Lecture One

Organic chemistry

Hydrocarbons

اعداد

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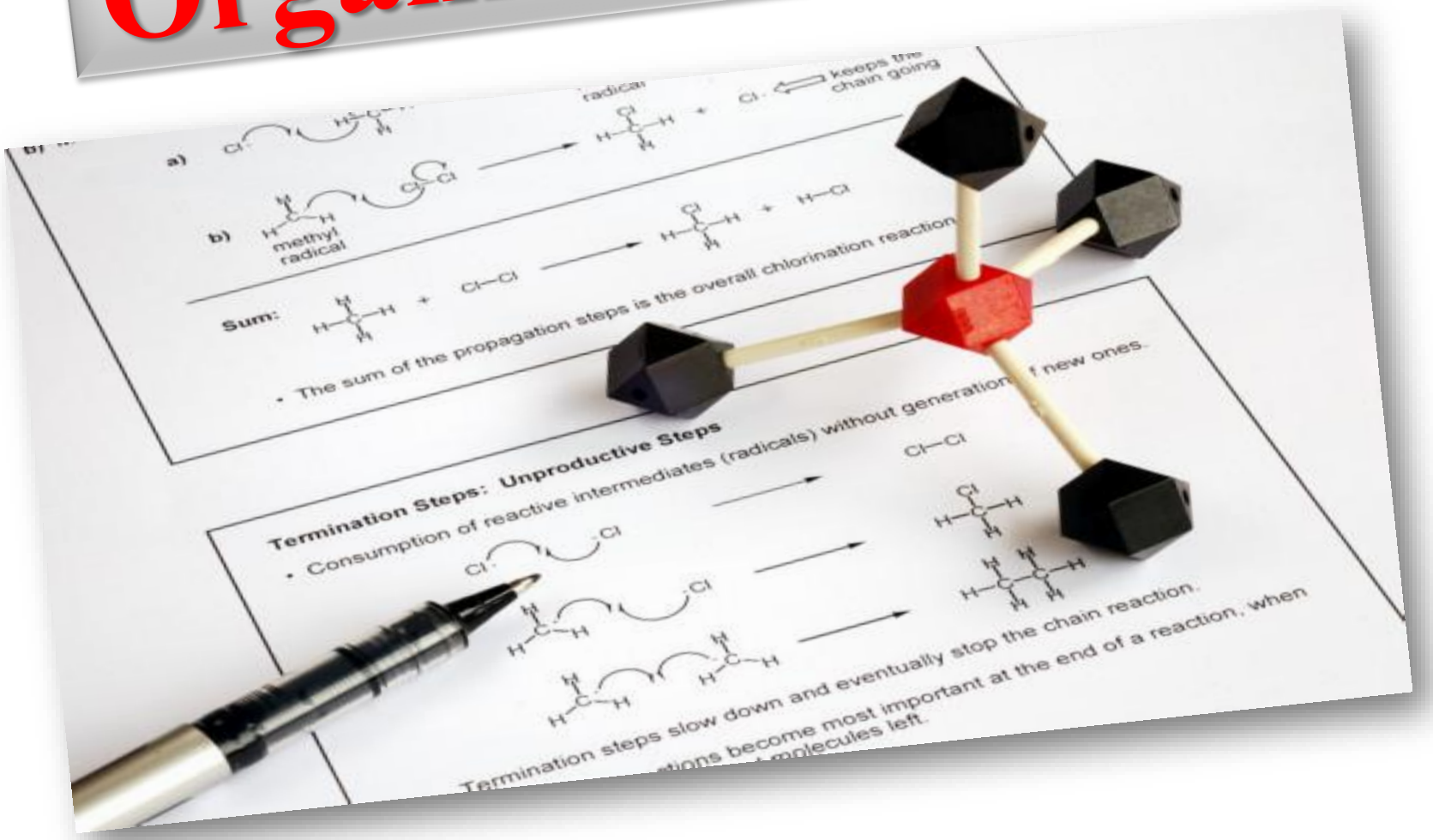
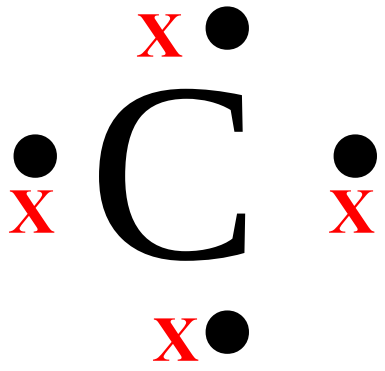
Organic Chemistry



Organic Chemistry- The study of carbon & carbon compounds

Draw an electron dot diagram of carbon.



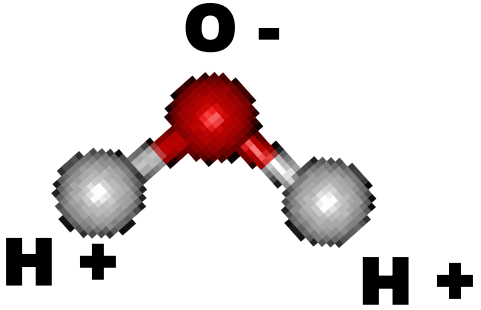
Carbon is able to form 4 covalent bonds (4 valence electrons) with other carbon or other elements.

Characteristics of Organic Compounds

- 1)They are nonpolar compounds – they do not dissolve in polar solvents like Water.

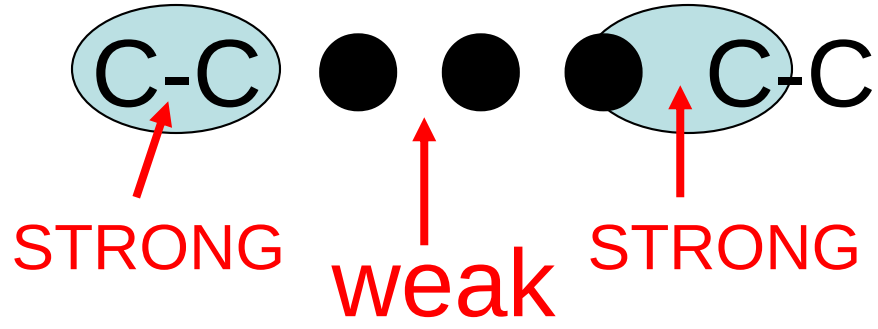
But dissolve in nonpolar solvents like benzene , ether & chloroform ,

2) The density for alkane is less than the density of water .



*remember the rule –
"likes dissolve likes"

3) They have low melting points – due to the weak intermolecular forces.

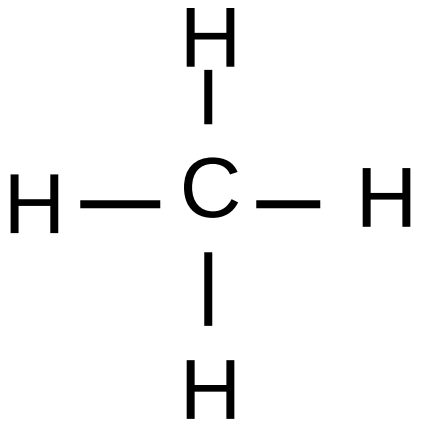


4) They react slower than ionic compounds – due to strong covalent bonds between atoms.

Structural Formulas –

A 2D model shows bonding patterns and shapes of molecules

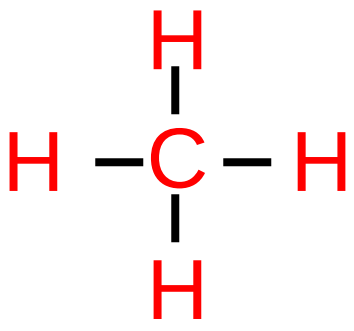
⇨ Carbon is found in the center



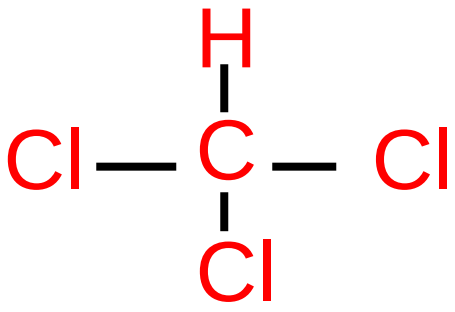
⇨ The short line – represents a pair of electrons.

Draw the structures for each organic compound

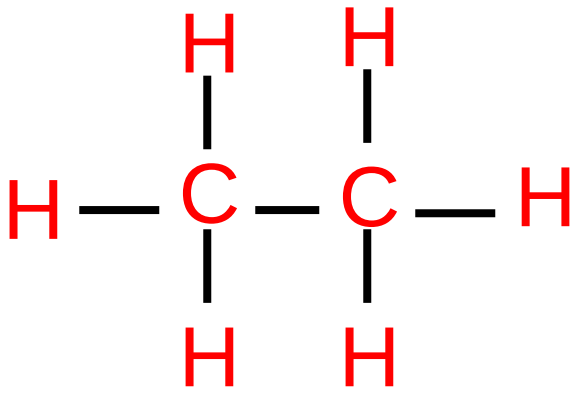
1. Methane: CH_4



2. Chloroform: $CHCl_3$



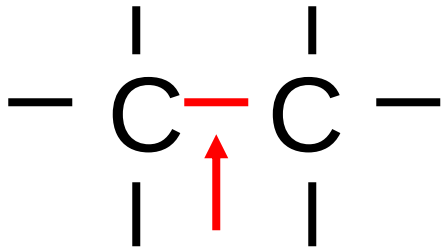
3. Ethane: C_2H_6

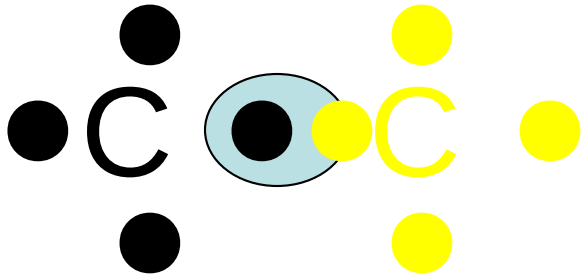


Remember : Carbon has **4** bonding sites.

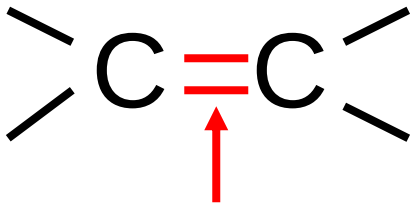
Types Of Bonds

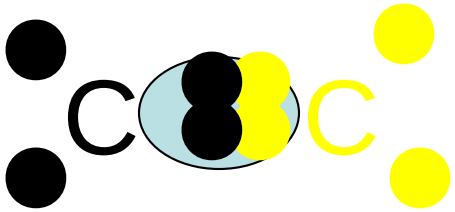
<u>Single Bond</u> – single covalent bond in which they share **1** pair of electrons. (2 e-)



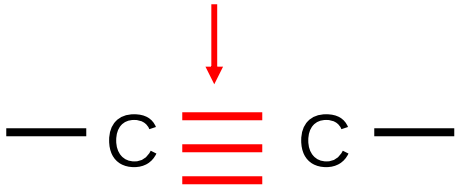


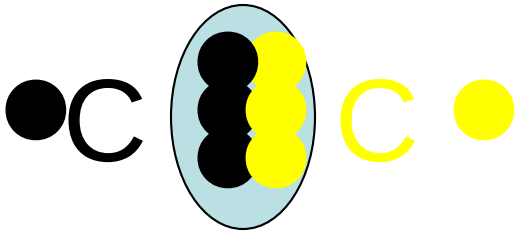
<u>Double Bond</u> – carbon atoms may share **2** pairs of electrons to form a double bond.





<u>Triple Bond</u> – carbon atoms may share **3** pairs of electrons to form a triple bond.

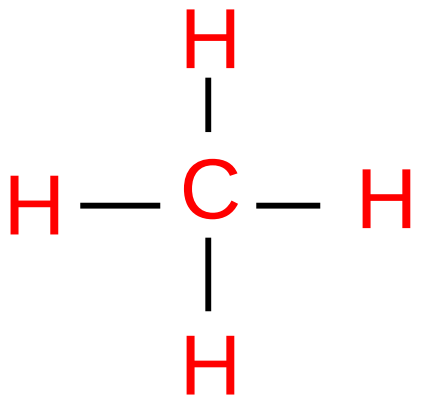




Types Of Compounds

Saturated Compound – organic compounds in which carbon atoms are bonded by SINGLE bonds.

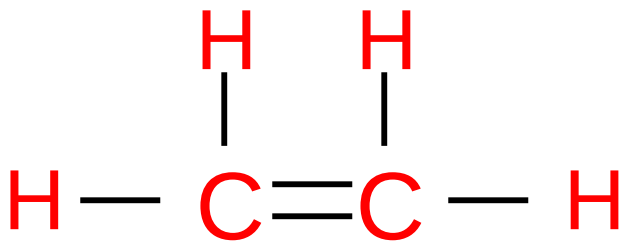
ex. Methane: CH_4



Types Of Compounds

Unsaturated Compound – compounds where carbon atoms have double or triple bonds.

ex. ethene: C_2H_4

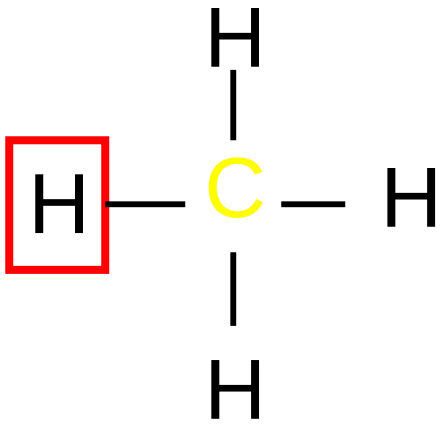


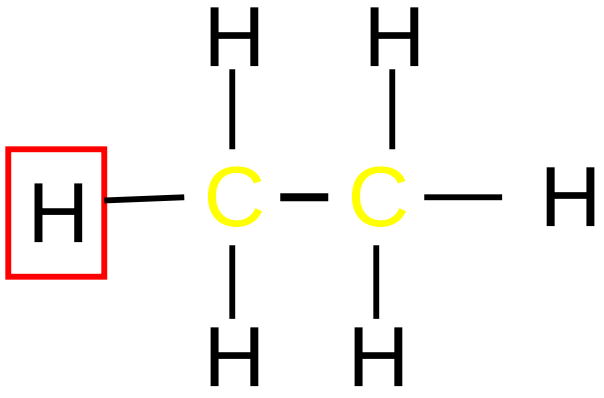
Homologous Series of Hydrocarbons

- Organic compounds can be classified into groups with related structures and properties.

***As size of molecule increases the boiling and freezing points increase.

Hydrocarbons are organic compounds that consist of only Carbon and Hydrogen atoms.





Organic Chemistry

It is the chemistry of the carbon compounds.

Hydro carbons

Are the compounds containing only two element hydrogen and Carbon?

One the basis of structure, hydrocarbons is divided into two main classes.

Hydrocarbon

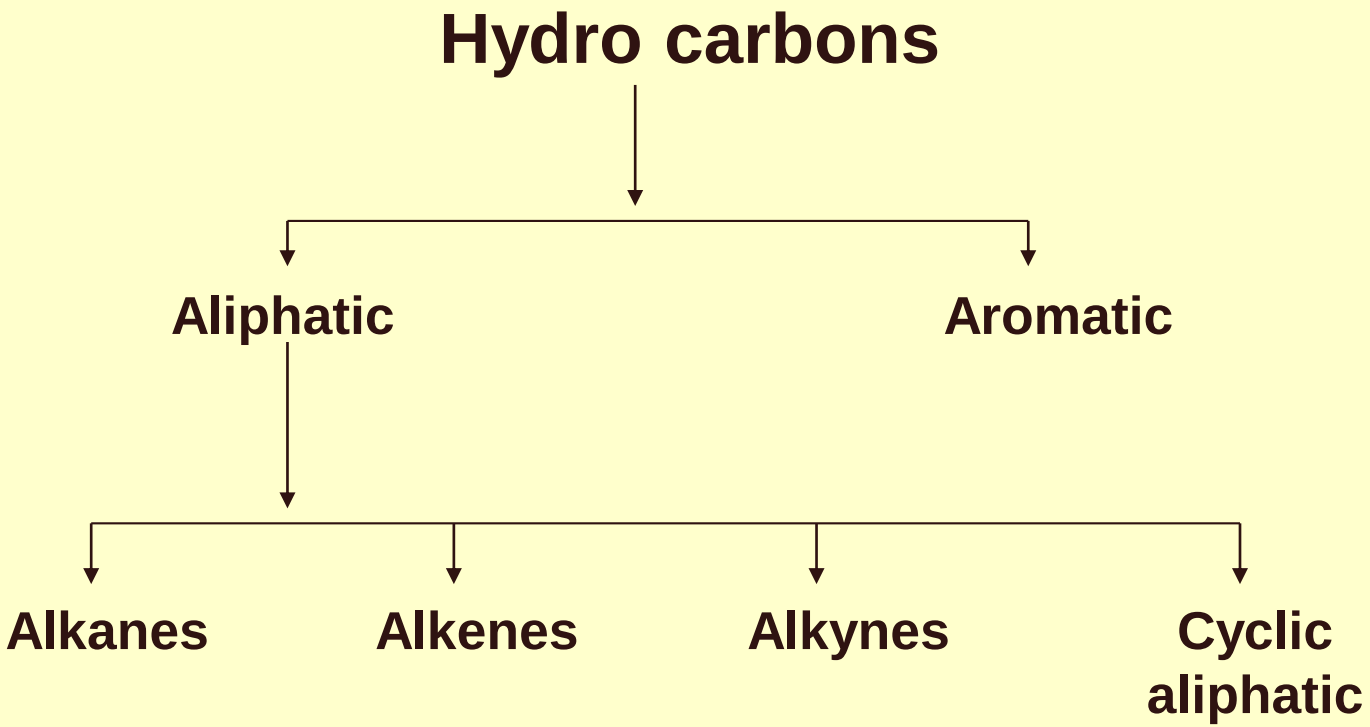
1-Aliphatic 2-Aromatic

1-Aliphatic Compounds with straight, branched or cyclic chains, which may be saturated or unsaturated

and it is divided into four main classes

1-Alkanes 2-Alkenes 3- Alkynes 4-Cyclic aliphatic

Hydro carbons



Base names

Prefix	Length of carbon chain
Meth	**1**
Eth	**2**
Prop	**3**
But	**4**
Pent	5
Hex	6
Hept	7
Oct	8
Non	9
Dec	10

Alkanes

Simplest members of the hydrocarbon family.

- contain only hydrogen and carbon
- only have single bonds

All members have the general formula of

$$C_nH_{2n+2}$$

Twice as many hydrogen as carbon + 2

Alkanes = C_nH_{2n+2}

- A saturated hydrocarbon contains 5 carbons. What is the formula?

$C_5H_{2(5)+2}$ = C_5H_{12}

- A saturated hydrocarbon contains 20 carbons. What is the formula?

$C_{20}H_{2(20)+2}$ = $C_{20}H_{42}$

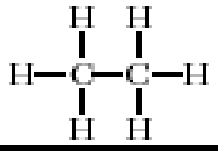
Saturated = Single bond

Alkanes

Table P
Organic Prefixes

Prefix	Number of Carbon Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Table Q
Homologous Series of Hydrocarbons

Name	General Formula	Examples	
		Name	Structural Formula
alkanes	C_nH_{2n+2}	ethane	

- CH_4 = methane
- C_2H_6 = ethane
- C_3H_8 = propane
- C_4H_{10} = butane
- C_5H_{12} = pentane

Alkanes

The smaller the compound the Lower Boiling point and Melting point is (less bonds to break)

Name	BP (°C)	MP (°C)	Density
Methane	-161.7	-182.6	0.424
Ethane	- 88.6	-172.0	0.546
Propane	- 42.2	-187.1	0.582
Butane	-0.5	-135.0	0.579
Pentane	36.1	-129.7	0.626
Hexane	68.7	- 94.0	0.659
Heptane	98.4	- 90.5	0.684
Octane	125.6	- 56.8	0.703
Nonane	150.7	-53.7	0.718
Decane	174.0	-29.7	0.730

Naming Organic Compounds

- Organic compounds are named according to the IUPAC (international union of pure & applied chemistry) system of nomenclature.

Alk**anes** – end in **ane**

Alk**enes** – end in **ene**

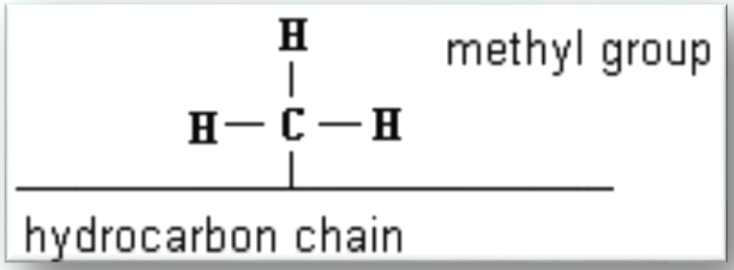
Alk**ynes** – end in **yne**

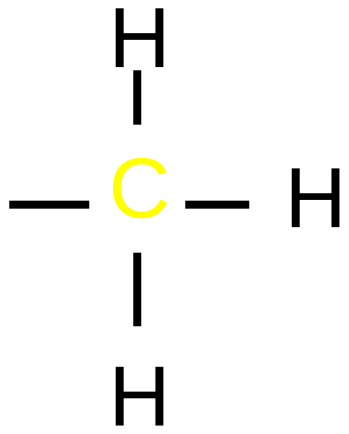
Alkyl groups C_nH_{2n+1}

Alkyl Groups – have one less hydrogen than the corresponding alkane. CH_3 is methyl – one less H than methane, CH_4 , C2H5- ethyl C3H7- propyl C4H9 - butyl C5H11- pentyl

The groups are named simply by dropping (ane) from the name of the corresponding alkane and replacing it by (yl)

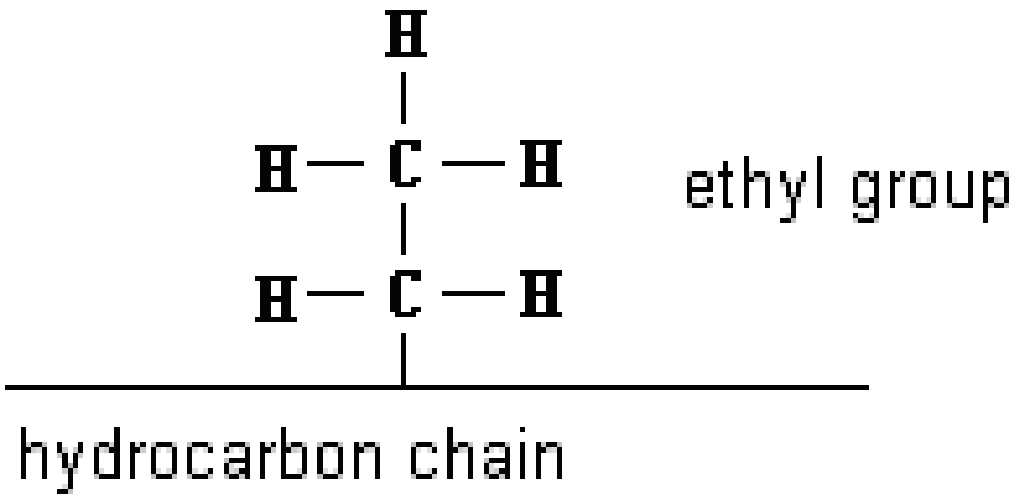
- An iso alkane is a compound in which all carbon atoms except one are from a continuous chain and that one carbon atom is attached to the next carbon





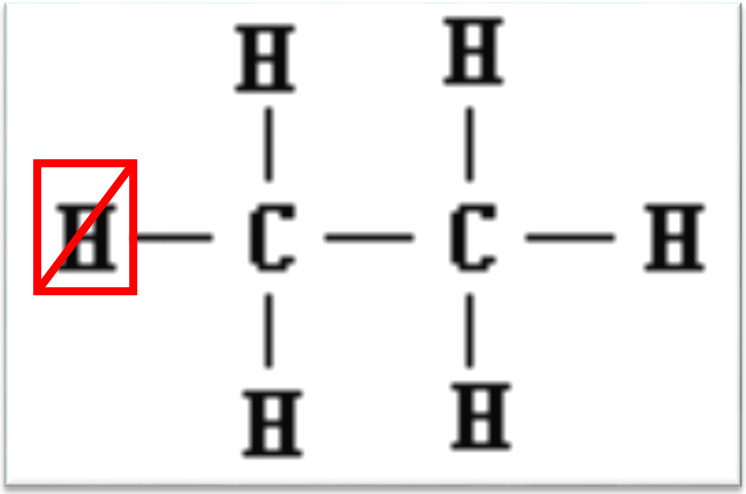
Draw methyl

- C_2H_5 is **ethyl** – one less H than ethane C_2H_6



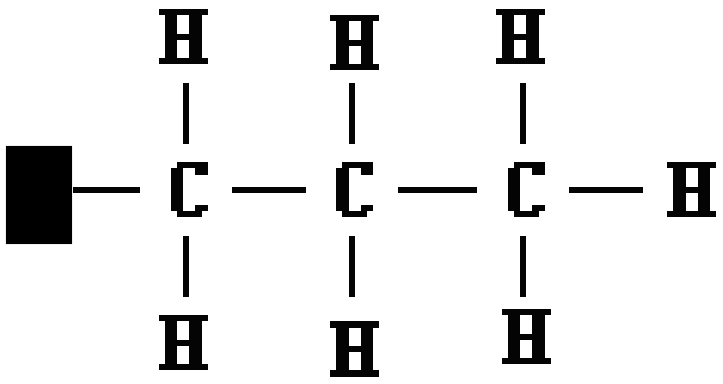
Condensed Formula:

CH_2CH_3

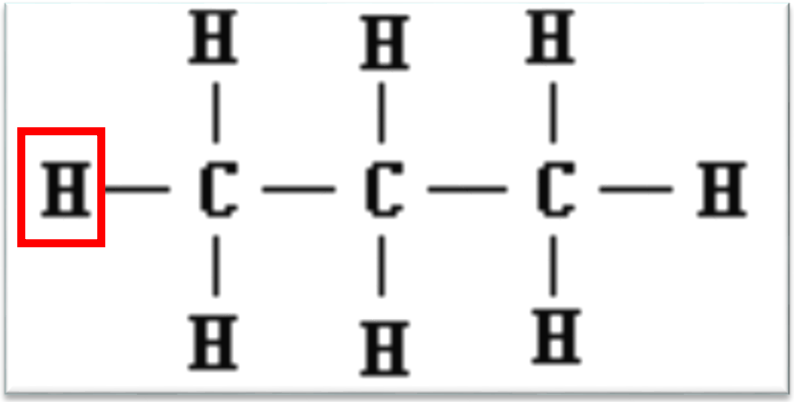


Ethane

- C_3H_7 is **propyl** – one less H than propane C_3H_8

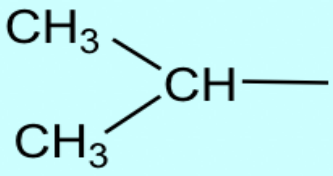


propyl

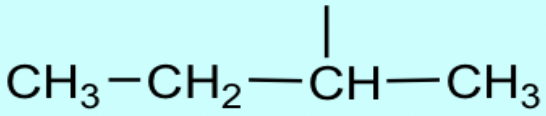


propane

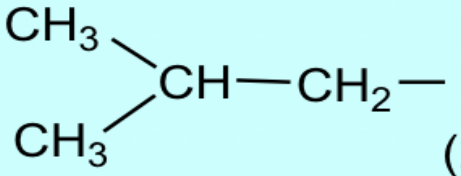
Branched alkyl groups:



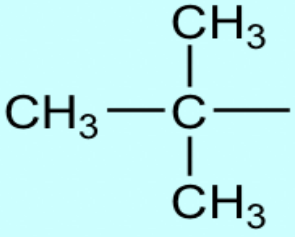
isopropyl
(1-methylethyl)



sec-butyl
(1-methylpropyl)



isobutyl
(2-methylpropyl)



tert-butyl
(1,1-dimethylethyl)

IUPAC Naming Branched Hydrocarbon Chains

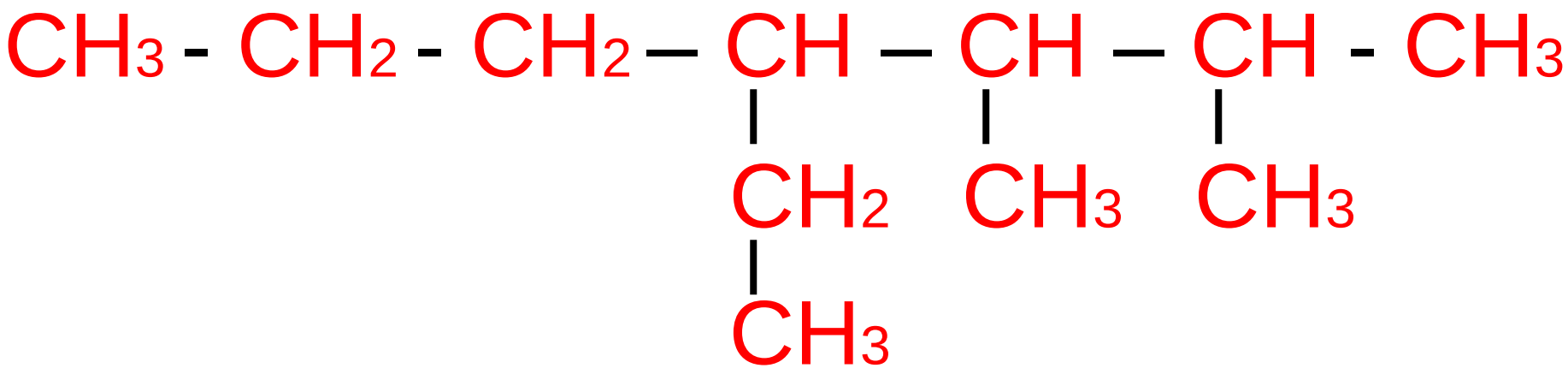
IUPAC : name of alkane :

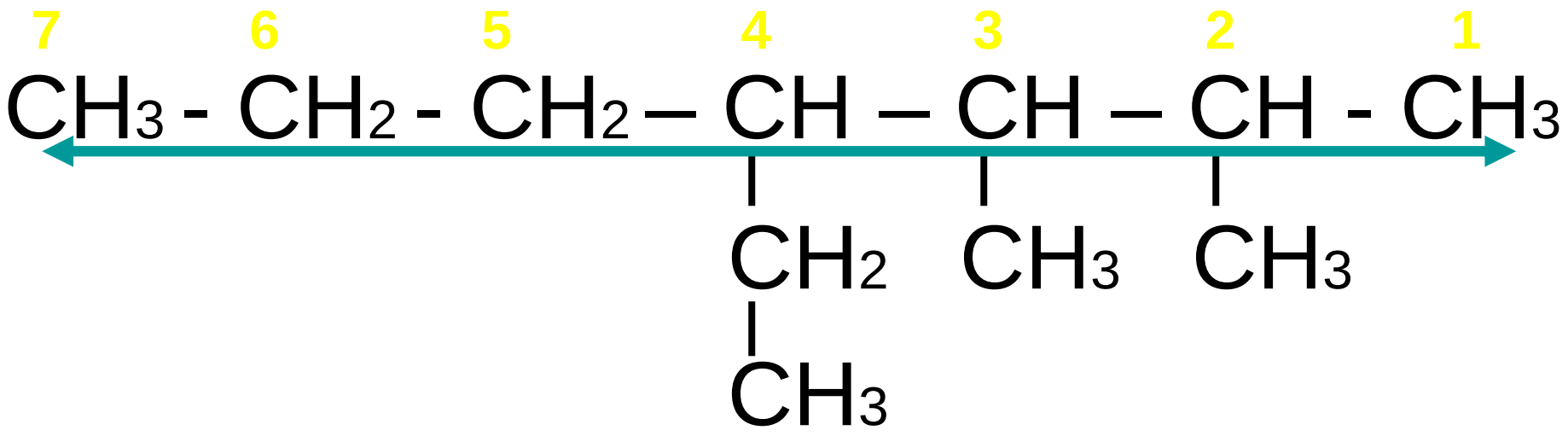
(IUPAC) main : (International union of pure & applied chemistry).

(C_1metha , C_2 etha,C_3propa,…….& soon) name the compound by adding (ane) .

If there are branches in chain choose the longest chain & add ane to the name .

Sometimes the hydrocarbon chains are not straight and sometimes they have other elements attached to them. Here is how they are named:

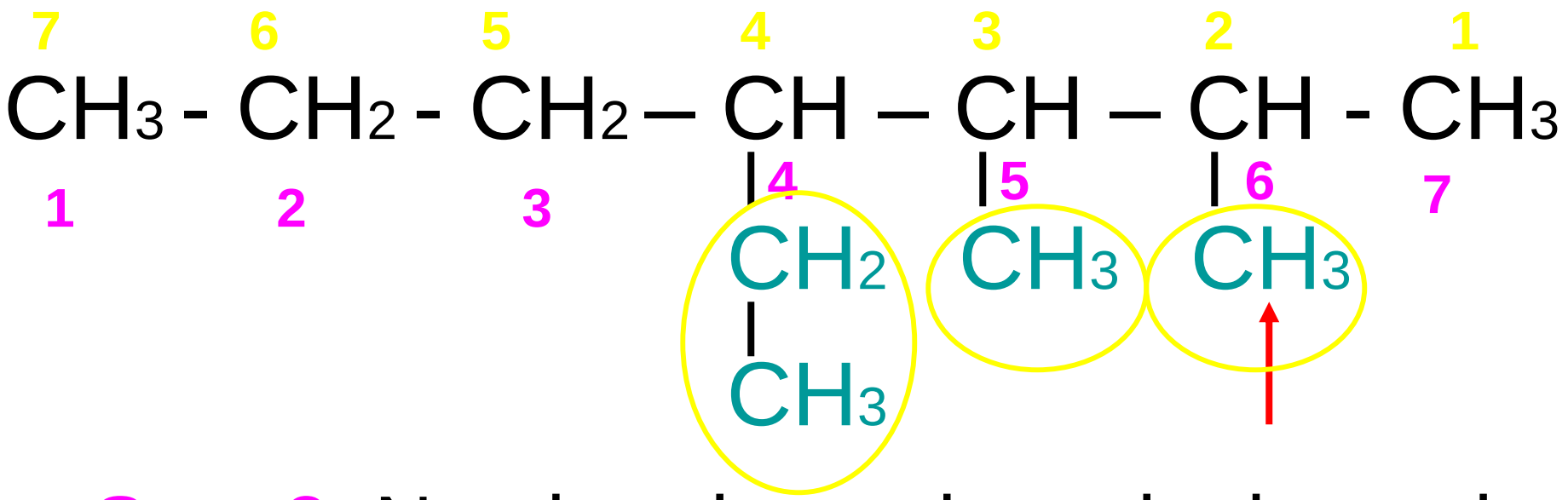




- Step 1: Find the longest continuous chain of carbons.

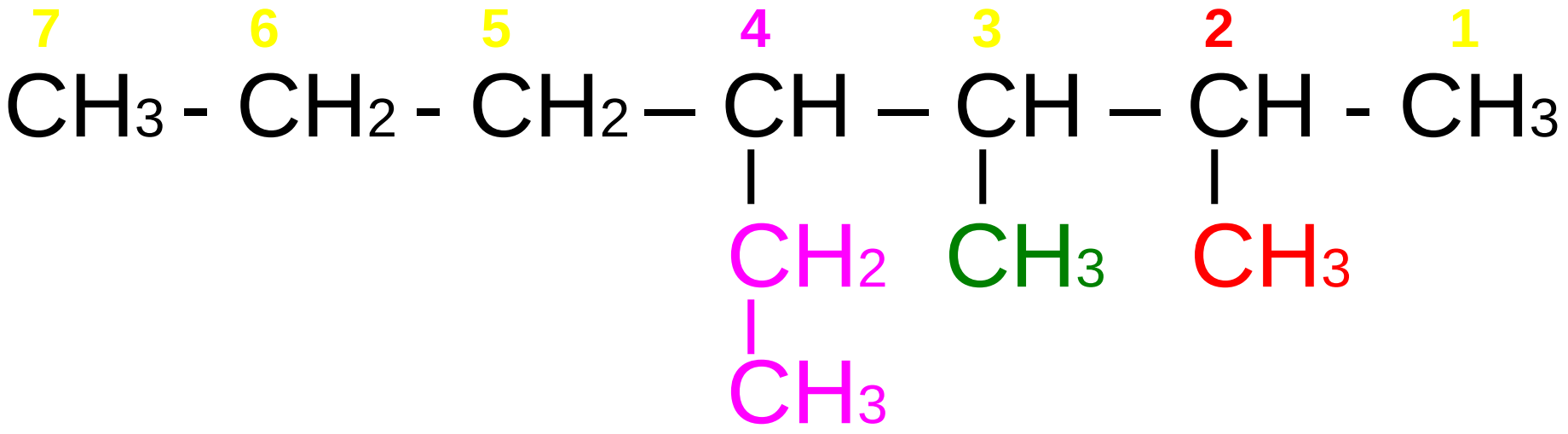
All bonds in the chain of carbons are single bonds so ending is…ane.

There are 7 continuous carbons, so the parent chain is heptane.



- Step 2: Number the carbons in the main sequence starting with the end that will give the attached groups the smallest #.

- This chain is numbered from right to left because there is a substituent closest to the right.



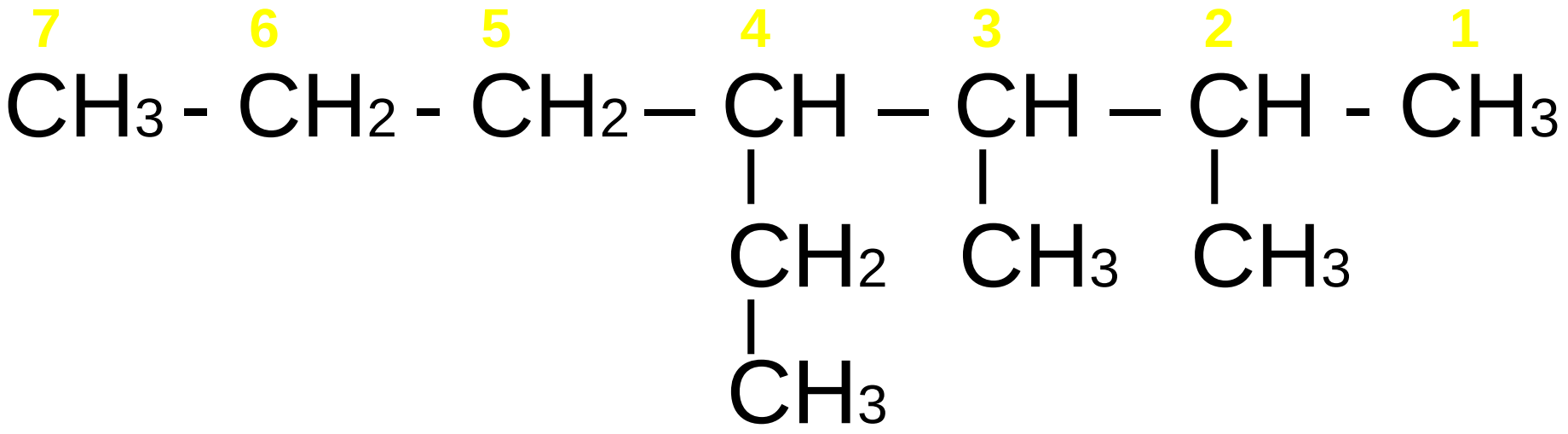
- Step 3 : Add numbers to the names of the groups to identify their positions on the chain.

- these numbers become prefixes to the parent chain.

In this ex. the positions are:

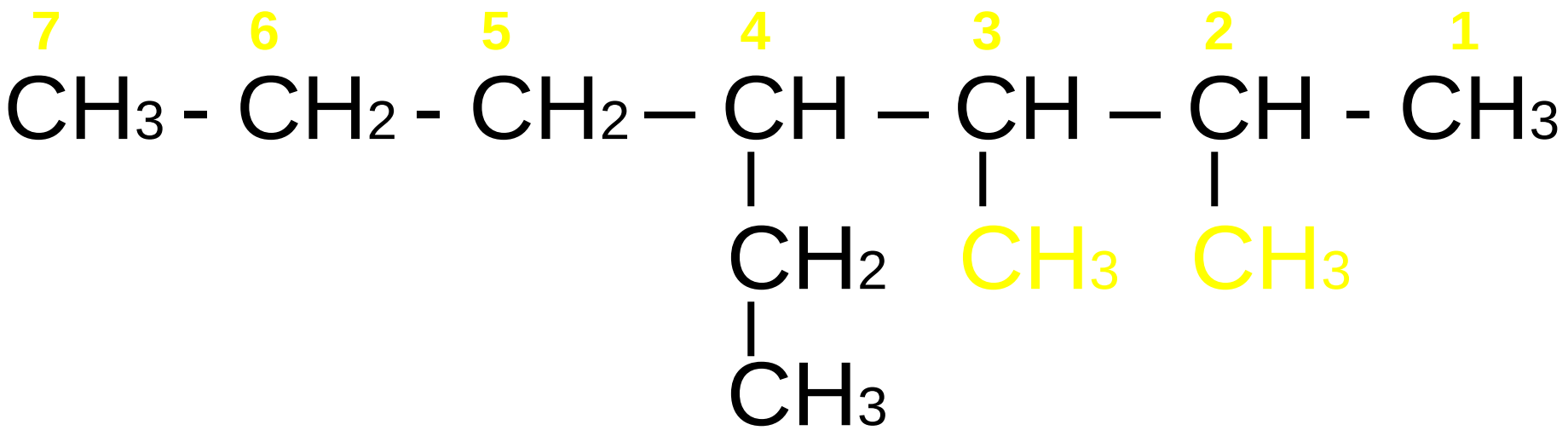
yl
~~ethane~~
$C_2H_{\cancel{6}\ 5}$

2- methyl, 3- methyl, 4- ethyl



- Step 4: Use prefixes to indicate the appearance of a group more than once in the structure.

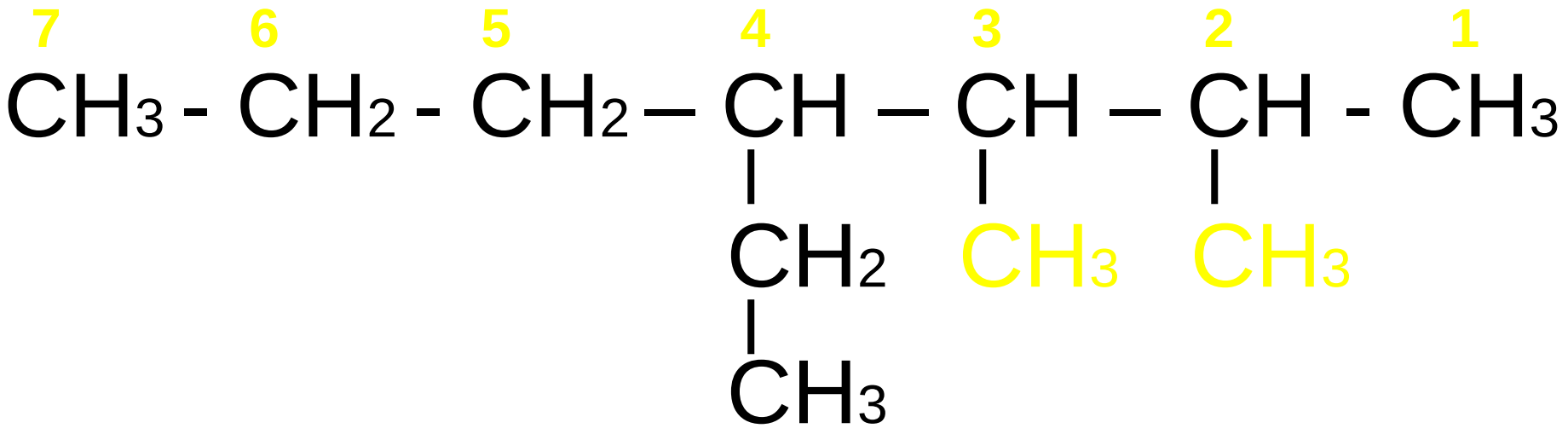
Di	=	twice
Tri	=	three times
Tetra	=	four times
Penta	=	five times



- This chain has 2 methyl groups so dimethyl is used.

Step 5: List the alkyl groups in alphabetical order.

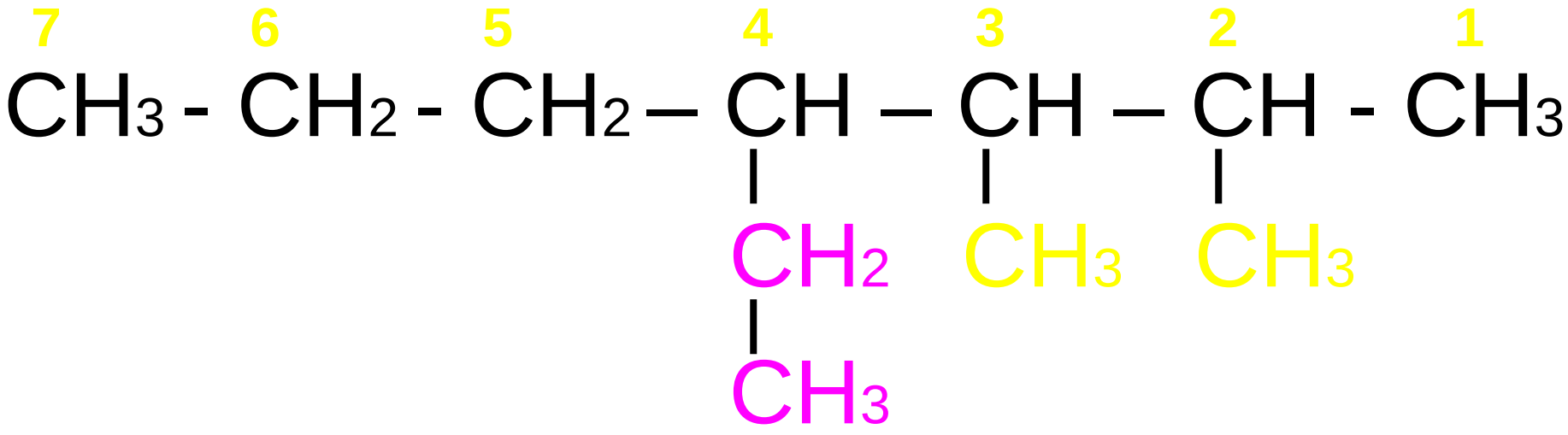
In this ex. dimethyl is listed before the ethyl.



Step 6: Use punctuation

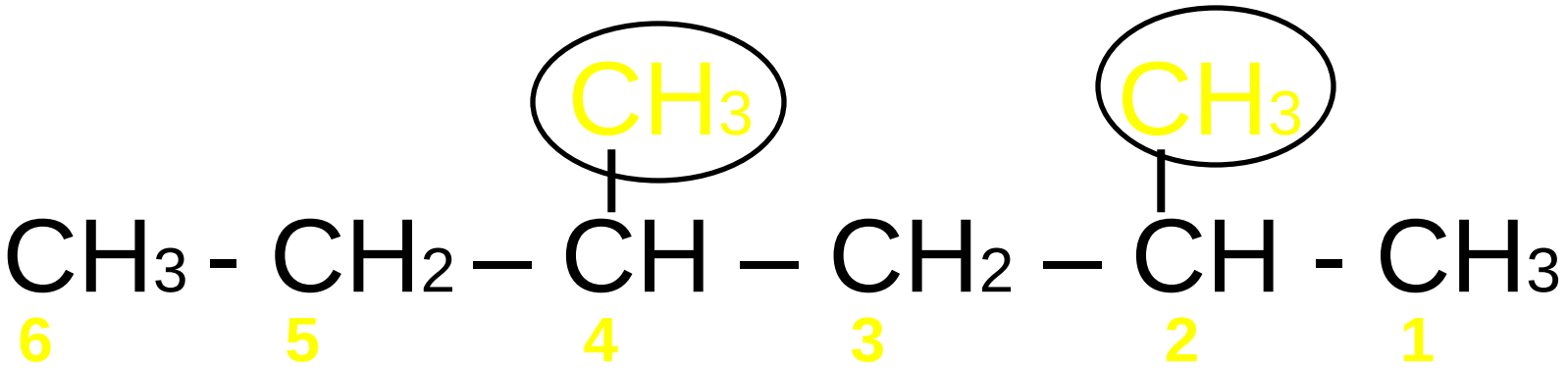
- use commas to separate numbers

-hyphens to separate numbers with words.



- The name of this compound is:

2,3-dimethyl – 4-ethyl heptane



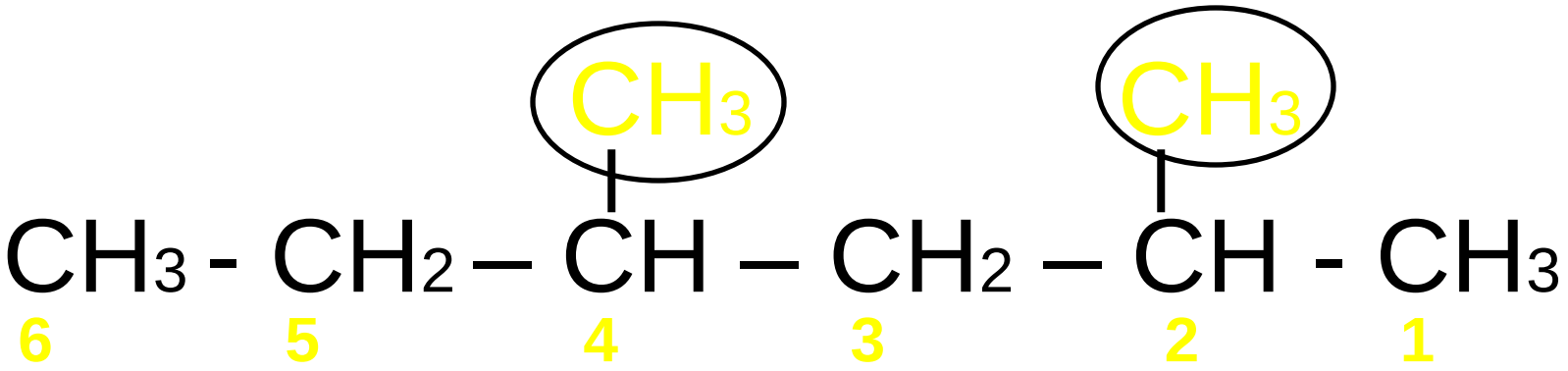
Step 1: 6 carbons = hex

All single bonds = ends in ane

So parent chain is hexane

Step 2: start numbering from right to left

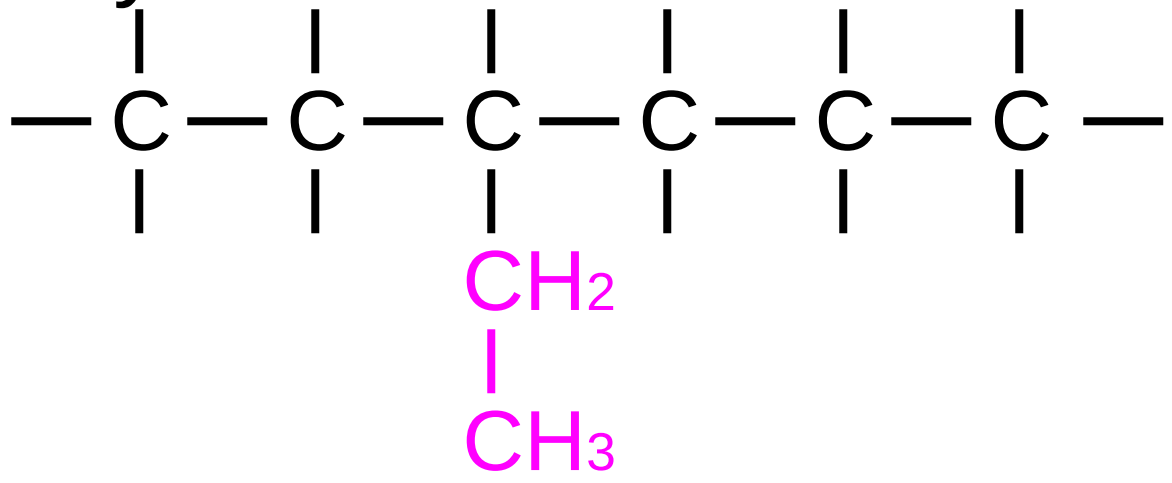
Step 3: 2 -methyl and 4-methyl



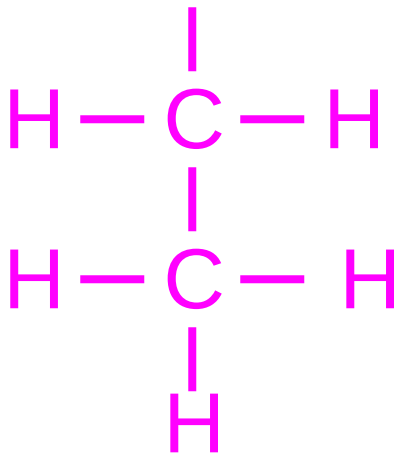
2,4 dimethyl hexane

Now start with name and draw the structure.

- 3-ethylhexane



You can place H's all around or just leave as is.

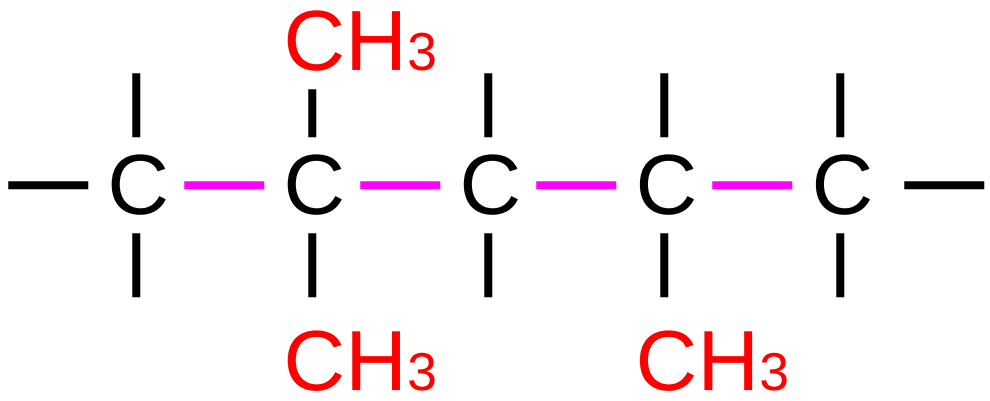


yl

~~ethane~~

$C_2H_{\cancel{6}\ 5}$

- 2,2,4-trimethylpentane



Other Organic Compounds

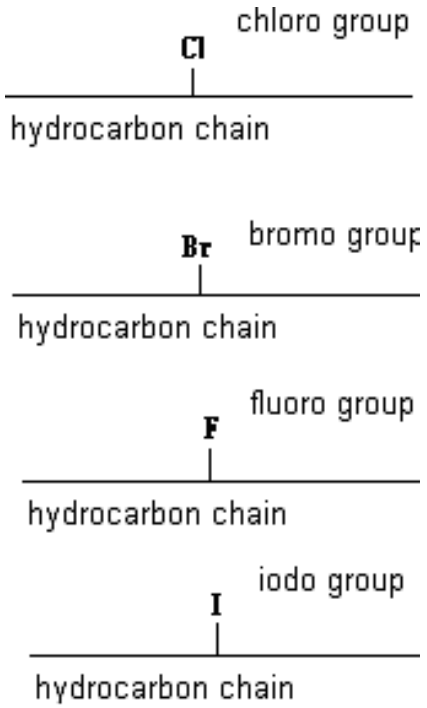
Functional Groups – specific groupings of atoms that give characteristic properties to organic compounds.

⇨ halides F (floro-)

Cl (chloro-)

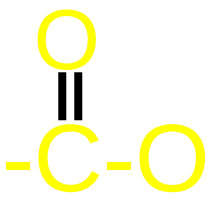
Br (bromo-)

I (iodo-)



What group do these belong to?

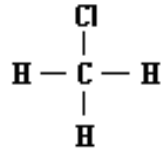
Halogens

- Alcohols -OH hydroxyl
- Organic acids -COOH carboxyl
- Aldehydes -CHO carbonyl
- Ketones 
- Ethers -O-
- Esters 
- Amines
- Amides

Halides

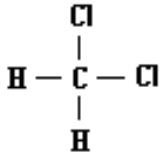
Cmpds that are formed when any halogen (F,Cl,Br,I) replaces an H atom in an alkane.

The functional group is the halide (F,Cl,Br,I)



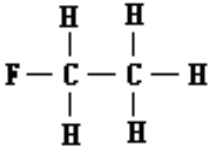
One carbon = methane
Chlorine = chloro

Chloro methane



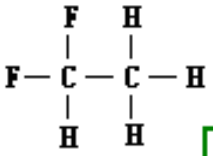
One carbon = methane
2 Cl's = dichloro

dichloro methane



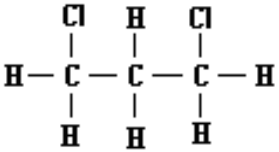
2 carbons = ethane
1 F = fluoro

fluoro ethane



2 carbons = ethane
2 F's = difluoro
Both on 1st carbon = 1,1

1,1 difluoro ethane



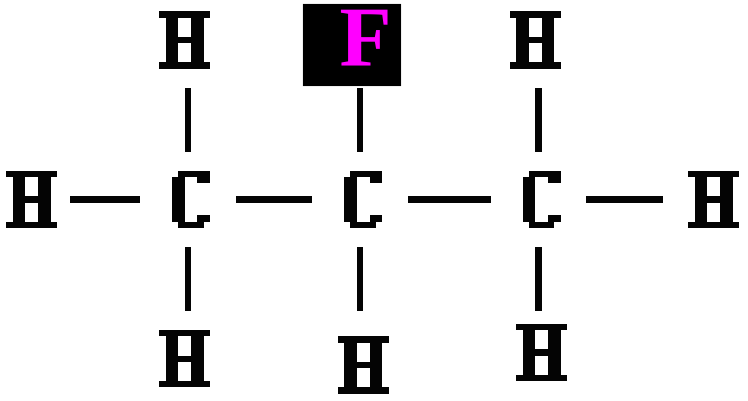
3 carbons = propane
2 Cl's = dichloro
One on 1st C, other on 3rd C = 1,3

1,3 dichloro propane

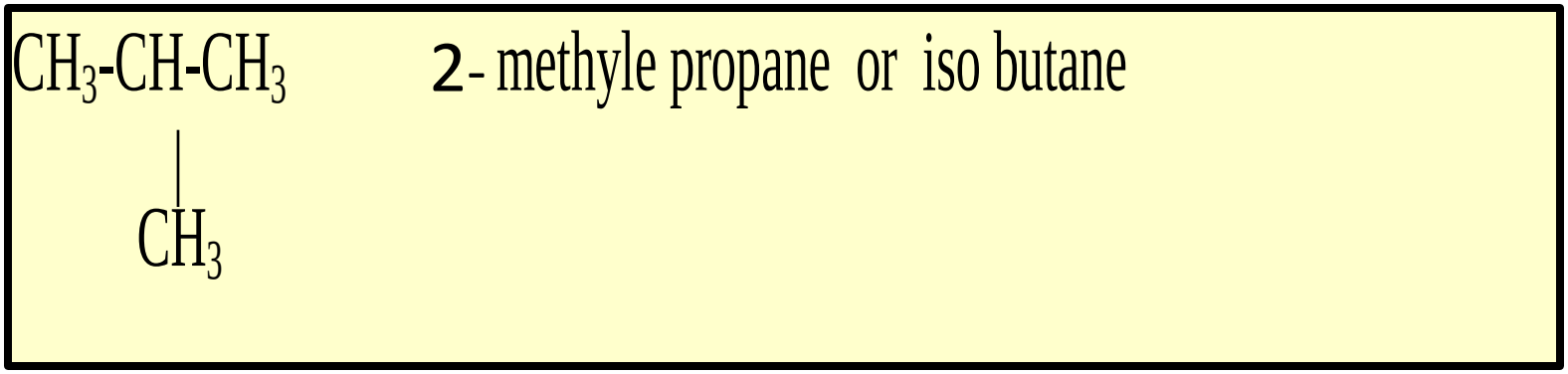
Halides

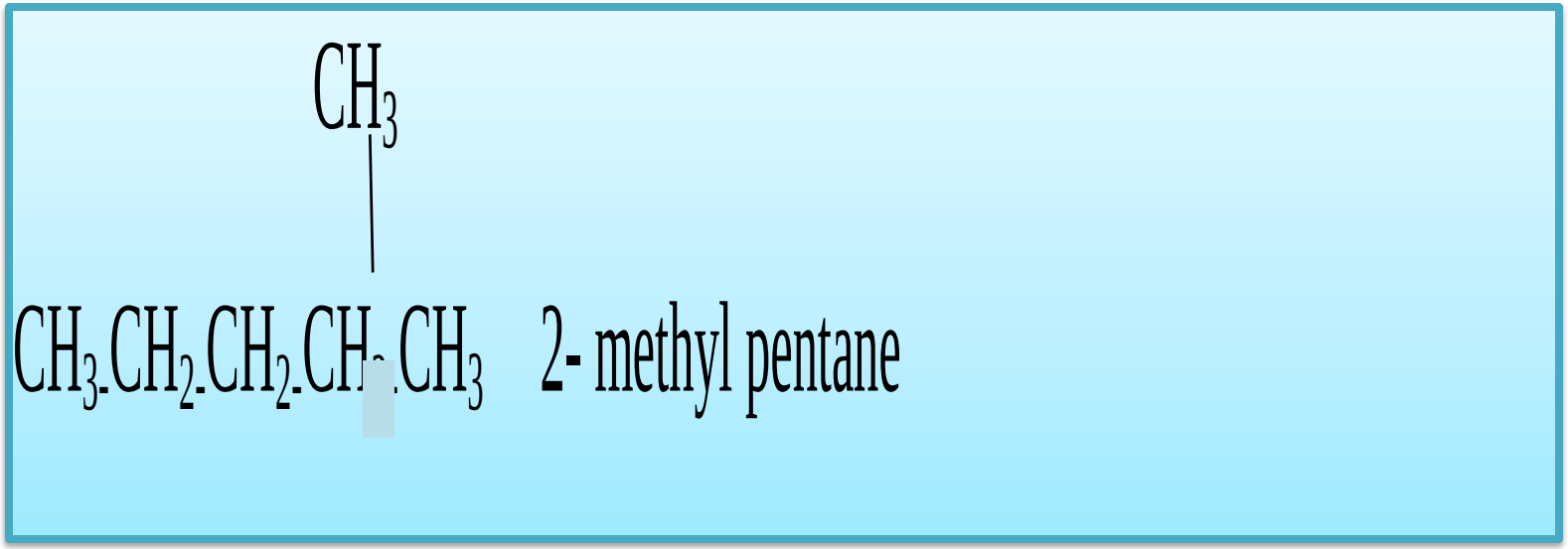
- They are named by citing the location of the halogen attached to the chain

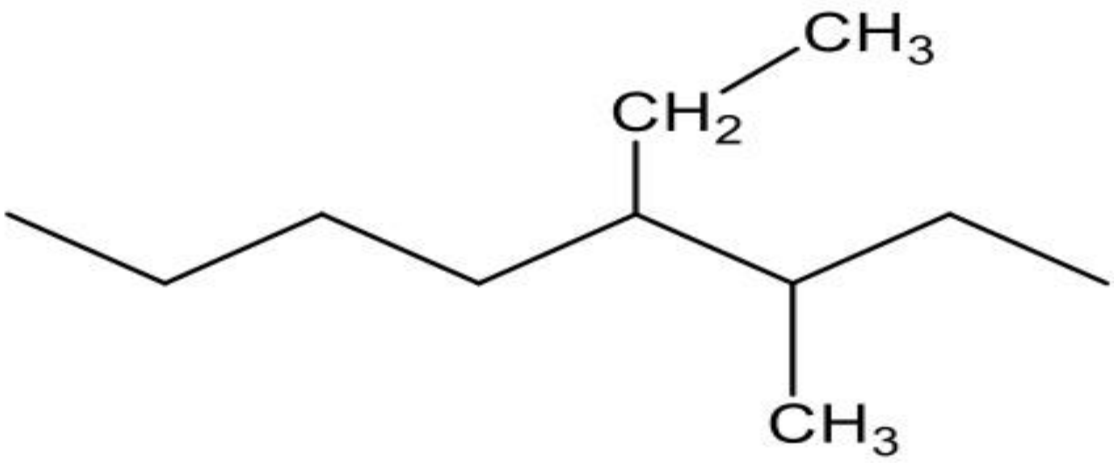
Drop the “ine” and add “o”

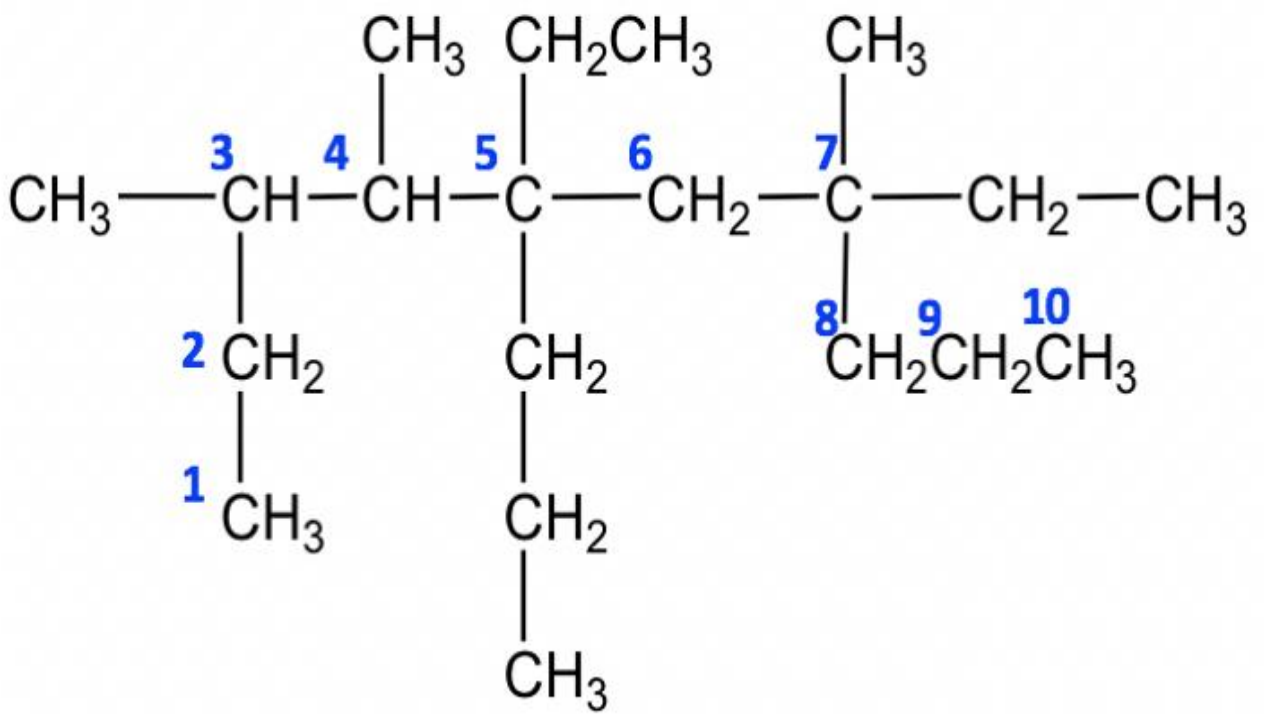


2- floropropane

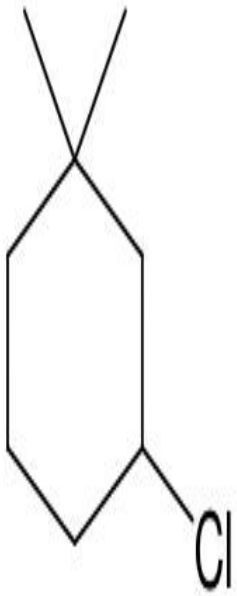

CH3-CH-CH3
CH3
2- methyle propane or iso butane


CH3
CH3.CH2.CH2.CH.CH3
2- methyl pentane

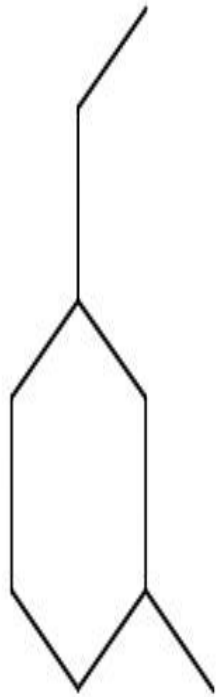

CH3
CH2
CH3



Find the parent chain correctly is the key step for naming this structure.

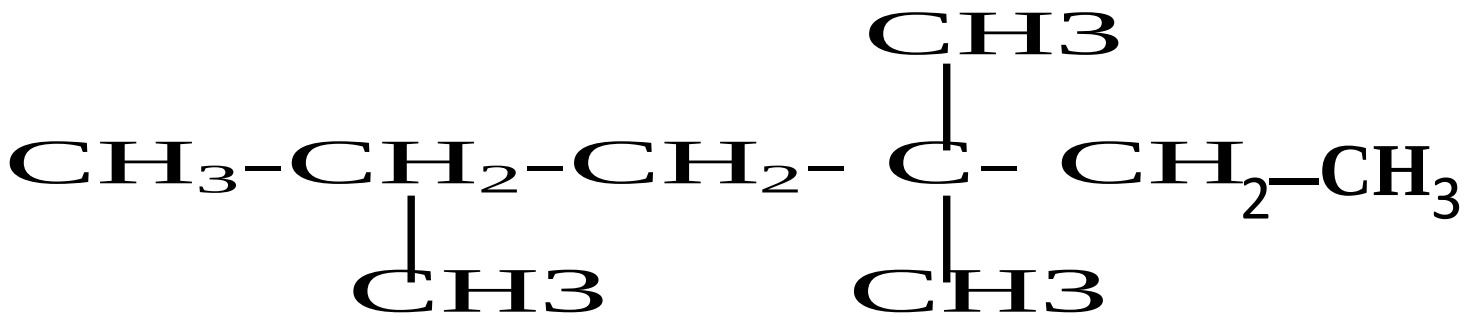


1,1-dimethyl-3-chlorocyclohexane



1-ethyl-3-methylcyclohexane

Give the name of this chemical structure:



Draw out the structure from the name and give the proper IUPAC name for the compounds.

a) 2,3-dimethylbutane

b) 4-ethylheptane

c) 3,3-dimethyl hexane

d) 3-Ethyl-3-MethylOctane

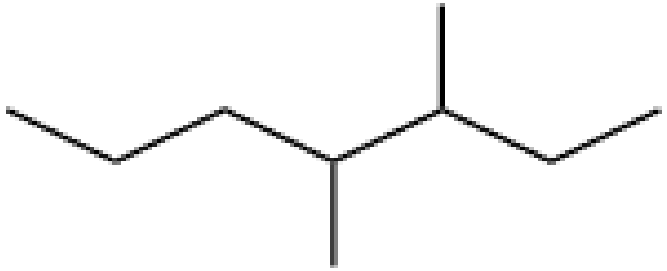
e) 2-propylnonane

f) 4,4-dibromohexane

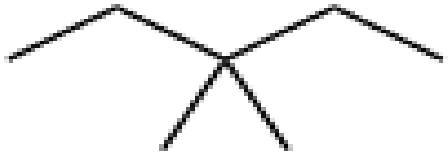
Give the proper IUPAC names of the following compounds.

a)

b)



c)



Physical properties

- 1-n- alkane having (C_1-C_4) are gases from (C_5-C_{17}) are liquids , alkane which contain more than (17C) are solid.
- 2- The boiling point (B.P) & melting point (m.p) increase with the increasing of the (M.Wt.) or long of chain .
- 3-Alkane are insoluble in water & other highly polar solvents but soluble in non polar solvents like benzene , ether & chloroform,all alkane has density less than H_2O .

Preparation of alkane:

Main source for prepared alkane by fractional distillation of oil.We have many labrotory methods for preparation.

1-Hydrogenation of alkenes:

- $C_nH_{2n}+H_2 \xrightarrow{Pt,Pd \text{ or } Ni} C_nH_{2n+2}$

$$CH_2=CH_2 + H_2 \xrightarrow{Pt,Pd \text{ or } Ni} CH_3CH_3$$

Preparation of alkane

2- Reduction of alkyl halides

RX+ Mg $\xrightarrow{\text{Dry ether}}$ **RMgX** $\xrightarrow{\text{HOH}}$ **RH + Mg(OH)X**

R= alkyl CH3, C2H5, , X = Cl ,Br , I. Dry ether= diethyl ether$(C_2H_5)_2O$

$CH_3CH_2Br + Mg \xrightarrow{\text{Dry eyher}} CH_3CH_2MgBr \xrightarrow{\text{HOH}} CH_3CH_3 + Mg(OH)Br$

(Methyl magnesium bromide) (ethane)

3-Special method for preparation of methane:

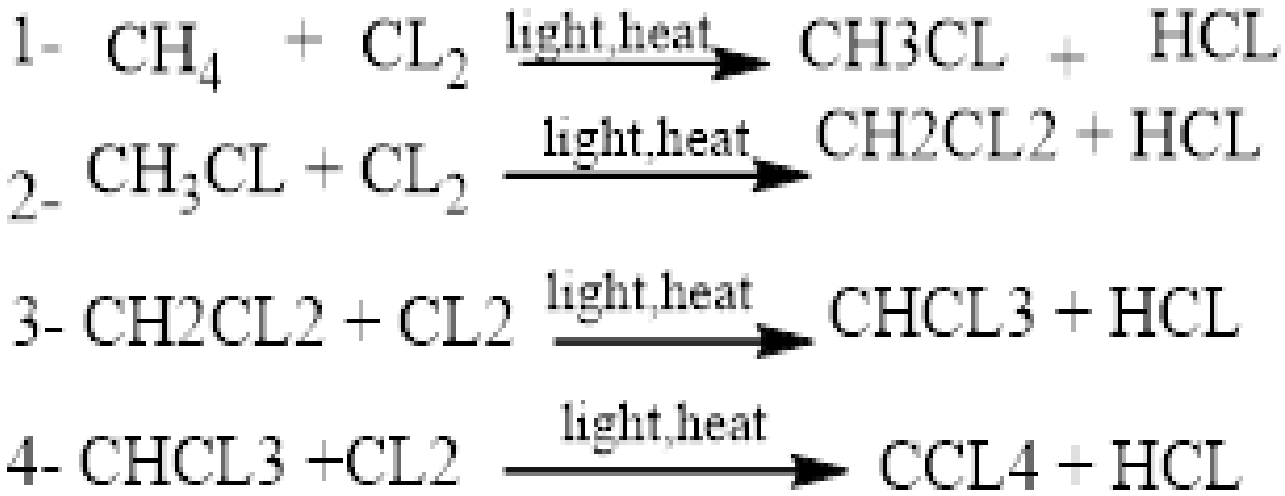
- **Labrotory preparation the reaction of sodium acetate with soda-lime (NaOH +CaO).**
- $CH_3COONa + NaOH + CaO \longrightarrow CH_4 + Na_2CO_3$

Reaction of Alkane

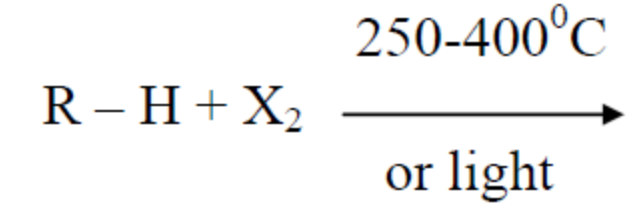
- Why alkane are less reactive?
- because it is saturated & not oxidized simply & not dissolve in H_2O & not react with acids &bases but react under condition like heat, light or in the presence of catalyst

1-Halogenation

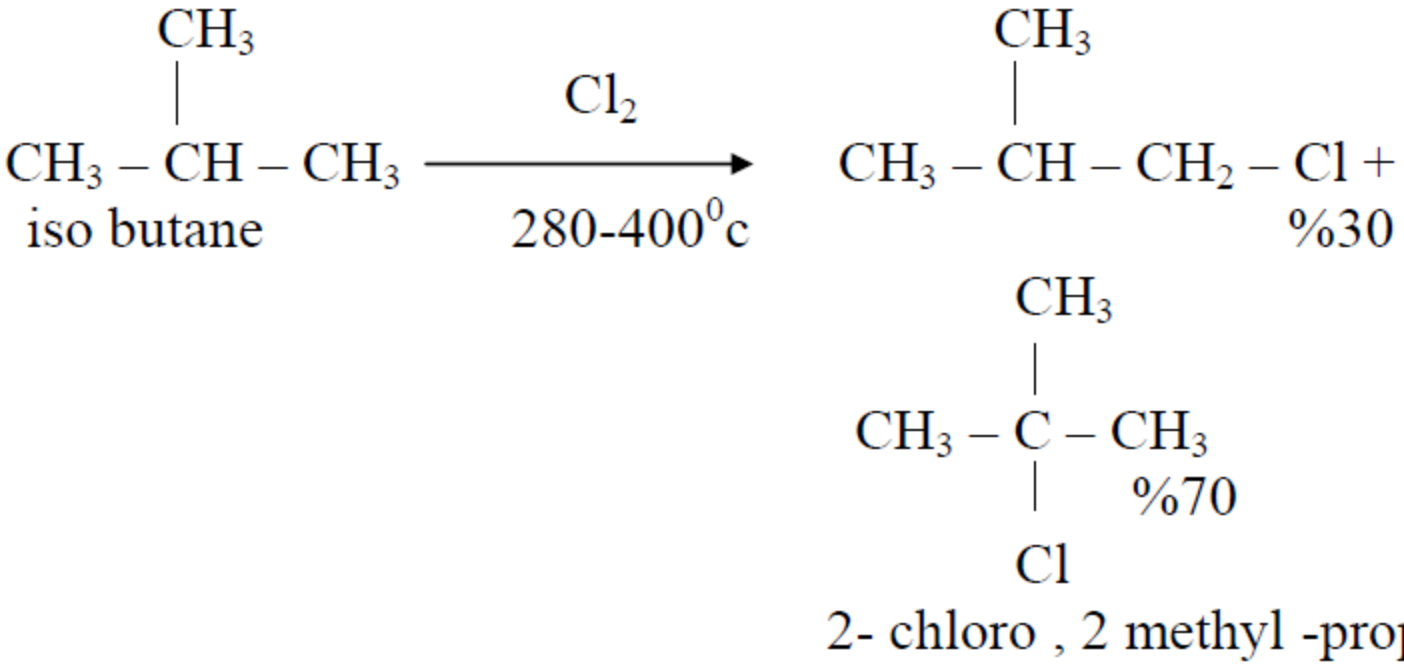
- The reactive chlorine atom attach another molecule &the reaction continue & its name radical reaction as followes:



1- Halogenations



Ex /



2- chloro , 2 methyl -propane

2- Combustion

$$C_n H_{2n+2} + O_2 \text{ (excess)} \xrightarrow{\text{flame}} nCO_2 + (n+1) H_2O + \text{Energy}$$

- Ex /

$$C_5 H_{12} + 8O_2 \xrightarrow{\text{flame}} 5CO_2 + 6H_2O + \text{Energy}$$

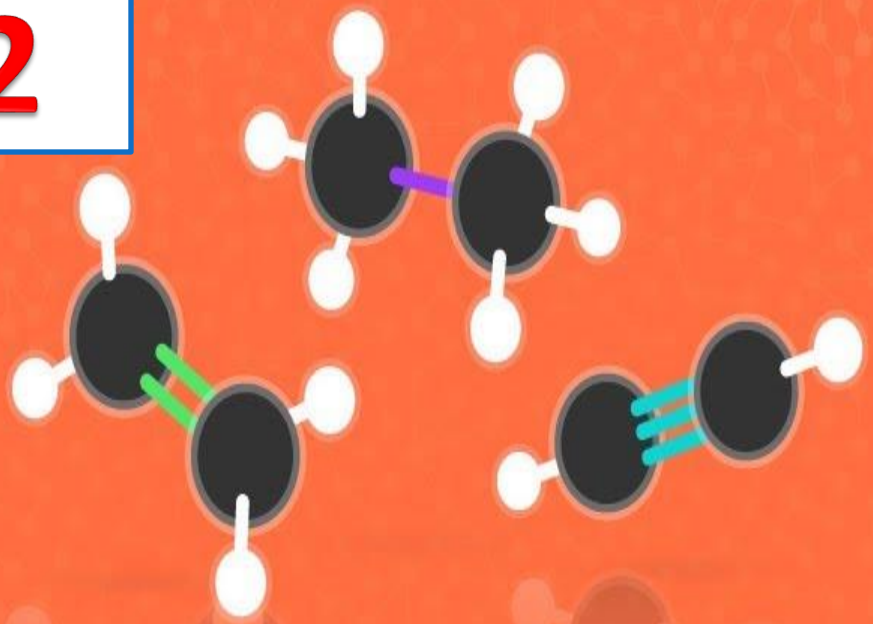
$\Delta H = -845$ HCal.

حرارة الاحتراق

2)Home work

- Prepare
- 1-$CH_3CH_2CH_3$ by hydration
- 2-$CH_3CH_2CH_2CH_3$ by Reduction of alkyl halides(Grignard reagent)

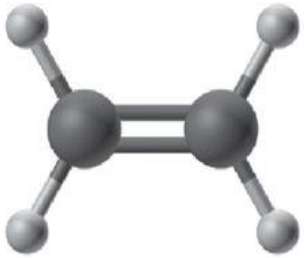
Lecture 2

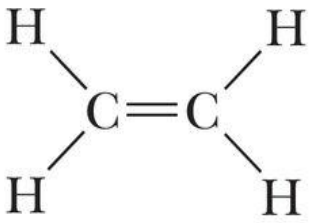


Sec 41-0 ALKENES & ALKYNES

Properties
Nomenclature
Stability
Reactions

- **Unsaturated Hydrocarbon:**
- **A hydrocarbon that contains one or more carbon-carbon double or triple bonds or benzene-like rings.**
  - **Alkene: contains a carbon-carbon double bond and has the general formula C_nH_{2n}.**
  - **Alkyne: contains a carbon-carbon triple bond and has the general formula C_nH_{2n-2}.**





Ethene
(an alkene)

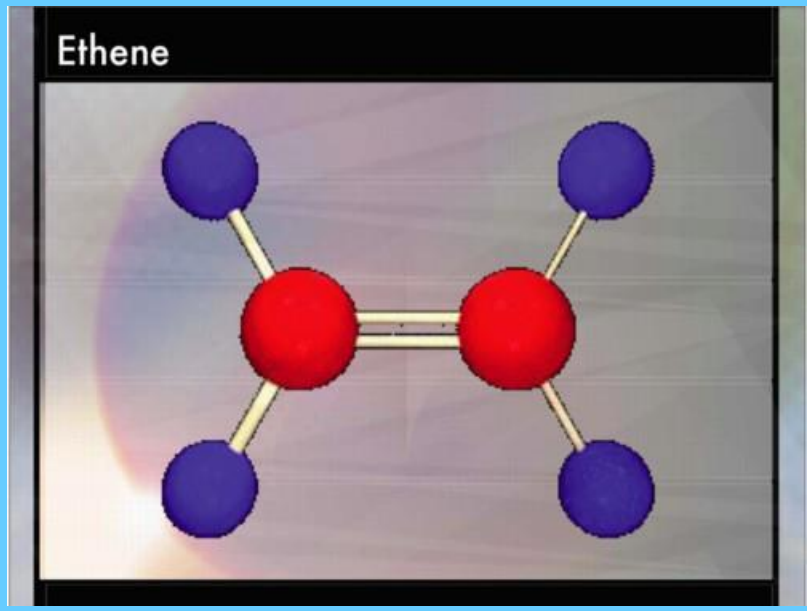
H—C≡C—H

Ethyne
(an alkyne)

Alk*enes*-*(Olefin)* – C_nH_{2n}

series of unsaturated hydrocarbons having one double bond (C=C)

- Also called ethylene series (IUPAC name is ethene)
- General formula C_nH_{2n}

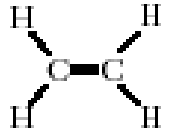


Alkenes

Table P
Organic Prefixes

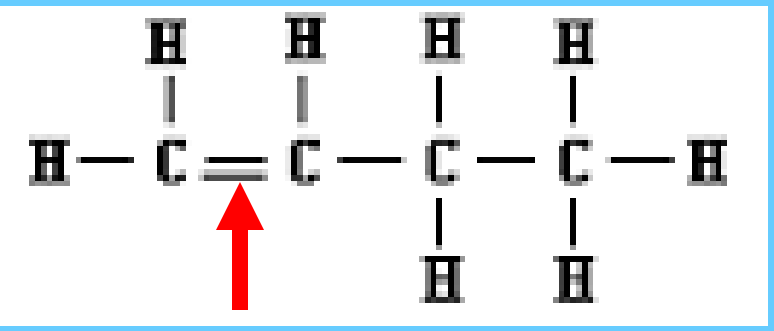
Prefix	Number of Carbon Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Table Q
Homologous Series of Hydrocarbons

Name	General Formula	Examples	
		Name	Structural Formula
alkenes	C_nH_{2n}	ethene	

- C_2H_4 = Ethene
- C_3H_6 = Propene
- C_4H_8 = Butene
- C_5H_{10} = Pentene
- To find the number of hydrogens, double the number of carbons.

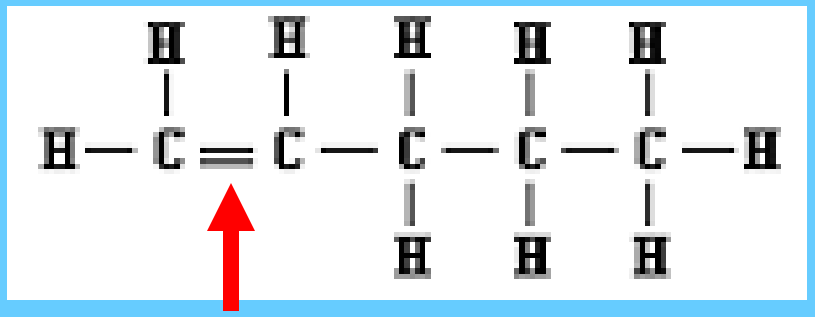
1-Butene



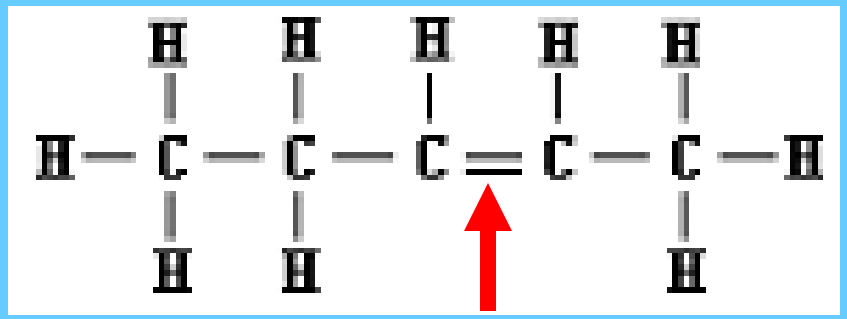
This is 1-butene, because the double bond is between the 1st and 2nd carbon from the end.

ISOMERS: Molecules have the same molecular formula, but have different structural formulas.

Pentene



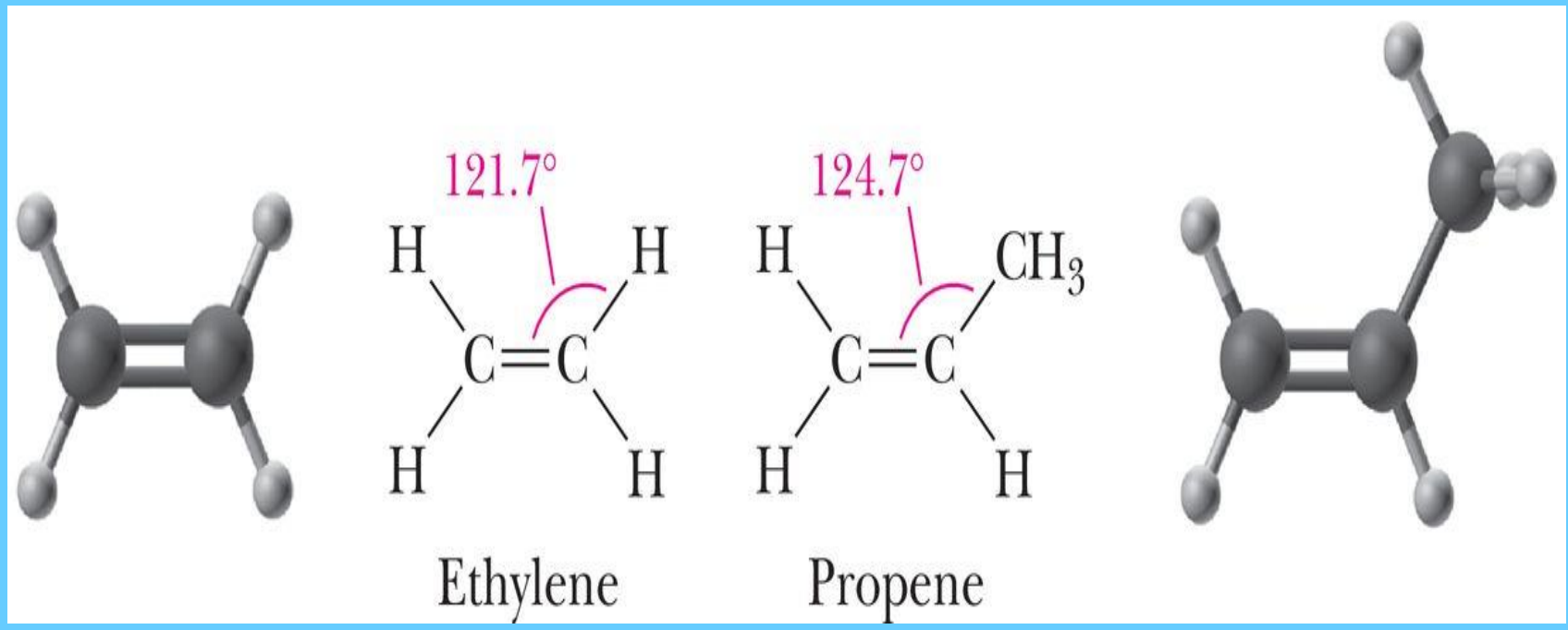
This is 1-pentene. The double bond is on the first carbon from the end.



This is another isomer of pentene. This is 2-pentene, just that the double bond is closer to the right end.

Structure of Alkenes

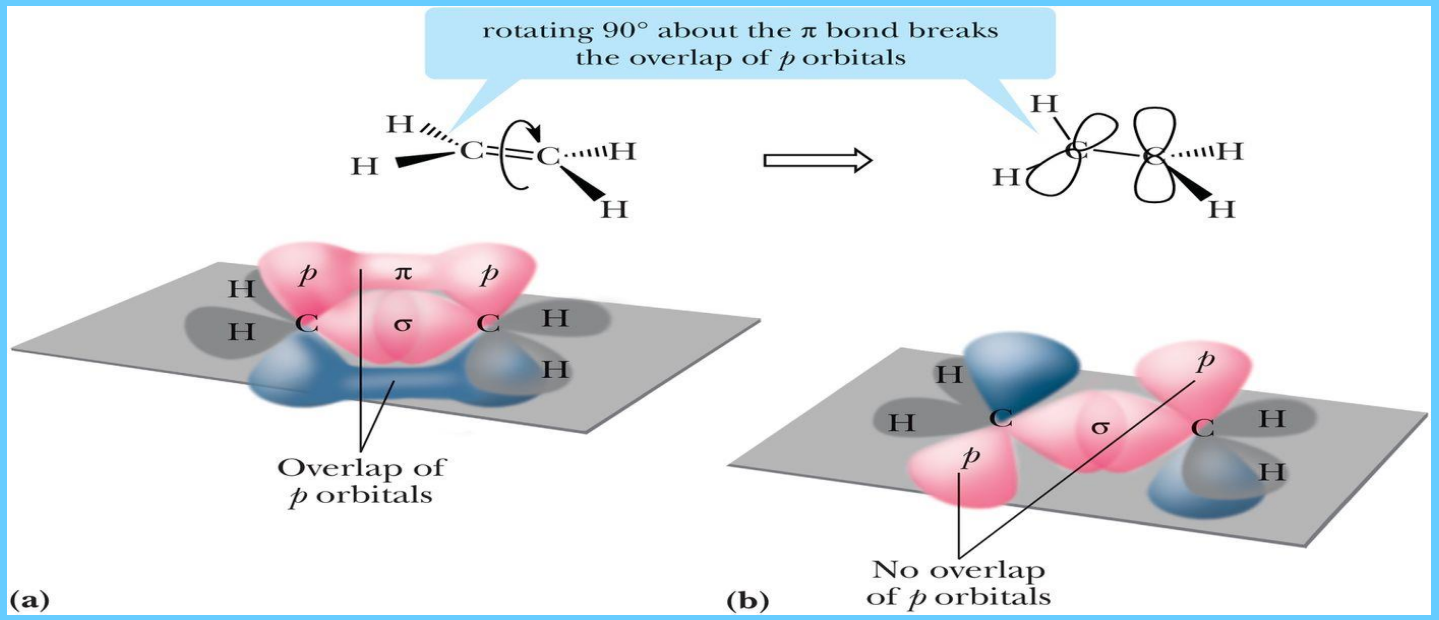
- **The two carbon atoms of a double bond and the four atoms bonded to them lie in a plane, with bond angles of approximately 120° .**



Structure of Alkenes

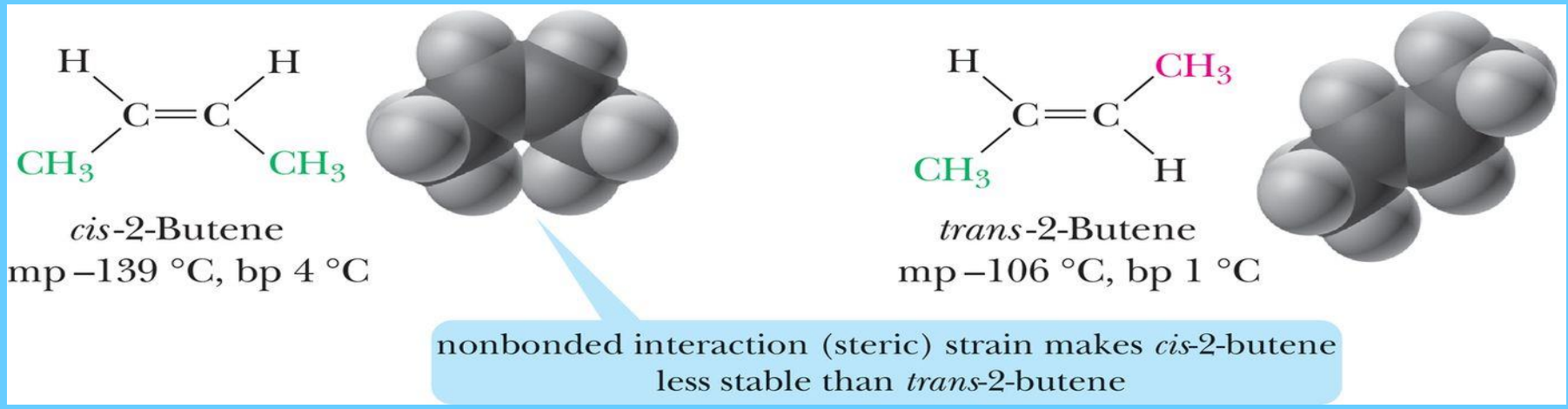
According to the orbital overlap model, a double bond consists of one s bond formed by overlap of sp^2 hybrid orbitals and one p bond formed by overlap of parallel 2*p* orbitals.

- ***Rotating by 90° breaks the pi bond.***



Cis-Trans Isomerism

- **Because of restricted rotation about a C–C double bond, groups on the carbons of a double bond are either *cis* or *trans* to each other.**
  - **Because of nonbonded interaction strain between alkyl substituents on the same side of the double bond, a *trans* alkene is more stable than an isomeric *cis* alkene.**

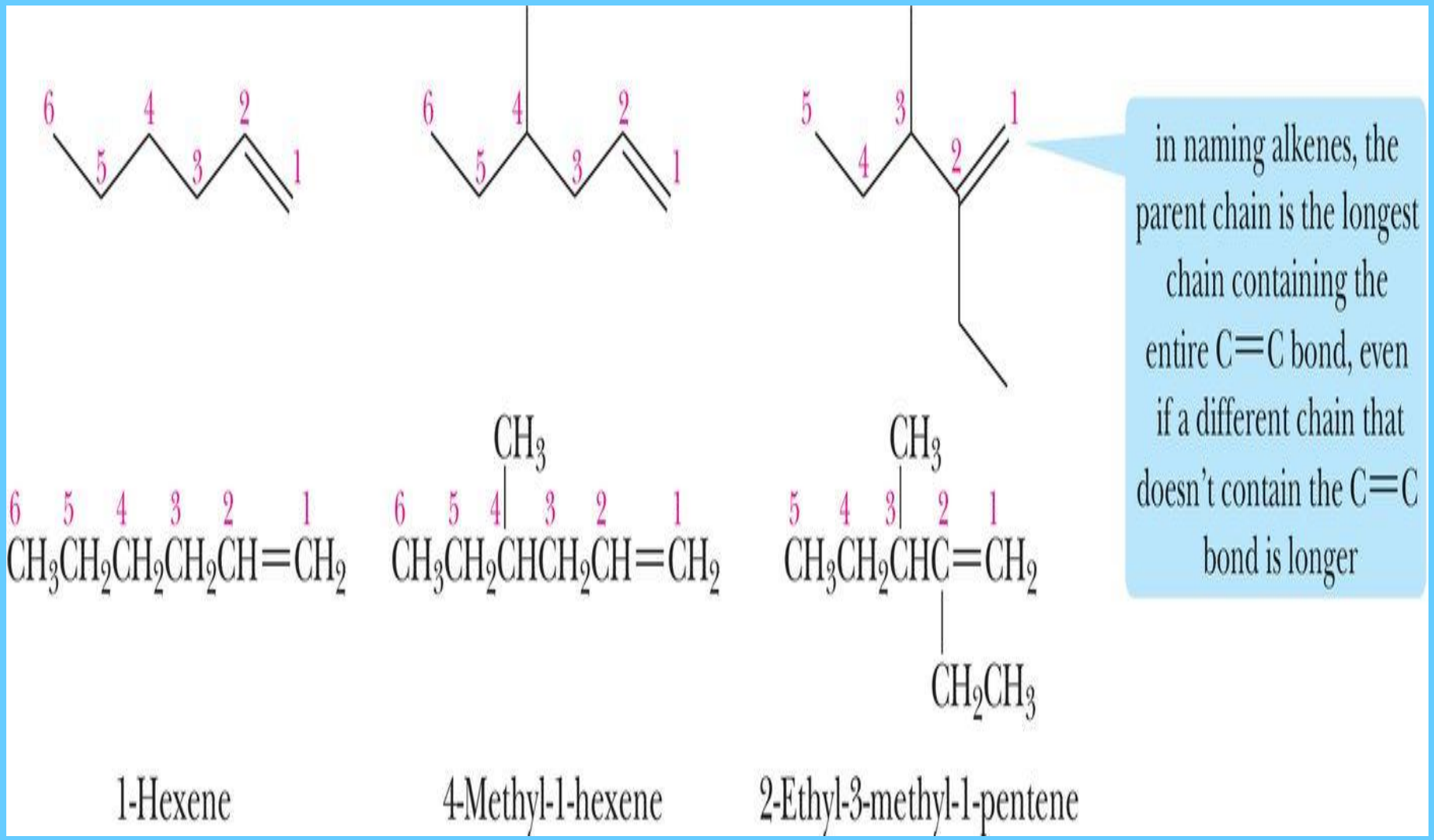


Nomenclature of Alkenes

- **IUPAC Nomenclature of alkenes**
  - **Use the infix -en- to show the presence of a carbon-carbon double bond.**
  - **Number the parent chain to give the first carbon of the double bond the lower number.**
  - **Follow IUPAC rules for numbering and naming substituents.**
  - **For a cycloalkene, number the atoms of the ring beginning with the two carbons of the double bond.**

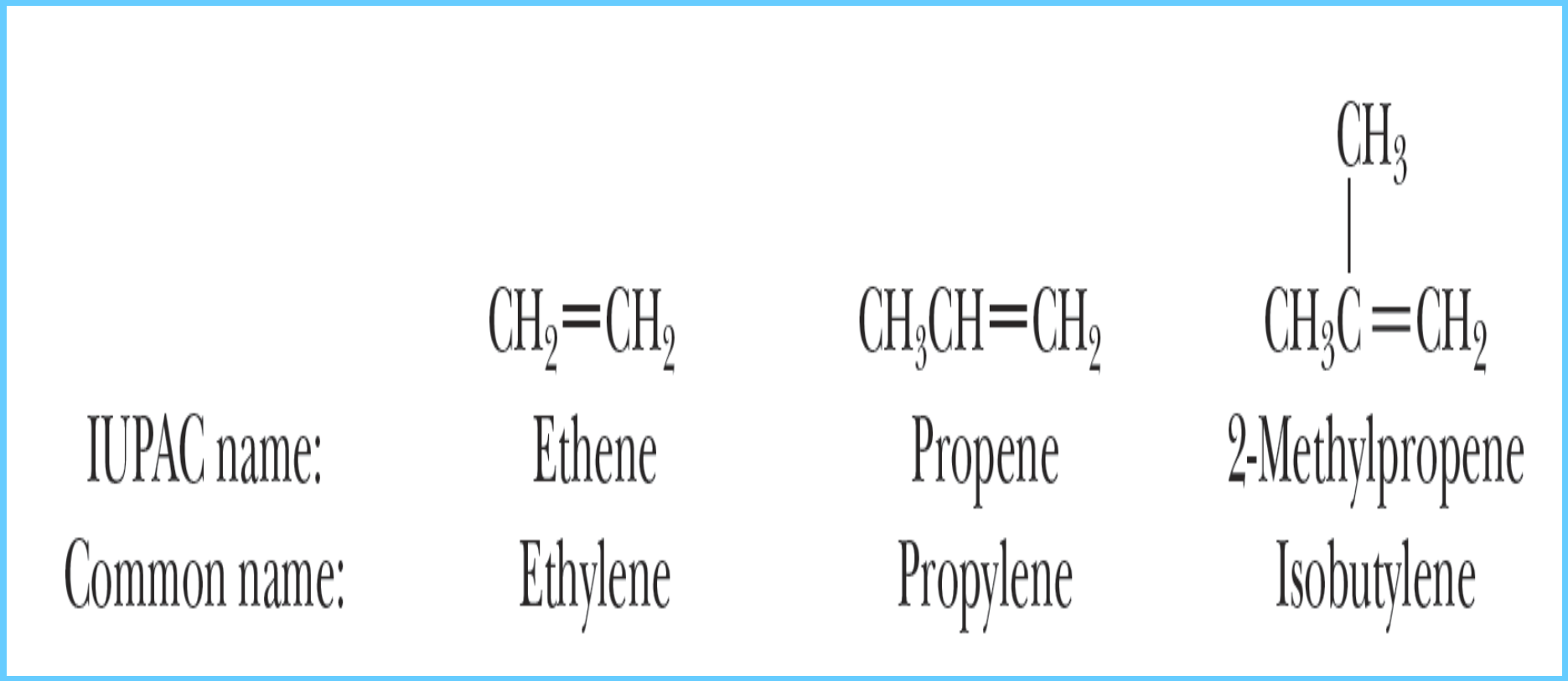
Nomenclature of Alkenes

- IUPAC nomenclature of alkenes



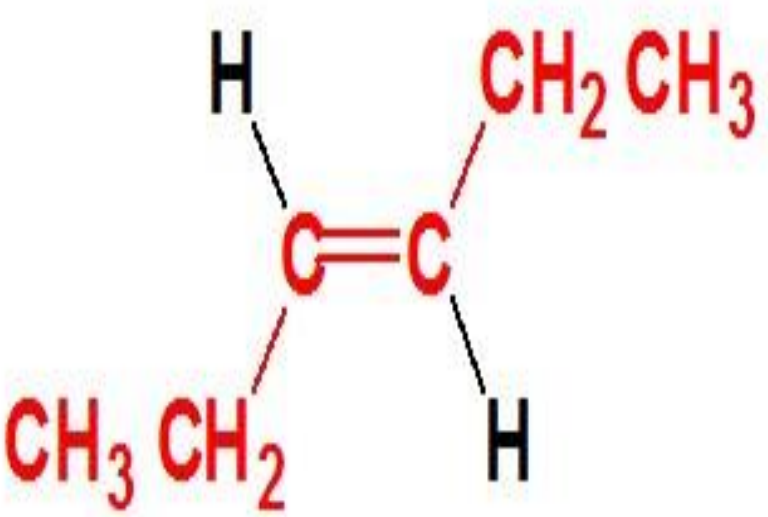
Nomenclature of Alkenes

- Some alkenes, particularly low-molecular-weight alkenes, are known almost exclusively by their common names.

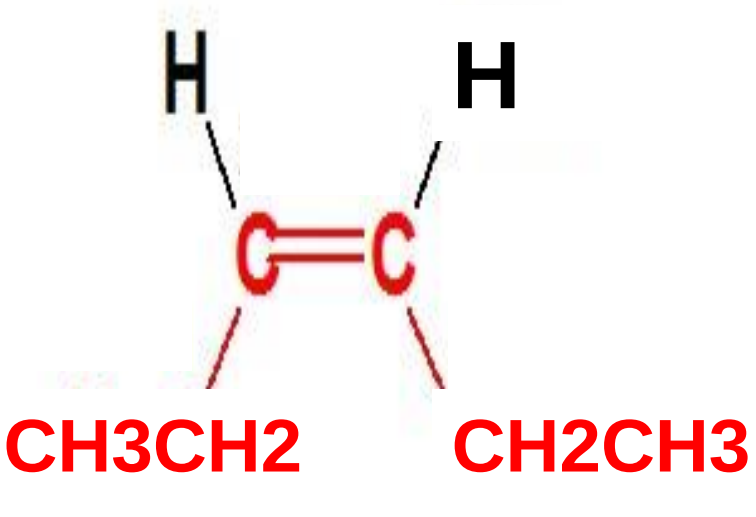


Configuration: *Cis-Trans*

- **The *cis-trans* system: Configuration is determined by the orientation of atoms of the main chain.**

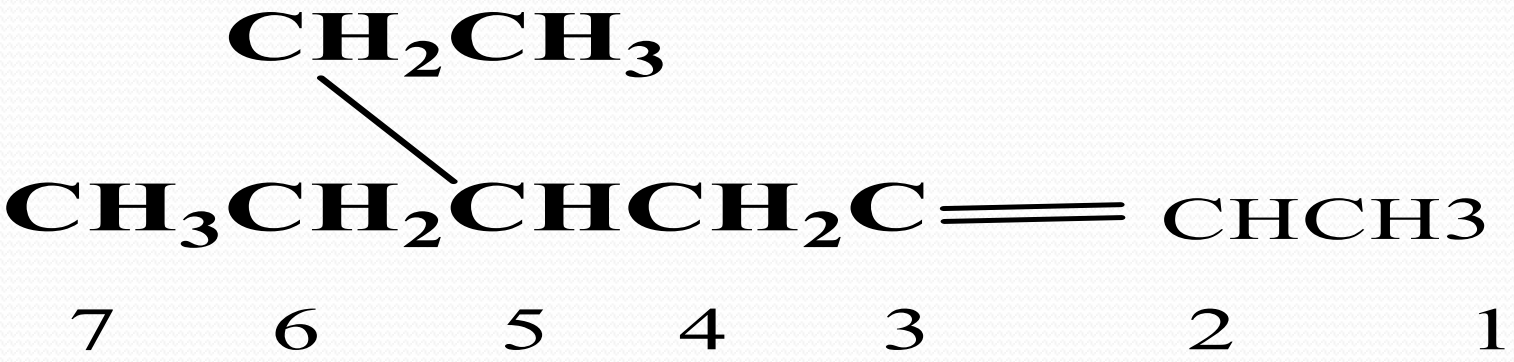


trans-3-Hexene



Cis-3-Hexene

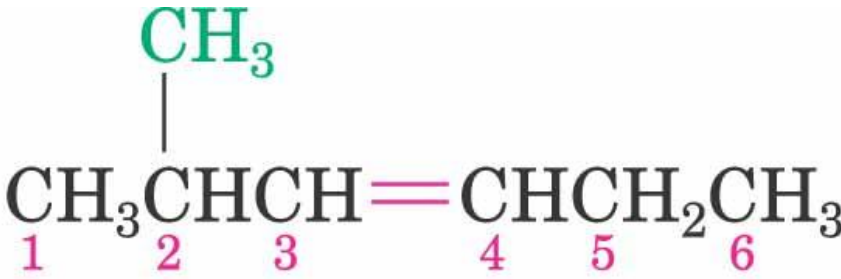
Example:

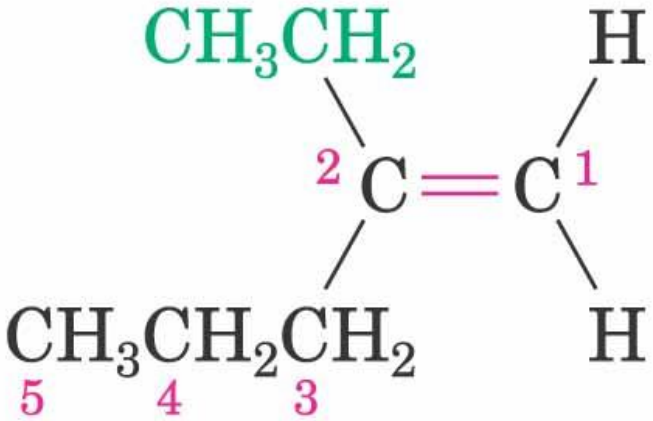


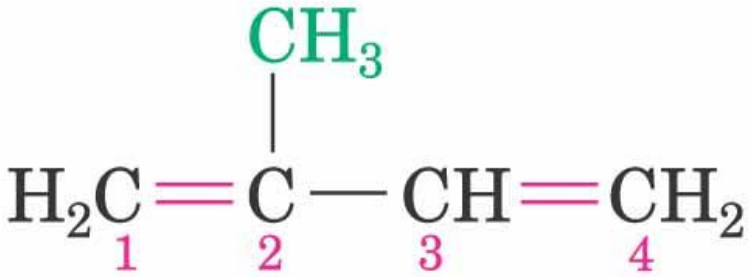
5-ethyle -2-heptene

-

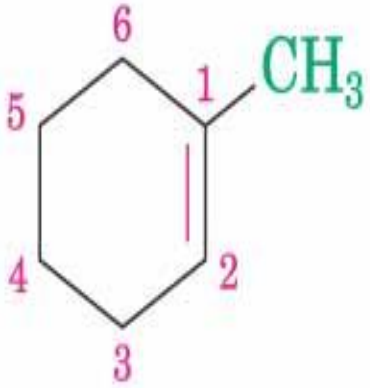

CH3CH2CH2CH=CHCH3
6 5 4 3 2 1

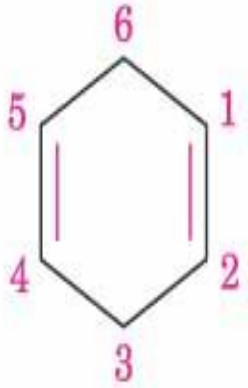

CH3
CH3CHCH=CHCH2CH3
1 2 3 4 5 6

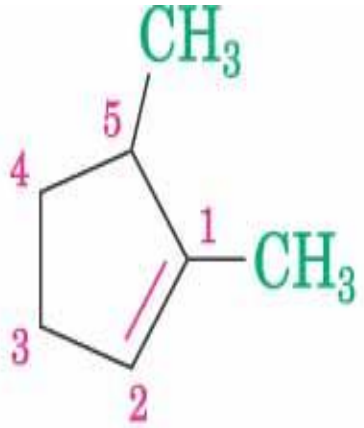

CH3CH2
H
2 C=C 1
CH3CH2CH2
H
5 4 3


CH3
H2C=C—CH=CH2
1 2 3 4

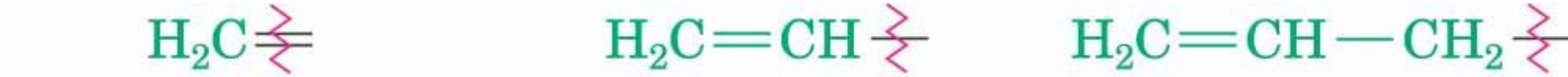
Cyclic alkenes



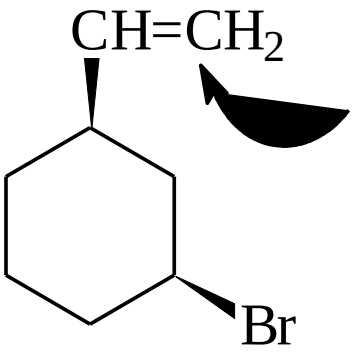




Alkyl Groups with π-Bonds

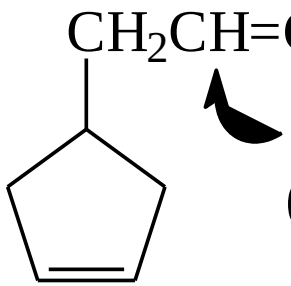


A *methylene* group **A *vinyl* group** **An *allyl* group**



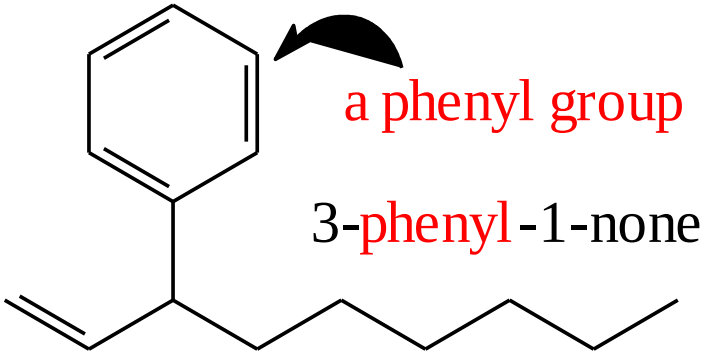
a vinyl group
(or ethenyl)

cis 1-bromo-3-vinyl cyclohexane



an allyl group
(or 2-propenyl)

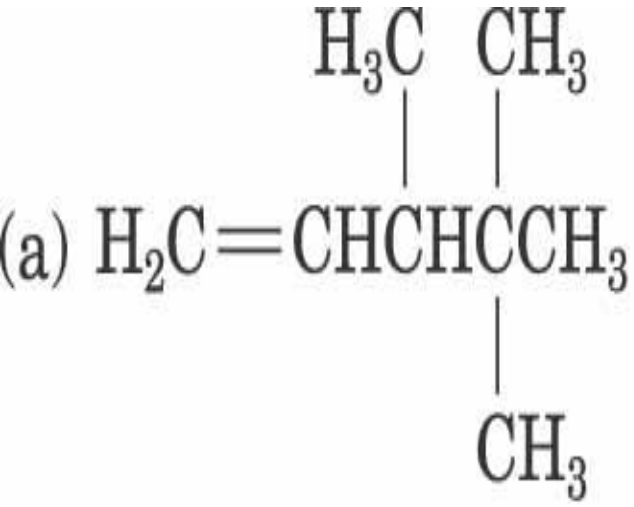
4-allyl cyclopentene

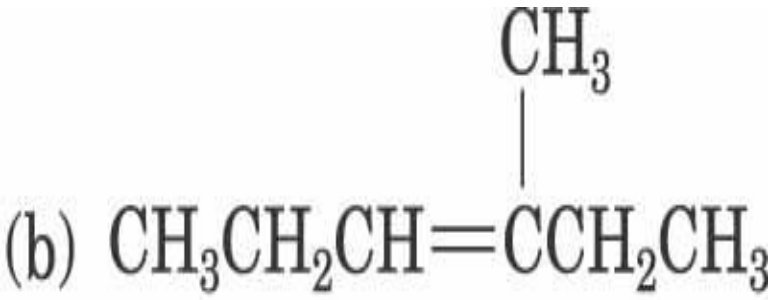


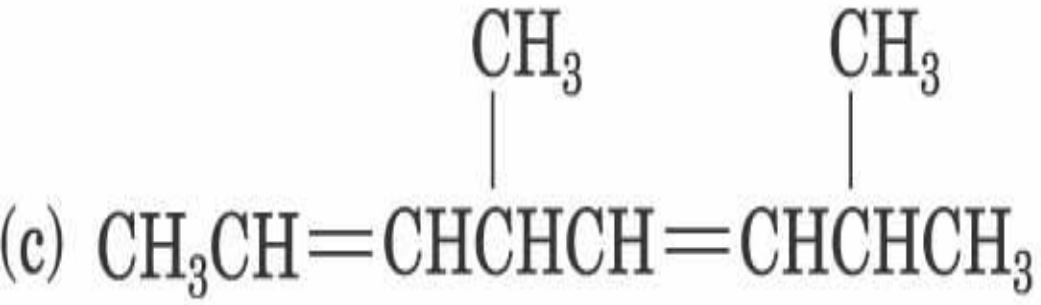
a phenyl group

3-phenyl-1-nonene

Name these Alkenes:

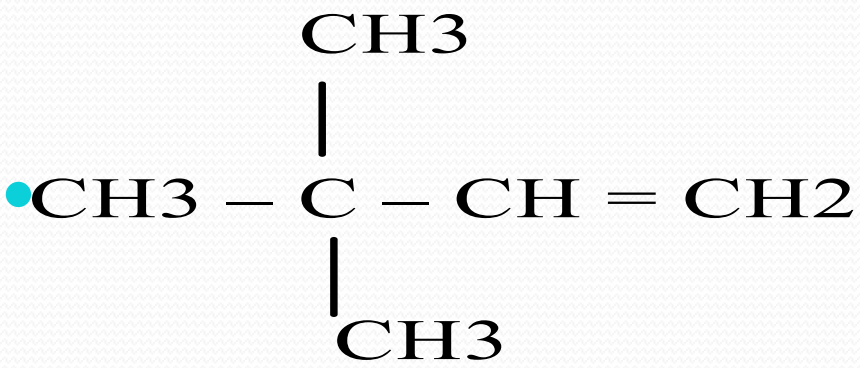




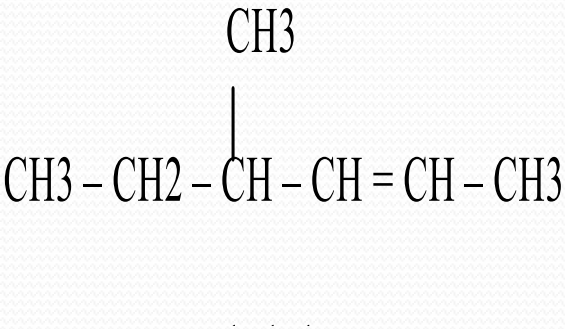


$CH_3 - CH_2 - CH = CH_2$

1-Butene



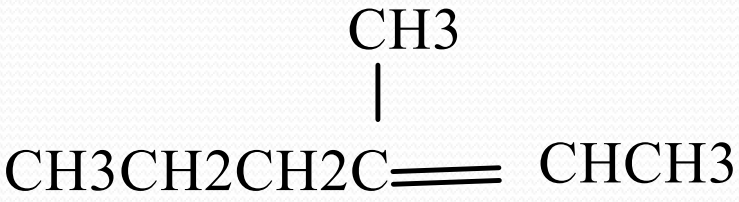
3,3-dimethyle butene

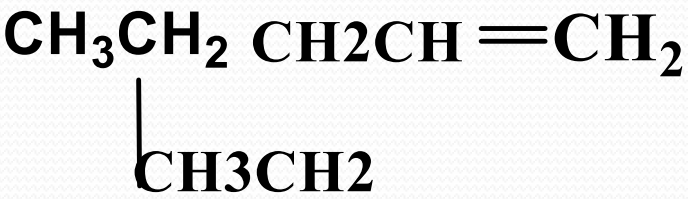


4-methyle-2-hexene

Home work

- Give the name of the following:

1- 

2- 

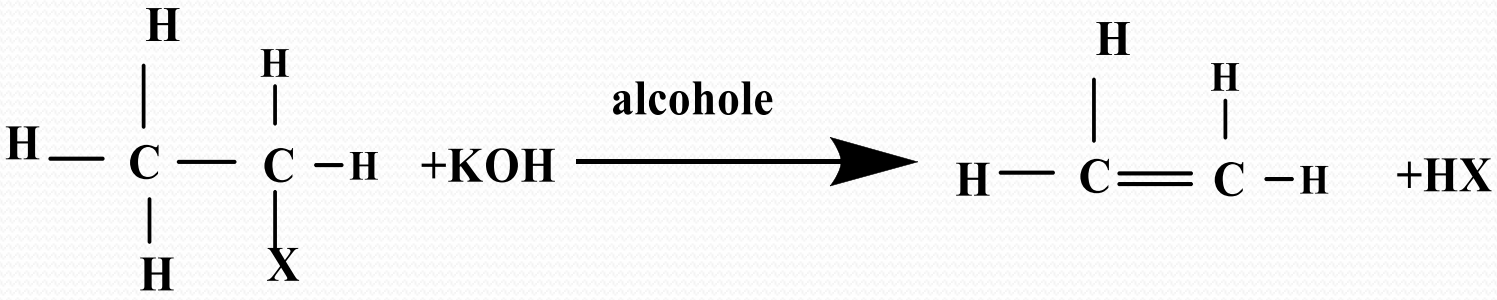
3- 

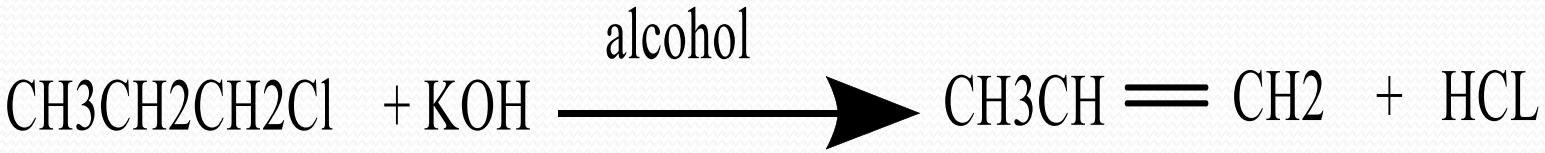
Physical properties

- 1-They are insoluble in water,but quite soluble in non polar solvents like benzene, ether, chloroform.
- 2-They are less dense than water.
- 3-The(B.P.) rise with increasing MWt. or chain no.Branching lower the B.P. the rise 20-30C° for each added carbon.
- 4-Complexes which contain 4 carbon atom (2C-4C)are gases while pentene,hexane….etc.are liquid.
- 5- Cis-trans isomer,which are chemically similar,but there are difference between its physical properties

Preparation of Alkenes

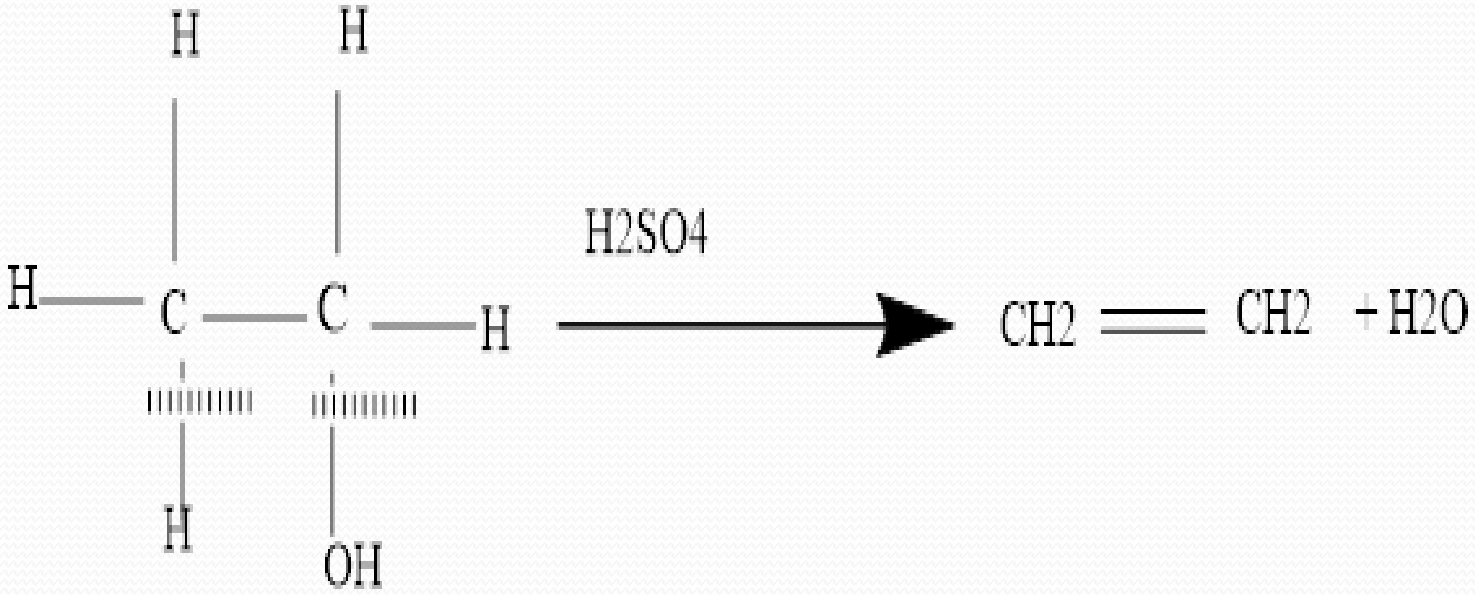
- **1) Dehydrohalogenation of alkyl halides**





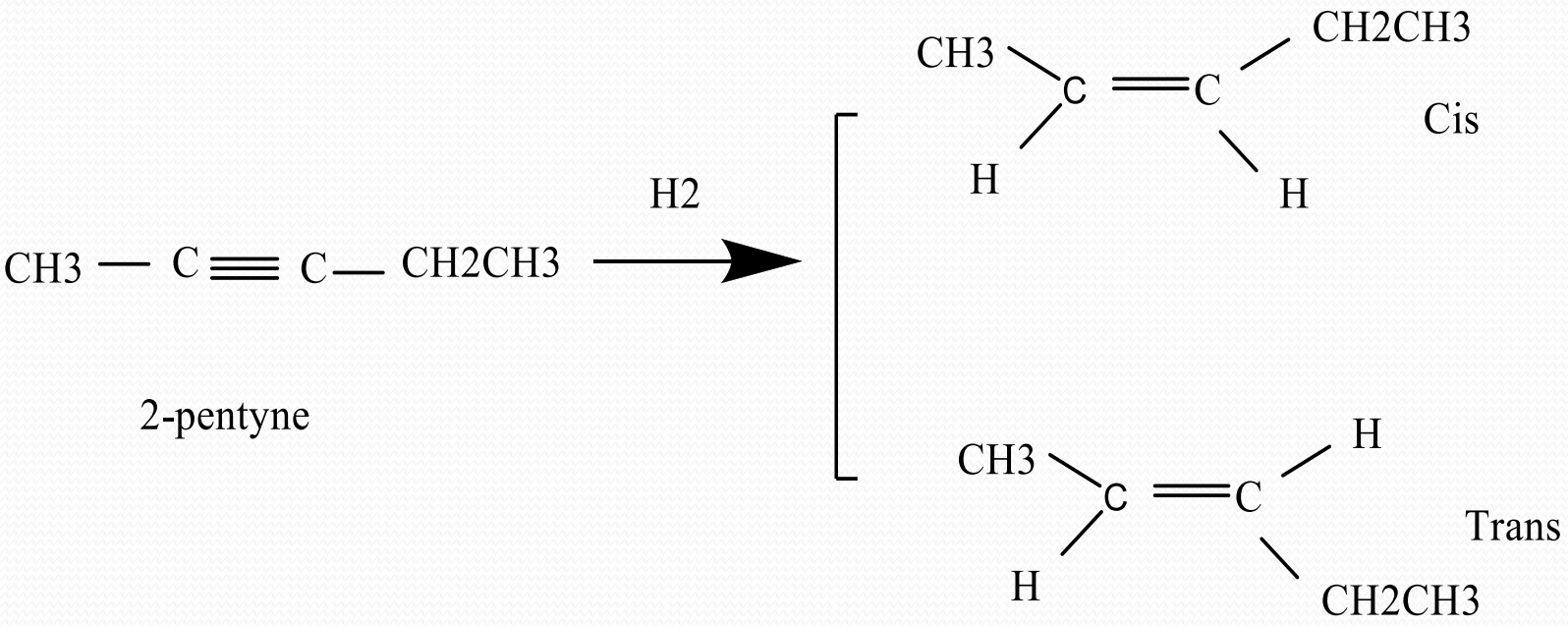
Preparation of Alkenes

- **2) Dehydration alcohol سحب جزينة ماء من الكحول**



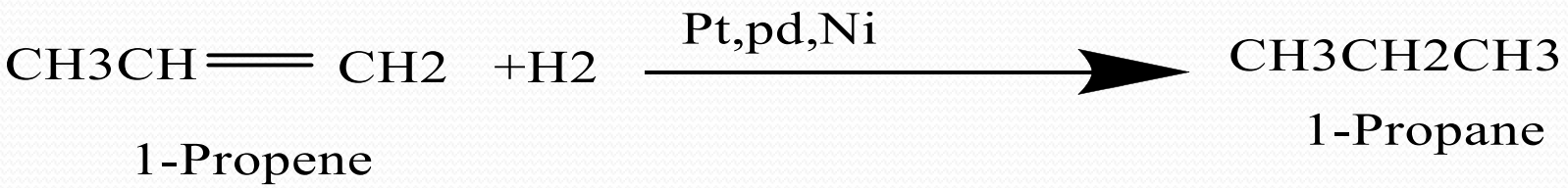
Preparation of Alkenes

- 3) **Reduction of alkynes اختزال الالكاينات**
-

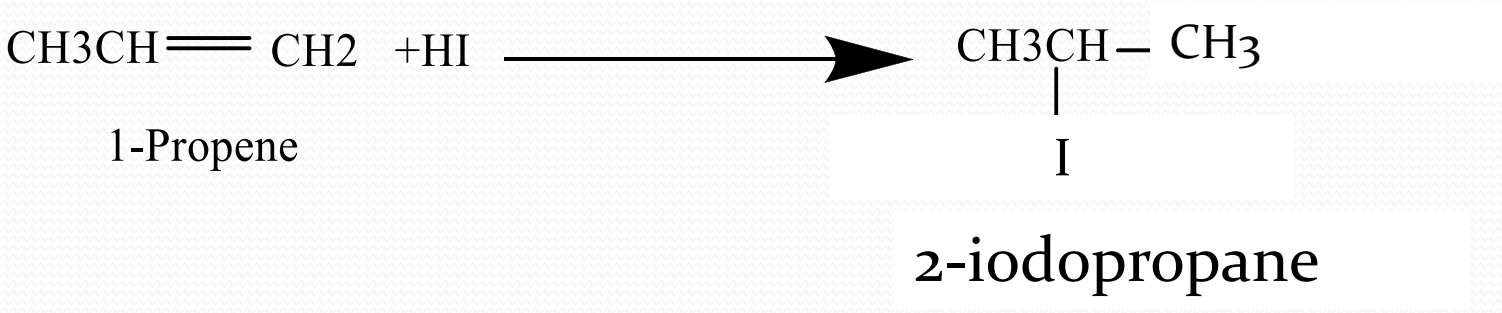


Reactions of alkenes تفاعلات الالكينات

1/ Addition of hydrogen



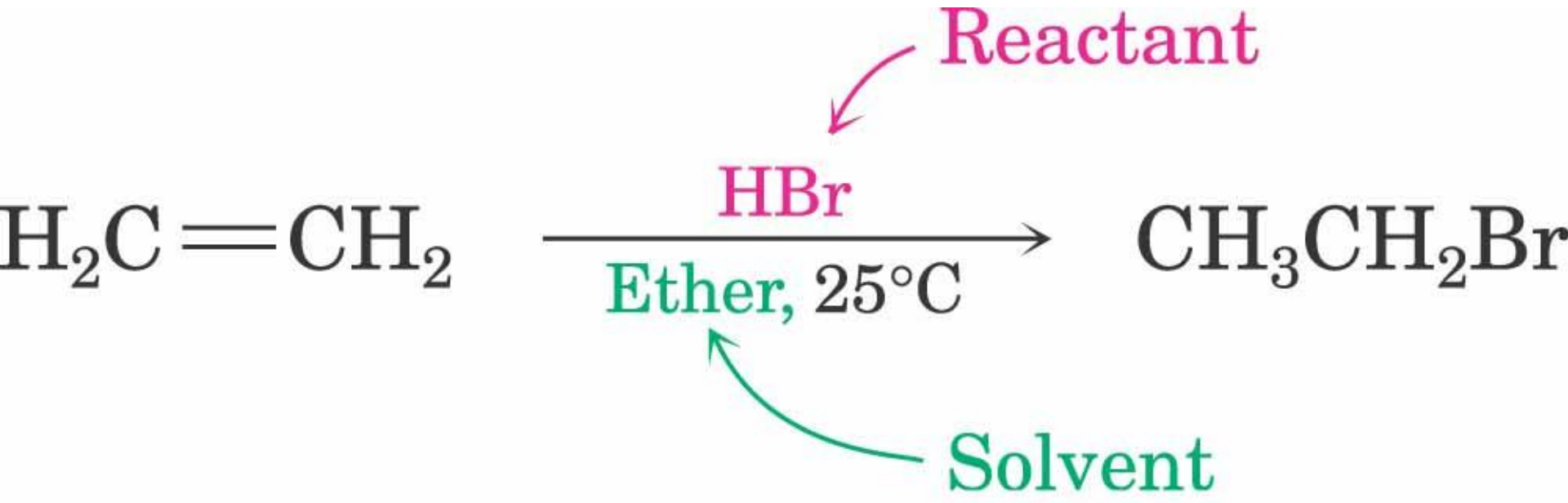
2/Addition of hydrogen halids



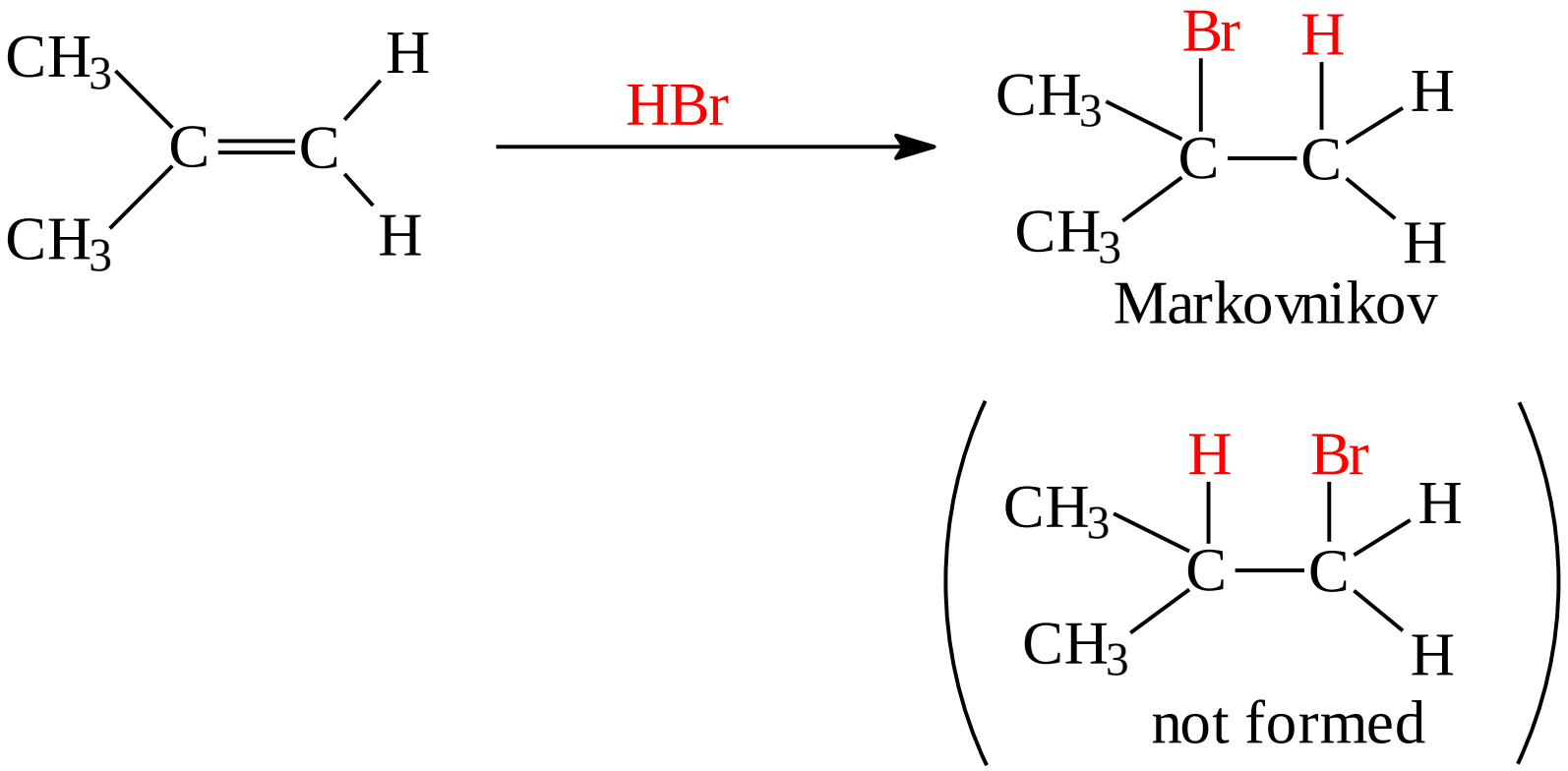
Markovnikov's Rule

The addition of H-X across a double bond results in the more highly substituted alkyl halide as the major product.

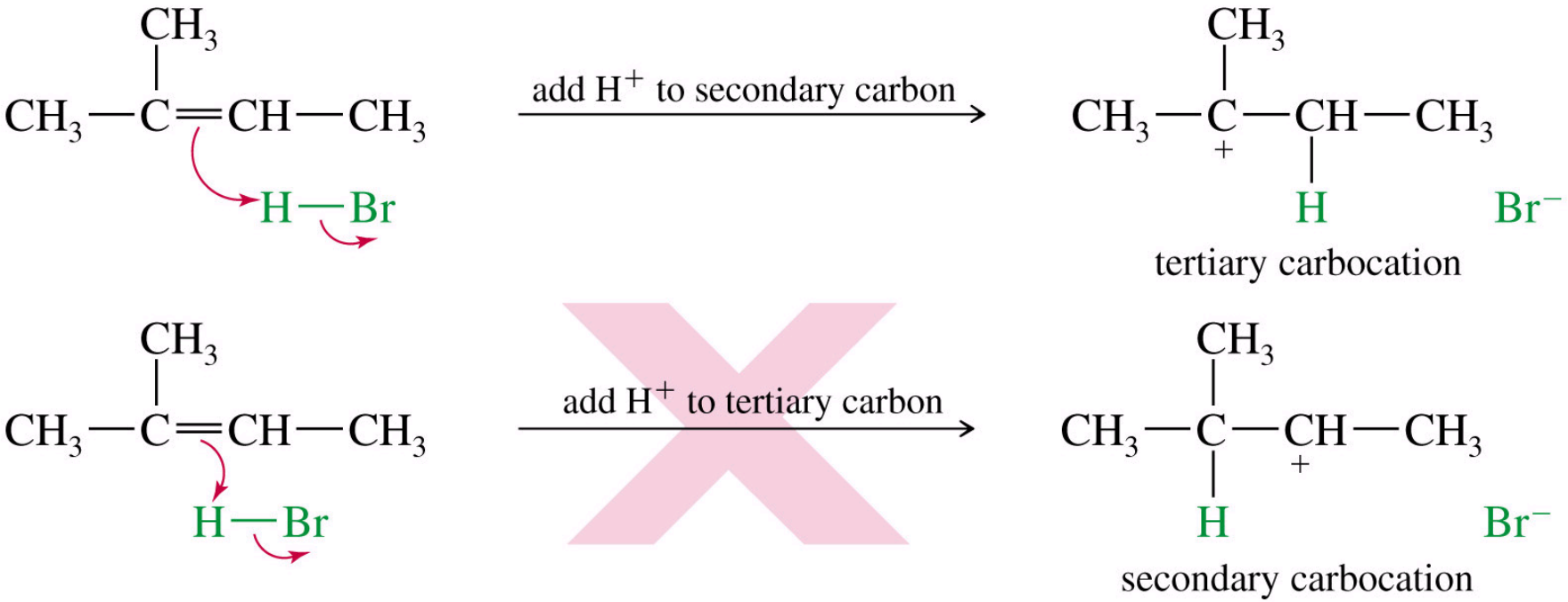
Depicting a Reaction

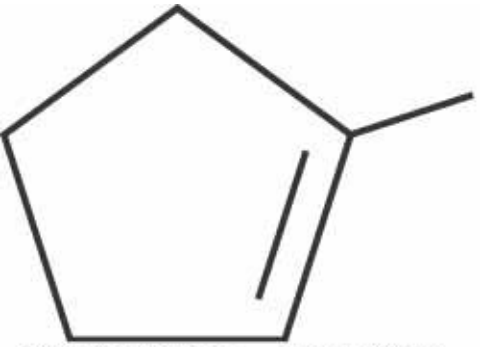


Addition of HBr or HCl
Markovnikov Addition

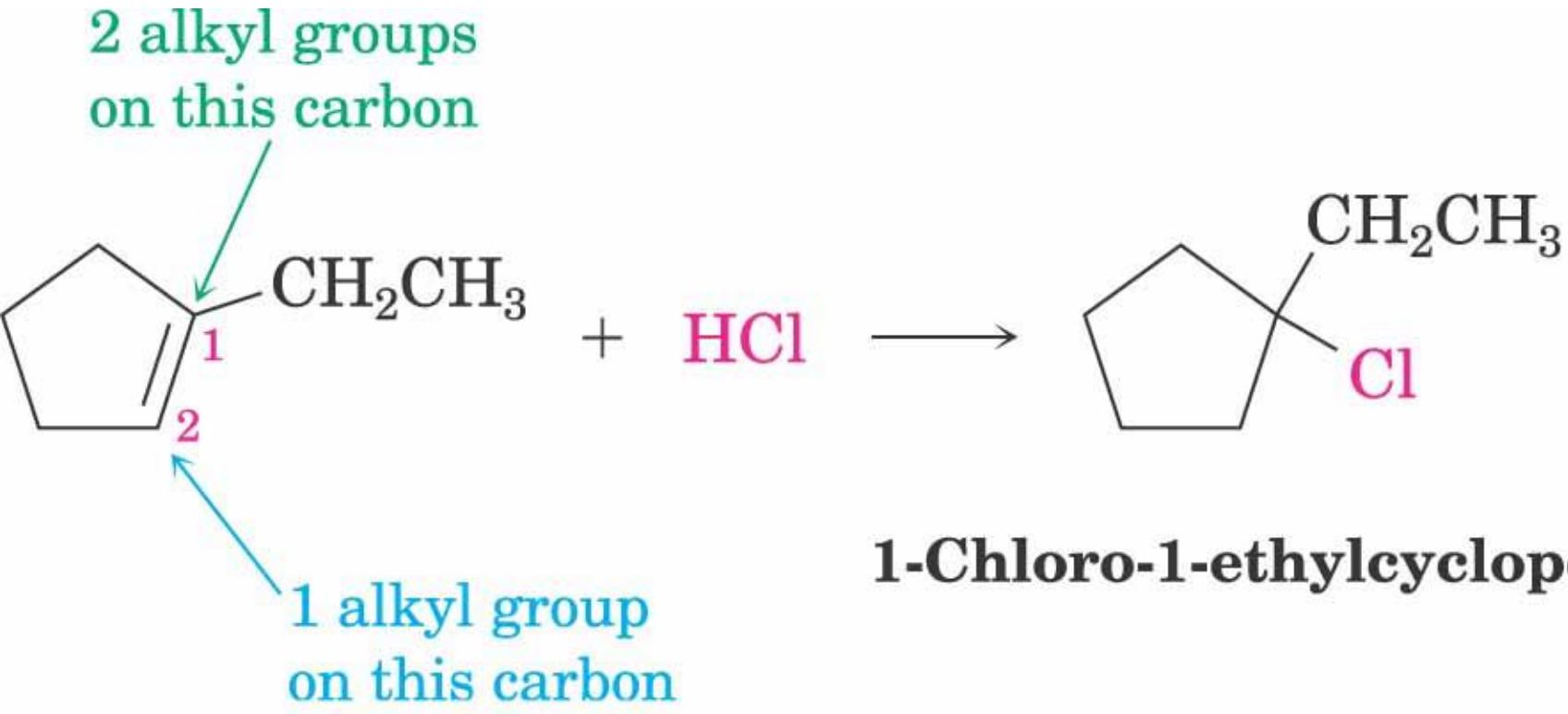


3º Carbocation forms Preferentially





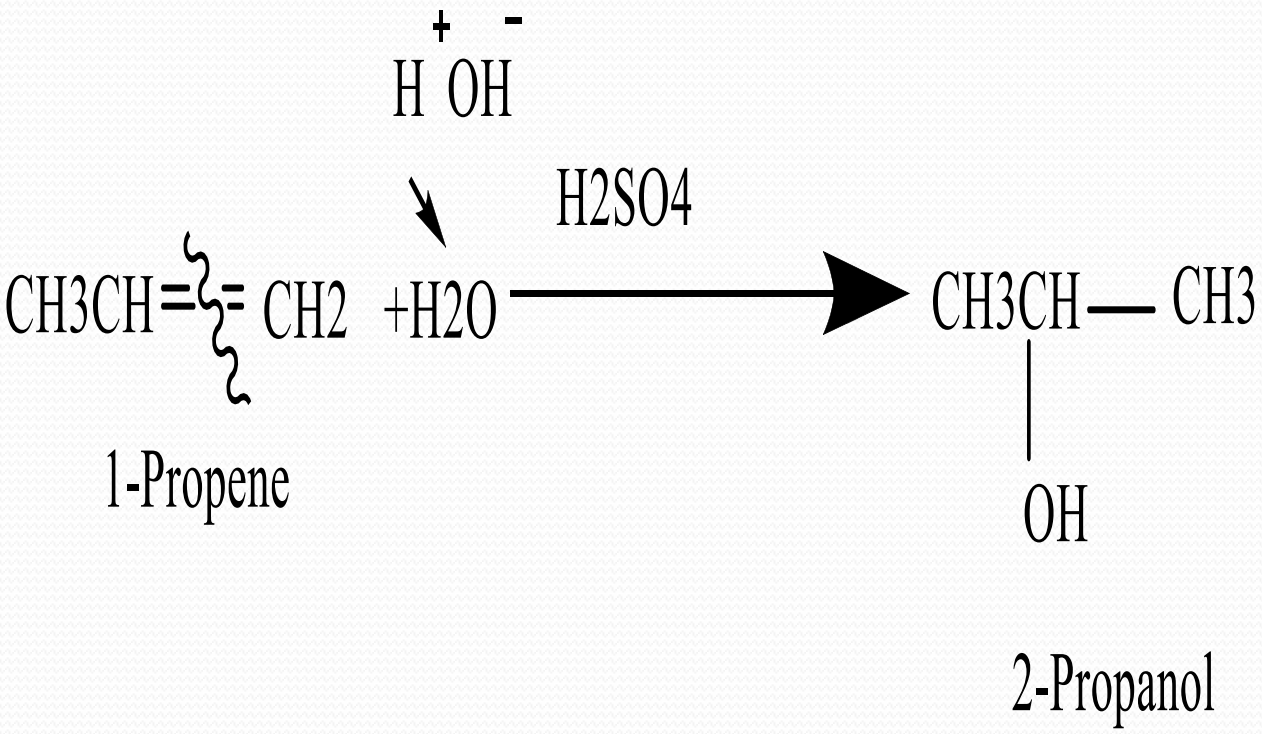
CH_2CH_3 + HCl ⟶ ?



1-Chloro-1-ethylcyclopentane

Reactions of alkenes تفاعلات الالكينات

3/Addition of water (hydration)



Lec -3-

Alkynes

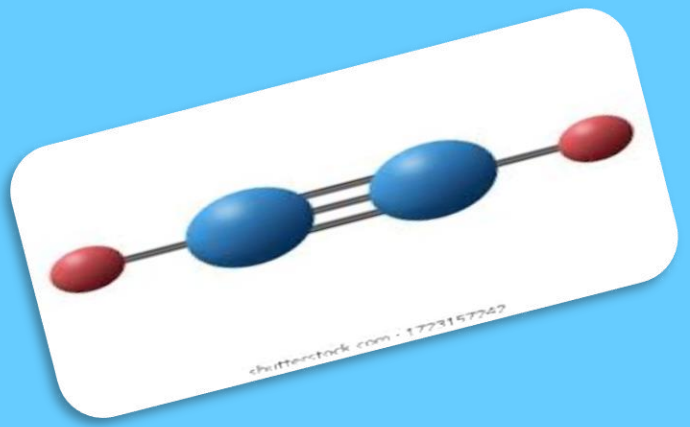
.1Introduction

.2Nomenclature of Alkynes

.3Physical Properties of Alkynes

.4Preparation of Alkynes

.5Reactions of Alkynes

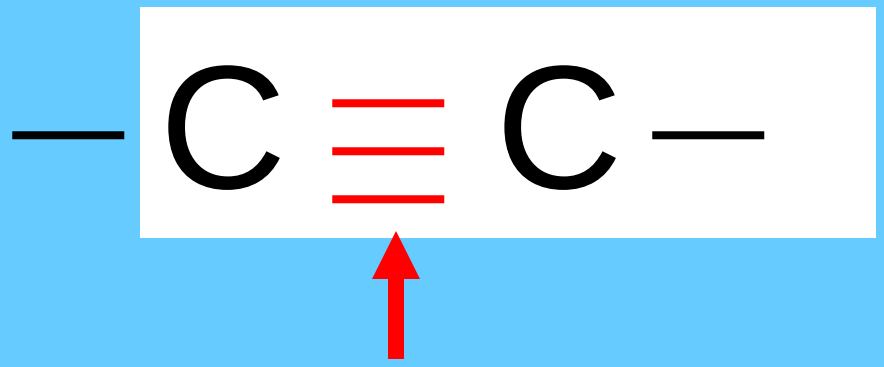


Alk*ynes* –

a series of unsaturated hydrocarbons that contain 1 triple bond.

- Also called the acetylene series

- General formula C_nH_{2n-2}



Alkynes

Table Q
Homologous Series of Hydrocarbons

Name	General Formula	Examples	
		Name	Structural Formula
alkynes	C_nH_{2n-2}	ethyne	H—C≡C—H

Table P
Organic Prefixes

Prefix	Number of Carbon Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

- C_2H_2 = Ethyne
- C_3H_4 = Propyne
- C_4H_6 = Butyne
- C_5H_8 = Pentyne

Structure of Alkynes

The functional group of an alkyne is a carbon-carbon triple bond.

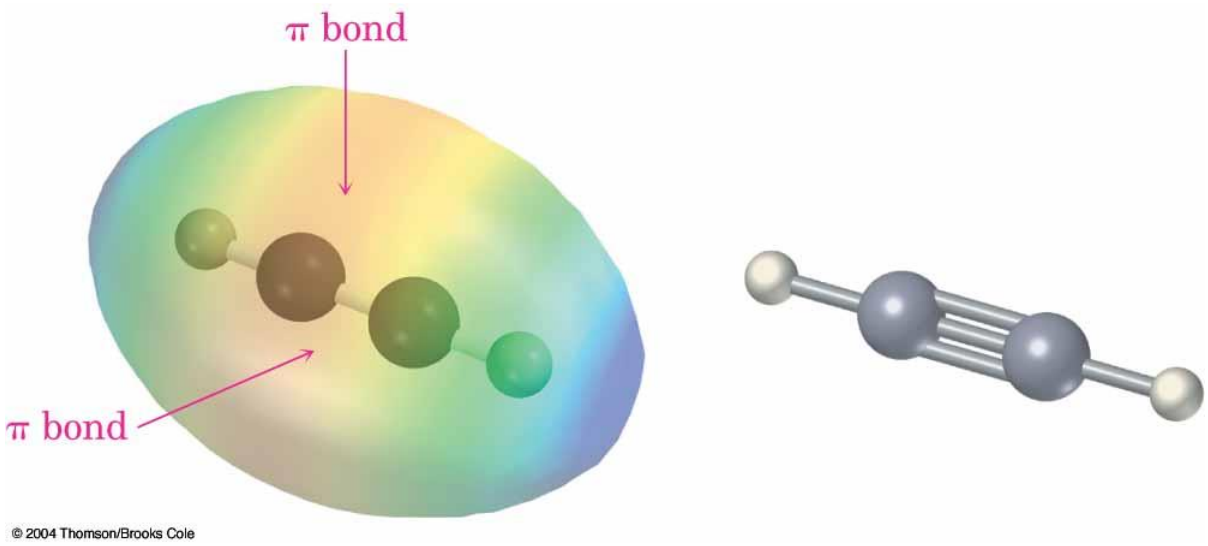
A triple bond consists of:

One s bond formed by the overlap of *sp* hybrid orbitals.

Two p bonds formed by the overlap of sets of parallel 2*p* orbitals.

Electronic Structure of Alkynes

- The triple bond is shorter and stronger than single or double
- Breaking a π bond in acetylene (HCCH) requires 318 kJ/mole (in ethylene it is 268 kJ/mole)

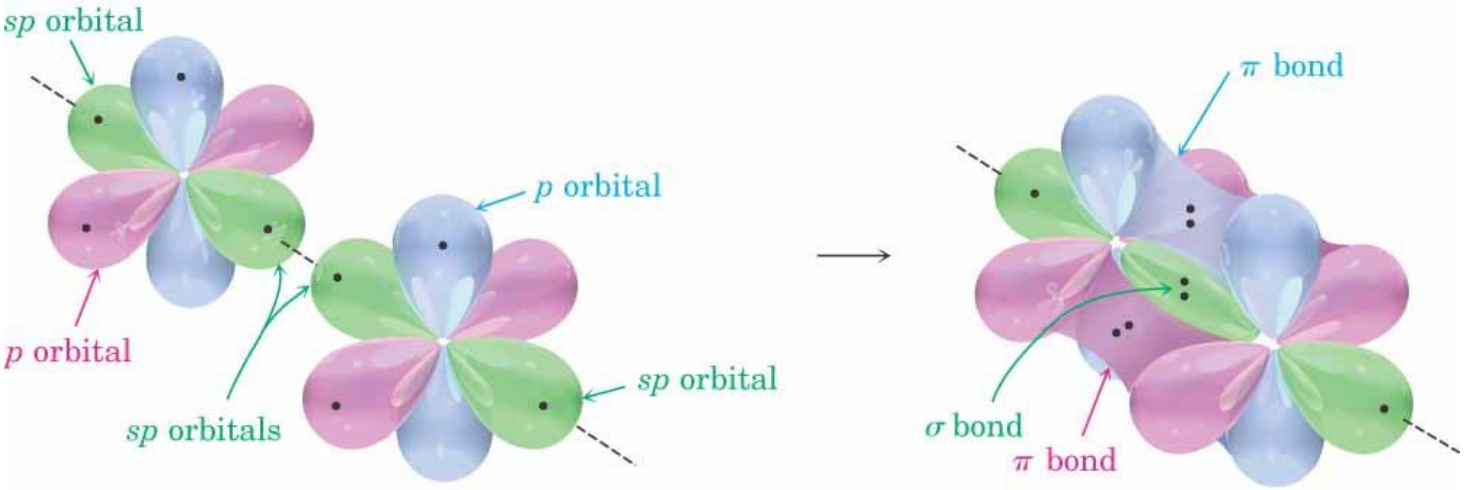


Electronic Structure of Alkynes

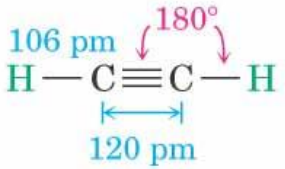
- Carbon-carbon triple bond results from an sp orbital on each C forming a sigma bond and unhybridized p_X and p_y orbitals forming a π bond

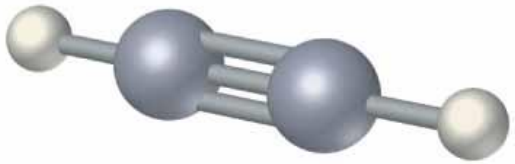
- The remaining sp orbitals form bonds to other atoms at 180º (linear geometry) to the C-C triple bond.

Electronic Structure of Alkynes



Carbon–carbon triple bond

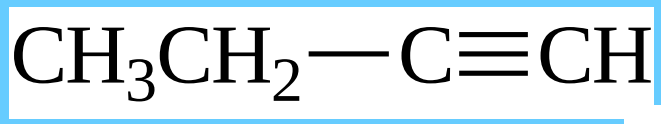




Nomenclature

IUPAC: alkyne
common: alkyl acetylene

- an internal alkyne



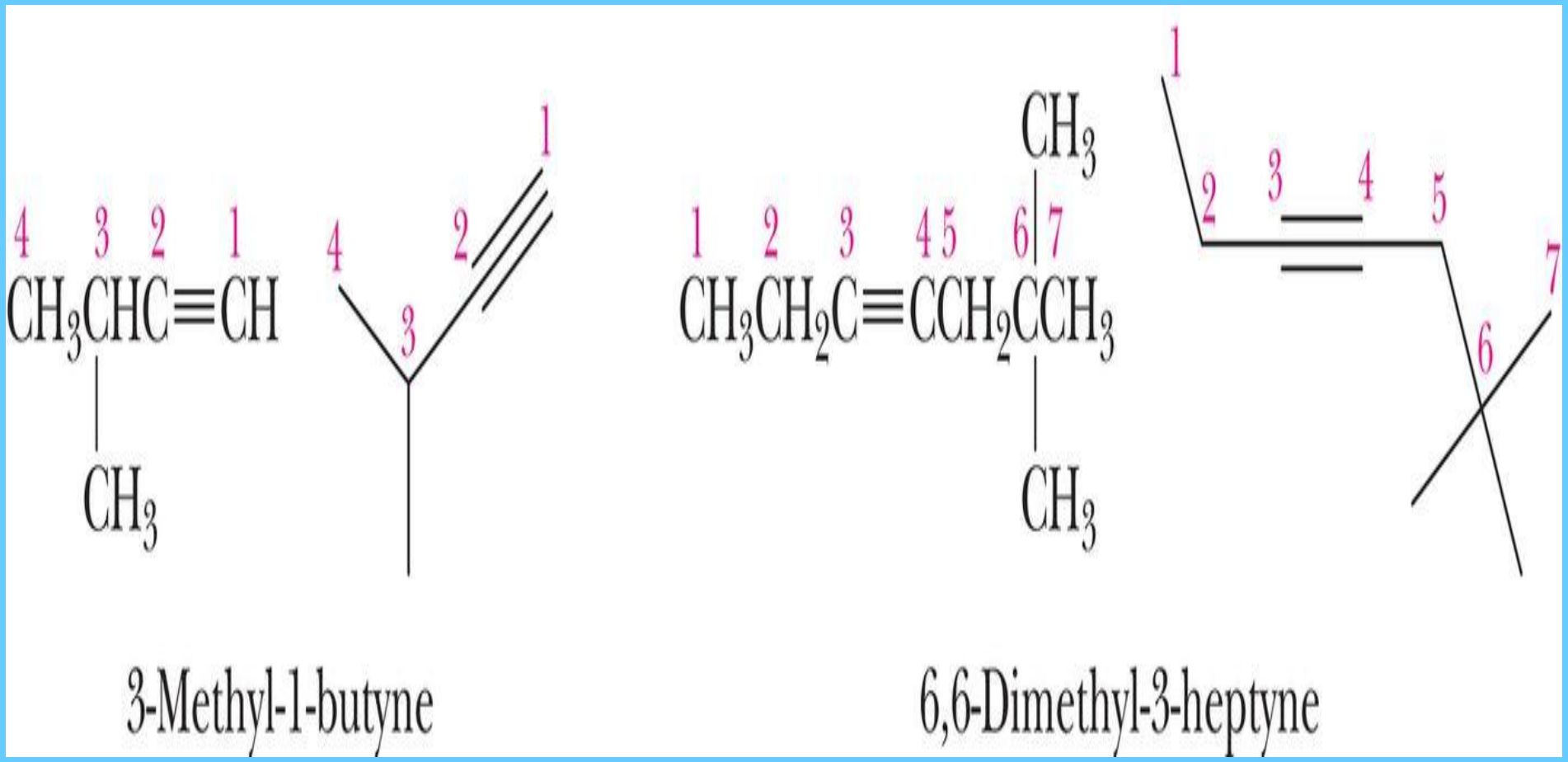
- a terminal alkyne

Nomenclature of Alkynes

- **IUPAC nomenclature of alkynes**
  - Use the infix **-yne** to show the presence of a carbon-carbon triple bond.
  - Number the parent chain to give the first carbon of the triple bond the lower number.
  - Follow IUPAC rules for numbering and naming substituents.

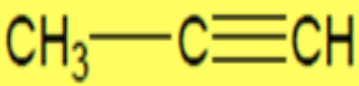
Nomenclature of Alkynes

- **IUPAC nomenclature of alkynes**



Alkynes : Common Nomenclature

Ethyne
[Acetylene]

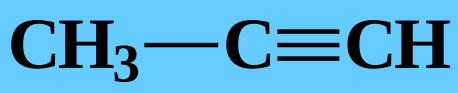


Propyne
[Methyl acetylene]

2-Butyne
[Dimethyl acetylene]

	$CH_3C{\equiv}CH$	$CH_3C{\equiv}CCH_3$	$CH_2{=}CHC{\equiv}CH$
IUPAC name:	Propyne	2-Butyne	1-Buten-3-yne
Common name:	Methylacetylene	Dimethylacetylene	Vinylacetylene

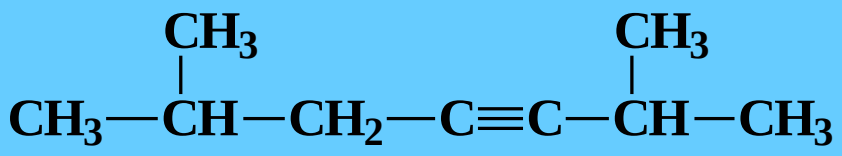
Name these:



propyne

5-bromo-2-pentyne

5-bromopent-2-yne

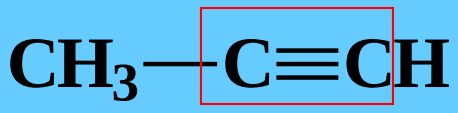


2,6-dimethyl-3-heptyne

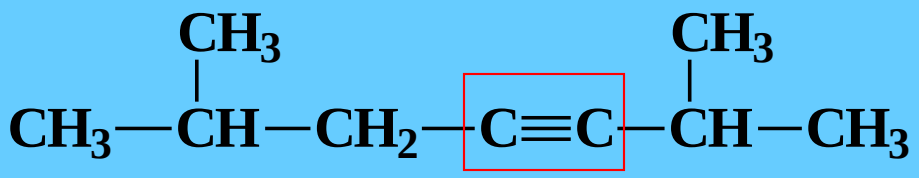
2,6-dimethylpept-3-yne

Common Names

Named as substituted acetylene.



methylacetylene
(terminal alkyne)



isobutylisopropylacetylene
(internal alkyne)

Physical Properties

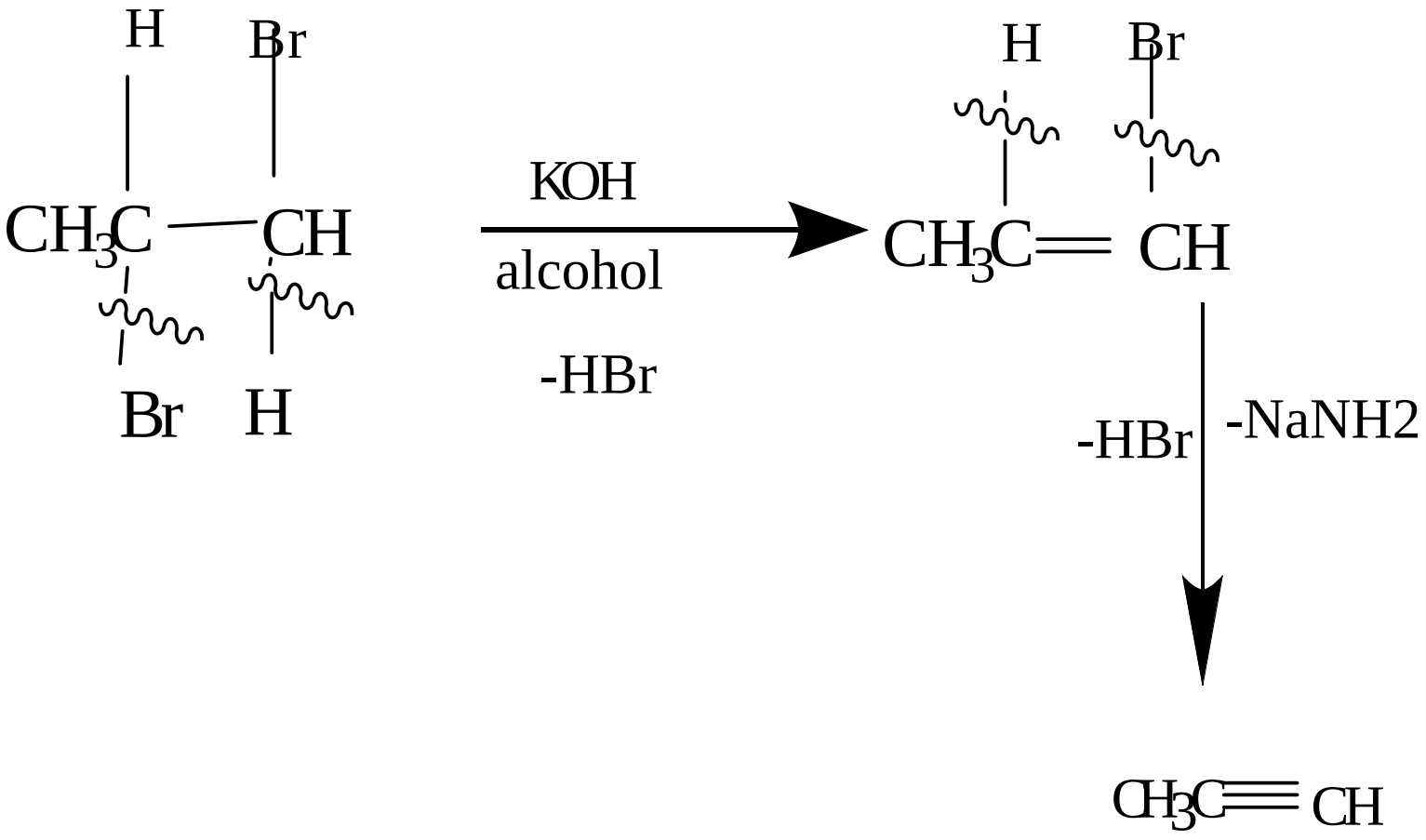
- Nonpolar, insoluble in water.
- Soluble in most organic solvents.
- Boiling points similar to alkane of same size.
- Less dense than water.
- Up to 4 carbons, gas at room temperature.

Preparation of Alkynes

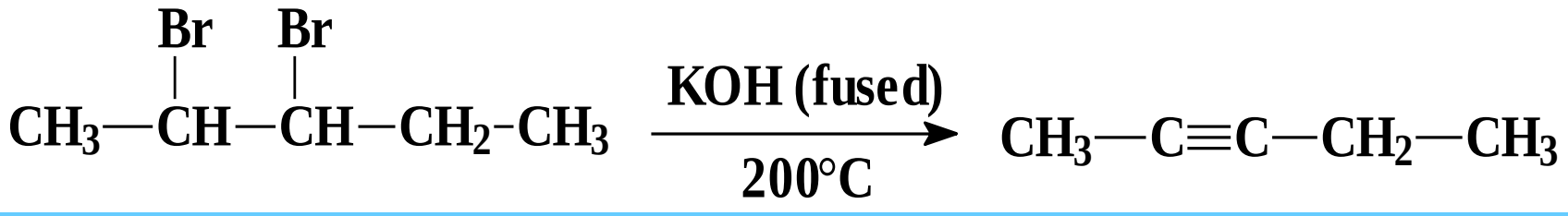
Synthesis by Elimination

- Removal of two molecules of HX from a vicinal dihalide produces an alkyne.
- First step (-HX) is easy, forms vinyl halide.
- Second step, removal of HX from the vinyl halide requires very strong base and high temperatures.

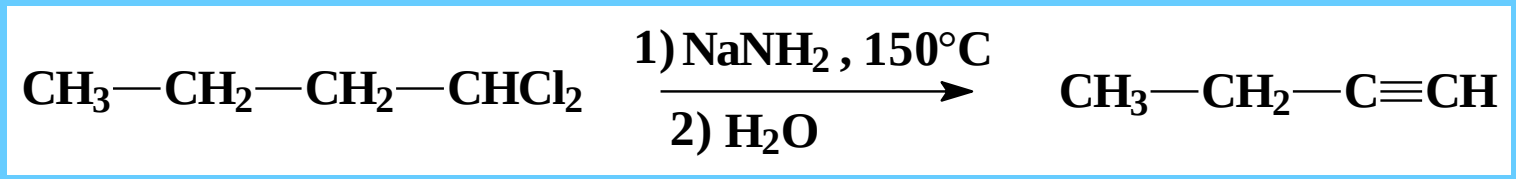
1-Dehydrohalogenations of alkyl di halides



Reagents for Elimination



- Molten KOH or alcoholic KOH at 200°C favors an internal alkyne.
- Sodium amide, $NaNH_2$, at 150°C, followed by water, favors a terminal alkyne.



2-Hydration of Calcium Carbide

$$CaO + 3C \xrightarrow{\Delta} CaC_2 + CO$$

$$CaC_2 + 2H_2O \longrightarrow HC \equiv CH + Ca(OH)_2$$

Reaction of Alkynes

Addition Reactions

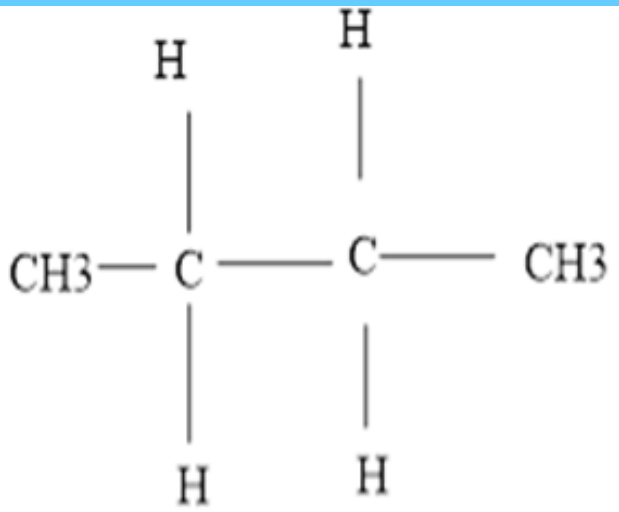
- Similar to addition to alkenes.
- Pi bond becomes two sigma bonds.
- Usually exothermic.
- One or two molecules may add.

TABLE 9-3 Approximate Bond Energies of Carbon–Carbon Bonds

Bond	Total Energy	Class of Bond	Approximate Energy
C—C	347 kJ (83 kcal)	alkane sigma bond	347 kJ (83 kcal)
C=C	611 kJ (146 kcal)	alkene pi bond	264 kJ (63 kcal)
C≡C	837 kJ (200 kcal)	second alkyne pi bond	226 kJ (54 kcal)

1-Addition of Hydrogen

- Three reactions:
- Add lots of H_2 with metal catalyst (Pd, Pt, or Ni) to reduce alkyne to alkane, completely saturated.
- Use a special catalyst, Lindlar's catalyst, to convert an alkyne to a **cis**-alkene.
- React the alkyne with sodium in liquid ammonia to form a **trans**-alkene.

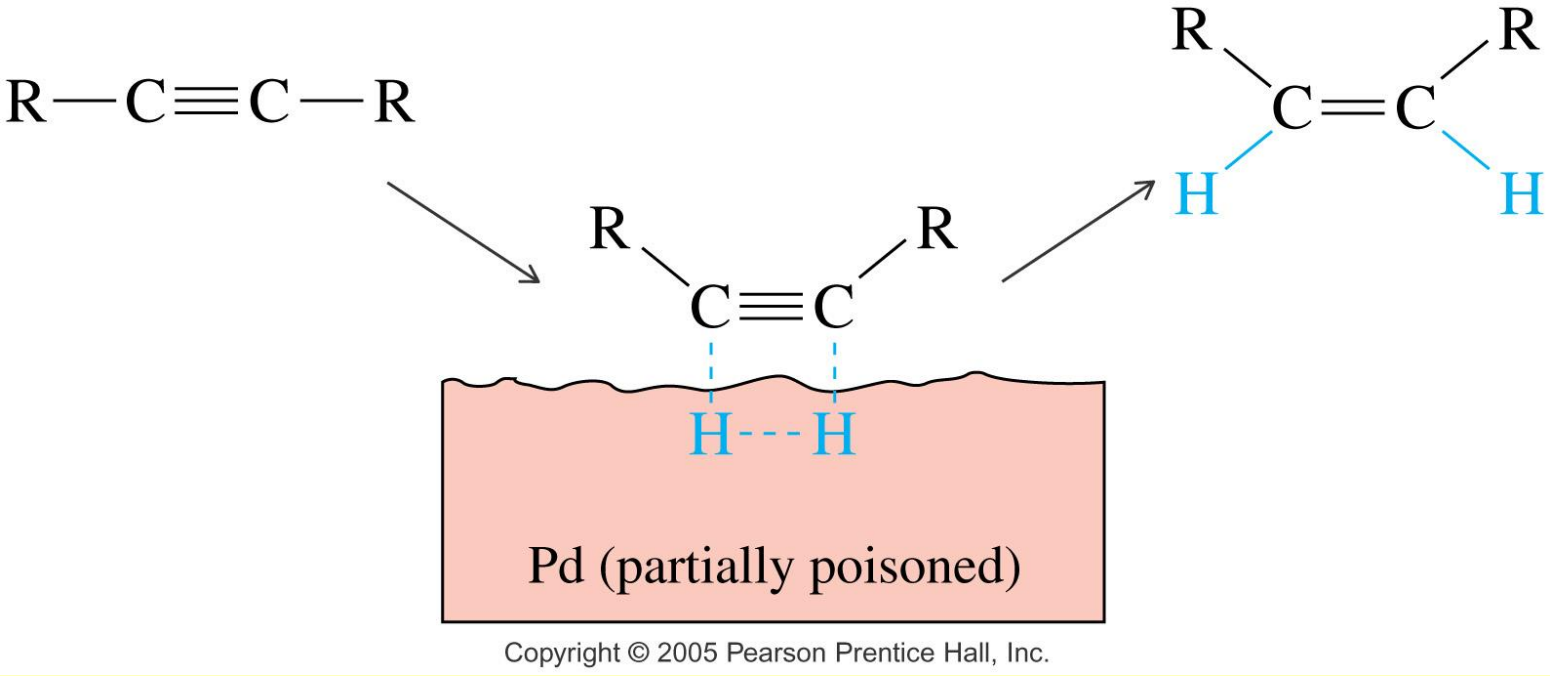
1- $CH_3C \equiv C-CH_3$ $\xrightarrow[Ni]{2H_2}$ 

2-Butyne

butane

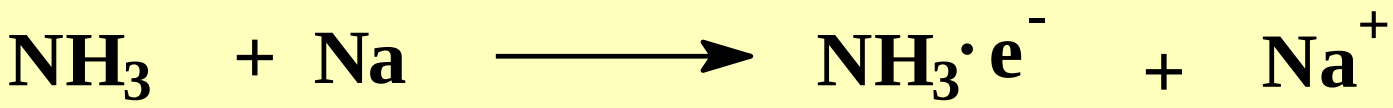
Lindlar's Catalyst

- Powdered $BaSO_4$ coated with Pd, poisoned with quinoline.
- H_2 adds syn, so **cis**-alkene is formed.



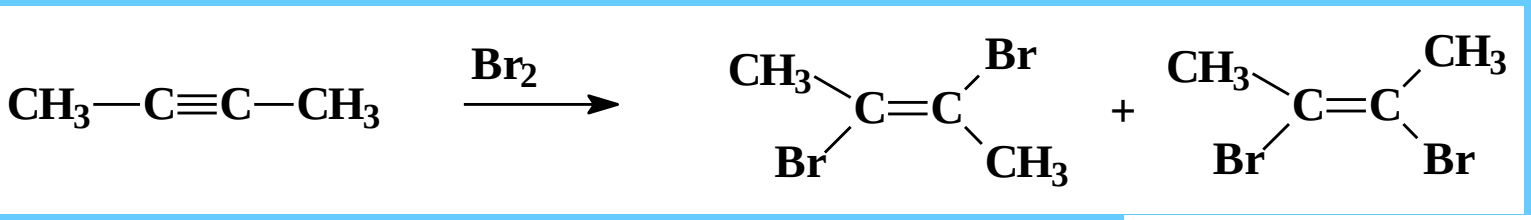
Na in Liquid Ammonia

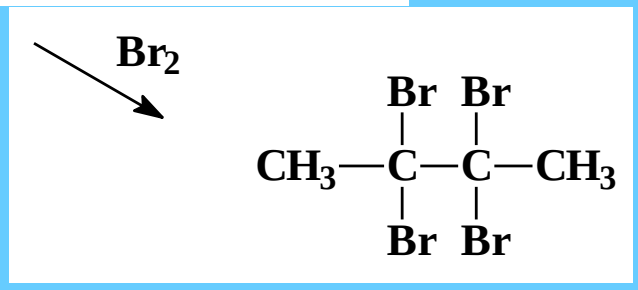
- Use dry ice to keep ammonia liquid.
- As sodium metal dissolves in the ammonia, it loses an electron.
- The electron is solvated by the ammonia, creating a deep blue solution.



2-Addition of Halogens

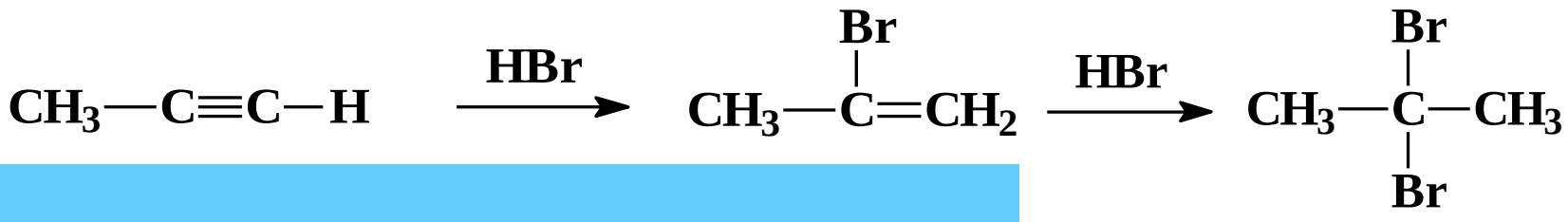
- Cl_2 and Br_2 add to alkynes to form vinyl dihalides.
- May add symmetrically or anti symmetrically, so product is mixture of **cis** and **trans** isomers.
- Difficult to stop the reaction at dihalide.



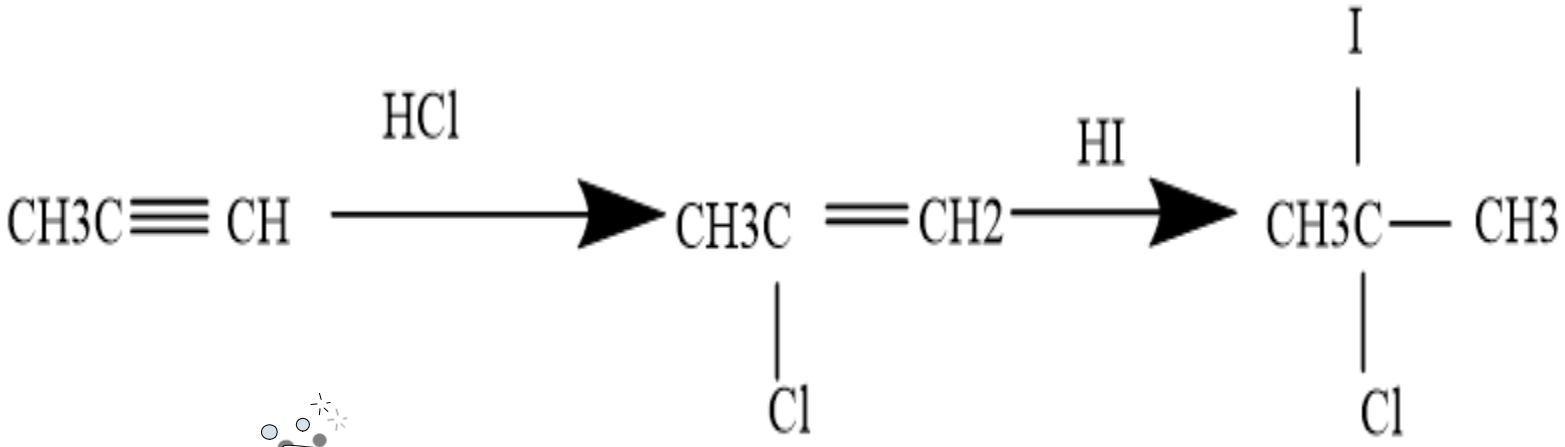


3-Addition of HX

- HCl, HBr, and HI add to alkynes to form vinyl halides.
- For terminal alkynes, Markovnikov product is formed.
- If two moles of HX is added, product is a geminal dihalide.



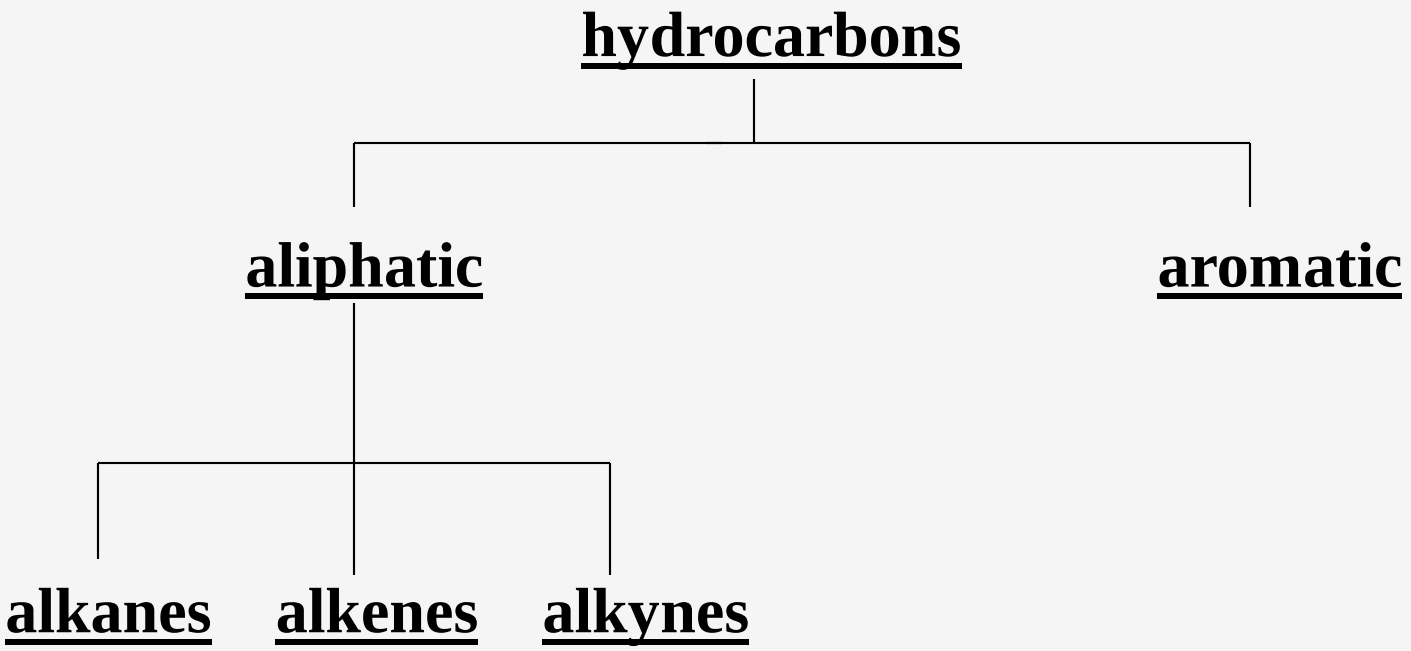
-Addition of hydro halides:



Lec-4-

Aromatic Hydrocarbon

Aromaticity



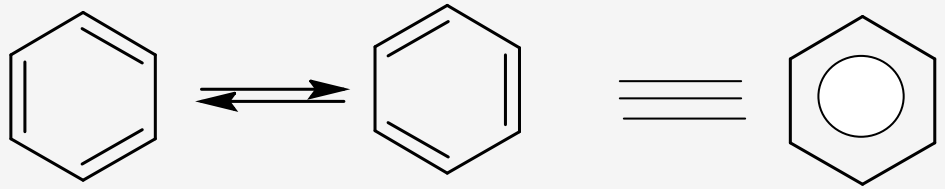
Aliphatic compounds: open-chain compounds and ring compounds that are chemically similar to open-chain compounds. Alkanes, alkenes, alkynes, dienes, alicyclics, etc.

Aromatic compounds: unsaturated ring compounds that are far more stable than they should be and resist the addition reactions typical of unsaturated aliphatic compounds. Benzene and related compounds.

Aromatic Hydrocarbons

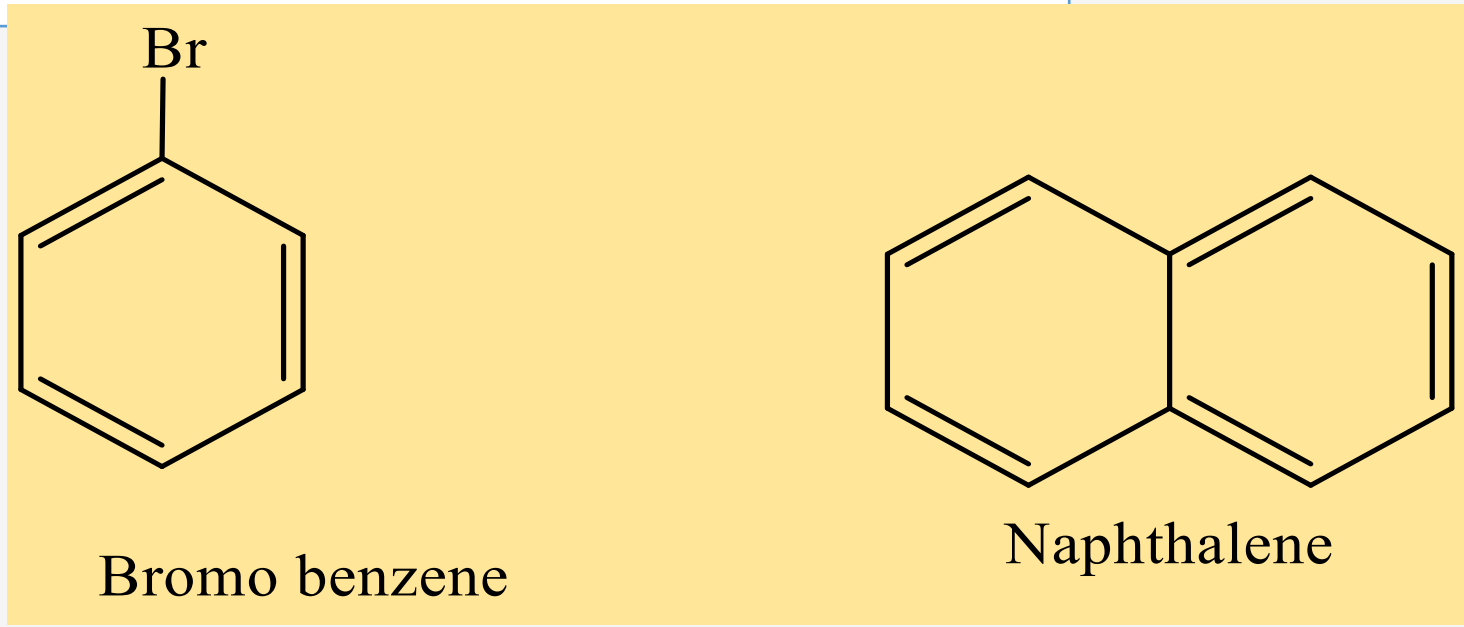
- Originally called **aromatic** due to fragrant odors, although this definition seems inaccurate as many products posses distinctly non-fragrant smells!

- Currently a compound is said to be aromatic if it has ***benzene-like in its properties***.



- Benzene is the *parent hydrocarbon of aromatic compounds*, because of their special chemical properties.

The name aromatic was applied to benzene and to compounds containing one or more benzene ring in their structures.



Properties of Aromatic compounds

1.High degree of un saturation .

2.Resistance to addition reactions .

3.up normal of stability.

The Structure of Benzene Ring

- Molecular formula = C_6H_6

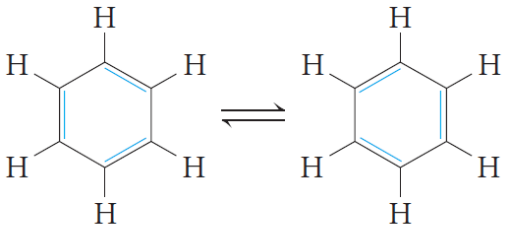
  The carbon-to-hydrogen ratio in benzene, suggests a highly unsaturated structure. **but its properties are quite different from those of open chain unsaturated hydro carbon .**

- *Benzene reacts mainly by substitution.*

  It does not undergo the typical addition reactions of alkenes or alkynes.

- **Kekulé Structure for Benzene**

  - *He suggested that*
    - *six carbon atoms are located at the corners of a regular hexagon, with one hydrogen atom attached to each carbon atom.*
    - *single and double bonds alternate around the ring (conjugated system of double bonds) and exchange positions around the ring.*

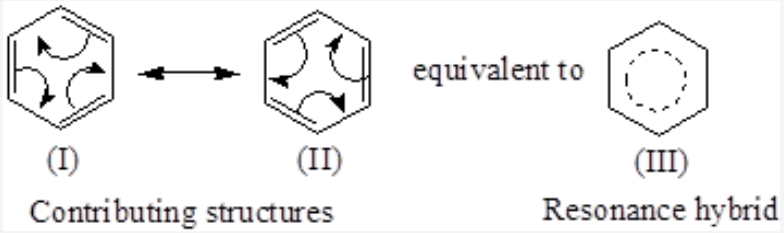


the Kekulé structures for benzene

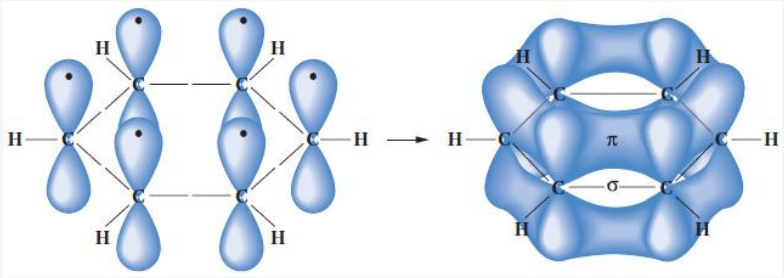
Benzene was intermediate between two structures that now we call resonance structure .

The Structure of Benzene Ring

- ***Resonance Model for Benzene.***



- *Benzene is planar.*
- *All of the carbon–carbon bond lengths are identical*: 1.39 Aº, intermediate between typical *single (1.54 Aº)* and *double (1.34 Aº)* carbon–carbon bond lengths.
- Each carbon is therefore sp^2-hybridized.
- Bond angles of 120°.



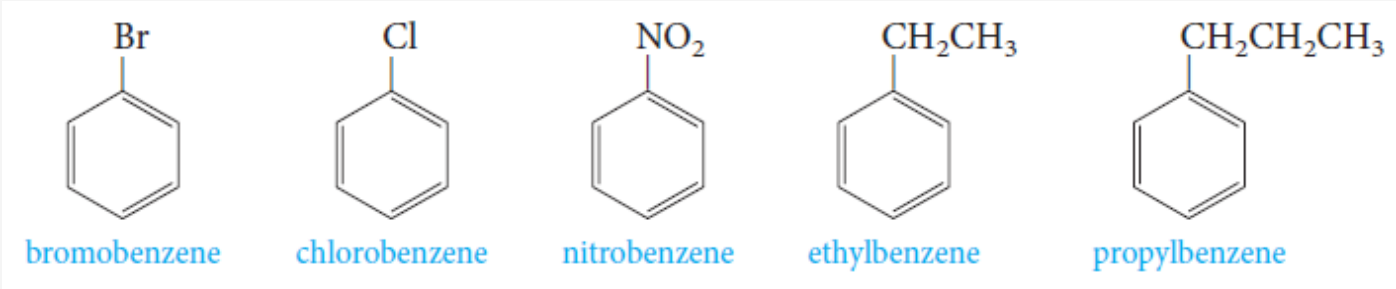
Aromatic Character (Aromaticity)

To be classified as aromatic, a compound must have:

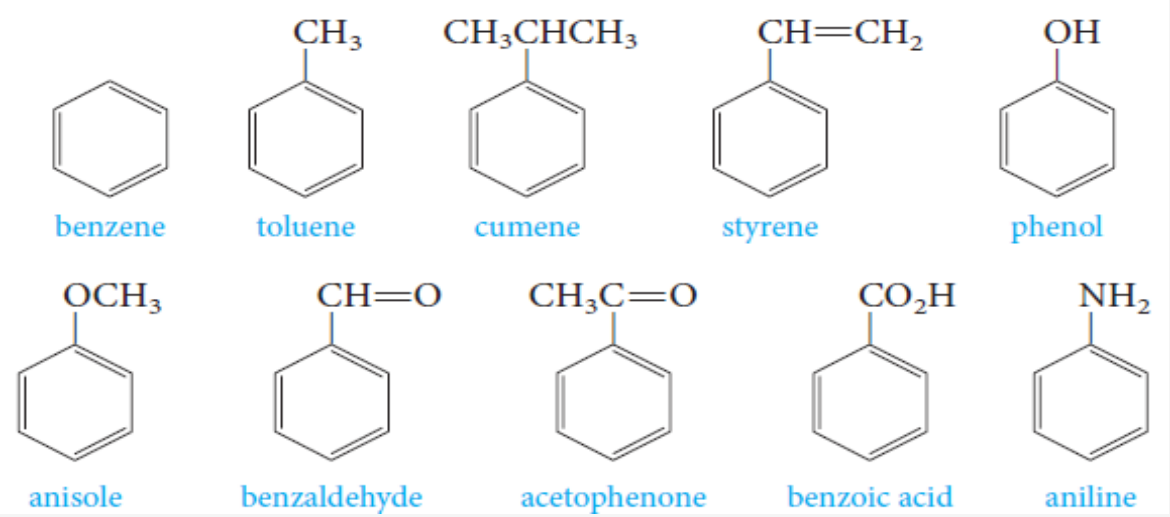
1. **Cyclic structure**
2. **Cyclic structure contains what looks like a continuous system of alternating double and single bonds**
3. **Aromatic compounds must be planar**

Monosubstituted Benzenes

- **Monosubstituted benzenes that do not have common names accepted by IUPAC are named as derivatives of benzene.**

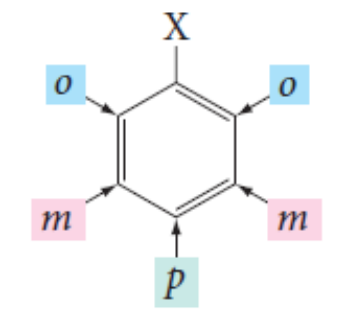


- **Common names are accepted by IUPAC (parent compounds).**

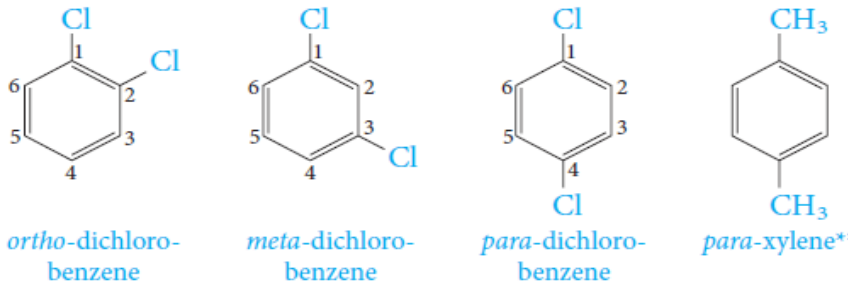


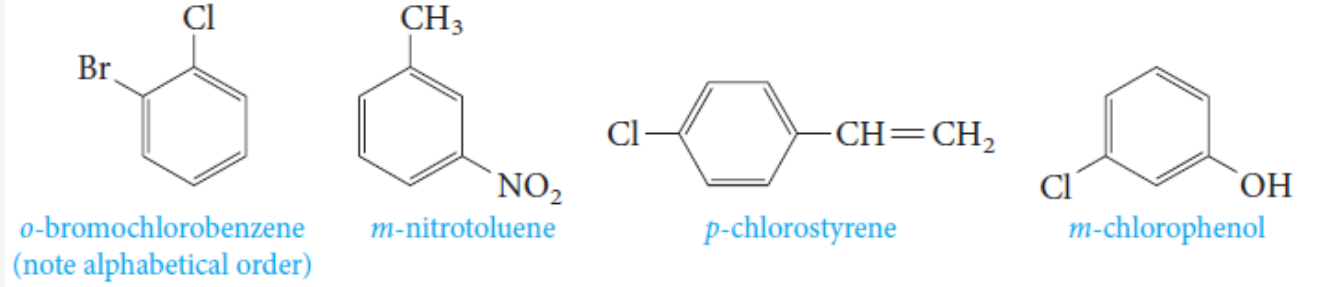
Disubstituted Benzenes

- **When two substituents are present, *three isomeric structures are possible*.**
  - **They are designated by the prefixes; *ortho-* (*o*-), *meta-* (*m*-) and *para-* (*p*-).**
  - **If substituent X is attached to carbon 1;**
    - ***o*- groups are on carbons 2 and 6,**
    - ***m*- groups are on carbons 3 and 5, and**
    - ***p*- groups are on carbon 4.**



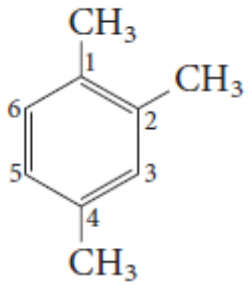
- **Examples;**



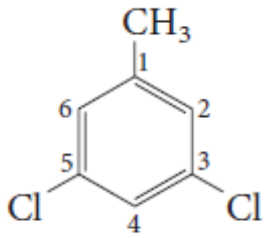


Polysubstituted Benzenes

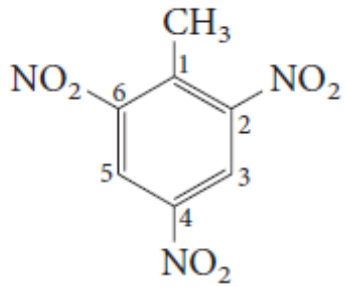
- **When more than two substituents are present, their positions are designated by numbering the ring.**



1,2,4-tri-methylbenzene

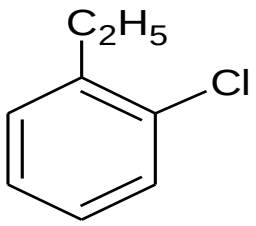


3,5-dichlorotoluene



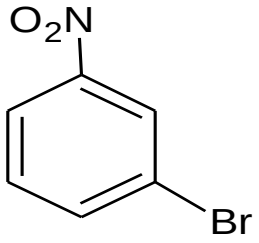
2,4,6-trinitrotoluene (TNT)

When the substituents are different, they are listed in alphabetical order



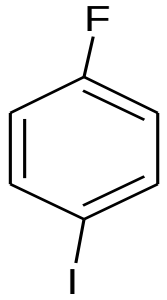
1-Chloro-2-ethylbenzene

o-Chloroethylbenzene



1-Bromo-3-nitrobenzene

m-Bromonitrobenzene

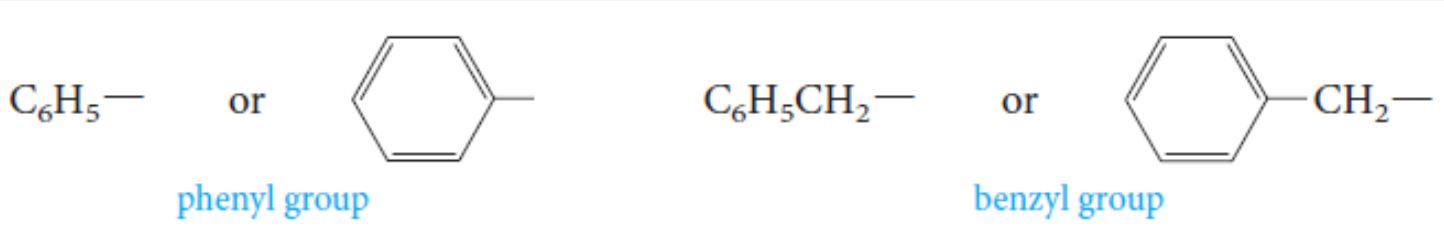


1-Fluoro-4-iodobenzene

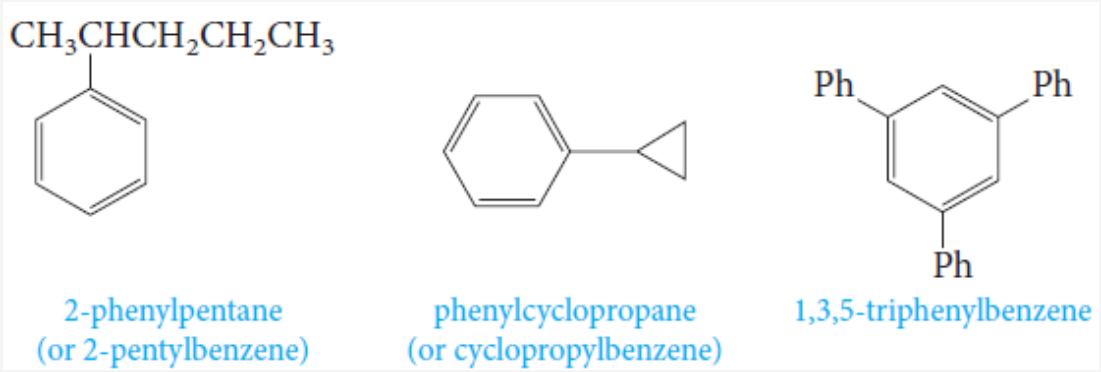
p-Fluoroiodobenzene

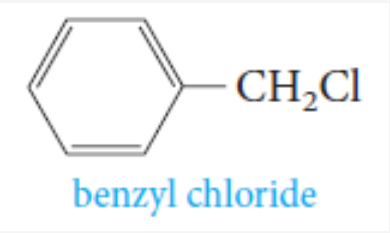
Nomenclature of Aromatic Compounds

- **Two groups with special names occur frequently in aromatic compounds; the phenyl group and the benzyl group.**



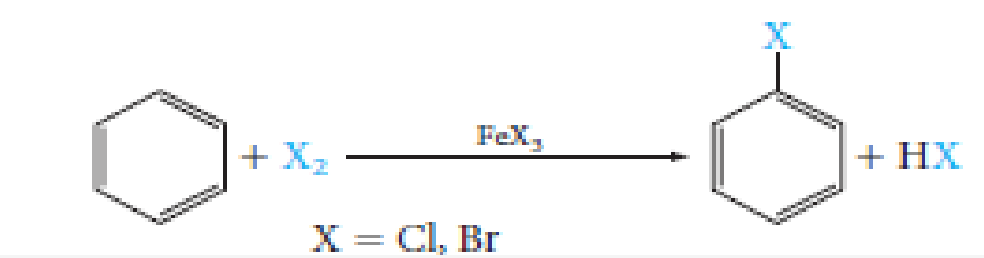
- **Examples;**



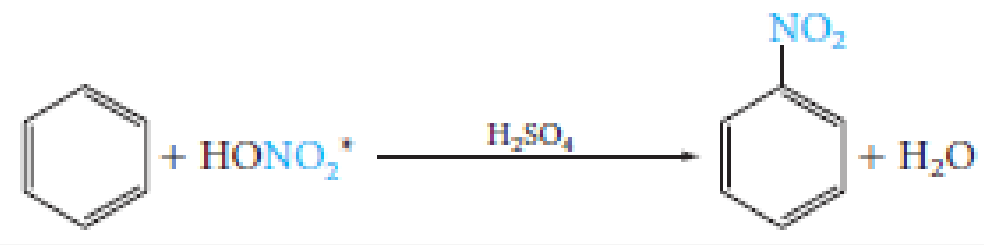


Substitution Reactions

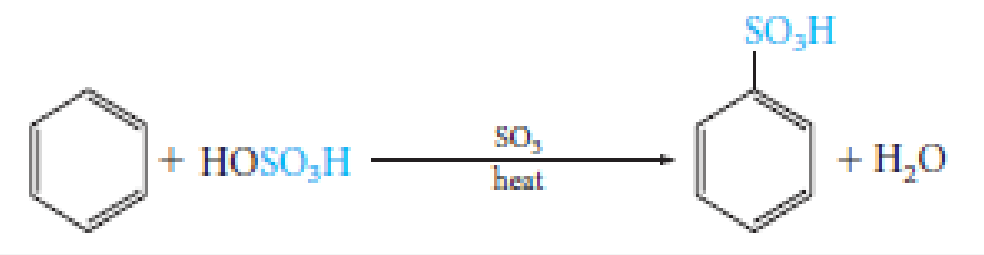
1) Halogenation



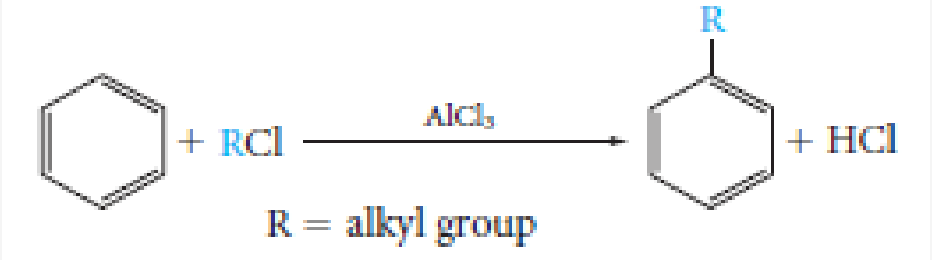
2) Nitration



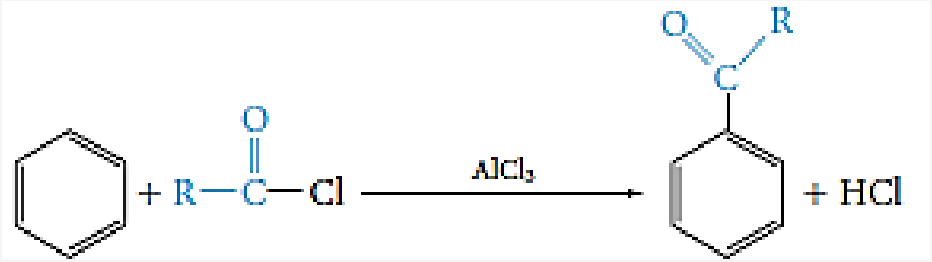
3) Sulfonation



4) Alkylation (Friedel-Crafts)

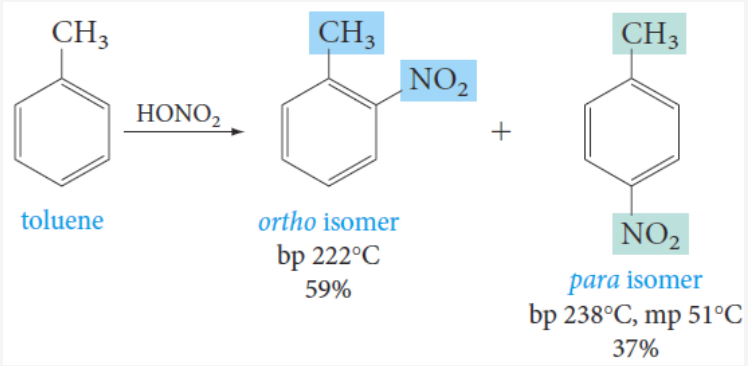


5) Acylation (Friedel-Crafts)

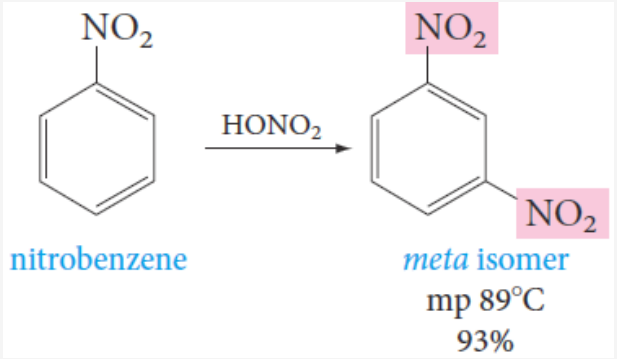


Disubstituted Benzenes: Orientation

- **Substituents already present on an aromatic ring determine the position taken by a new substituent.**
- **Example; nitration of toluene gives mainly a mixture of *o*- and *p*-nitrotoluene.**



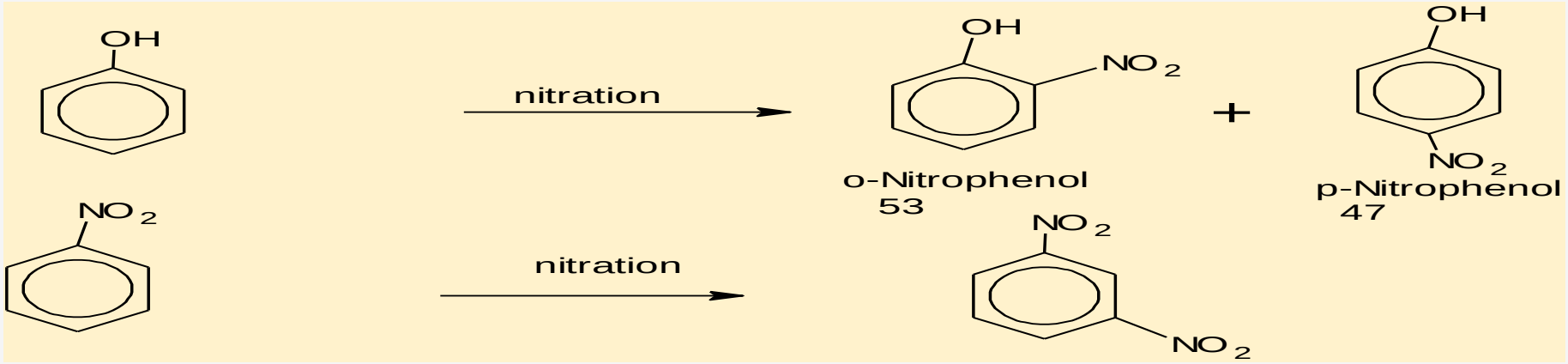
- **On the other hand, nitration of nitrobenzene under similar conditions gives mainly the *meta* isomer.**



Disubstituted Benzenes : Orientation

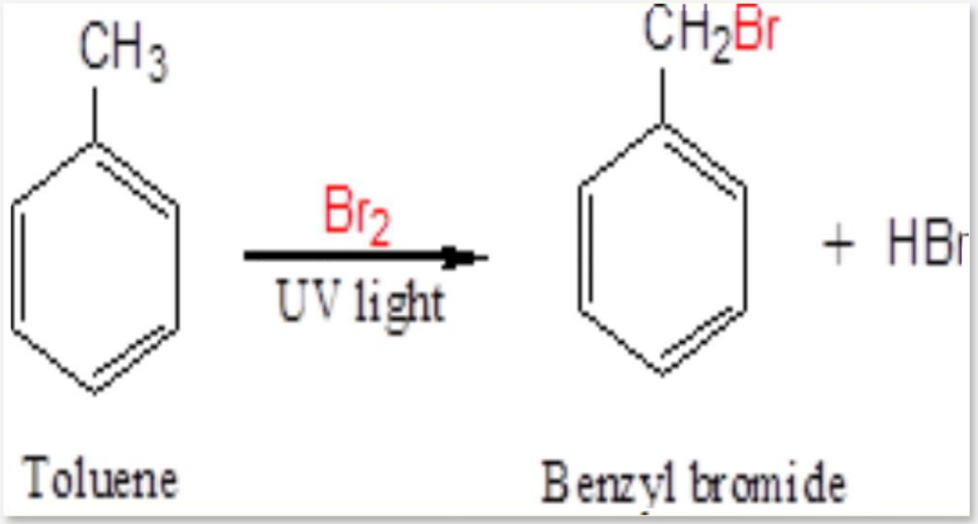
Orientation Effects of Substituents in Electrophilic Aromatic Substitution :

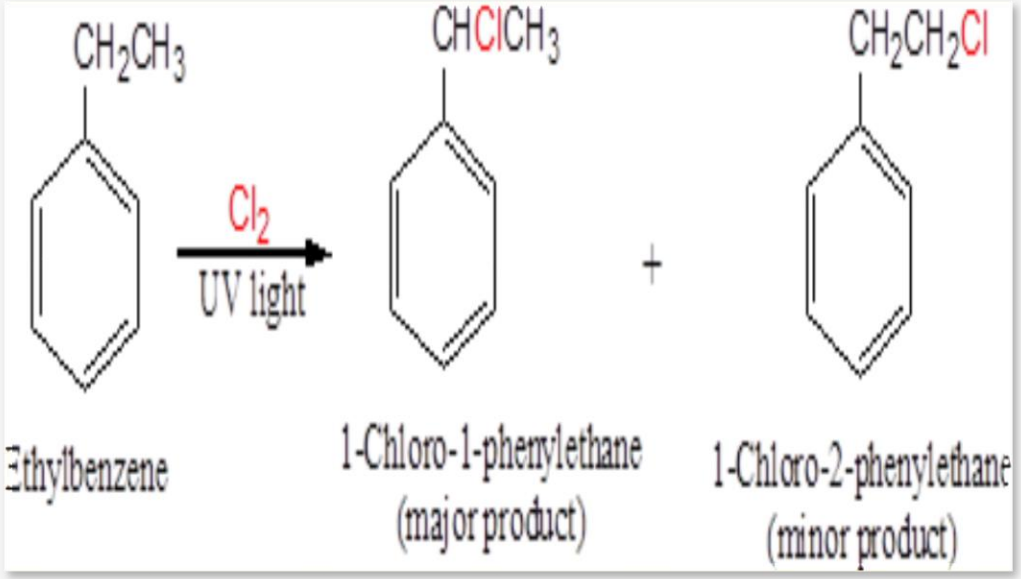
Ortho , para directors	Meta directors
-OH, -OR	$-NO_2$
$-NH_2$, -NHR, $-NR_2$	$-SO_3H$
$-C_6H_5$	-COOH, -COOR
$-CH_3$, -R (alkyl)	-CHO, -COR
-F, -Cl, -Br, -I	-CN



1. Halogenation of an Alkyl Side Chain

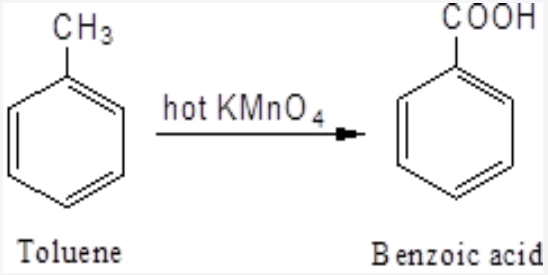
Side-Chain Reactions of Benzene-Derivatives

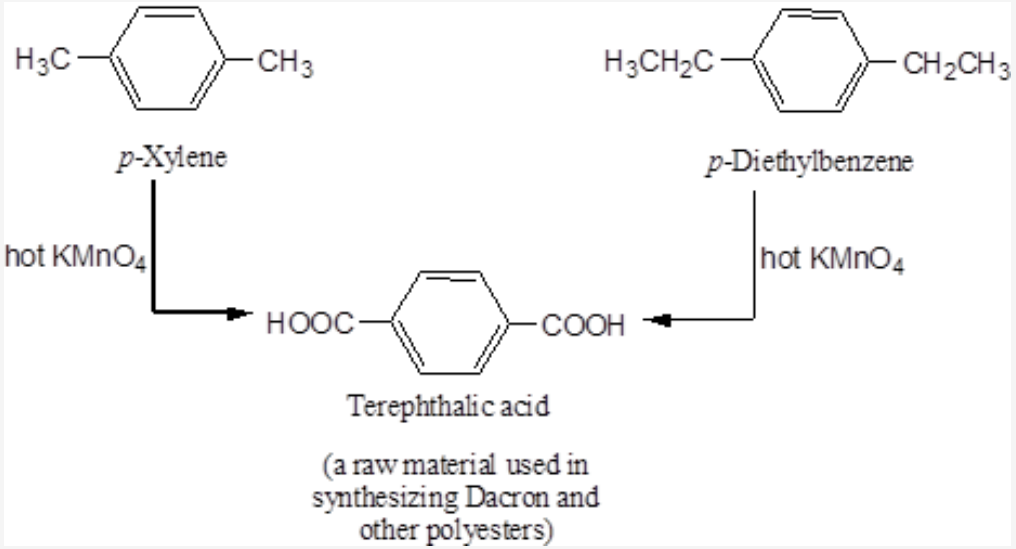




2. Oxidation of an Alkyl Side Chain

- **Conversion into a carboxyl group, -COOH, by treatment with hot potassium permanganate.**
- **Regardless the length of the alkyl chain, the product is always the same.**





Alcohols, Ethers, Alkyl Halides & Thiols

- ROH
- ROR
- RX
- RSH
  - All of these compounds contain a carbon atom that is singly bonded to a heteroatom (other than H or C)!
  - Alcohols & ethers can be considered organic derivatives of water
    - Replacing H(s) with one or two alkyl groups
    - HOH; ROH; ROR

Alcohols

- Are organic compounds in which one or more of the hydrogens is replaced with an – OH group.

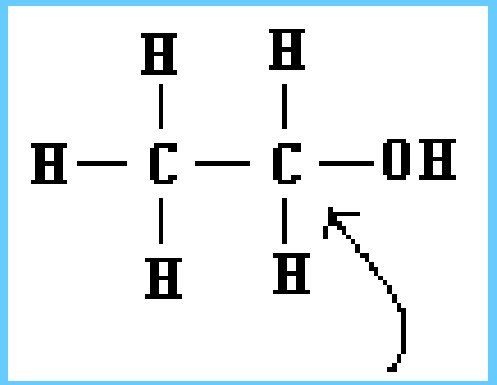
- OH group is called the hydroxyl group

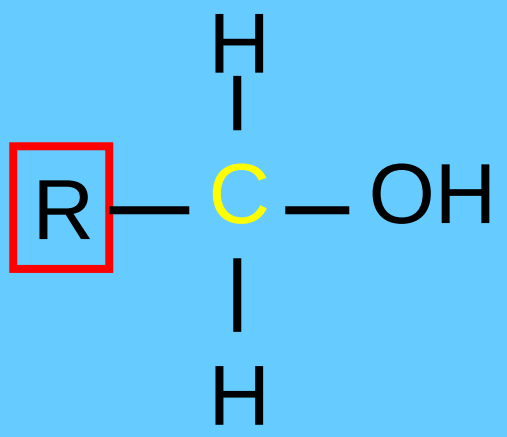
Table R
Organic Functional Groups

Class of Compound	Functional Group	General Formula	Example
alcohol	—OH	*R*—OH	$CH_3CH_2CH_2OH$ 1-propanol

Monohydroxyl Alcohols

-have one –OH group





Shortcut way to represent a primary alcohol

R-OH

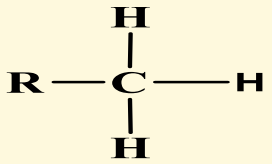
R stands for REST of the molecule

Alcohols

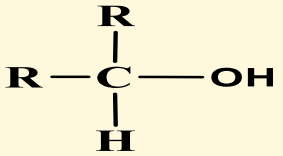
- **Structural Characteristics**
  - **R-OH -OH (hydroxyl = functional group)**

    -OH is bonded to a *saturated* C atom!

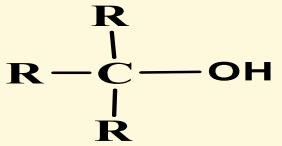
Classification of Alcohol



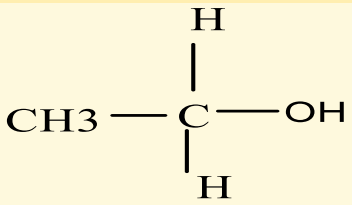
Primary (1°)



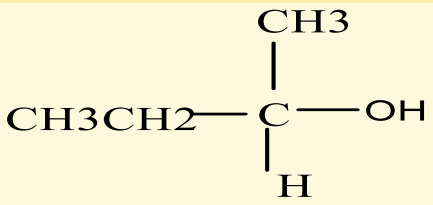
Secondary (2°)



Tertiary (3°)

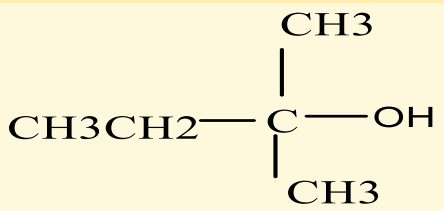


ethanol



Sec-butane alcohol

2-butanol



T-pentane alcohol

2-methyl-2-butanol

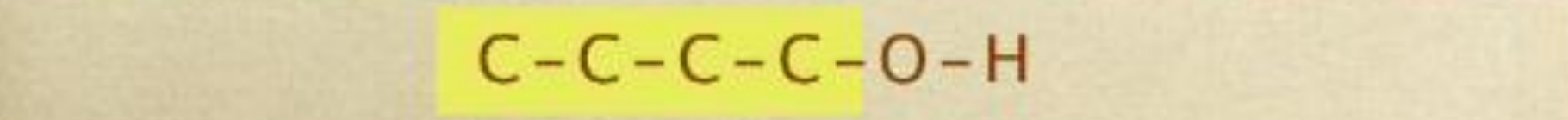
Alcohol Nomenclature

- IUPAC
  1. Name the longest chain (drop the “e” and add “ol” at the end) to which -OH is attached.
  2. number the chain from the end nearest the -OH* (number the position of the -OH group).
  3. Name/locate any substituents.
  4. For rings, -OH is on C number 1.

IUPAC naming of alcohols

- Replace the final “e” with “-ol”
  - methane → methanol → CH_3OH
  - ethane → ethanol → C_2H_5OH
  - propane → propanol → C_3H_7OH
  - butane → butanol → C_4H_9OH
  - pentane → pentanol → $C_5H_{11}OH$

Example



Base contains 4 carbon

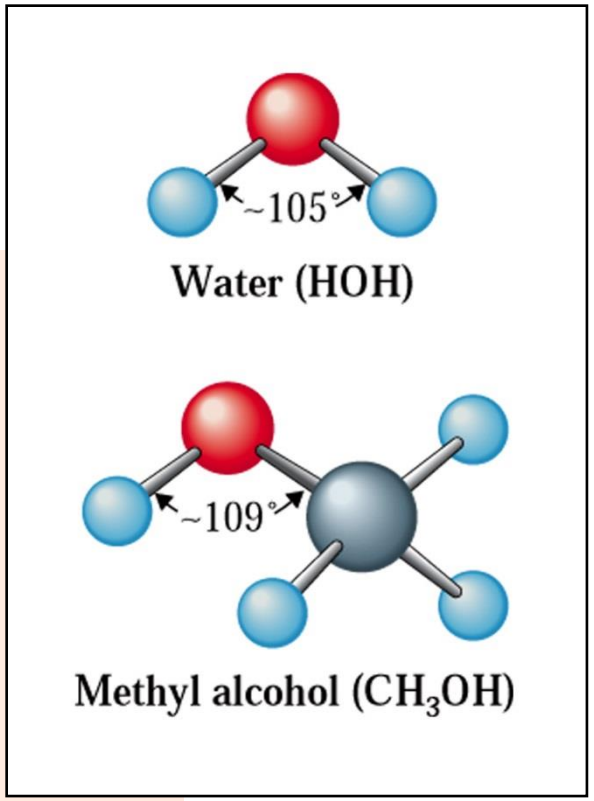
alkane name is butane

remove –e and add –ol

alcohol name – butanol

OH is on the first carbon so – 1–butanol

IUPAC naming examples

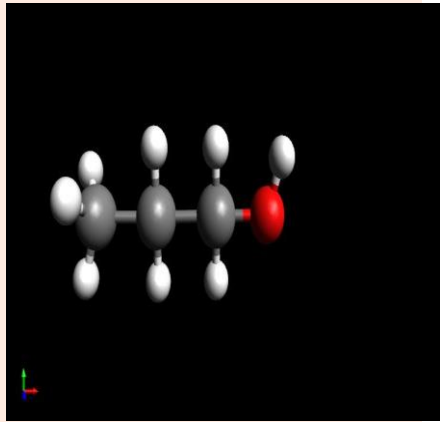


- Ex.: CH_3OH Methanol
- $CH_3CH_2CH_2OH$ 1-propanol

- CH_3CHCH_3
  |
  OH 2-propanol

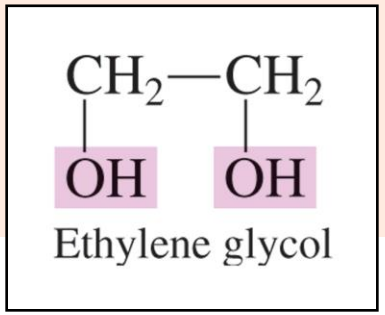
3,4-dimethylcyclohexanol

- Alcohols with >1 -OH groups
  - Ex.: CH_2CH_2
    | |
    OH OH 1,2-ethanediol

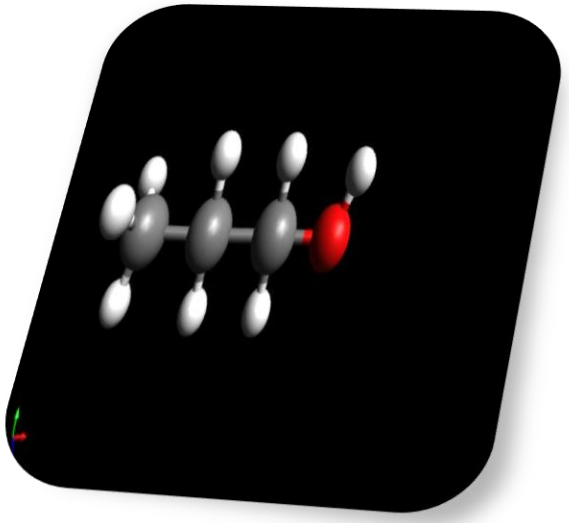


Alcohol Nomenclature

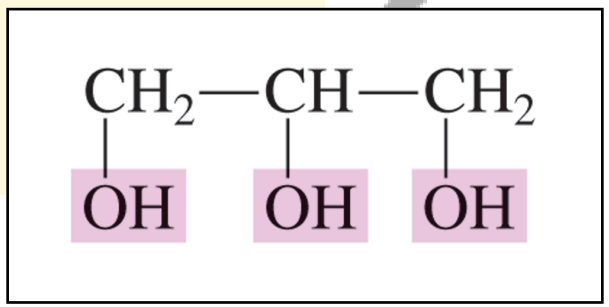
- Common (name “R” as an alkyl group)
  - Alkyl group name + alcohol
    - Ex.: CH_3OH Methyl alcohol
    - CH_3CHCH_3 Isopropyl alcohol
      |
      OH
  - Alcohols with >1 -OH groups
    - Ex.:



Important Common Alcohols



- IUPAC
  - Methanol
  - Ethanol
  - 2-propanol
  - 1,2-ethanediol
  - 1,2-propanediol
  - 1,2,3-propanetriol
- Common
  - Methyl alcohol
  - Ethyl alcohol
  - Isopropyl alcohol
  - Ethylene glycol
  - Propylene glycol
  - Glycerol (glycerin)

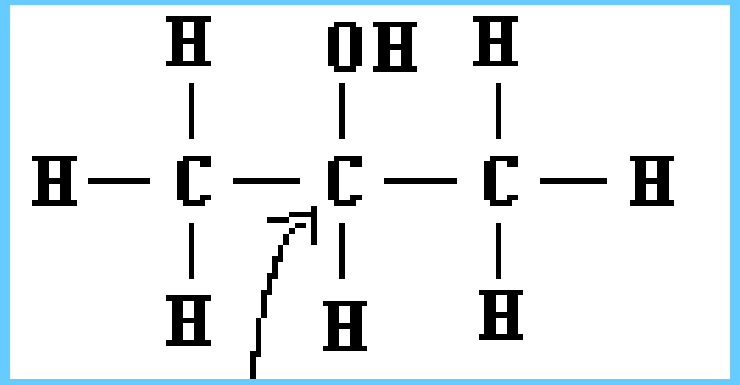


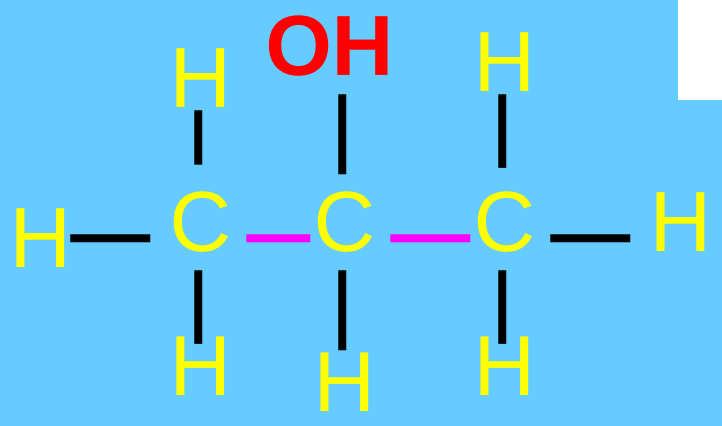
Constitutional Isomerism

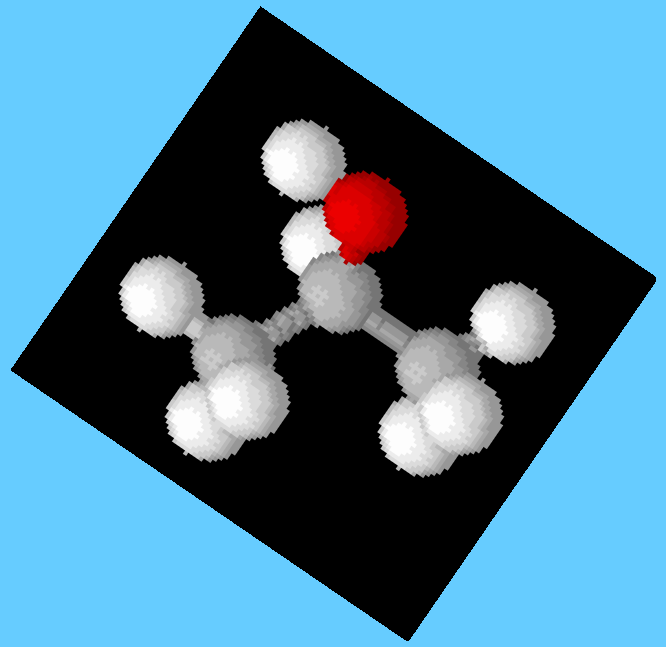
- Positional
  - Ex.: butanol 1-butanol
    2-butanol
- Skeletal
  - Ex.: butanol 2-butanol
    sec-butyl alcohol
    2-methyl-2-propanol
    tert-butyl alcohol

Formula	IUPAC Name	Common Name
One carbon atom (CH_3OH)		
$CH_3—OH$	methanol	methyl alcohol
Two carbon atoms (C_2H_5OH)		
$CH_3—CH_2—OH$	ethanol	ethyl alcohol
Three carbon atoms (C_3H_7OH); two constitutional isomers exist		
$CH_3—CH_2—CH_2—OH$	1-propanol	propyl alcohol
$CH_3—CH(OH)—CH_3$	2-propanol	isopropyl alcohol
Four carbon atoms (C_4H_9OH); four constitutional isomers exist		
$CH_3—CH_2—CH_2—CH_2—OH$	1-butanol	butyl alcohol
$CH_3—CH(CH_3)—CH_2—OH$	2-methyl-1-propanol	isobutyl alcohol
$CH_3—CH_2—CH(OH)—CH_3$	2-butanol	*sec*-butyl alcohol
$CH_3—C(CH_3)(CH_3)—OH$	2-methyl-2-propanol	*tert*-butyl alcohol

Ex. 2-propanol







Physical Properties of Alcohols

1. Alcohols have both Polar & Nonpolar character! (-OH) (alkyl)

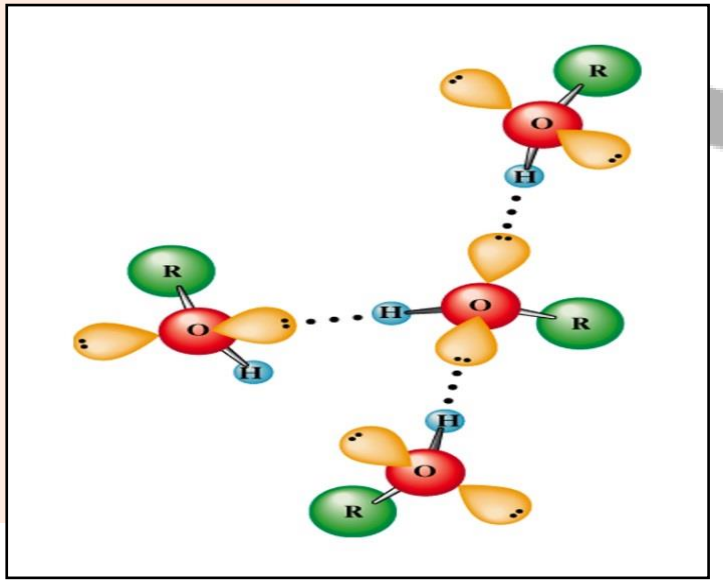
   Properties are determined by which portion dominates

   - Short chain (<6) - polar end dominates
   - Long chain (6+) - nonpolar end dominates

2. The boiling point increases with increasing number of C atoms ,and they usually decrease with branching.
3. Water solubility
   1. Short chain (<4) - soluble
   2. Long chain - insoluble

4. Alcohols can do Hydrogen bond polar (OH-groups are held together by inter molecular forces as those holding together water molecules).
   - (better with small chain alcohols)
   - affects BP & Solubility in Water

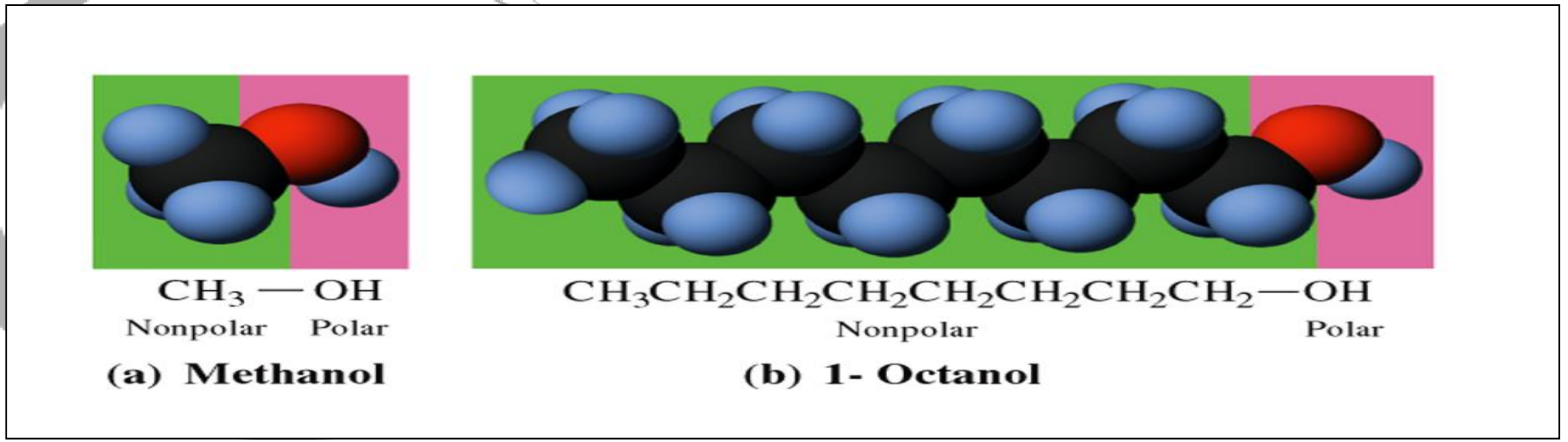
- Alkanes cannot make Hydrogen bond



Boiling Points of Alcohols

- Because alcohols hydrogen bond to each other, they have higher boiling points than alkanes of the same molecular weight.
- The boiling point of alcohols increases as the molecules become larger.

Name	Structure	Molecular Weight	Boiling Point
propane	$CH_3CH_2CH_3$	44.09 g/mol	-42.1°C
dimethyl ether	CH_3OCH_3	46.07 g/mol	-24°C
ethanol	CH_3CH_2OH	46.07 g/mol	78.3°C



- (a) The polar hydroxyl functional group dominates the physical properties of methanol.

- (b) Conversely, the nonpolar portion of 1- octanol dominates its physical properties.

Examples: Physical Properties of Alcohols

- Arrange the following substances in order of increasing boiling point and increasing solubility in water:
  - 2-butanol
  - 2-propanol
  - 2-methylpropane
  - 2-pentanol

Preparation of Alcohols

- Alcohols can be prepared in two major ways:

  Alkene hydration

  - Ex.: $CH_2=CH_2 + H_2O \xrightarrow{H2SO4} CH_3CH_2OH$

  - Hydrolyses of alkyl halides
    - Ex.: $CH_3CH_2{-}Cl + H_2O \xrightarrow{\triangle} CH_3CH_2OH + HCl$

Chemical Reactions of Alcohols

1. Combustion
   - $C_2H_5OH + 3O_2 \xrightarrow{\emptyset} 2CO_2 + 3H_2O + Energy$

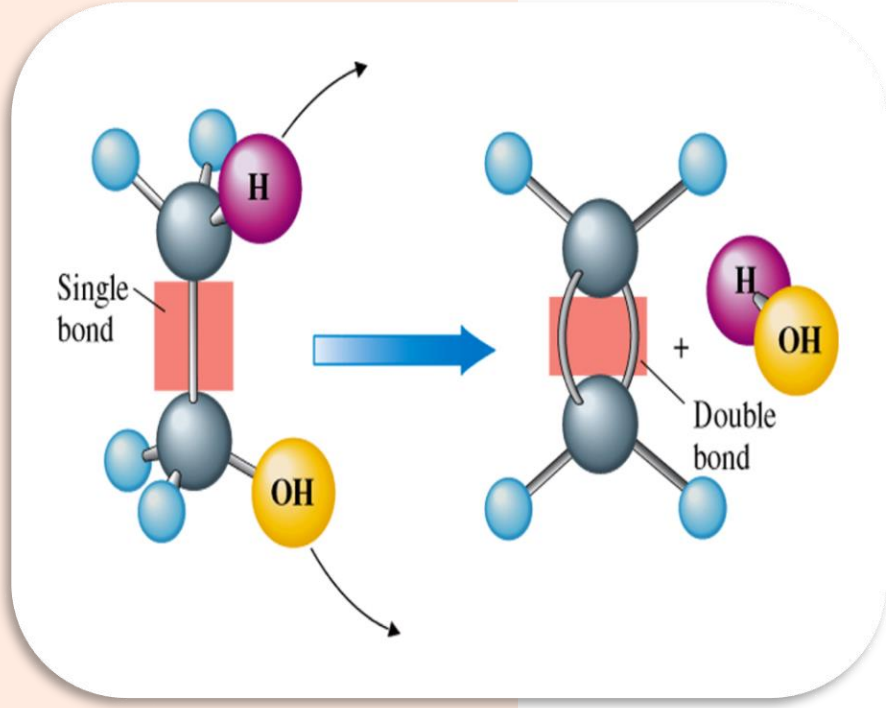
2. Dehydration!(Formation of olefins)

$$CH_3CH_2OH \xrightarrow{H2SO4} CH_2{=}CH_2 + H_2O$$

3. Reaction with Acids

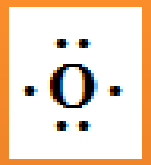
$$2ROH + H_2SO_4 \longrightarrow \underset{\textbf{ether}}{ROR} + H_2O$$

$$\underset{\textbf{methanol}}{2CH_3OH} + H_2SO_4 \xrightarrow{80^\circ C} \underset{\textbf{Dimethylether}}{CH_3OCH_3} + H_2O$$

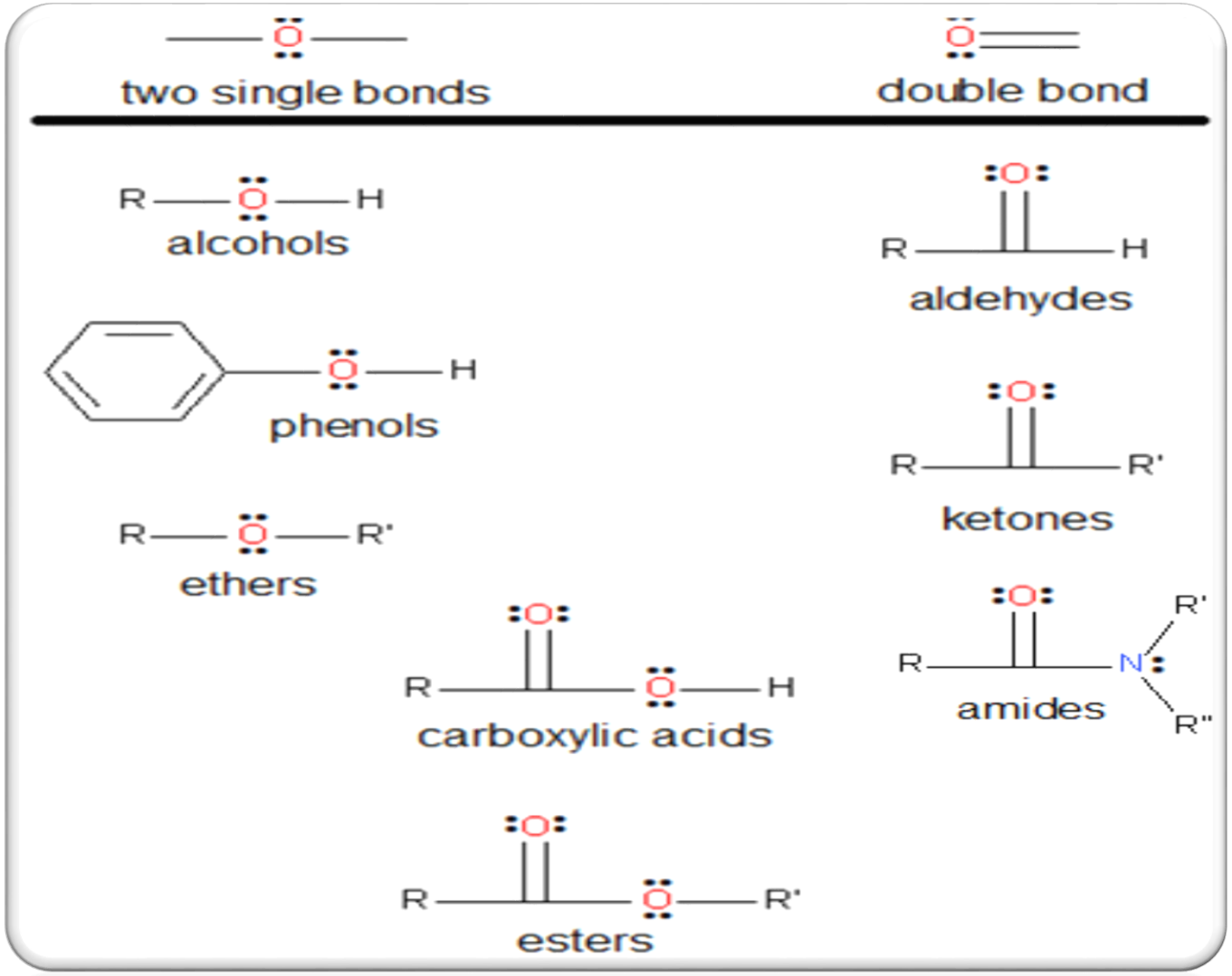


Bonding for oxygen atoms in organic compounds

- **Oxygen is commonly found in two forms in organic compounds:**



Oxygen is group 6A
Needs to form <u>two bonds</u>
to get an octet.



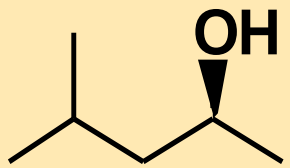
Alcohols - Nomenclature

Problem: Write the IUPAC name of each alcohol

(a) $CH_3(CH_2)_6CH_2OH$

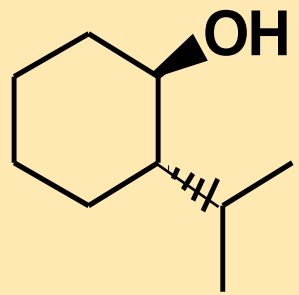
octanol

(b)



4-methyl-2-pentanol

(c)

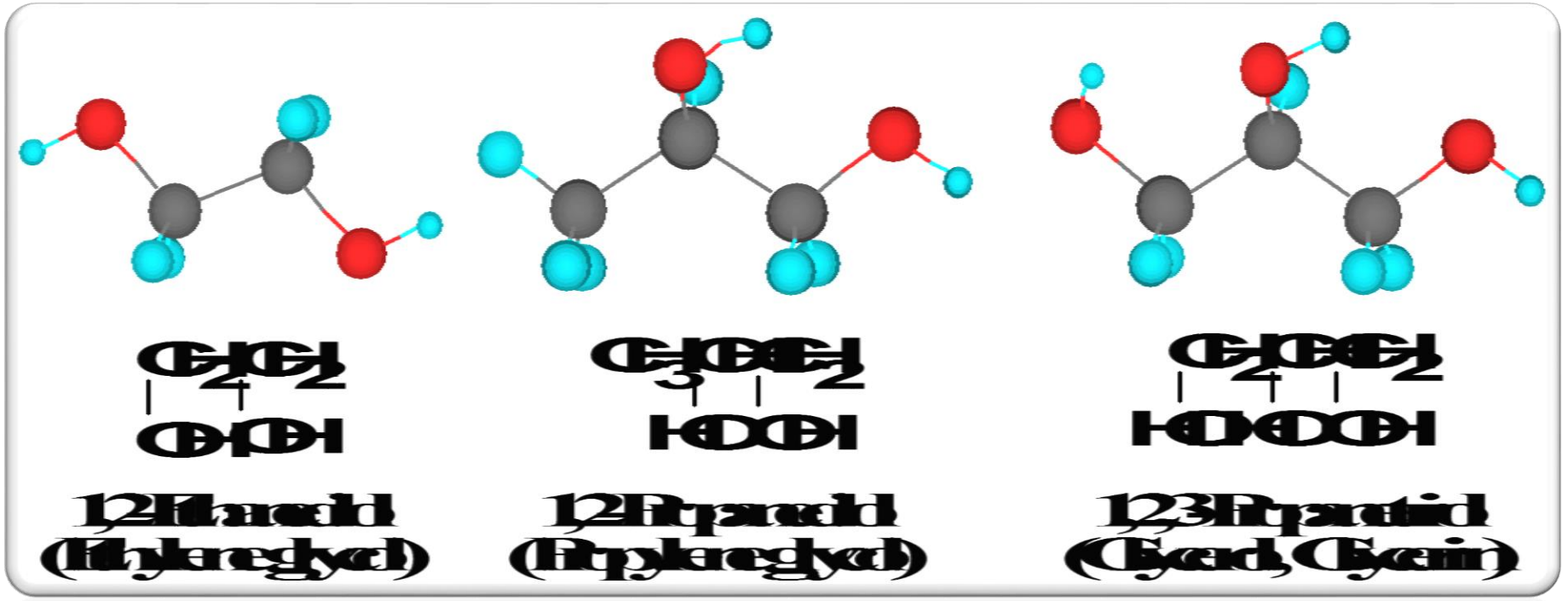


2-isopropaylcyclohexanol

Alcohols - Nomenclature

Compounds containing

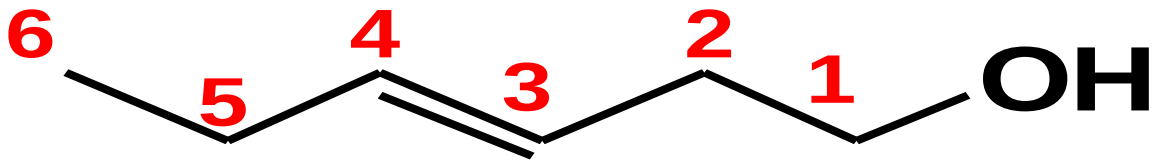
- two -OH groups are named as diols,
- three -OH groups are named as triols, etc.



Alcohols - Nomenclature

Unsaturated alcohols

- the double bond is shown by the infix -en-
- the hydroxyl group is shown by the suffix -ol
- number the chain to give OH the lower number

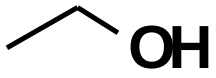


trans-3-hexene-1-ol

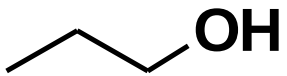
(*E*)-3-hexene-1-ol

Alcohols - Nomenclature

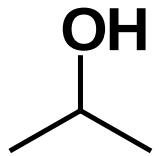
Examples:



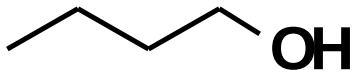
Ethanol
(Ethyl alcohol)



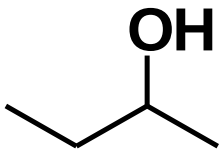
1-Propanol
(Propyl alcohol)



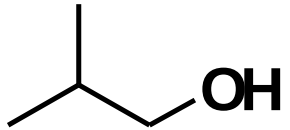
2-Propanol
(Isopropyl alcohol)



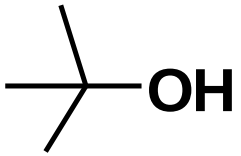
1-Butanol
(Butyl alcohol)



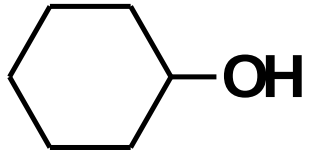
2-Butanol
(*sec*-Butyl alcohol)



2-Methyl-1-propanol
(Isobutyl alcohol)

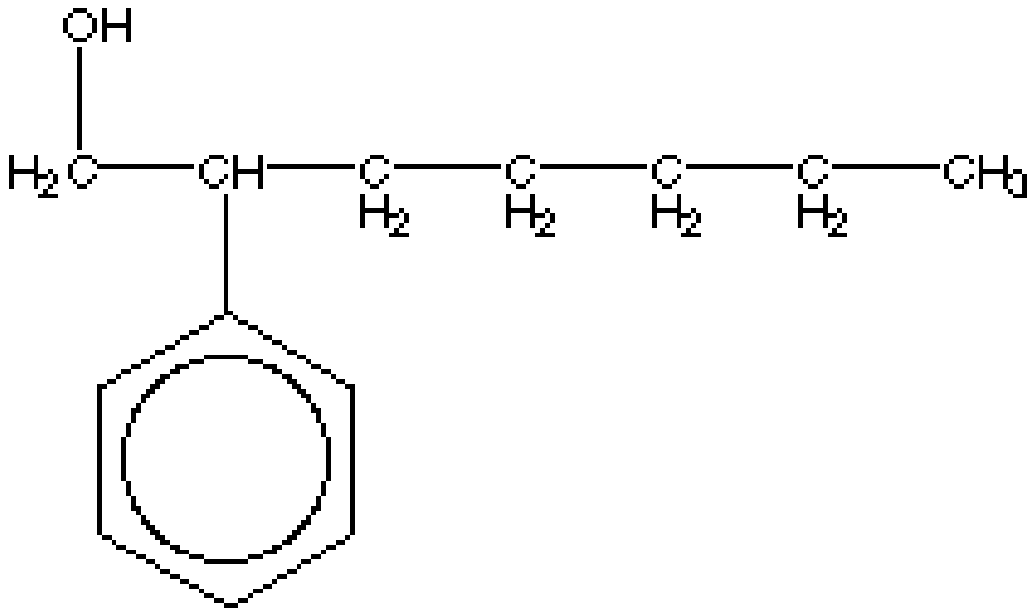


2-Methyl-2-propanol
(*tert*-Butyl alcohol)



Cyclohexanol
(Cyclohexyl alcohol)

Name the alcohol

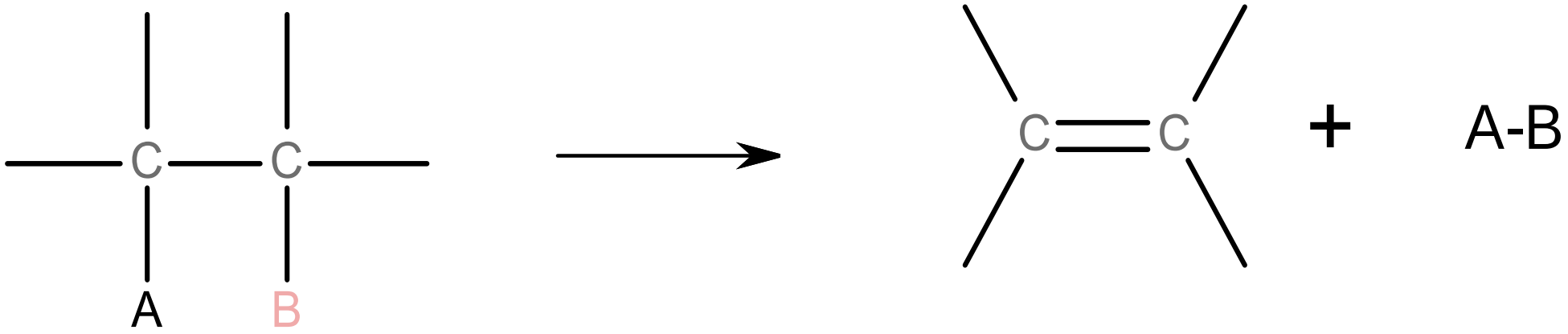


2-phenyl-1-heptanol

Chemical reactions of alcohols

Elimination reactions

- ***In general*, these kinds of reactions (eliminations) proceed as follows:**

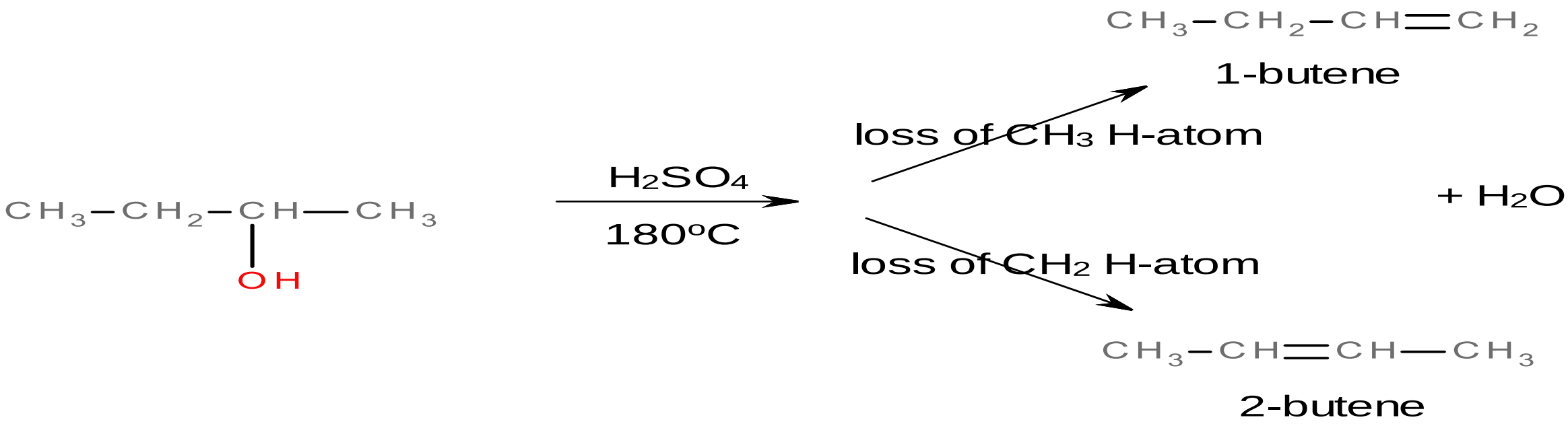


Two atoms (or groups of atoms) on neighboring carbons are removed, leaving a multiple bond between these carbon atoms

Chemical reactions of alcohols

Elimination reactions

- **If there is more than one adjacent carbon atom from which loss of a H-atom can occur, there will be more than one possible alkene dehydration product:**

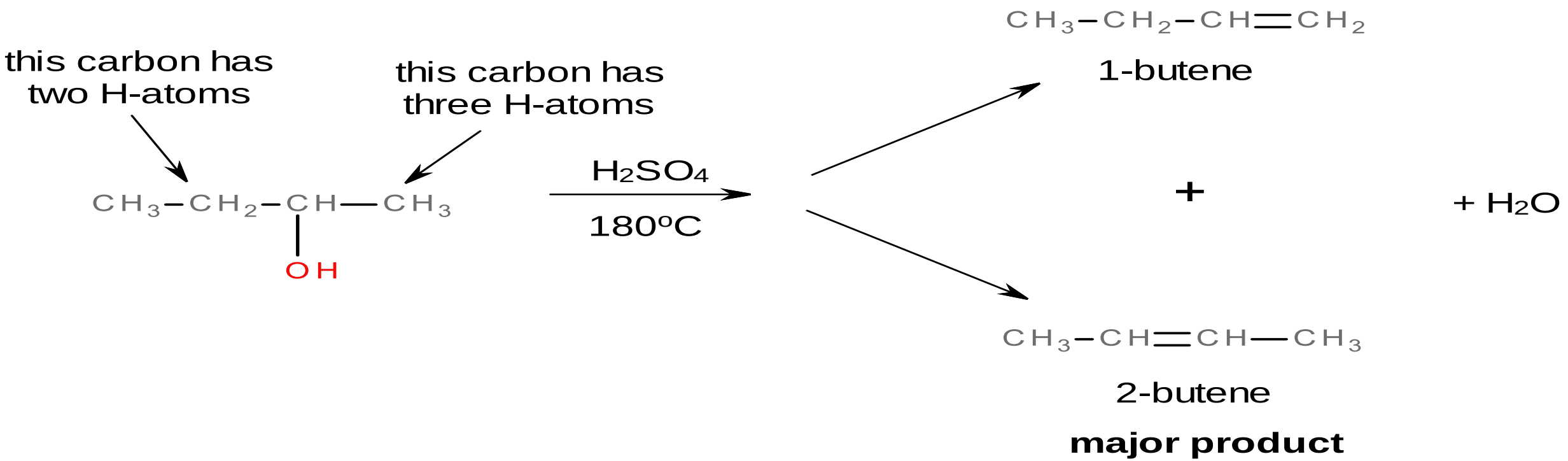


Use Zaitsev's Rule to predict which alkene will be produced in the greater amount

Chemical reactions of alcohols

Elimination reactions

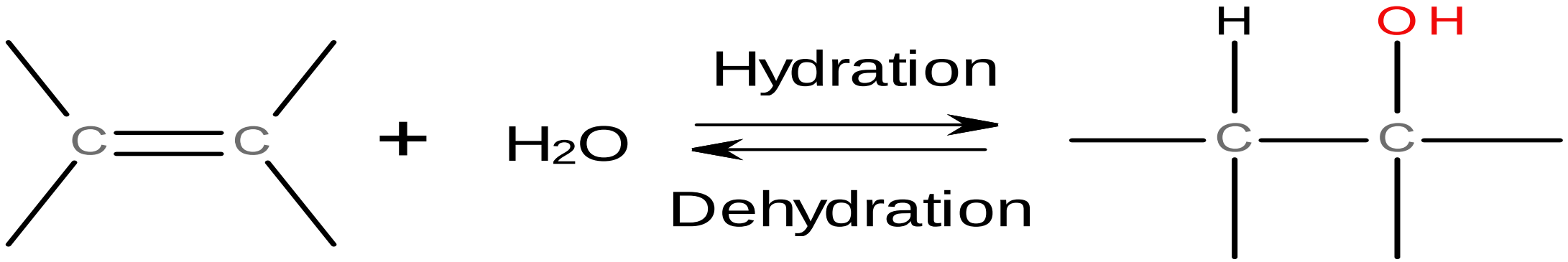
- **Zaitsev's Rule (for alcohol dehydrations): for cases where more than one alkene product might be formed from an elimination reaction, the hydrogen atom tends to be removed from the carbon that already possesses the fewest hydrogens.**



Chemical reactions of alcohols

Elimination reactions

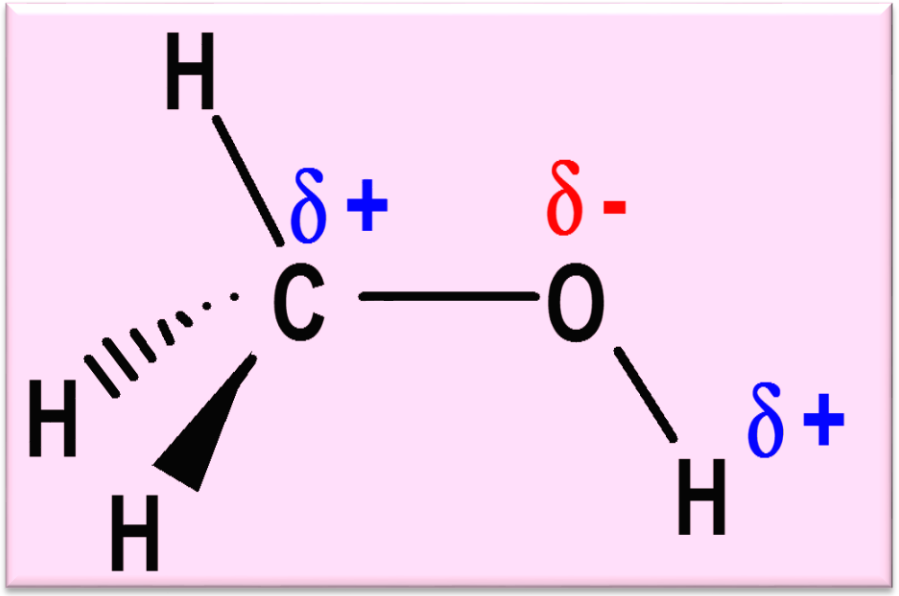
- **The alcohol dehydration reaction (like all chemical reactions) is an equilibrium. Since it occurs through elimination of an H_2O molecule, conditions that favor H_2O loss (dry conditions (concentrated H_2SO_4), high temperatures) favor alkene formation.**
- **On the other hand, if this reaction were run in dilute H_2SO_4, alcohol formation would be favored.**

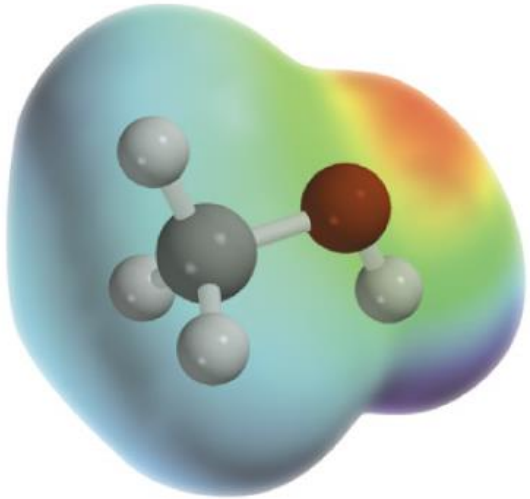


Physical Properties

Alcohols are polar compounds

- both the C-O and O-H bonds are polar covalent

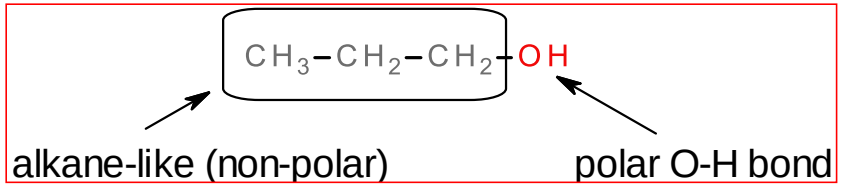




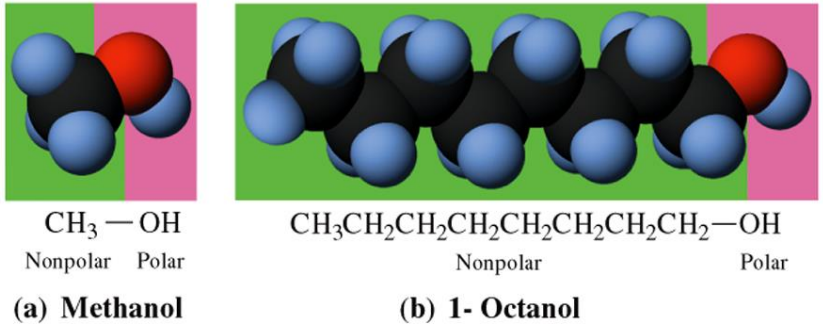
Physical properties of alcohols

- **Alcohols consist of:**
  - **a non-polar (alkane-like) chain**
  - **a polar hydroxyl group**

  Thus, alcohols might be water-soluble, or not (depending on the length of the carbon chain).



- **We already saw that the <u>boiling points</u> of alkanes increase with increasing chain length. The same is true for alcohols.**
- **Alcohols with more than one hydroxyl group (polyhydroxy alcohols) have higher boiling points than monoydroxy alcohols.**



<u>Boiling points</u>

Ethane: **-89°C** ← London forces

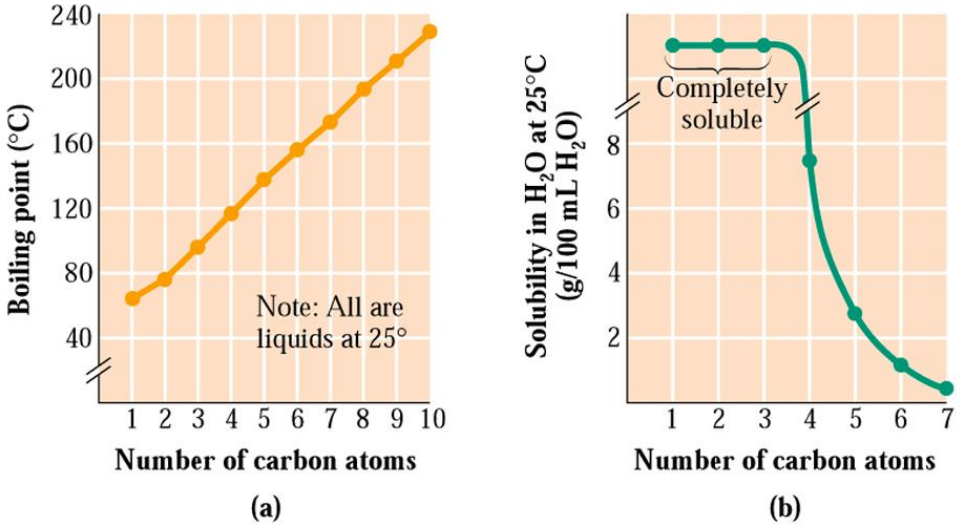
Methanol**: 65°C** ← London + H-bonding

Ethanol: **78°C** ← London + H-bonding

1,2-Ethane diol: **197°C** ← London + more H-bonding

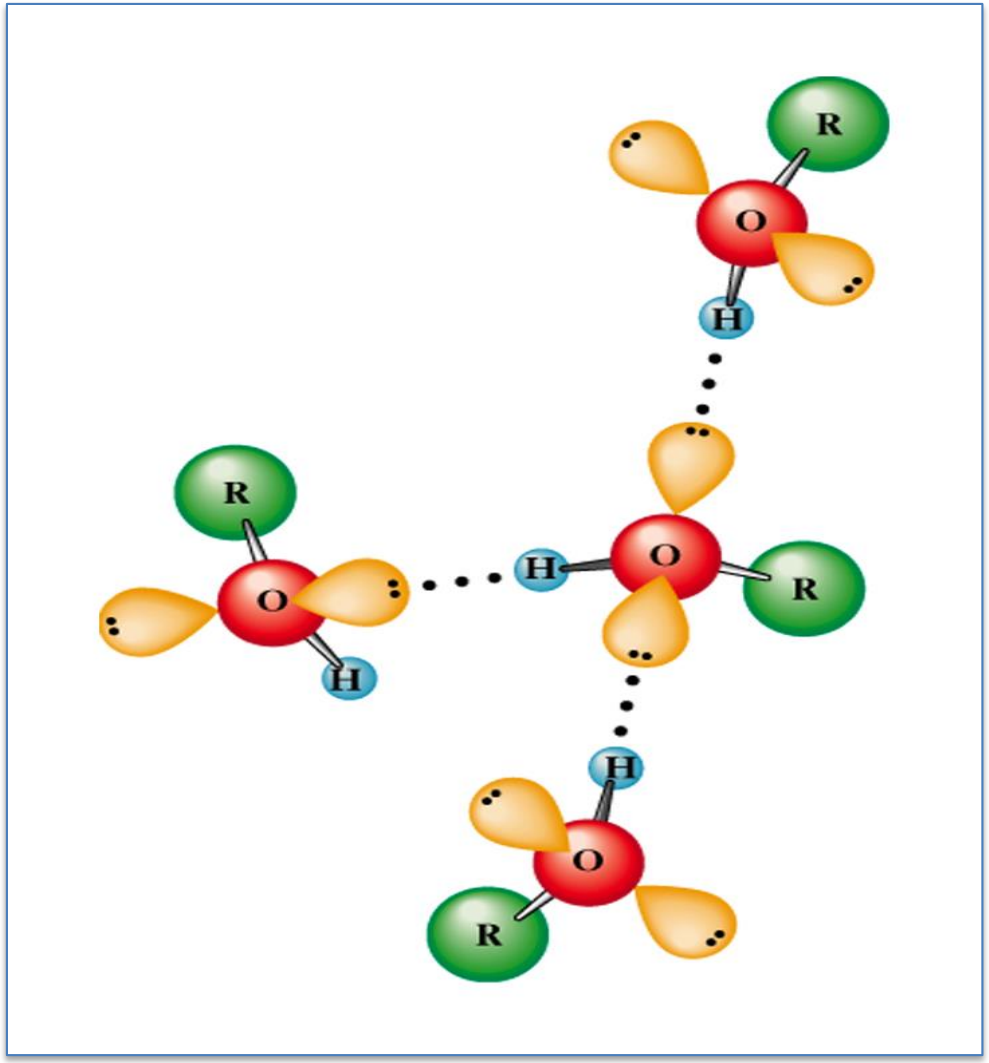
Physical properties of alcohols

- The water-solubility of alcohols depends on the length of the alkyl chain in the alcohol.
- Monohydroxy alcohols having chains longer than three carbons are not very water-soluble.
- Polyhydroxy alcohols are more soluble because they have more opportunities for hydrogen-bonding with water.



Physical properties of alcohols

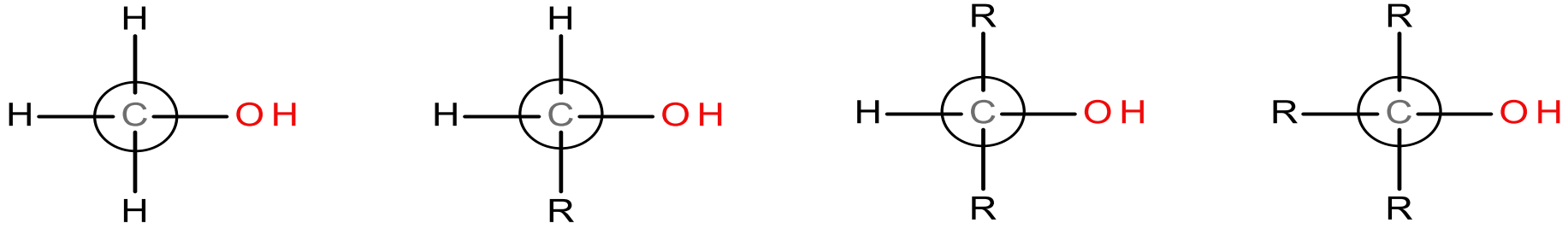
- **Alcohols have higher boiling points than alkanes of the same chain length (because they hydrogen bond to each other; the intermolecular forces for alkanes are only London forces)**
- **Alcohols of a given chain length are far more water-soluble than alkanes.**



Remember: H-bonding is the strongest intermolecular force

Classification of alcohols

- **Alcohols may be classified as 1º, 2º, or 3º, by considering the number of carbons *bound to the hydroxy-bearing carbon*.**



R = a saturated carbon group (e.g. alkyl substituent)

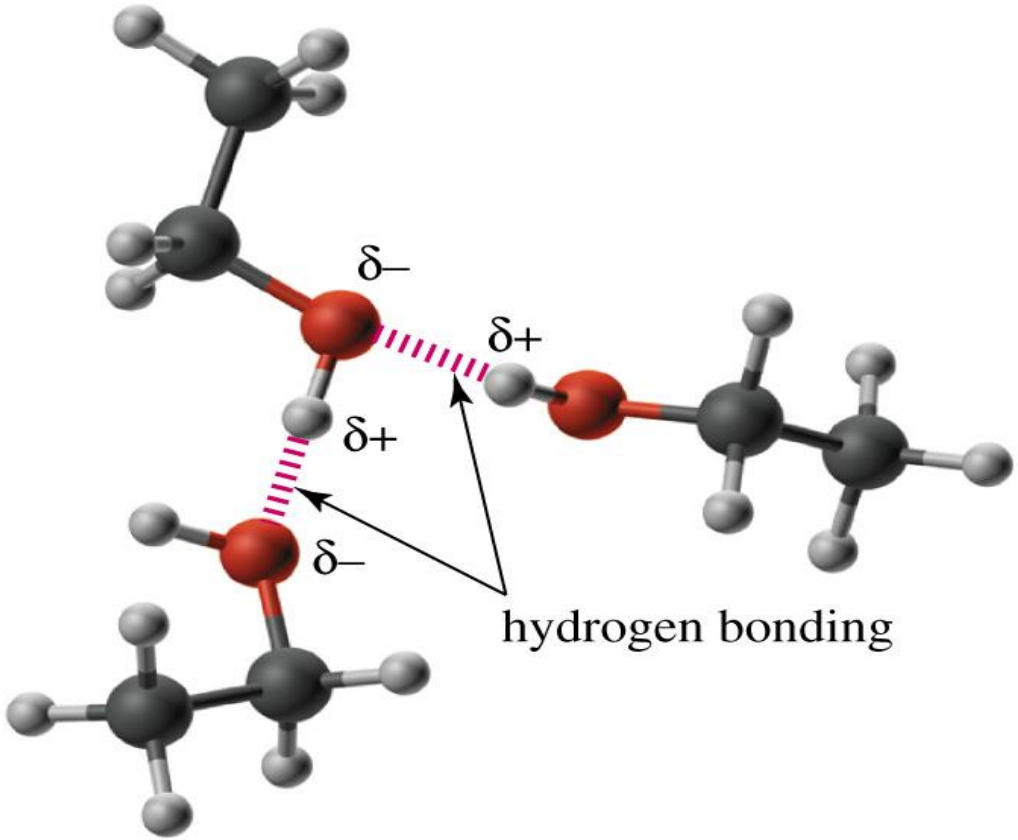
- **Although alcohols are able to H-bond, their ability to do so becomes impaired by other carbon atoms near the hydroxy group. The more carbon groups that are bound to the hydroxy-bearing carbon, the more they get in the way of H-bonding (steric hindrance).**

Hydrogen Bonding

Alcohols associate in the liquid state by hydrogen bonding

Hydrogen bonding: the attractive force between a partial positive charge on hydrogen and a partial negative charge on a nearby oxygen, nitrogen, or fluorine atom

- **Figure 8.3 shows the association of ethanol molecules in the liquid state (only two of the three possible hydrogen bonds to the upper oxygen are shown here).**

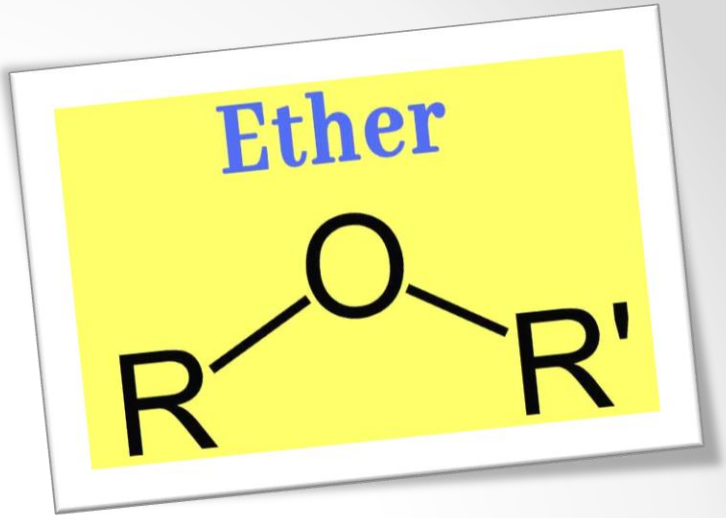


Boiling Points

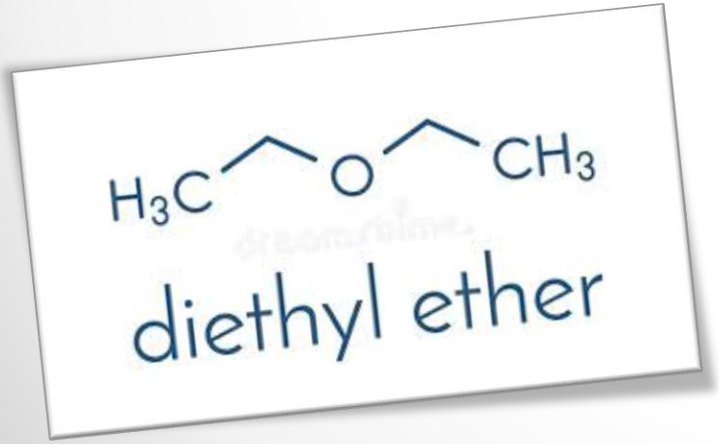
- alcohols have higher boiling points and are more soluble in water than hydrocarbons

Structural Formula	Name	Molecular Weight (g/mol)	Boiling Point (°C)	Solubility in Water
CH_3OH	methanol	32	65	infinite
CH_3CH_3	ethane	30	-89	insoluble
CH_3CH_2OH	ethanol	46	78	infinite
$CH_3CH_2CH_3$	propane	44	-42	insoluble
$CH_3CH_2CH_2OH$	1-propanol	60	97	infinite
$CH_3CH_2CH_2CH_3$	butane	58	0	insoluble
$CH_3CH_2CH_2CH_2CH_2OH$	1-pentanol	88	138	2.3 g/100 g
$HOCH_2CH_2CH_2CH_2OH$	1,4-butanediol	90	230	infinite
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane	86	69	insoluble

Lec. 6

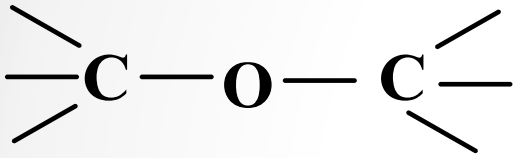


Ethers

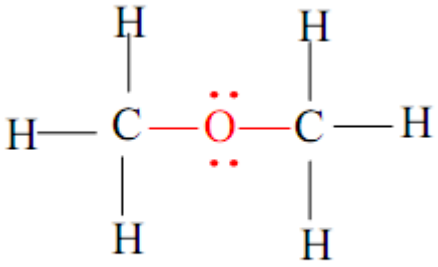


Ethers

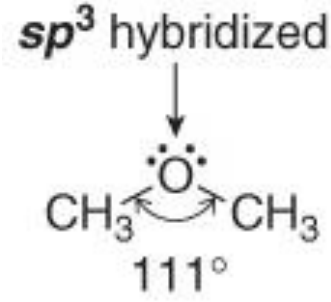
Ether is a class of organic compounds that contain an ether group R–O–R′. in which an oxygen atom is bonded to two organic group.



For the simplest ether, Dimethyl ether



Lewis structure



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Classification of Ethers

There are three kinds of ether known as :

(I) Alephatic

$$R—O—R$$

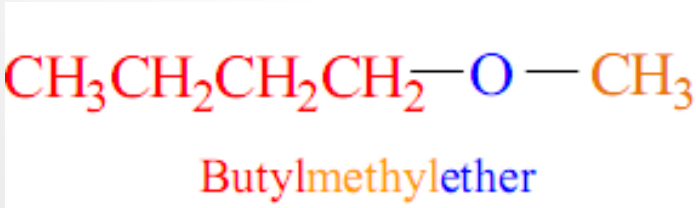
(II) Aromaic

$$Ar—O—Ar$$

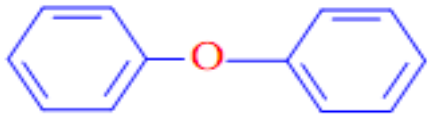
(III) Mixed

$$Ar—O—R$$

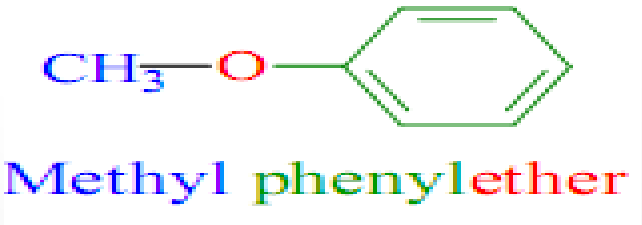
(I) Aliphatic Ethers



(II) Aromatic Ethers

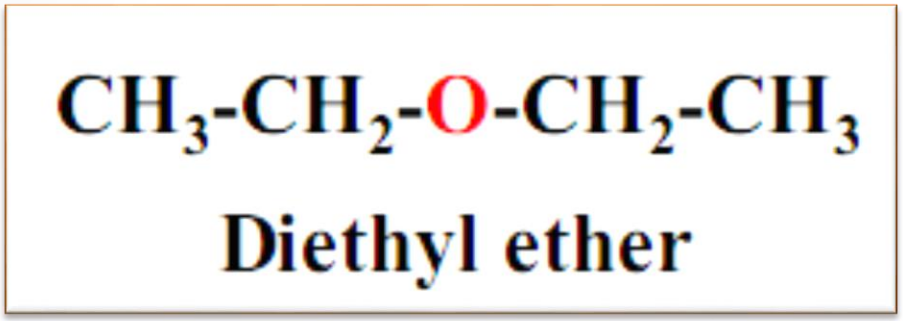


(III) Mixed Ethers

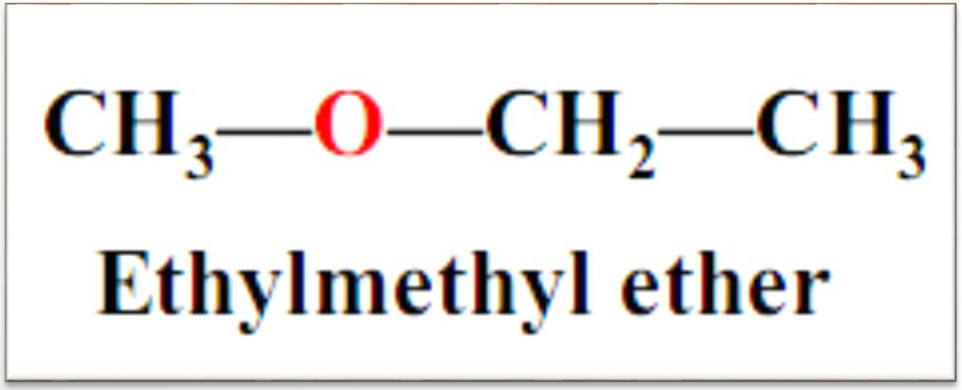


Types of Ethers

1- Simple Ethers or Symmetrical Ethers



2- Mixed Ethers or Unsymmetrical Ethers

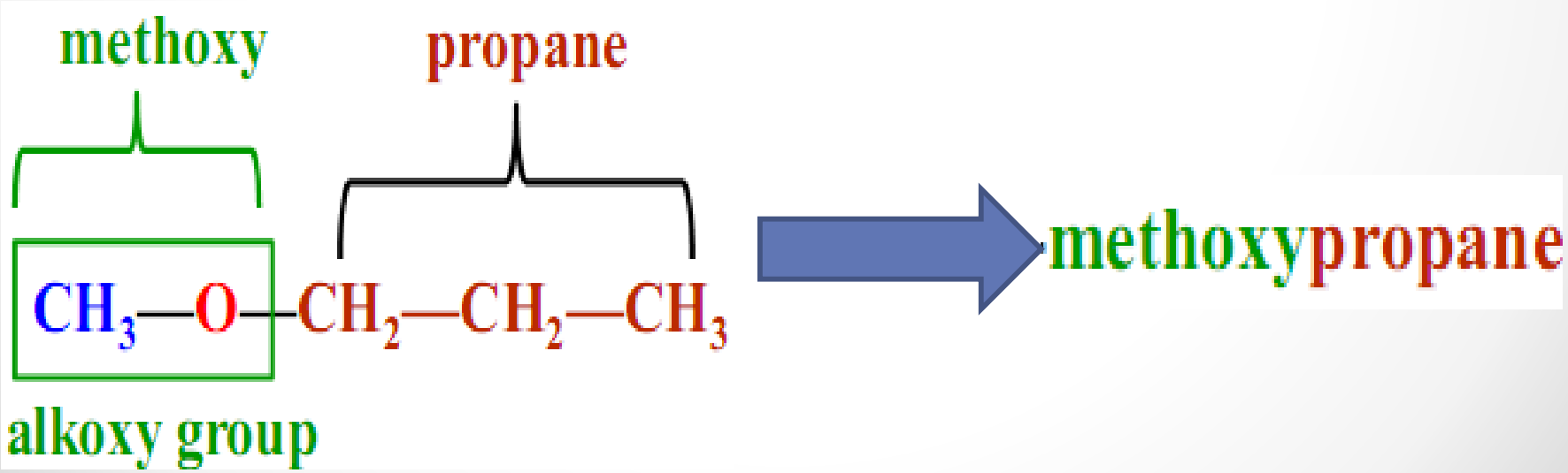


Nomenclature

IUPAC System

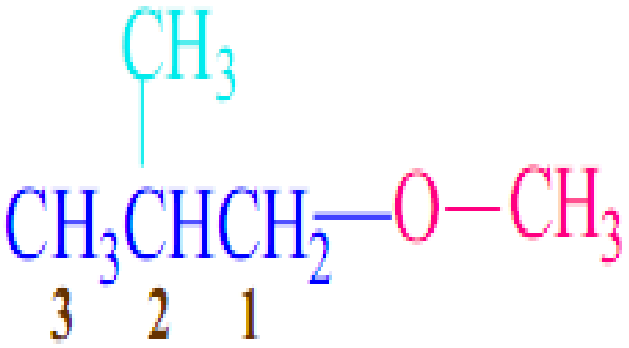
The shorter alkyl group and the oxygen are named as an alkoxy group attached to the longer alkane.

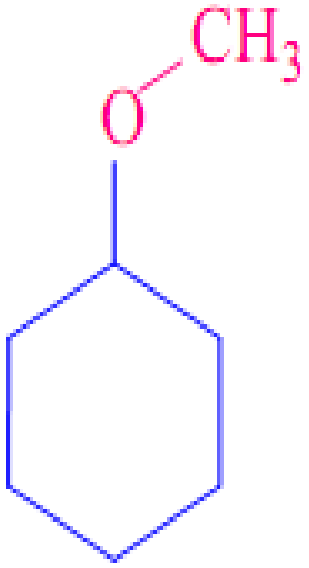
They are named as alkoxyalkanes.



IUPAC System

Examples:



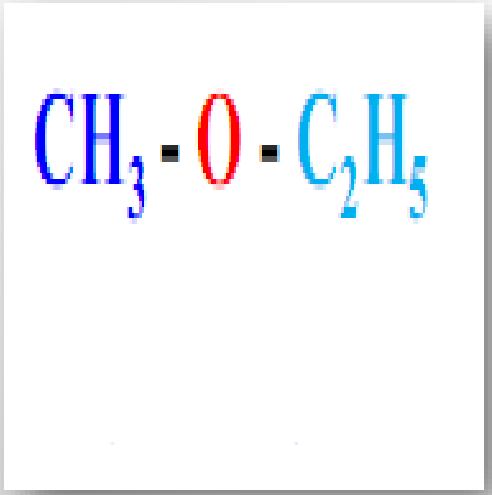


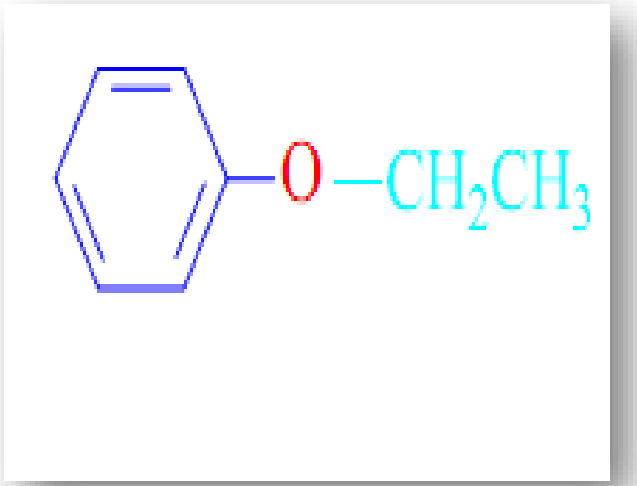
1-Methoxyisobutane

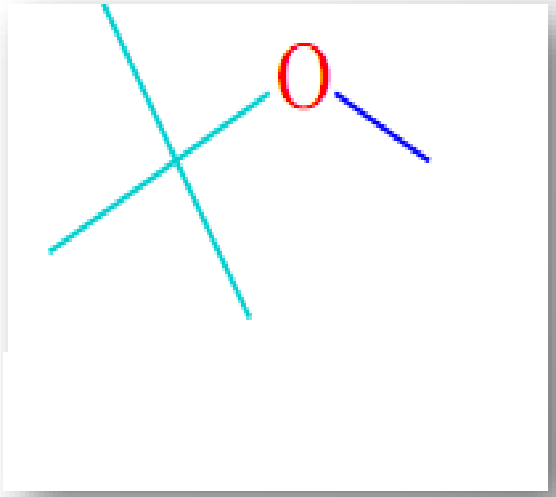
Common Names

The two-alkyl groups bonded to the functional group (- O -) are written alphabetically followed by the word ether.

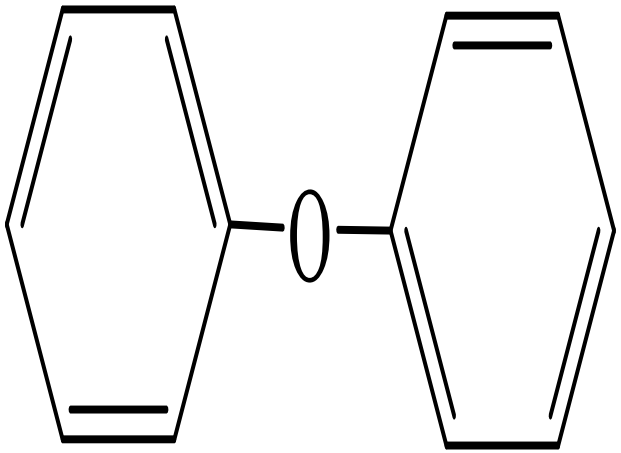
Examples:

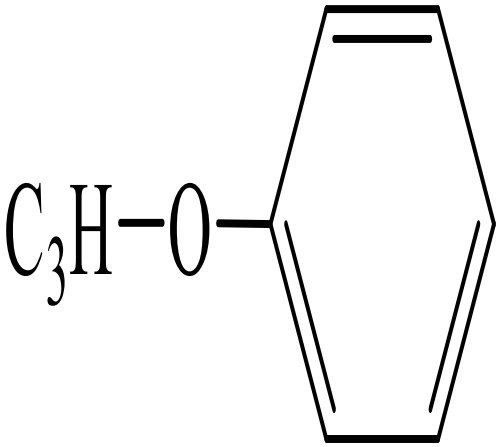


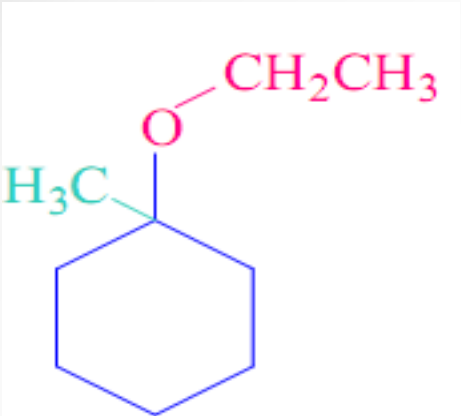


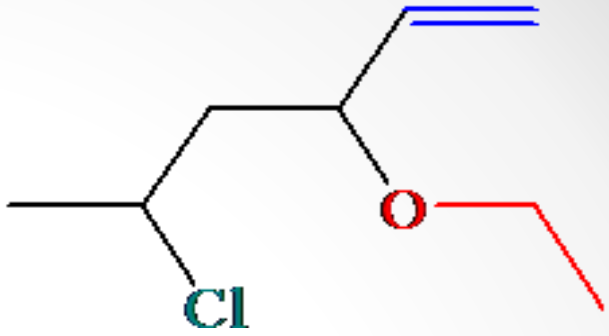


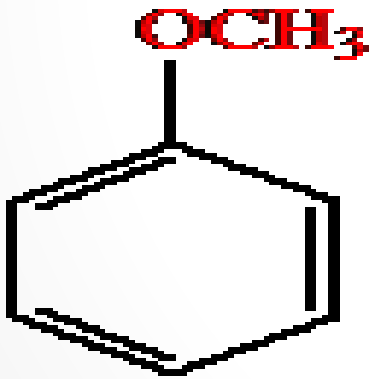
$C_3H-O-CH_3$

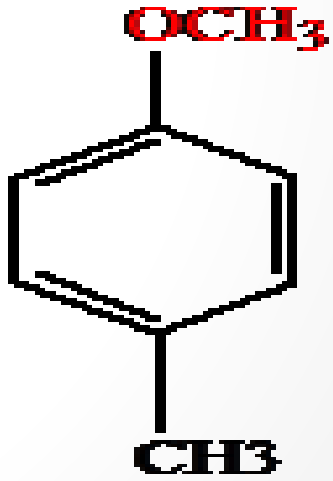





CH2CH3
O
H3C


O
Cl


OCH3


OCH3
CH3

Physical Properties

1. **Ethers posses a small dipole moment .**

   2- This weak polarity doesn't appreciably affect the boiling point of ethers Ex . B. P of n – heptane is 980C B. P of ethyl n – pentyl ether is 1000 c

   3- Di methyl ether and methyl ethyl ether are gases while di – ethyl ether and higher member of aliphatic ether are liquids . Aromatic ethers are liquids or solids.

   4- Ethyl ether has low boiling point 350 c and it is flameable. Also it is highly oxidized forming unvolatile peroxide – (H2O2).

Boiling Points of Ethers:

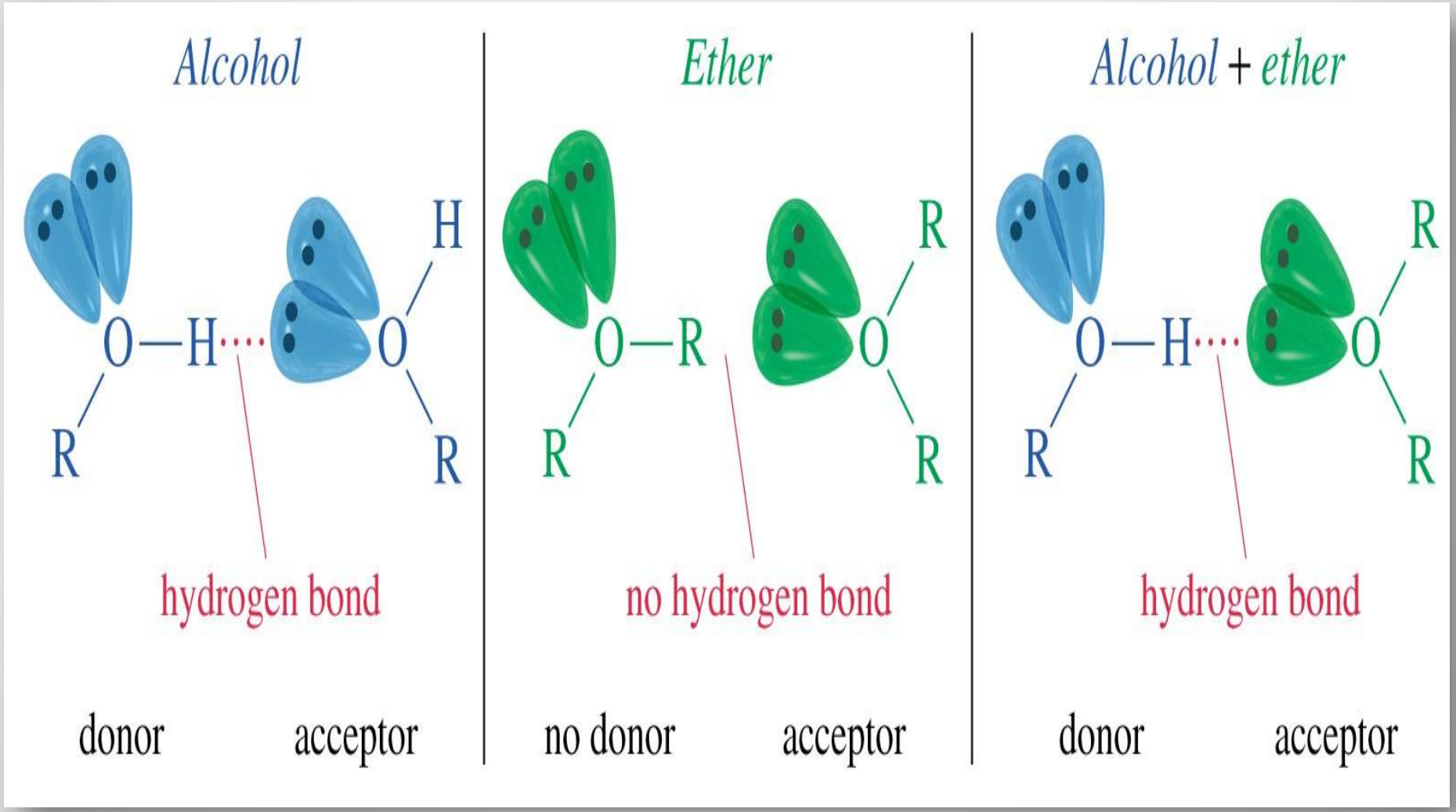
The hydrogen bonding that holds alcohol molecules strongly together is not possible for ethers .

hydrogen bonds cannot form between ether molecules

$CH_3CH_2CH_2CH_3$	$CH_3-O-CH_2CH_3$	$CH_3CH_2CH_2OH$
Butane	Methoxyethane	1-Propanol
(butane)	(ethyl methyl ether)	(Propyl alcohol)
M.W. = 58	M.W. = 60	M.W. = 60
b.p. = - 0.5°C	b.p. = 7.9 °C	b.p. = 97.2°C

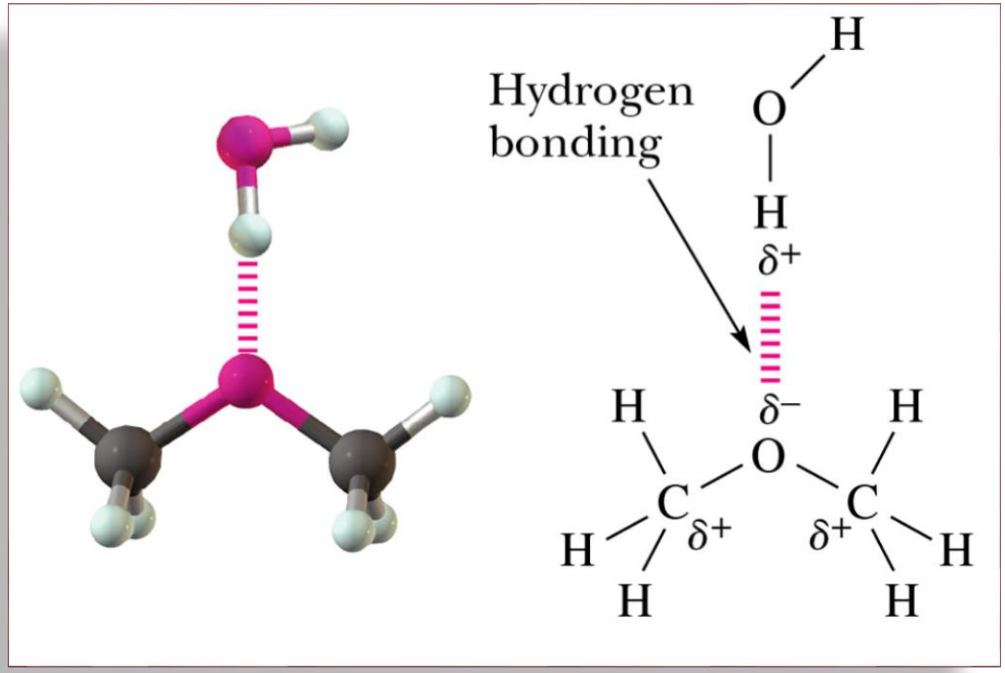
Comparisons of Physical Properties of Alcohols and Ethers

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water). Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols as shown in the table below.


Alcohol
O—H····
O
H
R
R
hydrogen bond
donor
acceptor
Ether
O—R
O
R
R
no hydrogen bond
no donor
acceptor
Alcohol + ether
O—H····
O
R
R
hydrogen bond
donor
acceptor

Solubility of Ethers:

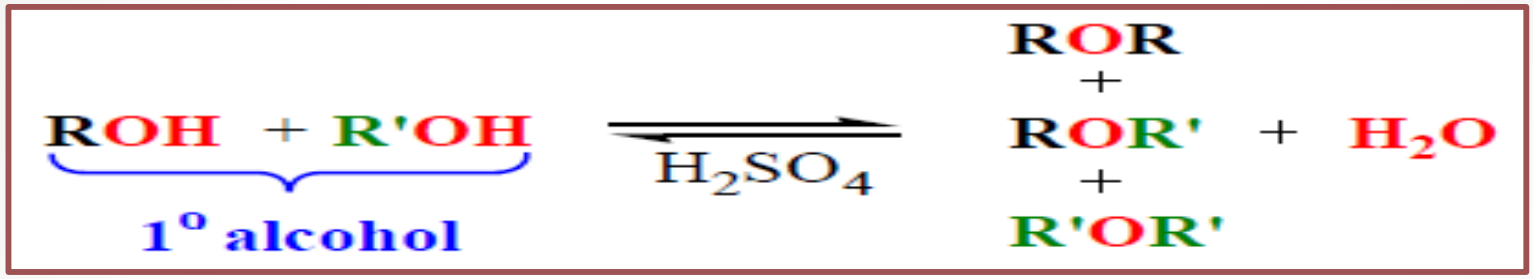
Ethers are soluble in water, due to their hydrogen bond formation with water molecules.

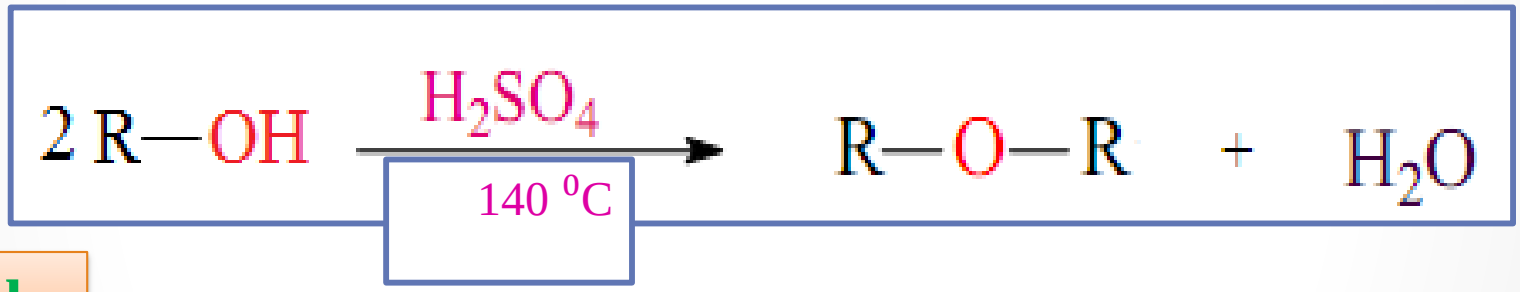


The solubility decreases with increase in the number of carbon atoms.

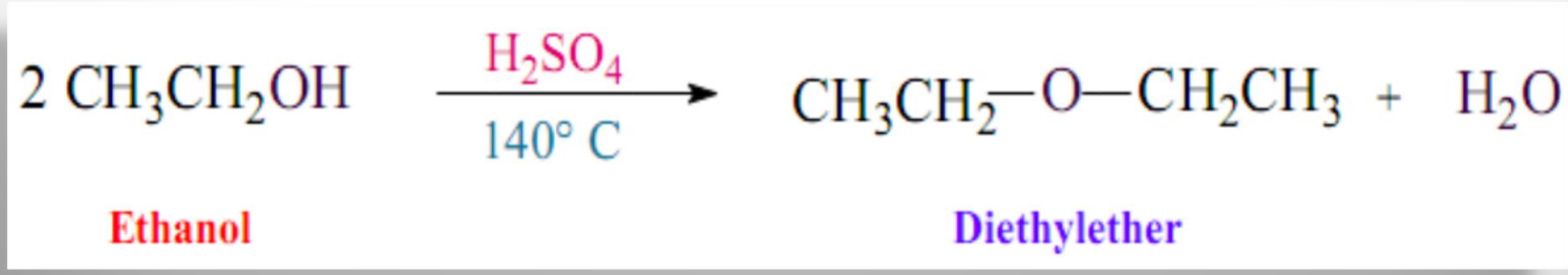
Preparation of Ethers

1- Dehydration of Alcohols

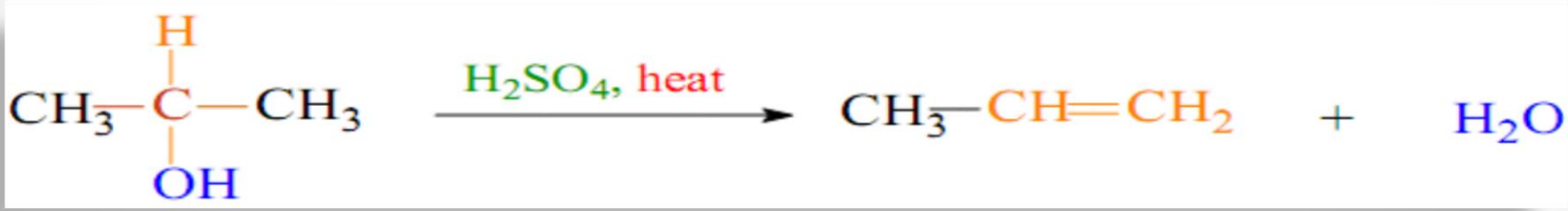


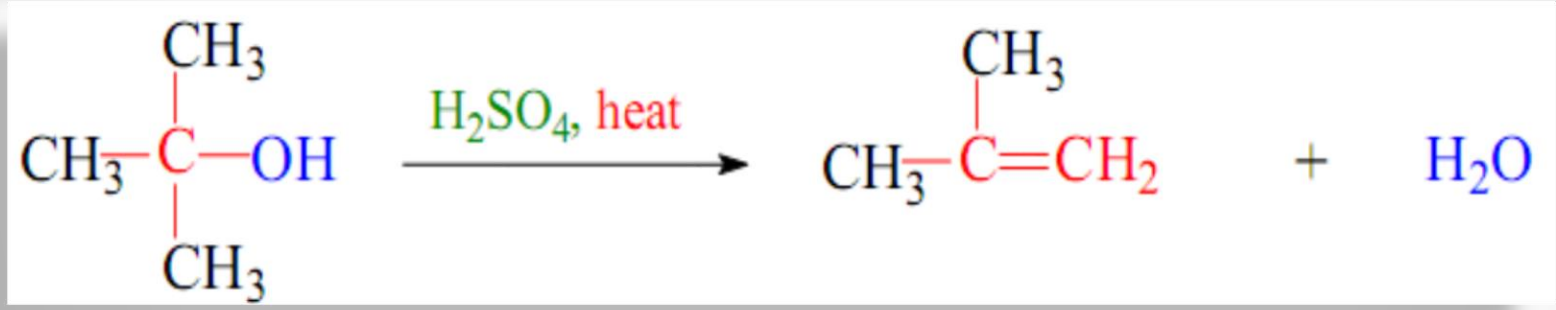


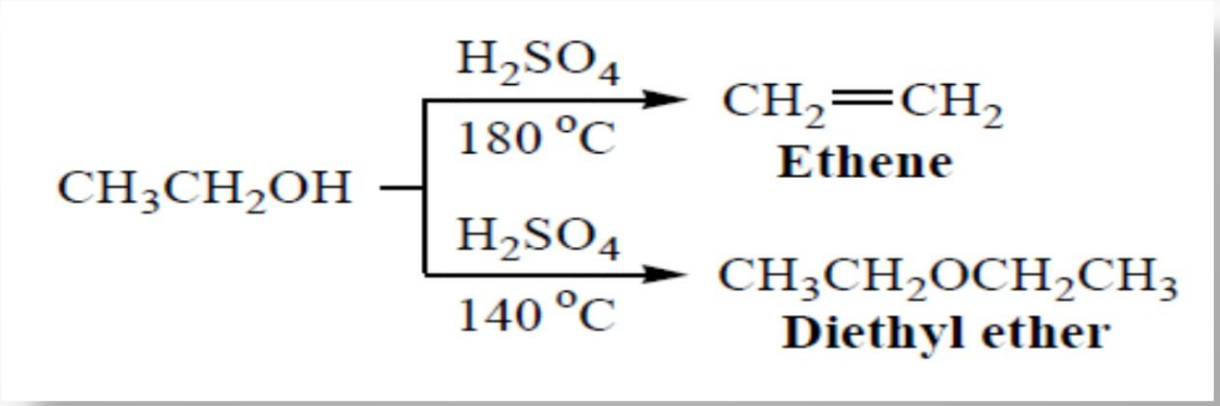
Example:



- **The dehydration of 2° and 3° alcohol is unsuccessful to get ethers as alkenes are formed easily.**

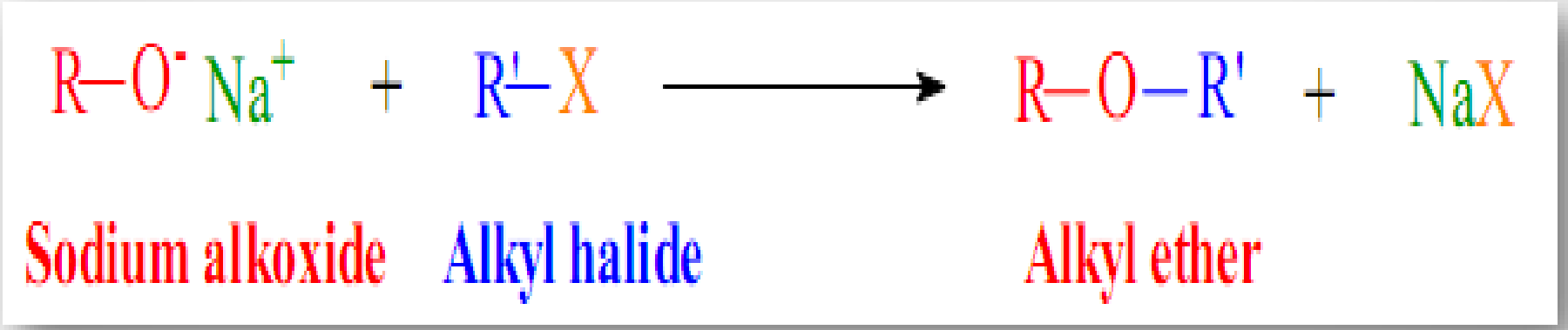


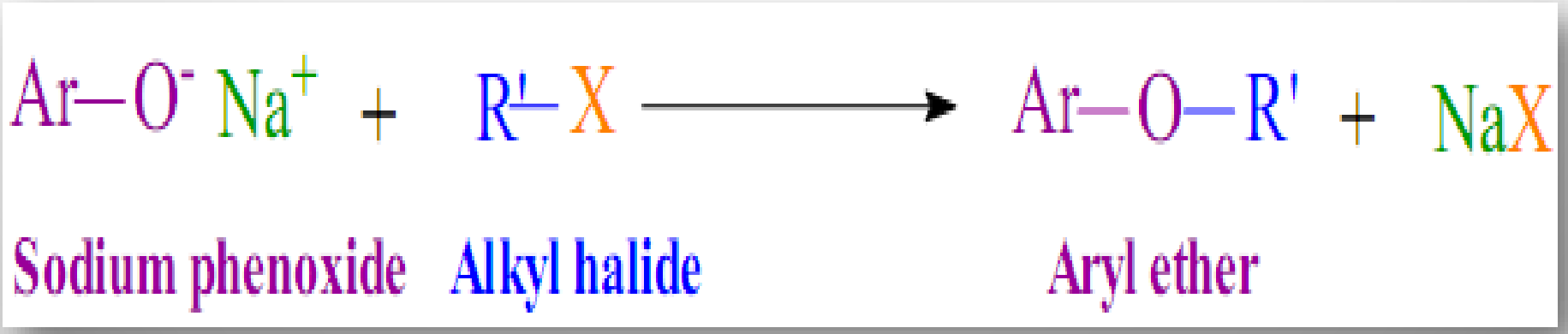


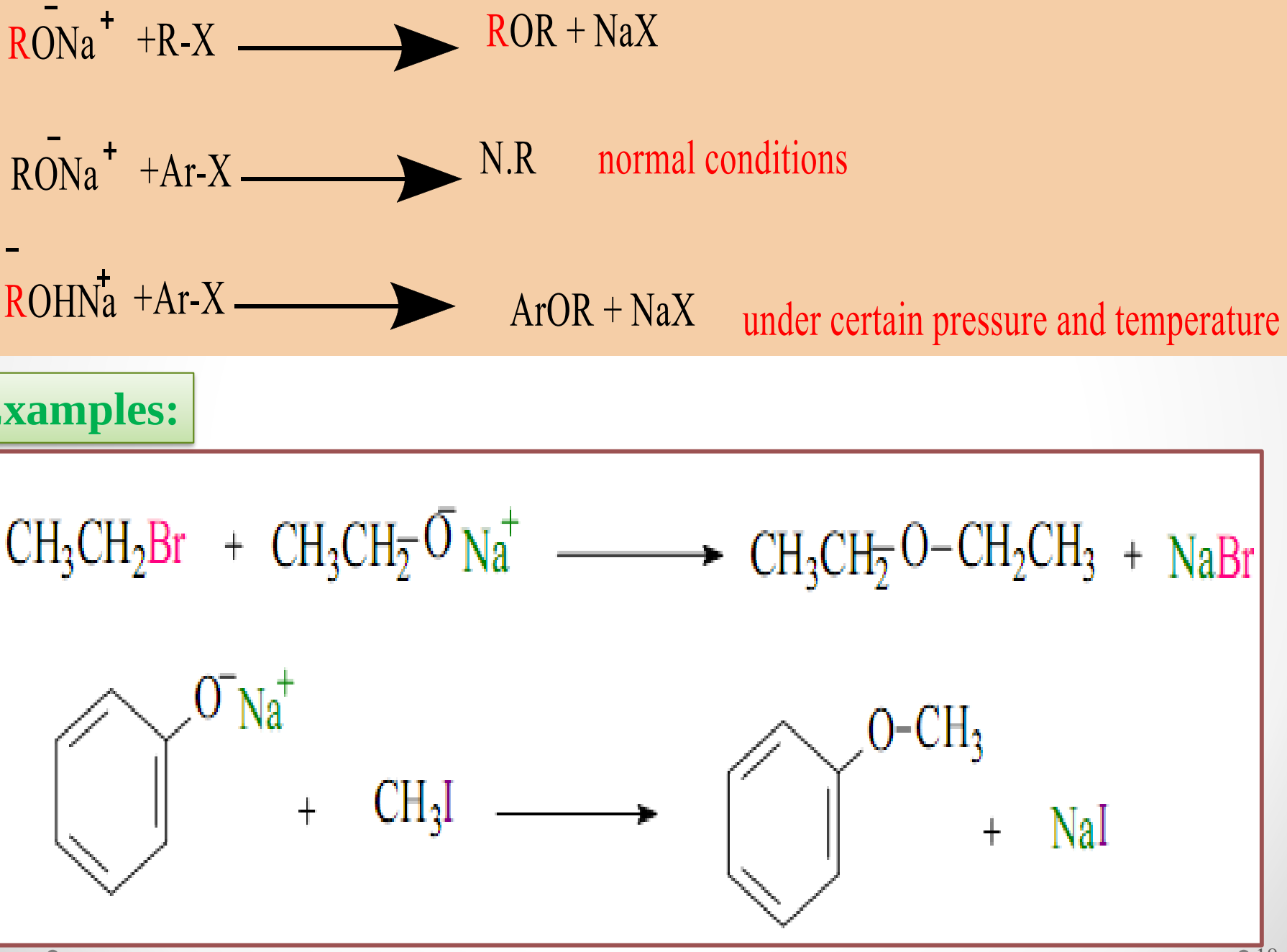


2- Williamson Synthesis

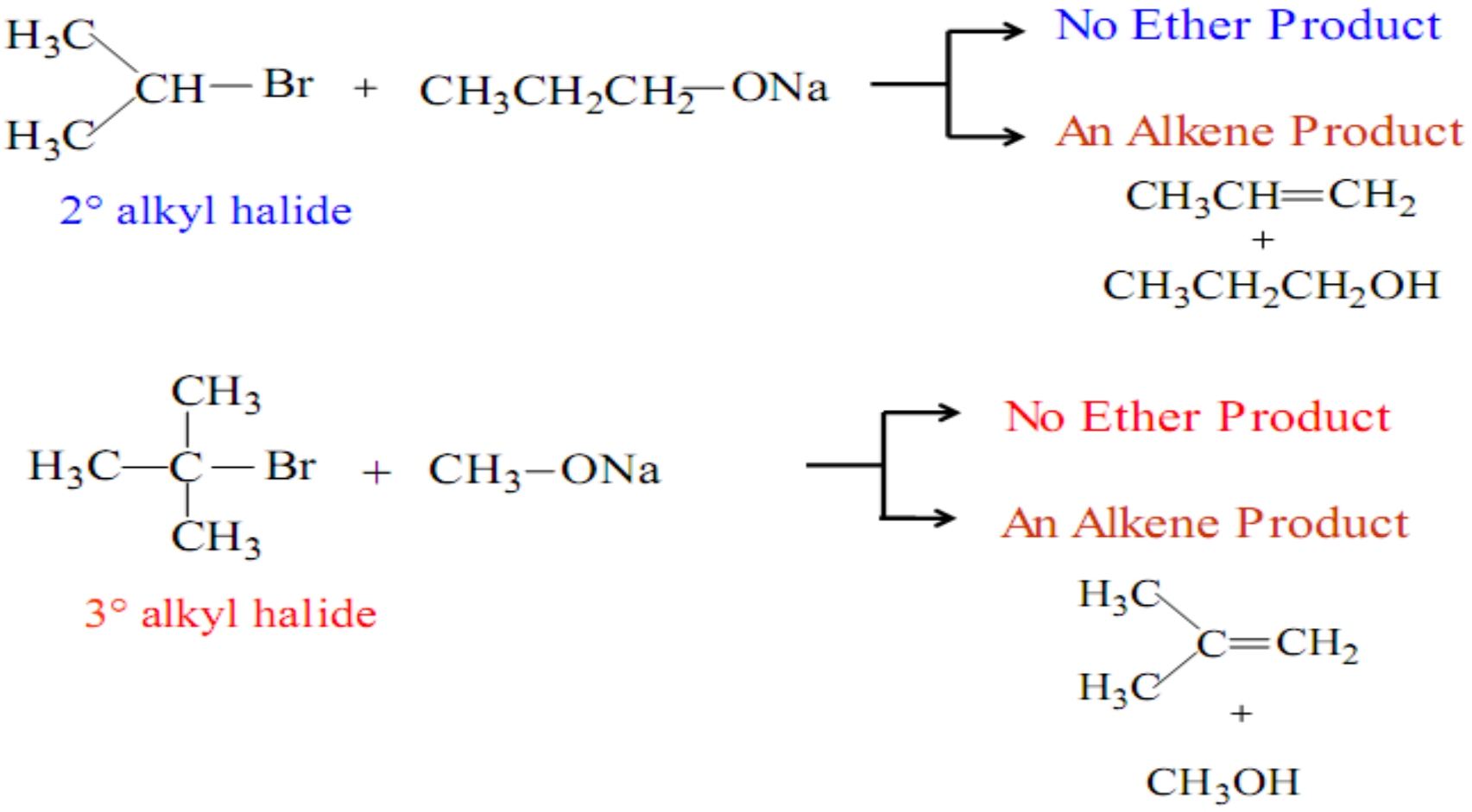
- **The reaction of a sodium alkoxide RONa or a sodium phenoxidex ArONa with an alkyl halide to form an ether.**
- **The reaction involves nucleophilic substitution of an alkoxide ion for a halide ion.**






RONa + R-X → ROR + NaX
RONa + Ar-X → N.R normal conditions
ROHNa + Ar-X → ArOR + NaX under certain pressure and temperature
Examples:
CH3CH2Br + CH3CH2O Na → CH3CH2O-CH2CH3 + NaBr
O Na + CH3I → O-CH3 + NaI

- **If a secondary (2°) or tertiary alkyl halide (3°) is used, an alkene is the only reaction product and no ether is formed.**



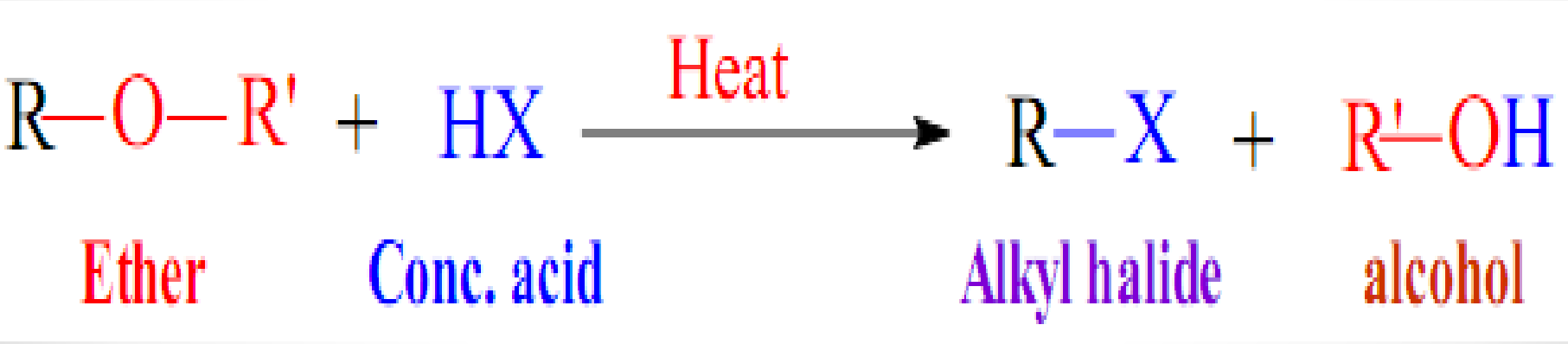
Reactions of Ethers

Cleavage of Ethers by Acids

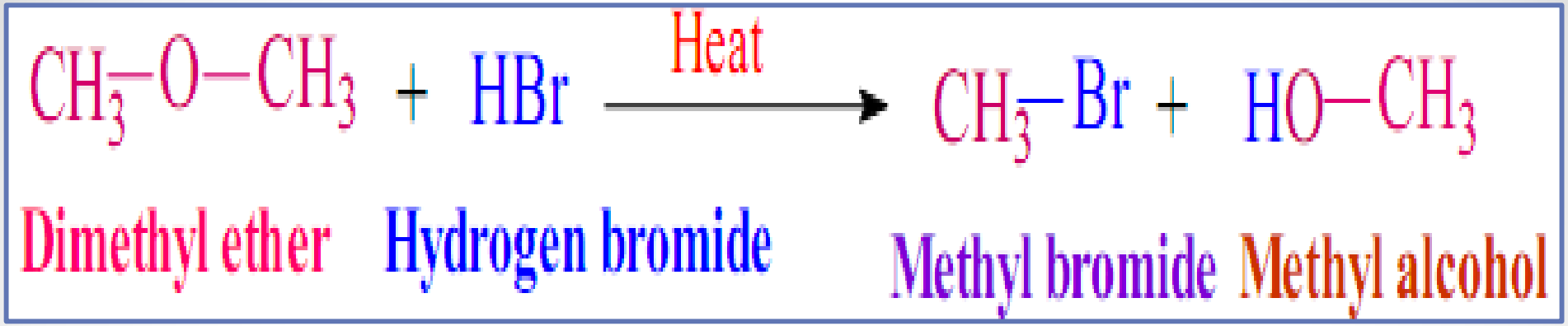
Substitution Reactions with strong acids HX,

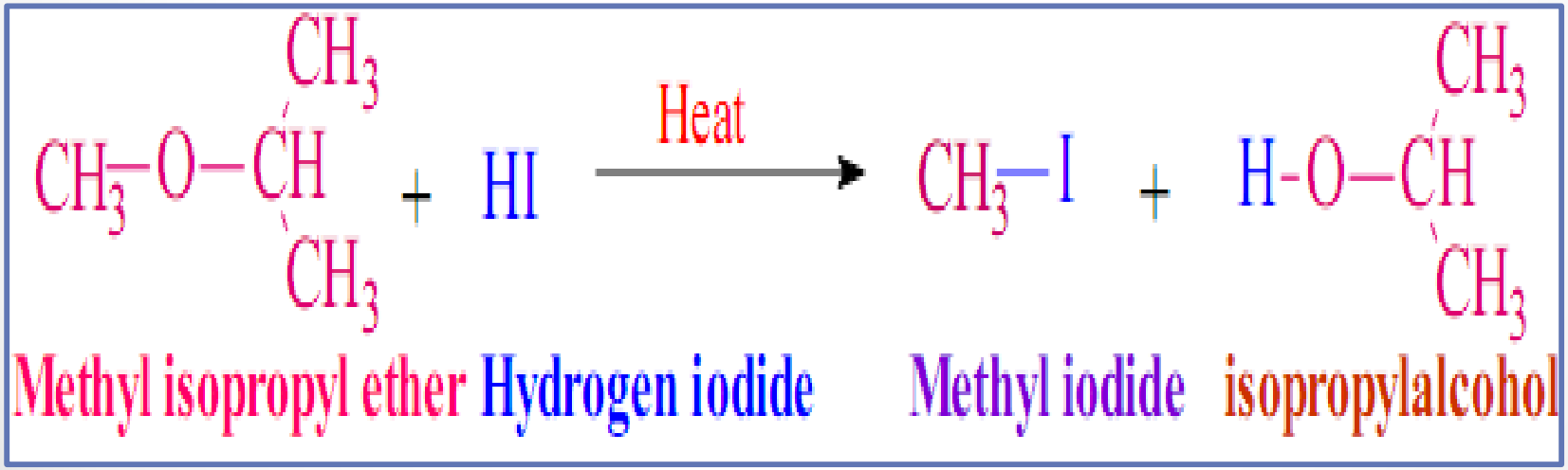
X could be; I or Br.

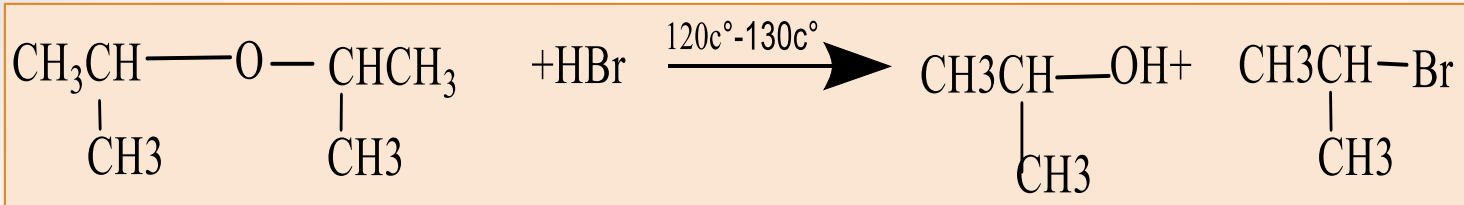
Ethers are cleaved by HX to an alcohol and a haloalkane



Examples:


CH3–O–CH3 + HBr
Heat
CH3–Br + HO–CH3
Dimethyl ether
Hydrogen bromide
Methyl bromide
Methyl alcohol

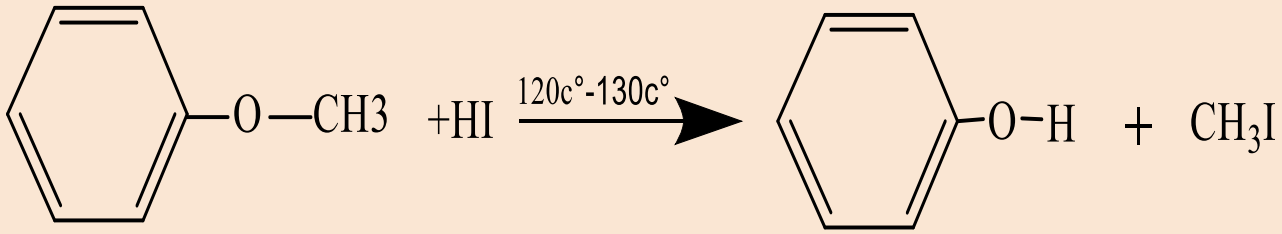

CH3–O–CH(CH3)2 + HI
Heat
CH3–I + H-O–CH(CH3)2
Methyl isopropyl ether
Hydrogen iodide
Methyl iodide
isopropylalcohol



Diethy Iisopropyl ether

2-propanol

2-bromo propane



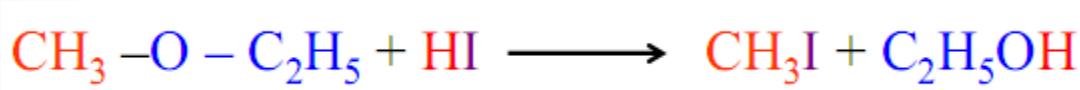
Methyl phenyl ether
or phenoxy methane

Phenol

ethyl iodide

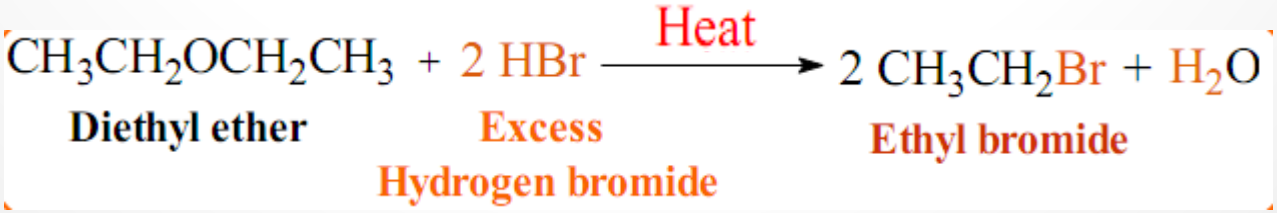
Point of cleavage:

- If both the alkyl groups are primary or secondary, the smaller alkyl group gets converted to the alkyl halide predominantly.

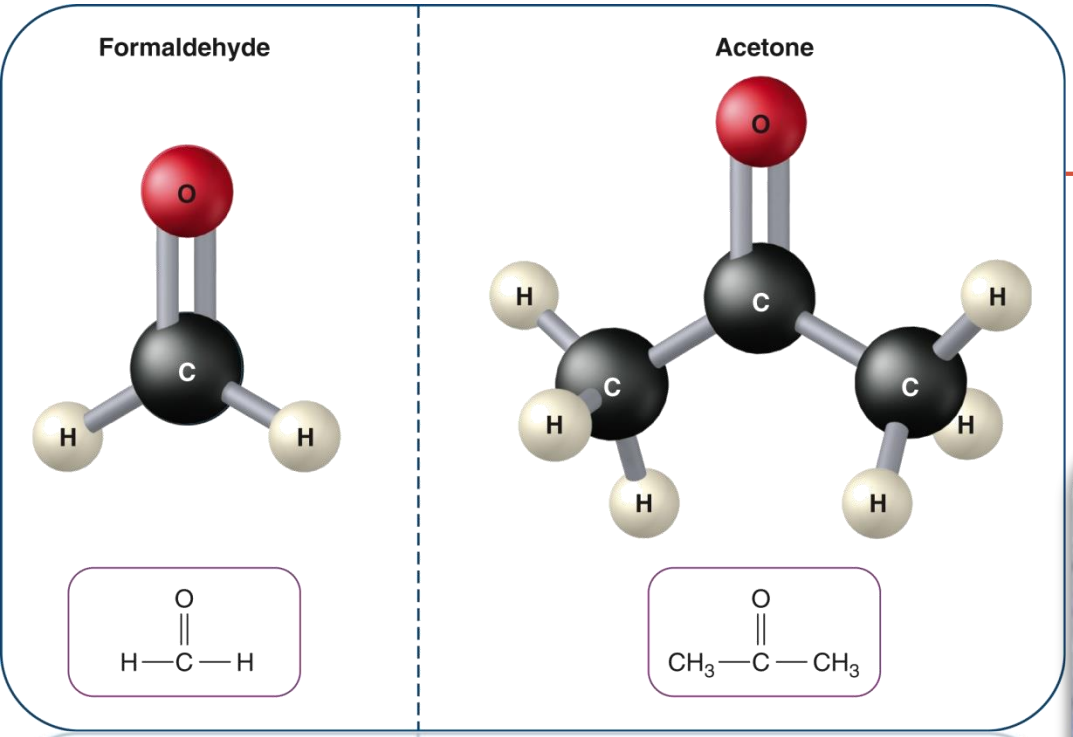


- If one of the alkyl group is tertiary, the point of cleavage is such that the tertiary alkyl halide is formed as the major product

- If two or more equivalents of acid are used further dehydration can occur on formed alcohols which may react further to form a second mole of alkyl halide.



ALDEHYDES AND KETONES

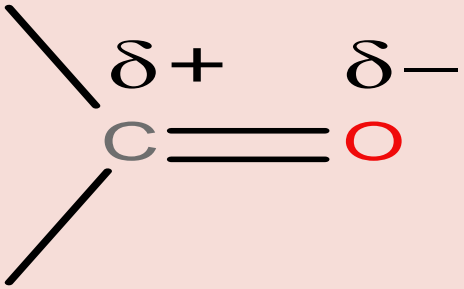


ALDEHYDES: STRUCTURE AND NOMENCLATURE

Aldehydes and ketones are organic compounds which incorporate a carbonyl functional group, C=O. The carbon atom of this group has two remaining bonds that may be occupied by hydrogen or alkyl or aryl substituents. If at least one of these substituents is hydrogen, the compound is an aldehyde RCHO or RCH=O. If neither is hydrogen, the compound is a ketone RCOR` (R and R`=alkyl or aryl).

The carbonyl group

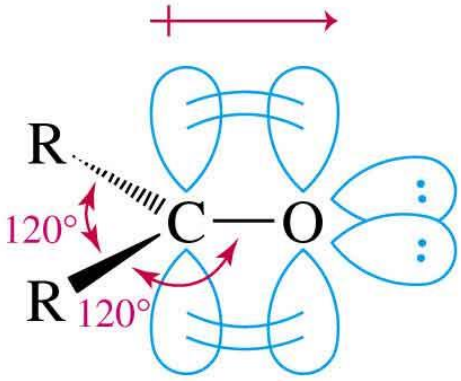
- Aldehydes and ketones are among the first examples of compounds that possess a C-O double bond .This group is called a carbonyl group, and it has very different chemical properties than a C-C double bond in alkenes:



- Because oxygen is more electronegative than carbon, the bond is polar.
- Bond angles are about 120^{o} around the carbon atom

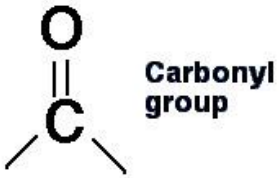
Carbonyl Structure

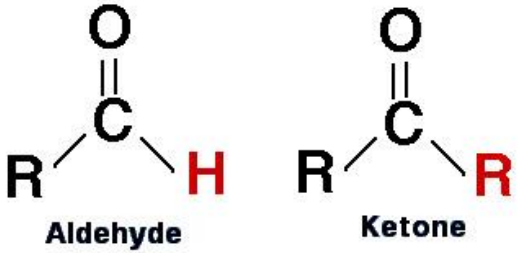
- **Carbon is sp^2 hybridized.**
- **C=O bond is shorter, stronger, and more polar than C=C bond in alkenes.**



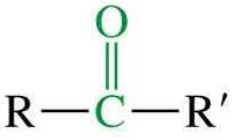
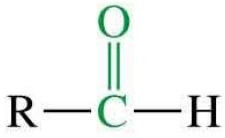
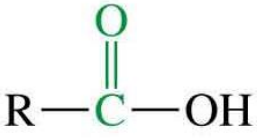
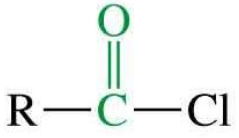
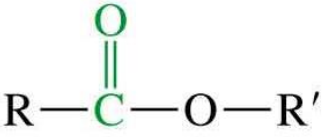
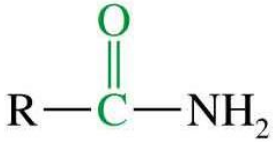
	length	*energy*
ketone C=O bond	1.23 Å	178 kcal/mol (745 kJ/mol)
alkene C=C bond	1.34 Å	146 kcal/mol (611 kJ/mol)

=>





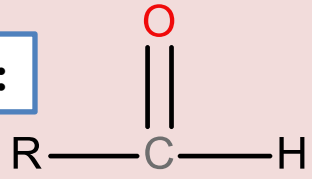
Some Common Classes Carbonyl Compounds

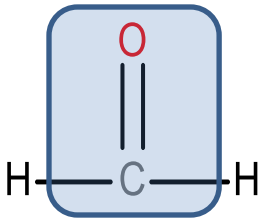
Class	General Formula	Class	General Formula
ketones		aldehydes	
carboxylic acids		acid chlorides	
esters		amides	

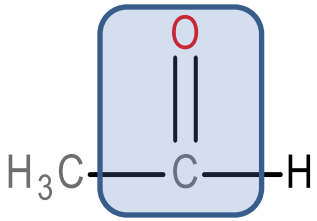
Compounds containing the carbonyl group

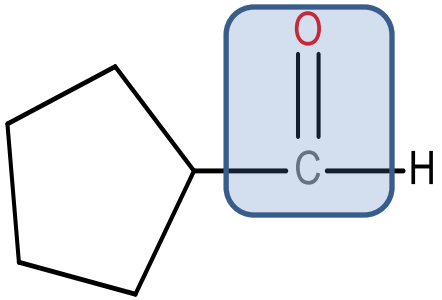
- The following classes of organic compounds involve the carbonyl group:
  - Aldehydes have a H-atom or a carbon substituent (alkyl, cycloalkyl, aromatic) bound to a CHO group (carbonyl group bound to a H-atom):

General formula for aldehyde:





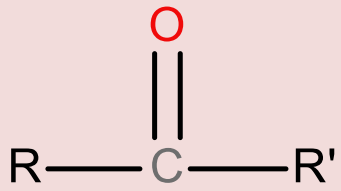


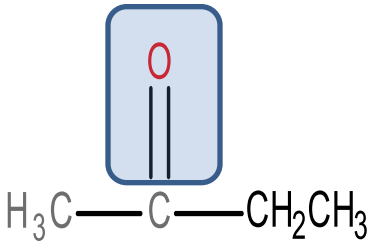


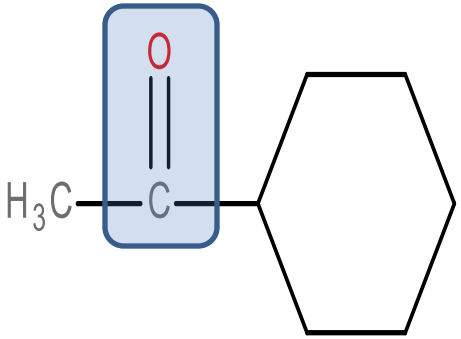
Compounds containing the carbonyl group

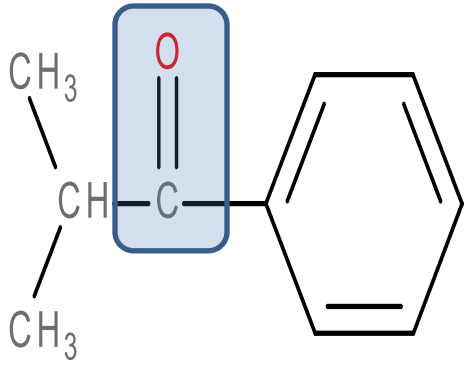
- Ketones have two carbon substituents (akyl, cycloalkyl, aromatic and not necessarily the same)

General formula for ketones:







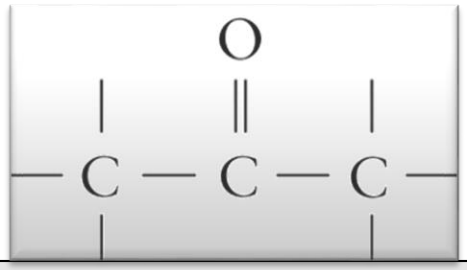


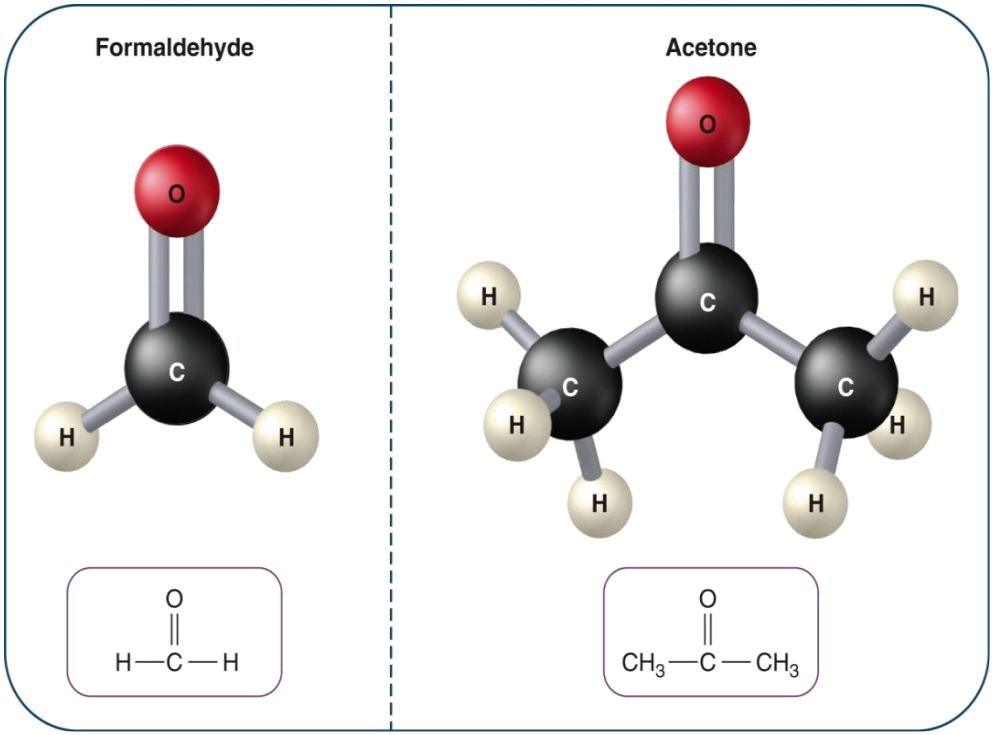
ALDEHYDES AND KETONES

- The **carbonyl group**:

- **Aldehydes** have at least one hydrogen attached to the **carbonyl group**.

- Ketones have two carbons attached to the **carbonyl group**.



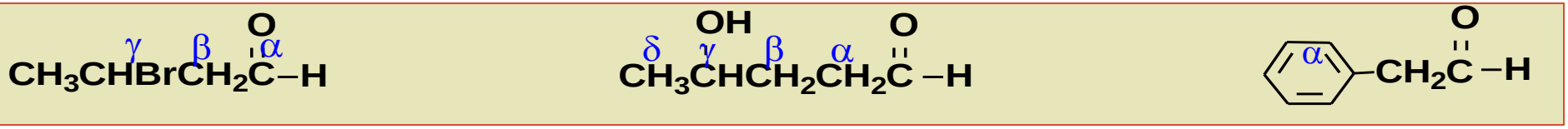


Common Names of Aldehydes

- **In the common system, aldehydes are named from the common names of the corresponding carboxylic acid.**
- **The '*ic acid*' ending is replaced with '*aldehyde*'.**
- **The aldehyde group is always at the end of a chain (terminal).**

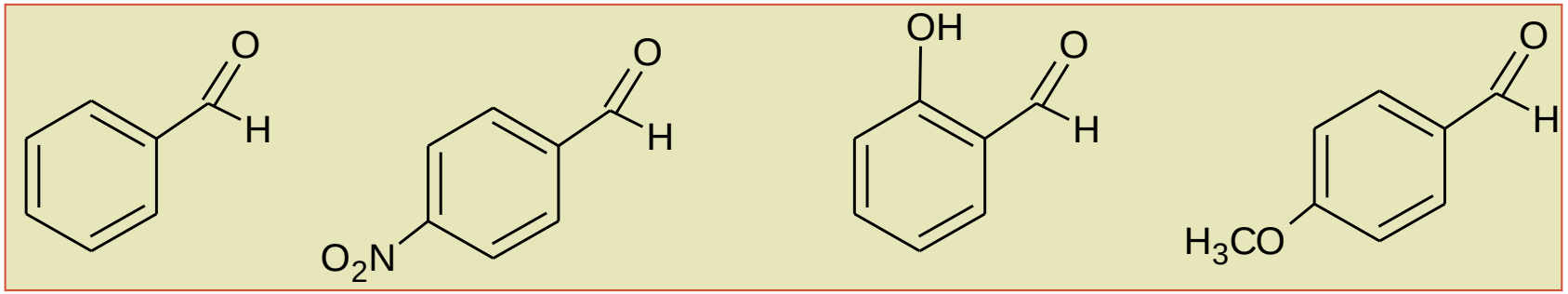
Structure	IUPAC name	Common name	Structure	IUPAC	Common name
HCO_2H	methanoic acid		HCHO	methanal	
CH_3CO_2H	ethanoic acid		CH_3CHO	ethanal	
$CH_3CH_2CO_2H$	propanoic acid		CH_3CH_2CHO	propanal	
$CH_3(CH_2)_2CO_2H$	butanoic acid		$CH_3(CH_2)_2CHO$	butanal	
$CH_3(CH_2)_3CO_2H$	pentanoic acid		$CH_3(CH_2)_3CHO$	pentanal	
$CH_3(CH_2)_4CO_2H$	hexanoic acid		$CH_3(CH_2)_4CHO$	hexanal	

- **Substituents locations are given using Greek letters (α, β, γ, δ, ε, ω.) beginning with the carbon *next to* the carbonyl carbon, the a-carbon.**



β-bromobutyraldehyde **γ-hydroxyvaleraldehyde** **α-phenylacetaldehyde**

- **Aromatic aldehydes are usually designated as derivatives of the simplest aromatic aldehyde, Benzaldehyde**



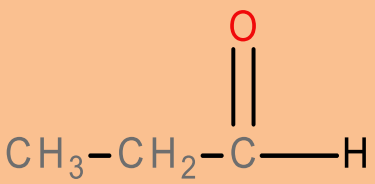
Benzaldehyde **p-Nitrobenzaldehyde** **o-Hydroxybenzaldehyde Salicylaldehyde** **p-Methoxybenzaldehyde Anisaldehyde**

IUPAC Nomenclature of Aldehydes

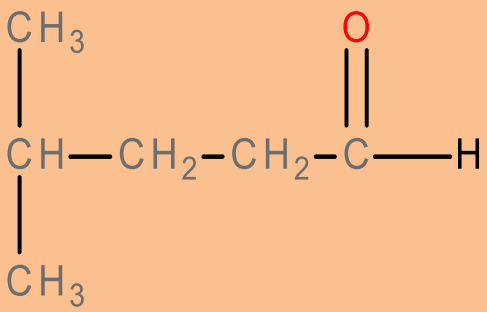
- **Select the longest continuous carbon chain that contains the C=O group and replace the ending -e by the suffix -al**
- **The CHO group is assigned the number "1" position and takes precedence over other functional groups that may the present such as –OH, C=C ……**
- **If the CHO group is bonded to a ring, name the ring and add the suffix *-carbaldehyde*.**

Nomenclature for aldehydes

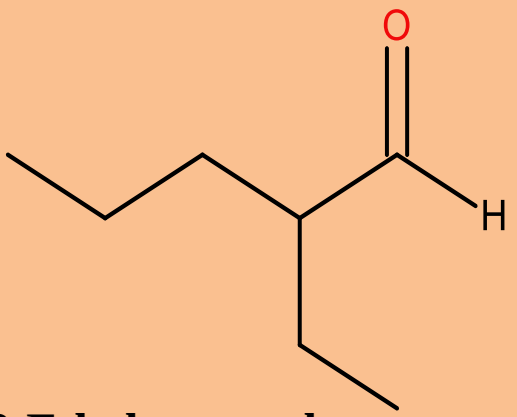
- **IUPAC rules:**
  - **Select as the parent chain the longest continuous chain that includes the carbonyl carbon**
  - **Name the parent chain by changing the corresponding alkane name (ending with “e”) to an ending with “al”**
  - **Number the parent chain assuming the carbonyl carbon is C-1**
  - **Identify substituents on the parent chain as before, at the beginning of the compound’s name.**



Propanal

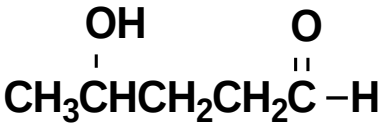


4-Methylpentanal

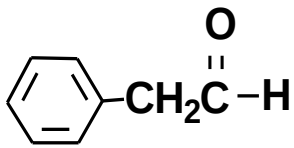


2-Ethylpentanal

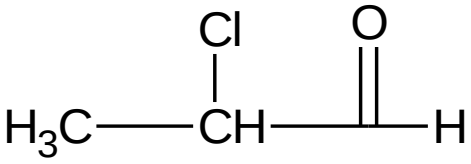
3-bromobutanal



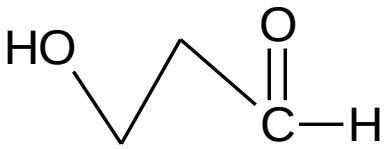
4-hydroxypentanal



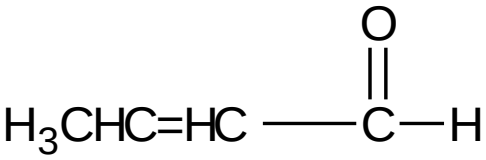
2-phenylethanal



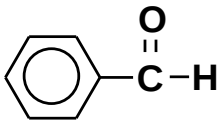
2-Chloropropanal



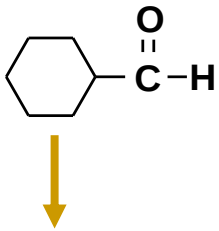
3-Hydroxypropanal



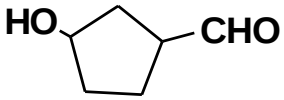
2-Butenal



benzenecarbaldehyde



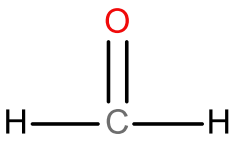
cyclohexanecarbaldehyde



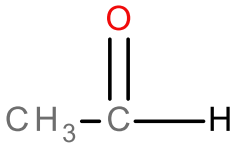
3-hydroxycyclopentanecarbaldehyde

Nomenclature for aldehydes

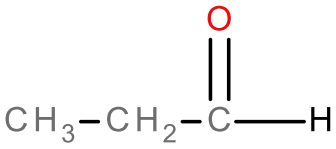
- For aldehydes having short carbon chains, the following common names are usually encountered:



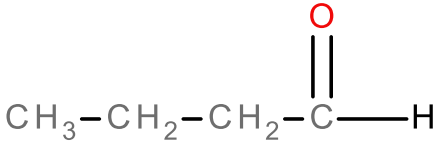
Formaldehyde (Methanal)



Acetaldehyde (Ethanal)



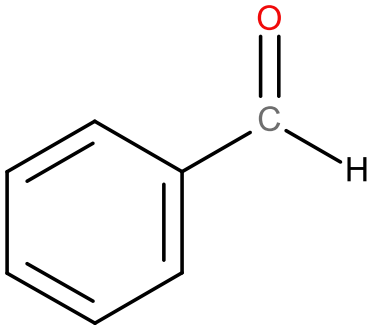
Propionaldehyde (Propanal)



Butyraldehyde (Butanal)

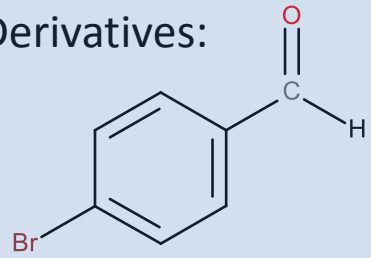
IUPAC

- The following aromatic aldehyde is called benzaldehyde:

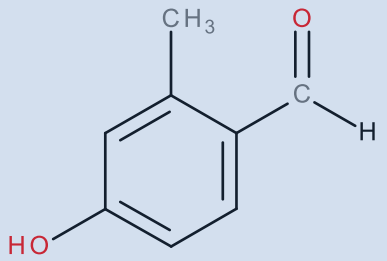


Benzaldehyde

Derivatives:



4-Bromobenzaldehyde



4-Hydroxy-2-methylbenzaldehyde

Nomenclature of Ketones

❖ **Common name:**

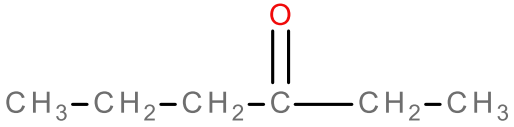
❑ **listing the alkyl substituents attached to the carbonyl group alphabetically, followed by the word ketone. As with aldehydes, substituents locations are given in common names using Greek letters (α, β, γ, δ, ε, ω.) beginning with the a-carbon.**

❖ **IUPAC system:**

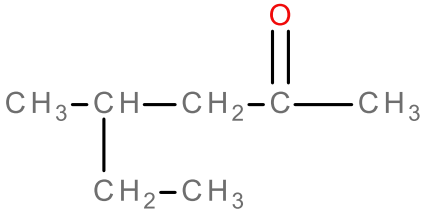
- **Find the longest chain containing the carbonyl group, and change the *-e* ending of the parent alkane to the suffix *-one*.**
- **Number the carbon chain to give the carbonyl carbon the lower number. Apply all of the other usual rules of nomenclature.**
- **Ketones are just below aldehydes in nomenclature priority.**
- **A ketone group is named as an 'oxo' substituent in an aldehyde.**

Nomenclature for ketones

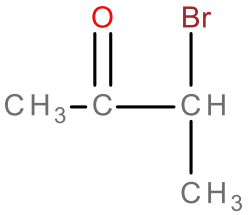
- IUPAC:
  - Select as the parent chain the longest continuous chain that involves the carbonyl carbon
  - Name the parent chain by removing the "e" from the corresponding alkane name and adding "one"
  - Number the chain to give the carbonyl group the lowest numbering. The number goes before the parent chain name
  - Determine the number and location of substituents and number them accordingly
  - For cyclic ketones, the carbonyl carbon is C-1 and the name begins with "cyclo"



3-Hexanone

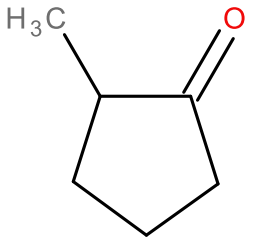


4-Methyl-2-hexanone



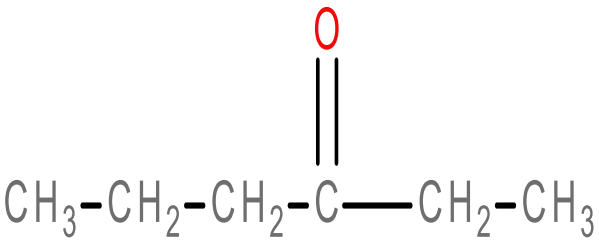
3-Bromo-2-butanone

2-Methylcyclopentanone

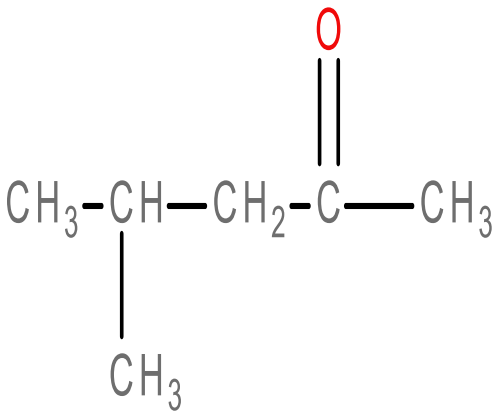


Nomenclature for ketones

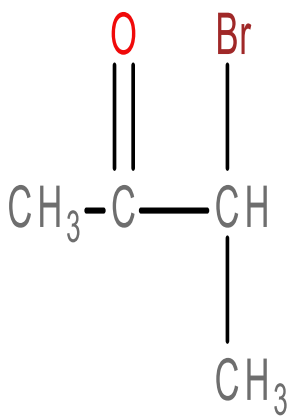
- The common system of naming ketones is similar to what we saw for ethers:



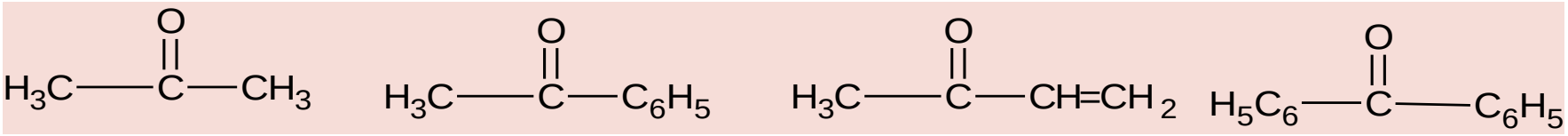
Ethyl propyl ketone



Isobutyl methyl ketone



1-Bromoethyl methyl ketone

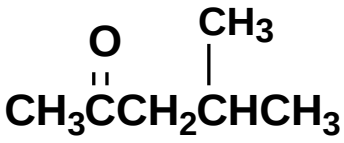


Common

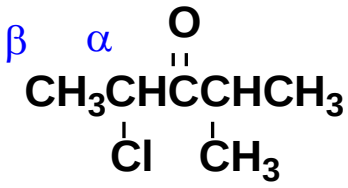
Dimethyl ketone	Methyl phenyl ketone	Methyl vinyl ketone	Diphenyl ketone
Acetone	Acetophenone		Benzophenone

IUPAC

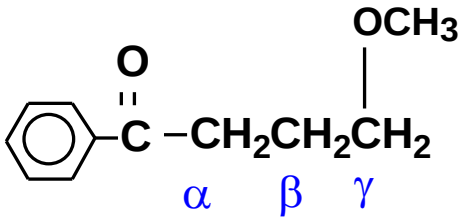
Propanone	Phenyl ethanone	3-Buten-2-one	Diphenylmethanone



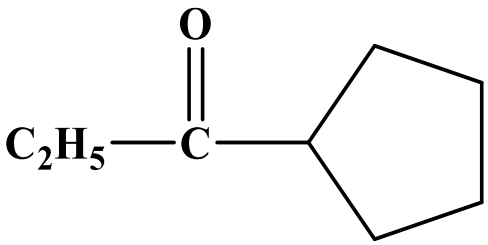
Methyl isobutyl ketone (MIBK)



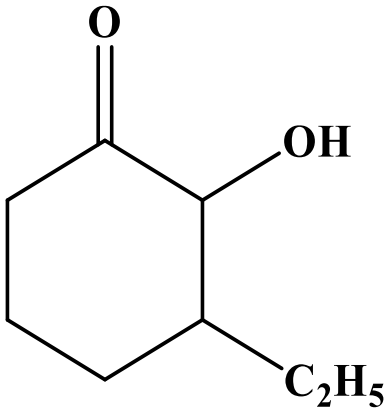
α-Chloroethyl isopropyl ketone



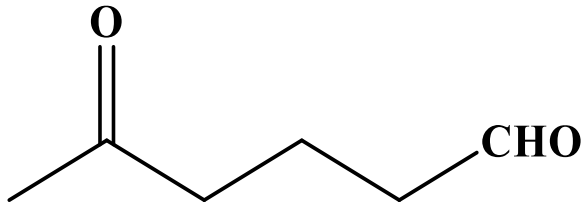
g-Methoxypropyl phenyl ketone



Cyclopentylpropanone



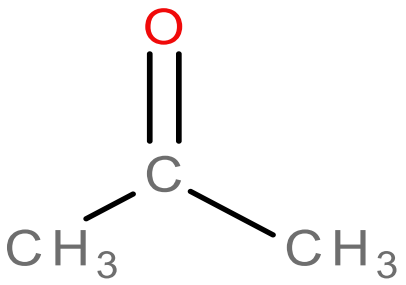
3-Ethyl-2-hydroxycyclohexanone



5-Oxohexanal

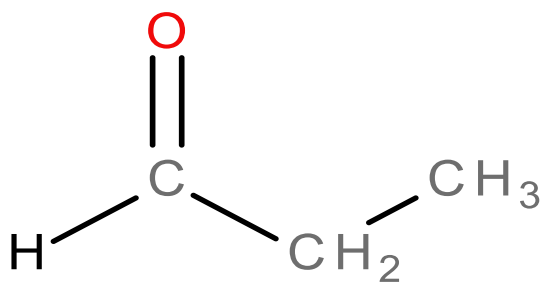
Isomerism for aldehydes and ketones

- Aldehydes and ketones that have a given number of carbon atoms are *functional group isomers*. (This is the third group of compounds we have seen that have this relationship; others were alcohols/ethers and thiols/thioethers)



Propanone

a ketone



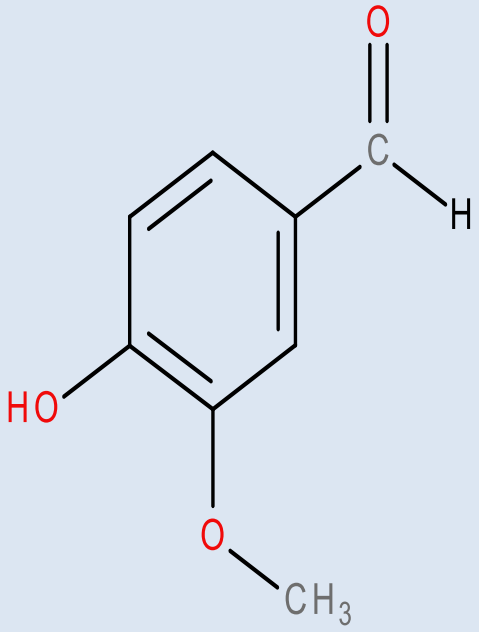
Propanal

an aldehyde

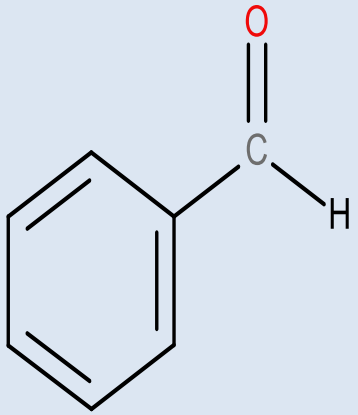
C_3H_6O

Common aldehydes and ketones

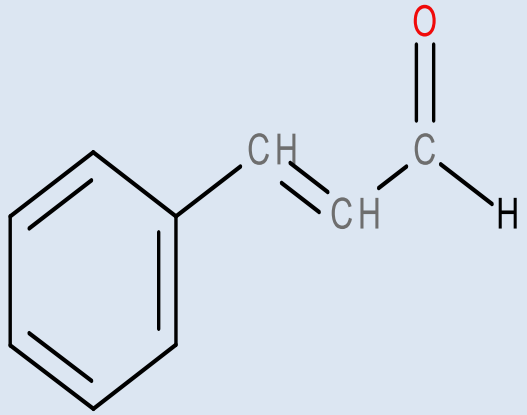
- Aldehydes are often recognizable by their "sweet" smells:



Vanillin
(vanilla flavoring)



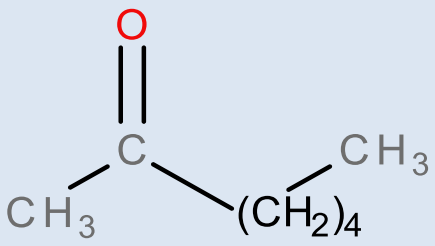
Benzaldehyde
(almond flavoring)



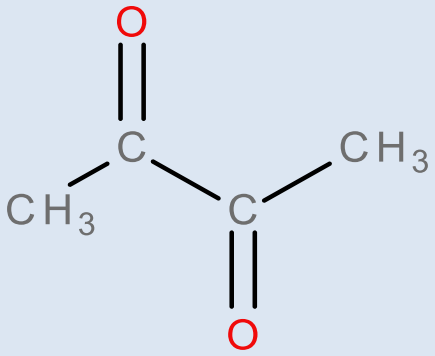
Cinnamaldehyde
(cinnamon flavoring)

Common aldehydes and ketones

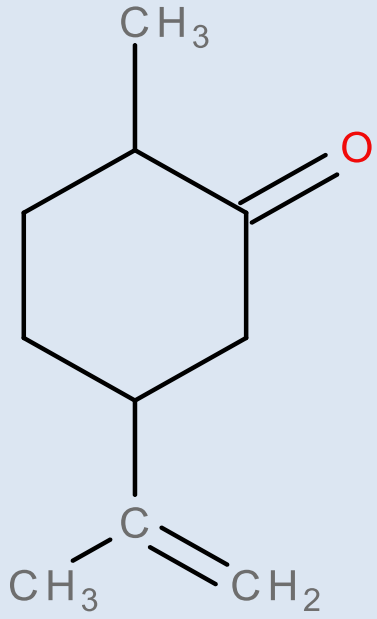
- Some ketones (e.g. acetone) have a “sweet” smell also). Other examples are:



2-Heptanone
(clove flavoring)

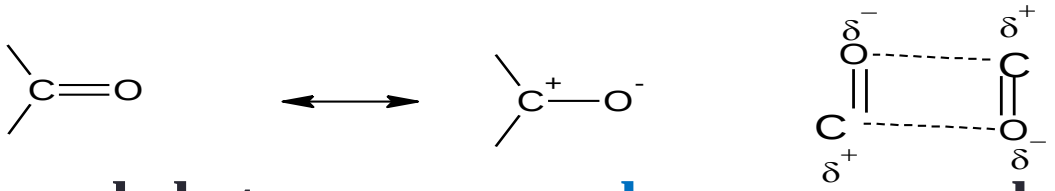


Butanedione
(butter flavoring)

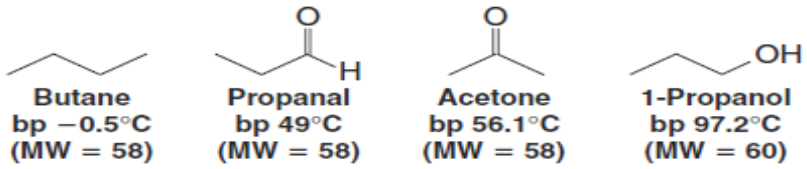


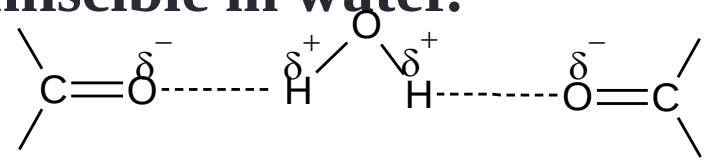
Carvone
(spearmint flavoring)

PHYSICAL PROPERTIES OF KETONES AND ALDEHYDE



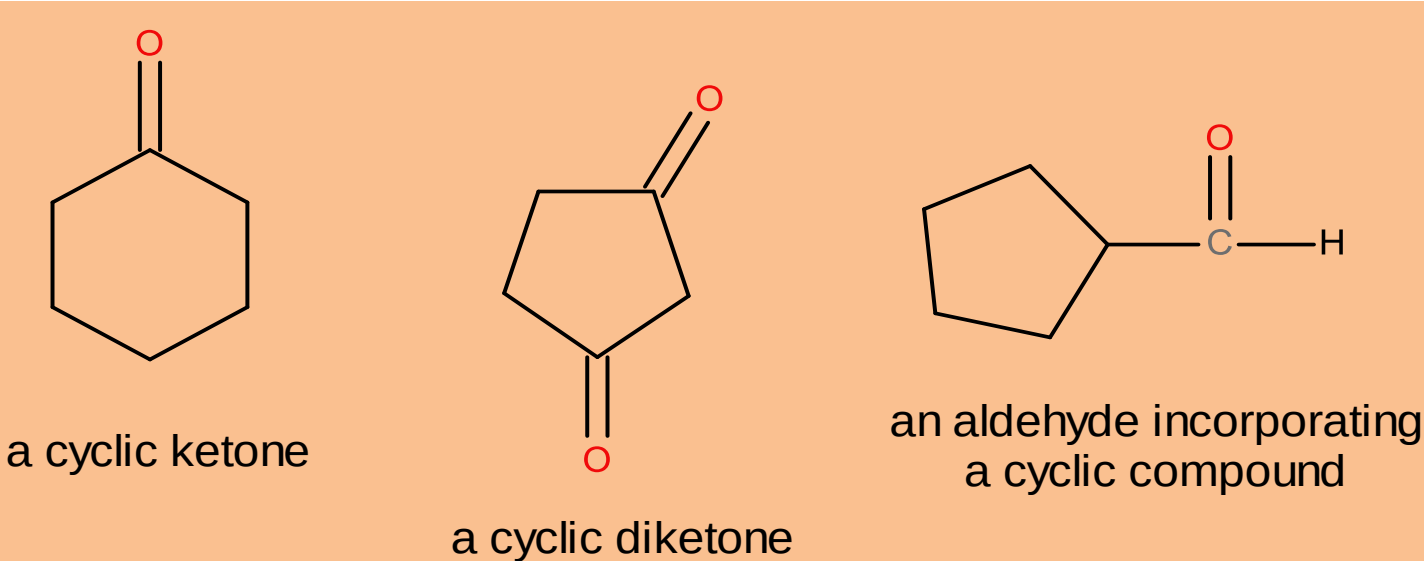
- **Aldehydes and ketones are polar compounds, Because the polarity of the carbonyl group.**
- **Polarization of CO group creates Dipole-dipole attractions between the molecules of aldehydes and ketones, resulting in higher boiling points than nonpolar alkanes and ether.**
- **aldehydes and ketones lower than alcohols Because Dipole-dipole attractions , are not as strong as interactions due to hydrogen bonding.**
- **The lower aldehydes and ketones are soluble. Acetone, formaldehyde and acetaldehyde are miscible in water.**





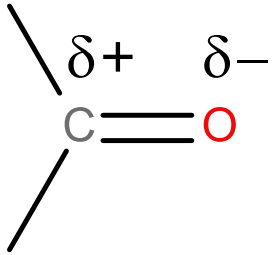
Aldehyde and ketone functional group

- Cyclic aldehydes are not possible, because in order for the carbonyl group to be part of the ring structure, two bonds to carbon groups would be required.
- Aldehydes may incorporate ring structures, but not be part of the ring.
- Also, note that cyclic ketones aren't heterocyclic compounds.



Physical properties of aldehydes and ketones

- Neither aldehydes nor ketones possess the ability to H-bond with other molecules like themselves. Consequently, boiling points for aldehydes and ketones are lower than for alcohols of similar molar mass.
- The C-O double bond in these molecules is polar, so dipole-dipole forces do exist. As a result, their boiling points tend to be higher than for alkanes of similar molar mass.

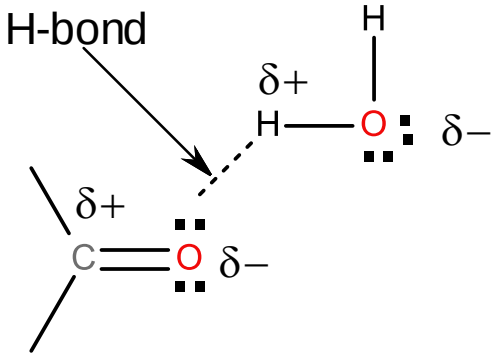


Physical properties of aldehydes and ketones

Type of Compound	Compound	Structure	Molecular Mass	Boiling Point (8°C)
alkane	ethane	$CH_3—CH_3$	30	−89
aldehyde	methanal	H—CHO	30	−21
alcohol	methanol	$CH_3—OH$	32	65
alkane	propane	$CH_3—CH_2—CH_3$	44	−42
aldehyde	ethanal	$CH_3—CHO$	44	20
alcohol	ethanol	$CH_3—CH_2—OH$	46	78
alkane	butane	$CH_3—CH_2—CH_2—CH_3$	58	−1
aldehyde	propanal	$CH_3—CH_2—CHO$	58	49
alcohol	1-propanol	$CH_3—CH_3—CH_2—OH$	60	97

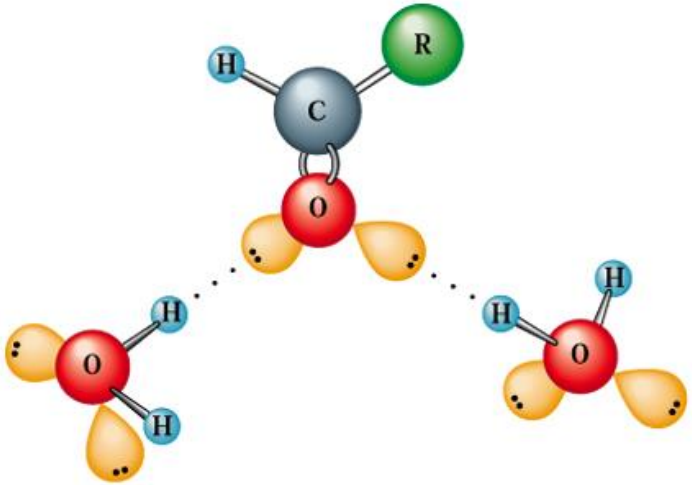
Physical properties of aldehydes and ketones

- Water molecules can interact (H-bond) with the non-bonding pairs of the carbonyl group oxygen atom, enabling aldehydes and ketones that have small carbon chain components to be water-soluble.

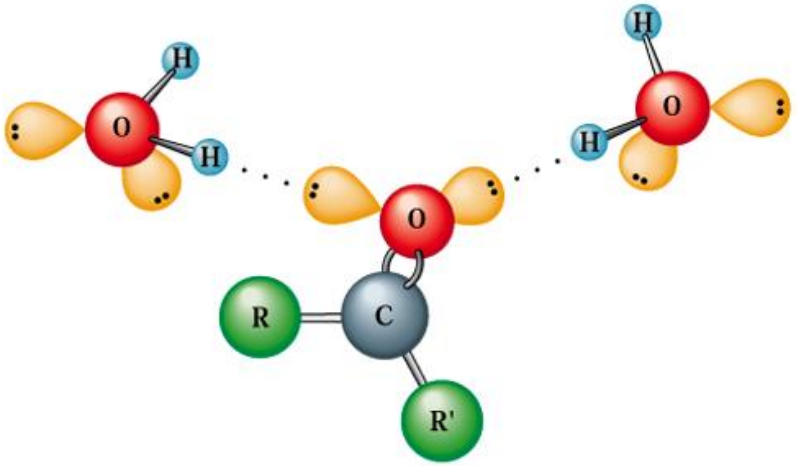


- As we saw for alcohols, the greater the carbon chain length, the lower the water-solubility (makes the molecule less polar)

Physical properties of aldehydes and ketones



(a) Aldehyde–Water Hydrogen Bonding



(b) Ketone–Water Hydrogen Bonding

Physical properties of aldehydes and ketones

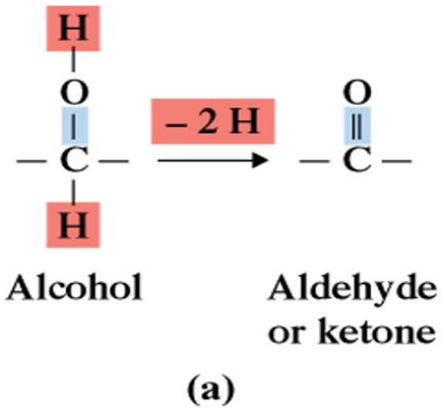
Number of Carbon Atoms	Aldehyde	Water Solubility of Aldehyde ($g/100\ g\ H_2O$)	Ketone	Water Solubility of Ketone ($g/100\ g\ H_2O$)
1	methanal	very soluble		
2	ethanal	infinite		
3	propanal	16	propanone	infinite
4	butanal	7	2-butanone	26
5	pentanal	4	2-pentanone	5
6	hexanal	1	2-hexanone	1.6
7	heptanal	0.1	2-heptanone	0.4
8	octanal	insoluble	2-octanone	insoluble

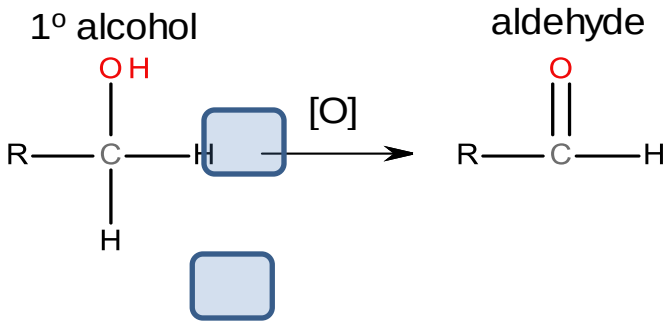
Comparing an aldehyde and a ketone of a given number of C-atoms, the ketone is generally more soluble. Why?

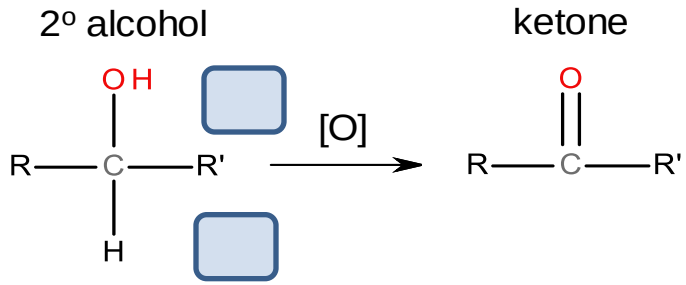
Preparation of aldehydes and ketones

- Oxidation of alcohols

- We saw already how alcohols can be oxidized to form aldehydes and ketones.
- Primary (1°) alcohols are oxidized to aldehydes (and subsequently to carboxylic acids)
- Secondary (2°) alcohols are oxidized to ketones



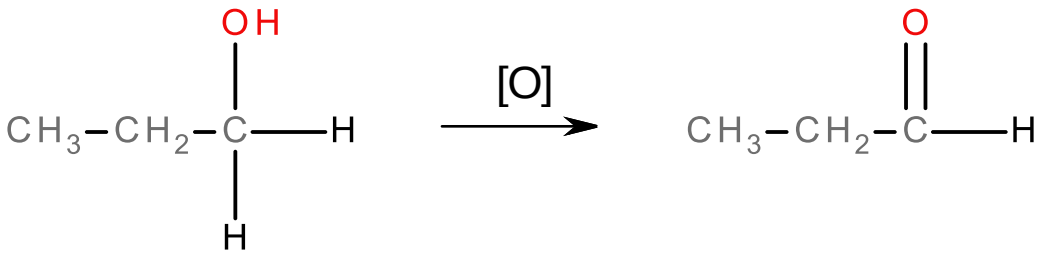




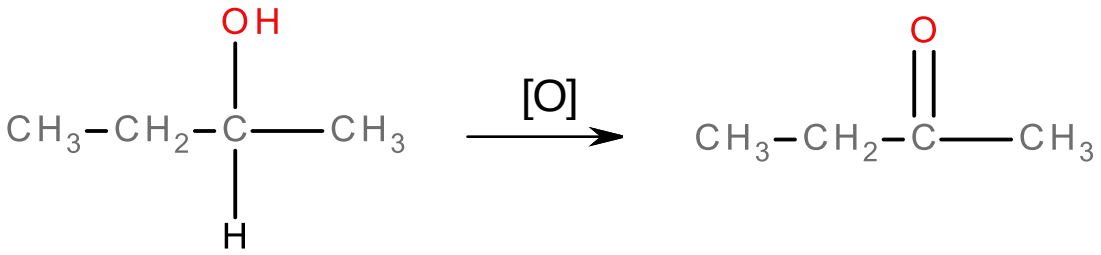
[O] = $KMnO_4$ or $K_2Cr_2O_7$

Aldehyde and ketone functional group

- As we saw, alcohols can be used to create aldehydes and ketones. Oxidation of a primary alcohol yields an aldehyde:



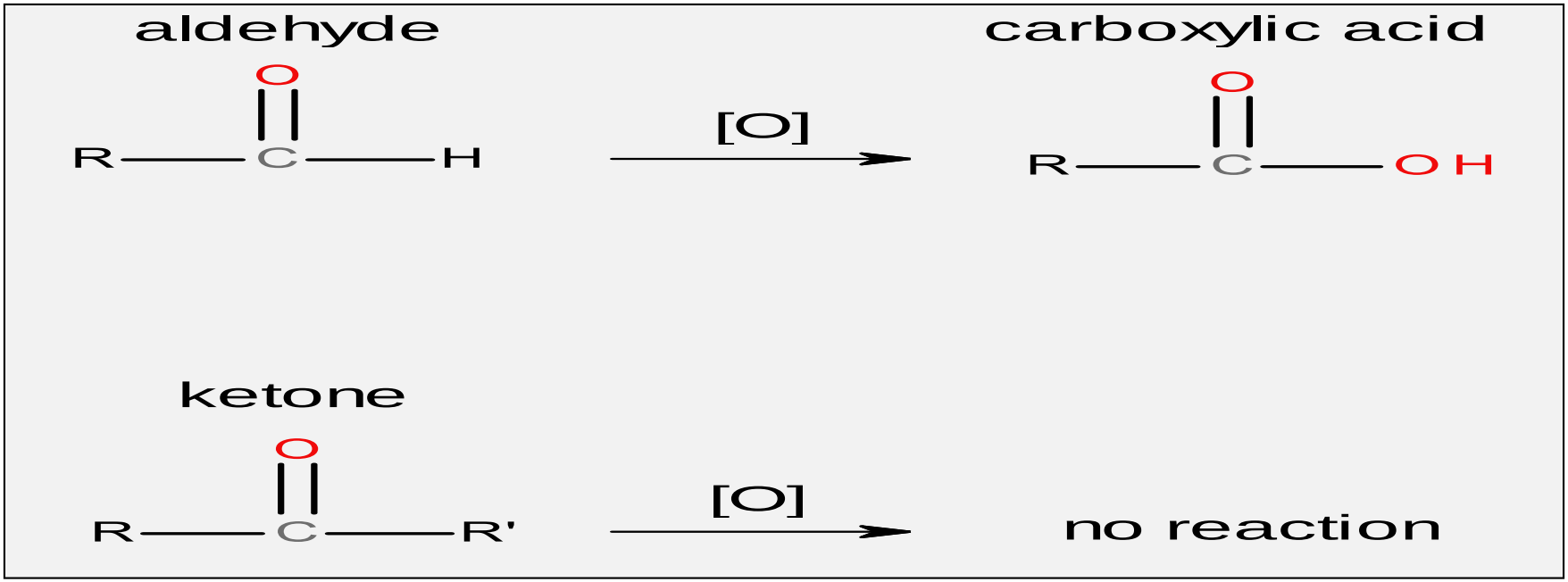
- And oxidation of a secondary alcohol yields a ketone:



Oxidation and reduction of aldehydes and ketones

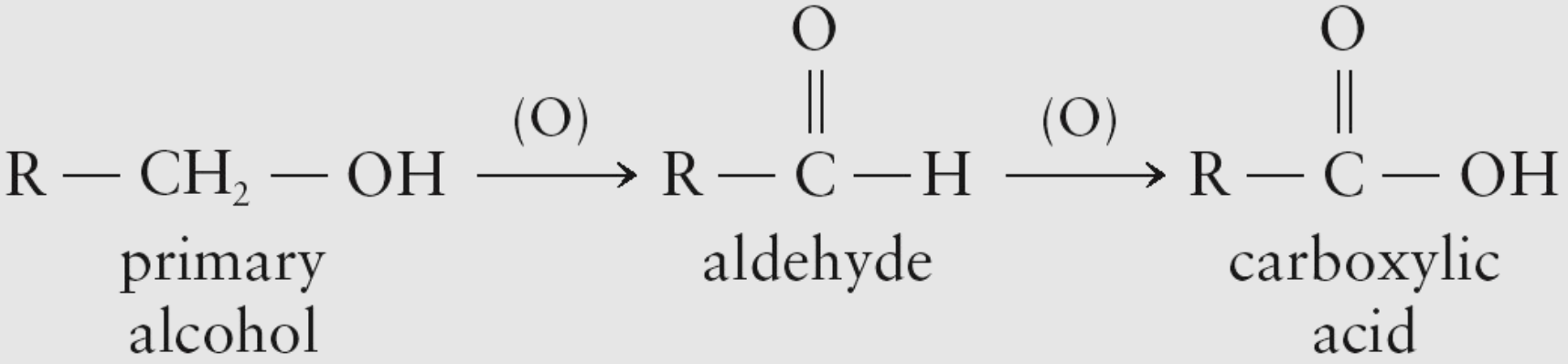
Oxidation reactions

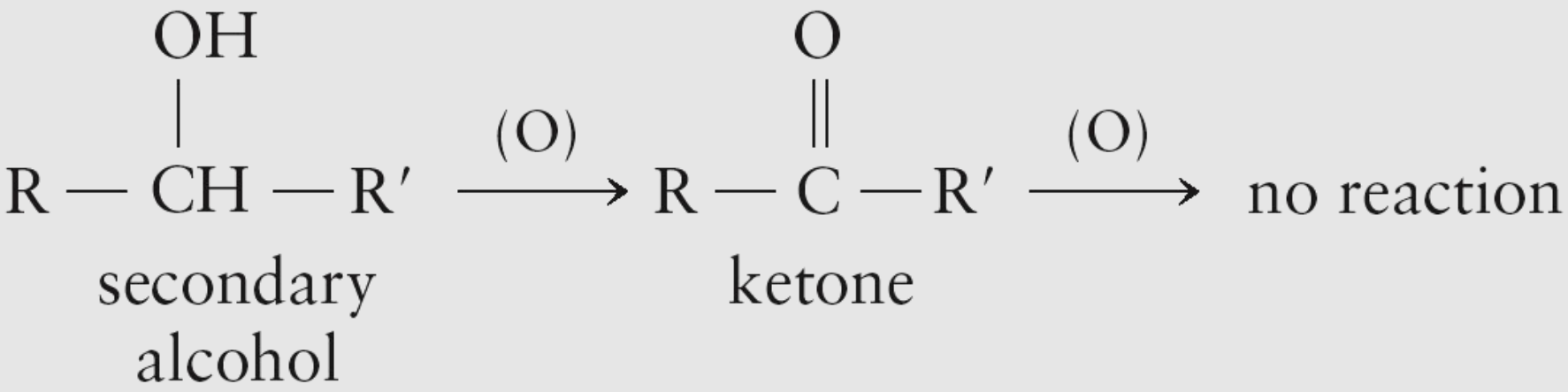
- Aldehydes can be oxidized easily to carboxylic acids
- Ketones are resistant to oxidation.



ALDEHYDE AND **KETONE** REACTIONS

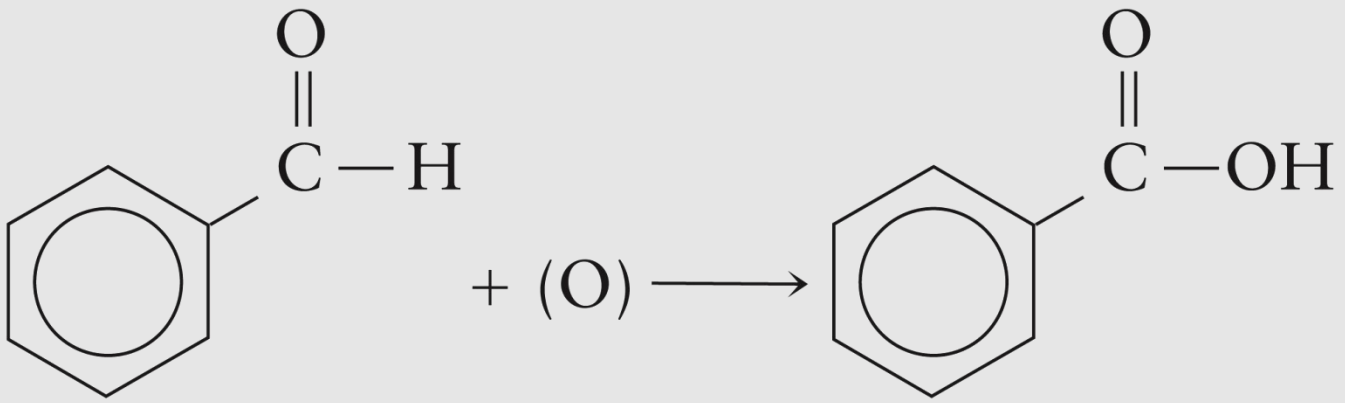
- Recall the oxidation of alcohols to produce **aldehydes** and **ketones**:



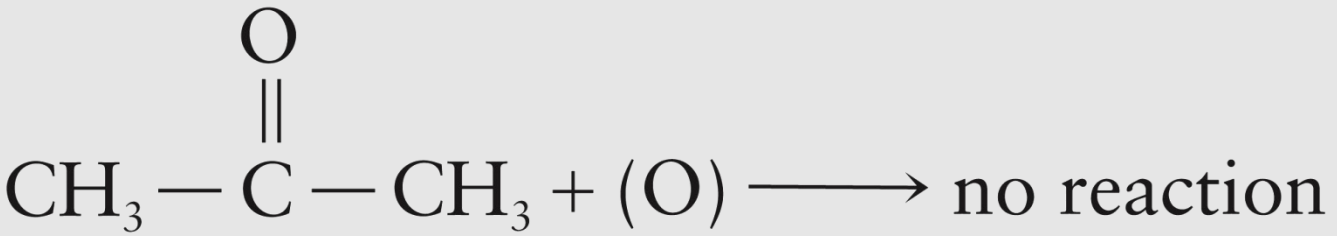


ALDEHYDE AND KETONE REACTIONS (continued)

- The difference in reactivity toward oxidation is the chief reason why **aldehydes** and **ketones** are classified in separated families.



benzaldehyde benzoic acid

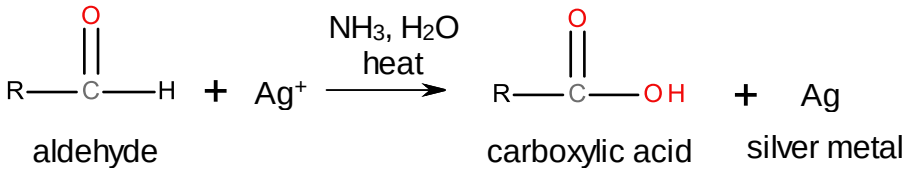


acetone

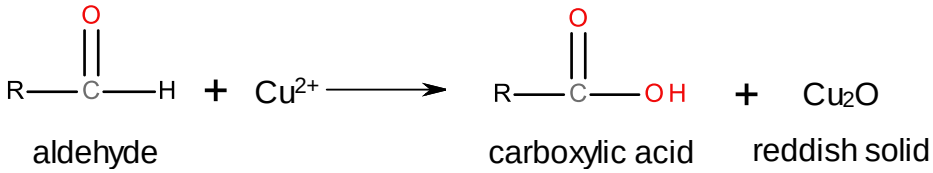
Oxidation and reduction of aldehydes and ketones

Oxidation reactions

- There are several tests that have been developed to determine the presence of aldehydes, based on their oxidation to carboxylic acids:
  - Tollen's test



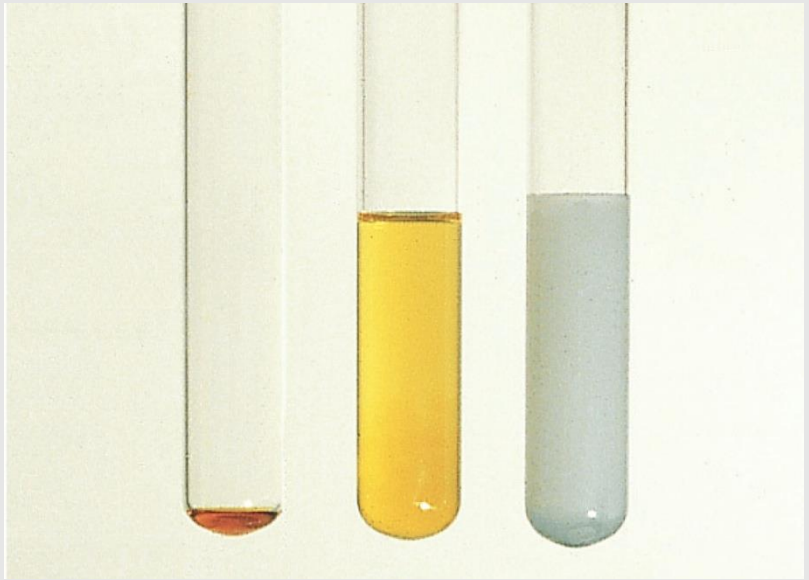
  - Benedict's test



ALDEHYDE AND KETONE REACTIONS (continued)

- The ease with which **aldehydes** are oxidized allows us to test for the presence of **aldehydes** with **Tollens' reagent** or **Benedict's reagent**.
- In general, **ketones** fail to react with these reagents.

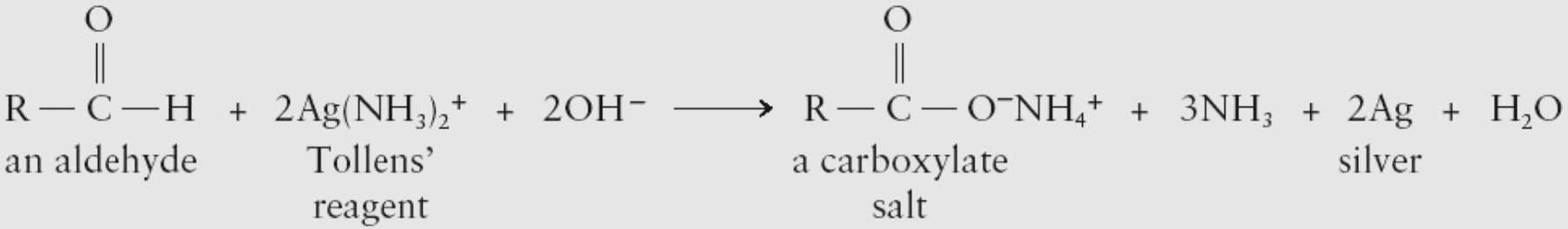
From left to right, three test tubes containing potassium dichromate ($K_2Cr_2O_7$), acetone, and benzaldehyde.



After the addition of equal amounts of $K_2Cr_2O_7$, the acetone remains unreacted, whereas the benzaldehyde is oxidized.

ALDEHYDE AND KETONE REACTIONS (continued)

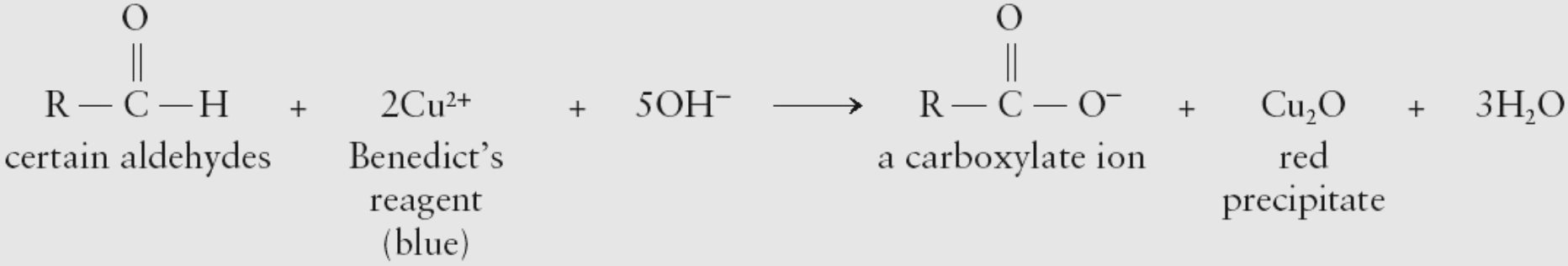
- In the presence of **aldehydes**, **Tollens' reagent** produces a silver coating on glass.

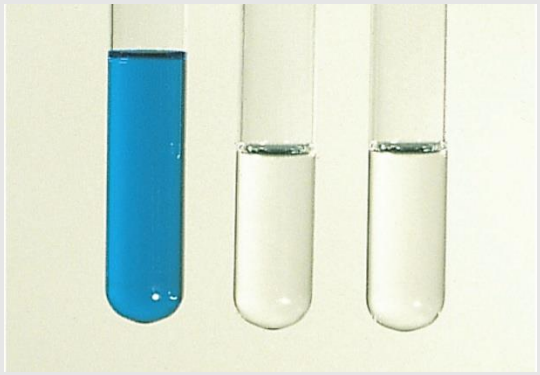


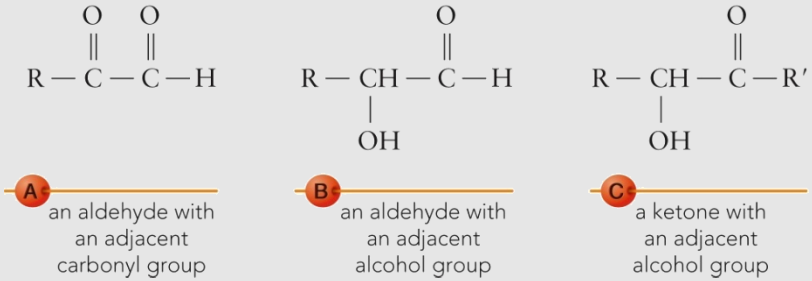
- This method is used to produce mirrors and silver ornaments.

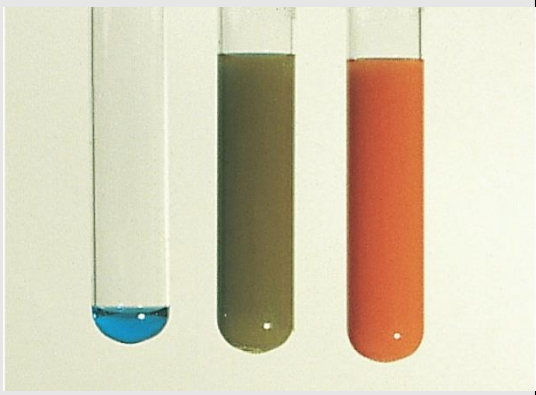
ALDEHYDE AND KETONE REACTIONS (continued)

- In the presence of **aldehydes**, **Benedict's reagent** produces a red precipitate.









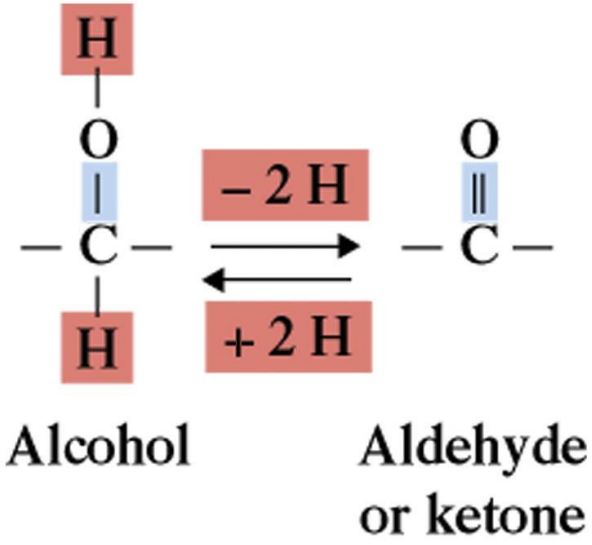
From left to right, three test tubes containing Benedict's reagent, 0.5% glucose solution, and 2.0% glucose solution.

The addition of Benedict's reagent from the first tube produces colors (due to the red Cu_2O) that indicate the amount of glucose present.

Oxidation and reduction of aldehydes and ketones

Reduction reactions

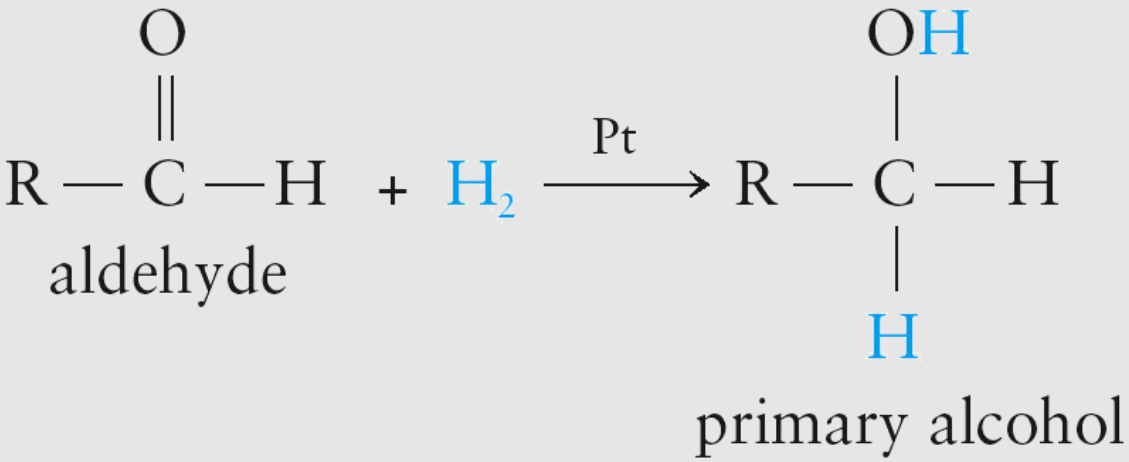
- Both aldehydes and ketones are easily reduced to alcohols with H_2 in the presence of a catalyst (Ni, Pt, Cu).

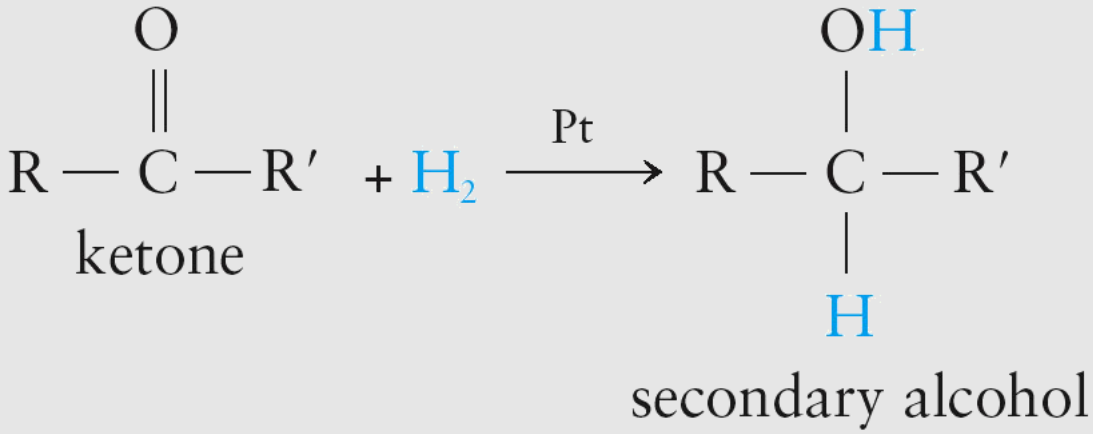


HSS Fig 15.1 Red'n

ALDEHYDE AND KETONE REACTIONS (continued)

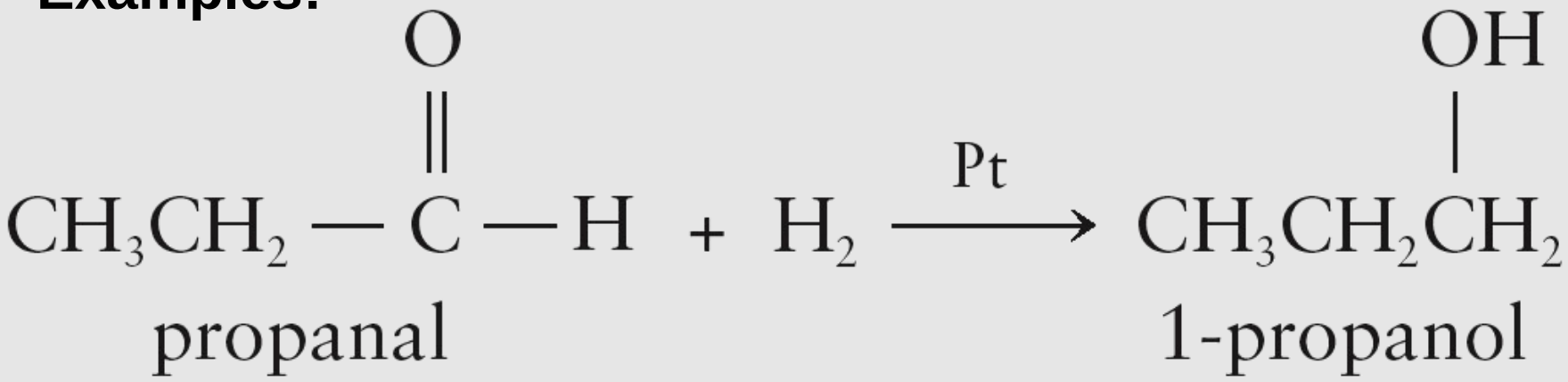
- The addition of H_2 in the presence of catalysts.



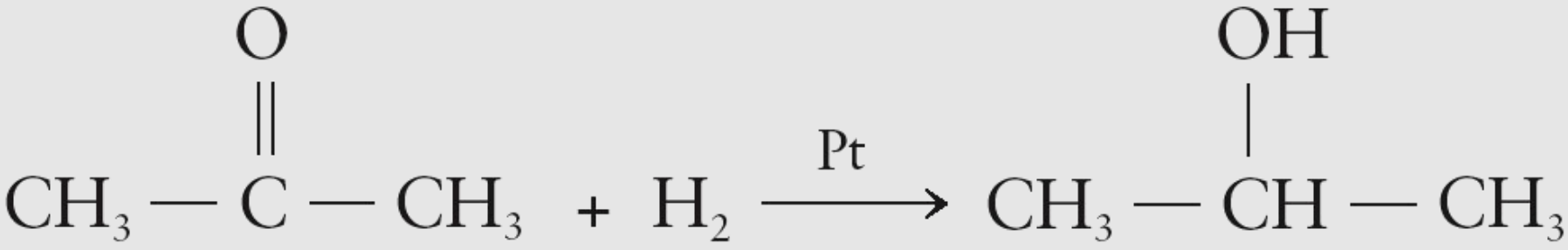


ALDEHYDE AND KETONE REACTIONS (continued)

- **Examples:**

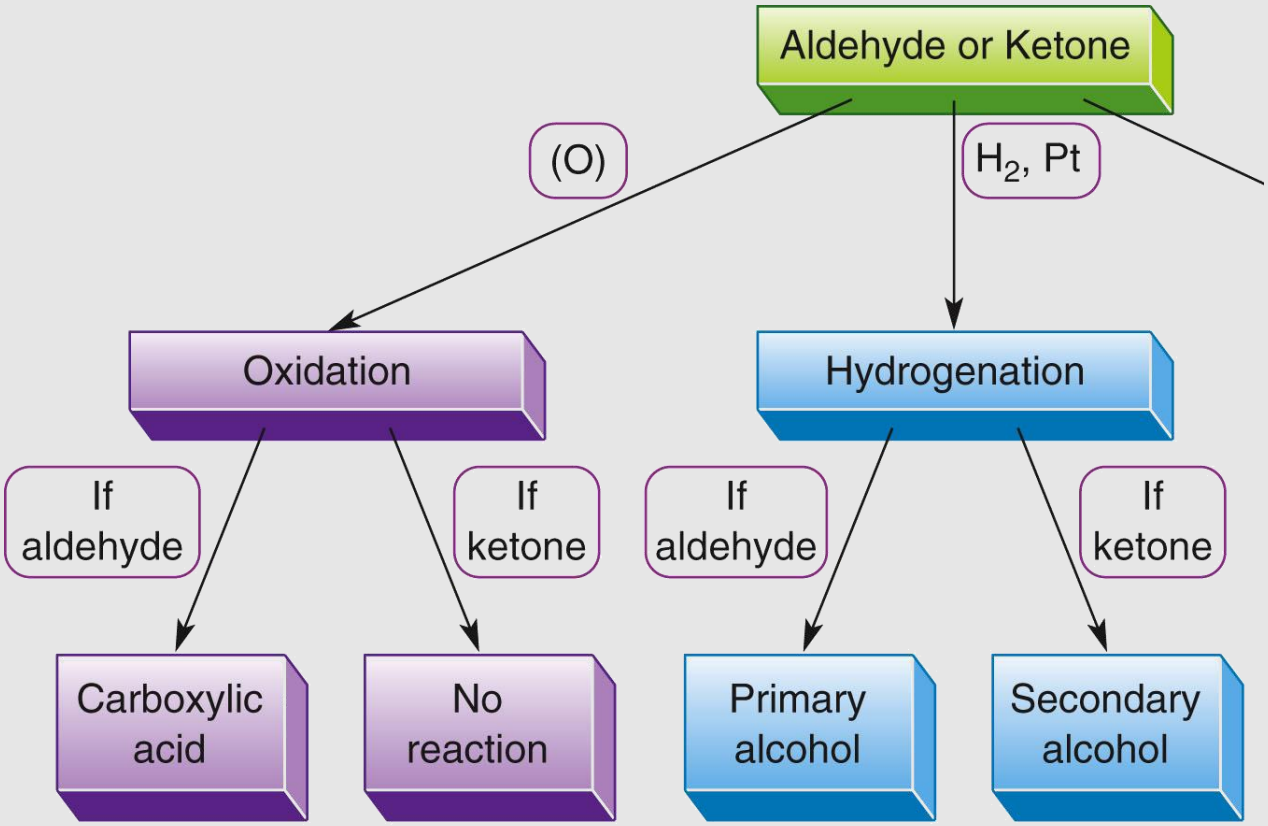


propanal 1-propanol



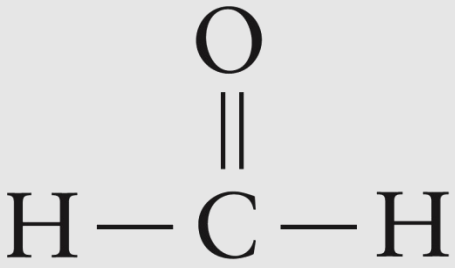
acetone 2-propanol

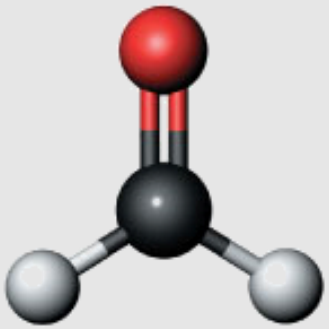
ALDEHYDE AND KETONE REACTION MAP

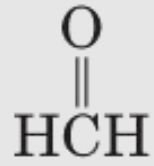


IMPORTANT **ALDEHYDES** AND **KETONES**

- Formaldehyde
  - Gas at room temperature
  - Formalin – 37% aqueous solution
  - Sterilizer
  - Embalming fluid
  - Starting material for plastics such as Formica and Bakelite



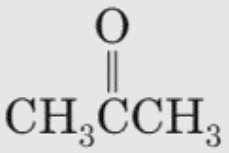




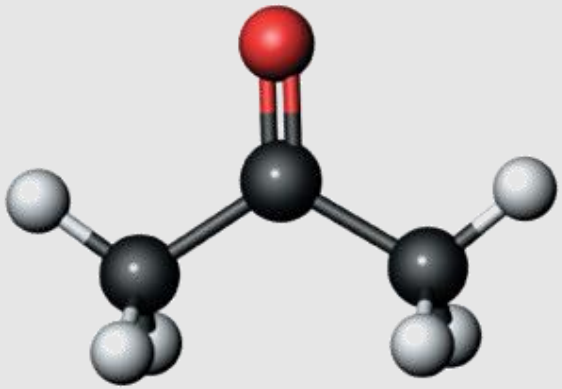
Methanal
(Formaldehyde)

IMPORTANT **ALDEHYDES** AND **KETONES** (continued)

- Acetone
  - Important organic solvent
  - Used in such things as nail polish remover
  - Miscible with water

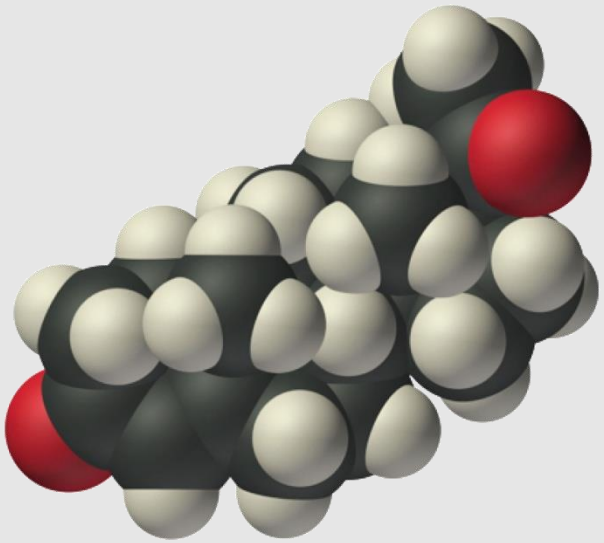


Propanone
(Acetone)

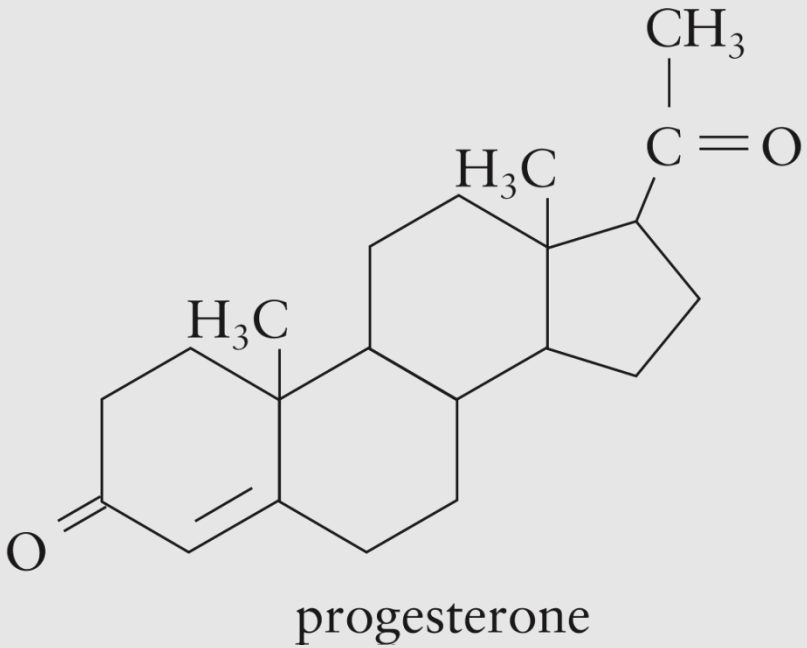


IMPORTANT **ALDEHYDES** AND **KETONES** (continued)

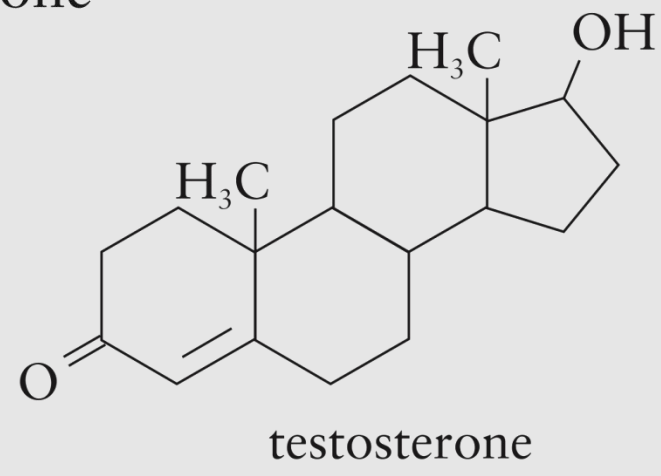
- Progesterone and testosterone (female and male sex hormones) are **ketones**.



Progesterone



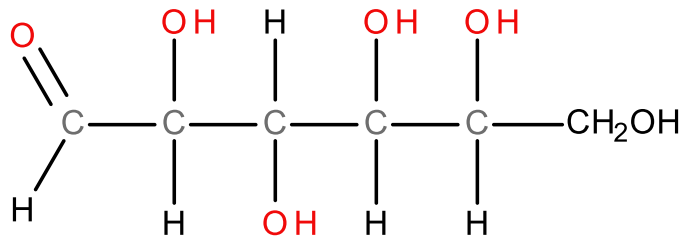
progesterone



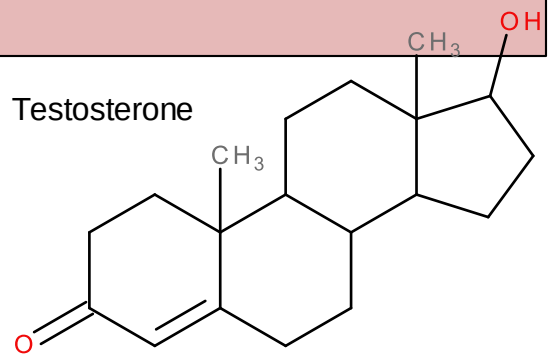
testosterone

Naturally occurring aldehydes and ketones

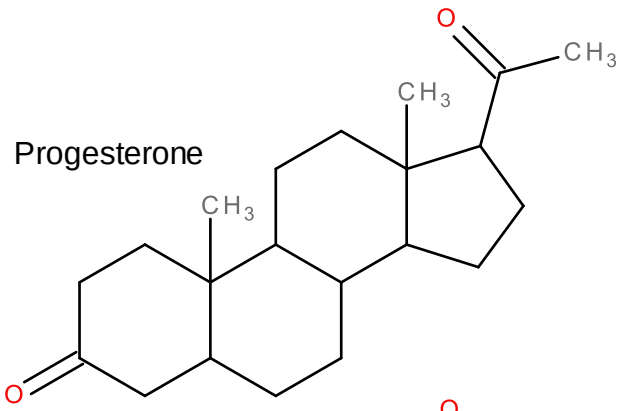
- A wide variety of biologically relevant molecules possess aldehyde and/or ketone functional groups:



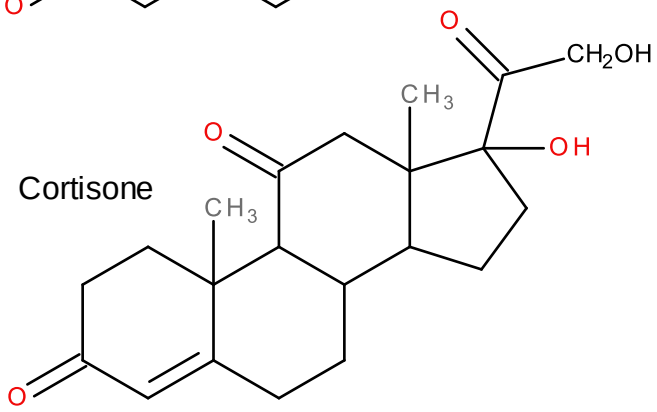
D-Glucose



Testosterone



Progesterone



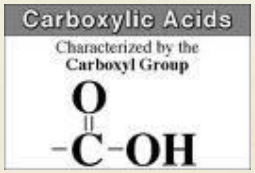
Cortisone

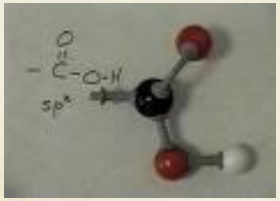
Lec.8

Carboxylic Acids, Esters & Amides

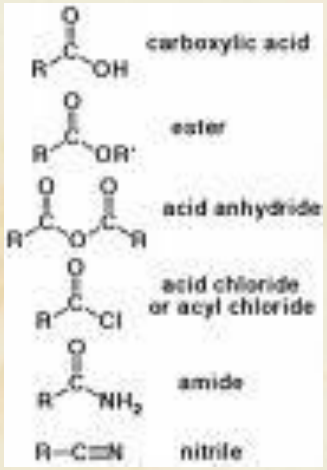
Carboxylic Acids

- Carboxyl group = functional group
  - -COOH

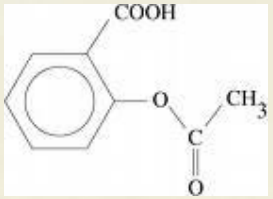




  - Easily produced through the oxidation of an aldehyde
- Carboxylic acid derivatives
  - **Ester**
  - Acid chloride
  - Acid anhydride
  - **Amide**

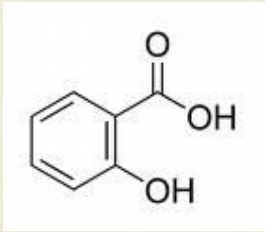


Aspirin

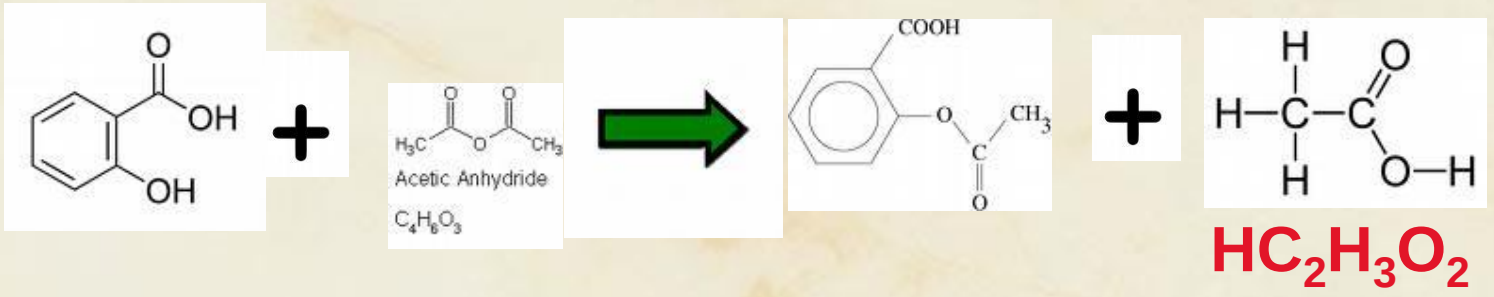


- Acetylsalicylic acid (an ester)

  is the active ingredient and is derived from salicylic acid.



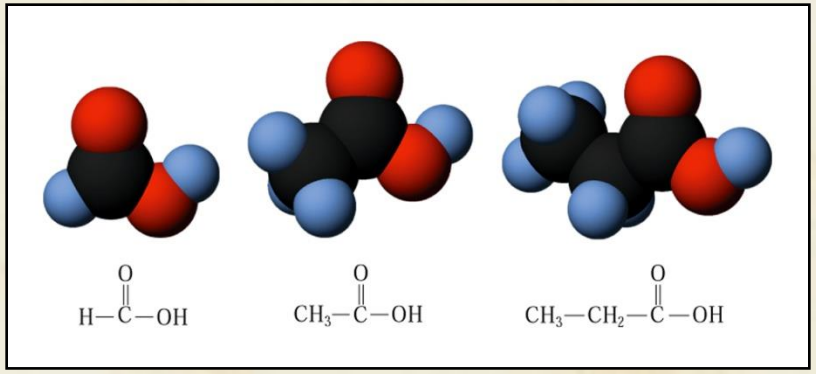
Synthesis reaction:

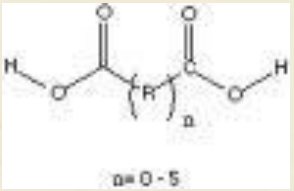


$HC_2H_3O_2$

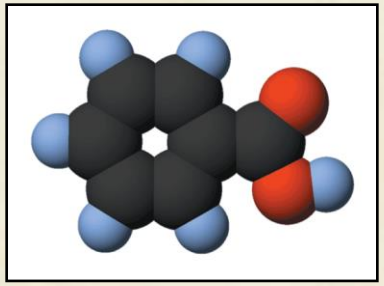
Carboxylic acids - Nomenclature

- IUPAC - resemble aldehyde rules (-COOH carbon is #1)
  - Parent chain is the longest that includes -COOH
  - Change “e” at the end of alkane name to “oic acid”
- Monocarboxylic acids (alkanoic acid)





- Dicarboxylic acids (alkanedioic acid)
- Aromatic carboxylic acids (benzoic acid)



Carboxylic acids - Nomenclature

Common - names are related to the common source of the acid

Valerian plant

- Monocarboxylic
  - *Formic* -->
  - *Acetic* -->
  - <--Propionic
    - "protos""pion" propionibacteria
  - Butyric
  - <--Valeric
  - Caproic -->

- Dicarboxylic
  - Oxalic
  - Malonic
  - Succinic
  - Glutaric
  - Adipic
  - Pimelic

Length of Carbon Chain	Structural Formula	Common Name[a]	IUPAC Name
C_1 monoacid	H—COOH	formic acid	methanoic acid
C_2 monoacid	CH_3—COOH	acetic acid	ethanoic acid
C_3 monoacid	CH_3—CH_2—COOH	propionic acid	propanoic acid
C_4 monoacid	CH_3—$(CH_2)_2$—COOH	butyric acid	butanoic acid
C_5 monoacid	CH_3—$(CH_2)_3$—COOH	valeric acid	pentanoic acid
C_6 monoacid	CH_3—$(CH_2)_4$—COOH	caproic acid	hexanoic acid

[a] The mnemonic "*F*rogs *a*re *p*olite, *b*eing *v*ery *c*ourteous" is helpful in remembering, in order, the first letters of the common names of these six simple saturated monocarboxylic acids.

Length of Carbon Chain	Structural Formula	Common Name[a]	IUPAC Name
C_2 diacid	HOOC—COOH	oxalic acid	ethanedioic acid
C_3 diacid	HOOC—CH_2—COOH	malonic acid	propanedioic acid
C_4 diacid	HOOC—$(CH_2)_2$—COOH	succinic acid	butanedioic acid
C_5 diacid	HOOC—$(CH_2)_3$—COOH	glutaric acid	pentanedioic acid
C_6 diacid	HOOC—$(CH_2)_4$—COOH	adipic acid	hexanedioic acid
C_7 diacid	HOOC—$(CH_2)_5$—COOH	pimelic acid	heptanedioic acid

[a] The mnemonic "*O*h *m*y, *s*uch *g*ood *a*pple *p*ie" is helpful in remembering, in order, the first letters of the common names of these six simple dicarboxylic acids.

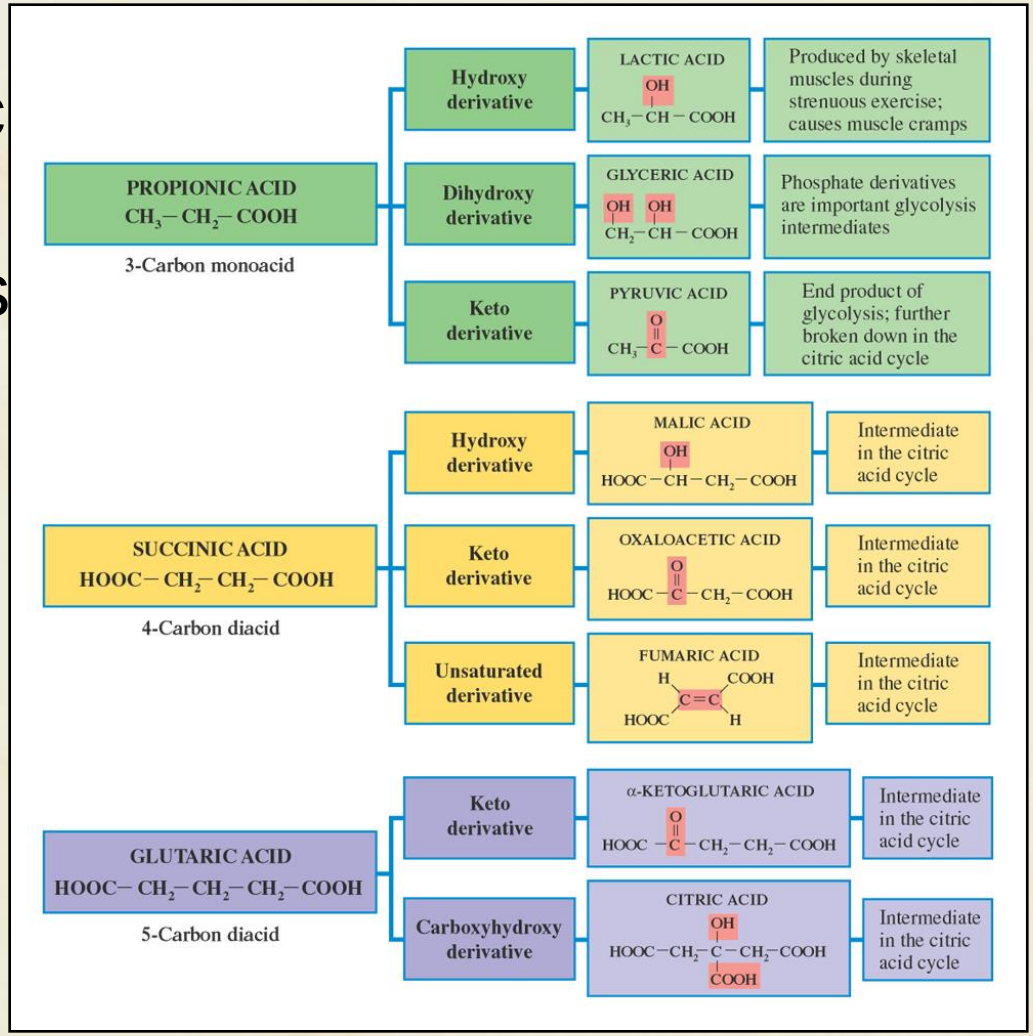
Polyfunctional acids - contain other functional groups

- Priority for naming compounds (by functional group)
  1. Carboxyl
  2. Carbonyl
     a) Aldehyde
     b) Ketone
  3. Alcohol
  4. Amine*
  5. Alkene
  6. Alkyne
  7. Alkoxy (ether)
  8. Alkyl
  9. Halogen

- Common P.A.s:
  - Unsaturated (with double bond)
  - Hydroxyl (with -OH group)
  - Keto (with carbonyl group)
  - *Amino (with amino (-NH_2) group)

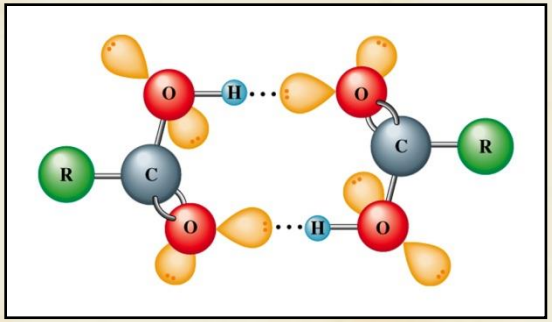
Metabolic Acids - intermediates in metabolic reactions

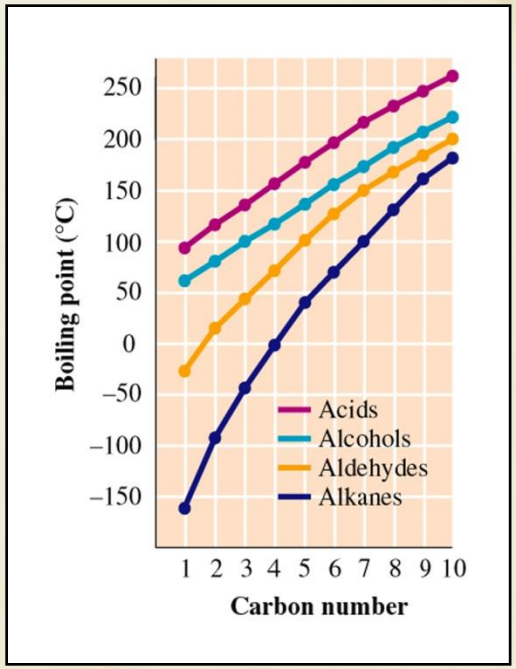
- Eight important suc acids are derived from 3 simple acids



Physical Properties

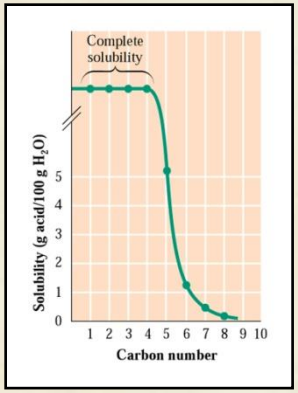
- Extremely Polar
  - High MP & BP
    - They readily form “dimers”





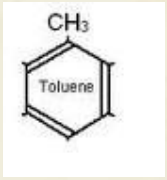
  - Soluble in water
    - For low # of C atoms

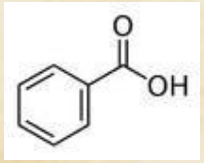
The solubility in water of saturated unbranched-chain carboxylic acids.



Preparation Reactions

- Aliphatic - Oxidation of 1˚ alcohol; oxidation of aldehyde
  - 1˚ alcohol --> aldehyde --> acid

- Aromatic - Oxidation of alkyl benzene
- 

[O] ›


Acidity of Carboxylic Acids

- R-COOH + H_2O <==> H_3O^+ + $R\text{-}COO^-$
- All are WEAK acids!

Acid	K_a	Percent Ionization (0.100 M Solution)
Formic	1.8×10^{-4}	4.2%
Acetic	1.8×10^{-5}	1.3%
Propionic	1.3×10^{-5}	1.2%
Butyric	1.5×10^{-5}	1.2%
Valeric	1.5×10^{-5}	1.2%
Caproic	1.4×10^{-5}	1.2%

- Carboxylate i
  - Ex. $HCOO^-$ (methanoate;formate)
  - CH_3COO^- (ethanoate; acetate) $C_2H_3O_2^-$

Carboxylic Acid Salts

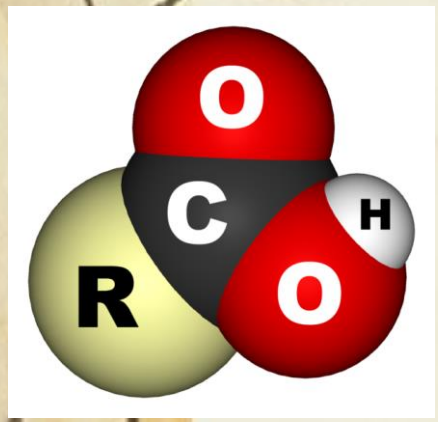
- C. Acid + Strong Base --> Salt + water
- R-COOH + NaOH --> $R\text{-}COO^{-}Na^{+}$ + H_2O

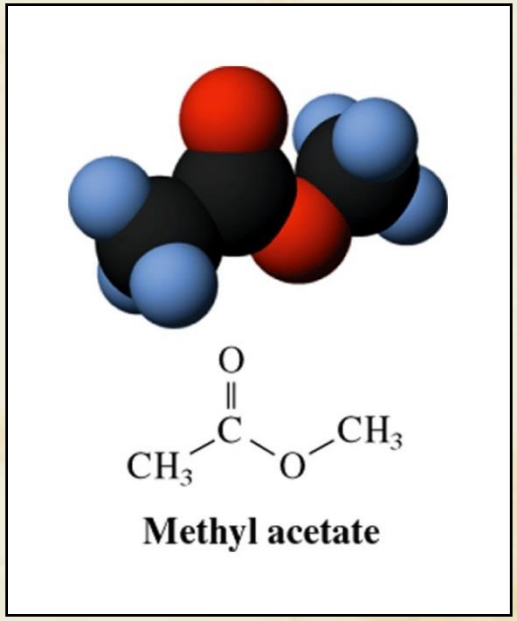
- C.A. Salt + Strong Acid --> C.A. + Inorganic salt
- Ex.: $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$

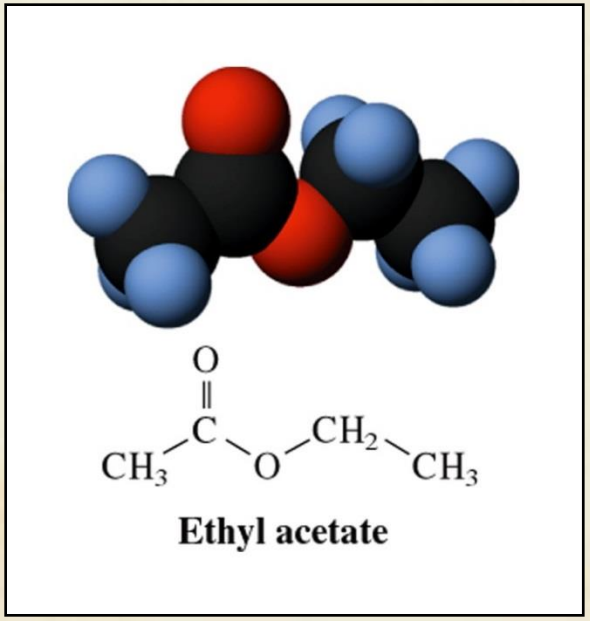
- These salts are even more soluble in water than their “parent” acids
- Since these salts raise pH, they are effective against certain microorganisms that require lower pH for their activity.

Esters

- These carboxylic acid derivatives have the -OH portion replaced by an -OR group.
  - R-COOR
  - Ex.

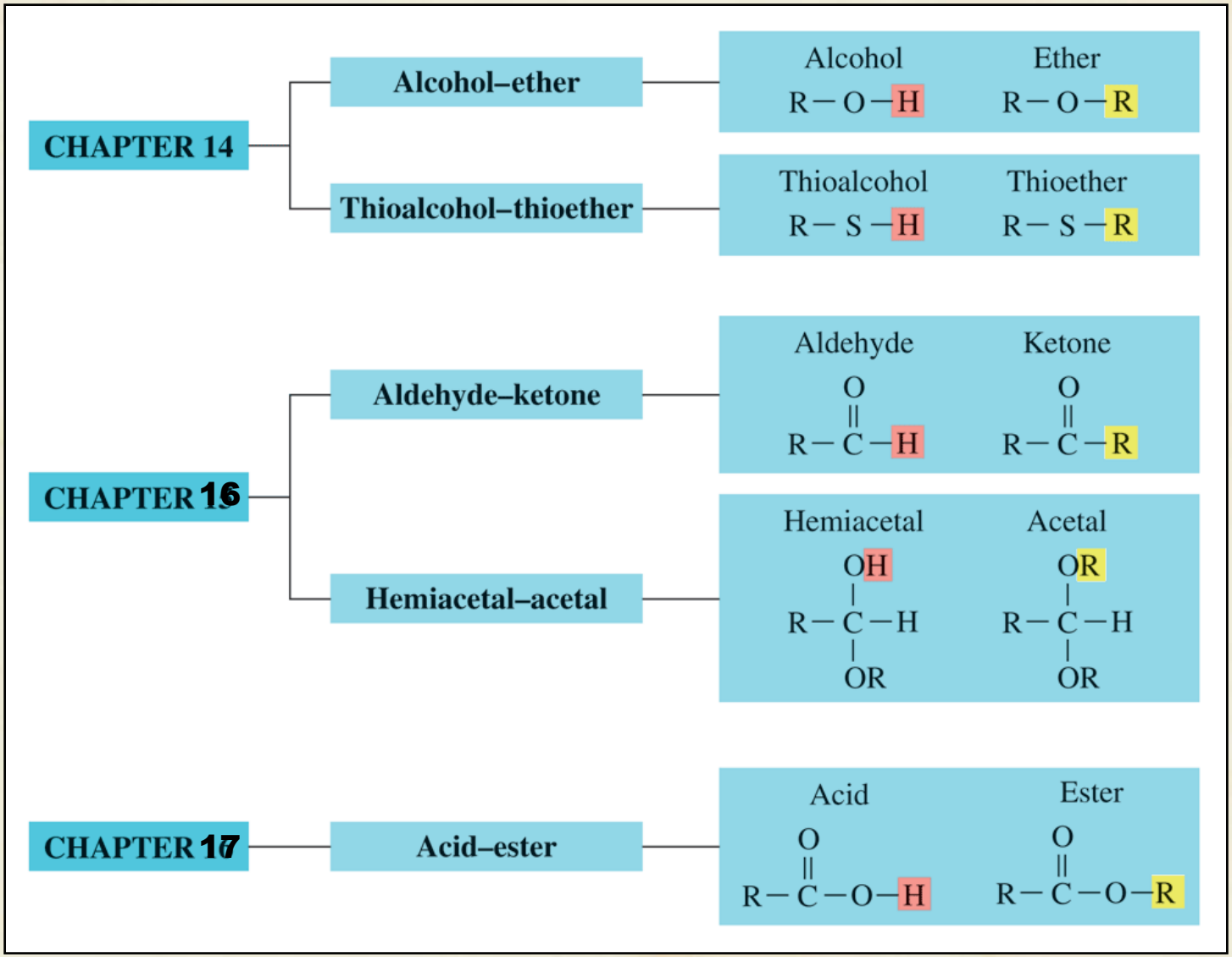






- Methyl ethanoate
- Ethyl ethanoate

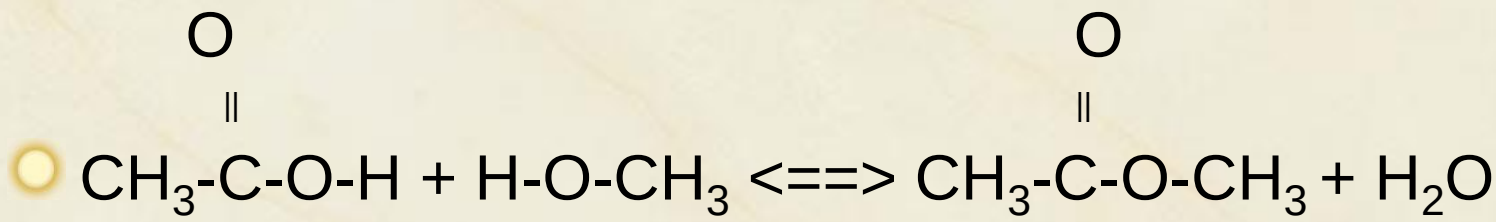
Functional Group Isomers



Esterification

in presence of acid catalyst

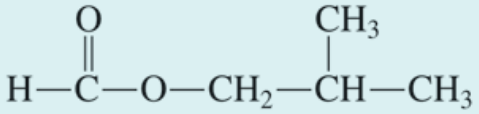
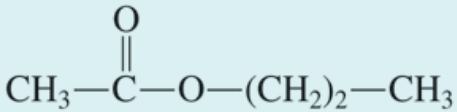
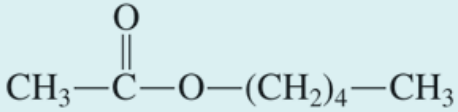
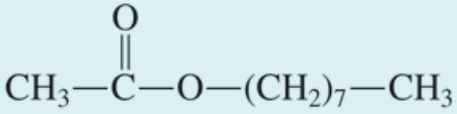
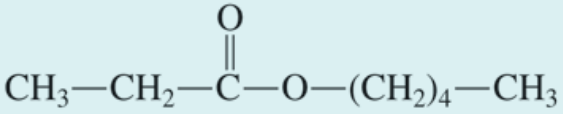
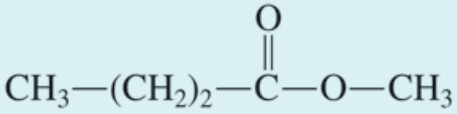
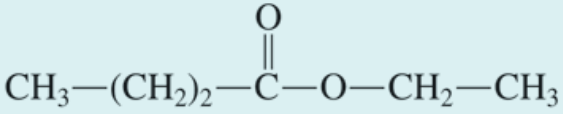
- Carboxylic acid + alcohol <==> Ester + water
  - RCOOH + HOR <==> RCOOR + HOH



Ester Nomenclature

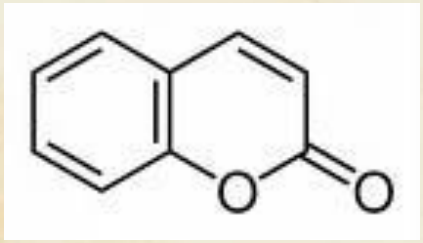
- IUPAC
  - Name the alcohol part 1st & acid part 2nd.
  - Alcohol part name = name of R group (alkyl) in the -OR portion of the ester.
  - Acid part name = drop “ic acid” ending of acid name and add suffix “ate”.
  - Alkyl alkanoate
- Common: same as for IUPAC, except change the common acid name to end in “ate”.

- Ex.: C-C-C-COOH + HOC <==> C-C-C-COOC + H_2O
- IUPAC
- Common

IUPAC Name	Structural Formula	Characteristic Flavor and Odor
isobutyl methanoate		raspberry
propyl ethanoate		pear
pentyl ethanoate		banana
octyl ethanoate		orange
pentyl propanoate		apricot
methyl butanoate		apple
ethyl butanoate		pineapple

Lactones - hydroxycarboxylic acids -->cyclic esters

- Self-esterification
  - IUPAC lactone names end in “olide”
- 3-hydroxypropanoic acid --> 3-propanolide
- 5-hydroxypentanoic acid --> 5-pentanolide
- Coumarin - newly mown hay odor

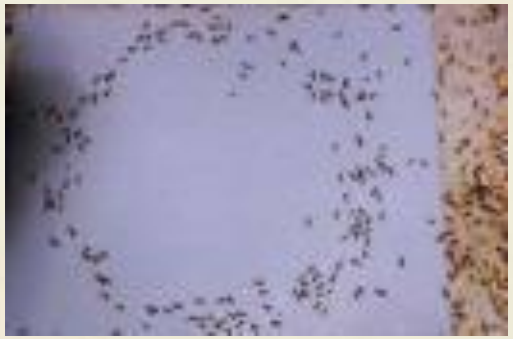


- Nepetalactone - catnip plant

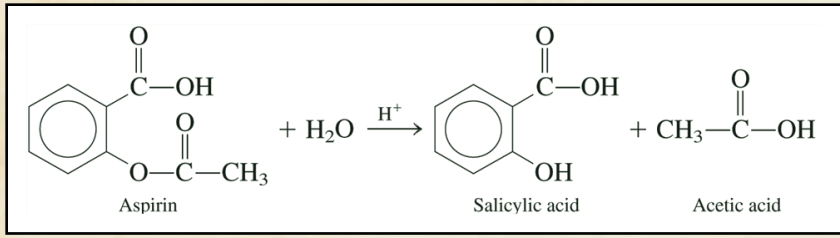
Common Esters

- Flavors/Fragrances
- Pheromones
  - Alarm
  - Trail
  - Sex
  - Deception
  - Releaser
  - Primer

IUPAC Name	Structural Formula	Characteristic Flavor and Odor
isobutyl methanoate	$H-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_3}{\underset{\|}{CH}}-CH_3$	raspberry
propyl ethanoate	$CH_3-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-CH_3$	pear
pentyl ethanoate	$CH_3-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-CH_3$	banana
octyl ethanoate	$CH_3-\overset{O}{\overset{\|}{C}}-O-(CH_2)_7-CH_3$	orange
pentyl propanoate	$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-CH_3$	apricot
methyl butanoate	$CH_3-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-CH_3$	apple
ethyl butanoate	$CH_3-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$	pineapple



- Medications
  - Benzocaine
    - Amino ester
  - Salicylic Acid Esters
    - Aspirin (acid rxn)
    - Oil of wintergreen (alcohol rxn)
      - SA + methanol --> Ester



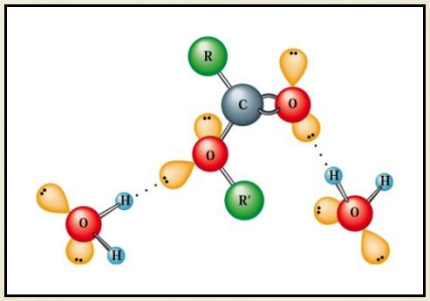
Isomerism

- Carboxylic acid - skeletal
- Ester - positional
- Functional group
  - Carboxylic acids & esters
    - Ex.: Ethyl propanoate & Pentanoic acid
  - Alcohol & ether
  - *Thiol & thioether*
  - Aldehyde & ketone
  - *Hemiacetal & acetal*

Physical Properties

- No Hydrogen bonds between esters
  - similar to ethers:)
  - Low BP

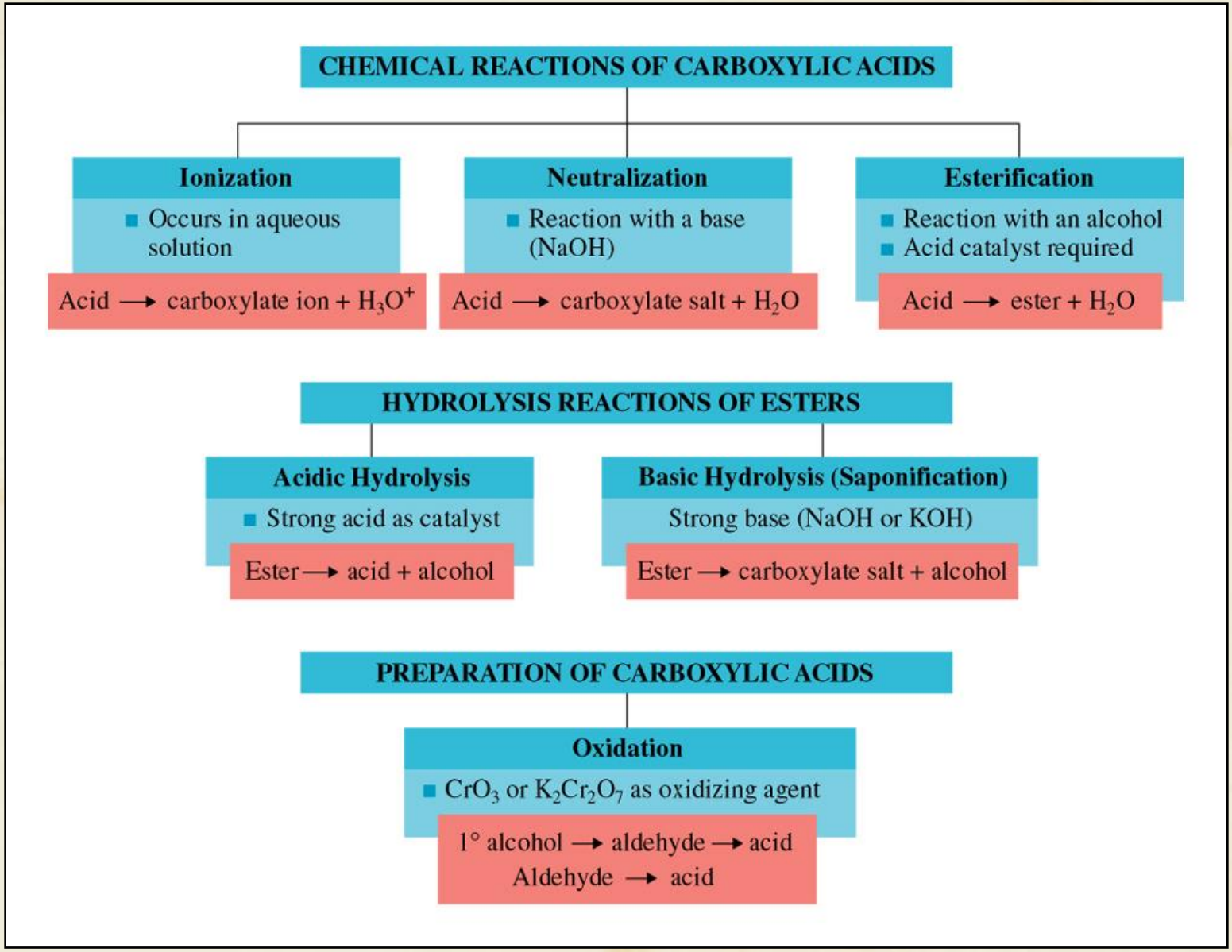
Name	Functional-Group Class	Molecular Mass	Boiling Point (°C)
diethyl ether	ether	74	34
ethyl formate	ester	74	54
methyl acetate	ester	74	57
butanal	aldehyde	72	76
1-butanol	alcohol	74	118
propionic acid	acid	74	141



- Hydrogen bonds possible between ester & water
  - Low MW esters are soluble

Chemical Reactions of Esters

- Ester hydrolysis (w/ strong acid as catalyst)- opposite of esterification
  - Ester + water <==> acid + alcohol
- Ester hydrolysis (with strong base)- Saponification
  - Ester + SB --> Carboxylate salt + alcohol

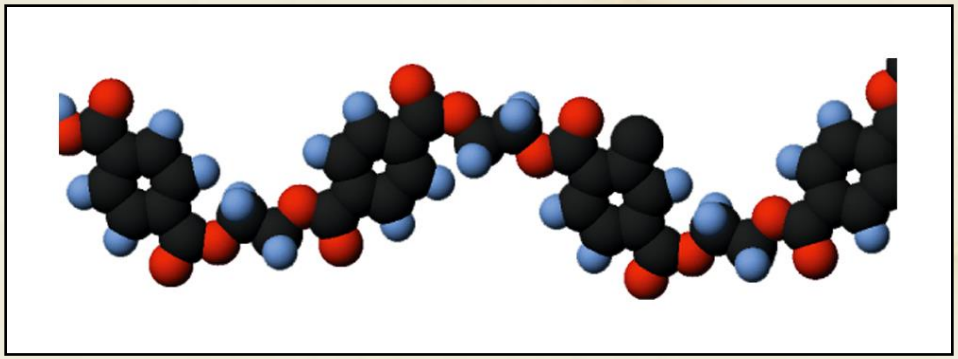

CHEMICAL REACTIONS OF CARBOXYLIC ACIDS
Ionization
Occurs in aqueous solution
Acid → carboxylate ion + H_3O^+
Neutralization
Reaction with a base (NaOH)
Acid → carboxylate salt + H_2O
Esterification
Reaction with an alcohol
Acid catalyst required
Acid → ester + H_2O
HYDROLYSIS REACTIONS OF ESTERS
Acidic Hydrolysis
Strong acid as catalyst
Ester → acid + alcohol
Basic Hydrolysis (Saponification)
Strong base (NaOH or KOH)
Ester → carboxylate salt + alcohol
PREPARATION OF CARBOXYLIC ACIDS
Oxidation
CrO_3 or $K_2Cr_2O_7$ as oxidizing agent
1° alcohol → aldehyde → acid
Aldehyde → acid

Sulfur Analogs of Esters

- Thioester: -SR group has replaced the -OR group

- RCOOH + RSH --> RCOSR + H_2O
- Ex.:
  - Methyl thiobutanoate (strawberry)
    C-C-C-COS-C
  - Acetyl coenzyme A!!
    C-COS-CoA

Polyesters



- **Most are condensation polymers** (for every monomer attached to the first monomer, a water molecule is produced)
  - Ex.: Poly(Ethylene Terephthalate) PET

HOOC- -COOH + HO-C-C-OH

Terephthalic acid + ethylene glycol

  - PET
    - Textile products (Dacron, etc.)
    - Plastics (Mylar, food wrapping material, etc.)
  - Ex.: glycolic acid + lactic acid <==> "lactomer" (surgical staple)

HO-C-COOH + HO-C-COOH <==> (-OC-COO-C-CO-)$_n$

C C

Acid Chlorides

-OH portion of carboxyl group is replaced by -Cl

- Naming
  - Replace “ic acid” with “yl chloride”
  - Ex. C-C-C-COOH
    - Butyric acid
    - Butanoic acid

C-C-C-COCl

Common-

IUPAC-

- Prep. Rxn.:
  - RCOOH + Inorganic chloride -->
- Hydrolysis: happens quickly**
  - $RCOCl + H_2O \rightarrow RCOOH + HCl$

Acid Anhydrides* -OH portion of carboxyl group is replaced by -OOCR group

*two carboxylic acid molecules bonded together after a water molecule is removed.

Ex.: 2Acetic Acid (CCOOH) --> Acetic Anhydride (CCOOOCC)

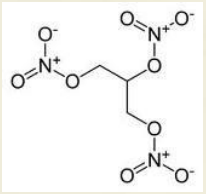
- RCOOH + HOOCR --> RCOOOCR + HOH
- * RCOCl + O^-OCR --> RCOOOCR + Cl^-
- Both Common & IUPAC names are formed by replacing “acid” with “anhydride”
  - CCOOOCC
  - CCCOOOCC
- Reactions:
  - Hydrolysis (quick): RCOOOCR + H_2O --> RCOOH + RCOOH
  - Ester Synthesis: ROH + RCOOOCR --> RCOOR + RCOOH

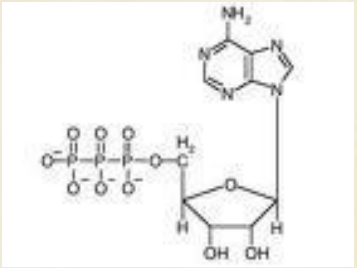
Esters & Anhydrides of Inorganic Acids

- Most important are Phosphate Esters - product of alcohol reacting with phosphoric acid.
  - Ex.: $H_3PO_4 + CH_3OH$ -->

- Phosphate mono (di, tri)esters
- Mono, di, or tri phosphate mono esters (AMP, ADP, ATP) ⬇

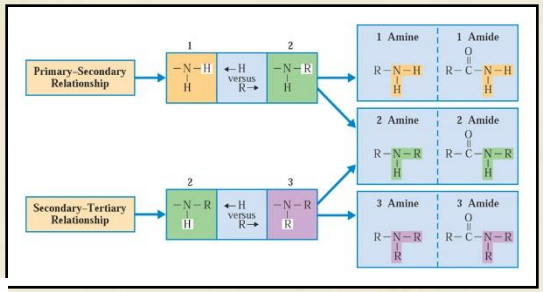
- Nitroglycerin

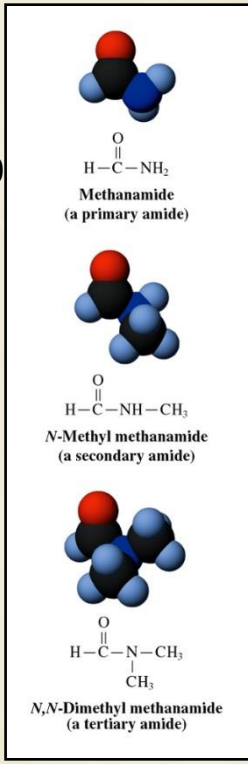




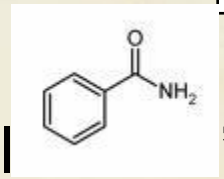
Amides

- Amides are carboxylic acid derivatives
  - OH group is replaced by an amino or substituted amino group
- 1˚ amide RCONH$_2$
- 2˚ amide RCONHR
- 3˚ amide RCONR$_2$

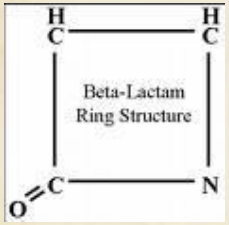




- Aromatic amide



- Cyclic amides = “l ”
  - (similar to cyclic esters = “lactones”)



Penicillin cpds have 4-membered lactam rings

Amide Nomenclature

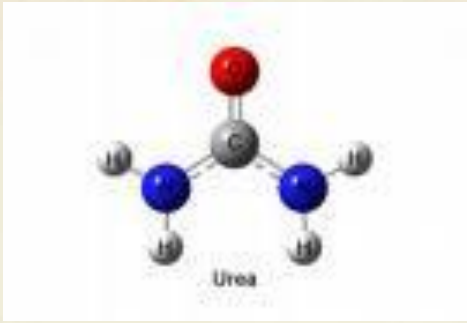
- Naming system (IUPAC vs. Common) is similar to that for carboxylic acids

1) Change the ending from “oic acid” or “ic acid” to “amide”.
   - Ex. Benzoic acid --> Benzamide

2) Names of groups attached to N (2˚ & 3˚) use an *N*-prefix as locator at front of name.

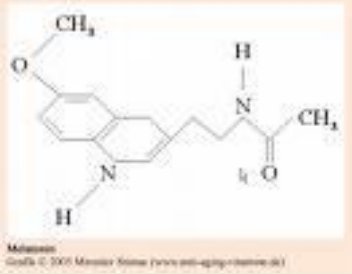
$HCONH_2$ CCCONHC

Some Important Amides

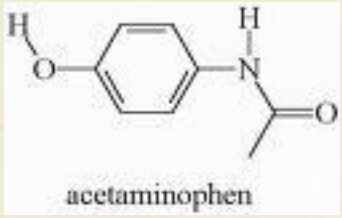


- Urea
  - $CO_2 + 2NH_3 \rightarrow (H_2N)_2CO + H_2O$

urea

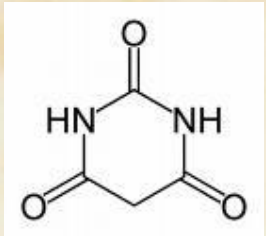


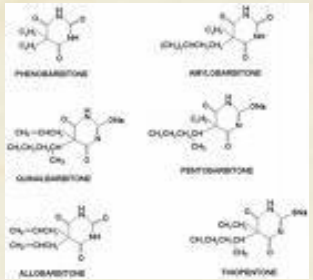
- Melatonin - polyfunctional amide



- Acetaminophen - pain reliever

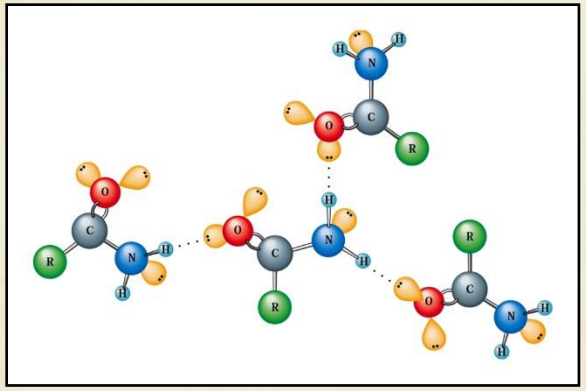
- Barbiturates - cyclic amides
  - Derivatives of barbituric acid





Physical Properties of Amides

- Not basic - due to polarity of adjacent carbonyl group
- BP - related to the degree of hydrogen bonding (note the difference between 1˚, 2˚, & 3˚)
- Water solubility
  - Low MW = soluble
  - High MW = less soluble



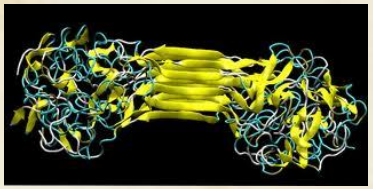
Preparation Reactions

- The "amidification" reaction must be carried out at 100+˚C, between a carboxylic acid and an amine (or ammonia).
- Ammonia + carboxylic acid --> 1˚ amide
- 1˚ amine + carboxylic acid --> 2˚ amide
- 2˚ amine + carboxylic acid --> 3˚ amide

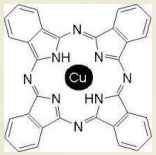
Amide Hydrolysis

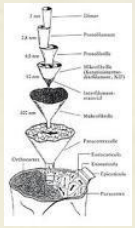
- Amide + water --> carboxylic acid + amine
- In acid:
  - Amide + water --> carboxylic acid + amine salt
  - RCONHR + HOH +HCl --> RCOOH + R-$NH_3^+Cl^-$
- In base:
  - Amide + SB --> carboxylic acid salt + amine
  - RCONHR + NaOH --> $RCOO^-Na^+$ + R-NH_2

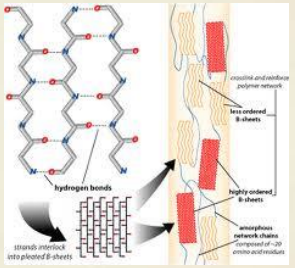
Polyamides



- Polyamide = condensation polymer of diamines + dicarboxylic acids

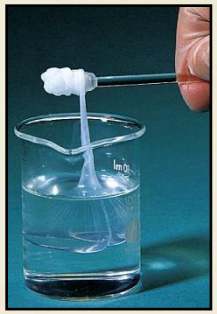




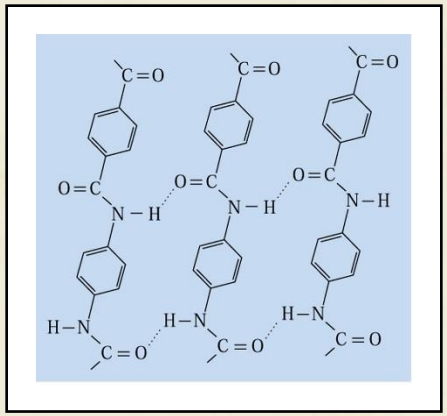


- Natural: wool,
- Synthetic: Nylon,

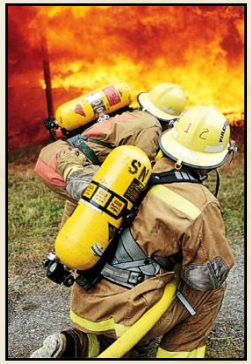
silk (proteins)



Kevlar



Nomex



Polyurethanes

- Polyurethanes are polymers that contain portions of both ester & amide functional groups