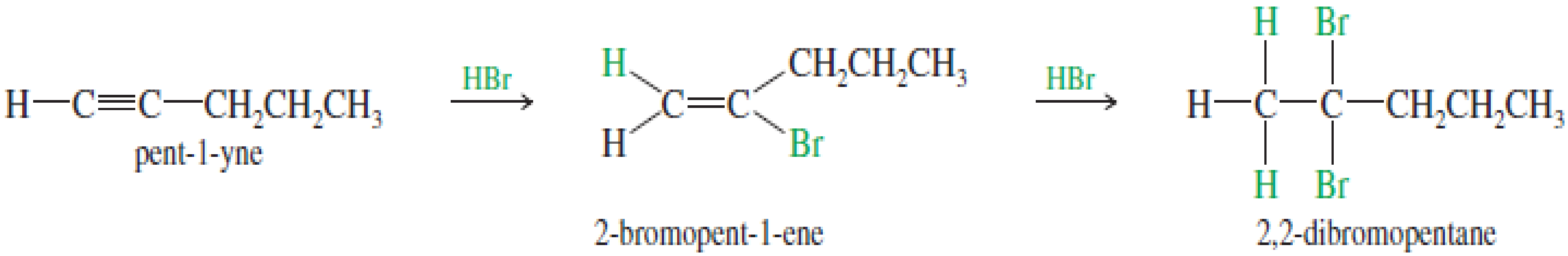
2-bromopent-1-ene (Markovnikov product)


pent-2-yne

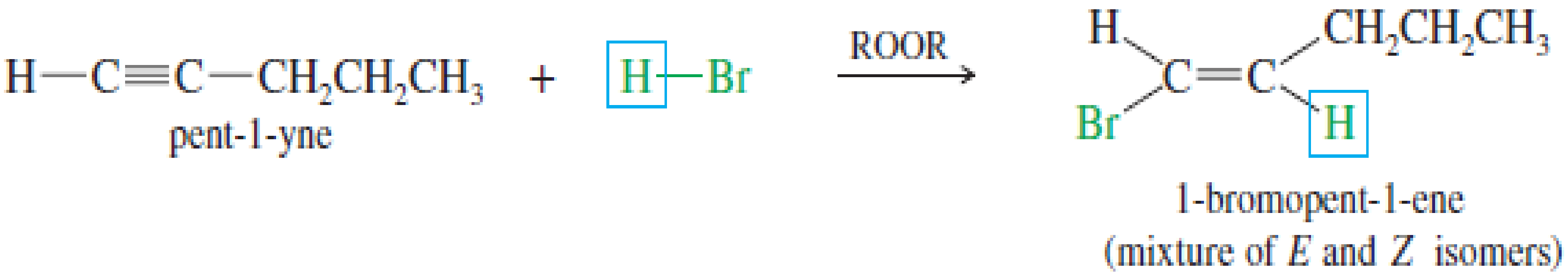
2-bromopent-2-ene (*E* and *Z* isomers)

3-bromopent-2-ene (*E* and *Z* isomers)

Reaction of alkynes



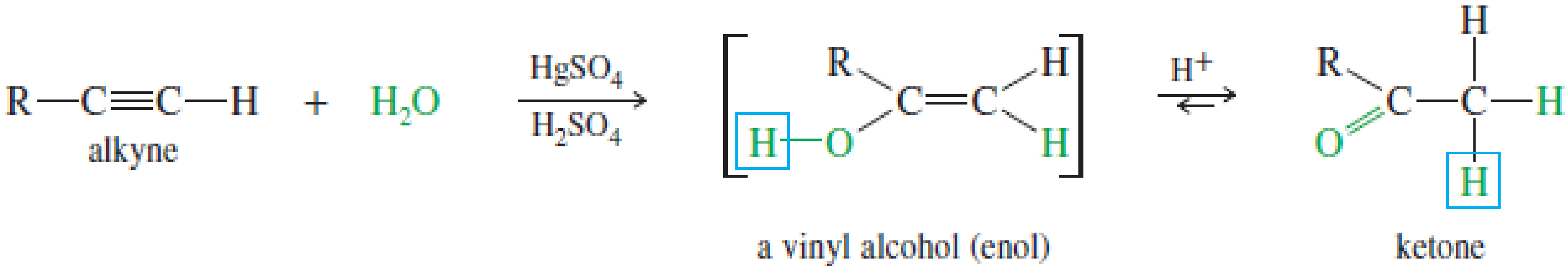
Peroxides catalyze a free-radical chain reaction that adds HBr across the double bond of an alkene in the anti-Markovnikov sense. A similar reaction occurs with alkynes, with HBr adding with anti-Markovnikov orientation.



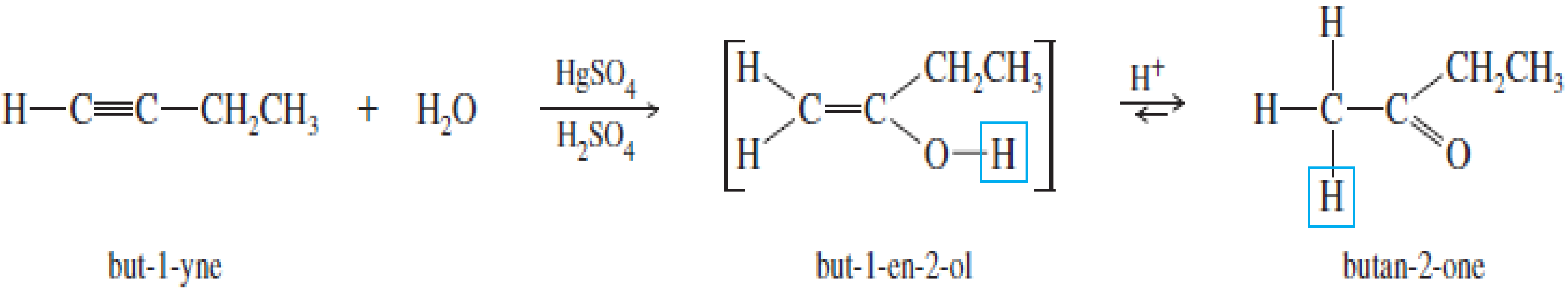
Reaction of alkynes

4- Hydration of alkynes to ketones and aldehydes:

Mercuric Ion-Catalyzed Hydration Alkynes undergo acid-catalyzed addition of water across the triple bond in the presence of mercuric ion as a catalyst.



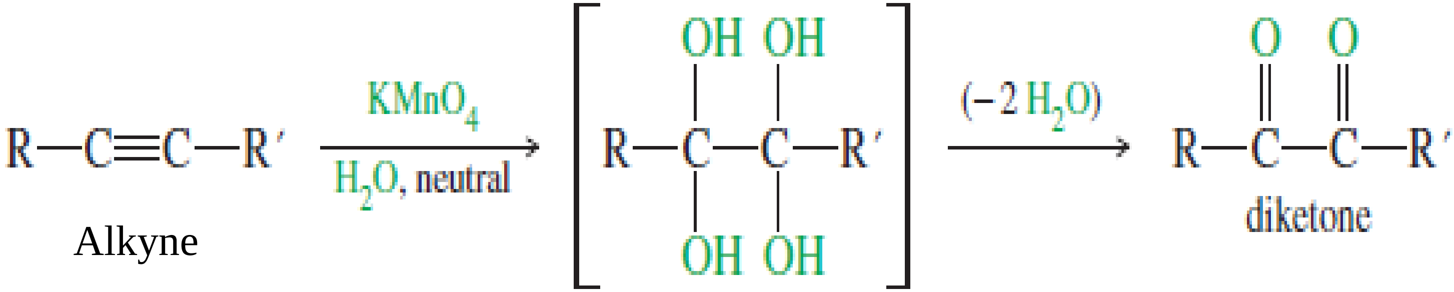
For example, the mercuric-catalyzed hydration of but-1-yne gives but-1-en-2-ol as an intermediate. In the acidic solution, the intermediate quickly equilibrates to its more stable keto tautomer, butan-2-one.



Reaction of alkynes

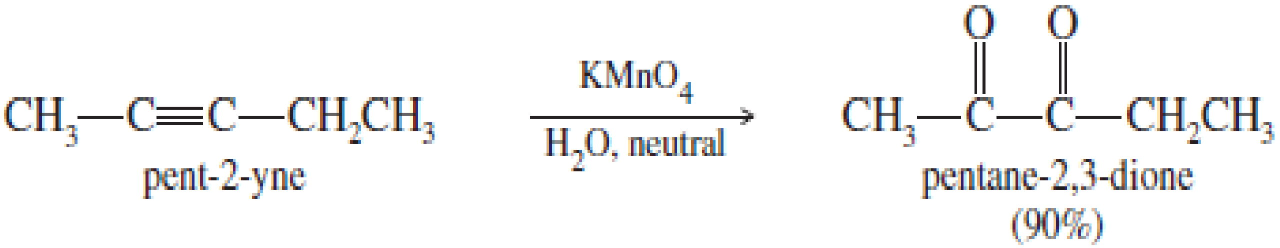
5- Oxidation of alkynes

a- Permanganate oxidations:



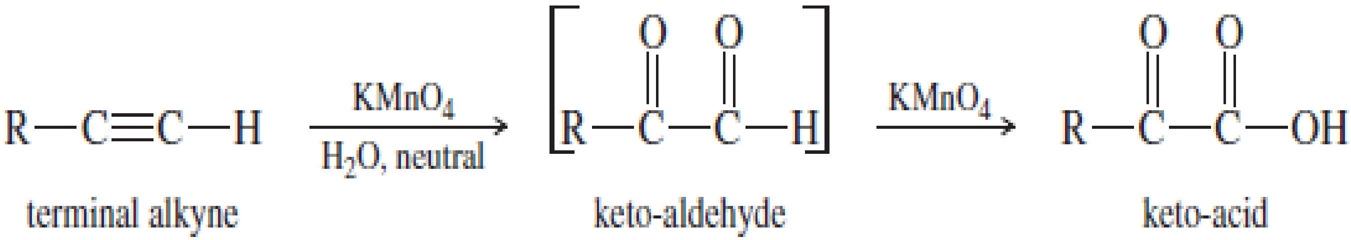
$$R-C\equiv C-R' \xrightarrow[H_2O,\ \text{neutral}]{KMnO_4} \left[R-\overset{OH}{\underset{OH}{C}}-\overset{OH}{\underset{OH}{C}}-R' \right] \xrightarrow{(-2\,H_2O)} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R'$$

For example, when pent-2-yne is treated with a cold, dilute solution of neutral permanganate, the product is pentane-2,3-dione.



$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow[H_2O,\ \text{neutral}]{KMnO_4} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

Terminal alkynes probably give a keto-aldehyde at first, but the aldehyde quickly oxidizes to an acid under these conditions.



$$R-C\equiv C-H \xrightarrow[H_2O,\ \text{neutral}]{KMnO_4} \left[R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H \right] \xrightarrow{KMnO_4} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

Reaction of alkynes

b-Ozonolysis:

Ozonolysis of an alkyne, followed by hydrolysis, cleaves the triple bond will gives two carboxylic acids.

Ozone

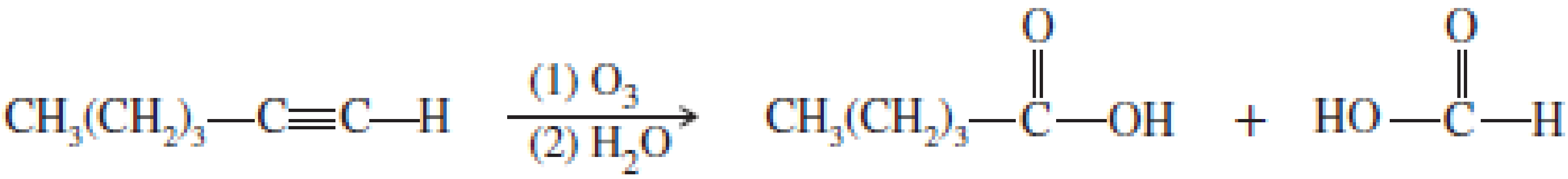
$$R{-}C{\equiv}C{-}R' \xrightarrow[\text{(2) } H_2O]{\text{(1) } O_3} R{-}COOH + R'{-}COOH$$

Alkyne Carboxylic acid

Examples:

$$CH_3{-}C{\equiv}C{-}CH_2CH_3 \xrightarrow[\text{(2) } H_2O]{\text{(1) } O_3} CH_3{-}COOH + CH_2CH_3{-}COOH$$

pent-2-yne acetic acid propionic acid



$$CH_3(CH_2)_3{-}C{\equiv}C{-}H \xrightarrow[\text{(2) } H_2O]{\text{(1) } O_3} CH_3(CH_2)_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH + HO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H$$

hex-1-yne pentanoic acid formic acid

Aromatics hydrocarbons

Aromatics hydrocarbons

- **Aromatics hydrocarbons:**

1-Aromatic term means compounds with spicy or sweet-smelling odors.

2-Aromatic compounds came to mean benzene (C_6H_6) and derivatives of benzene.

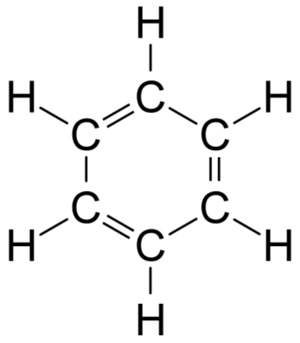
3- Substances that contained the C_6H_6 unit are with odorless and vile-smelling.

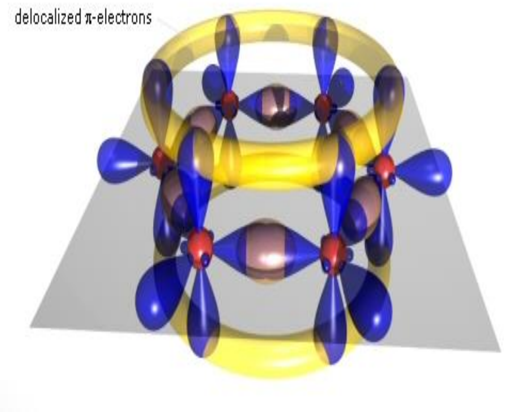
4-They are unsaturated hydrocarbons.

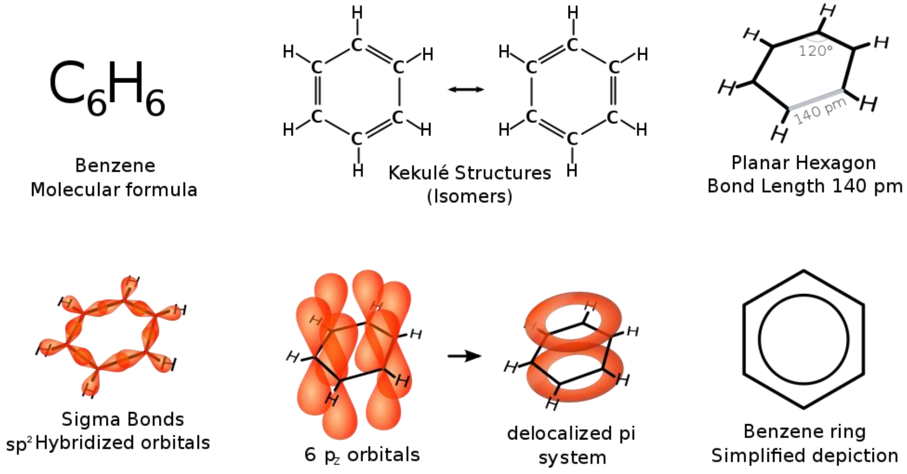
5-Characterized by alternate double bonds.

6-Their physical and chemical characteristics are different than aliphatics.

7- Each carbon atoms will have three *sp*^{2} hybridized orbitals and have one non-hybridized *p* orbital.





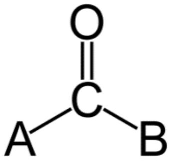


Aldehydes and Ketones

Carbonyl compounds

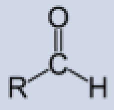
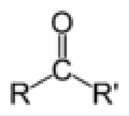
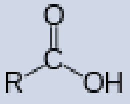
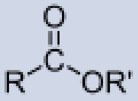
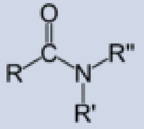
- **Definition of carbonyl compounds:**

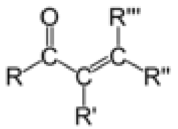
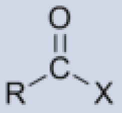
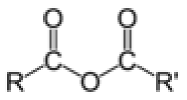
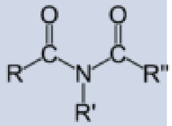
1. They are an organic compounds that contain the carbonyl group, which consists of a carbon-oxygen double bond.



2. The oxygen is called carbonyl oxygen and the carbon is called carbonyl carbon.

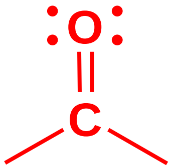
3. A carbonyl group characterizes the following types of compounds:

Compound	Aldehyde	Ketone	Carboxylic acid	Ester	Amide
Structure					
General formula	RCHO	RCOR'	RCOOH	RCOOR'	RCONR'R''

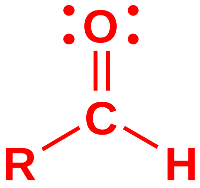
Compound	Enone	Acyl halide	Acid anhydride	Imide
Structure				
General formula	RC(O)C(R')CR''R'''	RCOX	$(RCO)_2O$	RC(O)N(R')C(O)R''

Aldehydes and Ketones

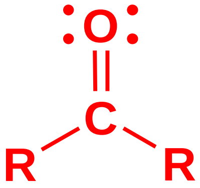
1. **Aldehydes** are organic compounds that carbonyl carbon of the carbonyl group is bonded to hydrogen, with general formula **RCHO.**
2. **Ketones** are organic compounds that carbonyl carbon of the carbonyl group is bonded to carbon, with general formula **RCOR´.**
3. The groups R and R´ may be aliphatic or aromatic.
4. They are widely distributed in nature.
5. They are involved in many biological reactions as starting materials or intermediates.



Carbonyl group



Aldehyde

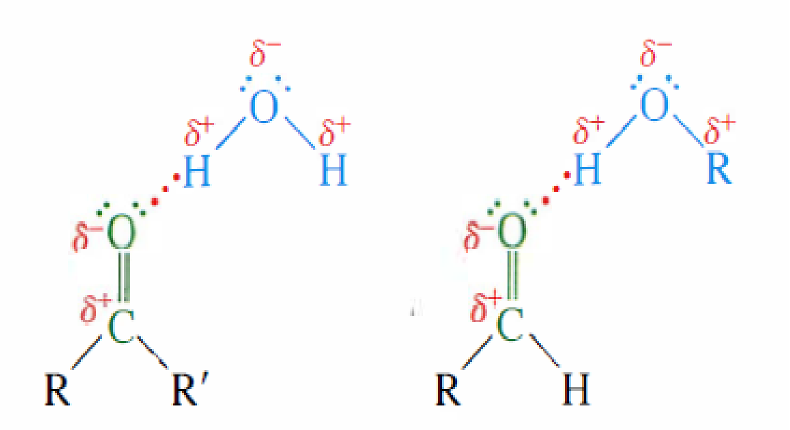


Ketone

Physical Properties of Aldehydes and Ketones

- **Solubility:**

Aldehydes and ketones are **soluble in water**, because of **hydrogen bonding between carbonyl group and water**.



Also they are **soluble in organic solvents** such as benzene, ether and carbon tetrachloride.

- **Boiling point**:

➢ Aldehydes and ketones are **polar compounds** due to the **polarity of carbonyl group** and hence they have **higher boiling points** than **non polar compounds (alkane, alkene and alkyne)** of comparable molecular weight.

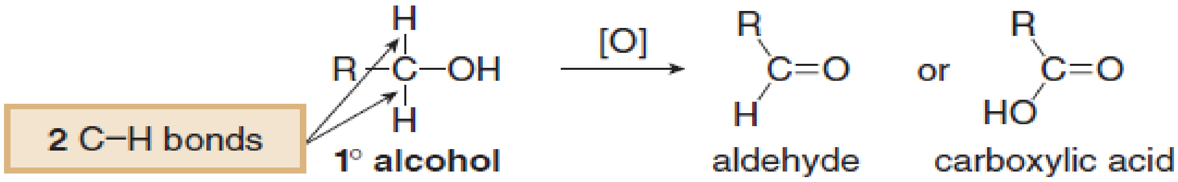
➢ They have **lower boiling points** than comparable **alcohols or carboxylic acids** due to the **intermolecular hydrogen bonding**.

Preparation of aldehydes & Ketones

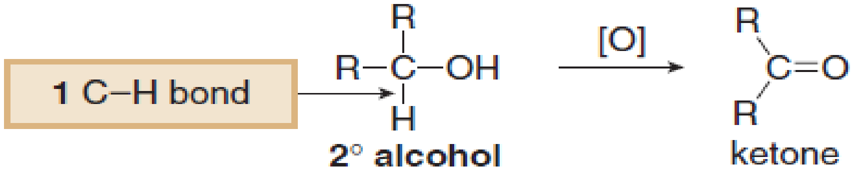
Introduction:

Alcohols are oxidized to a variety of carbonyl compounds, depending on the type of alcohol and reagent. Oxidation occurs by replacing the C–H bonds *on the carbon bearing the OH group* by C–O bonds.

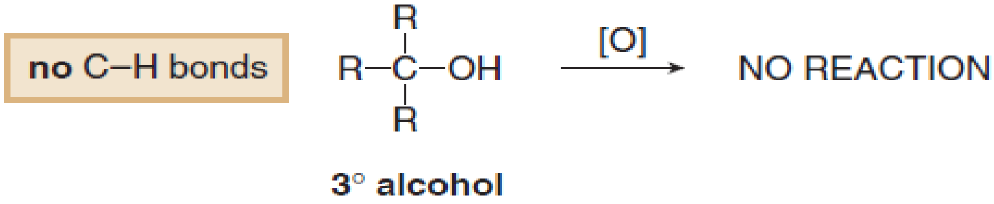
- 1° **Alcohols** are oxidized to either **aldehydes** or **carboxylic acids** by replacing either one or two C–H bonds by C–O bonds.



- 2° **Alcohols** are oxidized to **ketones** by replacing the one C–H bond by a C–O bond.



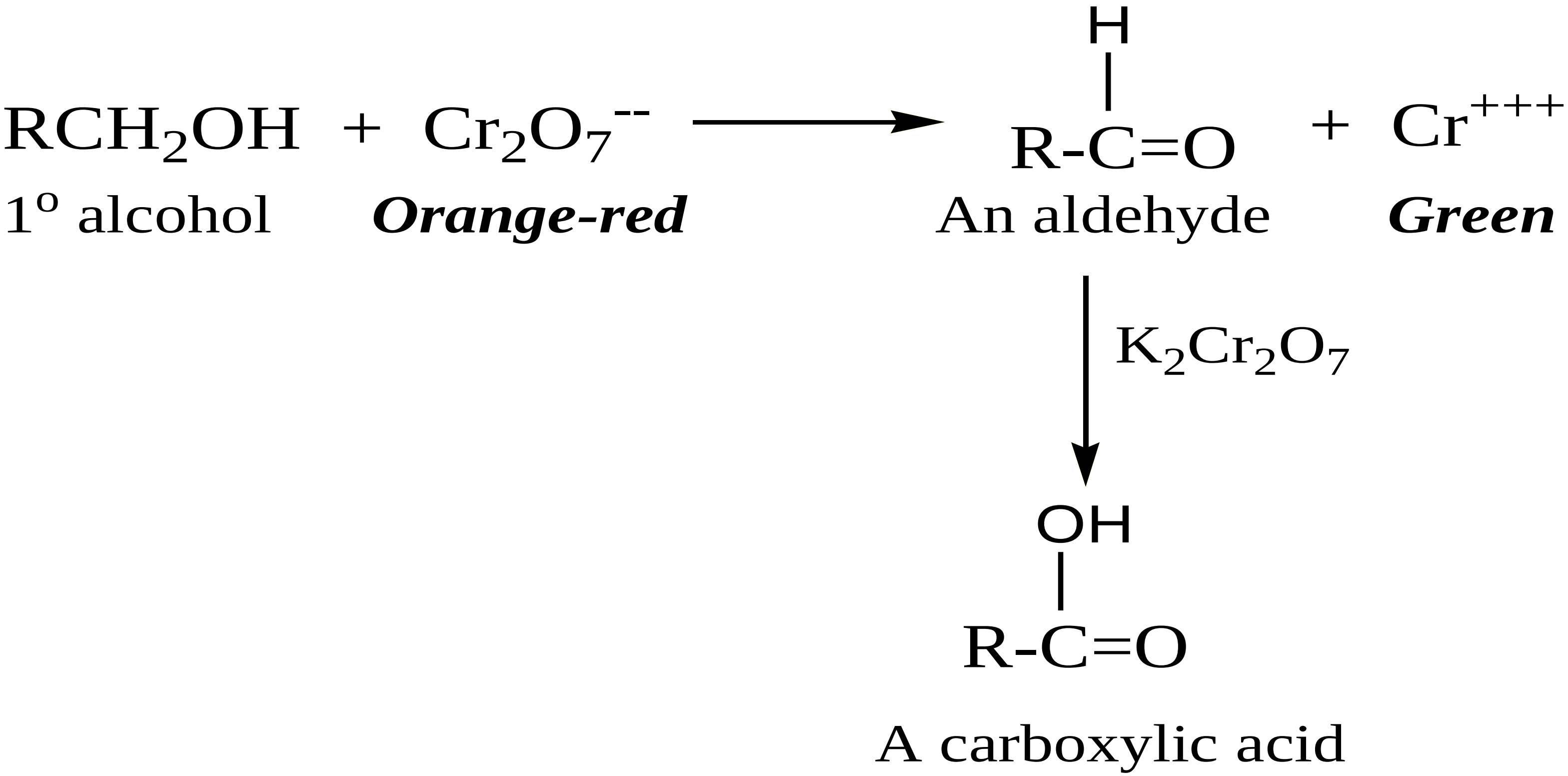
- 3° **Alcohols have no H atoms on the carbon with the OH group,** so they are not easily oxidized.



Preparation of aldehydes

1- Oxidation of primary alcohols:

[O] can be hot copper Cu or chromium oxide CrO_3 in pyridine (mild oxidizing agent) or by dichromic acid $H_2Cr_2O_7$ or potassium dichromic acid $K_2Cr_2O_7$.



$$RCH_2OH + Cr_2O_7^{--} \longrightarrow R\text{-}\overset{\overset{\displaystyle H}{|}}{C}=O + Cr^{+++}$$

1° alcohol **_Orange-red_** An aldehyde **_Green_**

$$\Big\downarrow K_2Cr_2O_7$$

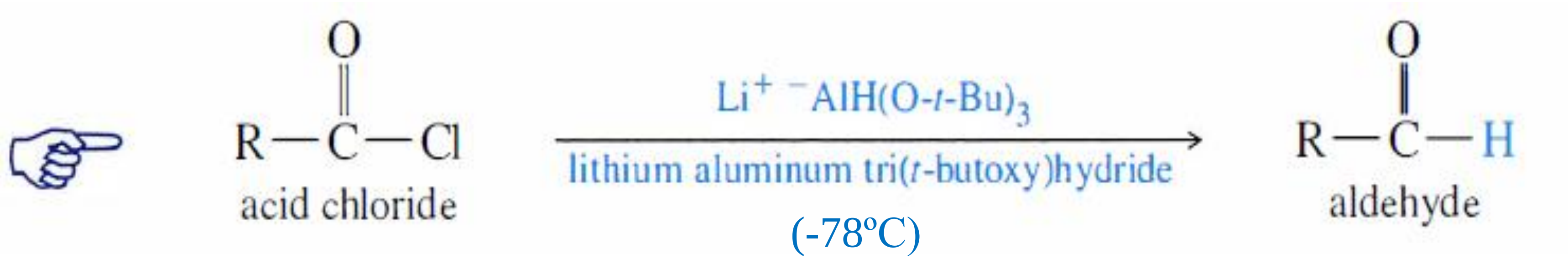
$$R\text{-}\overset{\overset{\displaystyle OH}{|}}{C}=O$$

A carboxylic acid

Preparation of aldehydes

2. Partial reduction of acid chlorides:

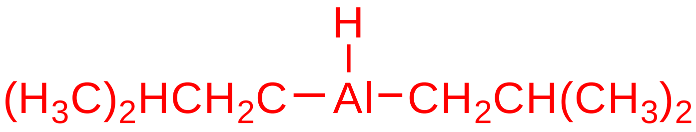
- **Strong reducing agents** (like **$LiAlH_4$**) reduce **acid chlorides** all the way to **primary alcohols**.
- **Lithium aluminum tri(*t*-butoxy)hydride** is a **milder reducing agent** that reacts faster with acid chlorides than with aldehydes. Reduction of **acid chlorides** with lithium aluminum tri(*t*-butoxy)hydride gives good yields of **aldehydes.**



(-78ºC)

Preparation of aldehydes

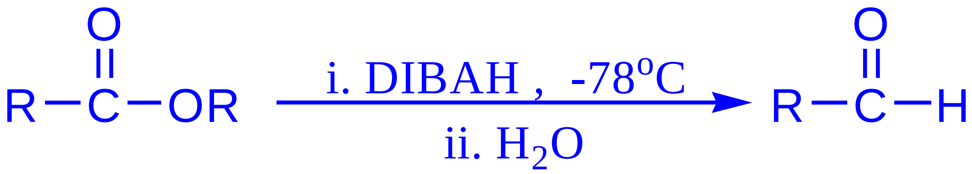
Diisobutylaluminium hydride
(*mild reducing agent*)



$$(H_3C)_2HCH_2C-\overset{\displaystyle H}{\overset{|}{Al}}-CH_2CH(CH_3)_2$$

3. Partial reduction of esters:

- Sterically bulky reducing agents, e.g. Diisobutylaluminium hydride **(DIBAH)**, can selectively reduce esters to aldehydes. The reaction is carried out at low temperature (-78ºC) in toluene.



$$R-\overset{\displaystyle O}{\overset{\|}{C}}-OR \xrightarrow[\text{ii. } H_2O]{\text{i. DIBAH , -78}^{o}\text{C}} R-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

Ester **Aldehyde**

4. Reduction of Nitriles:

Reduction of nitrile with a less powerful reducing reagent, e.g. **DIBAH**, produces aldehyde. The reaction is carried out at low temperatures (-78ºC) in toluene.

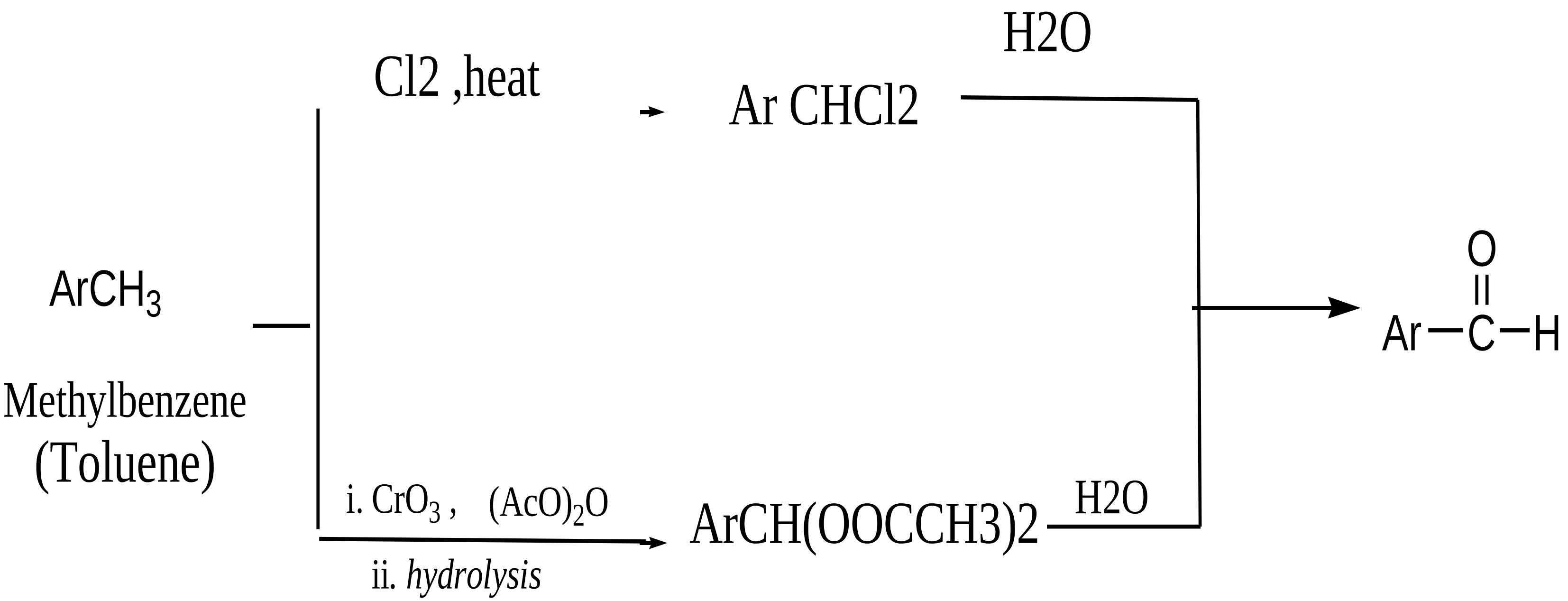
$$R-C\equiv N \xrightarrow[\text{ii. } H_2O]{\text{i. DIBAH}} R-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

Nitrile Aldehyde

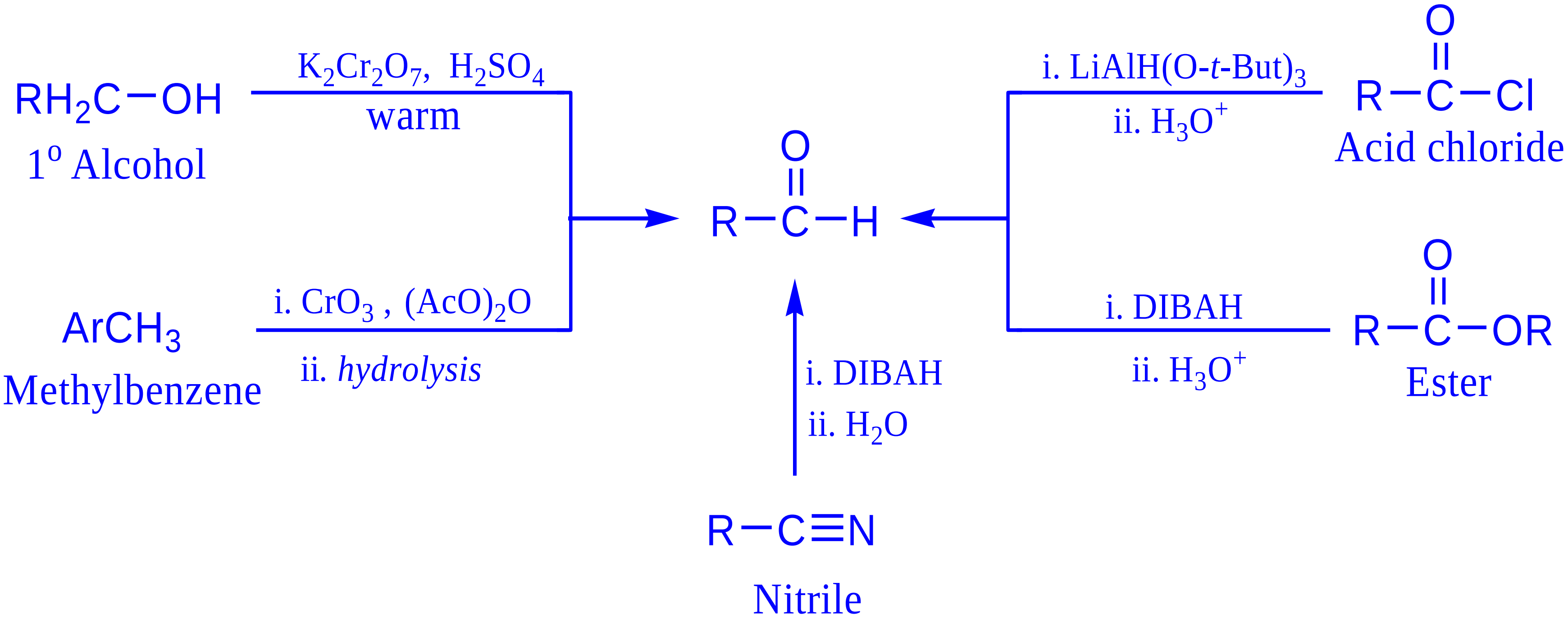
Preparation of aldehydes

5. Oxidation of methylbenzene:

Methylbenzene can be oxidized to give aldehydes by using of chromium oxide **CrO_3 and acetic anhydride then hydrolysis or by using of Cl_2 and heat.**



Review on preparation of aldehydes



RH_2C-OH

1° Alcohol

$K_2Cr_2O_7$, H_2SO_4

warm

$ArCH_3$

Methylbenzene

i. CrO_3 , $(AcO)_2O$

ii. *hydrolysis*

$R-\overset{O}{\overset{\|}{C}}-H$

i. $LiAlH(O\text{-}t\text{-}But)_3$

ii. H_3O^+

$R-\overset{O}{\overset{\|}{C}}-Cl$

Acid chloride

i. DIBAH

ii. H_3O^+

$R-\overset{O}{\overset{\|}{C}}-OR$

Ester

i. DIBAH

ii. H_2O

$R-C\equiv N$

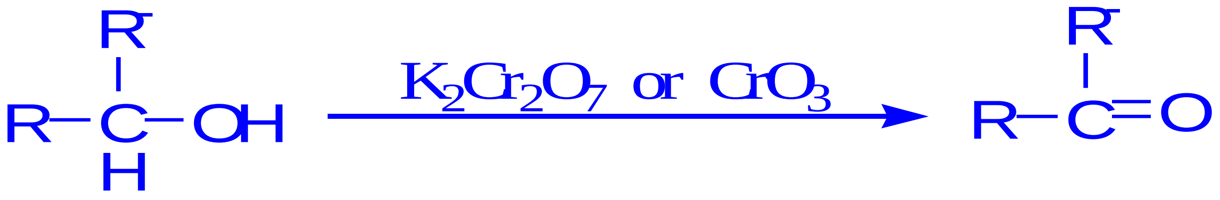
Nitrile

Preparation of ketones

1. Oxidation of Secondary alcohols:

Secondary alcohols are oxidized to ketones by hot copper Cu or chromium oxide CrO_3 in pyridine (mild oxidizing agent) or by dichromic acid $H_2Cr_2O_7$ or potassium dichromic acid $K_2Cr_2O_7$.

Hot permanganate MnO_4^- also oxidizes alcohols; it is rarely used for the synthesis of ketones.



$$R-\overset{R'}{\underset{H}{C}}-OH \xrightarrow{K_2Cr_2O_7 \text{ or } CrO_3} R-\overset{R'}{C}=O$$

A 2° alcohol

A ketone

Preparation of Aldehydes and Ketones

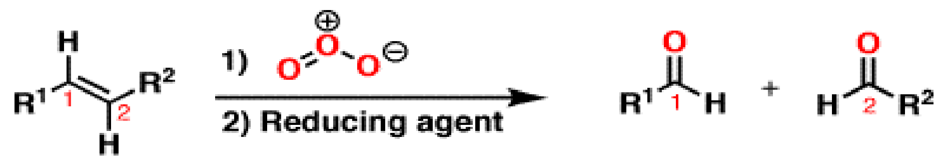
2- Ozonolysis of alkenes:

Cleavage of Carbon–Carbon double bond by Ozone:

Cleavage of an alkenes by ozone mean break both the **σ** and **π** bonds of the double bond to form two carbonyl groups in the presence of reducing or oxidizing agents. Depending on the number of R groups bonded to the double bond and presence of either reducing or oxidizing agents, **aldehydes or ketones or both; and carboxylic acids** instead of aldehydes will be yielded**.**

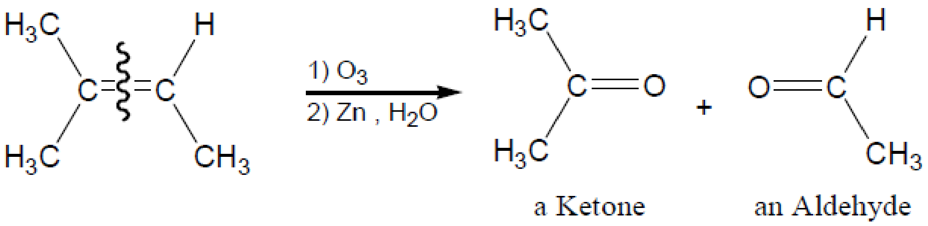
a) A reducing work-up, either Zn in acetic acid CH_3COOH or dimethyl sulfide $(CH_3)_2S$

Ozonolysis of alkenes with reductive workup



Alkene Aldehyde Aldehyde

(common reducing agents are zinc (Zn) or dimethyl sulfide $(CH_3)_2S$)

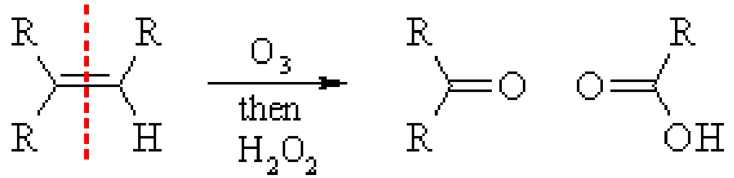


2-Methyl,2-butene

acetone
Dimethyl ketone

acetaldehyde
ethanal

b) An oxidizing work-up, usually hydrogen peroxide H_2O_2 (under these conditions, carboxylic acids are obtained instead of aldehydes).

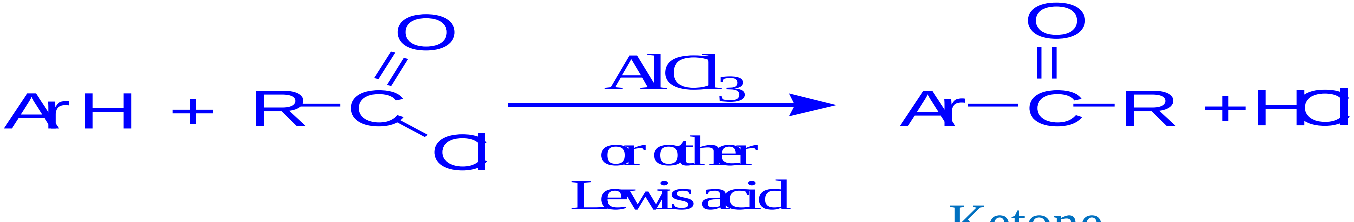


Alkene Ketone carboxylic acids

Preparation of Ketones

3. Friedel-Crafts acylation:

The Friedel-Crafts reaction involves the use of acid chlorides rather than alkyl halides. An acyl group (RCO–) becomes attached to the aromatic ring. Thus forming a ketone; the process is called acylation.

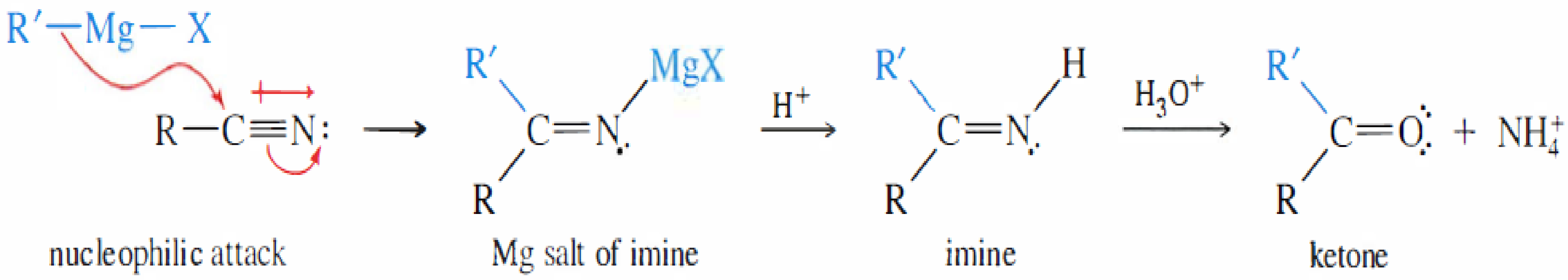


$$ArH + RCOCl \xrightarrow[\text{or other Lewis acid}]{AlCl_3} Ar\text{–}CO\text{–}R + HCl$$

Ketone

4- Synthesis of Ketones from Nitriles:

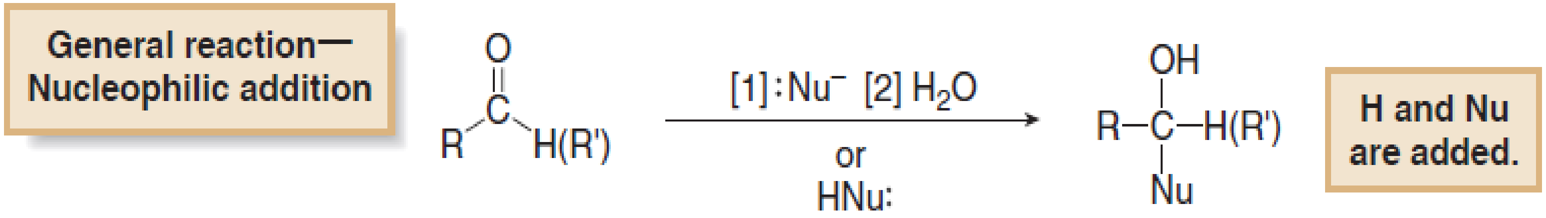
A Grignard or organomagnesium reagent attacks a nitrile to give the magnesium salt of an imine. Acidic hydrolysis of the imine leads to the ketone.



Reaction of Aldehydes and Ketones

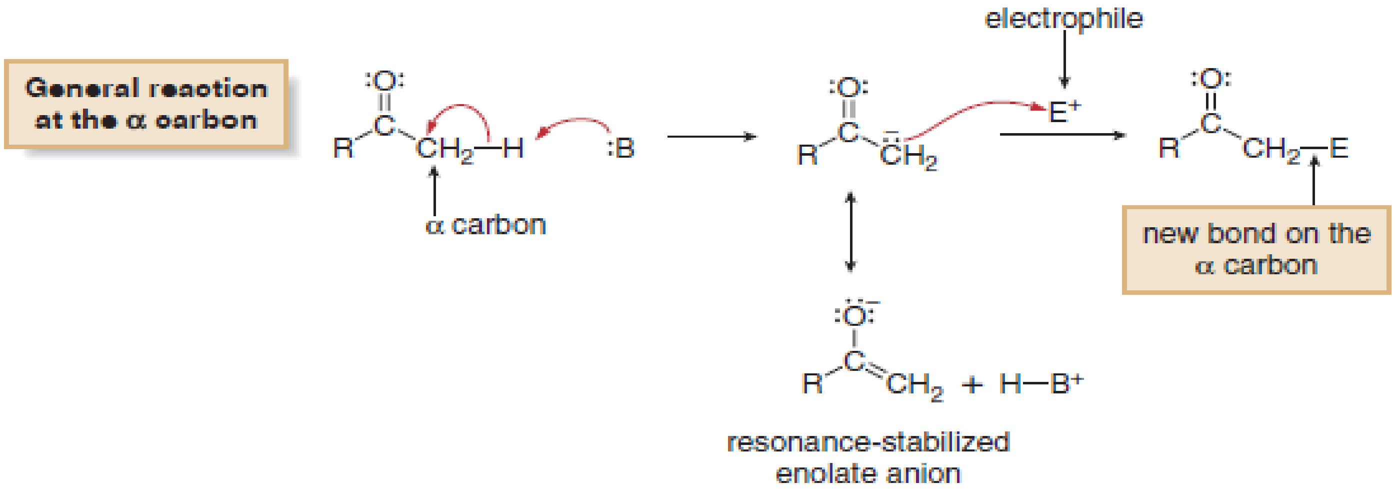
Aldehydes and Ketones undergo many reactions to give a wide variety of useful derivatives. There are two general kinds of reactions that aldehydes and ketones undergo:

[1] Reaction at the carbonyl carbon (Nucleophilic addition reactions).



[2] Reaction at the α carbon (Reaction involving acidic α-hydrogen).

A second general reaction of aldehydes and ketones involves reaction at the α carbon. A C–H bond on the α carbon to a carbonyl group is more acidic than many other C–H bonds, because reaction with base forms a resonance-stabilized enolate anion.

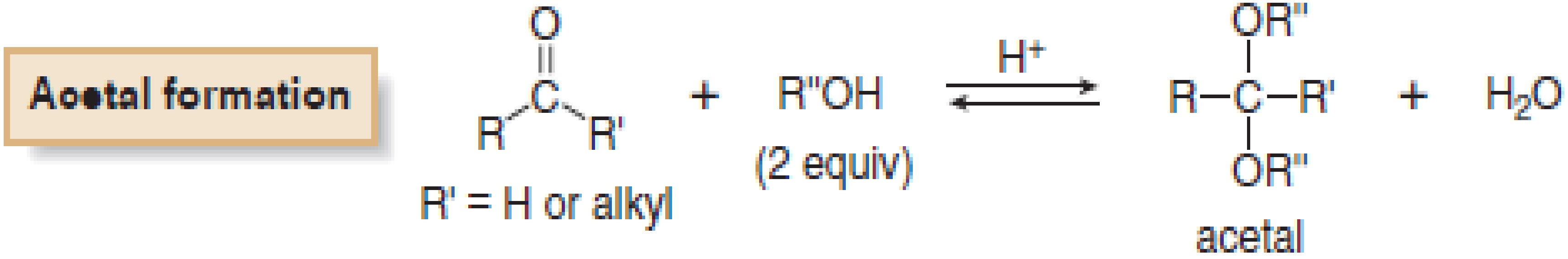


Reaction of Aldehydes and Ketones

[1] Reaction at the carbonyl carbon (Nucleophilic addition reactions):

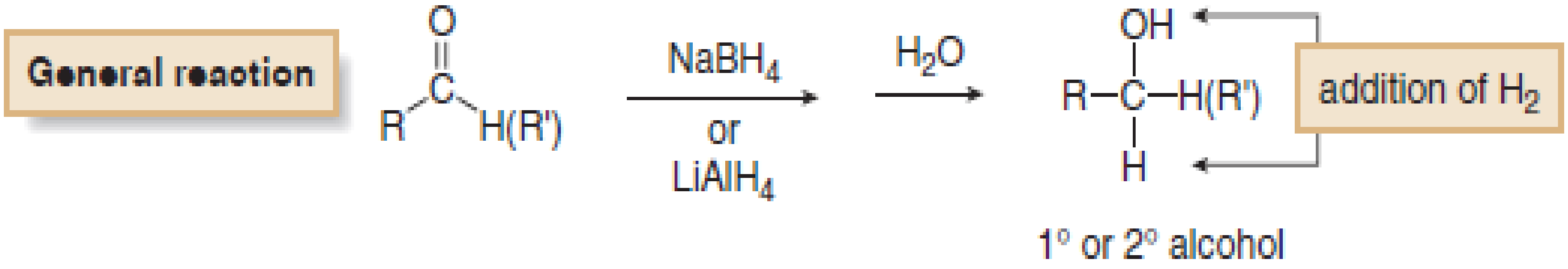
a) Addition of Alcohols (Acetal formation):

Aldehyde and ketone are react with *two* equivalents of alcohol to form acetal. In an acetal, the carbonyl carbon from the aldehyde or ketone is now singly bonded to two OR" (alkoxy) groups.



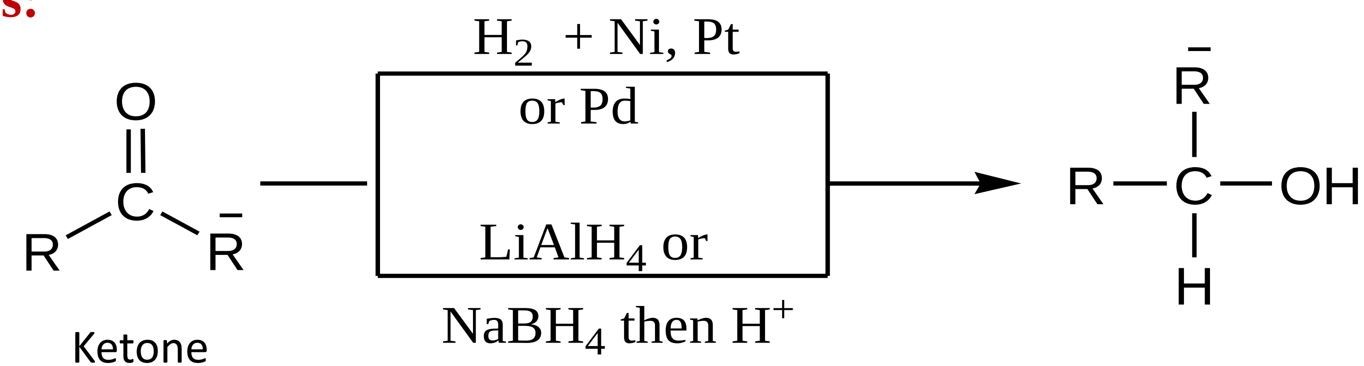
b) Nucleophilic Addition of H_2 (Reduction reaction):

Treatment of an **aldehyde or ketone** with either **Sodium borohydride ($NaBH_4$)** or **Lithium hydride ($LiAlH_4$)** followed by **protonation** forms a **1° or 2° alcohol**.



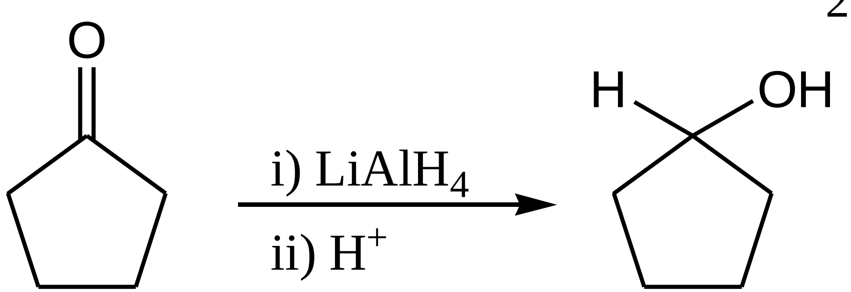
Reaction of Aldehydes and Ketones

Examples:



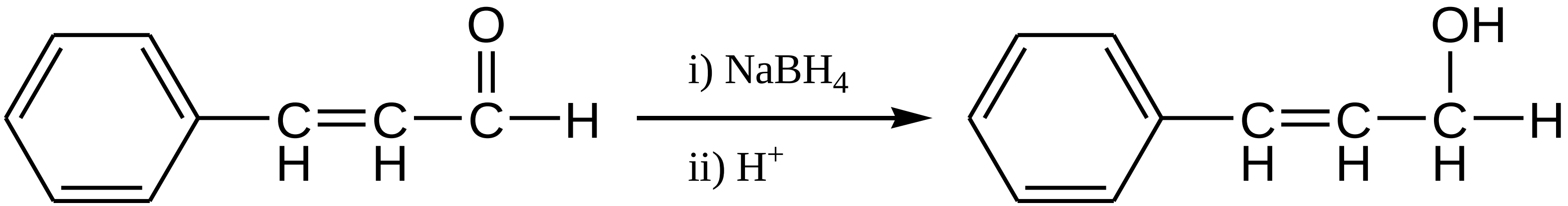
Ketone

2° Alcohol



Cyclopentanone

Cyclopentanol



3-Phenylacrylaldehyde
(Cinnamaldehyde)

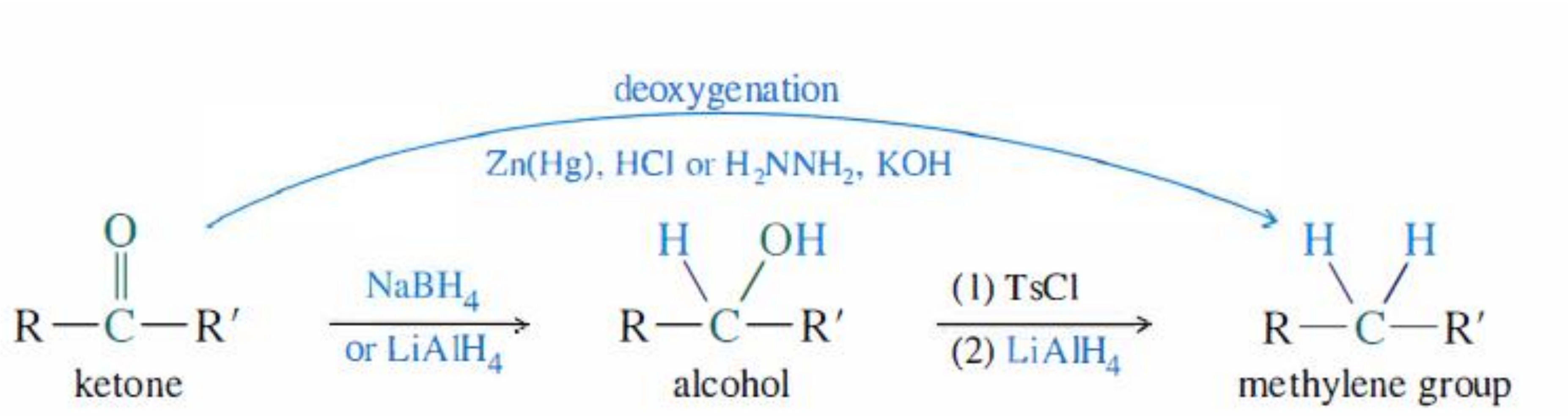
Cinnamyl alcohol

Reaction of Aldehydes and Ketones

c) Reduction to alkane (Deoxygenation of Ketones and Aldehydes):

i) Clemmensen reduction.

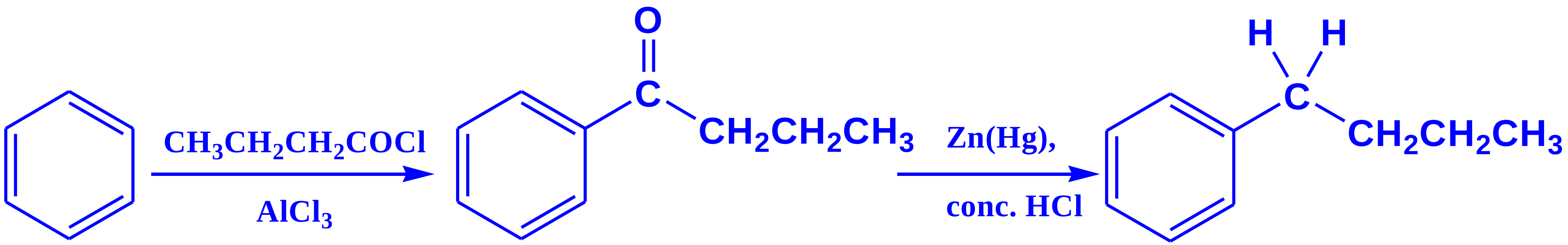
ii) Wolff–Kishner reduction.



Reaction of Aldehydes and Ketones

i) Clemmensen reduction:

The **Clemmensen reduction** is most commonly used to convert acylbenzenes (from Friedel-Crafts acylation) to alkylbenzenes, but it also works with other ketones or aldehydes that are **not sensitive to acid**. The carbonyl compound is **heated** with an excess of amalgamated zinc (zinc treated with mercury; **Zn (Hg)**, and concentrated hydrochloric acid **(HCl)**. The actual reduction occurs by a complex mechanism on the surface of the zinc.

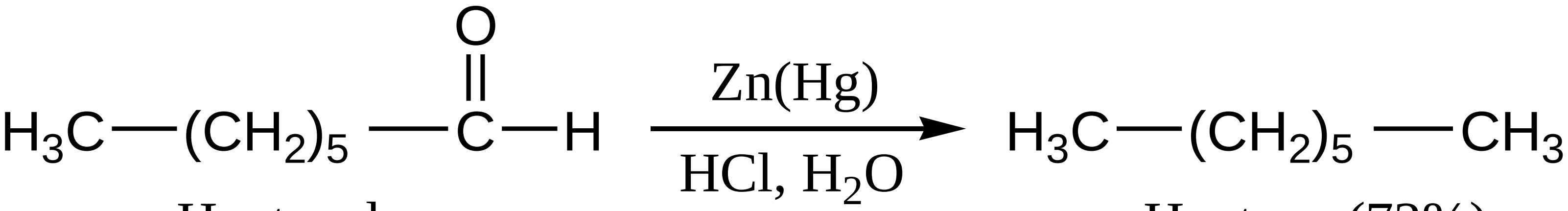


***n*-Butyrophenone** **_n_-Butylbenzene**

The **Clemmensen reduction** uses zinc and mercury in the presence of strong acid.

Reaction of Aldehydes and Ketones

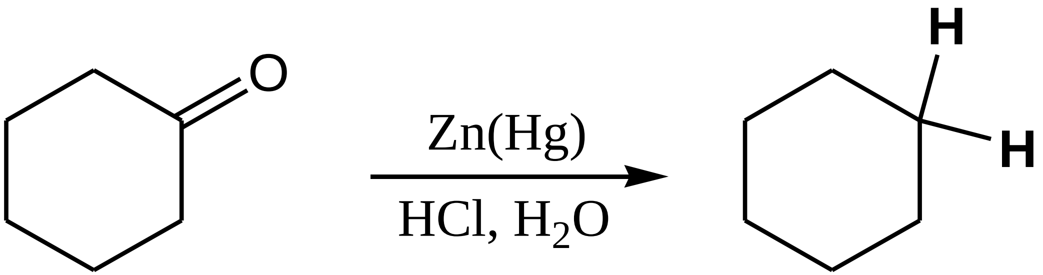
Examples:



$$H_3C-(CH_2)_5-\overset{O}{\overset{\|}{C}}-H \xrightarrow[HCl,\ H_2O]{Zn(Hg)} H_3C-(CH_2)_5-CH_3$$

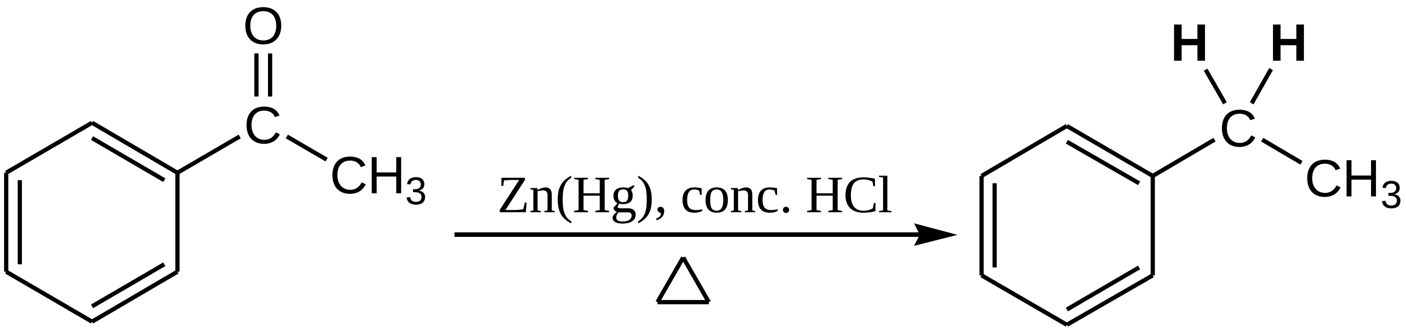
Heptanal

n-Heptane (72%)



Cyclohexanone

Cyclohexane (75%)



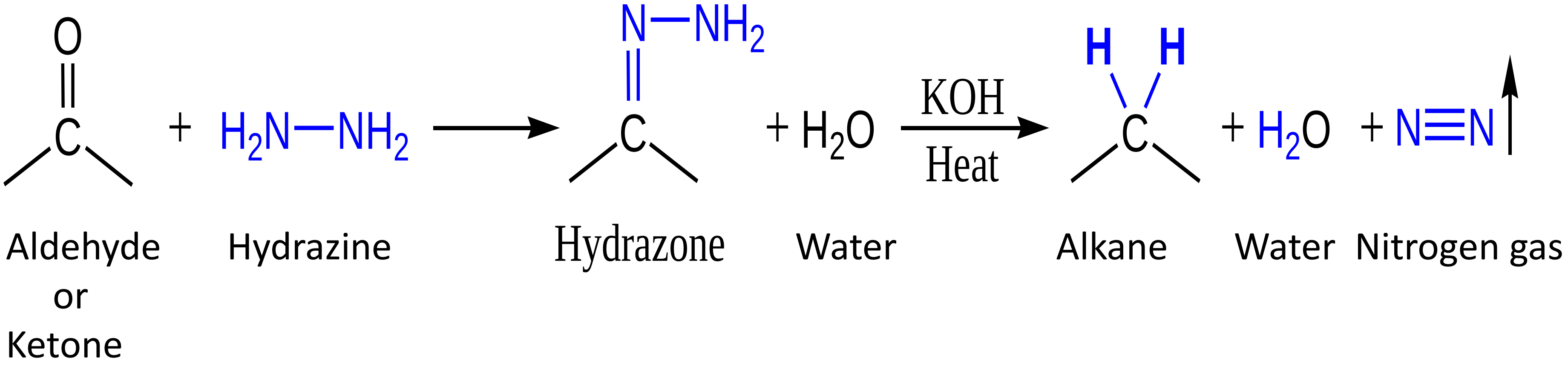
Acetophenone

1-Ethylbenzene

Reaction of Aldehydes and Ketones

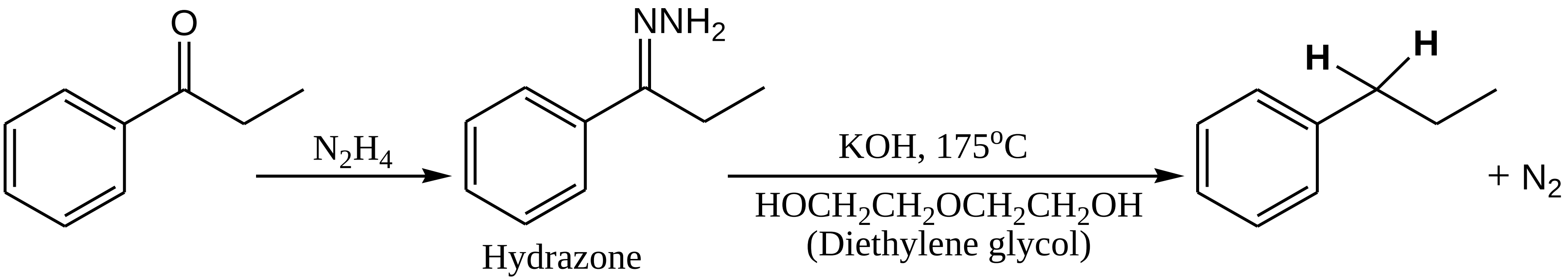
ii) Wolff–Kishner reduction:

Compounds that cannot survive treatment with hot acid can be deoxygenated using the **Wolff–Kishner reduction.** The ketone or aldehyde is converted to its **hydrazone**, which is **heated** with Hydrazine **(NH_2NH_2)**, and **strong base** such as **KOH**. Ethylene glycol, diethylene glycol, or another high-boiling solvent is used to facilitate the high temperature (140-200°C) needed in the second step.

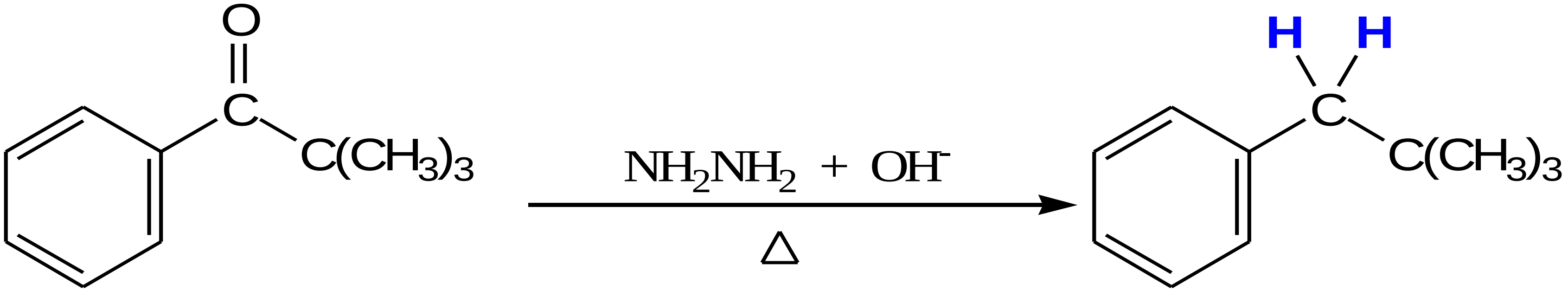


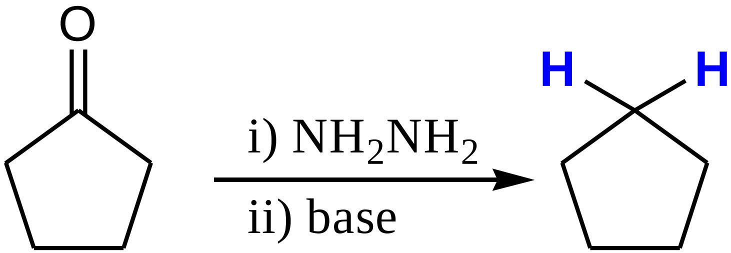
Reaction of Aldehydes and Ketones

Examples:



Hydrazone



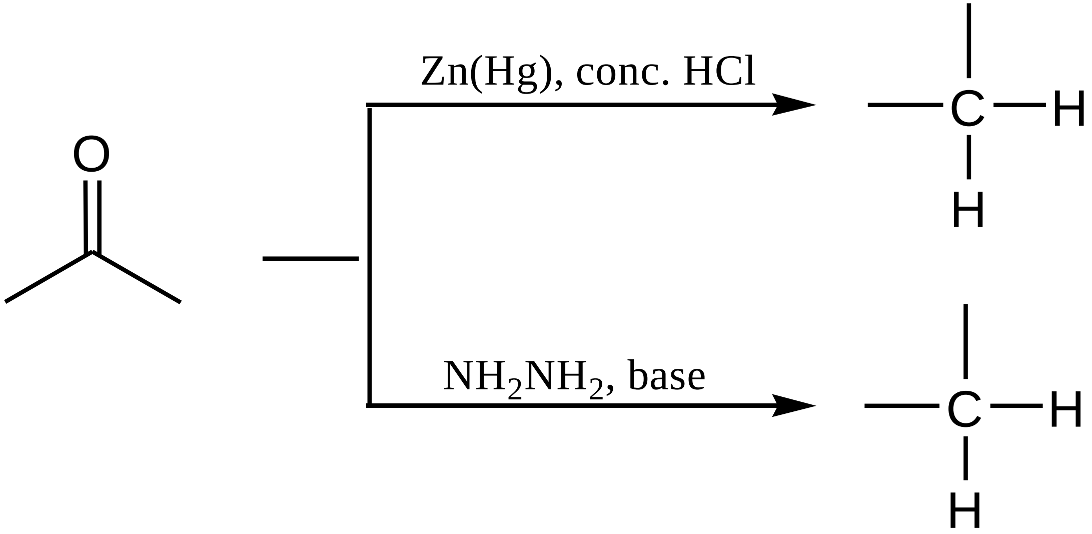


Cyclopentanone

Cyclopentane

Reaction of Aldehydes and Ketones

Summary:



Clemmensen reduction

for compounds sensitive to base

For compounds not sensitive to acid

Wolff-Kishner reduction

for compounds sensitive to acid

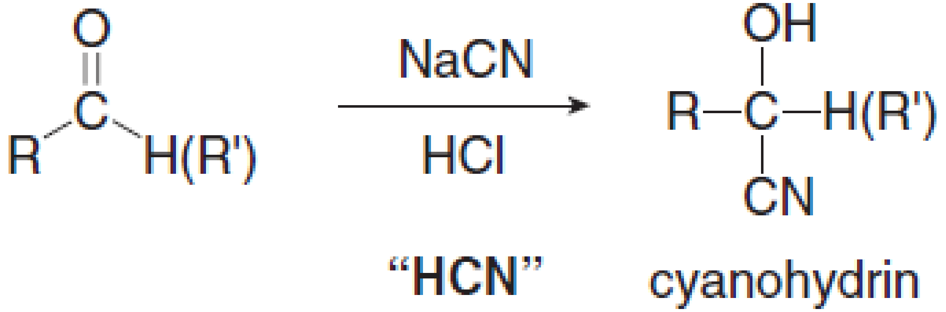
For compounds not sensitive to base

Reaction of Aldehydes and Ketones

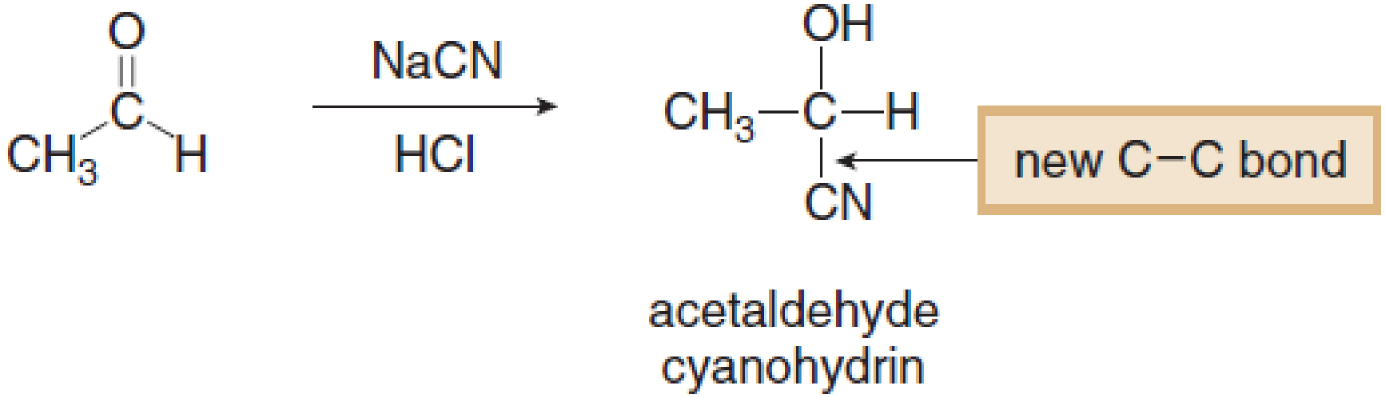
d) Nucleophilic Addition of CN⁻ :

Treatment of an aldehyde or ketone with **NaCN** and a strong acid such as **HCl** adds the elements of **HCN** across the **carbon–oxygen π bond**, forming a **cyanohydrin.**

Nucleophilic addition of HCN

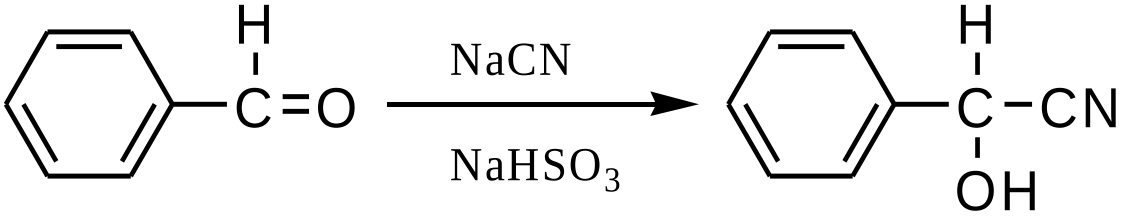


Example



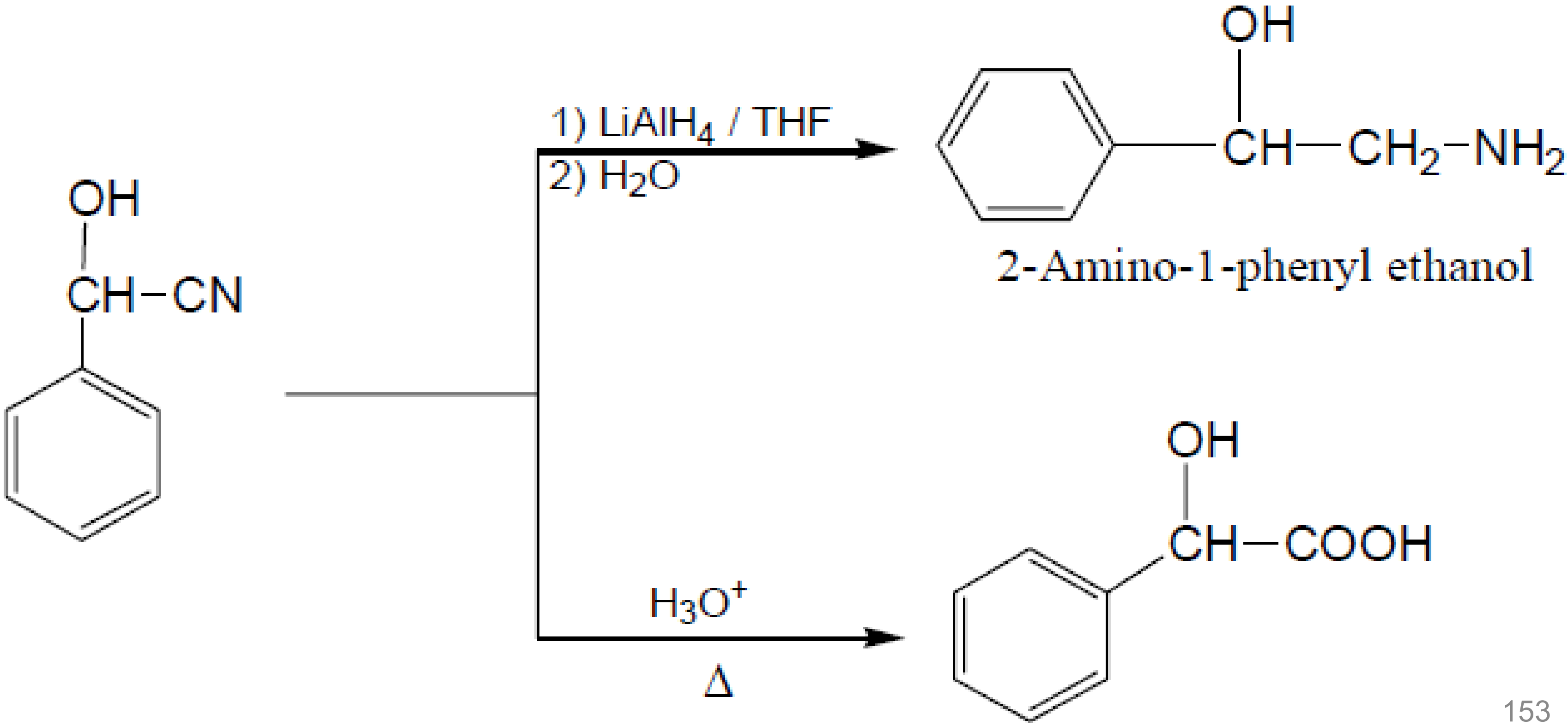
Reaction of Aldehydes and Ketones

Examples:



Benzaldehyde

Mandelonitrile

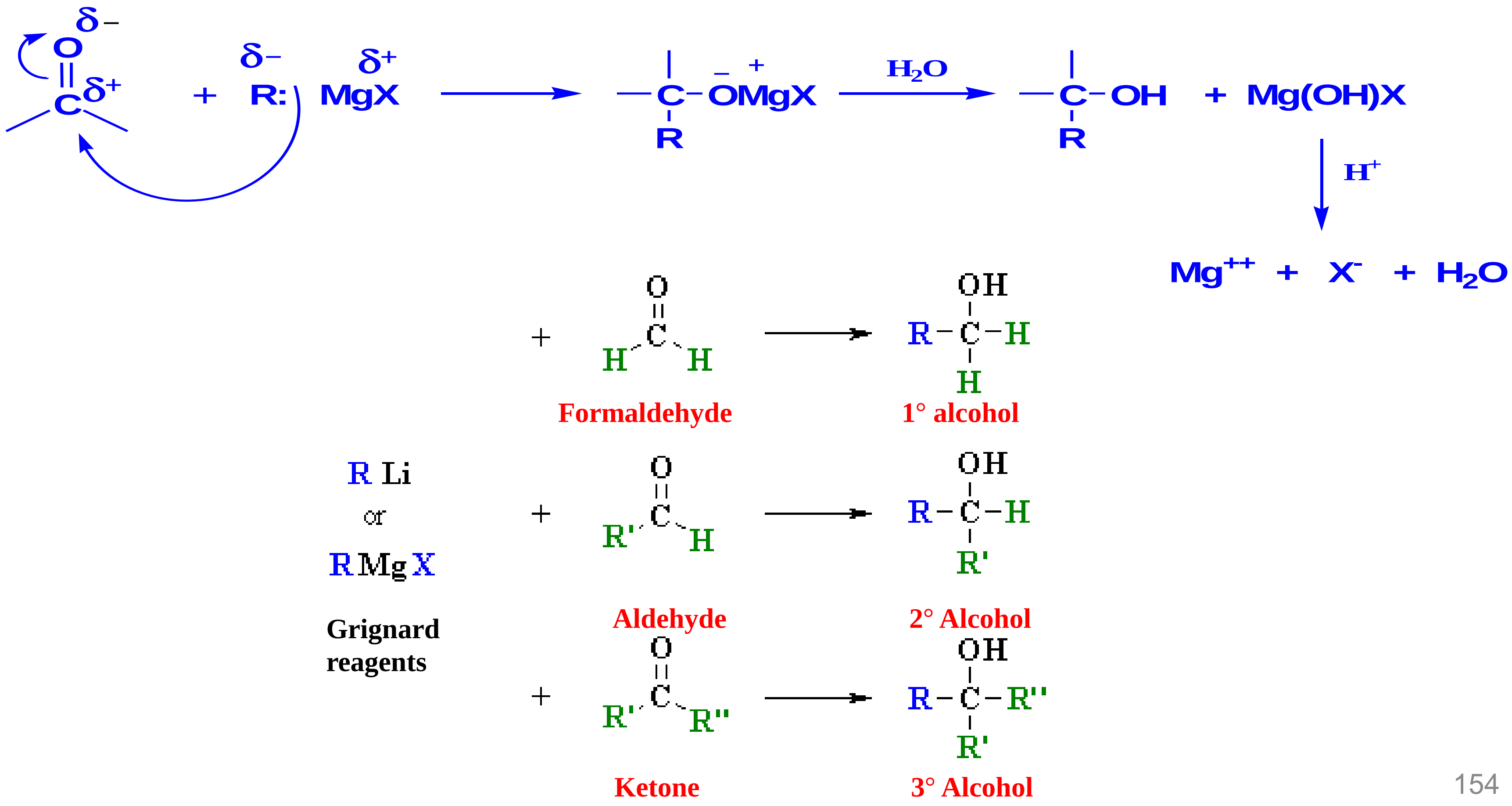


2-Amino-1-phenyl ethanol

Reaction of Aldehydes and Ketones

e) Addition of Grignard reagents (organometallic reagents R^-): Formation of alcohols:

The addition of Grignard reagents to aldehydes and ketones yields alcohols. The organic group, transferred with a pair of electrons from magnesium to carbonyl carbon, is a powerful nucleophile.

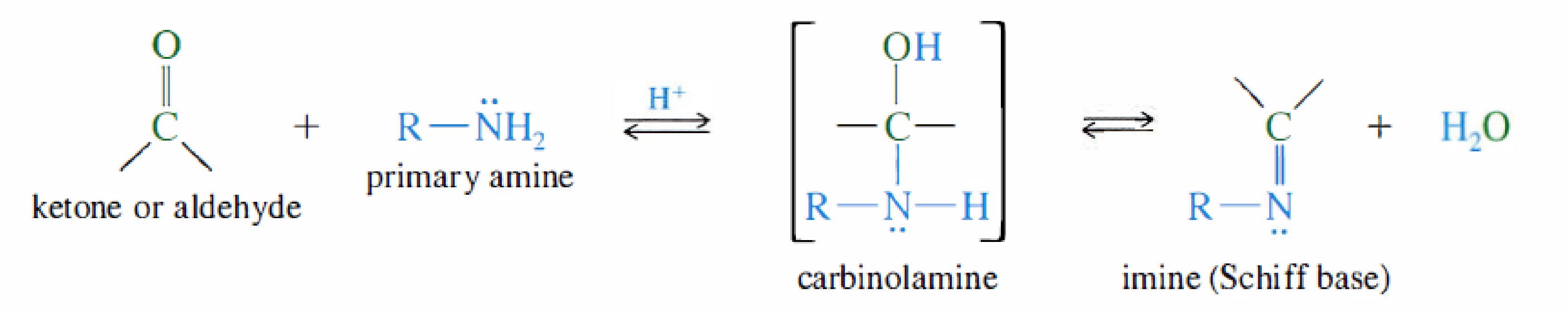


Reaction of Aldehydes and Ketones

f) Addition of derivatives of Ammonia (Formation of imine):

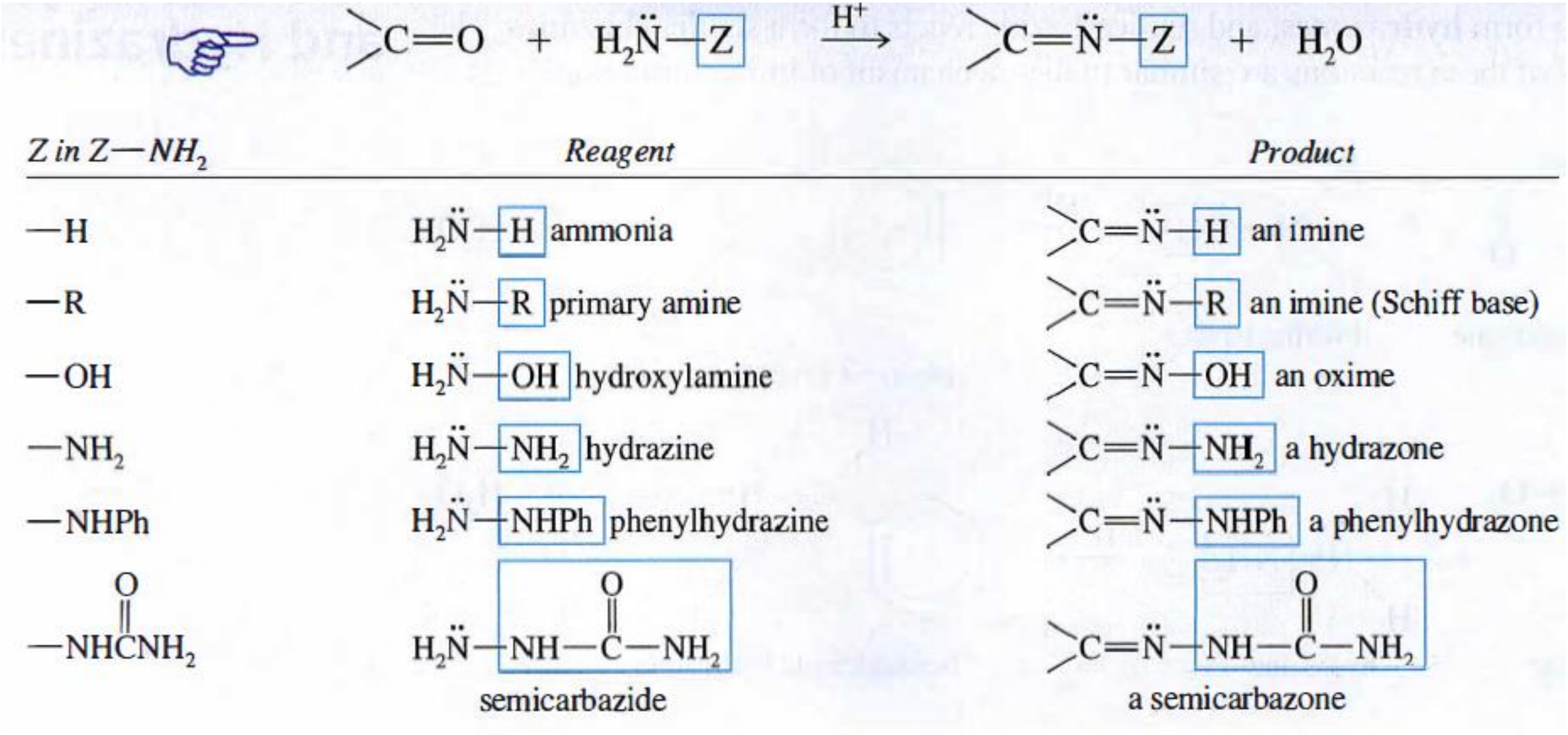
- ☞ Treatment of an aldehyde or ketone with a 1° amine affords an **imine** (also called a **Schiff base**).

- ☞ Nucleophilic attack of the 1° amine on the carbonyl group forms an unstable **carbinolamine**, which loses water to form an imine. The overall reaction results in **replacement of C=O by C=NR.**



Reaction of Aldehydes and Ketones

Addition of derivatives of Ammonia (Formation of imine):

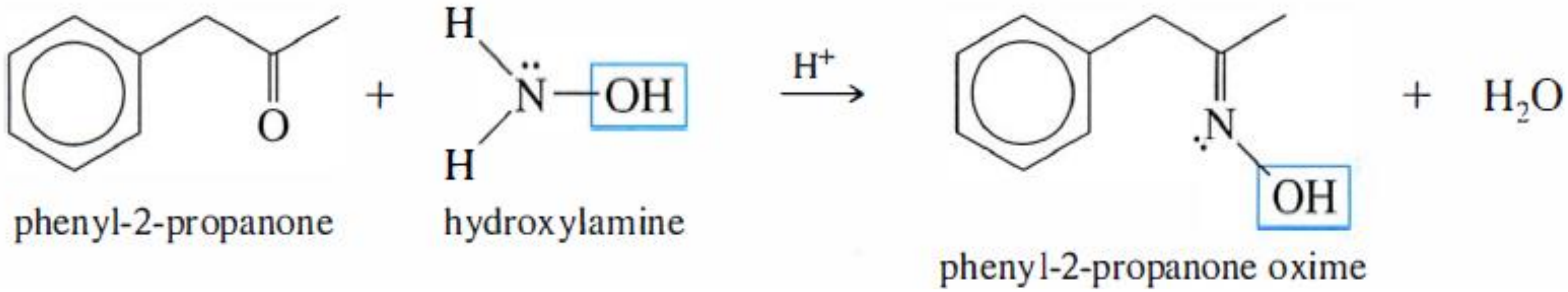


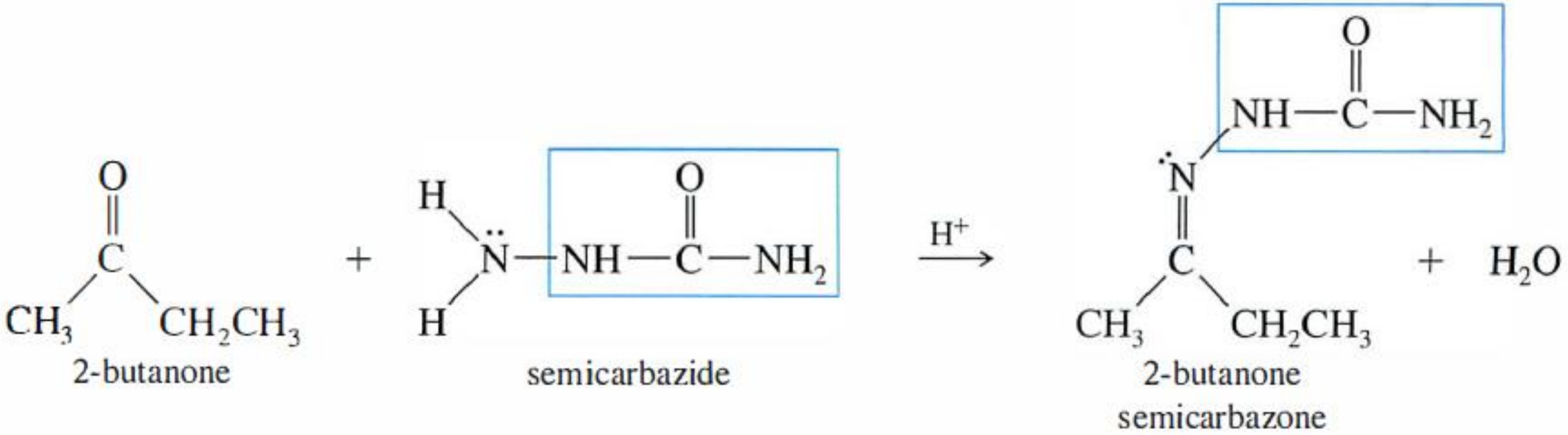
$$\rangle C=O + H_2\ddot{N}-\boxed{Z} \xrightarrow{H^+} \rangle C=\ddot{N}-\boxed{Z} + H_2O$$

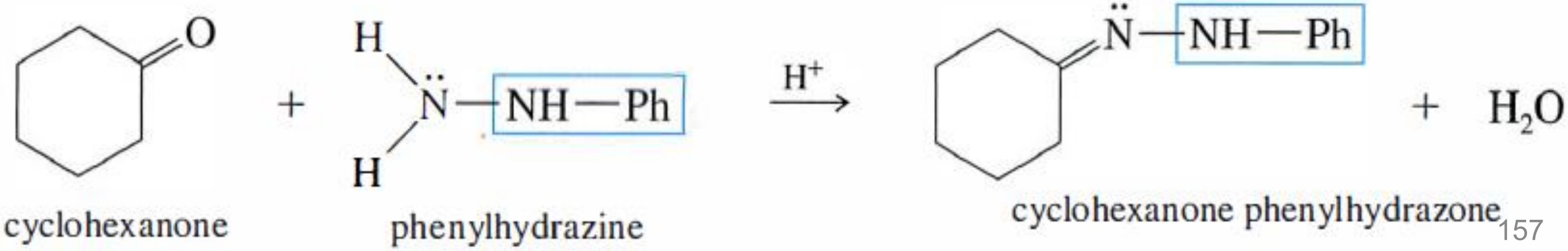
Z in Z—NH$_2$	*Reagent*		*Product*	
$-H$	$H_2\ddot{N}-\boxed{H}$	ammonia	$\rangle C=\ddot{N}-\boxed{H}$	an imine
$-R$	$H_2\ddot{N}-\boxed{R}$	primary amine	$\rangle C=\ddot{N}-\boxed{R}$	an imine (Schiff base)
$-OH$	$H_2\ddot{N}-\boxed{OH}$	hydroxylamine	$\rangle C=\ddot{N}-\boxed{OH}$	an oxime
$-NH_2$	$H_2\ddot{N}-\boxed{NH_2}$	hydrazine	$\rangle C=\ddot{N}-\boxed{NH_2}$	a hydrazone
$-NHPh$	$H_2\ddot{N}-\boxed{NHPh}$	phenylhydrazine	$\rangle C=\ddot{N}-\boxed{NHPh}$	a phenylhydrazone
$-NH\overset{\overset{O}{\|}}{C}NH_2$	$H_2\ddot{N}-\boxed{NH-\overset{\overset{O}{\|}}{C}-NH_2}$	semicarbazide	$\rangle C=\ddot{N}-\boxed{NH-\overset{\overset{O}{\|}}{C}-NH_2}$	a semicarbazone

Reaction of Aldehydes and Ketones

Examples:



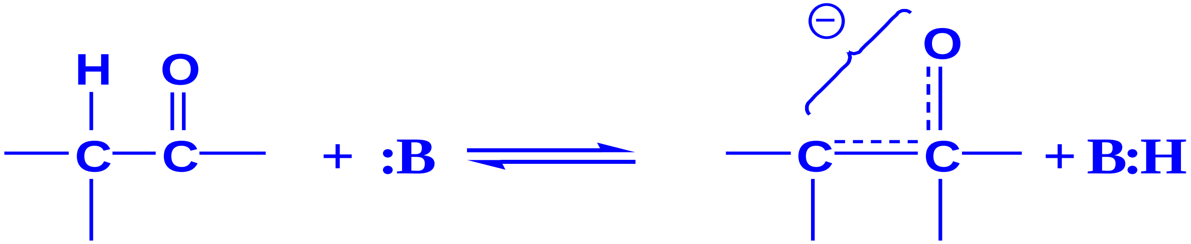




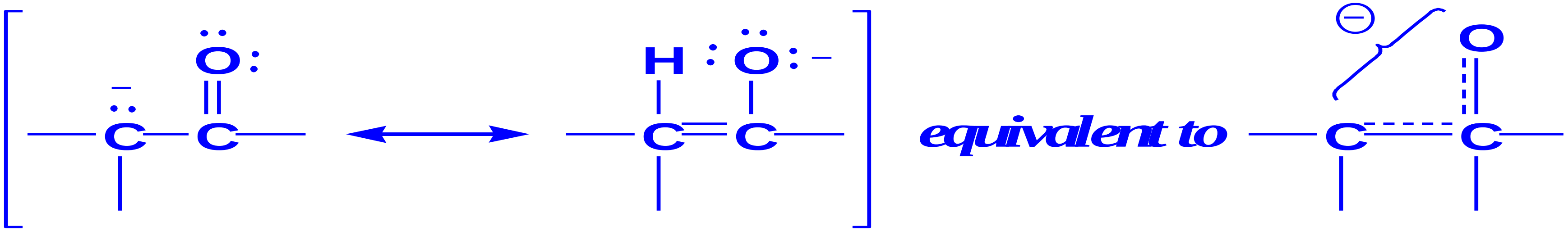
Reaction of Aldehydes and Ketones

[2] Reaction at the α carbon: Reaction involving acidic α-hydrogen:

- **The carbonyl strengthens the acidity of the hydrogen atoms attached to the α-carbon and, by doing this, gives rise to a whole set of chemical reactions.**
- **Ionization of an α-hydrogen, yields a carbanion (I) that is a resonance hybrid of two structures: Keto form and Enol form.**



(I)

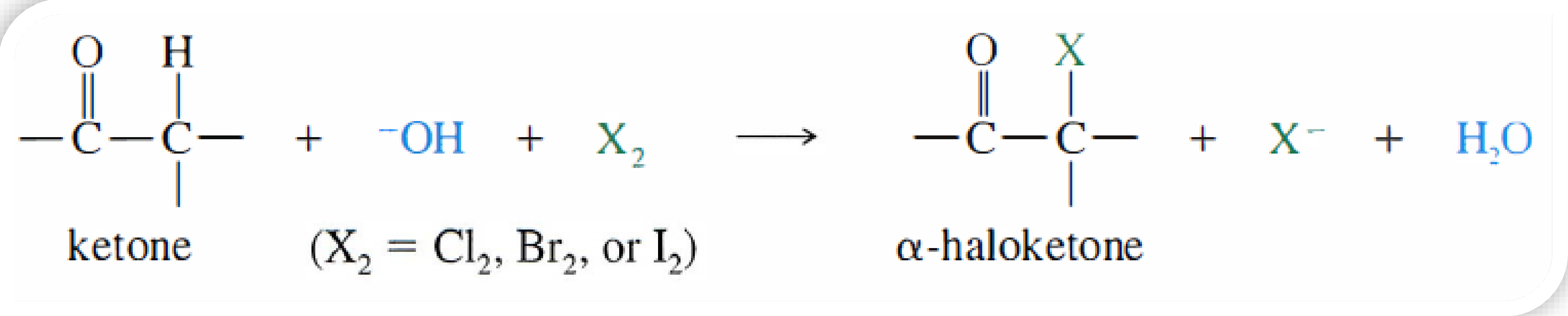


keto form *Enol form* (I)

Reaction of Aldehydes and Ketones

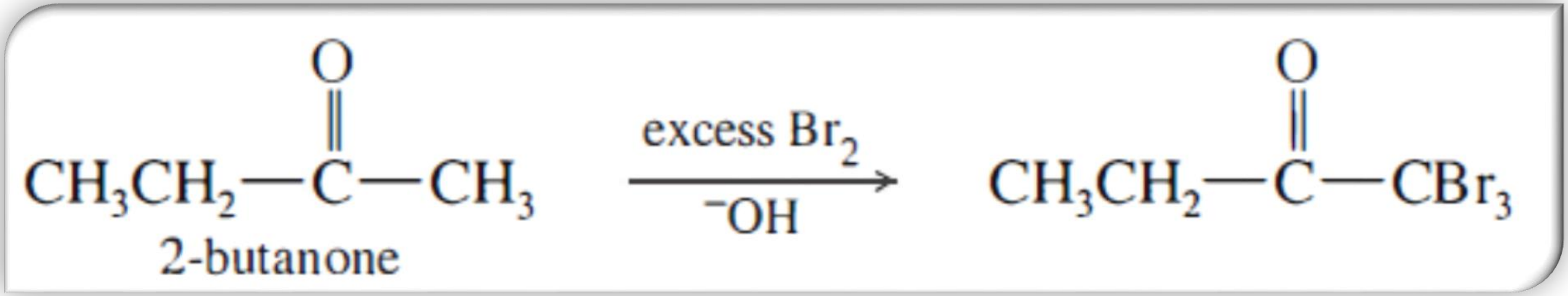
a) Halogenation of ketones:

- When a ketone is treated with a halogen and base, an **α-halogenation** reaction occurs.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{|}{C}}- \;+\; {}^{-}OH \;+\; X_2 \longrightarrow -\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle X}{|}}{\underset{|}{C}}- \;+\; X^{-} \;+\; H_2O$$

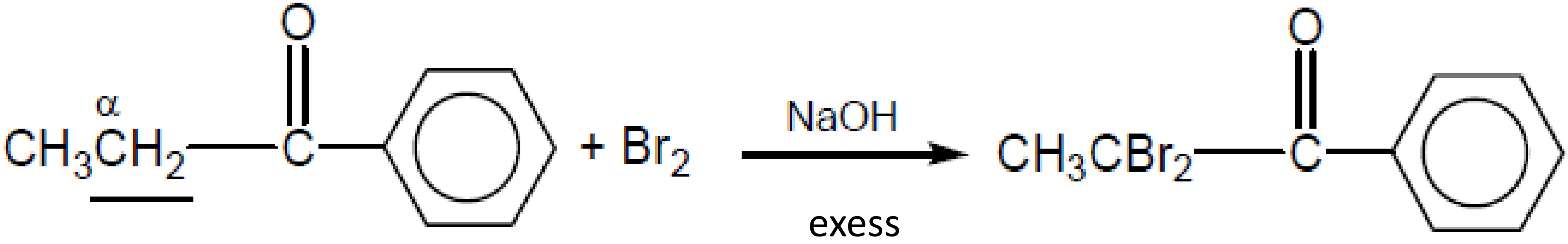
Examples:

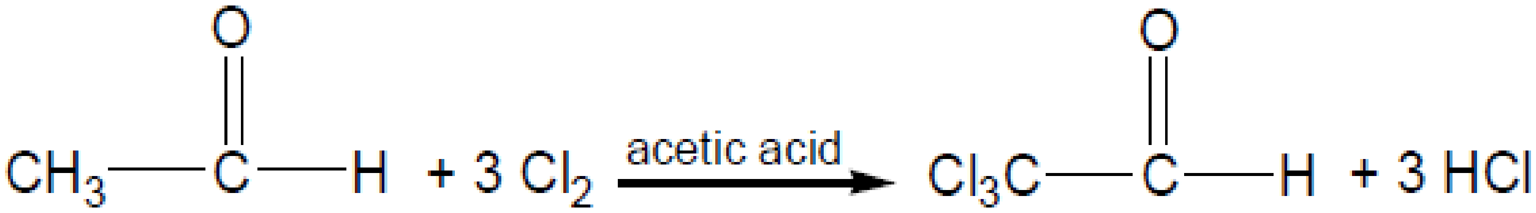


$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[{}^{-}OH]{\text{excess } Br_2} CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CBr_3$$

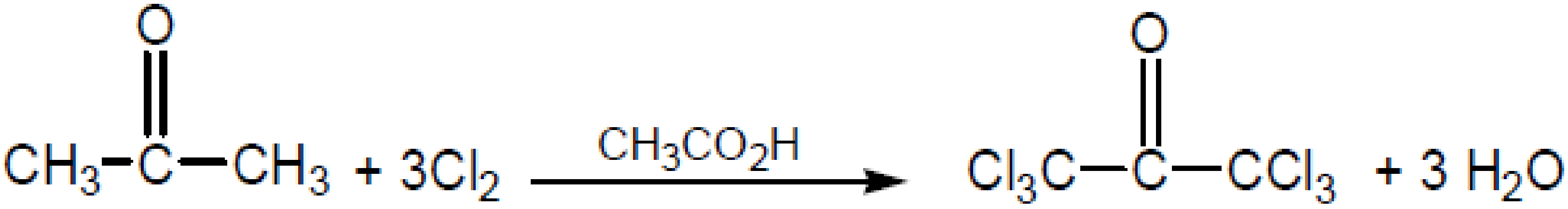
Reaction of Aldehydes and Ketones

Examples:





$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + 3\ Cl_2 \xrightarrow{\text{acetic acid}} Cl_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H + 3\ HCl$$



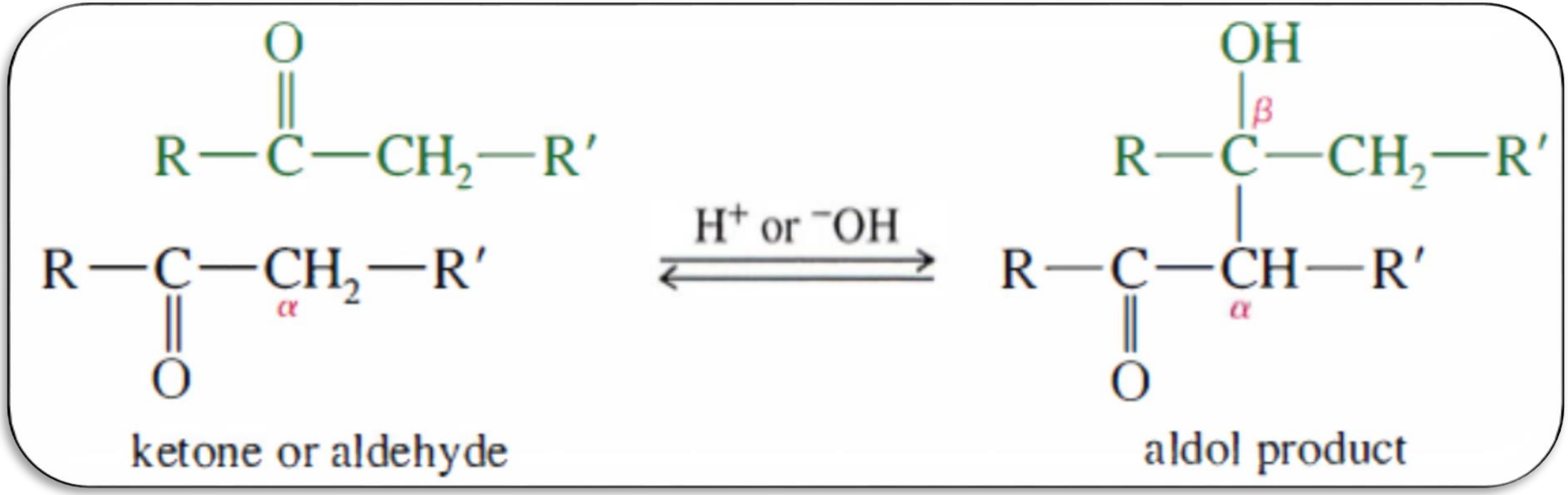
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3Cl_2 \xrightarrow{CH_3CO_2H} Cl_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CCl_3 + 3\ H_2O$$

Reaction of Aldehydes and Ketones

b) Aldol coandensation:

- Under the influence of **dilute base** or **dilute acid**, two molecules of an aldehyde or a ketone, which **contained α-hydrogen** , may combine to form a **β-Hydroxy aldehyde** or **β-Hydroxy ketone**. This reaction is called the **Aldol condensation**.

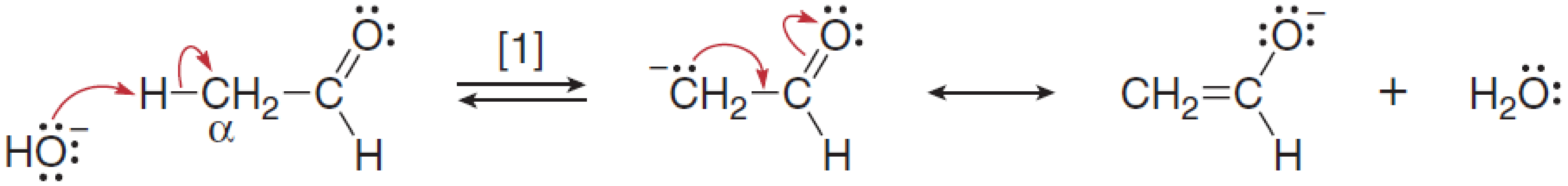
[redacted]



$$2\ R{-}\overset{O}{\overset{\|}{C}}{-}\underset{\alpha}{CH_2}{-}R' \xrightarrow[]{H^+ \text{ or } {}^-OH} R{-}\overset{OH}{\underset{\beta}{C}}(CH_2{-}R'){-}\underset{\alpha}{CH}(R'){-}\overset{O}{\overset{\|}{C}}{-}R$$

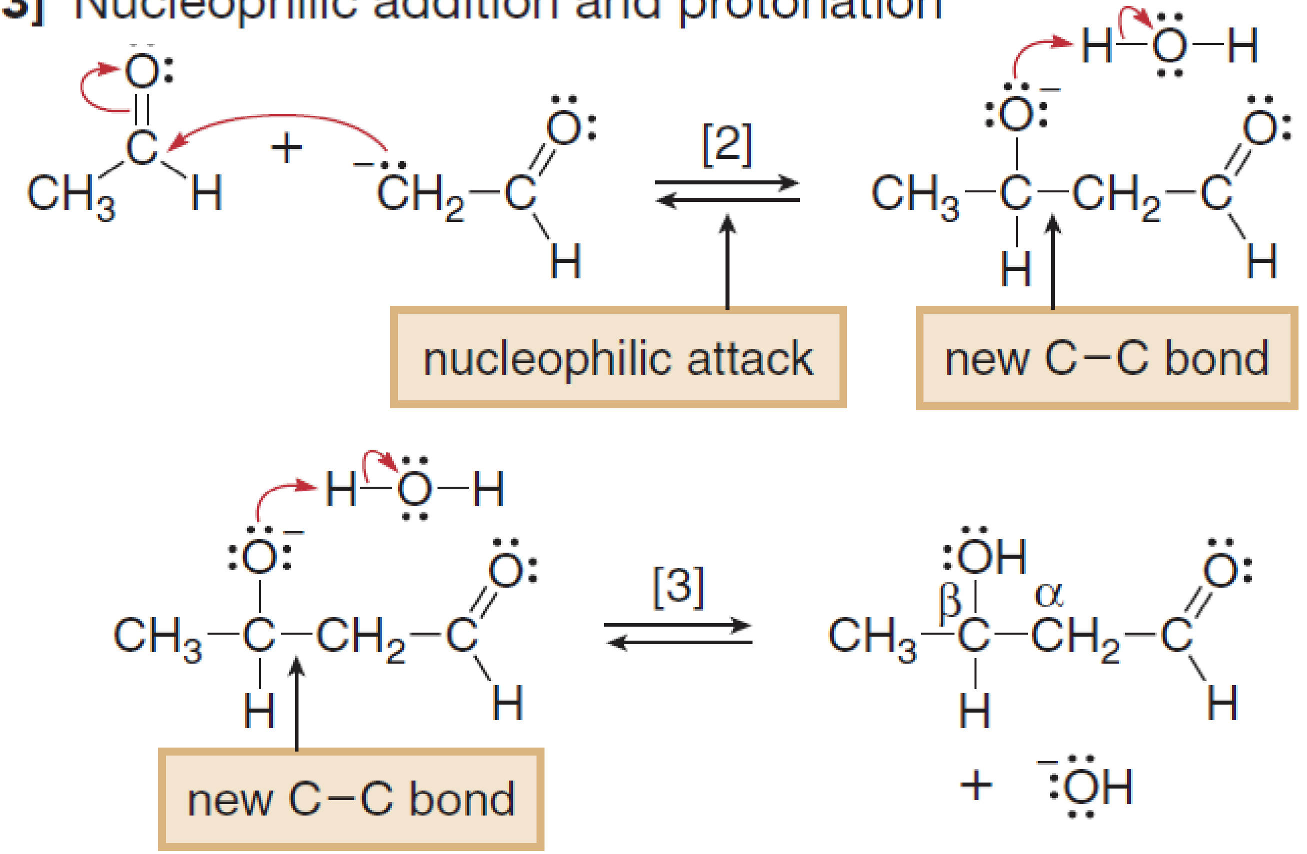
Mechanism:

Step [1] Formation of a nucleophilic enolate



resonance-stabilized enolate

Steps [2]–[3] Nucleophilic addition and protonation



nucleophilic attack

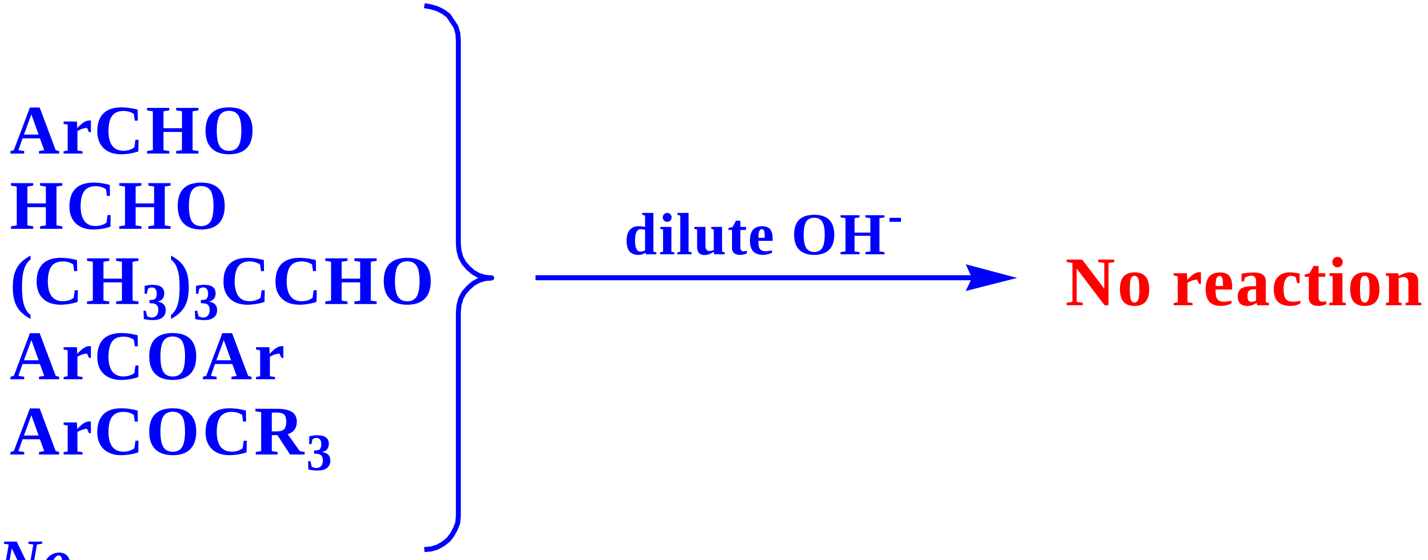
new C–C bond

new C–C bond

Reaction of Aldehydes and Ketones

☞ If **aldehyde or ketone** **does not contain an α-hydrogen**, a simple Aldol condensation **cannot take place**.

☞ ***For example:***



ArCHO
HCHO
$(CH_3)_3CCHO$
ArCOAr
$ArCOCR_3$

$$\xrightarrow{\text{dilute } OH^-}$$

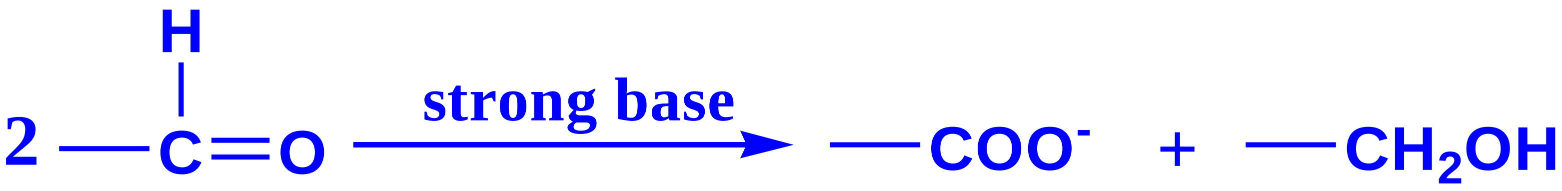
No reaction

No α -hydrogen atoms

Reaction of Aldehydes and Ketones

Cannizzaro reaction:

In the presence of **concentrated alkali**, **aldehydes** containing **no α-hydrogen** undergo **self-oxidation** and **reduction** to yield a mixture of an **alcohol** and a **salt of a carboxylic acid**. This reaction is known as the **Cannizzaro reaction**.



$$2\ —\overset{\overset{\displaystyle H}{|}}{C}{=}O \xrightarrow{\text{strong base}} —COO^{-} + —CH_2OH$$

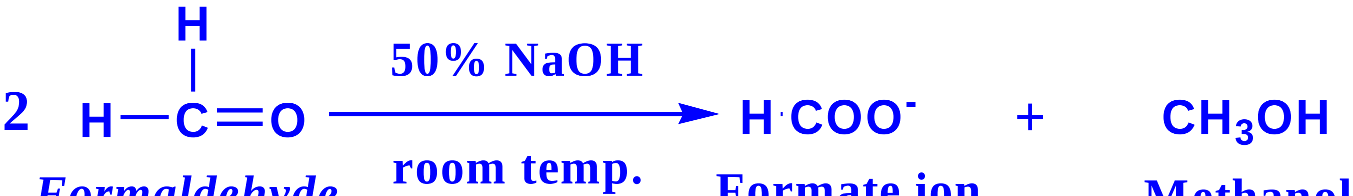
An aldehyde with
no α–hydrogen

Acid
salt

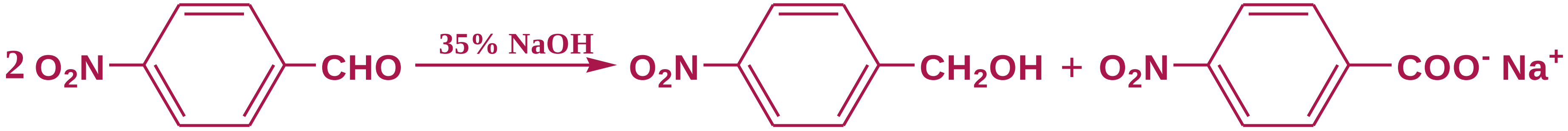
Alcohol

Reaction of Aldehydes and Ketones

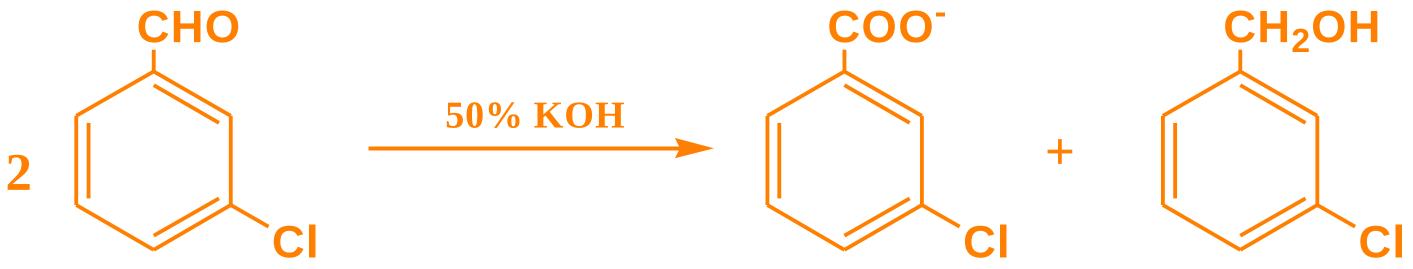
Examples:



Formaldehyde **Formate ion** **Methanol**



***p*-Nitrobenzaldehyde** ***p*-Nitrophenyl alcohol** **Sodium *p*-nitrobenzoate**



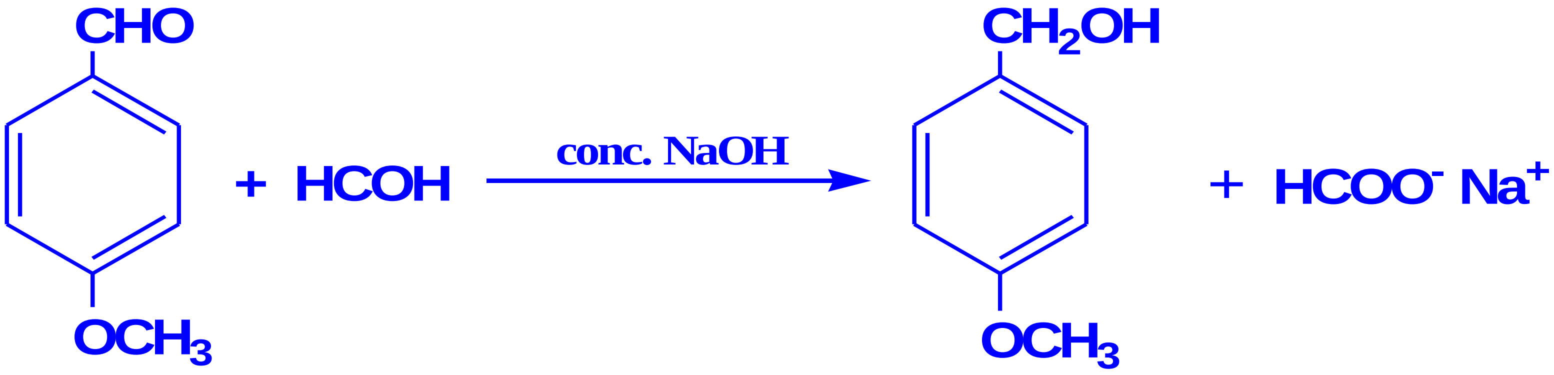
***m*-Chlorobenzaldehyde** ***m*-Chlorobenzoate ion** ***m*-Chlorobenzyl alcohol**

Reaction of Aldehydes and Ketones

Crossed Cannizzaro reaction:

☞ If **two different aldehydes** with **no α-hydrogen** undergo Cannizzaro reaction yield a mixture of products. This reaction is called **crossed Cannizzaro reaction**.

$$ArCHO + HCOH \xrightarrow{conc. NaOH} ArCH_2OH + HCOONa^+$$



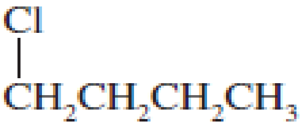
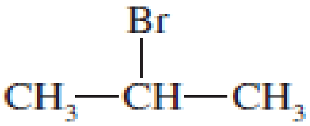
Anisaldehyde
***m*-Methoxybenzaldehyde**

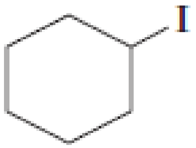
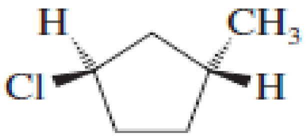
***m*-Methoxybenzyl alcohol**

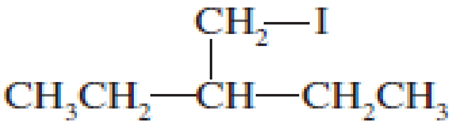
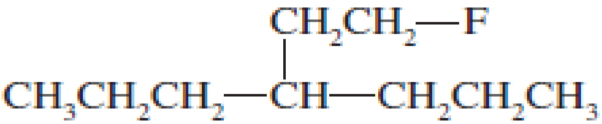
Alkyl halides

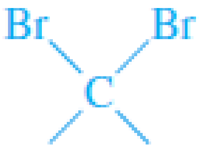
Alkyl halides

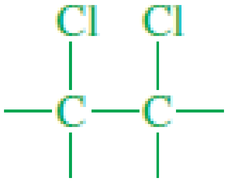
Alkyl halides: are compounds in which a halogen substituent is attached directly to an alkyl group.

	$CH_3CH_2{-}F$	 $\overset{Cl}{\overset{\vert}{C}}H_2CH_2CH_2CH_3$	 $CH_3{-}\overset{Br}{\overset{\vert}{C}}H{-}CH_3$
IUPAC name:	fluoroethane	1-chlorobutane	2-bromopropane
common name:	ethyl fluoride	*n*-butyl chloride	isopropyl bromide

		
IUPAC name:	iodocyclohexane	*trans*-1-chloro-3-methylcyclopentane
common name:	cyclohexyl iodide	(none)

	 $CH_3CH_2{-}\overset{CH_2{-}I}{\overset{\vert}{C}}H{-}CH_2CH_3$	 $CH_3CH_2CH_2{-}\overset{CH_2CH_2{-}F}{\overset{\vert}{C}}H{-}CH_2CH_2CH_3$
IUPAC name:	3-(iodomethyl)pentane	4-(2-fluoroethyl)heptane


a geminal dibromide

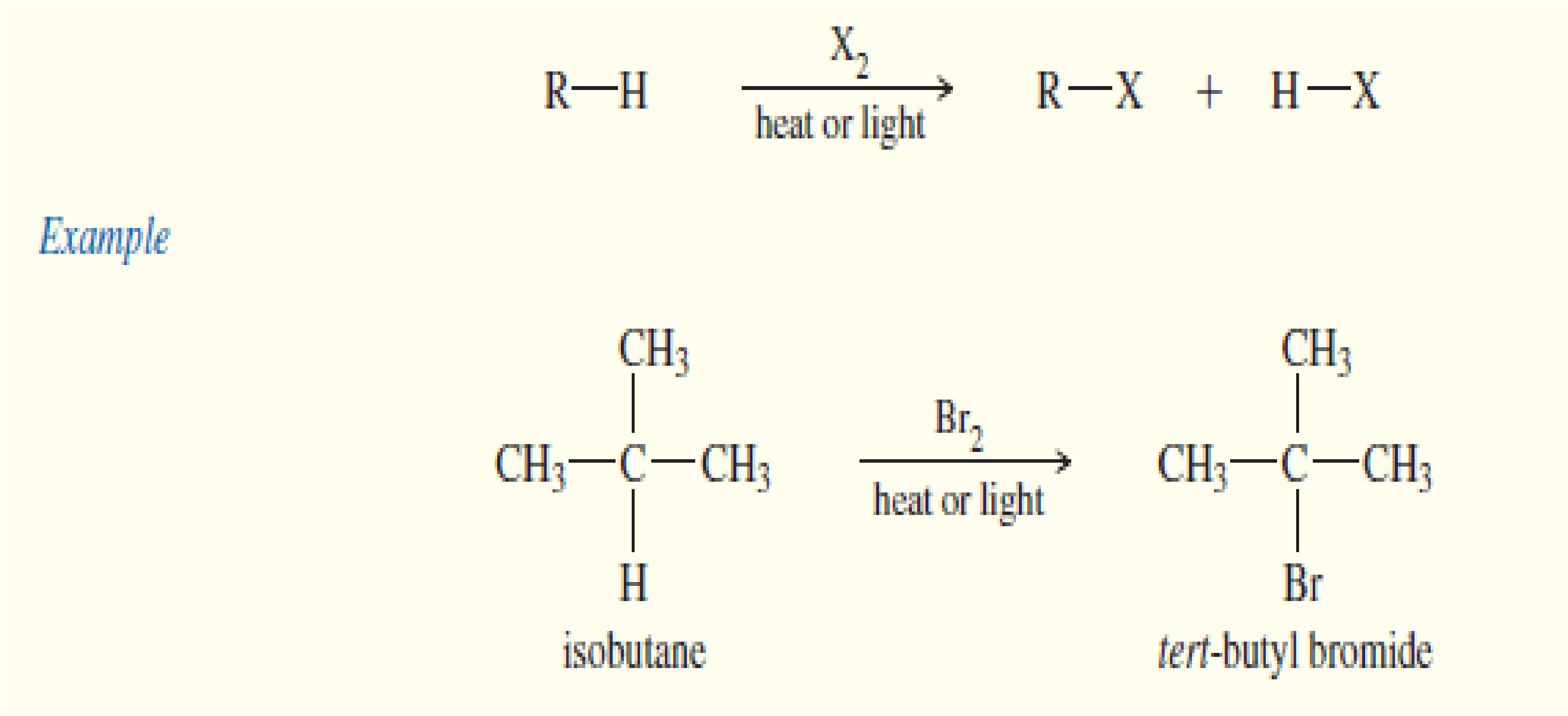

a vicinal dichloride

Physical properties of alkyl halides

- The physical properties of alkyl halides considerably differ from those of the corresponding alkanes. The strength and length of the carbon-halogen bond (C-X bond), the dipole moment and the boiling point of an alkyl halide are determined by the polarity of the bond as well as by the size of the various halogen atoms.
- The C-X bond strength decreases with an increase of the size of the halogen (X)
- Halogens (F, Cl and Br) are more electronegative than carbon. Consequently, carbon atoms that carry halogens are charged partially positive while the halogen is charged partially negative. The polarity of the C-X bond causes a measureable dipole moment.
- Molecules with higher molecular weights generally have higher boiling points because they are heavier (and therefore slower moving),

Preparation of alkyl halides

1- From alkanes: free-radical halogenation:



$$R{-}H \xrightarrow[\text{heat or light}]{X_2} R{-}X + H{-}X$$

Example

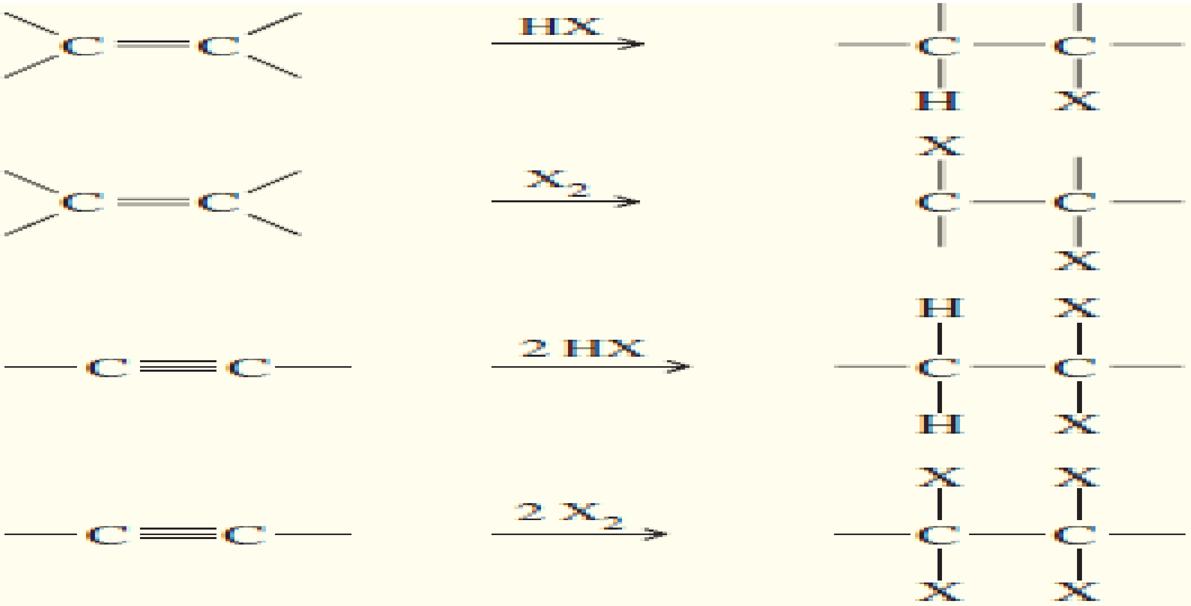
$$\begin{array}{c} CH_3 \\ | \\ CH_3{-}C{-}CH_3 \\ | \\ H \end{array} \xrightarrow[\text{heat or light}]{Br_2} \begin{array}{c} CH_3 \\ | \\ CH_3{-}C{-}CH_3 \\ | \\ Br \end{array}$$

isobutane

tert-butyl bromide

Preparation of alkyl halides

2- From alkenes and alkynes:



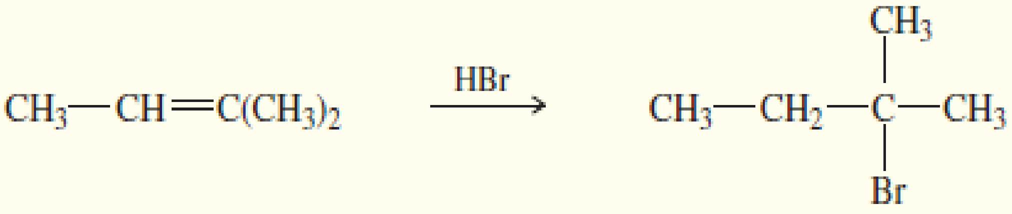
$$\mathrm{>C{=}C<} \xrightarrow{HX} \mathrm{-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{X}{C}}-}$$

$$\mathrm{>C{=}C<} \xrightarrow{X_2} \mathrm{-\overset{X}{\underset{|}{C}}-\overset{|}{\underset{X}{C}}-}$$

$$\mathrm{-C{\equiv}C-} \xrightarrow{2\,HX} \mathrm{-\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-}$$

$$\mathrm{-C{\equiv}C-} \xrightarrow{2\,X_2} \mathrm{-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-}$$

Examples:



$$CH_3-CH{=}C(CH_3)_2 \xrightarrow{HBr} CH_3-CH_2-\overset{CH_3}{\underset{Br}{C}}-CH_3$$

2-methylbut-2-ene 2-bromo-2-methylbutane

$$CH_3-CH{=}CH-CH_3 \xrightarrow{Cl_2} CH_3-CHCl-CHCl-CH_3$$

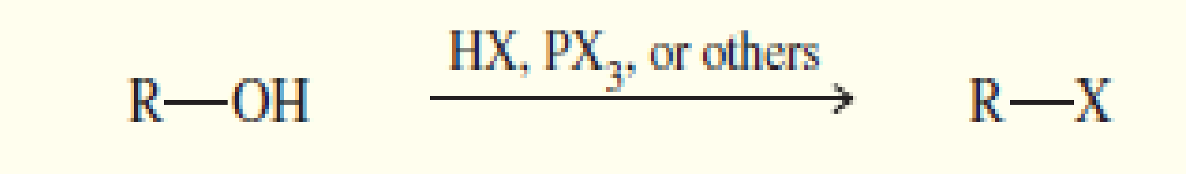
but-2-ene 2,3-dichlorobutane

$$H-C{\equiv}C-CH_2CH_2CH_3 \xrightarrow{2\,HBr} CH_3-CBr_2-CH_2CH_2CH_3$$

pent-1-yne 2,2-dibromopentane

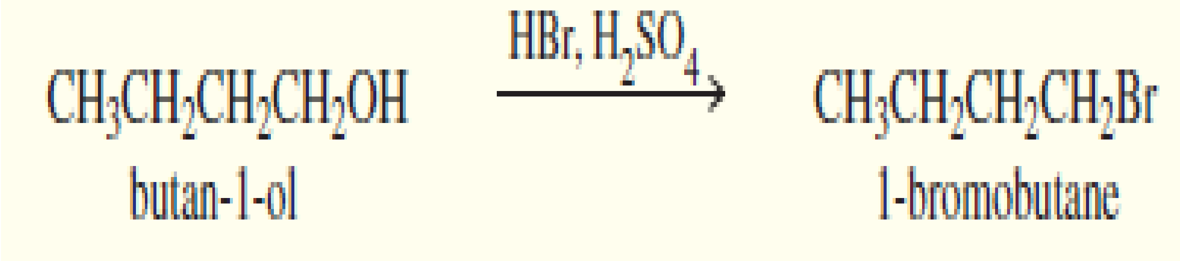
Preparation of alkyl halides

3- From alcohols:



$$R\text{—}OH \xrightarrow{HX,\ PX_3,\ \text{or others}} R\text{—}X$$

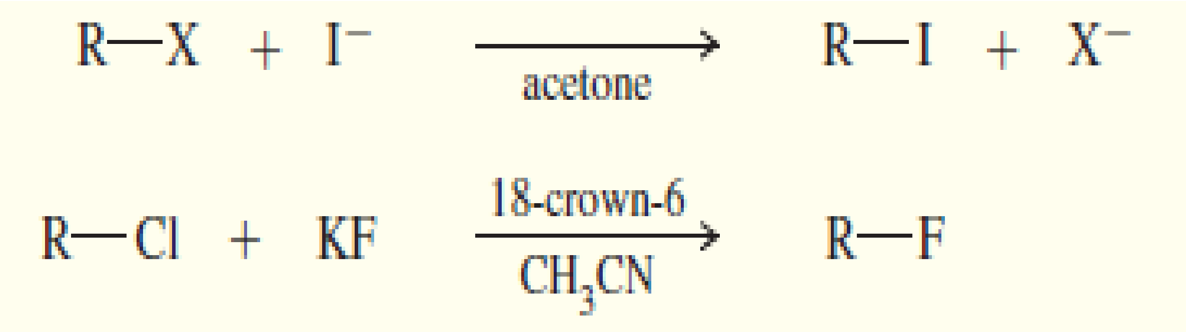
Example:



$$CH_3CH_2CH_2CH_2OH \xrightarrow{HBr,\ H_2SO_4} CH_3CH_2CH_2CH_2Br$$

butan-1-ol 1-bromobutane

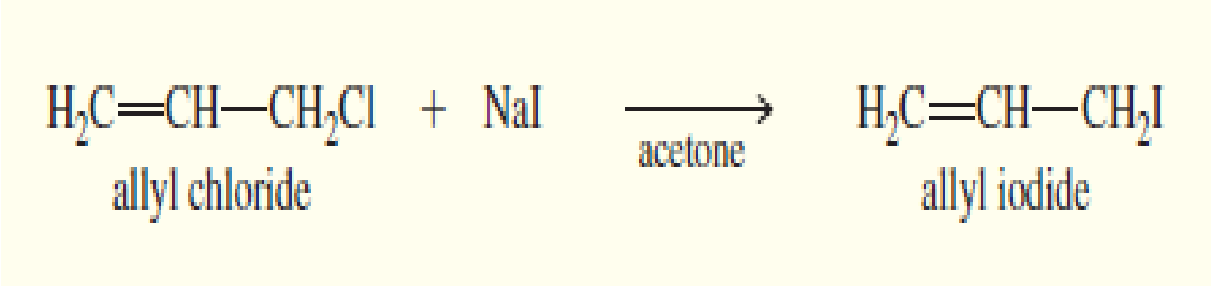
4- From other halides:



$$R\text{—}X + I^- \xrightarrow[\text{acetone}]{} R\text{—}I + X^-$$

$$R\text{—}Cl + KF \xrightarrow[CH_3CN]{\text{18-crown-6}} R\text{—}F$$

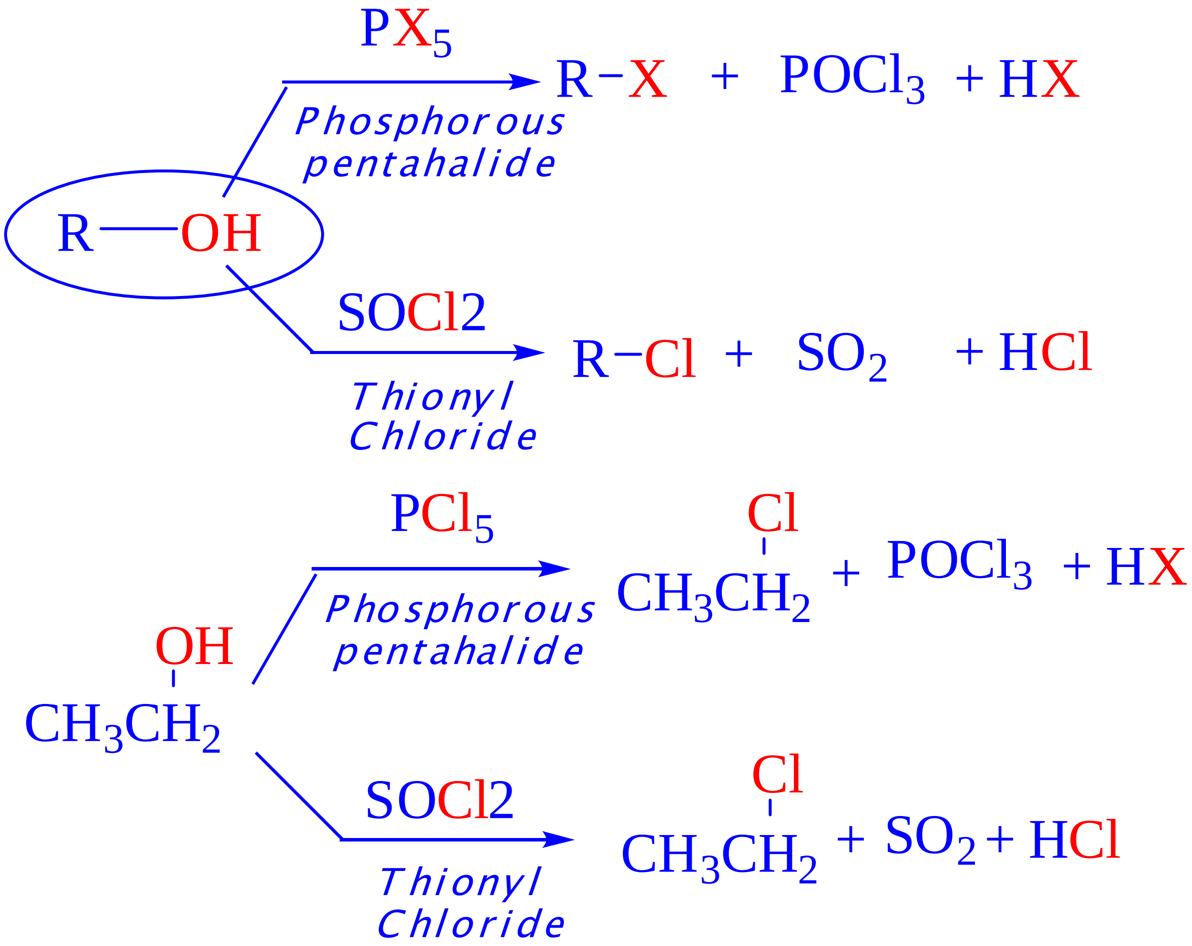
Example:



$$H_2C{=}CH\text{—}CH_2Cl + NaI \xrightarrow[\text{acetone}]{} H_2C{=}CH\text{—}CH_2I$$

allyl chloride allyl iodide

3- From Alcohols: By action of PX_5, PX_3 or $SOCl_2$ (in case of alkyl chlorides)



$$R-OH \xrightarrow[\text{Phosphorous pentahalide}]{PX_5} R-X + POCl_3 + HX$$

$$R-OH \xrightarrow[\text{Thionyl Chloride}]{SOCl2} R-Cl + SO_2 + HCl$$

$$CH_3\overset{OH}{CH_2} \xrightarrow[\text{Phosphorous pentahalide}]{PCl_5} CH_3\overset{Cl}{CH_2} + POCl_3 + HX$$

$$CH_3\overset{OH}{CH_2} \xrightarrow[\text{Thionyl Chloride}]{SOCl2} CH_3\overset{Cl}{CH_2} + SO_2 + HCl$$

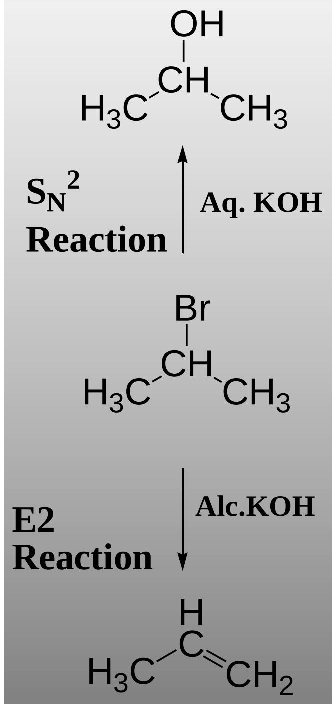
Chemical Reactions of Alkyl Halides

Reactivity of Alkyl Halides

The polarity of the carbon-halogen bonds

With the exception of iodine, all of the halogens are more electronegative than carbon. That means that the electron pair in the carbon-halogen bond will be dragged towards the halogen end, leaving the halogen slightly negative (δ-) and the carbon slightly positive (δ+).

General Notes



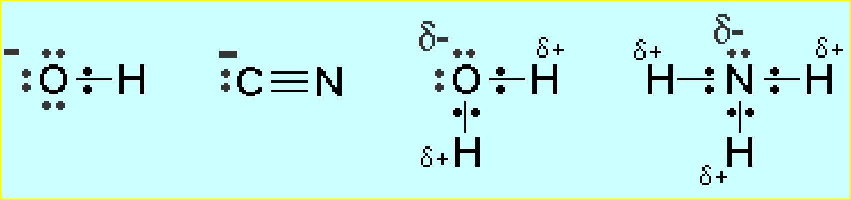
- RX react by *Nucleophilic Substitution* Reaction (S_N1 or S_N2), due to basicity of Halide atom.
- Some alkyl halides can react by *Elimination* reaction in the presence of very strong base: discussed in *page 10*.
- 1° and 2° alkyl halides react mainly by S_N.
- 3° alkyl halide tend to react by E reaction.
- Order of RX reactivity in S_N and E reactions is directly proportional to C-X bond strength.

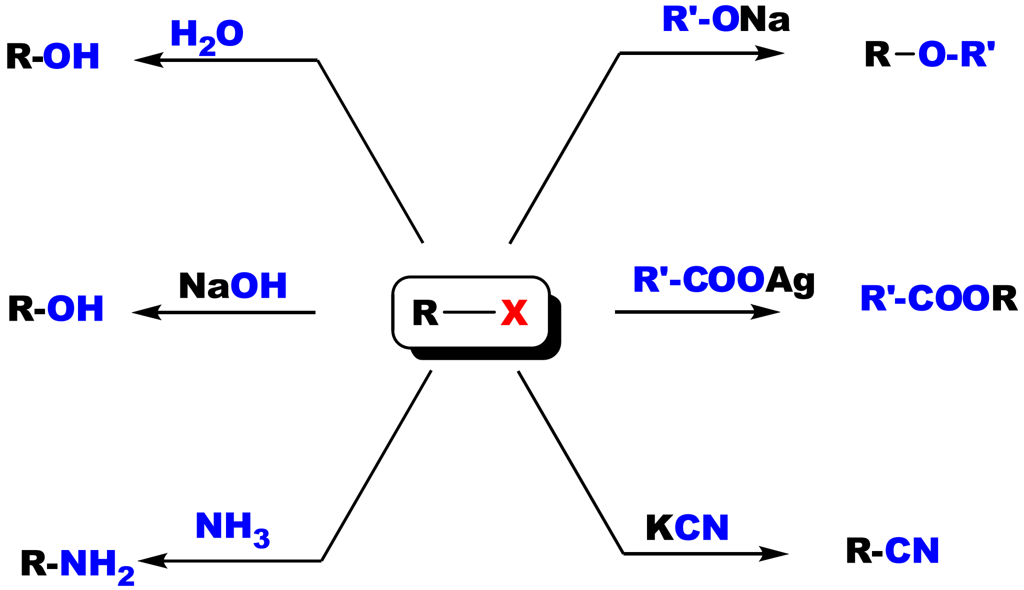
RI > RBr > RCl > RF

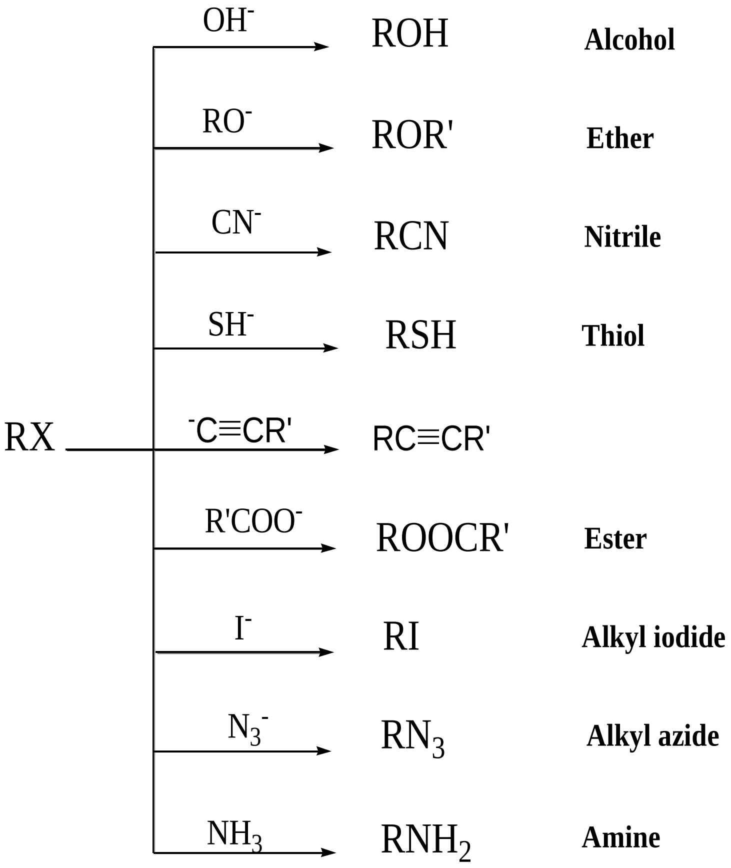
Nucleophilic Substitution Reactions SN

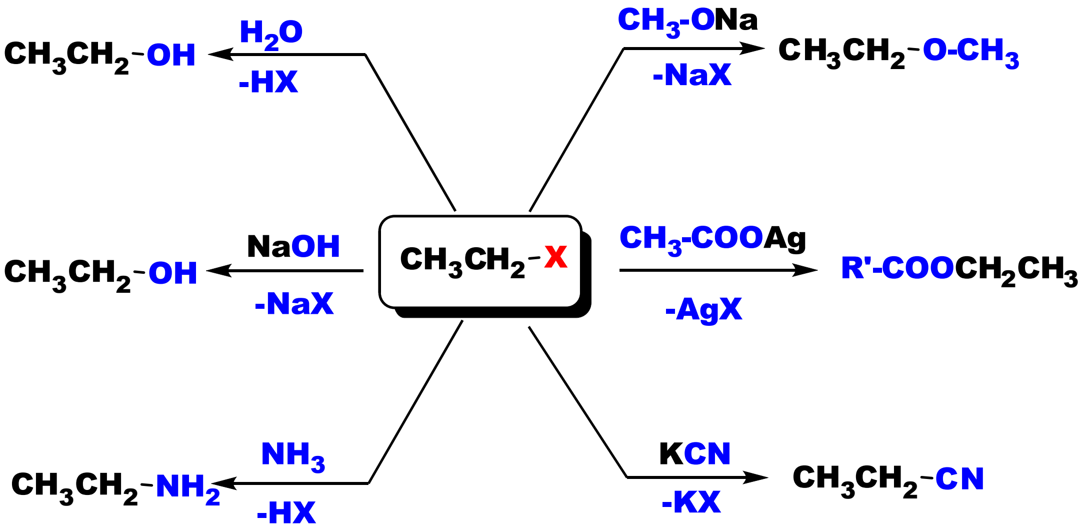
A nucleophile is a species (an ion or a molecule) which is strongly attracted to a region of positive charge in something else.

Nucleophiles are either fully negative ions, or else have a strongly δ^- charge somewhere on a molecule. The common nucleophiles are hydroxide ions, methoxide ions (CH_3O^-), cyanide ions, water and ammonia.




R-OH
H2O
R'-ONa
R–O-R'
R-OH
NaOH
R—X
R'-COOAg
R'-COOR
NH3
R-NH2
KCN
R-CN

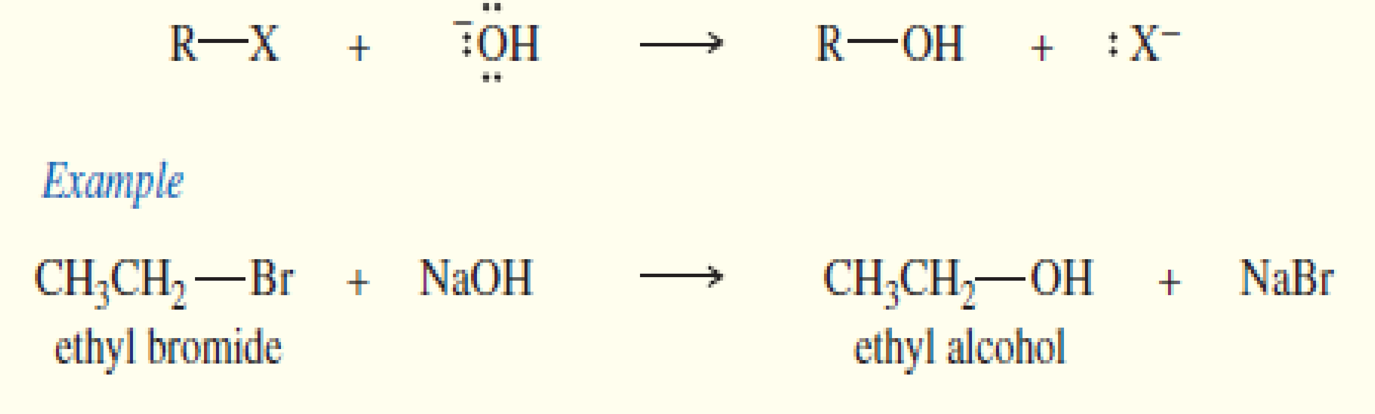

RX
OH-
ROH
Alcohol
RO-
ROR'
Ether
CN-
RCN
Nitrile
SH-
RSH
Thiol
-C≡CR'
RC≡CR'
R'COO-
ROOCR'
Ester
I-
RI
Alkyl iodide
N3-
RN3
Alkyl azide
NH3
RNH2
Amine


CH3CH2-OH
H2O
-HX
CH3-ONa
-NaX
CH3CH2-O-CH3
CH3CH2-OH
NaOH
-NaX
CH3CH2-X
CH3-COOAg
-AgX
R'-COOCH2CH3
CH3CH2-NH2
NH3
-HX
KCN
-KX
CH3CH2-CN

Reactions of alkyl halides

1- substitution reactions

a. Alcohol formation:



$$\mathrm{R{-}X} \quad + \quad {}^{-}{:}\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\mathrm{H} \quad \longrightarrow \quad \mathrm{R{-}OH} \quad + \quad {:}\mathrm{X}^{-}$$

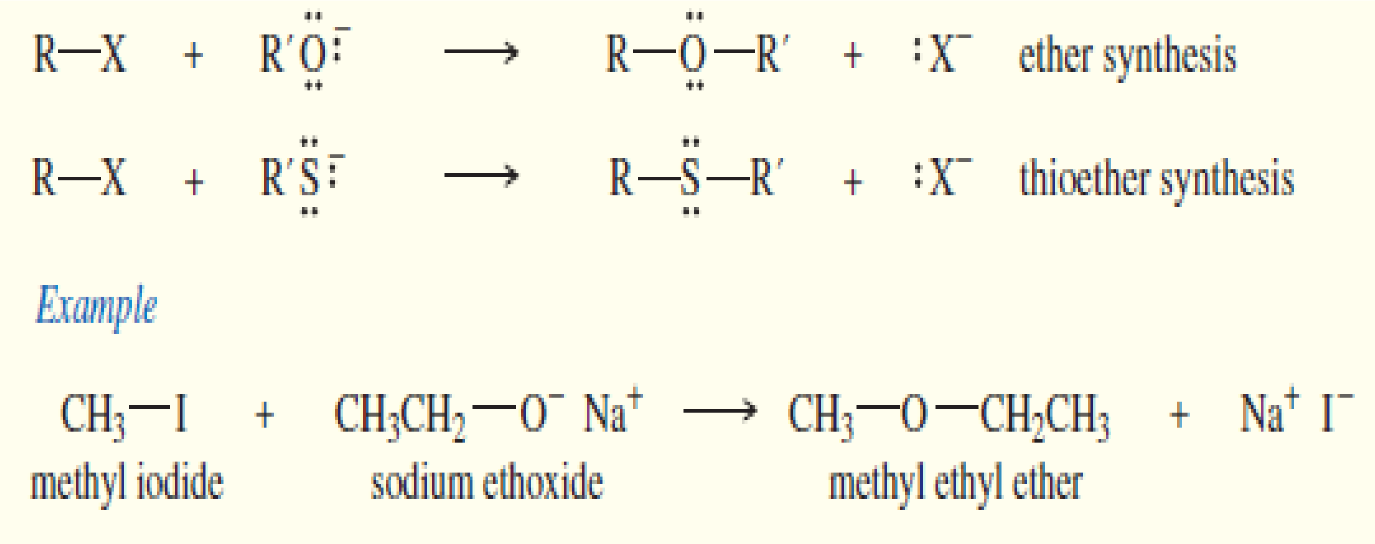
Example

$$\mathrm{CH_3CH_2{-}Br} \quad + \quad \mathrm{NaOH} \quad \longrightarrow \quad \mathrm{CH_3CH_2{-}OH} \quad + \quad \mathrm{NaBr}$$

ethyl bromide

ethyl alcohol

b. Williamson ether synthesis:



$$\mathrm{R{-}X} \quad + \quad \mathrm{R'}\ddot{\underset{\cdot\cdot}{\mathrm{O}}}{:}^{-} \quad \longrightarrow \quad \mathrm{R{-}}\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\mathrm{{-}R'} \quad + \quad {:}\mathrm{X}^{-} \quad \text{ether synthesis}$$

$$\mathrm{R{-}X} \quad + \quad \mathrm{R'}\ddot{\underset{\cdot\cdot}{\mathrm{S}}}{:}^{-} \quad \longrightarrow \quad \mathrm{R{-}}\ddot{\underset{\cdot\cdot}{\mathrm{S}}}\mathrm{{-}R'} \quad + \quad {:}\mathrm{X}^{-} \quad \text{thioether synthesis}$$

Example

$$\mathrm{CH_3{-}I} \quad + \quad \mathrm{CH_3CH_2{-}O^{-}\ Na^{+}} \quad \longrightarrow \quad \mathrm{CH_3{-}O{-}CH_2CH_3} \quad + \quad \mathrm{Na^{+}\ I^{-}}$$

methyl iodide

sodium ethoxide

methyl ethyl ether

Reactions of alkyl halides

c. Amine synthesis:

$$\mathrm{R{-}X} \quad + \quad \underset{\text{excess}}{:\mathrm{NH_3}} \longrightarrow \mathrm{R{-}NH_3^+\ X^-} \xrightarrow{:\mathrm{NH_3}} \underset{\text{amine}}{\mathrm{R{-}\ddot{N}H_2}} \quad + \quad \mathrm{NH_4^+\ :X^-}$$

Example

$$\underset{n\text{-propyl bromide}}{\mathrm{CH_3CH_2CH_2{-}Br}} \quad + \quad :\mathrm{NH_3} \longrightarrow \underset{n\text{-propylamine}}{\mathrm{CH_3CH_2CH_2{-}NH_2}} \quad + \quad \mathrm{NH_4^+\ {}^-Br}$$

d. Alkyne synthesis:

$$\underset{\text{acetylide ion}}{\mathrm{R{-}C{\equiv}C\colon^-}} \quad + \quad \mathrm{R'{-}X} \longrightarrow \underset{\text{alkyne}}{\mathrm{R{-}C{\equiv}C{-}R'}} \quad + \quad :\mathrm{X^-}$$

Example

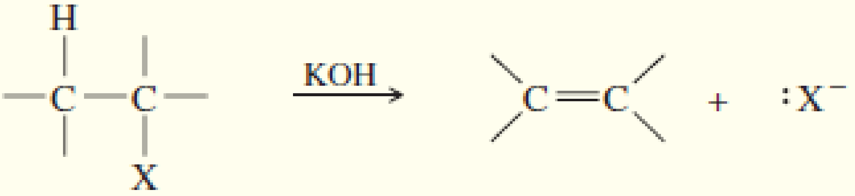
$$\underset{\text{propyne}}{\mathrm{CH_3{-}C{\equiv}C{-}H}} \quad + \quad \underset{\text{sodium amide}}{\mathrm{NaNH_2}} \longrightarrow \underset{\text{sodium propynide}}{\mathrm{CH_3{-}C{\equiv}C\colon^-\ Na^+}} \quad + \quad \mathrm{NH_3}$$

$$\underset{\text{propynide ion}}{\mathrm{CH_3{-}C{\equiv}C\colon^-\ \ Na^+}} \quad + \quad \underset{\text{ethyl iodide}}{\mathrm{CH_3CH_2{-}I}} \longrightarrow \underset{\text{pent-2-yne}}{\mathrm{CH_3{-}C{\equiv}C{-}CH_2CH_3}} \quad + \quad \mathrm{NaI}$$

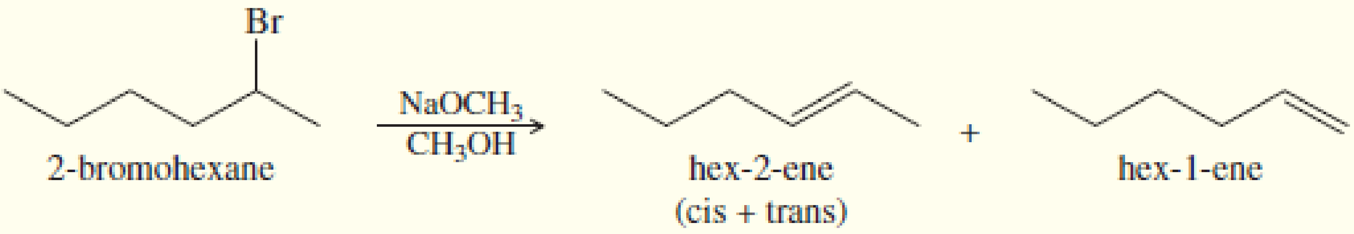
Reactions of alkyl halides

2- Elimination reactions:

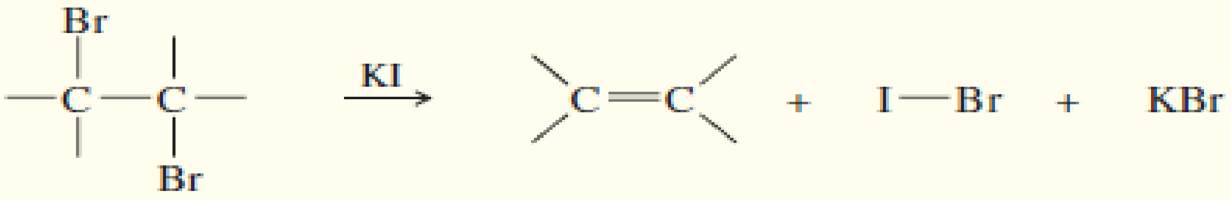
a. Dehydrohalogenation:



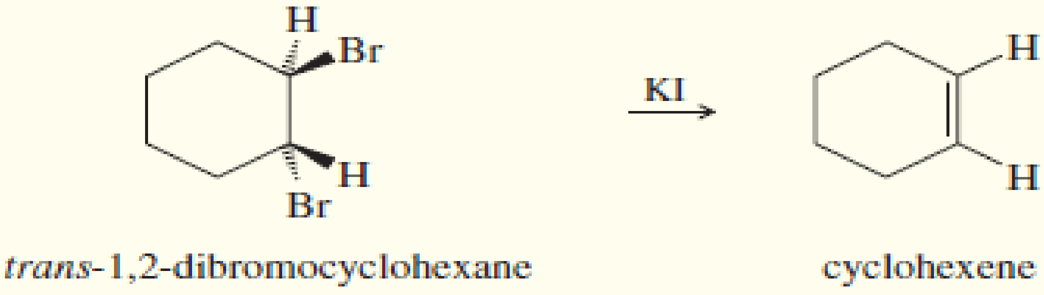
Example



b. Dehalogenation:



Example



Reactions of alkyl halides

3- Formation of Grignard reagents:

$$\underset{(X = Cl, Br, \text{ or } I)}{R-X} + Mg \xrightarrow{CH_3CH_2-O-CH_2CH_3} \underset{\substack{\text{organomagnesium halide} \\ \text{(Grignard reagent)}}}{R-Mg-X}$$

Example

bromocyclohexane → cyclohexylmagnesium bromide

$$R-X \xrightarrow[(2)\ H_2O]{(1)\ Mg \text{ or } Li} R-H$$

Example

$$\underset{n\text{-decyl bromide}}{C_9H_{19}-CH_2-Br} \xrightarrow[(2)\ H_2O]{(1)\ Mg,\ \text{ether}} \underset{n\text{-decane}}{C_9H_{19}-CH_3}$$

Alcohols

Alcohols

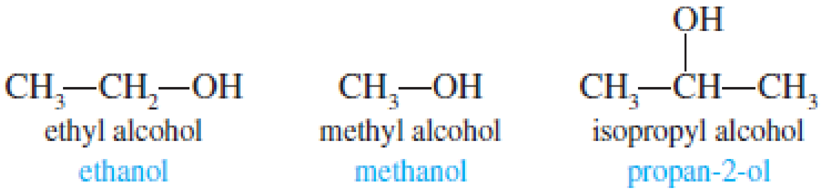
Introduction:

- **Alcohols:** are organic compounds containing hydroxyl groups.
- Alcohols viewed as organic derivatives of water.

H-O-H R-O-H

Water Alcohol

- Alcohols have a common functional group, the hydroxyl group, -OH.
- In alcohols the hydroxyl group is attached to an alkyl group, -R.



$CH_3{-}CH_2{-}OH$ ethyl alcohol ethanol

$CH_3{-}OH$ methyl alcohol methanol

$CH_3{-}\overset{OH}{CH}{-}CH_3$ isopropyl alcohol propan-2-ol

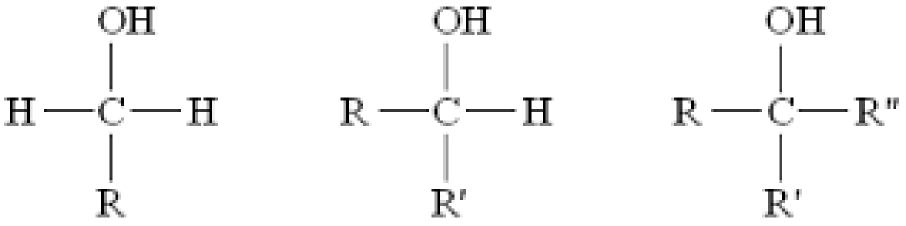
- When the hydroxyl group is attached to an aromatic ring, Ar, it is called phenol.

Ar-O-H

Phenol

Classification of alcohols:

- Alcohols are subdivided into three classes: primary (1°), secondary (2°) and tertiary (3°).
- The classification depends on the number of alkyl groups bonded to the carbon bearing the –OH , which called carbinol carbon.
- Primary alcohols have one alkyl group attached to the carbinol carbon.
- Secondary alcohols have two.
- Tertiary alcohols have three.

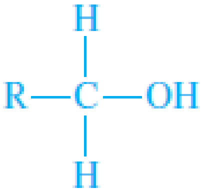
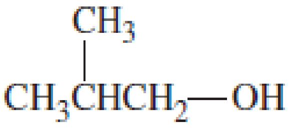
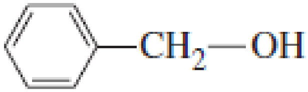
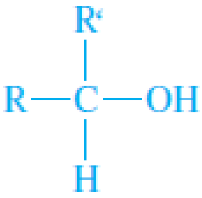
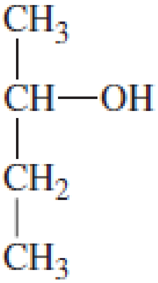
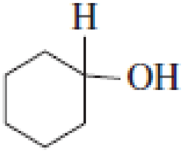
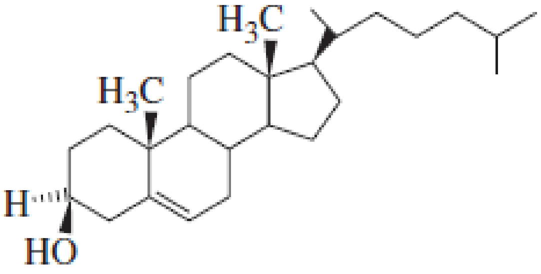
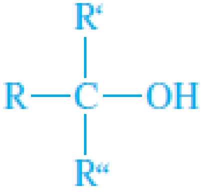
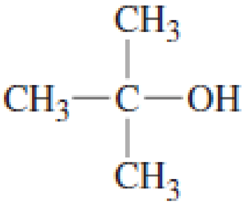
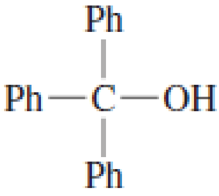
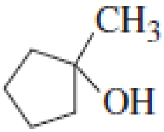
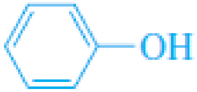
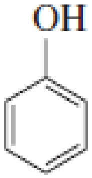
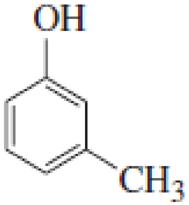
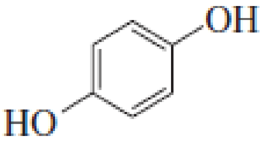


primary (1°) alcohol

secondary (2°) alcohol

tertiary (3°) alcohol

Alcohols

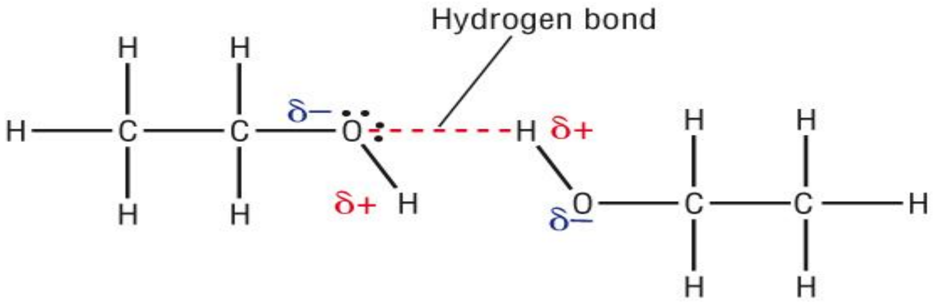
Type	*Structure*	*Examples*
Primary alcohol	 $R-\overset{H}{\underset{H}{C}}-OH$	CH_3CH_2-OH ethanol  $CH_3\overset{CH_3}{C}HCH_2-OH$ 2-methylpropan-1-ol  benzyl alcohol
Secondary alcohol	 $R-\overset{R'}{\underset{H}{C}}-OH$	 $\begin{array}{l} CH_3 \\ \vert \\ CH-OH \\ \vert \\ CH_2 \\ \vert \\ CH_3 \end{array}$ butan-2-ol  cyclohexanol  cholesterol
Tertiary alcohol	 $R-\overset{R'}{\underset{R''}{C}}-OH$	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$ 2-methylpropan-2-ol  $Ph-\overset{Ph}{\underset{Ph}{C}}-OH$ triphenylmethanol  1-methylcyclopentanol
Phenols		 phenol  3-methylphenol  hydroquinone

Physical properties alcohols

1- Solubility:

At room temperature the alcohols are liquids.

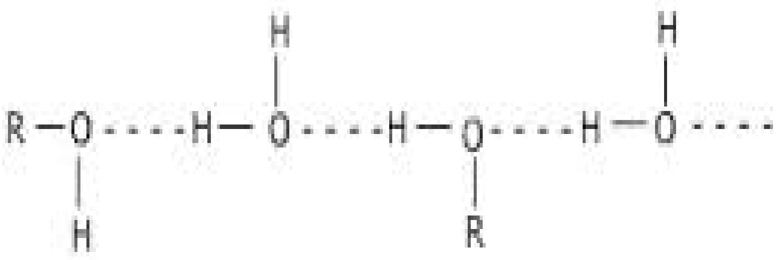
Alcohols are soluble in water unlike the alkanes due to alcohols ability to do hydrogen bond with water. As the number of carbons in the alcohol increases, the solubility in water decreases. The –O-H bond is highly polar.



2- Boiling point:

The boiling points increase with increase in molecular weights.

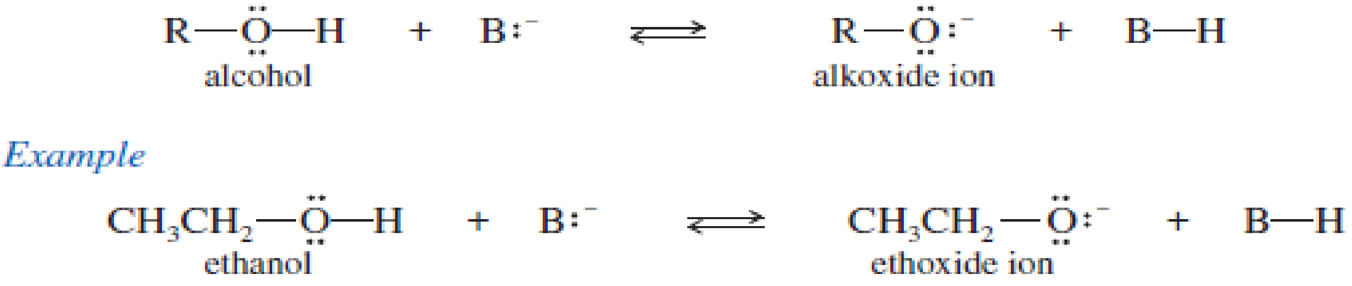
The values of boiling points of alcohols are higher than in alkanes due to presence of –OH group, which is able to do hydrogen bond between molecules.



Physical properties alcohols

3- Acidity of Alcohols and Phenols:

Like the hydroxyl proton of water, the hydroxyl proton of an alcohol is weakly acidic. A strong base can remove the hydroxyl proton to give an **alkoxide ion.**



$$\mathrm{R{-}\ddot{\underset{..}{O}}{-}H} + \mathrm{B:^-} \rightleftharpoons \mathrm{R{-}\ddot{\underset{..}{O}}:^-} + \mathrm{B{-}H}$$

alcohol — alkoxide ion

Example

$$\mathrm{CH_3CH_2{-}\ddot{\underset{..}{O}}{-}H} + \mathrm{B:^-} \rightleftharpoons \mathrm{CH_3CH_2{-}\ddot{\underset{..}{O}}:^-} + \mathrm{B{-}H}$$

ethanol — ethoxide ion

Alcohols as acids: formation of salt:

$$\underset{\text{Alcohol}}{\mathrm{ROH}} + \underset{\text{Sodium hydride}}{\mathrm{NaH}} \longrightarrow \underset{\text{Alkoxide salt}}{\mathrm{RO^-Na^+}} + \mathrm{H_2}$$

The Williamson synthesis of ethers:

$$\mathrm{R\text{-}O^-Na^+} + \mathrm{R'\text{-}X} \longrightarrow \mathrm{R\text{-}O\text{-}R'} + \mathrm{NaX}$$

Sodium alkoxide Alkyl halide Ether Sodium halide

Alkoxides are strong bases stronger than hydroxides, which is used in the synthesis of ethers R-O-R’.

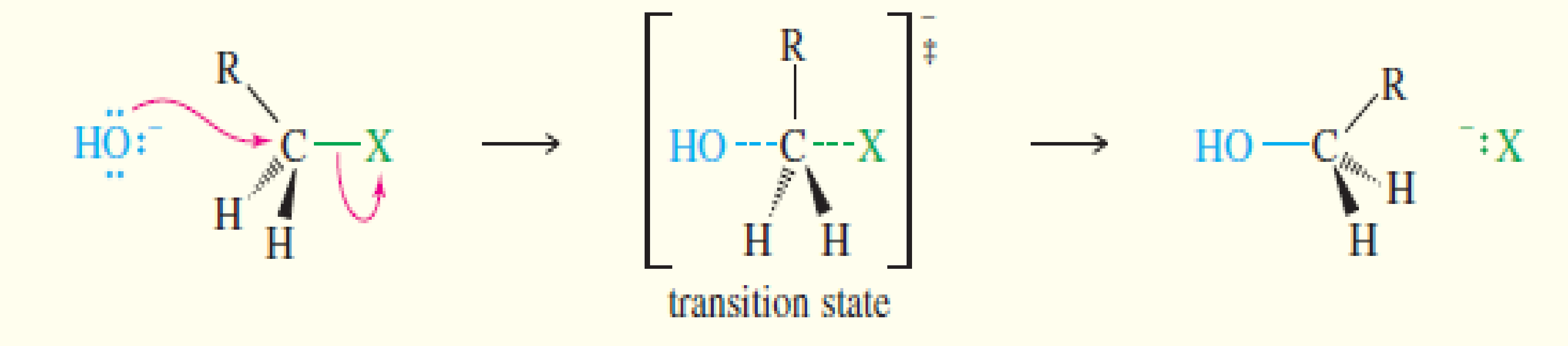
Alkoxyl group RO- , Hydroxyl group HO-

Preparation of alcohols

1- Nucleophilic substitution on an alkyl halide:

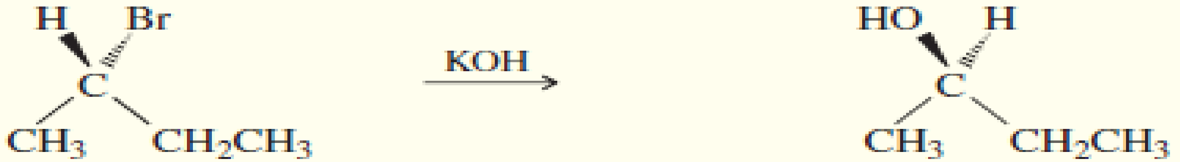
$$R\text{-}X + H\text{-}OH \longrightarrow R\text{-}OH + H\text{-}X$$

$$\underset{\text{1-bromopentane}}{CH_3CH_2CH_2CH_2CH_2Br} + {}^{-}OH \longrightarrow \underset{\text{pentane-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH} + Br^-$$



transition state

Example



(*S*)-2-bromobutane

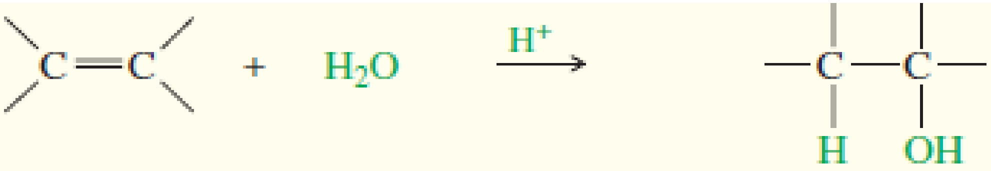
(*R*)-butan-2-ol, 100% inverted configuration
(plus elimination products)

Preparation of alcohols

2- From alkenes:

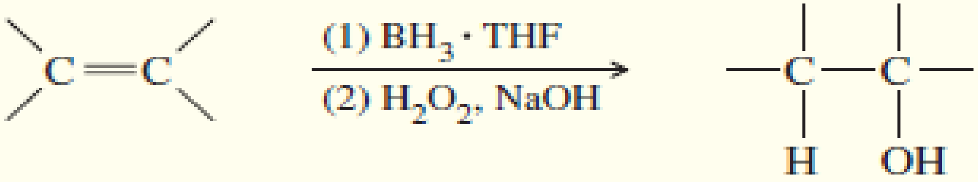
a. Acid-catalyzed Hydration of alkenes:

Water adds to alkenes in the presence of an acid catalyst following Markovnikov’s rule.



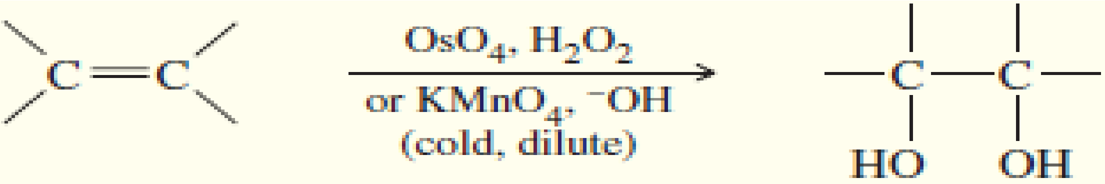
Markovnikov orientation

b. Hydroboration–oxidation:



syn addition, anti-Markovnikov orientation

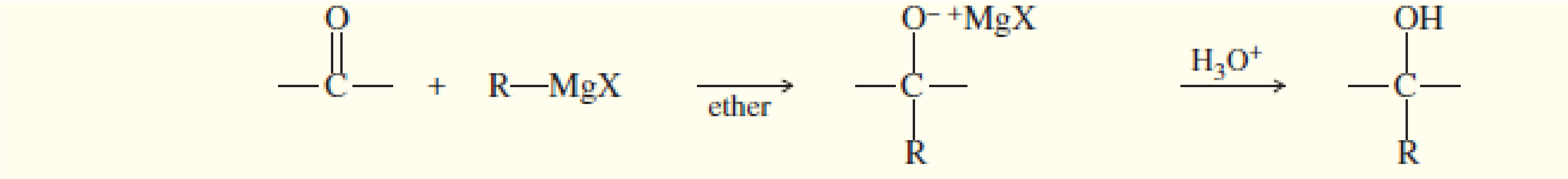
c. Dihydroxylation: synthesis of 1,2-diols from alkenes:



syn dihydroxylation

Preparation of alcohols

3- Addition of a Grignard reagent to carbonyl groups:

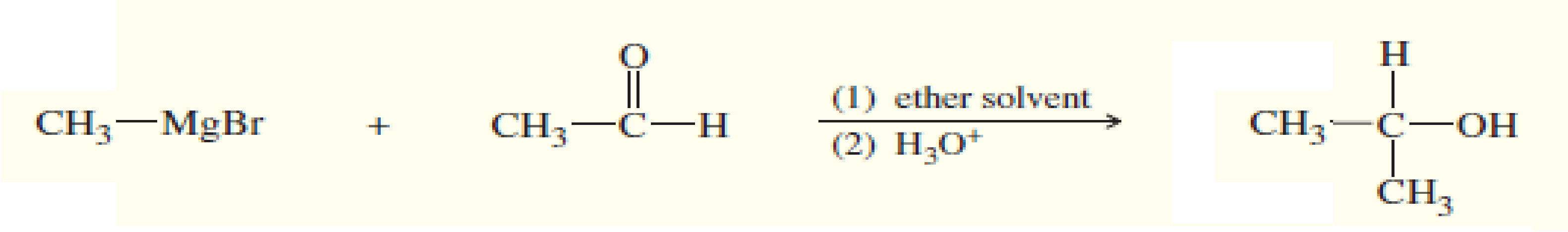


$$-\overset{\overset{\displaystyle O}{\|}}{C}- + R{-}MgX \xrightarrow[\text{ether}]{} -\overset{\overset{\displaystyle O^{-}\,{}^{+}MgX}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}- \xrightarrow{H_3O^+} -\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-$$

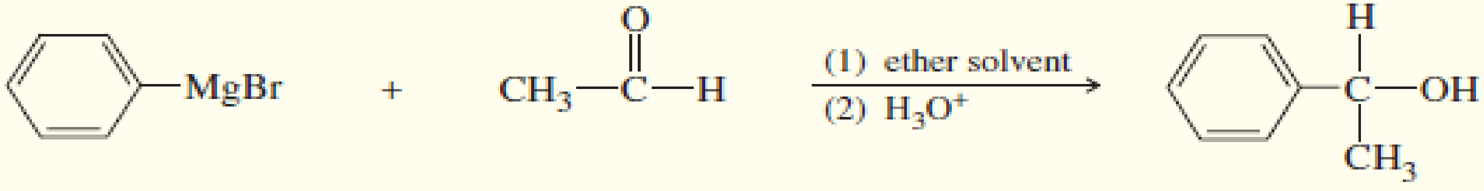
a. Addition to formaldehyde gives a primary alcohol:

$$\underset{\text{ethylmagnesium bromide}}{CH_3CH_2MgBr} + H_2C{=}O \xrightarrow[\text{(2) } H_3O^+]{\text{(1) ether solvent}} \underset{\text{propan-1-ol}}{CH_3CH_2{-}CH_2{-}OH}$$

b. Addition to an aldehyde gives a secondary alcohol:



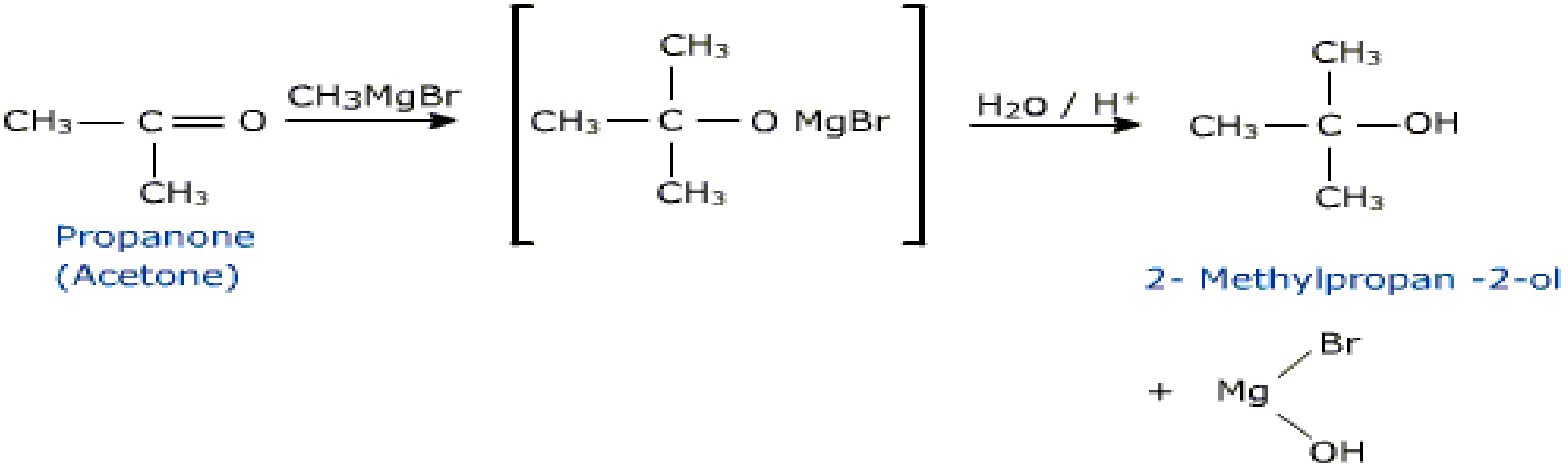
$$CH_3{-}MgBr + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H \xrightarrow[\text{(2) } H_3O^+]{\text{(1) ether solvent}} CH_3{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}OH$$



phenylmagnesium bromide — acetaldehyde — 1-phenylethanol

Preparation of alcohols

c. Addition to a ketone gives a tertiary alcohol:

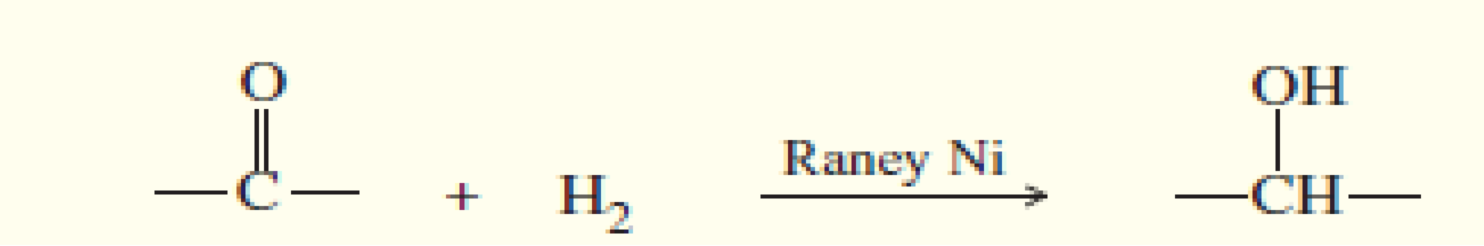


Propanone (Acetone)

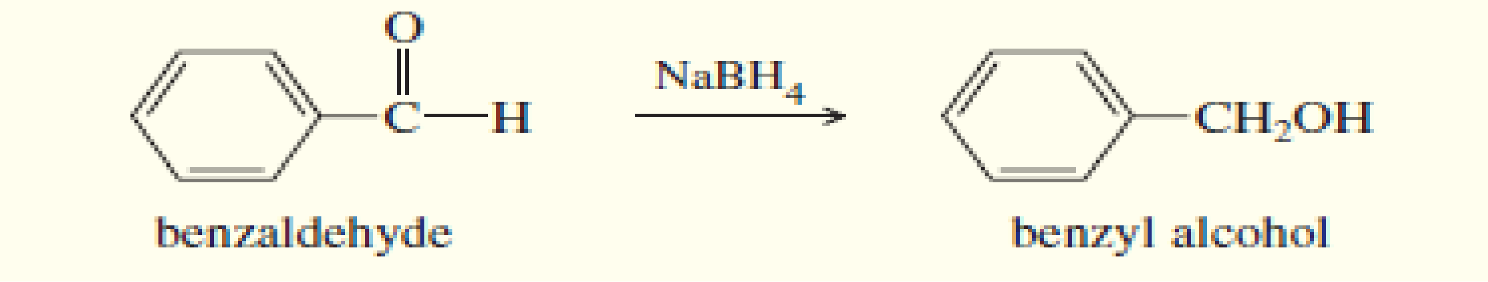
2- Methylpropan -2-ol

Preparation of alcohols

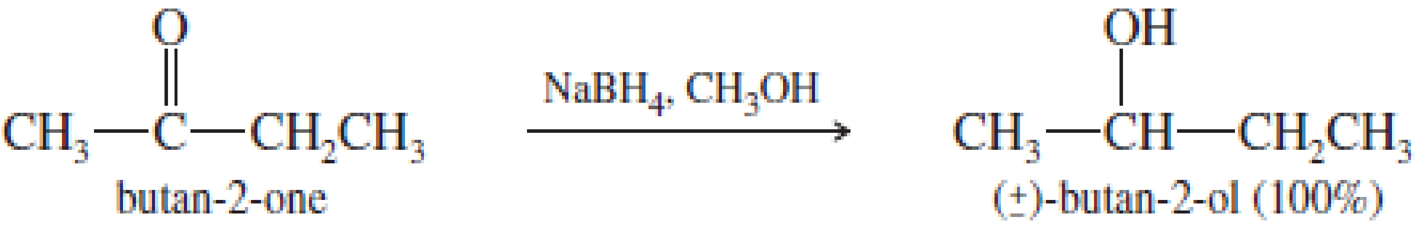
4- Reduction of carbonyl compounds:



a. Reduction of an aldehyde gives a primary alcohol:



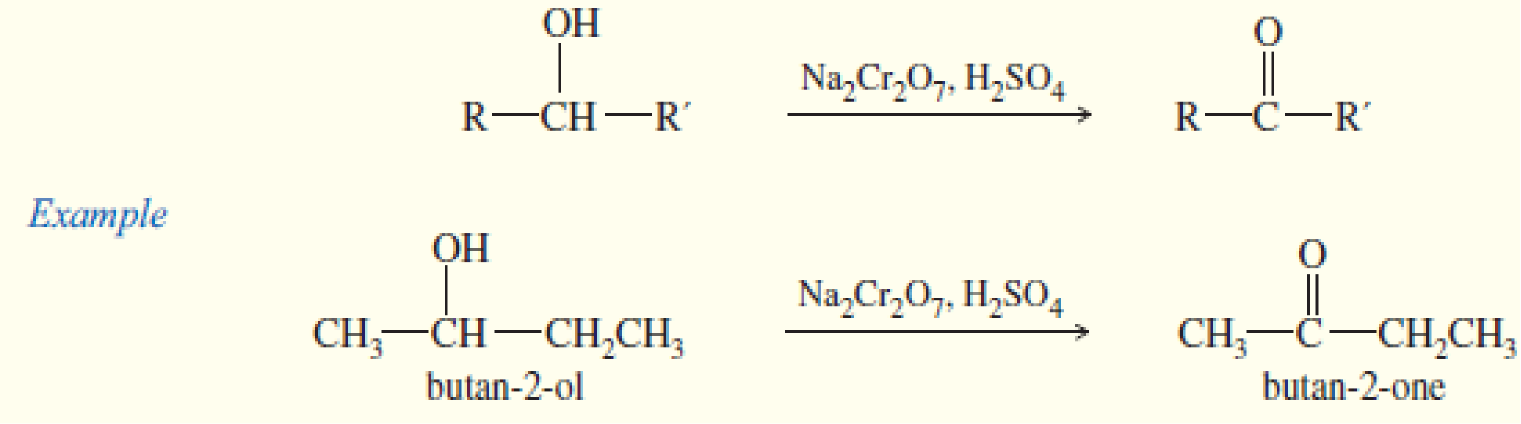
b. Reduction of a ketone gives a secondary alcohol:



Reactions of alcohols

1- Oxidation–reduction reactions:

a. Oxidation of secondary alcohols to ketones:

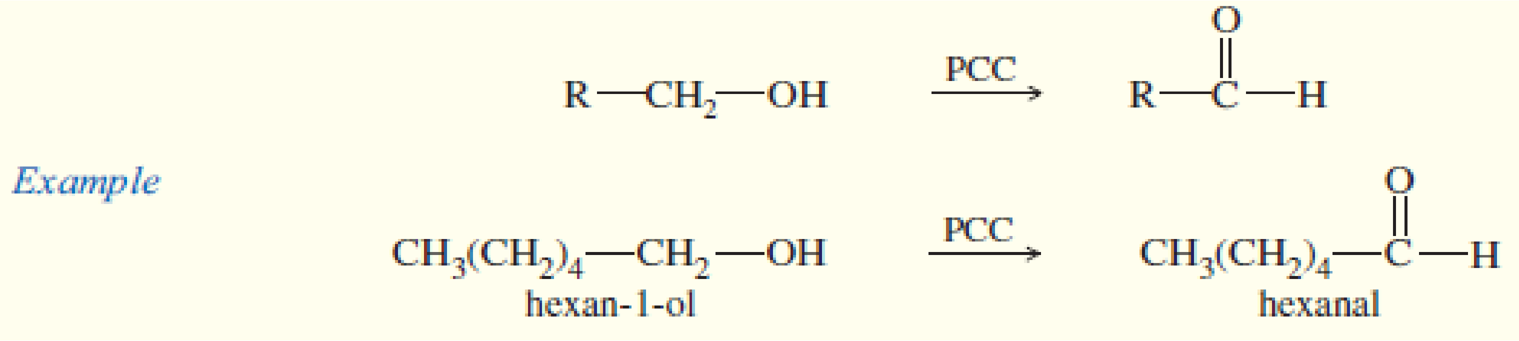


$$R-\overset{\overset{\displaystyle OH}{|}}{C}H-R' \xrightarrow{Na_2Cr_2O_7,\ H_2SO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

Example

$$\underset{\text{butan-2-ol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2CH_3} \xrightarrow{Na_2Cr_2O_7,\ H_2SO_4} \underset{\text{butan-2-one}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3}$$

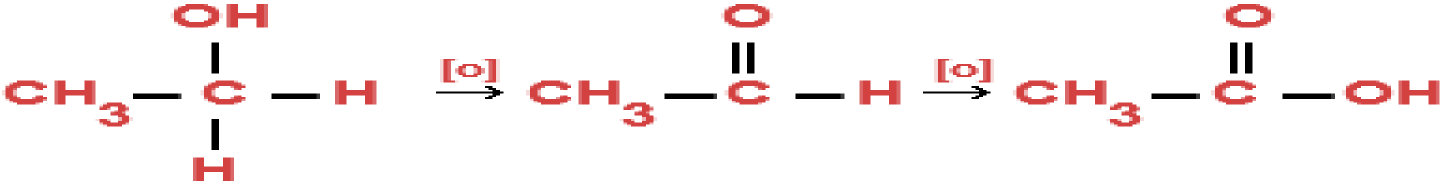
b. Oxidation of primary alcohols to aldehydes:



$$R-CH_2-OH \xrightarrow{PCC} R-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

Example

$$\underset{\text{hexan-1-ol}}{CH_3(CH_2)_4-CH_2-OH} \xrightarrow{PCC} \underset{\text{hexanal}}{CH_3(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \xrightarrow{[o]} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{[o]} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

A Primary Alcohol **An aldehyde** **A carboxylic acid**

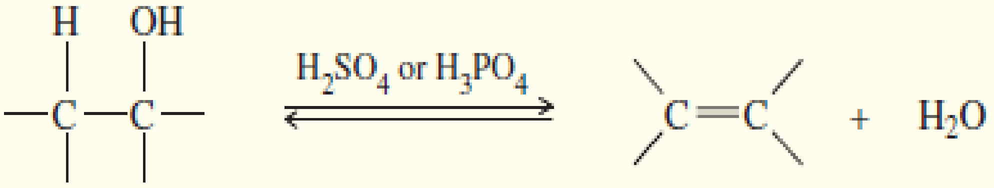
Reactions of alcohols

2- Conversion of alcohols to alkyl halides:

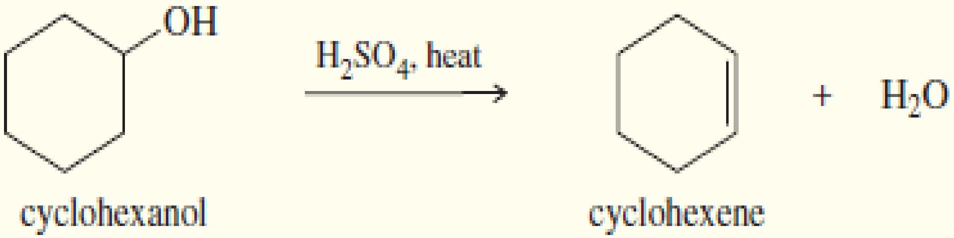
$$R—OH \xrightarrow{HBr \text{ or } PBr_3} R—Br$$

$$\underset{\textit{tert}\text{-butyl alcohol}}{(CH_3)_3CH—OH} \xrightarrow{HCl} \underset{\textit{tert}\text{-butyl chloride}}{(CH_3)_3C—Cl}$$

3- Dehydration of alcohols to form alkenes:

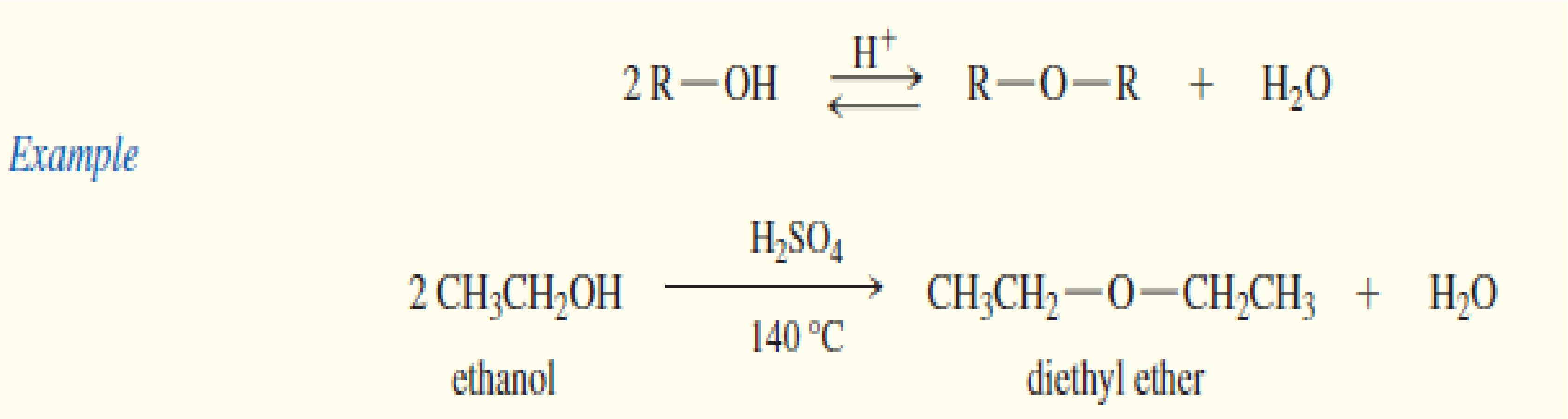


Example



Reactions of alcohols

4- Condensation of alcohols to form ethers (Dehydration of alcohols):

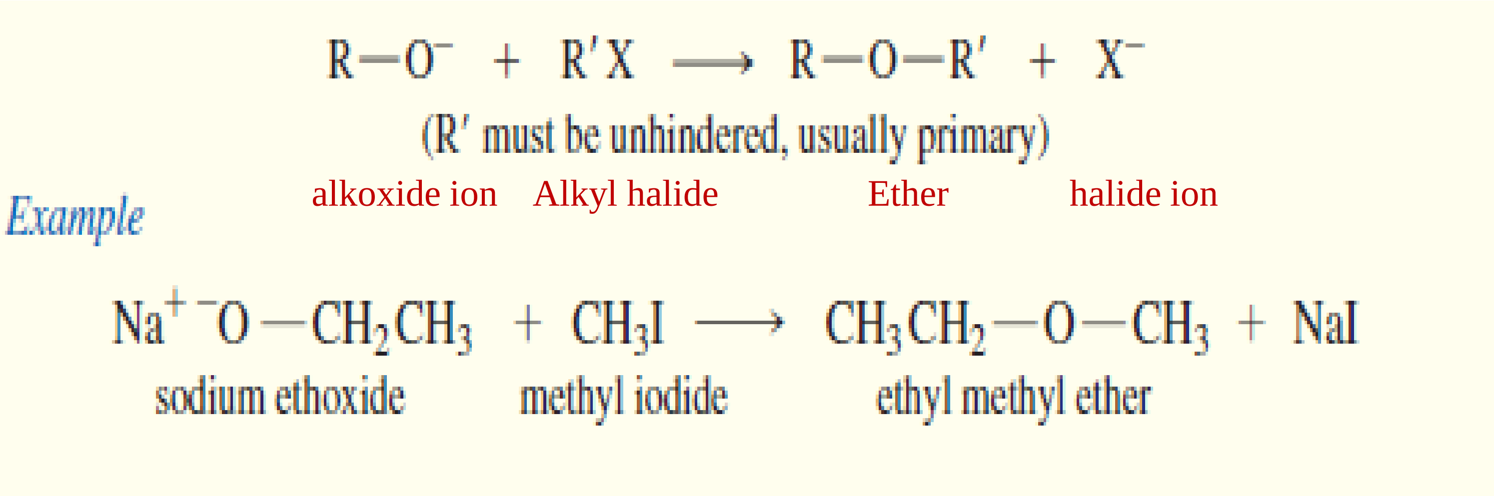


$$2\,R{-}OH \underset{}{\overset{H^+}{\rightleftharpoons}} R{-}O{-}R + H_2O$$

Example

$$\underset{\text{ethanol}}{2\,CH_3CH_2OH} \xrightarrow[140\,^\circ C]{H_2SO_4} \underset{\text{diethyl ether}}{CH_3CH_2{-}O{-}CH_2CH_3} + H_2O$$

5- Williamson ether synthesis:



$$R{-}O^- + R'X \longrightarrow R{-}O{-}R' + X^-$$

(R′ must be unhindered, usually primary)

alkoxide ion Alkyl halide Ether halide ion

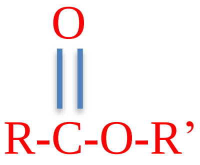
Example

$$\underset{\text{sodium ethoxide}}{Na^{+}\,{}^{-}O{-}CH_2CH_3} + \underset{\text{methyl iodide}}{CH_3I} \longrightarrow \underset{\text{ethyl methyl ether}}{CH_3CH_2{-}O{-}CH_3} + NaI$$

Reaction of alcohols

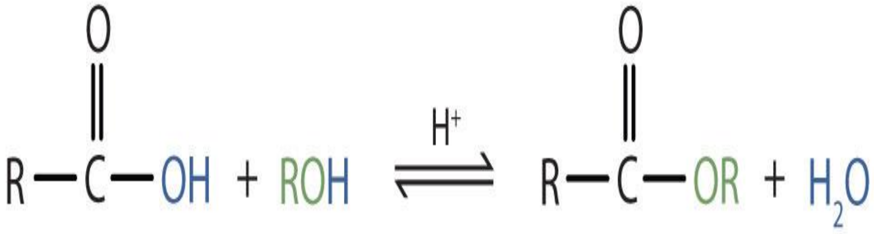
6- Esterification: formation of ester:

Reaction of carboxylic acid with alcohol will form ester.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'$$

Ester



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + ROH \overset{H^+}{\rightleftharpoons} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR + H_2O$$

Carboxylic acid Alcohol Ester

Ethers

Ethers and epoxides

- ## Introduction:

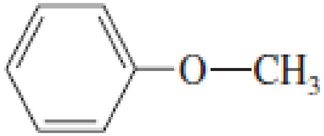
Ethers are molecules in which an oxygen atom is linked by single bonds to two organic groups. where R and R` may be alkyl groups or aryl (benzene ring) groups.

R-O-R’

Examples of ethers

$CH_3CH_2—O—CH_2CH_3$

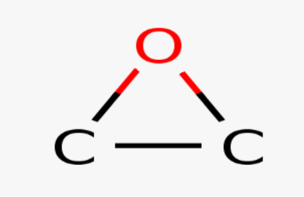
diethyl ether
(a symmetrical ether)

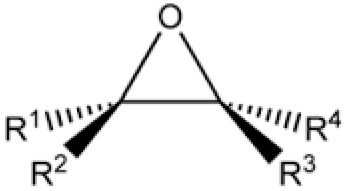


methyl phenyl ether
(an unsymmetrical ether)

tetrahydrofuran
(a symmetrical, cyclic ether)

Epoxides are cyclic ethers in which the ether oxygen is part of a three membered ring.





- ## Applications:

Anesthetic, herbicides, refrigerants, solvents and flavoring agents.

Physical properties of Ethers and epoxides

1- Physical state:

Dimethylether and ethyl methyl ether are gases at ordinary temperature .

The other lower homologes are colourless, pleasant smelling, volatile liquids with typical ether smell.

2- Solubility:

Solubility of ethers containing upto 3 carbon atoms are soluble in water due to their ability to do hydrogen bond with water molecules.

The solubility decreases with increase in the number of carbon atoms. The relative increase in the hydrocarbon portion of the molecule decreases the tendency of H-bond formation .

Solubility in water of ethers are much like alcohols of similar molecular weights, because the oxygen atom in ethers as in alcohols.

Ethers are soluble in organic solvents like alcohol, benzene, acetone etc .

3- Boiling point:

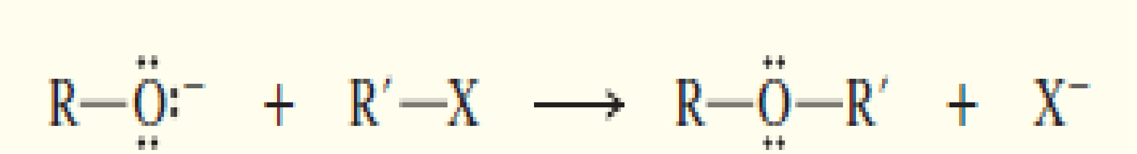
The C-O bonds in ether are polar and thus ethers have a net dipole moment .

Ethers have boiling points same as those of alkanes of comparable molecular weights due to weak polarity of ethers.

Boiling points of ethers are lower than those of alcohols because alcohols molecules are associated by hydrogen bonds while ether molecules are not.

Preparation of ethers

1. The Williamson ether synthesis:



$$R-\ddot{\underset{\cdot\cdot}{O}}:^- + R'-X \longrightarrow R-\ddot{\underset{\cdot\cdot}{O}}-R' + X^-$$

Alkoxide ion Alkyl halide Ether Halide ion

2. Bimolecular condensation of alcohols to form ethers (Dehydration of alcohols): industrial synthesis:

$$2\,R-OH \overset{H^+}{\rightleftharpoons} R-O-R + H_2O$$

R must be primary

Examples

$$\underset{\text{methyl alcohol}}{2\,CH_3OH} \xrightarrow{H_2SO_4,\ 140\,°C} \underset{\substack{\text{dimethyl ether}\\(100\%)}}{CH_3-O-CH_3} + H_2O$$

$$\underset{\text{ethyl alcohol}}{2\ CH_3CH_2OH} \xrightarrow{H_2SO_4,\ 140\,°C} \underset{\substack{\text{diethyl ether}\\(88\%)}}{CH_3CH_2-O-CH_2CH_3} + H_2O$$

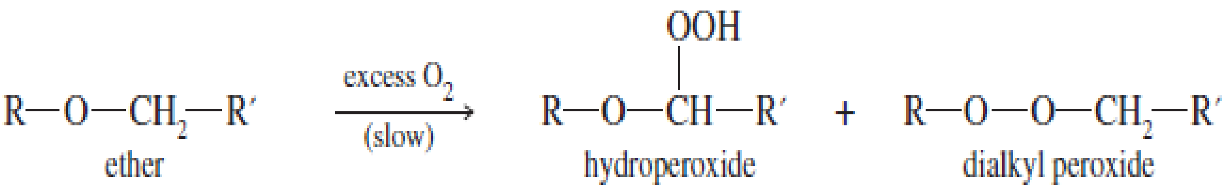
Reaction of ethers

1. Cleavage by HBr and HI:

$$R-O-R' \xrightarrow[(X = Br, I)]{\text{excess HX}} R-X + R'-X$$

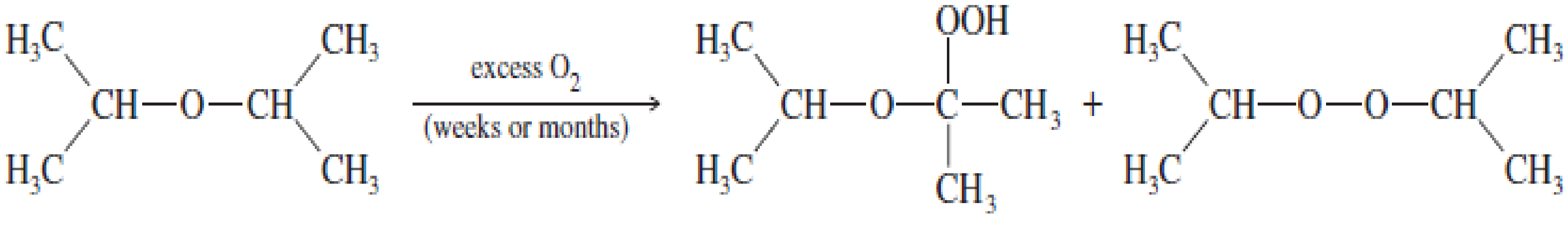
$$\underset{\text{ethyl methyl ether}}{CH_3CH_2-O-CH_3} \xrightarrow{\text{excess HX}} \underset{\text{ethyl iodide}}{CH_3CH_2I} + \underset{\text{methyl iodide}}{CH_3I}$$

2- Autoxidation of ethers:



$$\underset{\text{ether}}{R-O-CH_2-R'} \xrightarrow[\text{(slow)}]{\text{excess } O_2} \underset{\text{hydroperoxide}}{R-O-\overset{\overset{OOH}{|}}{CH}-R'} + \underset{\text{dialkyl peroxide}}{R-O-O-CH_2-R'}$$

Example



diisopropyl ether hydroperoxide diisopropyl peroxide

Thiols

Thiols

Introduction:

- ***Thiol*** is an organosulfur compound that contains a carbon-bonded ***sulfhydryl*** or ***sulphydryl*** (R–SH) group (where R represents an alkyl or other organic substituent).
- Thiols are the sulfur analogue of alcohols (that is, sulfur takes the place of oxygen in the hydroxyl group of an alcohol).
- The –SH functional group itself is referred to as either a ***thiol*** *group* or a ***sulfhydryl group***.

Properties:

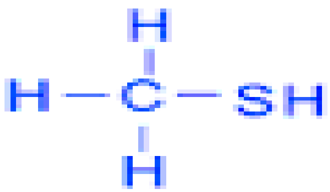
- Many thiols have strong odors resembling that of garlic or rotten eggs.
- Thiols are added to natural gas so leak can be detected.
- Natural gas (which in pure form is odorless), and the "smell of natural gas" is due to the smell of the thiol.

Thiols

Nomenclature of thiols:

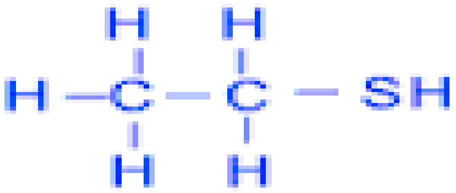
1) Thiol analogous to alcohols, the suffix –*thiol is added* rather than –*ol to the corresponding alkane.*

2) final -*e* of alkane name is remained, not dropped as with alcohols.



Methane Thiol

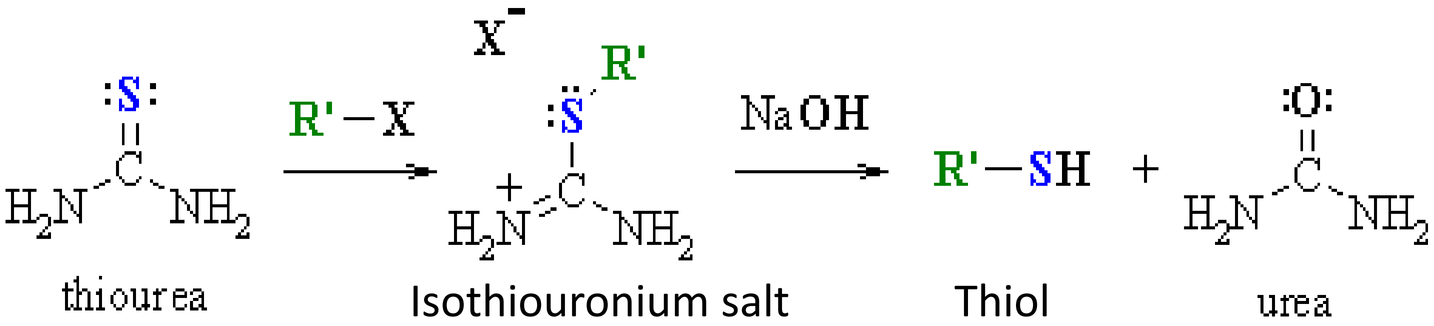
CH_3SH



Ethane Thiol

C_2H_5SH

Preparation of thiols from alkyl halides:



Thioethers

Introduction:

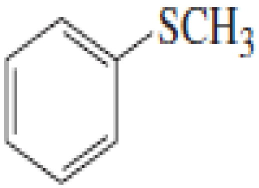
- A **thioether** is a functional group in organosulfur with the connectivity C–S–C. Like many other sulfur-containing compounds, volatile thioethers have rotten odors.
- A thioether is similar to an ether except that it contains a sulfur atom in place of the oxygen.
- The grouping of oxygen and sulfur in the periodic table suggests that the chemical properties of ethers and thioethers are somewhat similar.

Nomenclature of thioether:

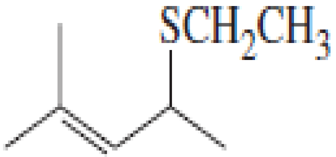
- Thioethers are sometimes called sulfides. The two organic substituents are indicated by the prefixes. $(CH_3)_2S$ is called dimethyl sulfide. Some thioethers are named by modifying the common name for the corresponding ether. For example, $C_6H_5SCH_3$ is methyl phenyl sulfide, but is more commonly called thioanisole, since its structure is related to that for anisole, $C_6H_5OCH_3$.

$CH_3—S—CH_3$

dimethyl sulfide



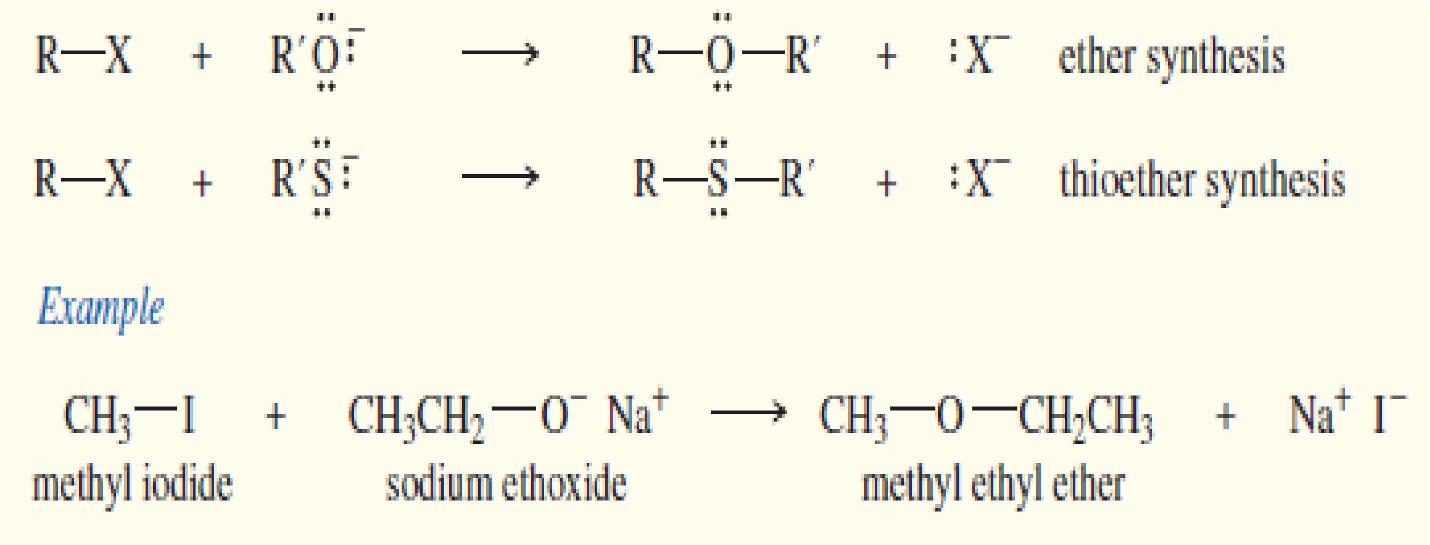
methyl phenyl sulfide



4-ethylthio-2-methylpent-2-ene

Preparation of thioethers

Williamson ether synthesis:

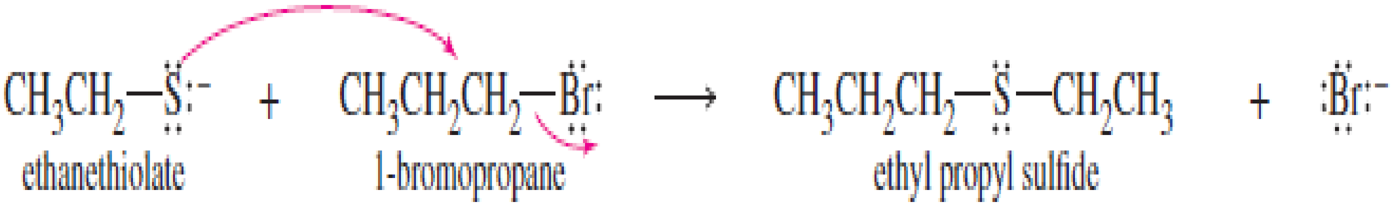


$$R{-}X \quad + \quad R'\underset{..}{\ddot{O}}{:}^- \quad \longrightarrow \quad R{-}\underset{..}{\ddot{O}}{-}R' \quad + \quad {:}X^- \qquad \text{ether synthesis}$$

$$R{-}X \quad + \quad R'\underset{..}{\ddot{S}}{:}^- \quad \longrightarrow \quad R{-}\underset{..}{\ddot{S}}{-}R' \quad + \quad {:}X^- \qquad \text{thioether synthesis}$$

Example

$$\underset{\text{methyl iodide}}{CH_3{-}I} \quad + \quad \underset{\text{sodium ethoxide}}{CH_3CH_2{-}O^-\ Na^+} \quad \longrightarrow \quad \underset{\text{methyl ethyl ether}}{CH_3{-}O{-}CH_2CH_3} \quad + \quad Na^+\ I^-$$



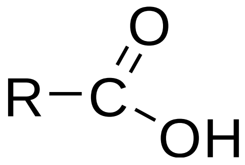
$$\underset{\text{ethanethiolate}}{CH_3CH_2{-}\underset{..}{\ddot{S}}{:}^-} \quad + \quad \underset{\text{1-bromopropane}}{CH_3CH_2CH_2{-}\underset{..}{\ddot{Br}}{:}} \quad \longrightarrow \quad \underset{\text{ethyl propyl sulfide}}{CH_3CH_2CH_2{-}\underset{..}{\ddot{S}}{-}CH_2CH_3} \quad + \quad {:}\underset{..}{\ddot{Br}}{:}^-$$

Carboxylic Acids

Carboxylic Acids

Introduction:

- Carboxylic acids is the most important class of organic acids
- All carboxylic acids contain the carboxyl group. The name is a combination of the two components of the group, -C=O, carbonyl, and –OH, hydroxyl.



$R\text{-}COOH$, $R\text{-}CO_2H$.

- Carboxylic acids are classified as aliphatic or aromatic depending on R group.

R-COOH (R = H or alkyl)

Ar-COOH (Ar = C_6H_5-)

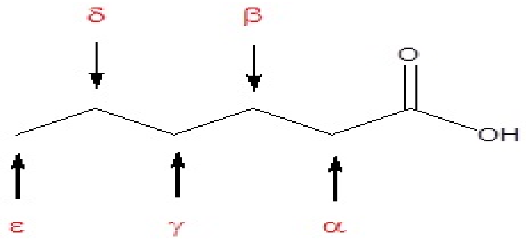
Nomenclature of carboxylic acids:

- The names are derived from Latin or Greek and relate to their natural sources. Formic acid is ant bite; acetic acid is vinegar; and butyric acid is rancid butter.
- Long straight-chain carboxylic acids with even numbers of carbons, which were first isolated from fats and waxes, are called fatty acids.
- In the IUPAC system the ending –e of the corresponding alkane is replaced by –oic acid.

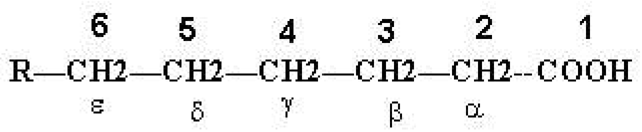
HCOOH	Methanoic acid
CH_3COOH	Ethanoic acid

Nomenclature of carboxylic acids

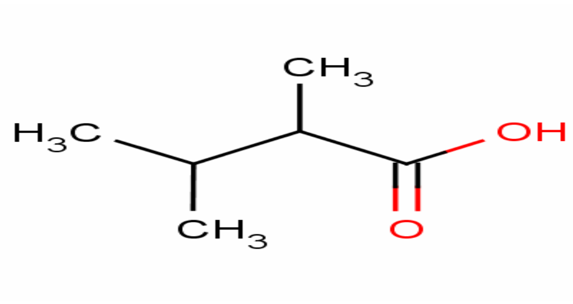
- If substituents are present on the acid chain, their positions are located by Greek letters
- The carbon adjacent to the carboxyl carbon is assigned the letter ∝ (alpha), the next carbon β (beta), and so on.



- In the IUPAC system numbers are used to assign positions. The carboxyl carbon is numbered 1, the next carbon 2, and so on.



$$\mathrm{R}-\underset{\varepsilon}{\overset{6}{\mathrm{CH2}}}-\underset{\delta}{\overset{5}{\mathrm{CH2}}}-\underset{\gamma}{\overset{4}{\mathrm{CH2}}}-\underset{\beta}{\overset{3}{\mathrm{CH2}}}-\underset{\alpha}{\overset{2}{\mathrm{CH2}}}--\overset{1}{\mathrm{COOH}}$$



∝, β−Dimethylbutyric acid
∝, β−Dimethylbutanoic acid

2,3-Dimethylbutyric acid
2,3-Dimethylbutanoic acid

HOOC-COOH
Ethanedioic acid
Oxalic acid

Carboxylic Acids

Formula	Common Name	Source	IUPAC Name	Melting Point	Boiling Point
HCO_2H	formic acid	ants (L. formica)	methanoic acid	8.4 ºC	101 ºC
CH_3CO_2H	acetic acid	vinegar (L. acetum)	ethanoic acid	16.6 ºC	118 ºC
$CH_3CH_2CO_2H$	propionic acid	milk (Gk. protus prion)	propanoic acid	-20.8 ºC	141 ºC
$CH_3(CH_2)_2CO_2H$	butyric acid	butter (L. butyrum)	butanoic acid	-5.5 ºC	164 ºC
$CH_3(CH_2)_3CO_2H$	valeric acid	valerian root	pentanoic acid	-34.5 ºC	186 ºC
$CH_3(CH_2)_4CO_2H$	caproic acid	goats (L. caper)	hexanoic acid	-4.0 ºC	205 ºC
$CH_3(CH_2)_5CO_2H$	enanthic acid	vines (Gk. oenanthe)	heptanoic acid	-7.5 ºC	223 ºC
$CH_3(CH_2)_6CO_2H$	caprylic acid	goats (L. caper)	octanoic acid	16.3 ºC	239 ºC
$CH_3(CH_2)_7CO_2H$	pelargonic acid	pelargonium (an herb)	nonanoic acid	12.0 ºC	253 ºC
$CH_3(CH_2)_8CO_2H$	capric acid	goats (L. caper)	decanoic acid	31.0 ºC	219 ºC

Carboxylic Acids

Common names:

HCO_2H	Formic acid	*L. formica ant*
CH_3CO_2H	Acetic acid	*L. acetum vinegar*
$CH_3CH_2CO_2H$	Propionic acid	*G. “first salt”*
$CH_3CH_2CH_2CO_2H$	Butyric acid	*L. butyrum butter*
$CH_3CH_2CH_2CH_2CO_2H$	Valeric acid	*L. valerans*

Dicarboxylic acids:

HOOC-COOH	Oxalic acid
$HO_2C\text{-}CH_2\text{-}CO_2H$	Malonic acid
$HO_2C\text{-}CH_2CH_2\text{-}CO_2H$	Succinic acid
$HO_2C\text{-}CH_2CH_2CH_2\text{-}CO_2H$	Glutaric acid
$HOOC\text{-}(CH_2)_4\text{-}COOH$	Adipic acid
$HOOC\text{-}(CH_2)_5\text{-}COOH$	Pimelic acid

Physical properties of carboxylic Acids

- Lower acids are colorless liquids and with sharp odors (vinegar, rancid butter or strong cheese, goat-like smell).

- They are soluble in water due to polarity and ability to do hydrogen bond with water molecules.

- Higher acids are wax-like solids and odorless.

- Aromatic acids are insoluble in water and odorless solids.

- High boiling points greater than alcohols due to ability to do hydrogen bond with another carboxylic acid.

Preparation of carboxylic acids

1. Oxidation of 1^o (primary) alcohols:

Oxidizing agents can be hot copper Cu or chromium oxide CrO_3 in pyridine (mild oxidizing agent) or by dichromic acid $H_2Cr_2O_7$ or potassium dichromic acid $K_2Cr_2O_7$.

$$\mathbf{RCH_2OH + K_2Cr_2O_7 \rightarrow RCOOH}$$

Example:

$$CH_3CH_2CH_2CH_2\text{-}OH \quad + \quad CrO_3 \rightarrow CH_3CH_2CH_2CO_2H$$

n-butyl alcohol
1-butanol

butyric acid
butanoic acid

Example:

$$CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2\text{-}OH \quad + \quad KMnO_4 \rightarrow CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCOOH$$

isobutyl alcohol
2-methyl-1-propanol

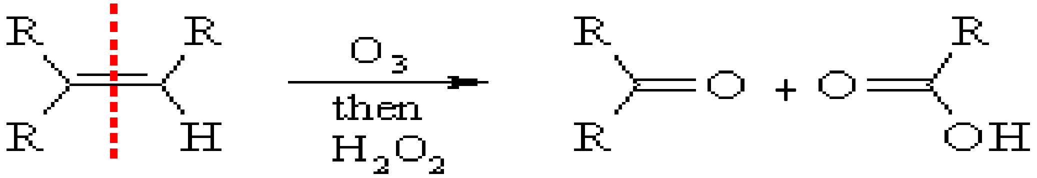
isobutyric acid
2-methylpropanoic acid

Preparation of carboxylic acids

2. **Oxidation of arenes**

ArR + $KMnO_4$, heat → ArCOOH

3. **Ozonolysis of alkenes: oxidiation of alkene with H_2O_2**



Alkene Ketone carboxylic acids

Preparation of carboxylic acids

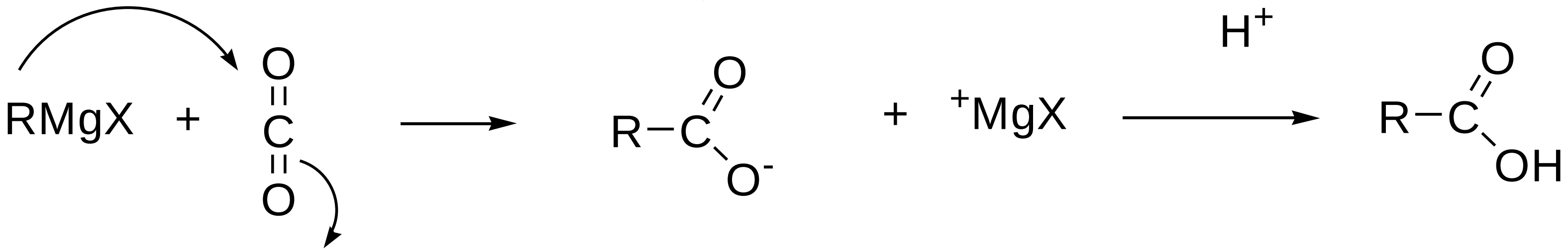
4. Carbonation of Grignard reagent:

Addition of Grignard reagents to carbon dioxide CO_2 to from carboxylic acids.

$$\mathbf{RMgX + CO_2 \rightarrow RCO_2MgX + H^+ \rightarrow RCOOH}$$

$$\text{R-X} \xrightarrow{\text{Mg}} \text{RMgX} \xrightarrow{CO_2} RCO_2MgX \xrightarrow{H^+} RCOOH$$

Increases the carbon chain by one carbon.



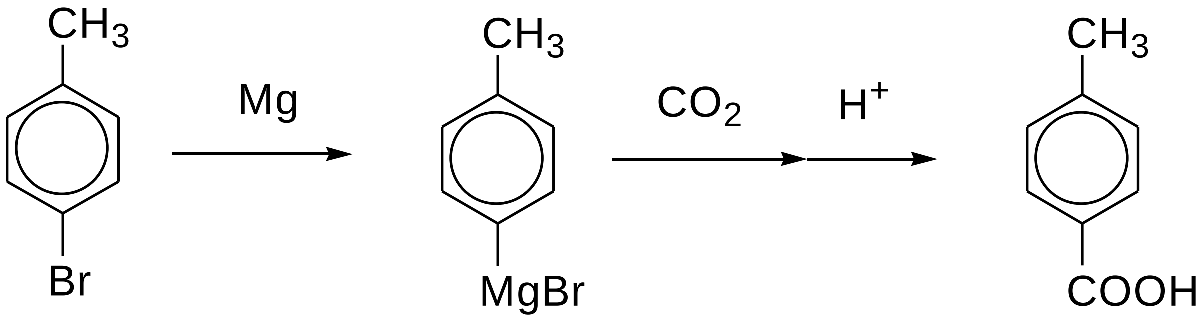
Example:

$$CH_3CH_2CH_2\text{-Br} \xrightarrow{\text{Mg}} CH_3CH_2CH_2MgBr \xrightarrow{CO_2} \xrightarrow{H^+} CH_3CH_2CH_2COOH$$

n-propyl bromide butyric acid

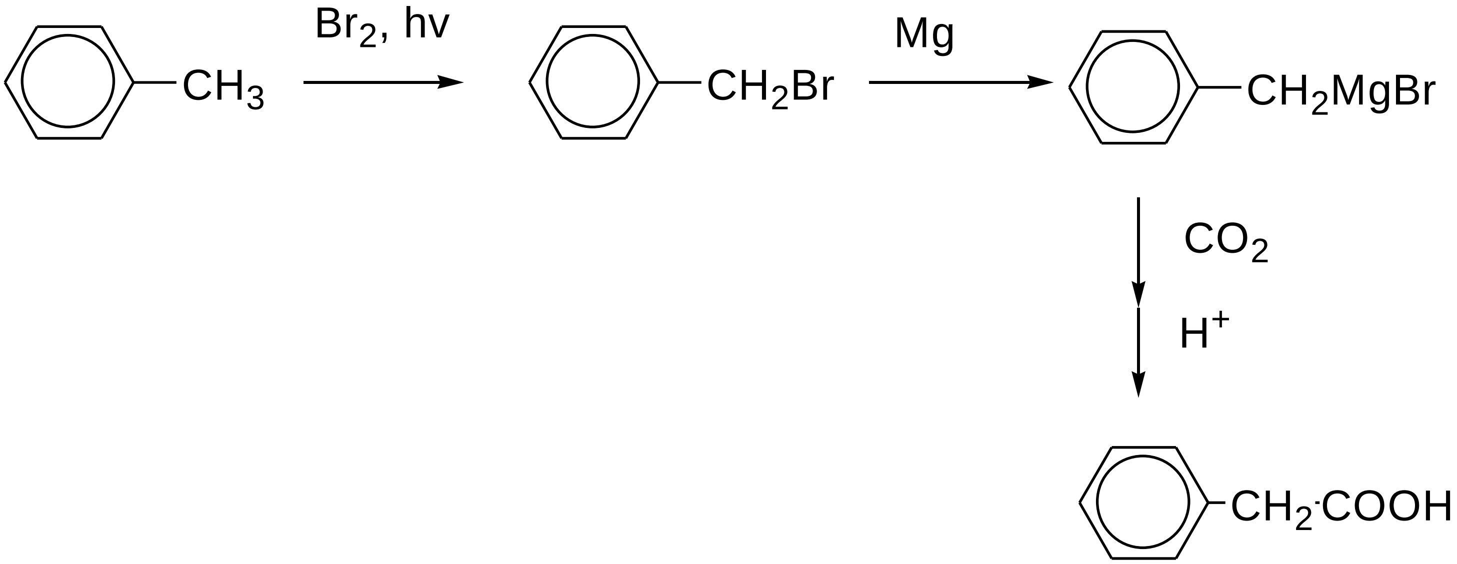
Preparation of carboxylic acids

Example:



p-toluic acid

Example:



phenylacetic acid

Preparation of carboxylic acids

5. Hydrolysis of a nitrile:

RCN + H_2O, H^+, heat → RCOOH

$$\text{R-C}\equiv\text{N} \xrightarrow[\text{heat}]{H_2O,\ H^+} \text{R-CO}_2\text{H}$$

$$\text{R-C}\equiv\text{N} \xrightarrow[\text{heat}]{H_2O,\ OH^-} \text{R-CO}_2^- + H^+ \rightarrow \text{R-CO}_2\text{H}$$

R-X + NaCN → R-CN + H^+, H_2O, heat → RCOOH

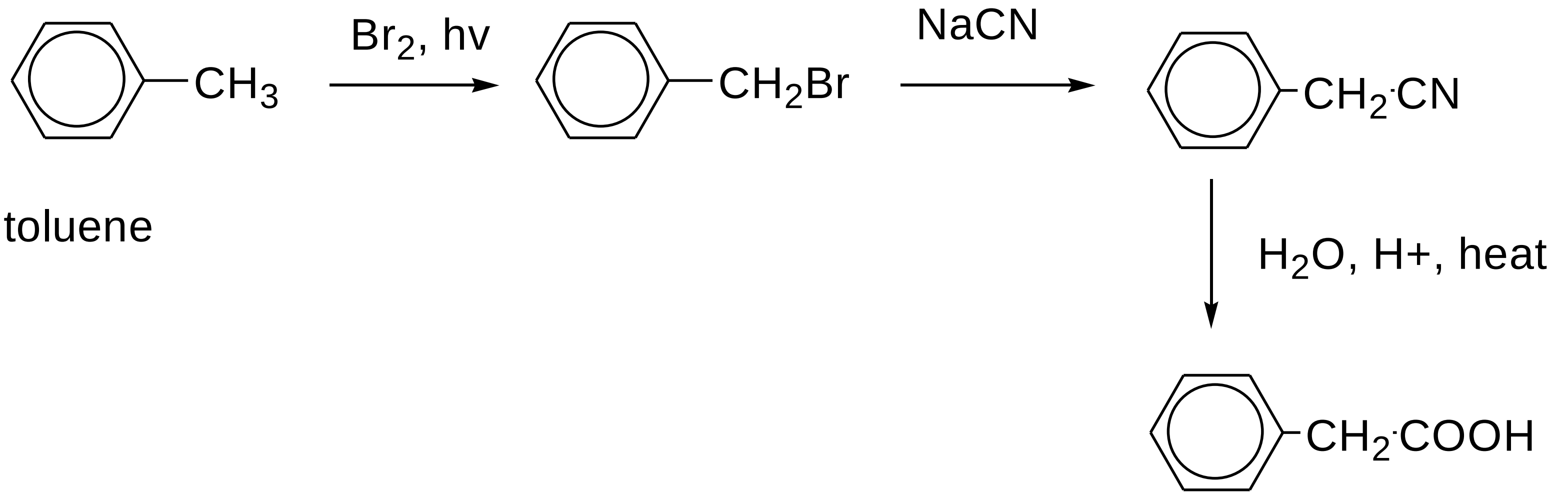
1^o alkyl halide

Adds one more carbon to the chain.

R-X must be 1^o or CH_3

Preparation of carboxylic acids

Example:



toluene

phenylacetic acid

Example:

$$CH_3CH_2CH_2CH_2CH_2CH_2\text{-}Br \xrightarrow{KCN} CH_3CH_2CH_2CH_2CH_2CH_2\text{-}CN$$

1-bromohexane

$$\downarrow H_2O,\ H+,\ heat$$

$$CH_3CH_2CH_2CH_2CH_2CH_2\text{-}COOH$$

heptanoic acid

Reaction of carboxylic acids

1. **As acids**
2. **Conversion into functional derivatives:**
   - **a) → Acid chlorides**
   - **b) → Esters**
   - **c) → Amides**
3. **Reduction**
4. **Alpha-halogenation**

Reaction of carboxylic acids

1. As acids:

Relative acid strength?

$CH_4 < NH_3 < HC \equiv CH < ROH < HOH < H_2CO_3 <$ **RCO_2H** $< HF$

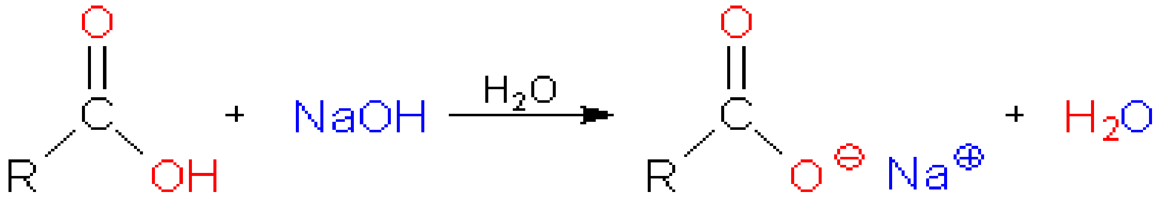
a) Reaction with active metals:

$RCO_2H + Na \rightarrow RCO_2^-Na^+ + H_2(g)$

b) Reaction with bases: salt formation:

Reaction of carboxylic acid (-ic) with sodium hydroxide will form sodium carboxylate (carboxylate salt) (-ate).

$RCO_2H + NaOH \rightarrow RCO_2^-Na^+ + H_2O$



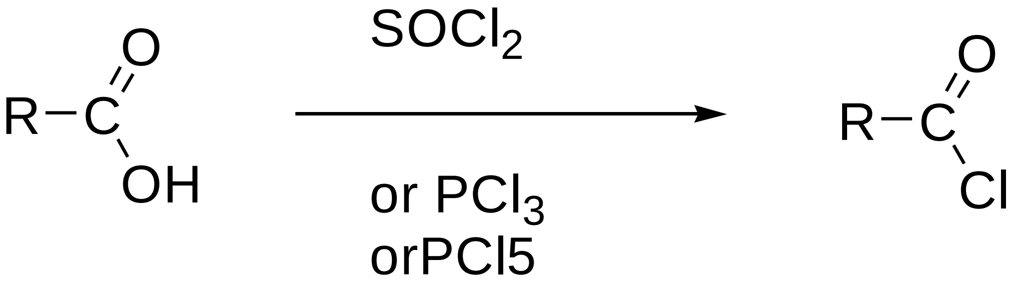
Carboxylic acid Sodium hydroxide Sodium carboxylate

Carboxylate salts are used commercially in a variety of application. Sodium acetate is used in dyeing. Sodium propionate and calcium propionate are used in bread to prevent molding. Sodium benzoate is a food preservative.

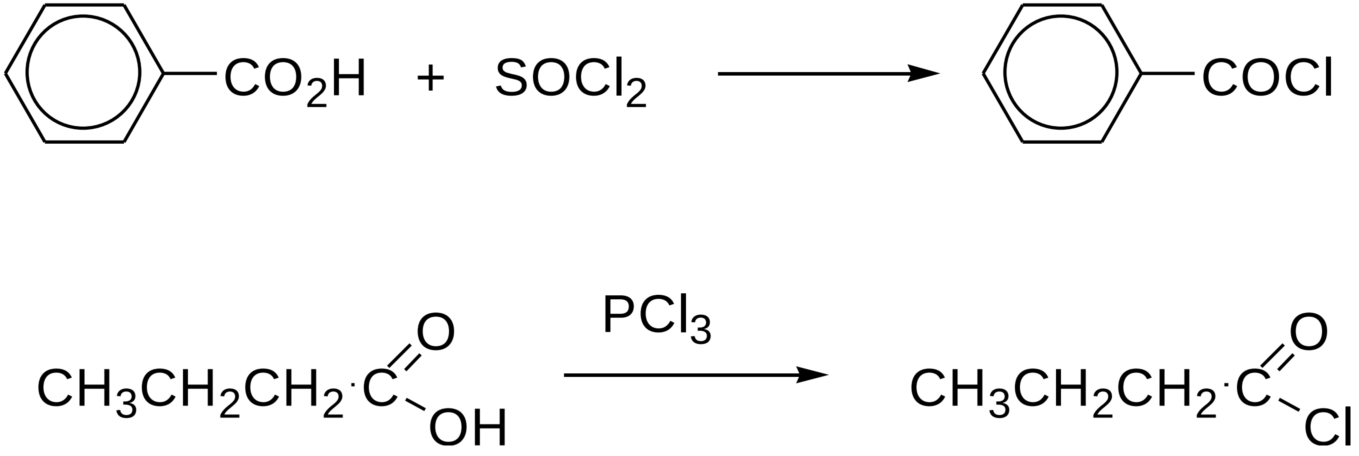
Reaction of carboxylic acids

2. Conversion into functional derivatives:

a) → acid chlorides



Examples:

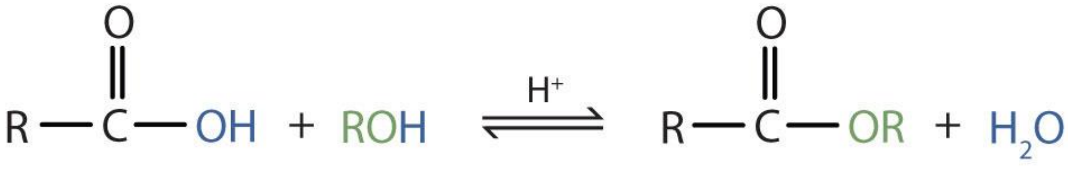


Reaction of carboxylic acids

b) → esters

Esterification: formation of ester:

Reaction of carboxylic acid with alcohol will form ester.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + ROH \xrightleftharpoons{H^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR + H_2O$$

Carboxylic acid Alcohol Ester

“direct” esterification:

$$RCOOH + R'OH \overset{H^+}{\leftrightarrows} RCO_2R' + H_2O$$

-reversible and often does not favor the ester

-use an excess of the alcohol or acid to shift equilibrium

-or remove the products to shift equilibrium to completion

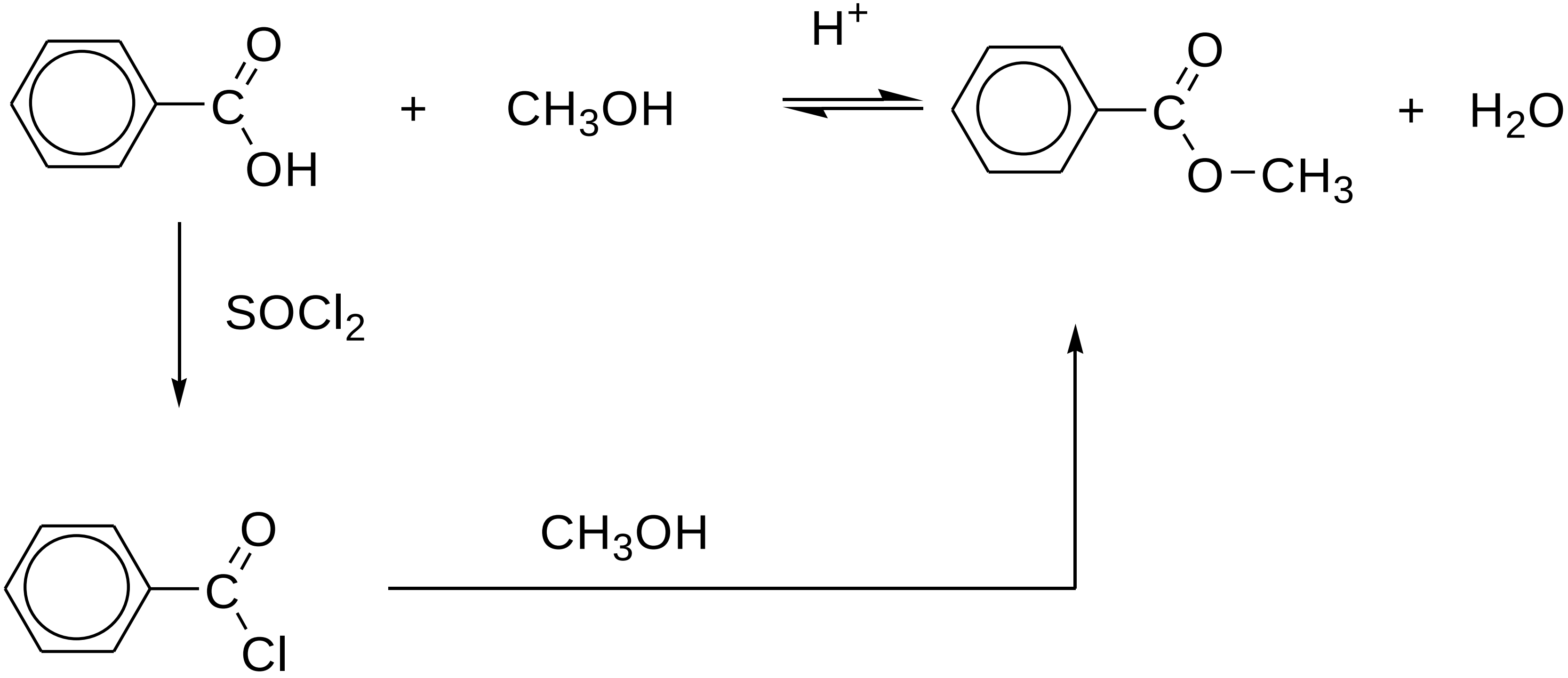
“indirect” esterification:

$$RCOOH + PCl_3 \rightarrow RCOCl + R'OH \rightarrow RCO_2R'$$

-convert the acid into the acid chloride first; not reversible

Reaction of carboxylic acids

Example:



Reaction of carboxylic acids

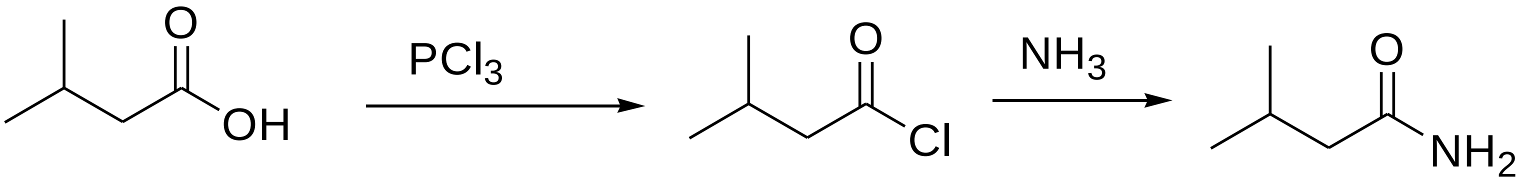
c) → amides

"indirect" only!

$RCOOH + SOCl_2 \rightarrow RCOCl + NH_3 \rightarrow RCONH_2$

amide

Example:



3-Methylbutanoic acid

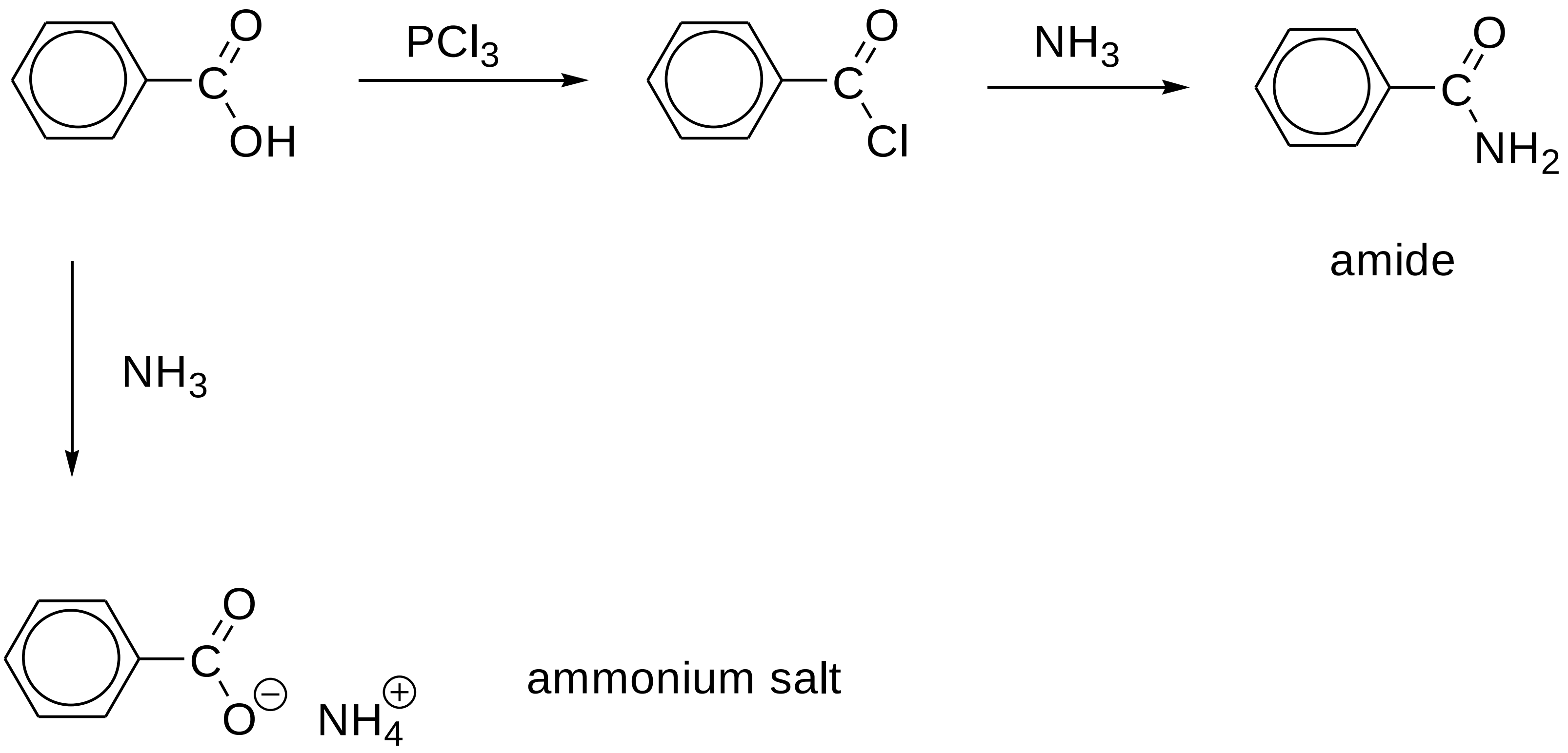
Directly reacting ammonia with a carboxylic acid results in an ammonium salt:

$RCOOH + NH_3 \rightarrow RCOO^{-}NH_4^{+}$

acid base

Reaction of carboxylic acids

Example:



amide

ammonium salt

Reaction of carboxylic acids

3. Reduction:

$$RCO_2H \quad + \quad LiAlH_4\text{; then } H^+ \quad \rightarrow \quad RCH_2OH$$

1° alcohol

Example:

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH \xrightarrow{LiAlH_4} \xrightarrow{H^+} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$$

Octanoic acid
(Caprylic acid)

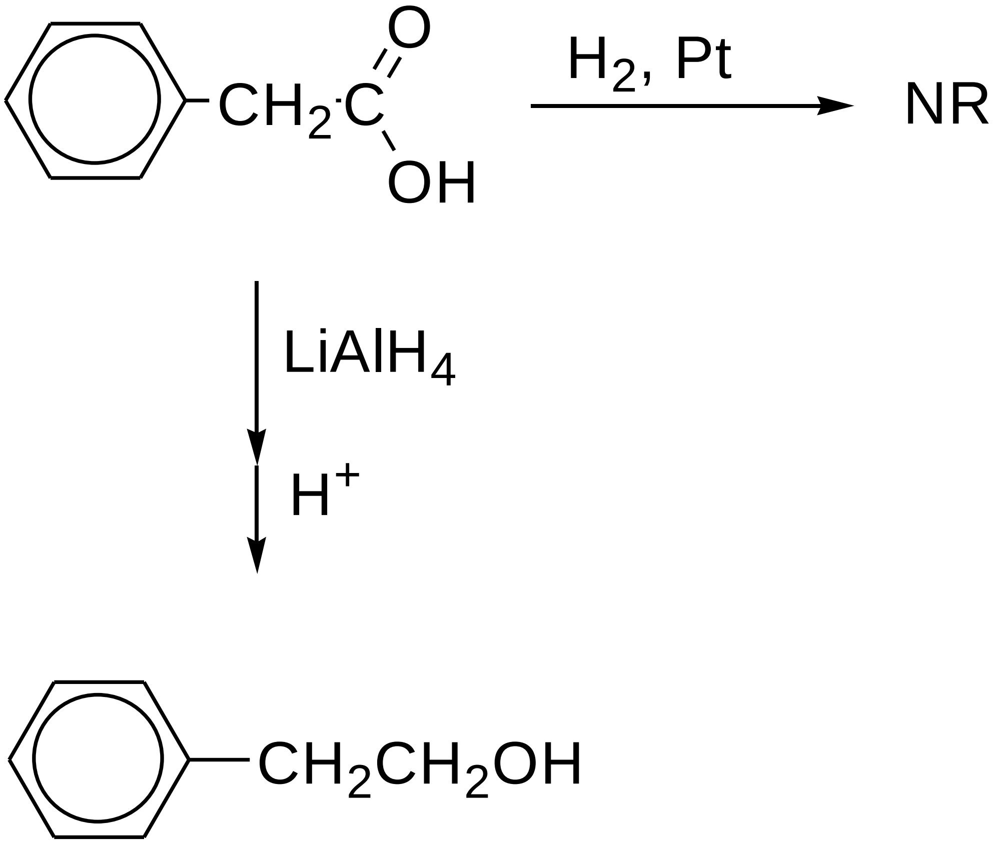
1-Octanol

Carboxylic acids resist catalytic reduction under normal conditions.

$$RCOOH \quad + \quad H_2\text{, Ni} \quad \rightarrow \quad NR$$

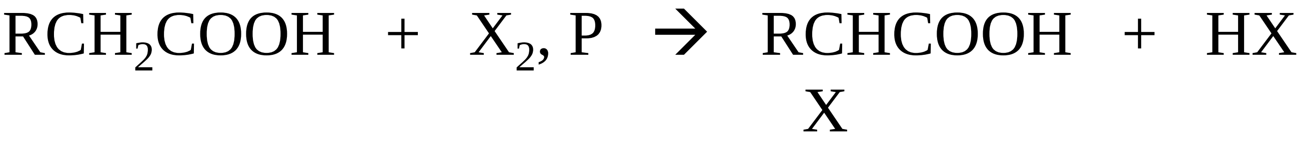
Reaction of carboxylic acids

Example:



Reaction of carboxylic acids

4. **Alpha-halogenation**: (Hell-Volhard-Zelinsky reaction)

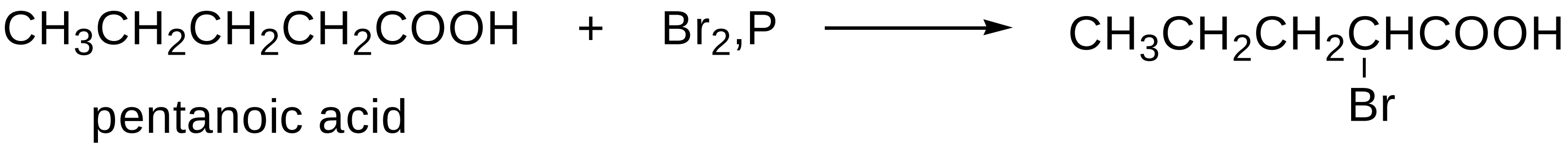


$$RCH_2COOH + X_2, P \rightarrow \underset{X}{RCHCOOH} + HX$$

α-haloacid

$X_2 = Cl_2, Br_2$

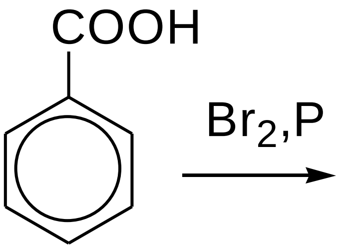
Example:



$$CH_3CH_2CH_2CH_2COOH + Br_2,P \longrightarrow CH_3CH_2CH_2\underset{Br}{C}HCOOH$$

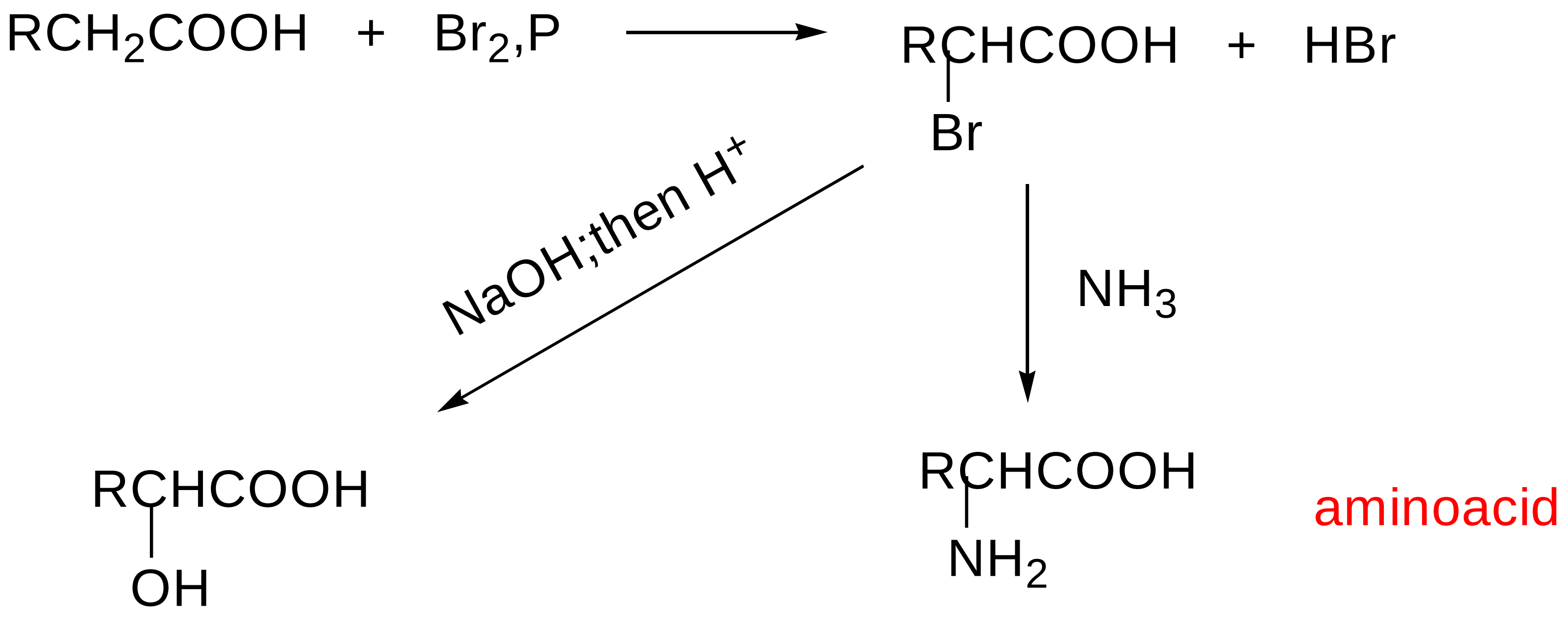
pentanoic acid

2-bromopentanoic acid



NR (no alpha H)

Reaction of carboxylic acids

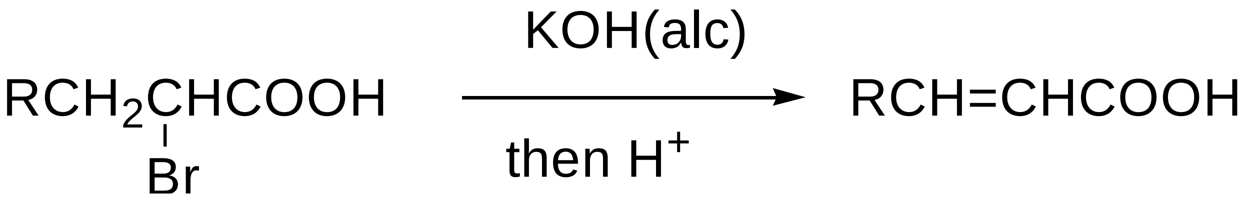


$$RCH_2COOH + Br_2,P \longrightarrow \underset{\displaystyle Br}{RCHCOOH} + HBr$$

$$\underset{\displaystyle Br}{RCHCOOH} \xrightarrow{NaOH;\text{then } H^+} \underset{\displaystyle OH}{RCHCOOH}$$

$$\underset{\displaystyle Br}{RCHCOOH} \xrightarrow{NH_3} \underset{\displaystyle NH_2}{RCHCOOH}$$

aminoacid



$$RCH_2\underset{\displaystyle Br}{C}HCOOH \xrightarrow[\text{then } H^+]{KOH(alc)} RCH{=}CHCOOH$$

Amines

Amines

Structure and Classification:

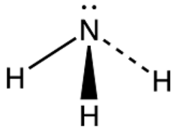
- Amines are compounds that derived from ammonia by replacement of one , two or three hydrogens by alkyl or aryl groups.

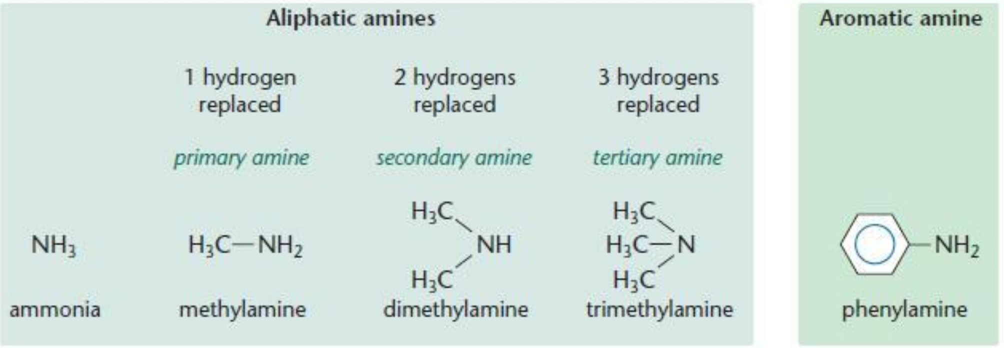
- Aliphatic amines contain only alkyl groups bonded directly to the nitrogen atom.

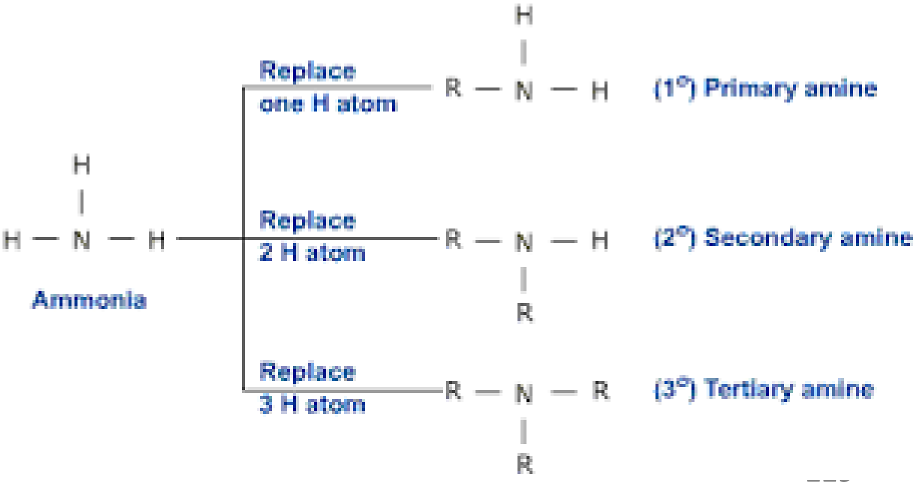
- Aromatic amines contain one or more aryl groups are bonded directly to the nitrogen atom.

- Amines are classified as 1 °, 2° *or* 3° depending to the number of R or Ar groups attached to the nitrogen atom.

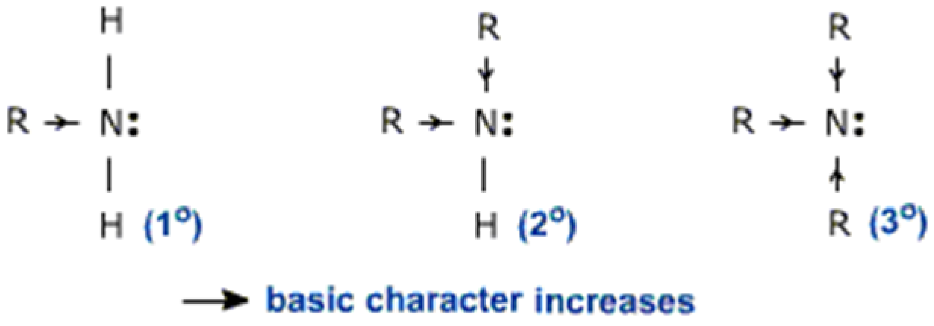
Ammonia NH_3

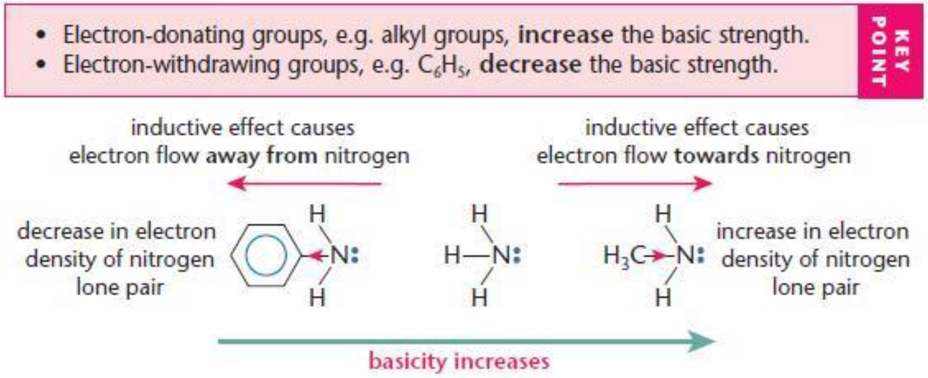






Amines




- Electron-donating groups, e.g. alkyl groups, **increase** the basic strength.
- Electron-withdrawing groups, e.g. C_6H_5, **decrease** the basic strength.

Importance:

- Amiens and their derivatives are important nitrogen compounds.
- They are used as intermediates in organic reactions and they are found in many biological systems.
- The amino acids that make up the proteins.
- The purine and pyrimidine bases that make up DNA and RNA the molecules of the genetic code.
- Amiens and their derivatives are used in drugs for treatment mental illness, chemotherapy an psychopharmacology.

Nomenclature of Amines

- Simple aliphatic amines are named by listing in alphabetical order the alkyl groups attached to the nitrogen atom and adding the suffix –amine all as one word.

CH_3NH_2	Methylamine
$CH_3\,CH_2NHCH_3$	Ethylmethylamine

- If two or three identical alkyl groups are attached to the nitrogen the prefix di- or tri- is added to the name of the amine.

$CH_3NH\,CH_3$	Dimethylamine
$CH_3\,CH_2NHCH_2CH_3$	Diethylamine

- If the amine is complicated the IUPAC system is used.
- The amino group (-NH2) is considered the substituent and its position on the chain is indicated by the lowest possible number.

$CH_3\,CH_2\overset{\overset{NH_2}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

3-Amino-5-methylhexane

$NH_2CH_2CH_2CH_2CH_2CH_2CH_2NH_2$

1,6-Diaminohexane

- The amino group is also considered a substituent if it is part of a molecule that contains another functional group.

$NH_2CH_2CH_2OH$

2-Aminoethanol

$CH_3\,\overset{\overset{NH_2}{|}}{C}HCOOH$

2-Aminopropanoic acid

Alanine

$NH_2CH_2CH_2CH_2OH$

3-Amino-1-propanol

Physical properties of Amines

- Low-molecular-weight aliphatic amines 1C to 3C are colorless gases that are soluble in water.
- They are like ammonia, they form basic solutions.
- They have unpleasant odors that resemble the odor of ammonia and dead fish.
- Amines containing 4C to 11C are liquids with unpleasant odor.
- Higher-molecular-weight amines are solids.
- All amines are capable of forming hydrogen bonds with water. Thus they are soluble in water. But amines with high molecular weights are insoluble in water and soluble in organic solvents.
- $1^\circ, and\ 2^\circ$ Amines possess a polarity (N-H) and capable to do hydrogen bonding with another molecules, thus their boiling points are higher than alkanes and lower than alcohols and carboxylic acids of similar molecular weight.
- 3° Amines are also polar compounds, but they are unable to do hydrogen bonding with another molecules. Thus they have lower boiling points than $1\ ^\circ, and\ 2^\circ$ of identical molecular weights.

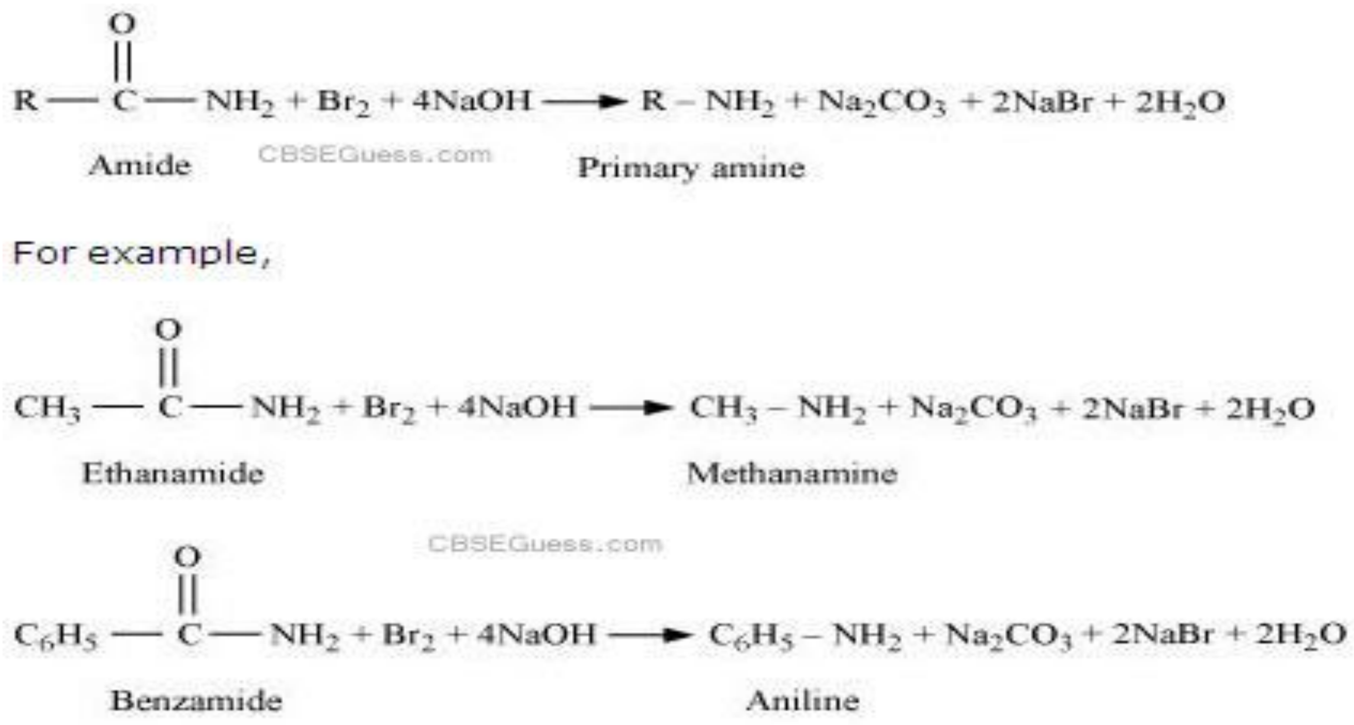
Preparation of Amines

1- Hoffmann bromamide reaction:

When an amide is treated with bromine in an aqueous solution of sodium hydroxide, a primary amine with one carbon atom less than the original amide is produced.

This degradation reaction is known as Hoffmann bromamide reaction.

This reaction involves the migration of an alkyl or aryl group from the carbonyl carbon atom of the amide to the nitrogen atom.



$$\underset{\text{Amide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Primary amine}}{R-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

For example,

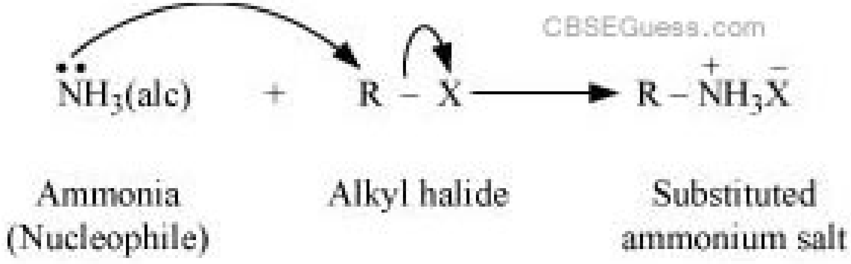
$$\underset{\text{Ethanamide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Methanamine}}{CH_3-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

$$\underset{\text{Benzamide}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Aniline}}{C_6H_5-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Preparation of Amines

~~2-~~Alkylation of Ammonia:

- When an alkyl halide is react with solution of ammonia, the halogen atom is replaced by an amino (−NH2) group.



$$\ddot{N}H_3(alc) + R-X \longrightarrow R-\overset{+}{N}H_3\overset{-}{X}$$

- When this substituted ammonium salt is treated with a strong base such as sodium hydroxide, amine is obtained.

$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow R-NH_2 + H_2O + NaX$$

Amine

- Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt as shown.

$$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4\overset{+}{N}\overset{-}{X}$$

(1°) (2°) (3°) Quaternary ammonium salt

Preparation of Amines

Reduction of Nitro compounds, Nitriles and Amides

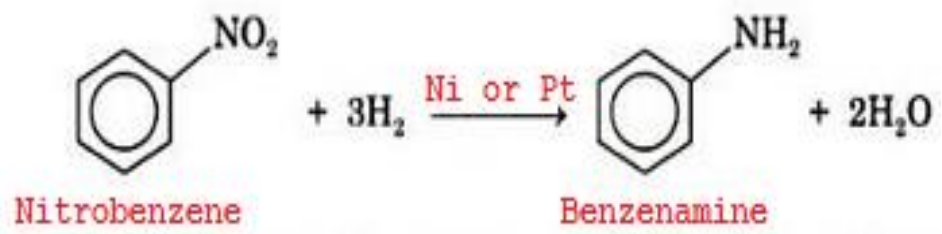
- Several classes of organic compounds that already contain nitrogen may be reduced to amines.
- Most commonly are nitro compounds, nitriles and amides.

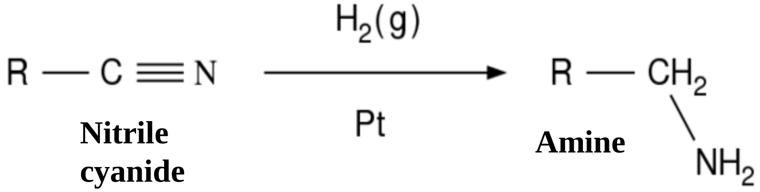
$$R{-}NO_2 + 3H_2 \xrightarrow{\text{Ni or Pt}} RNH_2 + 2H_2O$$

Nitro compound **Amine**

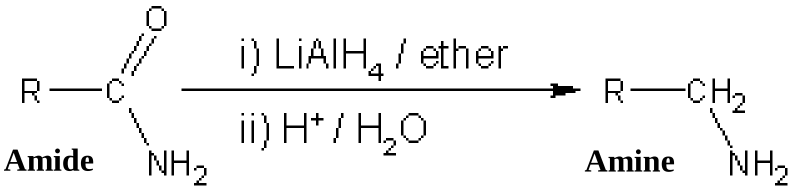
$$CH_3CH_2NO_2 + 3H_2 \xrightarrow{\text{Ni or Pt}} CH_3CH_2NH_2 + 2H_2O$$

Nitroethane Ethanamine





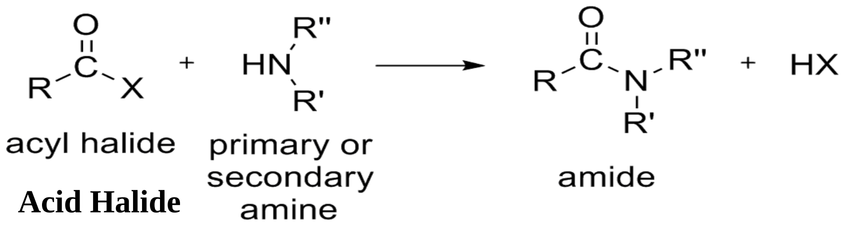
Nitrile cyanide **Amine**

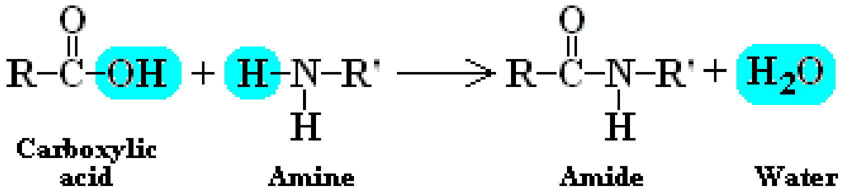


Amide **Amine**

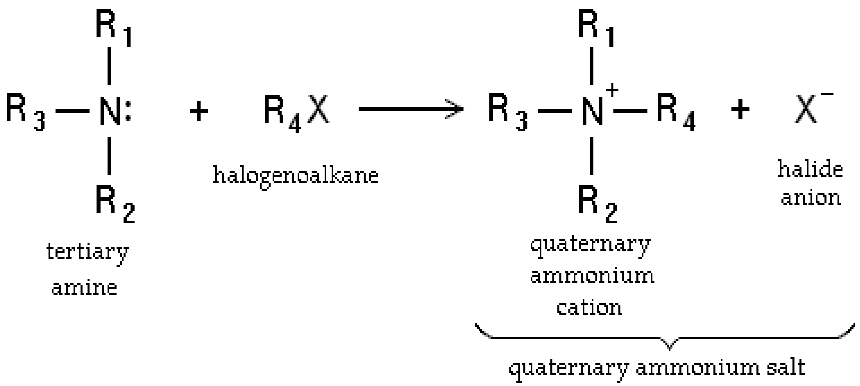
Reaction of Amines

1- Amide formation:





2- Alkylation:



Two quaternary ammonium salts of biological significance are choline and acetylcholine.

Choline found in egg yolk, meat and fish is essential to growth. It is also involved in carbohydrate and protein metabolism as will as in fat transport. It is also precursor of acetylcholine, a substance in the brain that transmits nerve impulses.

Thus, adding choline to the diet may help the elderly in the problem of memory loss.